Biosynthesis of α-Fe₂O₃-CdO Nanocomposites for Electrochemical Detection of Chloridazon Herbicide

Puthalapattu Aruna 1, Puthalapattu Reddy Prasad 2*, Punyasamudram Sandhya 3, N.V.S.S. Seshagiri Rao 4, Neelam Yugandhar Sreedhar 4

1 Electroanalytical Lab, Department of Chemistry, S.V. University, Tirupati-517502, A.P., India; arunaputhalapattu@gmail.com (P.A.);
2 Department of Chemistry, Institute of Aeronautical Engineering (IARE), Dundigal-500043, Hyderabad, India; prprasad@iare.ac.in (P.R.P.);
3 Department of Chemistry, Sri Padmavati Mahila Visvavidyalayam, Tirupati-517502, A.P., India; sanrchem@gmail.com (P.S.);
4 Department of Physics, Institute of Aeronautical Engineering (IARE), Dundigal-500043, Hyderabad, India; seshu.nvss2004@gmail.com (N.V.S.S.S.R.);
* Correspondence: prprasadchem@gmail.com (P.R.P.);

Abstract: Biosynthesised α-Fe₂O₃-CdO electrochemical nanosensor attained from Coriandrum sativum leaves extract and fabricated on the screen-printed electrode to detect chloridazon (CLZ) herbicide in agricultural food samples. Scanning electron microscopy, energy dispersive x-ray analysis, X-ray diffraction spectroscopy, cyclic voltammetry, and differential pulse voltammetry were used to investigate the α-Fe₂O₃-CdO electrochemical nanosensor. The optimization factors of the effect of pH, accumulation time, accumulation potential, and foreign substances were elevated. The α-Fe₂O₃-CdO/SPE electrochemical nanosensor shows the significant voltammetric response for the CLZ detection. Foreign substances did not considerably influence pesticide detection. Dynamic linear CLZ plot for a standard solution of CLZ was obtained in the concentration range of 0.1 to 36.00 µg·mL⁻¹ (R=0.995) with a limit of detection 0.059 µg·mL⁻¹ and a quantification limit of 0.179 µg·mL⁻¹. The proposed electrochemical nanosensor was used to detect CLZ in agricultural food samples and agreeable recovery results.

Keywords: chloridazon; electrode; nanosensor; herbicide; agricultural food.

© 2021 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Chloridazon (CLZ) (5-amino-4-bromo-2-phenylpyridazin-3(2H)-one) acts as a systemic leaf and soil herbicide by inhibiting the photosynthesis that belongs to the group of pyradazinone [1]. It was used for pre-plant, pre-emergence, and early post-emergence use to control annual broad-leaved weeds on sugar beets and red table beets [2]. Existing data indicate that CLZ is portable in various soil types, and in this way, it has the potential to enter surface and groundwater [2,3]. Uncertainty, it perseveres for a long time because its degradation is slow and harmful to the human being [4,5]; therefore, it is concerned with monitoring pesticides [6-8]. Many investigators have reported monitoring pesticide residues in food, water, and soil samples [9–16].

Voltammetric methods have been widely working on pesticide detection at bare electrodes [17]. Recently, the use of voltammetry on carbon paste electrode (CPE) [18], silver-
amalgam film electrode (Hg(Ag)FE) [19], bismuth film electrode (BiFE) [20], and screen printed electrode (SPE) [21] was described. Bare electrodes have limitations that are overcome by using electrodes whose surfaces are modified with specific conductivity species. The modified screen-printing technology is well established for the production of thick-film electrochemical transducers [22]. This technology allows the mass production of highly reproducible, disposable, single-use screen-printed electrodes (SPEs) at a reduced cost [22,23]. To increase sensitivity and selectivity in the pesticide determination, different modification procedures of usual electrodes were applied. Though metal oxide nanostructures are extensively applied in significant disciplines such as optoelectronics, catalysis, dye-sensitizer solar cell, and sensor applications [24-26] because they provide a high surface area to volume ratio, hydrothermal stability, and various oxidation states, they possess unique optical, magnetic and electronic properties [27].

