

Research Article

A modified sensitive palladium-copper oxide and multiwalled carbon nanotubes electrochemical sensor for detection of ametridione pesticide

V. Bebi

Electroanalytical Lab, Department of Chemistry, Sri Venkateswara University, Tirupati - 517502 (A.P.), India

P. Reddy Prasad

Electroanalytical Lab, Department of Chemistry, Sri Venkateswara University, Tirupati - 517502 (A.P.), India

K. Sudheer

Department of Chemistry, PES University, Bangalore - 560085 (Karnataka), India

P. Sandhya

Department of Chemistry, Sri Padmavati Mahila Visvavidyalayam, Tirupati - 517502 (A.P.), India

C. Nageswara Reddy

Department of Chemistry, Government Degree & P.G College, Puttur - 517583 (A.P.), India

N. Y. Sreedhar*

Electroanalytical Lab, Department of Chemistry, Sri Venkateswara University, Tirupati - 517502 (A.P.), India

*Corresponding author email: sreedhar_ny@rediffmail.com

Article Info

<https://doi.org/10.31018/jans.v13i3.2531>

Received: February 4, 2021

Revised: July 23, 2021

Accepted: July 28, 2021

How to Cite

Bebi, V. *et al.* (2021). A modified sensitive palladium-copper oxide and multiwalled carbon nanotubes electrochemical sensor for detection of ametridione pesticide. *Journal of Applied and Natural Science*, 13(3), 798 - 806. <https://doi.org/10.31018/jans.v13i3.2531>

Abstract

A glassy carbon electrode modified with sensitive palladium-copper oxide and multi-walled carbon nanotubes (Pd-CuO/MWCNTs) electrochemical nanosensor was used to detect ametridione pesticide in water samples. The morphological characteristics of Pd-CuO/MWCNTs were examined by Scanning electron microscope (SEM) and Energy dispersive x-ray analysis (EDX.) The ametridione pesticide under voltammetric investigation involves irreversible, four electron ($4e^-$) reduction, based on the protonation of the two carbonyl groups ($>C=O$). The voltammetric method was applied to detect ametridione in Britton-Robinson (BR) buffer solution at pH 5.0 as a supporting electrolyte. The limits of detection, quantification and concentration ranges of the proposed method were $0.0796 \mu\text{g}\cdot\text{mL}^{-1}$ (signal/noise=3), $0.5560 \mu\text{g}\cdot\text{mL}^{-1}$ and 0.1 to $10.0 \mu\text{g}\cdot\text{mL}^{-1}$, respectively. The electrochemical sensor was successfully applied to detect ametridione in tap, agricultural run-off and river water samples showing >98% mean recoveries.

Keywords: Ametridione, CuO, Morphology, Pesticide, Sensor

INTRODUCTION

Ametridione, 1-amino-3-(2,2-dimethylpropyl)-6-(ethylthio)-1,3,5-triazine-2,4(1H,3H)-dione is a triazinone group of herbicides class (Forouzesh *et al.*, 2015). Herbicides are the fastest-growing classes of agricultural chemicals that are extensively used throughout the world, owing to their high toxicity to pests (Beckie *et al.*, 2006; Legere *et al.*, 2000). The use of these herbicides

in agriculture leads to numerous benefits in production and an increase of quality (Sephenson *et al.*, 1990). However, due to intense usage, there is a possibility of leakage of these toxic compounds into the environment through water and/ or soil (Rich *et al.*, 2012). The residue of the herbicides long time exists in the environment and can generate pollution problems and potential hazards in human beings and animals (Selim *et al.*, 2003; Rayburn *et al.*, 2005). However, the promiscu-

ous analysis reveals residues of such pesticides in natural water and in foodstuffs (Kniss, 2017). Hence, rapid, reliable and inexpensive pesticide sensing becomes essential for public health protection in environmental monitoring. Electrochemical analysis of pesticides offers simple, rapid and cost-effective methods with a little sample pre-treatment steps (Pourakbari *et al.*, 2020; Costa *et al.*, 2017).

Among electroanalytical techniques, electrical conductivity is a determining factor in the choice of electrode material (Koksoy *et al.*, 2021; Gonçalves-Filho *et al.*, 2020; Thiago *et al.*, 2020). For more than a decade, the use of modified glassy carbon electrodes has been reported to be a good alternative when compared to other working electrodes for electro-analysis of organic and inorganic species (Baghayeri *et al.*, 2021; Vieira da Silva *et al.*, 2021; Bhvimane *et al.*, 2019). Hence, there is a wide variety of modified electrodes, developed for the determination of pesticides such as polyaniline modified glassy carbon electrodes, nano titanium dioxide polymer film modified GCE and poly (4-amino 3-hydroxy naphthalene sulphonic acid) modified GCE and nano TiO₂/Nafion composite etc., (Khadem *et al.*, 2020; Ha *et al.*, 2013; Jian-Chun *et al.*, 2011; Gamze *et al.*, 1997; Dan *et al.*, 2010; Esmail *et al.*, 2020; Ben Ali Hassine *et al.*, 2018). So, to improve the analytical figures of merit, there exists a need for highly sensitive sensors for early detection and accurate determination of ametrudione pesticide in water samples. Accordingly, there are no electro-analytical reports concerning the determination of ametrudione pesticide using Pd-CuO/MWCNTs modified glassy carbon electrode. The electrochemical characteristics of Pd-CuO/MWCNTs were thoroughly examined by cyclic and differential pulse voltammetry to elucidate the electro-catalytic ability of the modified glassy carbon electrode.

MATERIALS AND METHODS

Apparatus

Motrohm Autolab B.V. Netherlands provided the Autolab PG STAT 101 for electrochemical measurements. The working electrode was a three-electrode setup that included a modified glassy carbon electrode. The reference electrode was saturated Ag/AgCl/KCl, while the counter electrode was Pt wire. The electrode surface morphology was carried out using a scanning electron microscope (SEM) of OXFORD INCA PANTA FET X3 CARL ZEISS from Japan. The pH meter model ELICO LI-120, supplied by ELICO Ltd. Hyderabad, India, was used to determine the pH of the buffer solution.

