

Nanostructured Fe₂O₃-ZnO modified GCE nanosensor for dinobuton pesticide determination in environmental samples

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Abstract— Nanostructured Fe₂O₃-ZnO modified GCE electrochemical nanosensor has been developed for the determination of dinobuton pesticide in environmental samples. The electrochemical behavior of the dinobuton pesticide was examined by cyclic and differential pulse voltammetry. The conventional electrode signal was an estimable response on the Fe₂O₃-ZnO/GCE, due to noble electrical conductivity and the tolerable electrostatic interface between Fe₂O₃ and ZnO. Under the optimum conditions, a linear association was obtained from 0.05 to 30.00 µg•mL⁻¹ between the peak current and the concentration of dinobuton, significant detection limit of 0.01200 µg•mL⁻¹ and to a quantification limit of 0.03636 µg•mL⁻¹. The established procedure was magnificently applied to the determination of dinobuton pesticide in environmental (water and soil) samples.

Keywords— *Dinobuton, Pesticide, Voltammetry, Environmental samples*

I. INTRODUCTION

Dinobuton ((*RS*)-2-*sec*-butyl-4,6-dinitrophenyl isopropyl carbonate) is a bio- activated fungicide/acaricides group of dinitrophenyl group of pesticide [1]. It was the major component in been plants after either stem injection or foliar treatment. If the pesticides applied on soils, it persists for a long time, because its degradation is slow and it is harmful to the human being [2-5], therefore, there is necessary to monitoring of pesticides. Many monitoring techniques have been reported for the quantitative determination of pesticides such as spectrophotometry, capillary electrophoresis, high-performance liquid chromatography (HPLC), liquid chromatography-mass spectrometry (LC-MS), and ultra-performance liquid chromatography coupled to tandem mass spectrometry [6–15]. Thus, electrochemical methods offer a versatile stand for sensitive, selective and reproducible evaluating of pesticides. [16]

Consequently, nanomaterial modified electrodes have high electron transfer ability [17]. In particular, metal oxide nanomaterials exhibit unique physical and chemical properties due to their size and high density at the corner or edge surface sites. It's used for both their redox and acid/base properties in the context of absorption and catalysis [18, 19]. However, Fe₂O₃ and ZnO nanoparticles hold a lot of promise for applications in electrochemical fields because of the unusual structure, excellent adsorption, catalytic properties and inherent electrical conductivity [20, 21]. Then, Fe₂O₃-ZnO nanocomposites provide a potential application in electrochemistry due to their good conductivity, desirable biocompatibility and efficient surface modification to the

electrode surface to achieve the electrochemical properties. To the best of our acquaintance, there is no report based on using Fe₂O₃-ZnO modified electrodes for the determination of dinobuton. The presence of Fe₂O₃-ZnO nanocomposites may significantly improve the electrochemical performance. In the present study, the nanostructured Fe₂O₃-ZnO can be effortlessly prepared by sol-gel process. Cyclic and differential pulse voltammetry has been used to characterize the dinobuton pesticide in environmental samples using nanostructured electrochemical nanosensors (Fe₂O₃-ZnO/GCE, Fe₂O₃/GCE, ZnO/GCE and bare GCE). The nanostructured Fe₂O₃-ZnO/GCE electrochemical nanosensor was exhibit acceptable reproducibility and recovery for the quantify residues of dinobuton pesticide in environmental (water and soil) samples.

II. EXPERIMENTAL

A. Materials and Apparatus

ZnCl₂, FeCl₃•6H₂O, Nafion, H₃BO₃, H₃PO₄, glacial acetic acid were purchased from Merk Chemicals. All appropriate metal salts procured from SD fine chemicals. Dinobuton was procured from Beyer's chemicals, India. A stock solution of dinobuton (100 µg•mL⁻¹) was prepared by dissolving dinobuton in a suitable amount of dimethylformamide (DMF). All dilute solutions were freshly prepared daily from the stock solution. Doubled distilled water was used in the preparation of all solutions. Briton-Robison (BR) buffer solution ranging from pH 2.0 to 12.0 were prepared using 0.04 M boric acid, 0.04 M H₃PO₄, and 0.2 M NaOH. All the chemicals were analytical reagent grade.