In the present investigation, the nanostructured \( \alpha \)-Fe\(_2\)O\(_3\)-CdO electrochemical nanosensor can be effortlessly prepared from Coriandrum sativum leaves extract. An electrochemically investigated the CLZ pesticide in agricultural food samples using biosynthesized \( \alpha \)-Fe\(_2\)O\(_3\)-CdO/SPE electrochemical nanosensor. The \( \alpha \)-Fe\(_2\)O\(_3\)-CdO/SPE electrochemical nanosensor has shown satisfactory recovery results for the quantified residues of CLZ pesticide in agricultural food samples by DPV. Under the optimized voltammetric operational conditions, the established \( \alpha \)-Fe\(_2\)O\(_3\)-CdO/SPE electrochemical nanosensor exhibited a specific and excellent electrocatalytic performance with a good sensitivity, selectivity, and wide dynamic concentration range towards the quantification of CLZ.

2. Materials and Methods

CdCl\(_2\), FeCl\(_3\), FeCl\(_2\), Nafion, H\(_3\)BO\(_3\), H\(_3\)PO\(_4\), glacial acetic acid, NaOH, and glucose were purchased from Merck Chemicals. Dopamine, uric acid, hydroquinone, ascorbic acid, and urea were purchased from Sigma-Aldrich. Beyer’s chemicals provided the chloridazon. A stock solution of CLZ (1000 µg·mL\(^{-1}\)) was prepared by dissolving CLZ in a suitable amount of methanol. Briton-Robison (BR) buffer solution ranging from pH 2.0 to 12.0 was prepared using extra pure acetic acid, phosphoric acid, and boric acid. For adjusting the pH of the solution, perchloric acid and sodium hydroxide were used. All aqueous solutions were made with deionized water from the Millipore direct-Q water system. All of the substances were reagent-grade analytical compounds.

2.1. Apparatus.

Electrochemical quantifications were carried out in Auto-Lab consisting of the modified screen-printed electrode as a working electrode. Before an electrochemical investigation, the experimental solutions were degassed by purified nitrogen gas in the voltammetric cell for 2 min. Scanning electron microscopy (SEM) images were acquired using an FEI-quanta 200 scanning electron microscope with a 10 kV acceleration voltage. X-ray powder diffraction (XRD) spectroscopy was used to determine the crystal structure of the resultant products using an X’Pert-Pro MPD (Holland) D/max-\( \gamma \)AX-ray diffractometer with Cu K\( \alpha \) radiation (\( \lambda \)=0.154178). All the experiments were performed at 25±1 °C, and pH measurements were carried out with Hanna instruments (Italy) pH meter.
2.2. Preparation of Coriandrum sativum leaves extract.

Fresh leaves of Coriandrum sativum (kothimeera) were collected from a local market in Tirupati, Andhra Pradesh, India. The collected leaves were rinsed carefully with distilled water and left to dry for a few hours. Then, the dried leaves were powdered in a mortar, and 20 g of powdered leaves were mixed with 200 ml deionized water and heated at 80 °C using a heater-stirrer for 30 min. The mixture was then filtered and centrifuged to eliminate plant residues and contaminants before being preserved for further study.

2.3. Biosynthesis of α-Fe$_2$O$_3$-CdO.

A typical green process was applied to make the α-Fe$_2$O$_3$-CdO electrochemical nanosensor. For this, 50 mL aliquots of 0.03 mol L$^{-1}$ FeCl$_3$, 0.01 mol L$^{-1}$ CdCl$_2$ solutions were prepared and transferred into a 250 mL beaker under constant stirring. Meanwhile, 100 mL of coriander leaves extract was gradually added to the 250 mL beaker and stirred at 80 °C for 6 hours with a magnet stirrer. Then the pH is adjusted to reach a pH value of 10.0 by adding an amount of 0.02 mol L$^{-1}$ NaOH drop by drop under stirred conditions. The mixture was stirred until a solid product with a light brownish-black color was obtained. Later, the obtained solid product was filtered and washed with double deionized water and ethanol in sequence and dried in a vacuum at 100 °C at 12h. The brown-black α-Fe$_2$O$_3$-CdO was obtained by calcining the produced heterogeneous nanostructure at 350 °C for 3h at a heating rate of 1 °C min. α-Fe$_2$O$_3$ and CdO were prepared using the procedure described for comparison purposes.