Reagents and solutions

All the reagents of analytical grade or HPLC grade used in the present work were obtained from Merck Chemicals Ltd. Ametrudione (99 %) (Fig. 1.) was purchased

from Siddarth Inc. Hyderabad, India. MWCNTs (i.d.×length 2-15 nm×1-10 μm) purchased from DropSens. Pesticide stock solutions (1000 ppm) and subsequent dilutions were made with ultrapure water on a regular basis and kept in the refrigerator. Britton-Robinson (BR) buffer solution (acetic, boric and phosphoric acids) was made according to the literature (Costa *et al.*, 2017), and the pH values were adjusted (fm 2.0 to 12.0) by adding appropriate amounts of 1.0 mol L⁻¹ NaOH solution, and were employed as supporting electrolyte. All solutions were prepared by using ultra-purified water from a Millipore Milli-Q system (18.2 MΩ cm⁻¹). All electrochemical experiments were performed at room temperature (25 ± 1 °C).

Sample collection and preparation of water samples

River water samples were collected in the Swarnamukhi River at a depth of water 45 cm, as well as agricultural run-off and tap water samples from randomly selected locations in the Srikalahasti rural area, Chittoor district, Andhra Pradesh. Water samples were collected in the amber glass flasks, acidified with 0.5 mol L⁻¹ H₂SO₄, and filtered through a 0.45 μm membrane. Aliquots of standard herbicide solution prepared in acetonitrile were solubilised directly in the water samples at two concentration levels (10 and 25 μg·mL⁻¹) and these spiked samples were stored in the refrigerator. Before this analysis, the spiked samples were filtered through a 0.45 μm membrane and the pH of samples was adjusted to 5.0 and the samples were subjected to the voltammetric analysis without any pre-treatment step.

Preparation of Pd-CuO and Pd-CuO/MWCNTs

For the production of Palladium, CuO and palladium supported CuO nanoparticles *Theobroma cacao L. seeds* extract was used as both reducing and stabilising agent, and the nanocomposites were biosynthesised according to the literature approach (Nasrollahzadh *et al.*, 2016). For the synthesis of Pd, CuO and Pd/CuO nanocomposite, there is no surfactant, capping agent and template were utilised in this approach.

Prior to preparing Pd-CuO/MWCNTs nanocomposite, the MWCNTs were first oxidised in a 40 mL acidic combination of H₂SO₄/HNO₃ with a 3:1 ratio, then ultrasonicated for 5 hours. The oxidized MWCNTs were filtered and washed several times with ultra-pure water to eliminate the acidic contents, and then vacuum dried at 80 °C overnight. After that, the dried oxidized MWCNTs and Pd-CuO were sonicated for 30 min in acetone. The freshly generated Pd-CuO/MWCNTs nanocomposites were filtered and dried at 80 °C for 1 h. in a vacuum oven, then heated at 1°C/min to at 200° C in an oven. For comparison, Pd and CuO supported MWCNTs nanocomposites were also synthesized.

Preparation of Pd-CuO/MWCNTs/GCE

The GCE was first cleaned using 0.3 μm alumina powder using a BAS polishing kit followed by an ultrasonic bath in ethanol for 10 min. 10 mg of Pd-CuO/MWCNTs nanocomposites was ultrasonicated in 10 mL acetone and 10 μL of Pd-CuO/MWCNTs was then dropped on the surface of cleaned GCE and dried under the lamp for 30 minutes and rinsed in ultra-pure water several times. A similar procedure was repeated to modify the GCE with Pd, CuO and MWCNTs sensor for the electrocatalytic reduction of pesticide. Modified GCE was washed with ultrapure water and dried at room temperature for voltammetry study. A volume of 10.0 mL of Britton-Robinson (BR) buffer was added to the electrochemical cell for the experiments. Before the voltammetric measurements, the electrochemical solution was deoxygenated for 5 min using nitrogen gas.

RESULTS AND DISCUSSION

The morphology of the Pd-CuO/MWCNTs nanocomposites was investigated through the Scanning electron microscope technique (Fig. 2). The surface observed for the electrode fabricated with Pd, CuO and Pd-CuO/MWCNTs, appeared to be rougher, irregular in shape and size, which indicated that surface area was very large in SEM analysis (Fig. 2a & 2b). The palladium nanoparticles were observed in spherical shapes or clusters on the surface of MWCNTs with a diameter of around ~ 60 nm. However, the presence of patterned structures generated by globular crystals, which may be associated with the formation of aggregated particles. The diameter of a meandering form of carbon nanotubes was in the range of 10 nm, while the length could reach more than several micrometres. Fig. 2c clearly shows that Pd-CuO/MWCNTs with the granular structure were distributed on the GCE surface, whereas the bare GCE displayed a relatively smooth surface. Thus, MWCNTs on the electrode contributed to the enhancement of the surface area. The Pd-CuO/MWCNTs surface also was analysed by EDX and the results are shown in Fig. 3. The EDX spectroscopy

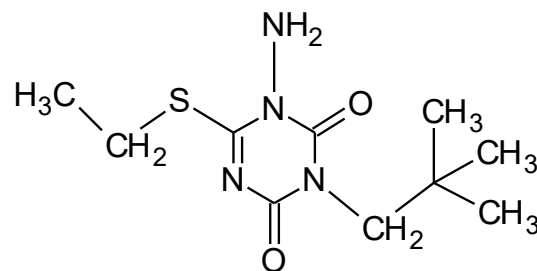


Fig. 1. Chemical structure of ametrudione pesticide (Choudhury et al., 2016).

showed that the nanocomposites were mainly composed of Cu, Pd, C and O elements.

The glassy carbon electrode was modified with Pd, MWCNTs, CuO and Pd-CuO/MWCNTs nanocomposites. Pd-CuO supported MWCNTs modified electrode for ametrudione detection was improved in terms of sensitivity, stability and mechanical asset. The cyclic voltammograms of ametrudione ($6.0 \mu\text{g}\cdot\text{mL}^{-1}$), in Britton-Robinson buffer at pH 5.0 and scan rate 50 mVs^{-1} . Fig. 4 compares cyclic voltammograms of ($6.0 \mu\text{g}\cdot\text{mL}^{-1}$) ametrudione at bare GCE, CuO/GCE, MWCNTs/GCE, Pd/GCE and Pd-CuO/MWCNTs/GCE. The reduction peak appeared at -1.12 V , which was due to the reduction of two carbonyl groups of the ametrudione and no oxidation peak was observed in the anodic branch that suggested that the process was irreversible. The cyclic voltammogram of Pd-CuO/MWCNTs/GCE in Fig. 4e reveals a significant background current, which indicated that the electrode had been effectively modified as seen by the substantial double-layer charging current. The CuO/GCE (Fig. 4b) did not exhibit a significant variation in their background currents compared to the MWCNTs (Fig. 4c). As shown in the figure, the peaks of pesticide at different potentials and the lowest peak potential were -1.12 V for the electrode Pd-CuO/MWCNTs/GCE, which was significant than the unmodified GCE. When the peak current of ametrudione was compared at these electrodes, the maximum peak current was $24.38 \mu\text{A}$, corresponding to the electrode of Pd-CuO/MWCNTs/GCE. This value was larger five times compared with the value recorded for the unmod-