Electrochemical measurements were carried out in Auto lab, three electrode systems consisting of modified glassy carbon electrode as a working electrode, Ag/AgCl (salt KCl) was used as a reference electrode and a platinum wire as an auxiliary electrode. The voltammetric study solutions were degassed prior to analysis by bubbling purified nitrogen gas through the voltammetric cell for 120 s. Scanning electron microscopy (SEM) images were taken on an FEI-quanta 200 scanning electron microscope with an acceleration voltage of 20 kV. All the experiments were performed at $25 \pm 1^\circ\text{C}$ and the pH measurements were carried out with Hanna instruments (Italy) pH meter.

B. Preparation of $\text{Fe}_2\text{O}_3\text{-ZnO}$ nanosensor

A typical sol-gel synthesis was applied for the preparation of $\text{Fe}_2\text{O}_3\text{-ZnO}$ nanostructure. For this synthesis, the 1:1 ratio of aqueous ZnCl_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution was prepared and slowly dropwise added ammonia solution (100 mL) under constant stirring. Subsequently sonicating for another 30 min, the mixture was transferred into a screw-capped glass bottle (1000 mL) and maintained at 100°C for 24 h. Later cooling down to room temperature, the obtained products were filtered and washed with double deionized water and ethanol in sequence, as well as dried in a vacuum at 80°C at 24h. The prepared $\text{Fe}_2\text{O}_3\text{-ZnO}$ nanostructure was calcined at 350°C for 2 h at a ramping rate of 1°C min to yield the brown-black $\text{Fe}_2\text{O}_3\text{-ZnO}$. For electrochemical comparison purpose, ZnO and Fe_2O_3 were procured.

C. Preparation of modified electrode

Before modification by drop-coating, the conventional glassy carbon electrode (GCE) was polished with alumina pastes of different sizes (1, then $0.05 \mu\text{m}$). They were then placed in a 1:1 ethanol-water solution and properly cleaned in a sonicator around 10 min to exclude any outstanding alumina particles. The 30 mg of $\text{Fe}_2\text{O}_3\text{-ZnO}$ was dispersed in 0.5 mL nafion (5%) and then in 1 mL ethanol by ultrasonication for 60 min to give uniform ZnO and Fe_2O_3 dispersions. The GCE surface was modified with $10 \mu\text{L}$ of nanostructured $\text{Fe}_2\text{O}_3\text{-ZnO}$ and dried at room temperature for 60 min to obtain used as a working electrode. Likewise, $\text{Fe}_2\text{O}_3/\text{GCE}$ and ZnO/GCE working electrode were used as a working electrode for comparison.

D. Environmental sample collection and preparation

Swarnamuki River water (Chittoor District, A.P., India), industrial wastewater (Renigunta area, A.P., India) and tap water samples were collected in 2.5 L brown glass bottles. Instantaneously after arrival in the working lab, the samples were filtered through 1 mm glass fiber filters and $0.45 \mu\text{m}$ cellulose acetate filters, consecutively, to remove the quiescent particles for following voltammetric analysis. Meanwhile, the soil samples were collected from the agricultural land area of two different places of Pakala, Chittoor District, and A.P. The soil was collected at 5-10 cm deep, sieved and stored in airtight plastic at -40°C until the soil sample would be analyzed. The soil samples were weighed 20 g and 60 ml of DMF was added to the soil. The

solution was transferred to a 100 ml beaker. Then, it was stirred for 60 min and sonicated for 5 minutes. The extract was filtered using a $0.2 \mu\text{m}$ filter paper. Further, the accurate spiked volumes of dinobuton ($10, 25$ and $50 \mu\text{g}\cdot\text{mL}^{-1}$) were added to the working sample for voltammetric measurement.