For an electrochemical measurement, the 20 mg of α-Fe$_2$O$_3$-CdO nanocomposite was dispersed in 0.5 mL nafion (2%) and made the paste for drop-casting. The SPE surface was modified with a slurry of α-Fe$_2$O$_3$-CdO paste and dried at room temperature for 60 min for using it as a working electrode. Similarly, α-Fe$_2$O$_3$/SPE and CdO/SPE working electrodes were prepared as a working electrode for assessment study.

2.4. Sample collection and preparation.

Meanwhile, the agricultural food samples were obtained from a local vegetable market in Rythu Bazar, Tirupati, Chittoor District, A.P. The food samples of spinach, lettuce, cauliflower, cucumber, and cabbage were washed with distilled water and stored in airtight plastic at −4 °C until evaluated. The chopped vegetable samples were weighed at 40 g and spiked with an appropriate amount of pesticide before resting for 30 minutes at room temperature. After that, 2 mL of acetonitrile was added, and the solution was homogenized by shaking for 20 min to ensure complete solvent evaporation. Then, the samples were centrifuged at 3600 rpm for 20 min, and the liquid supernatant was analyzed by voltammetry.

In the voltammetric cell, 10.0 mL of 6.0 µg/mL CLZ standard solution is transferred and added the required amount of BR buffer (pH 5.0). After attaining the voltammogram, required additions of standard solutions are added. After each addition, the voltammogram was recorded under similar experimental conditions. The accumulation time: 40 s; accumulation potential: -1.08 V; scan rate: 40 mVs$^{-1}$ and pulse amplitude: 30 mV are found to be the voltammetry optimum parameters for the detection of CLZ.
3. Results and Discussion

The α-Fe$_2$O$_3$-CdO electrochemical nanosensor was successfully attained via a modest and facile biosynthesis method. As synthesized α-Fe$_2$O$_3$-CdO electrochemical nanosensor morphological structure was investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), and energy-dispersive x-ray analysis (EDX). The morphology of α-Fe$_2$O$_3$-CdO nanocomposite was characterized by SEM at two different magnifications (Figure. 1). The typical SEM images of synthesized α-Fe$_2$O$_3$-CdO nanocomposites appeared carrying the formed α-Fe$_2$O$_3$-CdO nanocomposites, which are nearly spherical-like shapes with random distribution (see Figures. 1A & 1B). The SEM images reveal the rough and uneven surface of the nanocomposites, which exhibited the diameter of the particles around ~36 nm with a length of about 1 µm and 200 nm magnifications. The EDX patterns and corresponding atomic compositions for α-Fe$_2$O$_3$-CdO have been presented in Figure 1C. The atomic percentages reveal that the α-Fe$_2$O$_3$-CdO nanocomposites were successfully synthesized through the green procedure. Further lattice morphology and phase composition of α-Fe$_2$O$_3$-CdO are confirmed by powder XRD (Figure. 2). All the intense peaks of the face centered cubic CdO are observed in the recorded XRD; the peaks at 2 theta values of 29.4º, 33.6º, 43.5º, 49.5º, 53.2º, 66.2º and 69.3º matches with 210, 111, 202, 024,116, 311, and 222 peaks given by JCPDS card no. 65-2908 [28]. The XRD confirms the presence of CdO in a cubic lattice. The 202 and 024 peaks of α-Fe$_2$O$_3$ at 2 theta values of 43.5 and 49.5 indicate the presence of α-Fe$_2$O$_3$ in rhombohedral crystal lattice given by JCPDS card no.80-2377 [28]. Because of the low atomic weight, the α-Fe$_2$O$_3$-CdO peaks have modest intensities. The characterization characteristic diffraction peaks of the α-Fe$_2$O$_3$-CdO electrochemical nanosensor are completely comprised by the XRD patterns of α-Fe$_2$O$_3$-CdO nanomaterials, showing that the hybrid nanocomposites are successfully synthesized using α-Fe$_2$O$_3$ and CdO precursors [29]. In the spectrum of the α-Fe$_2$O$_3$-CdO sensor, a broad peak of graphitic-like carbon was also seen at 23º, as reported [30].