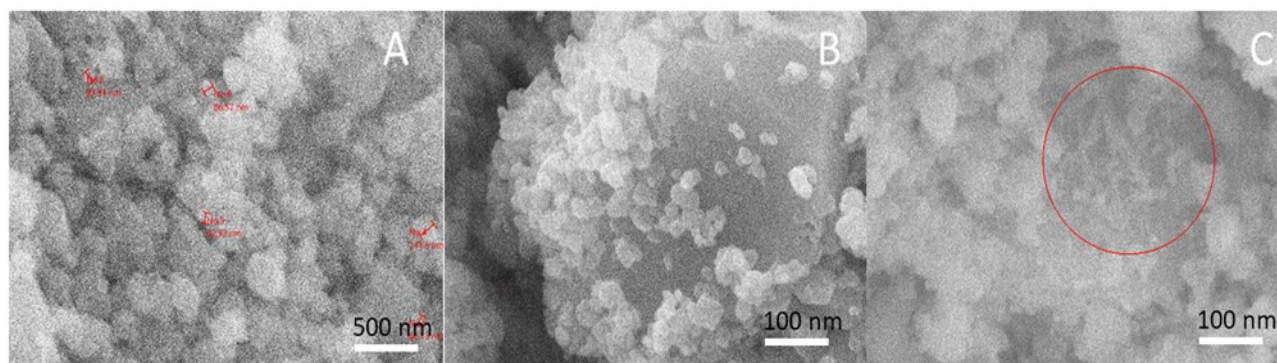


Fig. 2. Scanning electron microscope images of Pd (A), CuO (B) and Pd-CuO supported MWCNTs.

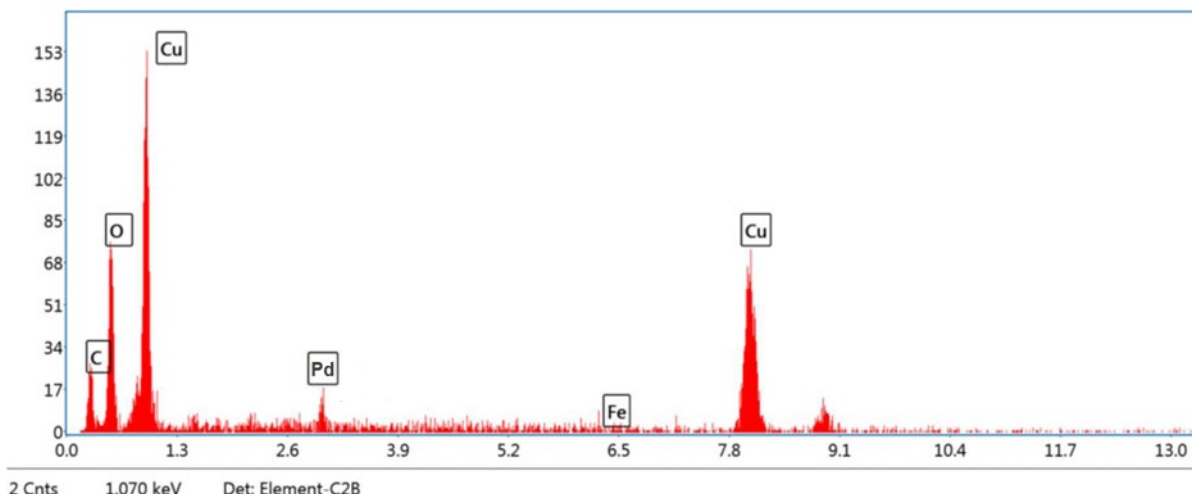


Fig. 3. EDX spectrum of Pd-CuO supported MWCNTs.

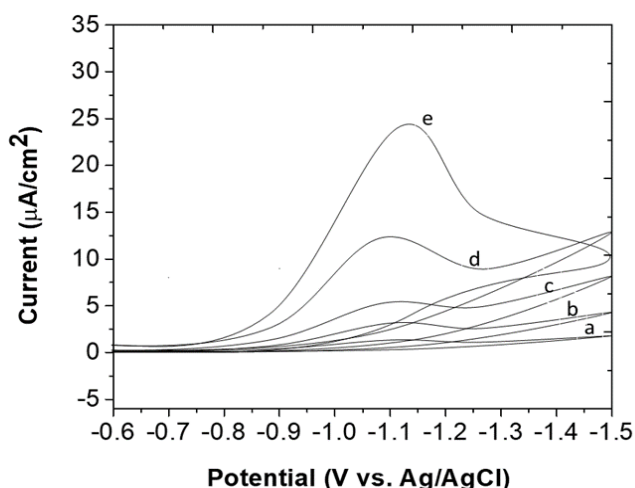


Fig. 4. Cyclic voltammograms for $5.0 \mu\text{g}\cdot\text{mL}^{-1}$ ametrudione at bare GCE (a), CuO/GCE (b), MWCNTs/GCE (c), Pd/GCE (d) and Pd-CuO/MWCNTs/GCE (e) in pH 5.0 (0.10 M of BR buffer); accumulation potential -1.1 V, accumulation time 100 s, pulse amplitude 50 mV and the scan rate 40 mV s^{-1} .

ified bare GCE (Fig. 4a). The CuO/GCE (Fig. 4b) and MWCNTs/GCE (Fig. 4c) also showed improvement in the peak current of ametrudione as twice as that of bare GCE, whereas the current for CuO/GCE was not significantly different to bare GCE. On the basis of the above results, the Pd-CuO, supported MWCTs was successfully immobilised on the GCE surface and synergistic electro-active character. Additionally, the electrochemical sensor provided high electro-catalytic activity because of their large surface area and an efficient electron transfer.