E. Voltammetric procedure

Aliquot solutions were prepared by dilution of the stock solution with a suitable amount of dimethylformamide. In the voltammetric cell, 5.0 ml of standard solution is transferred and made up to 5.0 ml of the BR buffer of pH 6.0. Afterward attaining the voltammogram required additions of standard solutions are added then voltammogram recorded after each addition under similar experimental parameters. The optimum conditions for the determination of dinobuton are found to be an accumulation time: 40 s; accumulation potential: -0.56 V ; scan rate: 50 mVs^{-1} , pulse amplitude: 25 mV, respectively.

III. RESULTS AND DISCUSSION

The surface morphology of $\text{Fe}_2\text{O}_3\text{-ZnO}$ nanocomposite was analyzed by scanning electron microscope. The typical SEM images of $\text{Fe}_2\text{O}_3\text{-ZnO}$ particles were evidently appeared carrying the formed $\text{Fe}_2\text{O}_3\text{-ZnO}$ nanoparticles as nearly spherical like shape with a uniform distribution of nanodeposits (Figs. 1a & 1b). The electrochemical behavior of $5.0 \mu\text{g}\cdot\text{mL}^{-1}$ dinobuton on varied electrodes was studied by cyclic and differential pulse voltammetry in $0.1 \mu\text{g}\cdot\text{mL}^{-1}$ BR buffer at pH 6.0. The electrochemical response at $\text{Fe}_2\text{O}_3\text{-ZnO}/\text{GCE}$ was more significantly noticeable in terms of peak current. This can be illuminated by the high electrical conductivity and electrostatic interactions between the Fe_2O_3 , ZnO, and a glassy carbon electrode.

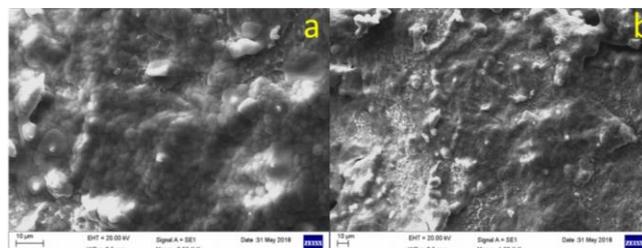


Figure 1. (a, b) SEM images of $\text{Fe}_2\text{O}_3\text{-ZnO}$ nanocomposite of two magnifications.

Fig. 2 showed the cyclic voltammogram of $\text{Fe}_2\text{O}_3\text{-ZnO}/\text{GCE}$ in $0.1 \mu\text{g}\cdot\text{mL}^{-1}$ pH 6.0 BR buffer solutions in the presence of $5.0 \mu\text{g}\cdot\text{mL}^{-1}$ of dinobuton were compared to that on the $\text{Fe}_2\text{O}_3/\text{GCE}$, ZnO/GCE and bare GCE. As can see on the cyclic voltammograms reduction peaks of dinobuton the bare GCE exhibit small reduction peak current at potential -0.50 V (Fig. 2a). Correspondingly, when GCE was modified with Fe_2O_3 , it was found that the reduction peak increased and potentially decreased at -0.57 V (Fig. 2b). This demonstrates that the electrochemical reduction process of $-\text{NO}_2$ on the GCE surface was inhibited by the conductive Fe_2O_3 film. On