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (A, B) SEM images of α-Fe$_2$O$_3$-CdO nanocomposite at two magnifications (C) EDX.

Using cyclic voltammetry in 0.1 mol L$^{-1}$ pH 5.0 BR buffer solutions in the presence of 6.0 µg·mL$^{-1}$ of CLZ at a scan rate of 40 mVs$^{-1}$, the electrochemical behavior of CLZ at bare SPE, α-Fe$_2$O$_3$/SPE, CdO/SPE, and α-Fe$_2$O$_3$-CdO/SPE is investigated (Figure. 3). As seen in the cyclic voltammogram, utilizing bare SPE produced no reduced peak current ($I_{pc}$) (Figure. [Figure 3](https://example.com/figure3.png)).
3 curve a). On the CdO/SPE (Figure. 3 curve b), the less reduction peak currents have formed due to reduced electron transfer between the electrodes, suggesting the CdO substances’ low sensitivity on the SPE. When the SPE was modified with α-Fe₂O₃, it was found that the reduction peak current has been increased at -1.0 V (Figure. 3 curve c) because of the small size and high surface area of the nanoparticle enhanced the electron mobility. On the other hand, on α-Fe₂O₃-CdO/SPE (Figure. 3 curve d) at -1.08 V, a well-defined redox peak current of CLZ is significantly enhanced, which is more prominent than those obtained at the bare SPE, α-Fe₂O₃/SPE, and CdO/SPE. This indicates that α-Fe₂O₃ and CdO have a considerable influence on the SPE’s electron transfer kinetics. The enhanced electron transport due to the biosynthesized entangled α-Fe₂O₃-CdO structure and the good affinity of CLZ with α-Fe₂O₃-CdO can be attributed to the improved performance of the α-Fe₂O₃-CdO/SPE combination nanocomposite. The rate-determining phase of CLZ’s electrochemical process is seen in Figure 4 [31].

The differential pulse voltammetric response of 6.0 µg·mL⁻¹ CLZ (pH 5.0 BR buffer) at bare SPE, CdO/SPE, α-Fe₂O₃/SPE, and α-Fe₂O₃-CdO/SPE is examined as shown in Figure 5. After 3 min of open-circuit accumulation in a pH 5.0 BR buffer, a slight reduction peak on -1.0 V at CdO/SPE (Figure. 5 curve b) developed, which is better than bare SPE (Figure. 5 curve a). Under differential voltammetric conditions, feeble reduction peak current appeared at α-Fe₂O₃/SPE (Figure. 5 curve c); though, it has been significantly increased at the α-Fe₂O₃-CdO modified SPE (Figure 5 curve d). The peak current increase may have been caused by the fact that the biosynthesized α-Fe₂O₃-CdO nanocomposite has a high surface area and forms a perfect film on the SPE surface. Compared with CdO/SPE and α-Fe₂O₃/SPE the reduction peak current for the α-Fe₂O₃-CdO coated SPE increases significantly under comparable conditions, and the reduction peak potential does not change much. The remarkable peak current enhancement is undoubtedly attributed to the extraordinary properties of biosynthesized α-Fe₂O₃ and CdO, such as good electronic properties, high aspect ratio, and strong absorptive ability. This result further confirms that the α-Fe₂O₃-CdO nanocomposites have a superior activity for catalytic of CLZ reduction. Therefore, carbon mediated nanocomposites screen-printed electrode improves the electrocatalytic activity. Thus, the sensitivity of the α-Fe₂O₃-CdO electrochemical nanosensor can be improved greatly to determine CLZ in agricultural food samples.
The influence of supporting electrolytes and pH on DPV for 6.0 µg·mL⁻¹ CLZ with α-Fe₂O₃-CdO/SPE was evaluated in various supporting electrolytes, including 0.1 M Britton-Robinson buffer, 0.1 M sodium acetate–acetic acid buffer, 0.1 M phosphate buffer, carbonate buffer, and borate buffer solution. The maximum peak current was obtained using 0.1 M Britton-Robinson buffer/acetonitrile (10:1, V/V) as the supporting electrolyte among the various buffers examined in the pH range of 2.0–12.0. As shown, the current density increased with pH values by increasing until a maximum value of pH 5.0 had arrived, and then the current density decreased when the pH value still increased from 5.5. This kind of phenomenon is because the CLZ pesticide and H⁺ are both required in the irreversible reduction, but the electrode structure can be destroyed if the acidity is too low. Thus, the best voltammetric signal in terms of sensitivity (peak height) was obtained at pH 5.0 (Britton-Robinson buffer) with acetonitrile supporting electrolyte media (10:1 V/V) as shown in Figure 6.