The differential pulse voltammetric response of $6.0 \mu\text{g}\cdot\text{mL}^{-1}$ ametrudione studied at Pd-CuO/MWCNTs with Britton-Robinson buffer at pH 5.0 as a supporting electrolyte the pulse amplitude of 30 mV and scan rate of 50 mVs^{-1} is shown in Fig. 5. At bare GCE (Fig. 5a), no obvious reduction peak was attained for $6.0 \mu\text{g}\cdot\text{mL}^{-1}$

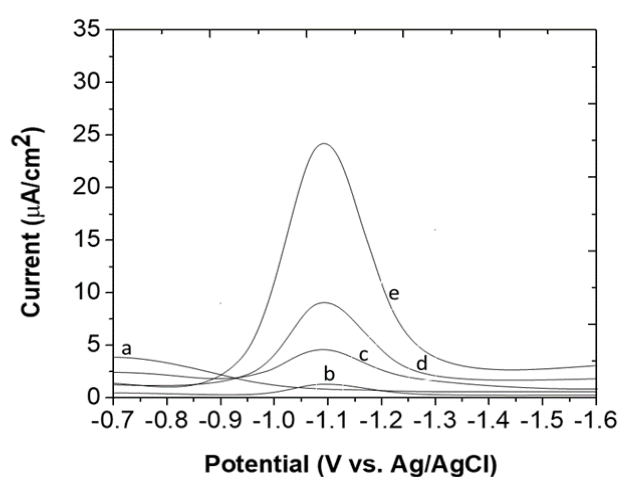


Fig. 5. Differential pulse voltammograms for $6.0 \mu\text{g}\cdot\text{mL}^{-1}$ ametrudione at bare GCE (a), CuO/GCE (b), MWCNTs/GCE (c), Pd/GCE (d) and Pd-CuO/MWCNTs/GCE (e) in pH 5.0 (0.10 M of BR buffer); accumulation potential -1.1 V, accumulation time 100 s, pulse amplitude 50 mV and the scan rate 40 mV s^{-1} .

ametrudione pH 5.0. At fabricated CuO/GCE (Fig. 5b) and MWCNTs/GCE (Fig. 5c), the small reduction peak current was observed expressively significant than the bare GCE reduction current. The Pd/GCE (Fig. 5d) showed a respectable reduction peak current that appeared due to great electron mobility. Furthermore, the enrichment of the reduction peak current of the Pd-CuO/MWCNTs modified GCE, was acquired owing to the expectant area and great electrical conductivity of the ametrudione (Fig. 5e). Therefore, the differential pulse voltammograms were observed for bare GCE, CuO/GCE, Pd/GCE, and MWCNTs/GCE. It was found not to be so effective for reducing ametrudione.

Optimum parameters on the response of ametrudione

The influence of pH of the medium significantly enhanced the reduction of the peak current of ametrudi-

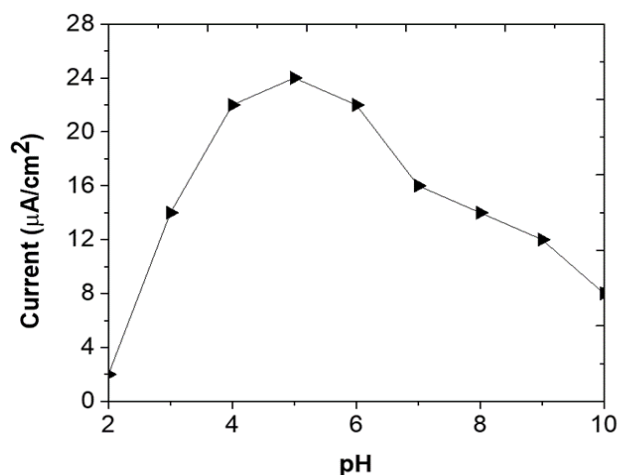


Fig. 6. Effect of pH on the electrochemical response of the Pd-CuO/MWCNTs/GCE; accumulation potential -1.1 V, accumulation time 100 s, pulse amplitude 50 mV and the scan rate 40 mV s $^{-1}$.

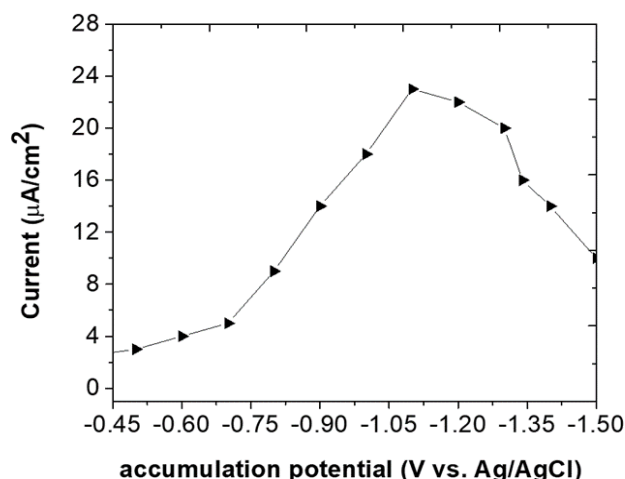


Fig. 7. Effect of accumulation potential on the electrochemical response of ametrudione at Pd-CuO/MWCNTs/GCE; accumulation time 100 s, pulse amplitude 50 mV and the scan rate 40 mV s $^{-1}$.

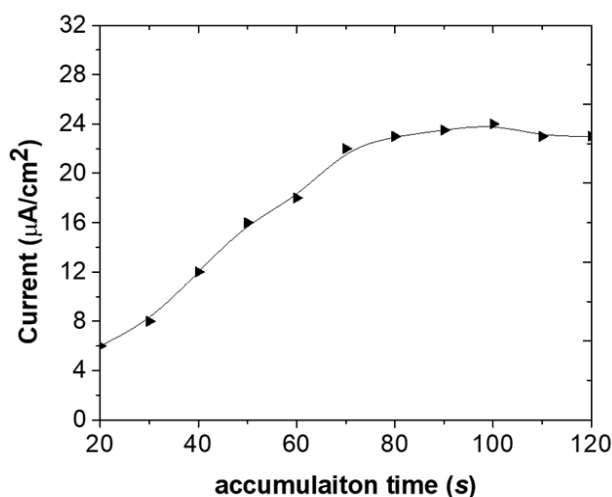


Fig. 8. Effect of accumulation time on the electrochemical response of ametrudione at Pd-CuO/MWCNTs/GCE; accumulation potential -1.1 V, pulse amplitude 50 mV and the scan rate 40 mV s $^{-1}$.

