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Improving the Sensitivity of Fipronil Electrochemical Detection with Imprinted Polymers Polyaniline Modified of Nano FeO.TiO_2

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Abstract: Fipronil, a widely used pesticide, has raised concerns due to its potential adverse effects on the environment and human health. To address this issue, developing sensitive detection methods for fipronil is crucial. This study focuses on a new electrochemical sensor based on nano ilmenite (FeO.TiO_2) and polyaniline (PANi) molecularly imprinted polymers (MIP) for highly improving the sensitivity of fipronil detection. This study prepares a new electrochemical sensor by a simple surface modification of a molecularly imprinted polymer on GPE/FeO.TiO_2 electrode. FeO.TiO_2@MIP composites were modified on a graphene paste electrode (GPE/FeO.TiO_2@MIP), and fipronil molecules were removed from PANi layers by cyclic voltammetry at the potential range of 0.8-1.2 V. The MIP was evaluated by scanning electron microscopy-energy dispersive X-ray (SEM-EDX) and subsequently ensured by cyclic voltammetry to verify the successful synthesis. The as-prepared electrode (encoded as GPE/FeO.TiO_2@MIP) is greatly sensitive to fipronil solution, with a linear range from 0.1 to 1.0 mg/mL and a detection limit of 0.19 mg/mL. The proposed sensor presents an auspicious performance capable of effectively detecting insecticide remnants. It demonstrates exceptional sensitivity and high stability.

Keywords: GPE/FeO.TiO_2@MIP; nanoilmenite; molecularly imprinted polymer; electrochemical sensor; fipronil.

1. Introduction

Currently, the use of pesticides for pest control is becoming wider in agricultural products. Regardless, its excessive use to protect agricultural products from pest attacks could induce environmental pollution, such as air, water, and soil [1]. Fipronil, as one of the most important systemic insecticides, is widely used to control various types of pests [2,3]. Furthermore, fipronil residues endanger human health due to their toxicity. In this case,

monitoring fipronil insecticide and its residue is highly desirable. Different analytical techniques have been established for the determination of fipronil, such as gas chromatography (GC) [4], high-performance liquid chromatography (HPLC), [5] spectrophotometric [6], and electrochemical sensors [7]. Among the mentioned methods, electrochemical sensors have received greater attention and offer various advantages such as low cost, fast response, sensitivity, selectivity, and simple technique in recent years [8,9].

As we all know, one important point for preparing an electrochemical sensor is to discover new modifier materials that can improve the performance of electrodes. Nano ilmenite ($FeO.TiO_2$) has been proven to be a superior semiconductor oxide material due to its high photoactivity under UV lights and high surface area [10–12]. Moreover $FeO.TiO_2$ has excellent chemical and physical properties and is non-toxic, eco-friendly, and low-cost, rendering it compatible with various wide applications such as electrochemical sensors, photocatalysis, catalytic applications, DSSC devices, and so on [13–15]. In addition, in this work, we choose graphene as the material substrate due to its high conductivity and ease of modification [16,17]. Although several studies have been conducted on using carbon as an electrochemical sensor material, graphene is more conductive than carbon [18,19]. Even though the usage of TiO_2 has been widely investigated in electrochemical sensors, its sensitivity and selectivity in sensors for detecting various dangerous low-level pollutants are unsavory [20–22].

In this work, we reported using PANi-based MIP on graphene paste electrode (GPE) modified of nano ilmenite ($FeO.TiO_2$). GPE offers high sensitivity for detecting analytes due to the large surface area of the graphene material [23,24]. This makes them ideal for use in electrochemical sensors. Moreover, GPE has a wide potential range, which allows for the detection of both oxidative and reductive species. On the other hand, the presence of nano ilmenite in GPE can enhance its electrochemical performance. When ilmenite is reduced to nano size, it can be used as a catalyst to improve the electrochemical behavior of the GPE. This truly strengthens the novelty of the present studies, wherein a highly sensitive MIP-based sensor was developed to detect fipronil insecticides.