Figure 3. Cyclic voltammogram of CLZ at bare SPE (a), CdO/SPE (b), α-Fe₂O₃/SPE (c), α-Fe₂O₃-CdO/SPE (d); pH: 5.0 (BR buffer/acetonitrile); accumulation potential: -1.08 V; accumulation time: 40 s; scan rate: 40 mVs⁻¹, pulse amplitude: 30 mV; concentration: 6.0 µg·mL⁻¹.

Figure 4. Electrochemical reduction mechanism of CLZ.

To improve the method's sensitivity and limit of detection, the effect of accumulation potential and accumulation time on the DPV signal has been studied. Figure 7 shows the influence of the accumulation potential on the peak height that has been studied from −0.2 to −1.6V, and strong adsorption at −1.0 V was observed, so this potential was used as the accumulation potential for all the measurements. The consequence of accumulation time t_acc (sec.) on the differential pulse peak current of the first peak CLZ in BR buffer of pH 5.0 is investigated. As shown in Figure 8, an accumulation time of 40 s, at −1.0 V generated a significant peak current. The influence of the scan rate (E) on the electrochemical reduction of 6.0 µg·mL⁻¹ CLZ using DPV was studied in the range of 10-100 mVs⁻¹ on the α-Fe₂O₃-CdO/SPE. When a scan rate of 40 mVs⁻¹ was applied, plotting log i_p versus log v gave a straight
line with a slope of 0.91 (r = 0.995) close to 1, which is the expected slope for an ideal reaction surface species. The effect of pulse parameters on CLZ voltammetric response has been calculated. Another important parameter involved in DPV is the pulse amplitude (E_a). The effect of DPV pulse amplitude on the reduction peak current of 6.0 µg·mL⁻¹ CLZ in 0.1 M of BR buffer/acetonitrile was studied from 20–100 mV and modulation time of 25–75 ms respectively. The highest reduction currents have been obtained for the pulse amplitude of 30 mV and modulation time of 20 ms that have been used for further measurements.

Figure 5. Differential pulse voltammogram of CLZ at bare SPE (a) CdO/SPE (b), α-Fe₂O₃/SPE (c), α-Fe₂O₃-CdO/SPE (d); pH: 5.0 (BR buffer/acetonitrile); accumulation potential: -1.08 V; accumulation time: 40 s; scan rate: 40 mVs⁻¹, pulse amplitude: 30 mV; concentration: 6.0 µg·mL⁻¹.

Figure. 6. Effect of pH on the differential pulse voltammetry of CLZ at α-Fe₂O₃-CdO/SPE; accumulation time: 40 s; accumulation potential: -1.08 V; accumulation time: 40 s; scan rate: 40 mVs⁻¹, pulse amplitude: 30 mV; concentration: 6.0 µg·mL⁻¹.

The effects of some of the organic and inorganic foreign species on the voltammetric detection of CLZ were investigated by using α-Fe₂O₃-CdO/SPE at pH 5.0 (BR buffer) with acetonitrile supporting electrolyte (10:1 V/V). The electrocatalytic reduction response of the electrochemical sensor of α-Fe₂O₃-CdO towards (1.0, 6.0 and 15 µg·mL⁻¹) of CLZ and foreign species, i.e., dopamine, uric acid, caffeic acid, glucose, hydroquinone, catechol, carbofuran, ascorbic acid, urea, bisphenol, Cl⁻, Br⁻, I⁻, CO₃²⁻, PO₄³⁻, NO₃⁻, Cu²⁺, SO₄²⁻, Ca²⁺, Mg²⁺ and Zn²⁺ were studied, and the results were given as a plot in Figure 9. As shown in the bar chart, the electrochemical nanosensor delivered an excellent current response to CLZ; however,
negligible replies were observed for all the foreign species. Thus, the foreign species study clearly revealed that $\alpha$-Fe$_2$O$_3$-CdO/SPE electrochemical nanosensor has good anti-interference ability and can be used for the selective detection of CLZ in agricultural food samples.