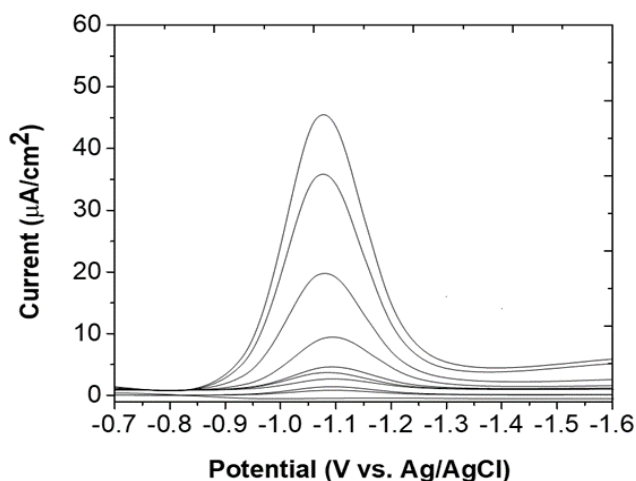


Fig. 9. Differential pulse voltammograms recorded at Pd-CuO/MWCNTs/GCE for different concentrations of ametrudione (0, 0.1, 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 8.0 and 10.0 $\mu\text{g}\cdot\text{mL}^{-1}$ (from bottom to top)); in pH 5.0 (BR buffer); accumulation potential -1.1 V, accumulation time 100 s, pulse amplitude 50 mV and the scan rate 40 mV s $^{-1}$.

one. The effect of pH on the reduction peak current of ametrudione investigated in the range of pH 2.0-12.0 with Britton-Robinson buffer indicated that process, responsible for this behaviour, must be the reduction of the carbonyl group in the ametrudione and the maximum peak, which was observed at pH 5.0 on Pd-CuO/MWCNTs/GCE. It indicates that the proton concentration in the acidic solution was superior for the reduction of carbonyl group of ametrudione. Moreover, the peak potential of ametrudione shifted negatively constantly with the increase of pH and as seen in Fig. 6. As a result, Britton-Robinson buffer (pH 5.0) was considered as the most suitable accompanying electrolyte for further investigation. Through the electrochemical reduc-

tion of ametrudione, the pH implies protonation of the reactive portion of the molecule. This behaviour suggests that protons are involved in chemical processes during the electrochemical reduction of ametrudione. Based on these results, Scheme 1 depicts an electrochemical reduction of ametrudione involving the same number of protons and electrons.

The optimisation of the differential pulse voltammetry parameters is essential to achieve the best conditions of the electrochemical analysis of ametrudione at Pd-CuO/MWCNTs/GCE electrode. The effect of scan rate on the differential pulse voltammetric responses at Pd-CuO/MWCNTs/GCE using Britton-Robinson buffer as a supporting electrolyte showed that the scan rate, the

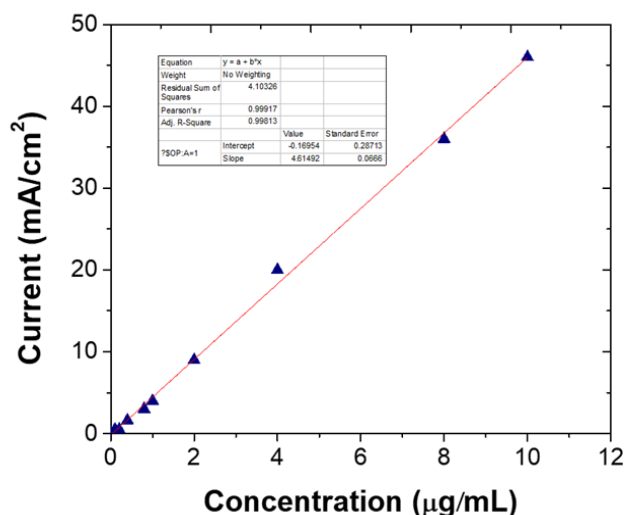


Fig.10. Calibration curve of ametrudione at Pd-CuO/MWCNTs/GCE; in pH 5.0 (BR buffer); accumulation potential -1.1 V, accumulation time 100 s, pulse amplitude 50 mV and the scan rate 40 mV s⁻¹.

current response, and increasing the scan rate from 0 mVs⁻¹ to 150 mVs⁻¹, such gave the maximum response at 50 mVs⁻¹. The reduction peak of ametrudione is observed in the potential range of -0.5-1.6 V shifting more towards negative potential with an increasing scan rate. The deposition potential was chosen at -1.11 V, which corresponds to the reduction potential for ametrudione under optimum conditions (Fig. 7). This intriguing study indicated electrochemical reduction of ametrudione pesticide products on DPV's maximum peak current. Hence, the enhanced absorption and the accumulation of ametrudione on the Pd-CuO/MWCNTs/GC electrode after its pre-treatment at -1.1 V can be exploited here to increase the sensitivity of the DPV significantly. Fig. 8 shows that the signal has a prolongation of the accumulation time up to 100 s. The peak current increased rapidly with the increase of accumulation time and almost reached a platform after 100 s. For analytical purposes, Pd-CuO/MWCNTs/GC electrode was initially pre-treated for 100 s into the solution of 6.0 µg·mL⁻¹ of ametrudione. Before it was used for measuring the concentration of ametrudione to achieve down to the low ppm-level, Britton-Robinson buffer solution was used. The additional preconcentration time of 100 s was em-

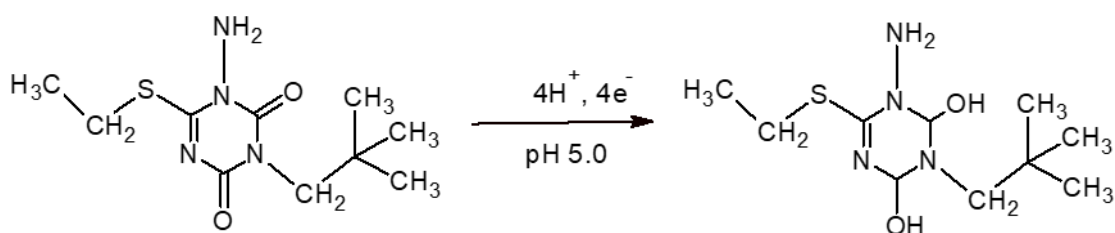
Table 1. Results for the interference study regarding some inorganic and biomolecules on the voltammetric reduction of 6.0 µg·mL⁻¹ at Pd-CuO/MWCNTs/GCE.

