**RESEARCH ARTICLE**

# Voltammetric Detection of Diazinon Insecticide at Ferrocene-Graphene/Nafion Modified Glassy Carbon Electrode

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**ABSTRACT:** In this study, ferrocene was used to modify a glassy carbon electrode, which was fixed with an appropriate amount of nafion solution. The -C-O-C- and -COOH functional groups were detected in the ferrocene/graphene composite, which indicated that graphene was oxidized to graphene oxide, making it more hydrophilic, dispersible and compatible with polymers, thus increasing the diazinon detection rate. The optimal conditions for diazinon detection were found using cyclic voltammetry (CV): a scan rate of 50 mV/s, pH 6.6, and 0.1 mol/L PBS buffer solution. Differential pulse voltammetry (DPV) shows that the concentrations of diazinon are $1\times10^{-6}$ – $1.2\times10^{-5}$ mol/L, and there is a good linear relationship between the peak current and the concentration: Ipa ($\mu$A)=2.0578 c($\mu$M) -38.2518, $R^2$ = 0.9971; the detection limit is $1.2\times10^{-9}$ mol/L. This modified electrode has good stability, repeatability and operability and can be applied to detect actual samples.

**Keywords:** Ferrocene, Nafion, Diazinon, Differential pulse voltammetry

## 1. INTRODUCTION

Diazinon (O,O-diethyl O-2-isopropyl6-methyl pyrimidin -4-yl phosphorothioate), as an organophosphorus insecticide and an extremely toxic insecticide, often used widely on cultivation of various types of crops such as apple, rice, grapes, pistachios, palm, citrus and pear. Diazinon is also poisonous for aquatics, mammals, and some non-target insects. High doses of diazinon can cause muscle tremors, nausea, dimness of vision and difficult breathing. It can cause harmful effects on skin, lungs, gastrointestinal tract and nervous system. Moreover, diazinon has been identified as a potential chemical mutagen and it is proved that diazinon is highly toxic to fish and water organisms [1–3].

According to what was explained qualitative and quantitative analysis methods for organophosphates (Ops) and especially for diazinon is very serious for human health and environmental control. Common techniques applied for Ops, detection are gas chromatography and high-performance liquid chromatography (HPLC), mass spectrometry method, spectrophotometry, infrared spectroscopy and an enzyme immunoassay [4-9]. Though these methods are suitably sensitive and highly reproducible and show low detection limits, because of some problems such as very expensive techniques, time-consuming methods, complicated laboratory equipment, low speed analysis under field conditions and requiring trained man power, developing of new, simple, inexpensive and sensitive quantifying methods is still a critical subject in analytical chemistry [1-3]. Among the all reported methods, those that are based on electrochemical techniques [10-13] have been more interested because of their several advantages such as ease of use, cost effectiveness, fast measurement, high sensitivity, and capable of application in field conditions, and so on.

Up to now a few electrochemical methods have been reported for determination of diazinon such as nafion modified glassy carbon electrode, biosensors and DNA-composed carbon nanotube electrode [2, 13]. Graphene has a large surface area, good dispersity and strong electric conductivity. Ferrocene can participate in the gain and loss of electrons and undergo redox reactions. This new assembled

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modified electrode perfectly combines the advantages of graphene and ferrocene. In addition, this electrode has a simple structure, it is easy to make, and the manufacture cost is low. In the detection of diazinon, it has a low detection limit, and there is a good linear relationship in a wide linear range. It is convenient, economically efficient and effective, which contributes to its practicability.

## 2. EXPERIMENTAL DETAILS

### 2.1. Chemicals

Nafion®-perfluorinated ion-exchange powder (15 wt % solution in a mixture of lower aliphatic alcohols and water (10%)) was obtained from Aldrich. Diazinon and all other compounds used were of ACS-certified reagent grade and were used without further purification. Aqueous solutions were prepared with doubly distilled deionized water. Unless otherwise mentioned, a phosphate buffer of pH 6.6 was used for all electrochemical measurements. Lake water was collected from the Karakaya Dam Lake. The samples were taken in glass bottles, filtered through a 0.45-μm nylon filter, and stored at 4°C.

### 2.2. Instrumentation

All electrochemical experiments were carried out using a BAS 100 B model computerized electrochemical analyzer (Bioanalytical Systems, Inc., West Lafayette, IN, USA). Experiments were conducted in a three-electrode cell with a glassy carbon disc (geometric area: 6.85 mm², BAS) as the working electrode, a platinum coil as the auxiliary electrode, and an Ag/AgCl reference electrode. Deaeration was performed by purging with nitrogen.