![Graph](https://doi.org/10.33263/BRIAC124.57725784)

**Figure 7.** Effect of accumulation potential on the differential pulse voltammetric determination of CLZ at $\alpha$-Fe$_2$O$_3$-CdO/SPE; pH: 5.0 (BR buffer/acetonitrile); accumulation time: 40 s; scan rate: 40 mVs$^{-1}$, pulse amplitude: 30 mV; concentration: 6.0 µg·mL$^{-1}$.

![Graph](https://biointerfaceresearch.com/)

**Figure 8.** Effect of accumulation time on the differential pulse voltammetric determination of CLZ at $\alpha$-Fe$_2$O$_3$-CdO/SPE; pH: 5.0 (BR buffer/acetonitrile); accumulation potential: -1.08 V; scan rate: 40 mVs$^{-1}$, pulse amplitude: 30 mV; concentration: 6.0 µg·mL$^{-1}$.

The stability of the developed electrochemical nanosensor of $\alpha$-Fe$_2$O$_3$-CdO has been monitored when not used, and it was kept in the laboratory for 5 days. Through five days storage period, the electrode signals for a solution of CLZ (6.0 µg·mL$^{-1}$) were noted and compared with its response on the first day. According to the results, peak current had a small change (approx. 3%), showing its significant stability. Subsequent reproducibility and repeatability of the developed electrochemical nanosensor, the DPV responses of 6.0 µg·mL$^{-1}$ of CLZ (Britton-Robison buffer/acetonitrile (10:1, V/V)) for 5 successive times were evaluated. The developed electrochemical nanosensor exhibits appreciable repeatability with an RSD of ~1.11% for five repetitive measurements. Further, the developed electrochemical nanosensor exhibits satisfactory reproducibility of $\alpha$-Fe$_2$O$_3$-CdO electrode.
The stability of the developed electrochemical nanosensor of α-Fe₂O₃-CdO has been monitored when not used, and it was kept in the laboratory for 5 days. Through five days storage period, the electrode signals for a solution of CLZ (6.0 µg·mL⁻¹) were noted and compared with its response on the first day. According to the results, peak current had a small change (approx. 3%), showing its significant stability. Subsequent reproducibility and repeatability of the developed electrochemical nanosensor, the DPV responses of 6.0 µg·mL⁻¹ of CLZ (Britten-Robison buffer/acetonitrile (10:1, V/V)) for 5 successive times were evaluated. The developed electrochemical nanosensor exhibits appreciable repeatability with an RSD of ~1.11% for five repetitive measurements. Further, the developed electrochemical nanosensor exhibits satisfactory reproducibility of α-Fe₂O₃-CdO electrode.

3.1. Applications.

Under the optimized voltammetric conditions, the developed α-Fe₂O₃-CdO/SPE electrochemical nanosensor was applied for electrochemical detection of CLZ. Figure 10 displayed the DPV of the α-Fe₂O₃-CdO/SPE in 0.1 M pH 5.0 Britten-Robison buffer/acetonitrile supporting electrolyte at a potential range from −0.2V to −1.6V in the presence of various CLZ concentrations (0, 0.05, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0, 24.0, 28.0 and 36.0 µg·mL⁻¹). As shown in the figure, the peak current density increased with the increase of CLZ concentration, suggesting that the presence of the CLZ can enhance the reaction on the modified electrode, which can be speculated that CLZ had a high binding affinity with CdO and α-Fe₂O₃ hybrid nanocomposites.