Interfering species	Tolerance (µg·mL ⁻¹)*
Na ⁺ , NH ₄ ⁺	1000
OH ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , Cl ⁻	1000
Citric acid	500
Ascorbic acid	400
Urea	300
Thiodicarb	20

*the level with maximum concentration of foreign for deviation less than $\pm 5\%$.

ployed before each measurement. The selected pre-treatment time is enough to obtain a stable analytical signal. Accordingly, the optimum conditions for recording a maximum developed and sharpened peak for ametrudione are accumulation time 100 sec, accumulation potential -1.1 V, scan rate 50 mVs⁻¹, pulse amplitude 30 mV, and optimum temperature 25 °C. Furthermore, it should be noted that Pd-CuO nanoparticles are electro-catalyst which in synergism with a developed surface area of MWCNTs enables the successful application of this sensor for the determination of ametrudione pesticide.

Under the voltammetric conditions, the selectivity of the Pd-CuO/MWCNTs/GCE sensor was evaluated by testing its electrochemical response to 6.0 µg·mL⁻¹ (pH 5.0) ametrudione pesticide in the presence of interfering substances. The known amounts of NH₄⁺, Na⁺, K⁺, Ca²⁺, Ag⁺, HCO₃⁻, SO₄²⁻, CO₃²⁻, Cl⁻, NO₃⁻, urea, ascorbic acid and thiodicarb on the determination of ametrudione in water samples indicated that the thiodicarb is one of the most common compounds that interacted with ametrudione in water samples. The electrochemical reduction of ametrudione had negligible influence with a twenty-fold excess of thiodicarb and the results are summarised in Table 1. The developed sensor behaved selectively with respect to ametrudione because there were no significant changes in the peak current for ametrudione reduction ($< \pm 5\%$) in the presence of interfering species.



Scheme 1. Electrochemical reduction mechanism of ametrudione.

Voltammetric performance on the determination ametrudione

Based on the optimised parameter, a typical differential pulse voltammogram recorded in various concentration ranged from $0.10 \mu\text{g}\cdot\text{mL}^{-1}$ to $10 \mu\text{g}\cdot\text{mL}^{-1}$ at Pd/MWCNTs/GCE as shown in Fig. 9. The peak currents showed a linear dependence on the concentration range from $0.10 \mu\text{g}\cdot\text{mL}^{-1}$ to $10 \mu\text{g}\cdot\text{mL}^{-1}$ of ametrudione on Pd-CuO/MWCNTs/GCE. Fig.10 represents the calibration plot recorded using the standard addition method. The linear equation was $I (\mu\text{A}) = 0.169 + 4.614 C \mu\text{g}\cdot\text{mL}^{-1}$ with a correlation coefficient of 0.998. The detection limit ($\text{LOD} = 3(\text{sd})/b$) and quantitation of limit ($\text{LOQ} = 10(\text{sd})/b$) were determined, where sd being the standard deviation of the intercept and b denoting the slope of the calibration graph. On Pd-CuO/MWCNTs/GCE electrochemical sensor, the LOD and LOQ of ametrudione were found to be $0.0796 \mu\text{g}\cdot\text{mL}^{-1}$ and $0.5560 \mu\text{g}\cdot\text{mL}^{-1}$, respectively.

The practicality of the developed method was validated by measuring ametrudione in spiked samples of tap, agricultural runoff and river water. To avoid the matrix effect, the standard addition method was used to carry out the quantitative assays. Moreover, the determinations were performed in quintuple to check the precision of the assays. In order to check the precision of the method, five replicate analyses of each sample,

were carried out. The average recoveries obtained in water samples were 97.6–99.9% (Table 2) with a relative standard deviation of 1.69%, respectively. The suggested electrochemical characteristics, such as dynamic range, LOD and LOQ are compared with other conventional metaloxide-based sensors as shown in Table 3. Obviously, the proposed Pd-CuO/MWCNTs/GCE electrochemical sensor had an excellent linear range, LOD, and LOQ values comparable to reported values in the literature. Therefore, the CuO/MWCNTs/GCE sensor has good constancy and high electron kinetics to consider as an alternative electrochemical sensor.

The repeatability of the established Pd-CuO/MWCNTs/GCE sensor was verified by taking five successive determinations with a fixed amount of $6.0 \mu\text{g}\cdot\text{mL}^{-1}$ of ametrudione on the same day under ideal conditions. The Pd-CuO/MWCNTs/GCE sensor achieved in retaining 98.0% of the initial peak response on average peak current. These findings validated the advanced Pd-CuO/MWCNTs/GCE sensor high repeatability, large surface area, and precision. The difference between measurements taken under different conditions on a subject is referred to as reproducibility. In the voltammetric signals, minimal variations with an equivalent standard deviation value (RSD) of 1.72% were observed within the day at ambient temperatures. In addition, the electrode reproducibility was persistently ex-

Table 2. Application of the recommended method to the determination of ametrudione in water samples.

Sample	Amount added ($\mu\text{g}\cdot\text{mL}^{-1}$)	Amount found ($\mu\text{g}\cdot\text{mL}^{-1}$)	Recovery* (%)	Standard deviation
Tap water	10.0	9.80	98.0	0.014
	25.0	24.6	98.4	0.025
Agricultural run-off Water	10.0	9.99	99.9	0.450
	25.0	24.9	99.6	0.160
River water	10.0	9.92	99.2	0.065
	25.0	24.4	97.6	0.020

*n=5 (no. of determinations)

Table 3. Comparison of the proposed electrochemical sensor with the reported electrochemical sensors for the electrochemical analysis of various pesticides.

Technique	Modified electrode	Linear concentration range	Limit of detection	Ref.
DPV	CPE	6.7-117.4 μM	2.04 μM	Papp <i>et al.</i> , 2009
CV	NH ₂ -SBA-15/CPE	0.3-18 μM	0.05 μM	Thiago <i>et al.</i> , 2016
SWV	PGC	1.25-100 μM	2.8 μM	Brahim <i>et al.</i> , 2018
CV	GCE	10.9-1956 μM	30.1 μM	Guzsvany <i>et al.</i> , 2005
SWV	MWCNT/GCE	0.2-60 μM	0.08 μM	Salehzadesh <i>et al.</i> , 2016
DPV	SiO ₂ /MWCNTs/RuPc	3-66 μM	1.62 μM	Canevari <i>et al.</i> , 2016
DPV	Pd-CuO/MWCNTs/GCE	0.1 to 10.0 $\mu\text{g}\cdot\text{mL}^{-1}$	0.0796 $\mu\text{g}\cdot\text{mL}^{-1}$	Present Work

CPE: carbon paste electrode; **NH₂-SBA-15/CPE:** Amino-functionalized SBA-15/carbon paste electrode; **SWV:** Square wave voltammetry; **PGC:** pre-treated glassy carbon electrode; **SiO₂/MWCNTs/RuPc:** ruthenium phthalocyanine on silica-coated multi-walled carbon nanotubes.

aminated over the course of three days, and the RSD level was discovered to be ~1.4%. This study exposes the modification of glassy carbon electrodes with Pd-CuO/MWCNTs nanoparticles, showing greater constancy and reproducibility.