### 2.3. Preparation of the Ferrocene/Nafion composite material

Accurately weighed 0.004 g of ferrocene was completely dissolved in anhydrous ethanol. Subsequently, 0.02 g of graphene was added under mild stirring, and the mixture was stirred for 3 hours in a water bath at 25°C. Following this, 0.356 g of graphite powder and 0.038 g of polyvinylidene fluoride were added. The mixture was sonicated for 1 hour to ensure even distribution within the composite material and then stirred for an additional 12 hours at room temperature, protected from air and light.

### 2.4. Preparation of the Ferrocene/Nafion-modified electrode (FNME)

A bare glassy carbon electrode was polished with 1, 0.3, and 0.05 μm aluminum oxide powder in the same direction on wet suede. The electrode was then ultrasonically cleaned

for 3 minutes with ethanol and distilled water and allowed to dry naturally. Subsequently, 8 μL of the prepared ferrocene/graphene composite was pipetted onto the polished bare glassy carbon electrode, spread evenly, and allowed to dry naturally. A 15% Nafion solution was then pipetted using a micro-injector and dispersed onto the surface of the ferrocene/graphene composite at room temperature, followed by natural drying. The ferrocene/graphene-modified electrode was placed in a buffer solution (pH=6.6) until a layer of polymer film formed. The potential was reduced for one minute to complete the formation of the ferrocene/graphene-modified electrode.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical behavior of diazinon on the modified electrodes

To investigate the electrochemical behavior of diazinon, three different electrodes were prepared: a bare glassy carbon electrode, a graphene-modified electrode, and a ferrocene/graphene-modified electrode. The cyclic voltammetry (CV) responses of these electrodes were measured in a phosphate buffer solution (PBS) containing 10 μM diazinon (pH 6.6) at a scan rate of 5 mV/s.

As shown in Fig. 1, the bare glassy carbon electrode (a) exhibited no significant redox peaks for diazinon, indicating minimal electrochemical activity. The graphene-modified electrode (b), however, showed noticeable redox peaks with a peak-to-peak separation of 0.32 V, demonstrating enhanced electron transfer but still limited reversibility.

In contrast, the ferrocene/graphene-modified electrode (c) exhibited significantly higher peak currents with a peak-to-peak separation reduced to 0.0059 V, indicating excellent reversibility and efficient electron transfer. The substantial improvement in electrochemical performance can be attributed to the synergistic effects of graphene's large surface area and ferrocene's redox mediation, which facilitate faster electron transfer and higher detection sensitivity for diazinon.