To show the validation of the proposed method, the analytical features of the method, such as linear range of the calibration curve, detection limit, limit of quantification, accuracy, and precision was examined. Figure 11 shows the voltammograms of CLZ in the concentration range of 0.1–36.0 µg·mL⁻¹. Under the optimum conditions, the calibration graph for the determination of CLZ is obtained with a correlation coefficient of 0.995. The regression equation for the line was \( i_p = aC \ (CLZ) + b \) (n = 4), where C is the concentration of CLZ in µg·mL⁻¹ and (i) is the peak current intensity difference (at the peak potential −1.08 V) between the analyte and the blank voltammograms. The slope of the line \( b = 0.6152 \pm 0.0137 \) and the intercept of the line \( a = 0.0906 \pm 0.238 \) with a R.S.D = 1.01% were also obtained.
Figure 10. Differential pulse voltammograms of CLZ at α-Fe₂O₃-CdO/SPE obtained under optimized conditions, for CLZ concentration from (A) to (L): 0, 0.1, 0.5, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0, 24.0, 28.0 and 36.0 µg mL⁻¹ at pH: 5.0 (BR buffer/acetonitrile); accumulation potential: -1.08 V; accumulation time: 40 s; scan rate: 40 mVs⁻¹, pulse amplitude: 30 mV; concentration: 6.0 µg mL⁻¹.

Figure 11. Linear curve for the CLZ determination by differential pulse voltammetry at α-Fe₂O₃-CdO/SPE. pH: 5.0 (BR buffer/acetonitrile); accumulation potential: -1.08 V; accumulation time: 40 s; scan rate: 40 mVs⁻¹, pulse amplitude: 30 mV.

The proposed α-Fe₂O₃-CdO electrochemical nanosensor was further utilized to determine CLZ in agricultural food samples. The standard addition method was used to examine the reliability and accuracy of the proposed method; diverse volumes of CLZ standard additions were spiked into the agricultural food samples at the concentration of 5.0 and 25 µg mL⁻¹, respectively. The recoveries of CLZ in various (Spinach, Lettuce, Cauliflower, Cucumber, and Cabbage) spiked content of agricultural food samples were evaluated, and the results were presented in Table 1. Five replicate analyses of each sample were carried out to confirm the method’s precision. In agricultural food samples, average recoveries ranged from 94.0-99.6 %, with an RSD of ~1.0 %. Furthermore, the significant voltammetric characteristics of LOD and linear range were compared to modified electrodes previously reported. The proposed α-Fe₂O₃-CdO/SPE shows notable competitiveness to some previously reported electrodes (Table 2).
Table 1. Application of the recommended method to determine CLZ in Agricultural food samples at α-Fe$_2$O$_3$-CdO/SPE; pH: 5.0 (BR buffer/acetoni trile); accumulation potential: -1.08 V; accumulation time: 40 s; scan rate: 40 mVs$^{-1}$, pulse amplitude: 30 mV.

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>Amount added (µg mL$^{-1}$)</th>
<th>Amount found (µg mL$^{-1}$)</th>
<th>Recovery* (%) ± S.D</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinach leaves</td>
<td>5.0</td>
<td>0.48</td>
<td>96.0±0.083</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>24.9</td>
<td>99.6±0.210</td>
<td>0.84</td>
</tr>
<tr>
<td>Lettuce</td>
<td>5.0</td>
<td>0.47</td>
<td>94.0±0.069</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>24.6</td>
<td>98.4±0.220</td>
<td>0.90</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>5.0</td>
<td>0.49</td>
<td>98.0±0.075</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>24.9</td>
<td>99.6±0.180</td>
<td>0.72</td>
</tr>
<tr>
<td>Cucumber</td>
<td>5.0</td>
<td>0.48</td>
<td>98.0±0.011</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>24.6</td>
<td>98.4±0.064</td>
<td>0.26</td>
</tr>
<tr>
<td>Cabbage</td>
<td>5.0</td>
<td>0.49</td>
<td>98.0±0.090</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>24.7</td>
<td>98.8±0.140</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*n=4 (no. of determinations); S.D= Standard Deviation; RSD= Relative Standard Deviation

Table 2. Comparison of the biosynthesized α-Fe$_2$O$_3$-CdO/SPE electrochemical sensor with other reported electrodes for detection of pesticides.