2. Materials and Methods

2.1. Synthesis of $FeO.TiO_2$@MIP electrode.

The sol-gel method was chosen to synthesize nano ilmenite ($FeO.TiO_2$) because it is a one-step synthesis [7] to generate uniform, smaller, and colloidally stable sol of nanoparticles. According to this method, 4 mL of TTIP, 0.5 mL of acetylacetonate, and 15 mL of 99% ethanol were mixed as solution A, while solution B contains 15 mL of ethanol, 2 mL of DI water, and 1 mL of acetic acid. Furthermore, the mixture was stirred for 3 hours at 50°C and maintained. Subsequently, 1 mL of $Fe(NO_3)_3$ was added to obtain the colloidal $FeO.TiO_2$. Moreover, the sole was evaporated for 48 hours and furnaced at 80°C for 30 minutes.

The preparation of graphene paste electrode/$FeO.TiO_2$-modified molecularly imprinted polymer (GPE/$FeO.TiO_2$@MIP) was conducted using a simple polymerization process with a cyclic voltammetry technique. The experiment was carried out in a 10 mM aniline solution containing 1 M $MgSO_4$ supporting electrolyte with a potential range of 0.8-1.2 V, scan rate 0.5 V/s, and 10 cyclic. Then, in the same way, the measurement was conducted in aniline concentrations of 1 mM, 3 mM, 5 mM, 7 mM, and 10 mM. Finally, after the polymerization process, the template molecule was removed by electrolysis method in 1 M $MgSO_4$ supporting electrolyte solution with a cyclic voltammetry technique. It should be noted that the

GPE/FeO.TiO_2 modified non-molecularly imprinted polymers (GPE/FeO.TiO_2@NIPs) were prepared under the same situations represented above but without adding an aniline template. All polymerization processes utilized GPE/FeO.TiO_2 electrode as the working electrode, Ag/AgCl as the reference electrode, and platinum wire (Pt) as the auxiliary electrode.

2.2. Fipronil detection.

The detection of fipronil using the GPE/FeO.TiO_2@MIP electrode was carried out using three electrodes with the Cyclic Voltammetry (CV) method. Previously, the GPE/FeO.TiO_2@MIP electrode performance was examined using 0.01 M $K_3[Fe(CN)_6]$ solution to see the electrodes' characteristics in producing redox peak currents. Meanwhile, the detection of fipronil was performed in an electrochemical cell containing 25.0 mL of 1.0 M $MgSO_4$ and fipronil solution. Then the electrochemical response was investigated from a potential range of +0.8 to -0.8 V with a scan rate from 0.02 Vs to 0.5 Vs.

2.3. Characterization and measurements.

The morphologies and composition of the as-synthesized sample were evaluated by using scanning electron microscope-energy dispersive x-ray (SEM, FEI Quanta 450 ESEM, USA). The crystal structure and size were analyzed by X-ray diffraction (SHIMADZU Maxima, X-7000). Furthermore, the electrochemical properties were examined using a DY2100B potentiostat, as displayed in Figure 1.