### 3.2. Effect of pH on the electrochemical behavior of diazinon

The influence of scan rates on the electrochemical behavior of diazinon was studied using cyclic voltammetry in a PBS buffer solution (pH 6.6) containing $1 \times 10^{-5}$ mol/L diazinon. The CV responses were recorded at different scan rates ranging from 0.001 V/s to 0.02 V/s, as shown in Fig. 2. The peak current increased significantly with increasing scan rates, with the oxidation peak shifting slightly in the positive direction.
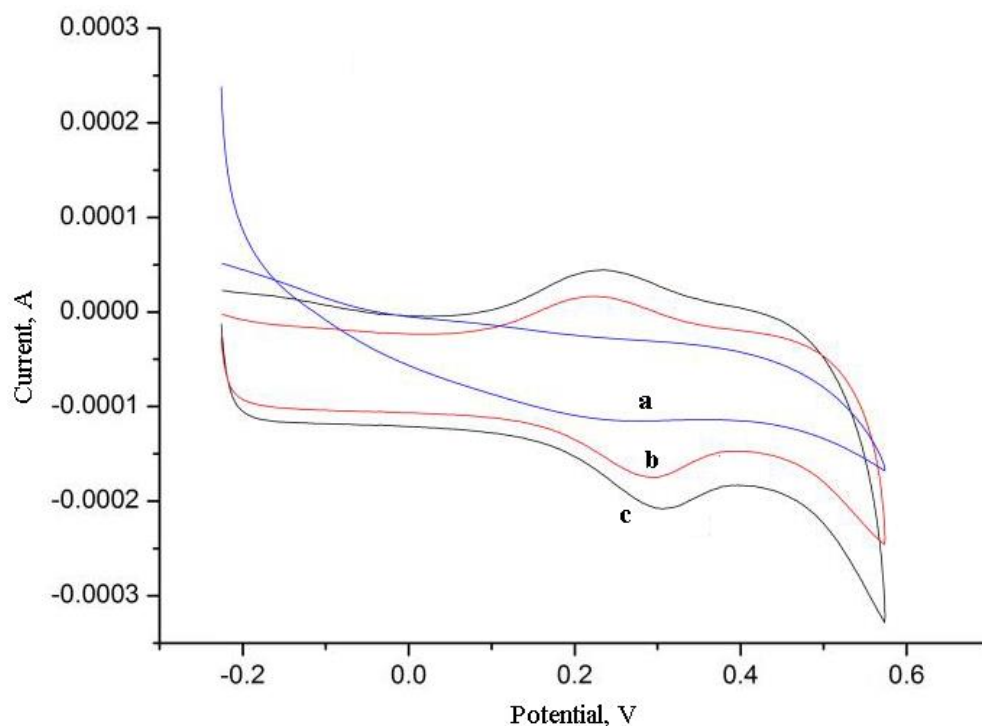
**Fig. 1.** Cyclic voltammograms of the (a) bare glassy carbon electrode, (b) graphene-modified electrode and (c) ferrocene/graphene-modified electrode in 0.1 mol/L PBS buffer solution (pH 6.47) with 10 µM diazinon at a scan rate of 50 mV/s.
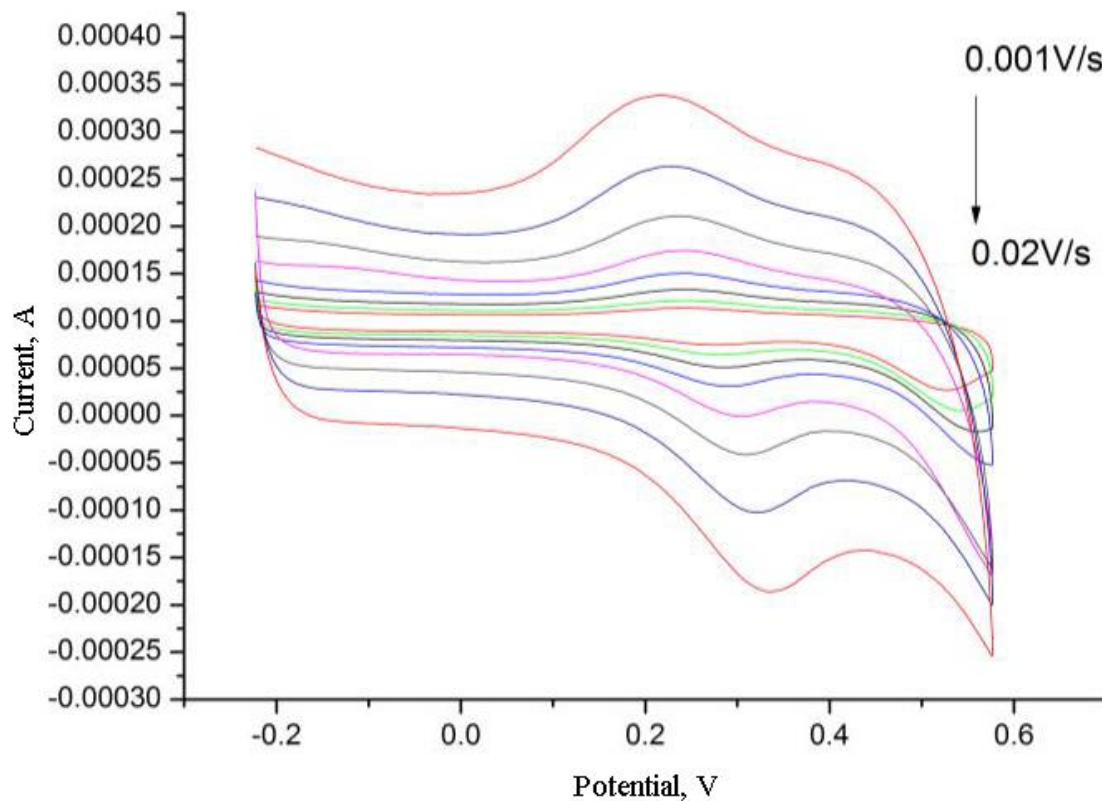


**Fig. 2.** Cyclic voltammogram of the ferrocene/graphene-modified electrode in 0.1 mol/L PBS buffer solution (pH 6.47) containing 10 µM diazinon with a scan rate of 0.001-0.02 V/s.