the ZnO/GCE shown the good reduction potential peak current appeared. Indicating that the ZnO have great influence on improving the electron transfer kinetic of the GCE (Fig. 2c). When the GCE was modified with Fe₂O₃-ZnO, reduction peak current significantly increased more and the reduction potential slightly move to at -0.56 V (Fig. 2d), which was more prominent than those obtained at the bare GCE, Fe₂O₃/GCE and ZnO/GCE. Moreover, one can see that the combination of Fe₂O₃ into ZnO nanocomposites possess more prominent peak current, indicating that the use of Fe₂O₃, ZnO can significantly improve the electron transfer amongst Fe₂O₃-ZnO and the GCE. Consequently, these showed the Fe₂O₃-ZnO/GCE gave the highest controlled response. The improved performance of the Fe₂O₃-ZnO/GCE combination nanocomposite can be attributed to the excellent affinity of dinobuton with Fe₂O₃-ZnO and the enhanced electron transfer due to the formation of entangled Fe₂O₃-ZnO structure. The electrochemical mechanism of dinobuton is shown in Fig. 3. The average time required for the proposed sensor to reach a steady potential value within ± 1 mV of the final equilibrium value after successive immersion in series inside dinobuton solution was studied.

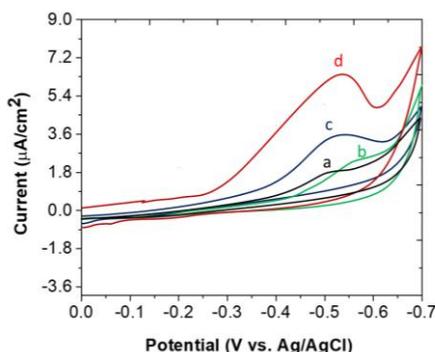


Figure 2. Typical cyclic voltammogram of dinobuton at bare GCE (a), Fe₂O₃/GCE (b), ZnO/GCE (c), Fe₂O₃-ZnO/GCE (d); accumulation time: 40 s; pH: 6.0; accumulation potential: -0.56 V; scan rate: 50 mVs⁻¹, pulse amplitude: 25 mV; concentration: 5.0 µg•mL⁻¹.

The voltammetric response of 5.0 µg•mL⁻¹ dinobuton at four different electrodes were examined by differential pulse voltammetry. In a pH 6.0 BR buffer and after 3 min of open-circuit accumulation, a low reduction peak appeared on -0.54 V at the bare GCE (Fig. 4a). Under identical conditions, feeble reduction peak current appeared at a Fe₂O₃/GCE (Fig. 4b), ZnO/GCE (Fig. 4c); though, it significantly increased at the Fe₂O₃-ZnO coated GCE (Fig. 4d). The peak current increase may have been caused by the fact that the Fe₂O₃-ZnO forms a perfect film on the GCE surface, and thus enhance electron transfer. The bare GCE, Fe₂O₃/GCE and ZnO/GCE the reduction peak for the Fe₂O₃-ZnO coated GCE increases significantly under comparable conditions, and the reduction peak potential does not change much. The remarkable peak current enhancement undoubtedly attributes to the extraordinary

properties of Fe₂O₃ and ZnO, such as subtle electronic properties, high aspect ratio, and strong absorptive ability.

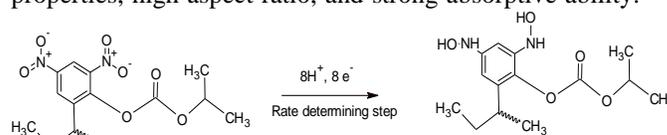


Figure 3. Electrochemical reduction mechanism of dinobuton

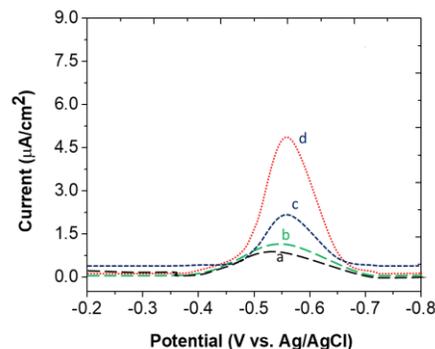


Figure 4. Differential pulse voltammogram of dinobuton at bare GCE (a), Fe₂O₃/GCE (b), ZnO/GCE (c), Fe₂O₃-ZnO/GCE (d); accumulation time: 40 s; pH: 6.0; accumulation potential: -0.56 V; scan rate: 50 mVs⁻¹, pulse amplitude: 25 mV; concentration: 5.0 µg•mL⁻¹.