Conclusion

The electrochemical reduction of ametrudione pesticide in water (river water, tap, agricultural run-off) samples were achieved successfully by differential pulse voltammetry. An electrochemical sensor of Pd-CuO/MWCNTs can be easily prepared and fabricated on a glassy carbon electrode for ametrudione detection. The proposed sensor has shown to be a fairly efficient technique for rapid and sensitive determination of ametrudione pesticide at a glassy carbon electrode improved with palladium supported multiwalled carbon nanotubes. The obtained Pd-CuO/MWCNTs sensor possessed a decent morphology with fast electron-transport and enabled advantageous electrocatalytic behaviour to reduce ametrudione with relatively low detection and quantitation limits. Sensing features of Pd-CuO/MWCNTs/GCE towards ametrudione were found to be superior in comparison to the bare GCE, MWCNTs/GCE, CuO/GCE and Pd/GCE, respectively. The Pd-CuO/MWCNTs/GCE electrochemical sensor offered a low detection limit, quantification limit, good reproducibility, easy construction and short response time for the reduction of ametrudione.

Conflict of interest

The authors declare that they have no conflict of interest.

REFERENCES

1. Baghayeri, M., Amirhassan, A., Maryam, F., Marzieh, N. & Ali, E. (2021). Electrochemical detection of bisphenol a on a MWCNTs/CuFe₂O₄ nanocomposite modified glassy carbon electrode. *Materials Chemistry and Physics*, 261, 124247. <https://doi.org/10.1016/j.matchemphys.2021.124247>.
2. Beckie, H.J., Harker, K.N., Hall, L.M., Warwick, S.I., Legere, A., Sikkema, P.H., Clayton, G.W., Thomas, A.G., Leeson, J.Y., Seguin-Swartz, G. & Simard, M.J. (2006). A decade of herbicide-resistant crops in Canada. *Canadian Journal of Plant Science*, 86,1243-1264. <https://doi.org/10.4141/P05-193>.
3. Ben Ali Hassine, C. & Barhoumi, H. (2018). Electrochemical study of a glassy carbon electrode modified by poly-4-nitroaniline-reduced/murexide and its sensitivity for metal ions. *Analytical Biochemistry*, 560, 30-38. <https://doi.org/10.1016/j.ab.2018.08.023>.
4. Bhvimane, S.J., Mruthyunjayachari, C.D., Malathesh, P., Mounesh, P., Sharankumar, T.M. & Venugopala Reddy, K.R. (2019). Electrochemical sensing based MWCNT-Cobalt tetra substituted sorbaamide phthalocyanine onto the glassy carbon electrode towards the determination of 2-Amino phenol: A voltammetric study, *Sensors and Actuators B: Chemical*, 301, 127078. <https://doi.org/10.1016/j.snb.2019.127078>.
5. Brahim, M.B., Elahmadi, M.F., Ammar, H.B. & Samet, Y. (2018) Determination of ultra-trace amounts of neonicotinoid insecticide imidacloprid by cyclic and square wave voltammetric methods using pretreated glassy carbon electrode. *Glob. Nest J.* 20, 628-636. <https://doi.org/10.30955/gnj.002509>.
6. Canevari, T.C., Prado, T.M., Cincotto, F.H. & Machado, S.A.S. (2016) Immobilization of ruthenium phthalocyanine on silica-coated multi-wall partially oriented carbon nanotubes: Electrochemical detection of fenitrothion pesticide. *Mater. Res. Bull.* 76, 41–47, <http://dx.doi.org/10.1016/j.materresbull.2015.12.007>.
7. Choudhury, P.P., Singh, R., Ghosh, D. & Sharma, A.R. (2016). Herbicide use in Indian agriculture. *ICAR-Directorate of Weed Research, Jabalpur, Madhya Pradesh*, 110.
8. Costa, D.J.E., Santos, J.C.S., Sanches-Brando, F.A.C., Ribeiro, W.F., Salazar-Banda, G.R. & Araujo, M.C.U. (2017). Boron-doped diamond electrode acting as a voltammetric sensor for the detection of methomyl pesticide, *Journal of Electroanalytical Chemistry*, 789, 100-107. <https://doi.org/10.1016/j.jelechem.2017.02.036>.
9. Dan, Du., Xiaxue, Ye., Jie, Cai., Juan, Liu. & Aidong, Z. (2010). Acetylcholinesterase biosensor design based on carbon nano tube-encapsulated polypyrrole and polyaniline copolymer for amperometric detection of organophosphates, *Biosens. Bioelectron.*, 25, 2503-2508. <https://doi.org/10.1016/j.bios.2010.04.018>.
10. Esmail, S., Amir, H.K., Shahdost-fard, F., Ebrahim, N., Plonska-Brzezinska, M.E., Rahimi-Nasrabadi, M. & Farhad, A. (2020). A glassy carbon electrode modified with carbon nanoions for electrochemical determination of fentanyll, *Materials Science and Engineering, C*, 110, 110684. <https://doi.org/10.1016/j.msec.2020.110684>.
11. Forouzesh, A., Zand, E., Soufizadeh, S. & Foroushani, S.S. (2015). Classification of herbicides according to chemical family for weed resistance management strategies – an update. *European Weed Research Society*, 55, 334-358. <https://doi.org/10.1111/wre.12153>.
12. Gamze, E. & Ersin karagozler, A. (1997). Investigation and comparison of the electrochemical behaviour of some organic and biological molecules at various conducting polymer electrodes, *Talanta* 44, 2011-2018. [https://doi.org/10.1016/S0039-9140\(96\)02196-0](https://doi.org/10.1016/S0039-9140(96)02196-0).
13. Gonçalves-Filho, D., Gonçalves Silva, C.C. & De Souza, D. (2020). Pesticides determination in foods and natural waters using solid amalgam-based electrodes: Challenges and trends, *Talanta*, 212, 120756. <https://doi.org/10.1016/j.talanta.2020.120756>.
14. Guzsvany, V.J., Gaal, F.F., Bjelica, L.J. & Okresz, S.N. (2005). Voltammetric determination of imidacloprid and thiamethoxam. *J. Serbian Chem. Soc.*, 70, 735–743. <https://doi.org/10.2298/JSC0505735G>.
15. Ha, T.J., Hong, M.H., Park, C.S. & Park, H.H. (2013). Gas sensing properties of ordered mesoporous TiO₂ film enhanced by thermal shock induced cracking. *Sens. Actuator B Chem*, 181, 874-879. <https://doi.org/10.1016/j.snb.2013.02.093>.