A linear relationship was observed between the peak current (both oxidation Ipa and reduction Ipc) and the square root of the scan rate for scan rates between 0.001 V/s and 0.005 V/s, indicating that the redox behavior of diazinon on the ferrocene/graphene-modified electrode is diffusion-controlled. For scan rates between 0.005 V/s and 0.02 V/s, the peak current showed a positive correlation with the scan rate, suggesting adsorption-controlled behavior. Based on these observations, a scan rate of 0.005 V/s was selected for further experiments to optimize the background current and enhance the signal-to-noise ratio.

## 3.3. Effect of pH on the electrochemical behavior of Diazinon

The effect of pH on the electrochemical behavior of diazinon was evaluated using differential pulse voltammetry (DPV) in a PBS buffer solution containing $1 \times 10^{-5}$ mol/L diazinon. The peak current responses at different pH values are shown in Fig. 3.

The peak current increased as the pH value increased from 5.60 to 6.47, reaching a maximum at pH 6.6. Beyond this point, the peak current gradually decreased with further increases in pH. This behavior can be attributed to the repulsion of neutral and anionic particles by the Nafion film at lower pH values, which reduces the adsorption capacity of diazinon on the modified electrode. At higher pH values, the increase in $OH^-$ concentration leads to partial charging of diazinon molecules, reducing their adsorption on the

electrode surface and thereby decreasing the peak current. The optimal pH for diazinon detection was determined to be 6.6.

## 3.4. Determination of the selectivity for Diazinon

### 3.4.1. Differential pulse relationship of diazinon with different concentrations

Differential pulse voltammetry was used to analyze diazinon in a 0.1 mol/L PBS buffer solution (pH 6.6) at various concentrations. As shown in Fig. 4, the peak current increased with increasing diazinon concentration, indicating higher diffusion and adsorption rates of diazinon on the ferrocene/graphene-modified electrode. At low concentrations ($1.2 \times 10^{-6}$ mol/L), the oxidation peak current remained at -0.72 µA, demonstrating the high sensitivity of the electrode for diazinon detection.

### 3.4.2. Linear Range and Detection Limit of Diazinon

As illustrated in Fig. 5, a linear relationship was observed between the peak current and diazinon concentration in the range of $1 \times 10^{-6}$ to $1.2 \times 10^{-5}$ mol/L. The linear regression equation was Ipa (µA) = 2.0578x - 38.2518 (µmol/L), with a correlation coefficient ($R^2$) of 0.9971. The detection limit, calculated as three times the standard deviation, was $1.2 \times 10^{-9}$ mol/L, indicating the high sensitivity of the ferrocene/graphene-modified electrode for diazinon detection.
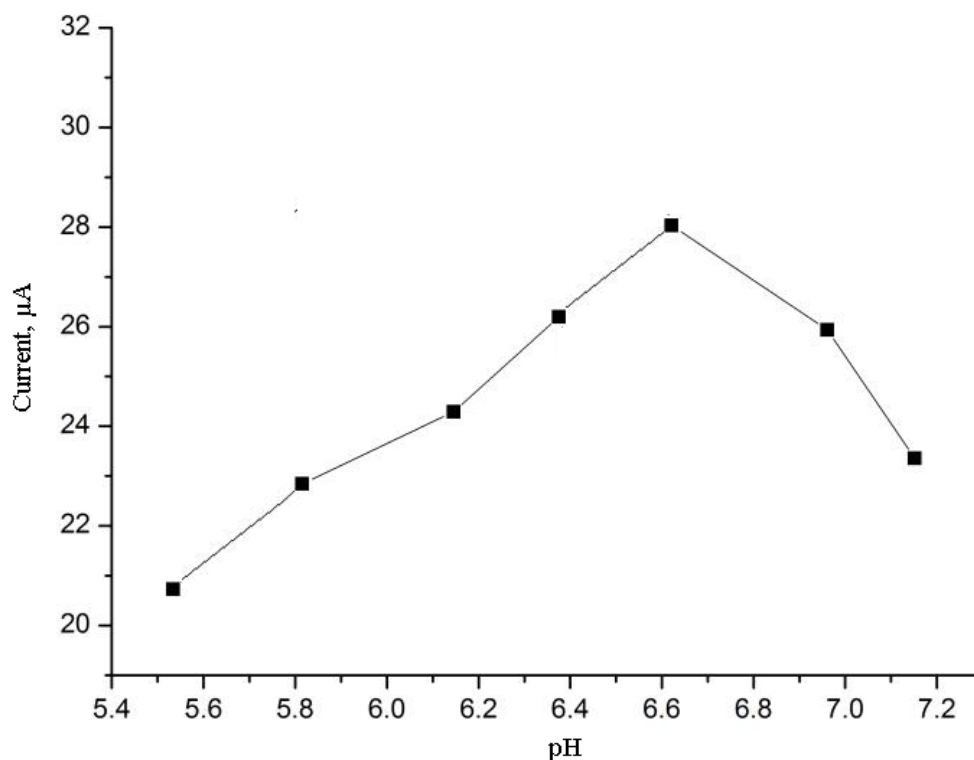