A. The effect of pH

The test solution on the peak current of dinobuton voltammograms was studied by applying Universal, Britton–Robinson, phosphate and acetate buffer solutions. Among the various investigated buffers in the pH range of 2.0–12.0, the best voltammetric signal in terms of sensitivity (peak height) was obtained at pH 6.0 using BR buffer as shown in Fig. 5. At pH values lower than 5, the reduction of hydronium ion (H₃O⁺) may cause a decrease in the intensity of peak current. At pH values greater than 6 the decomposition of dinobuton causes sensitivity reduction. Therefore, the peak potentials of dinobuton are found to be pH dependent and shift towards more negative values with increase in pH indicating the involvement of protons in the reduction process.

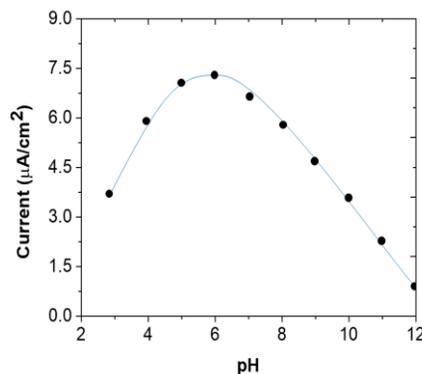


Figure 5. Effect of pH on the differential pulse voltammetry of dinobuton at Fe₂O₃-ZnO/GCE; accumulation time: 40 s; pH: 6.0; accumulation potential: -0.56 V, scan rate: 50 mVs⁻¹, pulse amplitude: 25 mV; concentration: 5.0 µg•mL⁻¹.

In order to improve the sensitivity and limit of detection of the method, the effect of accumulation potential and accumulation time on the DPV signal has been studied. Fig. 6, shows the influence of the accumulation potential on the peak height was studied from -0.2 to -1.0 V and strong adsorption at -0.56 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 dinobuton in BR buffer of pH 6.0 is investigated. As shown in Fig. 7, accumulation time of 40 s, at -0.56 V generated significant peak current. The influence of the scan rate (v) on the peak current (i_p) and peak potential (E_p) with in the range 10–100 mVs^{-1} was carried out. When a scan rate of 50 mVs^{-1} was applied, plotting $\log i_p$ versus $\log v$ gave a straight line with a slope of 0.899 ($r = 0.9998$) close to 1, which is the expected slope for an ideal reaction of surface species. The effect of pulse parameters on dinobuton voltammetric response has been calculated. The pulse amplitude in the range of 10–100 mV and modulation time of 25–75 ms have been examined. The highest reduction currents have been obtained for the pulse amplitude of 25 mV and modulation time of 25 ms that have been used for further measurements.

The influences of some foreign species on the voltammetric determination of 5.0 $\mu g \cdot mL^{-1}$ dinobuton were investigated by using Fe_2O_3 -ZnO modified glassy carbon electrode at pH 6.0 BR buffer and varying amounts of the foreign substances using DPV. The concentration of the pesticides and the interfering ions were taken in 1:1 ratio. The inorganic ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO^- , SO_4^{2-} and HSO_4^- do not interfere with the dinobuton reduction signal. Other biomolecules and pesticides such as glucose, fenitrothion and parathion are not potential effects on Fe_2O_3 -ZnO/GCE. Thus, Fe_2O_3 -ZnO/GCE shows good selectivity and sensitivity to the dinobuton determination.