16. Jian-Chun, Ma. & Wei-De, Z. (2011). Gold nanoparticle-coated multiwall carbon nanotube-modified electrode for electrochemical determination of methyl parathion, *Microchim Acta*, 175, 309–314. <https://doi.org/10.1007/s00604-011-0681-5>.
17. Khadem, M., Fardbod, F., Norouzi, P., Abbas Rahimi, F., Mohammad Reza, G., Rasoul, Y. & Seyed, J.S. (2020). Voltammetric determination of carbofuran pesticide in biological and environmental samples using a molecularly imprinted polymer sensor, a multivariate optimization, *Journal of Analytical Chemistry*, 75 (5), 669-678. <https://doi.org/10.1134/S1061934820050068>.
18. Kniss, A.R. (2017). Long-term trends in the intensity and relative toxicity of herbicide use, *Nature Communications*, 8 (14865), 1-7. <https://doi.org/10.1038/ncomms14865>.
19. Koksoy, B., Akyuz, D., Senocak, A., Durmus, M. & Demirbas, E. (2021). Sensitive, simple and fast voltammetric determination of pesticides in juice samples by novel BODIPY-phthalocyanine-SWCNT hybrid platform, *Food and Chemical Toxicology*, 147, 1118886. <https://doi.org/10.1016/j.fct.2020.111886>.
20. Legere, A., Beckie, H.J., Stevensorn, F.C. & Thomas, A.G. (2000). Survey of management practices affecting the occurrence of wild oat (*Avena fatua*) resistance to acetyl-CoA carboxylase inhibitors. *Weed Technology* 14, 366-376. [https://doi.org/10.1614/0890-037X\(2000\)014\[0366:SOMPAT\]2.0.CO;2](https://doi.org/10.1614/0890-037X(2000)014[0366:SOMPAT]2.0.CO;2).
21. Nasrollahzadh, M. (2016). Pd/CuO nanoparticles as a highly effective catalyst for the cyanation of aryl halides under ligand-free conditions. *Tetrahedron Letters*, 57 (3):337-339. <https://doi.org/10.1016/j.tetlet.2015.12.019>.
22. Papp, Z., Svancara, I., Guzsavny, V., Vytras, K. & Gaal, F. (2009). Voltammetric determination of imidacloprid insecticide in selected samples using a carbon paste electrode. *Microchim. Acta*, 166, 169–175. <https://doi.org/10.1007/s00604-009-0181-z>.
23. Pourakbari, Z., Aliakbar, A. & Sheykhani, M. (2020). A metal-catech composite electrode for determination of paraquat in various samples by Ad-differential pulse cathodic stripping voltammetry, *Talanta* 212, 120793. <https://doi.org/10.1016/j.talanta.2020.120793>.
24. Rayburn, A. L., Moody, D.D. & Freeman, J.L. (2005). Cytotoxicity of technical grade versus formulations of atrazine and acetochlor using mammalian cells. *Bulletin of Environmental Contamination and Toxicology*, 75(4), 691–698. <https://doi.org/10.1007/s00128-005-0807-8>.
25. Rich, J.D., Gabriel, S.M. & Schultz-Norton, J.R. (2012). In vitro effects of herbicides and insecticides on human breast Cells. *International Scholarly Research Notices*, 2012, 1-9. <https://doi.org/10.5402/2012/232461>.
26. Salehzadeh, H., Ebrahimi, M., Nematollahi, D. & Salarian, A.A. (2016). Electrochemical study of fenitrothion and bifenox and their simultaneous determination using multi-walled carbon nanotube modified glassy carbon electrode. *J. Electroanal. Chem.* 767, 188–194, <http://dx.doi.org/10.1016/j.jelechem.2016.02.011>.
27. Selim, H.M. (2003). Retention and runoff losses of atrazine and metribuzin in soil. *Journal of Environmental Quality*, 32 (3), 1058–1071. <https://doi.org/10.2134/jeq2003.10.58>.
28. Sepsenon, G.R., Dykstra, M.D., McLaren, R.D. & Hamill, A.S., (1990). Agronomic practices influencing triazine-resistant weed distribution in Ontario. *Weed Technology*, 4 (1), 199-207. <https://doi.org/10.1017/S0890037X00025227>.
29. Sira, L.R., de Lima, F., Cardoso, C.A.I. & Arruda, G.J. (2015). Electrochemically pretreated zeolite-modified carbon-paste electrodes for determination of linuron in an agricultural formulation and water. *Electrochimica Acta*, 151, 609-618. <https://doi.org/10.1016/j.electacta.2014.11.008>.
30. Subbalaskhamma, M. & Jayarama Reddy, S. (1994). Electrochemical behavior of formetanate and chloridimeform pesticides. *Electroanalysis*, 6, 612-615. <https://doi.org/10.1002/elan.1140060716>.
31. Thiago, C. C., Thiago, M.P., Fernando, H. C. & Sergio, A.S.M. (2016). Immobilization of ruthenium phthalocyanine on silica-coated multi-wall partially oriented carbon nanotubes: Electrochemical detection of fenitrothion pesticide. *Materials Research Bulletin*, 76, 41-47. <https://doi.org/10.1016/j.materresbull.2015.12.007>.
32. Thiago, M.B.F.O., Francisco W.P.R., Camila P.S., Giancarlo, R.S., Pedro de, L., Adriana N.C. & Simone, M. (2020). Current overview and perspectives on carbon-based (bio) sensors for carbamate pesticides electroanalysis. *TrAC Trends in Analytical Chemistry*, 124, 115779. <https://doi.org/10.1016/j.trac.2019.115779>.
33. Vieira da Silva, L., Nicholas, D.S., Andresa, K.A.A., Dave Di, E.R.S., Ana Caroline, F.S., Mesaque, C.F., Dimas, J.P.L., Phabyanno, R.L. & Marilia, O.F.G. (2021). A new electrochemical sensor based on oxidized capsaicin/multi-walled carbon nanotubes/glassy carbon electrode for the quantification of dopamine, epinephrine, and xanthurenic, ascorbic and uric acids, *Journal of Electroanalytical Chemistry*, 881, 114919. <https://doi.org/10.1016/j.jelechem.2020.114919>.