**Fig. 3.** Relationship between the pH value and the peak current in a solution of 10 µM diazinon.
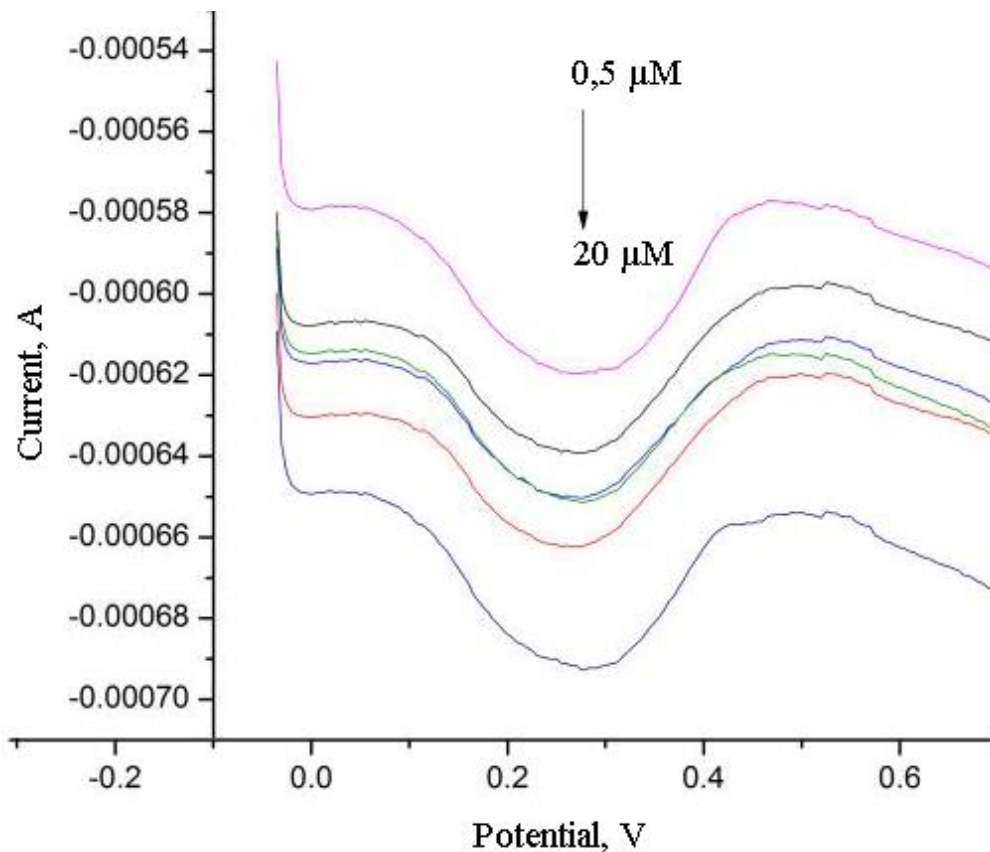
**Fig. 4.** Differential pulse voltammogram of diazinon with different concentrations in 0.1 mol/L PBS buffer solution (pH 6.6).
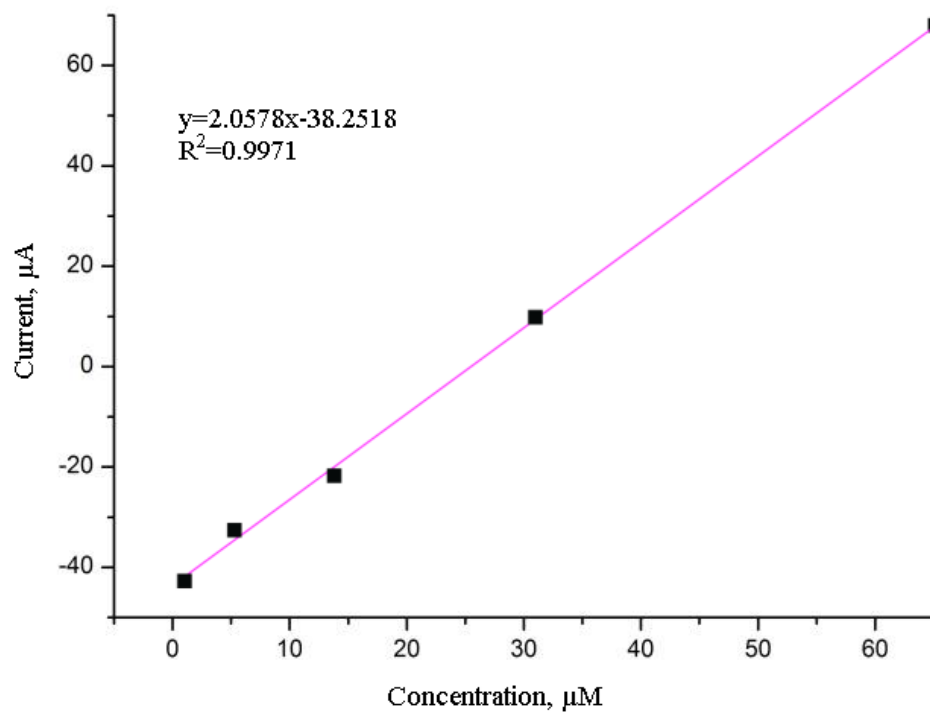