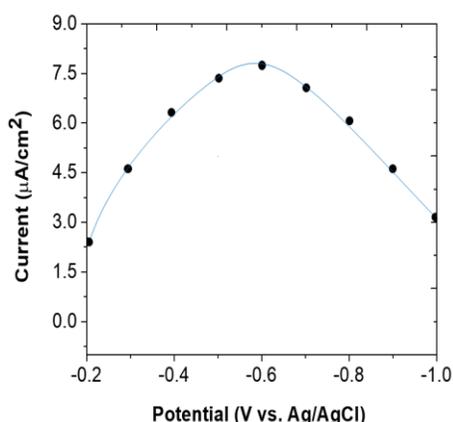


Figure 6 Effect of accumulation potential on the differential pulse voltammetric determination of dinobuton at Fe_2O_3 -ZnO/GCE; accumulation time: 40 s; pH: 6.0; accumulation potential: -0.56 V, scan rate: 50 mVs^{-1} , pulse amplitude: 25 mV; concentration: 5.0 $\mu g \cdot mL^{-1}$.

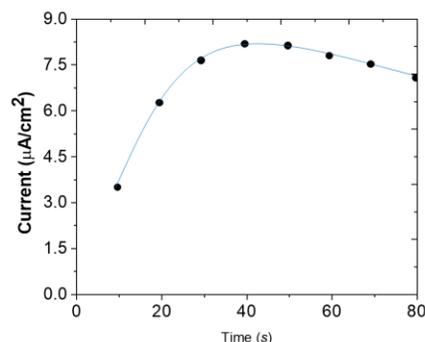


Figure 7. Effect of accumulation time on the differential pulse voltammetric determination of dinobuton Fe_2O_3 -ZnO/GCE; accumulation time: 40 s; pH: 6.0; accumulation potential: -0.56 V, scan rate: 50 mVs^{-1} , pulse amplitude: 25 mV; concentration: 5.0 $\mu g \cdot mL^{-1}$.

B. Applications

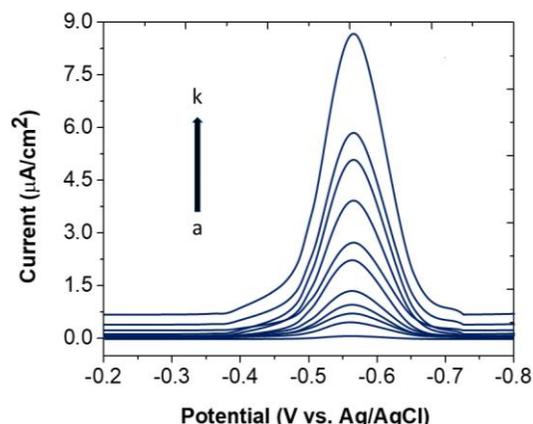


Fig. 8. Differential pulse voltammograms of dinobuton at Fe_2O_3 -ZnO/GCE obtained under optimized conditions, for dinobuton concentration from (A) to (k): 0, 0.05, 0.5, 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0, and 30.0 $\mu g \cdot mL^{-1}$ at pH 6.0, accumulation potential: -0.56 V; scan rate: 50 $mV s^{-1}$; pulse amplitude: 25 mV.

The quantitative determination of dinobuton has been performed by DPV. There is a well-defined peak of dinobuton reduction at -0.565 V on Fe_2O_3 -ZnO/GCE in BR buffer pH 6.0 on differential pulse voltammograms. Fig. 8 displayed the effect of different dinobuton concentration (0, 0.05, 0.5, 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0, 30.0 $\mu g \cdot mL^{-1}$) on differential pulse voltammetry behavior of the Fe_2O_3 -ZnO/GCE in 0.1 M pH 6.0 BR buffer solution. As shown in the figure the peak current density increased with the increase of dinobuton concentration, suggesting that the presence of the dinobuton can enhance the reaction on the modified electrode, which can be speculated that dinobuton had a high binding affinity with ZnO with Fe_2O_3 hybrid nanocomposites. Thus provides a diverse sensing mechanism for dinobuton electrochemical detection.