<table>
<thead>
<tr>
<th>Modified electrodes</th>
<th>Technique/method</th>
<th>Linear range</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO/rGO/GCE</td>
<td>DPV</td>
<td>0.5-200 µM</td>
<td>0.037 µM</td>
<td>[30]</td>
</tr>
<tr>
<td>CP-SPE</td>
<td>DPV</td>
<td>0.1-1000 µM</td>
<td>0.08 µM</td>
<td>[32]</td>
</tr>
<tr>
<td>ZXCPE</td>
<td>DPV</td>
<td>1.0-100 µM</td>
<td>0.3 µM</td>
<td>[33]</td>
</tr>
<tr>
<td>MoS$_2$/NPs/GCE</td>
<td>DPV</td>
<td>1.0-55 ng µL$^{-1}$</td>
<td>0.32 ng µL$^{-1}$</td>
<td>[34]</td>
</tr>
<tr>
<td>AuNPs/DNA/GE</td>
<td>DPV</td>
<td>1-100 µM</td>
<td>1.30 µM</td>
<td>[35]</td>
</tr>
<tr>
<td>PGC</td>
<td>CV</td>
<td>5-500 mg L$^{-1}$</td>
<td>8.7 mg L$^{-1}$</td>
<td>[36]</td>
</tr>
<tr>
<td>BiFE</td>
<td>DPV</td>
<td>9.5 – 200 µM</td>
<td>2.9 µM</td>
<td>[37]</td>
</tr>
<tr>
<td>Hg(Ag)FE</td>
<td>SWV</td>
<td>3.55-185.6 µM</td>
<td>1.05 µM</td>
<td>[38]</td>
</tr>
<tr>
<td>Boran-doped diamond</td>
<td>SWV</td>
<td>4.95-36.7 µM</td>
<td>4.1 µM</td>
<td>[39]</td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$-CdO/SPE</td>
<td>DPV</td>
<td>0.1-36 µg mL$^{-1}$</td>
<td>0.059 µg mL$^{-1}$</td>
<td>This Work</td>
</tr>
</tbody>
</table>

SWV: square wave voltammetry; CV: cyclic voltammetry; rGO: reduced graphene oxide; CP-SPE: carbon paste-screen printed electrode; GCE: glassy carbon electrode; BiFE: Bismuth-film electrode; Hg(Ag) FE: silver-amalgam film electrode; ZxCPE: zeolite X modified carbon paste electrode, DNA: deoxyribonucleic acid.

4. Conclusions

The modest, good sensitive conventional α-Fe$_2$O$_3$-CdO/SPE electrochemical nanosensor was efficaciously applied for CLZ determination in agricultural food samples. The influence of scan rate, diverse concentration, and pH of the electrolytes was studied. Under the voltammetric optimized operating conditions, the α-Fe$_2$O$_3$-CdO/SPE electrochemical nanosensor showed a good linear range, low detection limit, and excellent electrical conductivity, which leads to a fast electron transfer rate. Moreover, the practical applicability of the biosynthesized nanosensor was demonstrated as it gave good (94.0% to 99.6%) recoveries of CLZ in agricultural food samples with an RSD of ~1.11%. The experimental results are conventional in that the proposed method has great potential for fast, modest, high sensitivity, selectivity, low cost, strong stability, and reproducibility for the detection of CLZ.

Funding

This research received no external funding.

Acknowledgments

We are grateful to Prof. N.Y. Sreedhar, Department of Chemistry, Sri Venkateswara University, Tirupati, for instrumentation support.
Conflicts of Interest

The authors declare that there is no conflict of interest for this manuscript publication.

References


https://biointerfaceresearch.com/
ode for voltammetric monitoring of solar photodegradation of
–
35.
36.
37.
–

32.
31.
30.
29.
28.
27.
26.
25.
24.
22.
21.
20.
19.
18.
17.
16.
15.
14.
13.
12.
11.
10.
9.
8.
7.
6.
5.
4.
3.
2.
1.

https://biointerfaceresearch.com/