$$y=2.0578x-38.2518$$
$$R^2=0.9971$$

**Fig. 5.** Linear relationship between oxidation peak current and diazinon concentration in 0.1 mol/L PBS buffer solution, pH 6.6.

**Table 1.** Determination of the Diazinon Recovery.

| Sample | Theoretical value (µM) | Determined value (µM) | RSD (%) | Recovery (%) |
|--------|------------------------|-----------------------|---------|--------------|
| 1 | 1 | 0.958 | 5.3 | 95.5 |
| 2 | 2 | 1.916 | 5.2 | 95.8 |
| 3 | 5 | 4.745 | 4.9 | 94.9 |
| 4 | 10 | 9.48 | 4.8 | 94.8 |
| 5 | 20 | 19.24 | 4.2 | 96.2 |

\* RSD: relative standard deviation

### 3.5. Reproducibility of the ferrocene/graphene-modified electrode

The reproducibility of the ferrocene/graphene-modified electrode was evaluated by performing 10 consecutive scans in a PBS buffer solution containing diazinon (pH 6.6). The relative standard deviation (RSD) of the oxidation peak current was only 3.2%, indicating excellent reproducibility. Additionally, the sensor's performance remained stable, with only a 7.1% decrease in peak current after two weeks, demonstrating the good stability and reproducibility of the electrode.

### 3.6. Recovery rate of diazinon

The recovery rate of diazinon was tested using five water samples from Karakaya Lake. The initial tests showed no diazinon in the samples. Known concentrations of diazinon were then spiked into the samples using a stepwise dilution method, and the results are presented in Table 1. Each sample was tested in triplicate, and the RSD for the five groups did not exceed 10%. The recovery rates ranged from 94% to 96.2%, demonstrating the accuracy, reliability, and applicability of the electrochemical sensor for detecting diazinon in real water samples.

### 4. CONCLUSION

In this study, a ferrocene/graphene composite-modified glassy carbon electrode was successfully fabricated and evaluated for its performance in detecting diazinon. The modification significantly enhanced the electron transfer rate and electro-catalytic performance, resulting in high-efficiency detection of diazinon. The use of ferrocene in conjunction with graphene created a synergistic effect that improved the overall sensitivity and responsiveness of the sensor. The electrochemical performance of the modified electrode was assessed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). These techniques confirmed that the ferrocene/graphene composite provided a significant increase in the peak currents and improved the reversibility of the redox reactions, indicating efficient electron transfer and enhanced catalytic activity. The combination of high sensitivity, broad detection range, excellent stability, and practical applicability makes this sensor a valuable tool for environmental monitoring and potentially other applications requiring the detection of trace amounts of analytes. Future work could explore the adaptation of this sensing platform for detecting other environmental contaminants, further expanding its utility and impact.

### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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