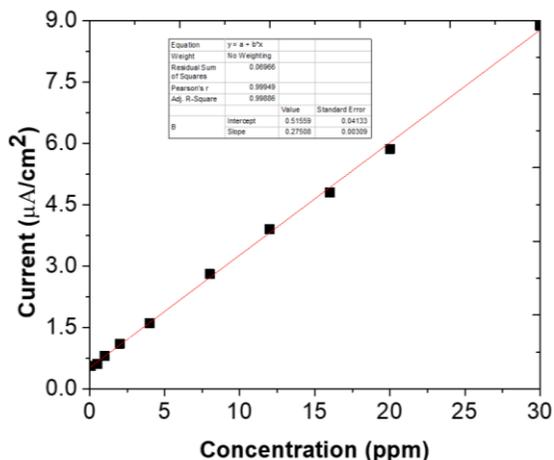


Figure 9. The linear plot for the dinobuton determination by differential pulse voltammetry at Fe₂O₃-ZnO/GCE.

In order to show the validation of the proposed method, the analytical features of the method such as the linear range of the calibration curve, limit of detection, limit of quantification, accuracy, and precision were examined. Fig. 9 shows the voltammograms of dinobuton in the concentration range of 0.05–30.0 µg·mL⁻¹. Under the optimum conditions, the calibration graph for the determination of dinobuton is obtained with a correlation coefficient of 0.9992. The regression equation for the line was $i_p = aC(\text{dinobuton}) + b$ (n = 10), where C is the concentration of dinobuton in µg·mL⁻¹ and (i) is the peak current intensity difference (at the peak potential -0.56 V) between the analyte and the blank voltammograms. The slope of the line $b = 0.51559 \pm 0.0037$ which shows a R.S.D. = 3.0 % and the intercept of the line $a = 0.27506 \pm 0.0401$ with a R.S.D. = 2.6% were also obtained.

In furtherance to examining the validity of the method, the proposed procedure was applied for the determination of dinobuton in environmental samples (water and soil). Recovery tests were used to examine the reliability and accuracy of the method, different amounts of dinobuton were spiked into the water and soil samples. The spiked content of different samples was evaluated and the results were presented in Table 1 and Table 2. In order to check the precision of the method, ten replicate analyses of each sample were carried out. The average recoveries obtained in water and soil samples were 97.8-99.8% and 98.8-99.8% with a relative standard deviation of 0.10-0.22% and 0.09-0.26% respectively.

Table 1. Application of the recommended method to the determination of dinobuton in various water samples

Name of the sample	Amount added (µg.mL ⁻¹)	Amount found (µg.mL ⁻¹)	Recovery* (%)	RSD (%)
Tap water	10.0	09.9	99.0	0.14
	25.0	24.9	99.6	0.18
	50.0	48.9	97.8	0.16

Industrial wastewater	10.0	09.8	98.0	0.22
	25.0	24.8	99.2	0.12
	50.0	49.2	98.4	0.19
River water	10.0	09.9	99.0	0.14
	25.0	24.8	99.2	0.12
	50.0	49.9	99.8	0.10

*n=10 (no. of determinations)

Table 2. Application of the recommended method to the determination of dinobuton in soil samples

Name of the sample	Amount added (µg·mL ⁻¹)	Amount found (mg)	Recovery* (%)	RSD (%)
Soil-I	10.0	09.6	96.0	0.20
	25.0	24.9	99.6	0.14
	50.0	49.8	99.6	0.14
Soil-II	10.0	09.9	99.0	0.10
	25.0	24.7	98.8	0.26
	50.0	49.9	99.8	0.09

*n=10 (no. of determinations)

IV. CONCLUSION

In this work, the bare GCE, ZnO/GCE and Fe₂O₃/GCE nanosensor were applied for dinobuton examined. The Fe₂O₃-ZnO/GCE nanosensor exhibited significantly a good linear range and low detection limit in determination of dinobuton in environmental samples. Moreover, the practical applicability of the nanosensor was demonstrated as it gave good 97.8% to 99.8% recoveries of dinobuton in water and soil samples respectively. The experimental results have established that this system has advantages such as simple function, high sensitivity, selectivity, low cost, long-term stability and good reproducibility with satisfactory results for dinobuton pesticide determination in various water and soil sample analysis.

Conflict of interests

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

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