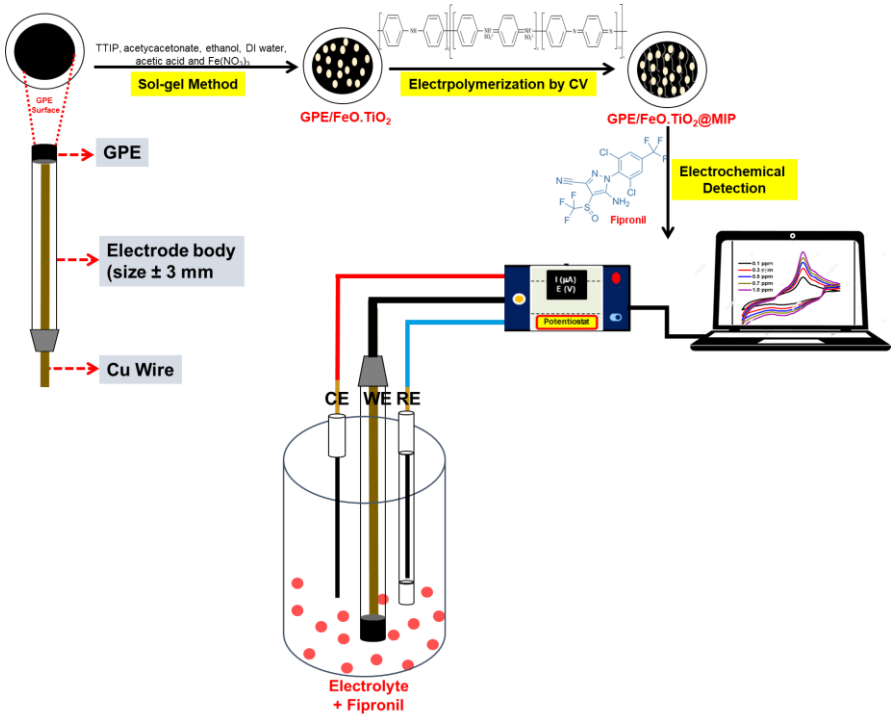

Figure 1. Illustration schematic of fipronil detection using cyclic voltammetry technique.

3. Results and Discussion

3.1. Characterization of GPE/FeO.TiO_2@MIP composite.

In the XRD characterization of FeO.TiO_2, a unique diffraction pattern consisting of diffraction peaks, was obtained—the diffraction pattern of FeO.TiO_2 has diffraction peaks corresponding to the crystal phases of FeO and TiO_2. These phases can be identified by

comparing the positions of the diffraction peaks to known standard diffraction patterns. The XRD pattern of the sample shows typical peaks of $FeO.TiO_2$ with an angle of 2θ at 37°, 38.60°, 78.79° and 75.10° respectively, which corresponds to the Miller index (012), (110), (113), and (024). This finding aligns well with previous studies [7]. Moreover, the crystallinity patterns of the prepared sample indicated characteristic peaks similar to the crystalline anatase structure of TiO_2, which are visible at 2θ at 25.35°, 37.80°, 48.12°, 53.90°, 55.12°, 62.74°, and 70.39° respectively, conform with JCPDS file No.21-1272. The particle size of $FeO.TiO_2$ was assigned by the Scherrer equation as 4.4780 nm.

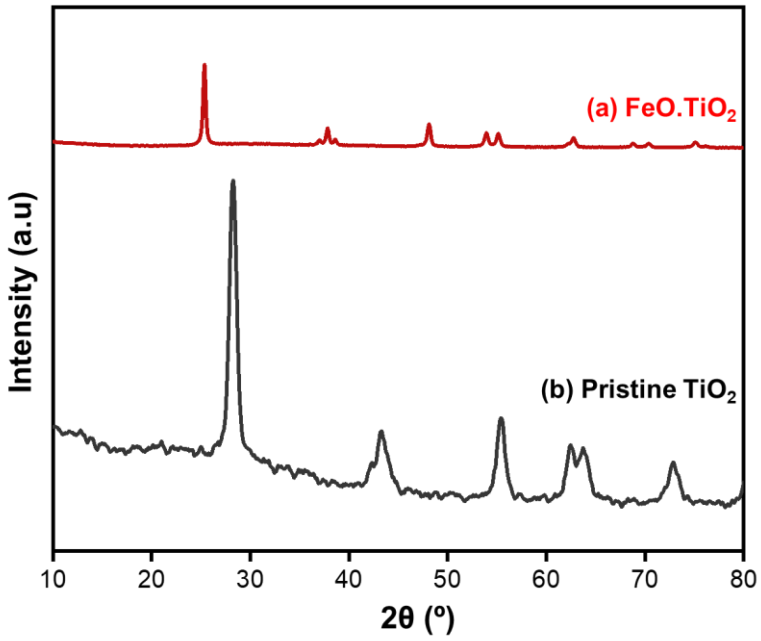

Figure 2. XRD patterns of **(a)** $FeO.TiO_2$; **(b)** pristine TiO_2

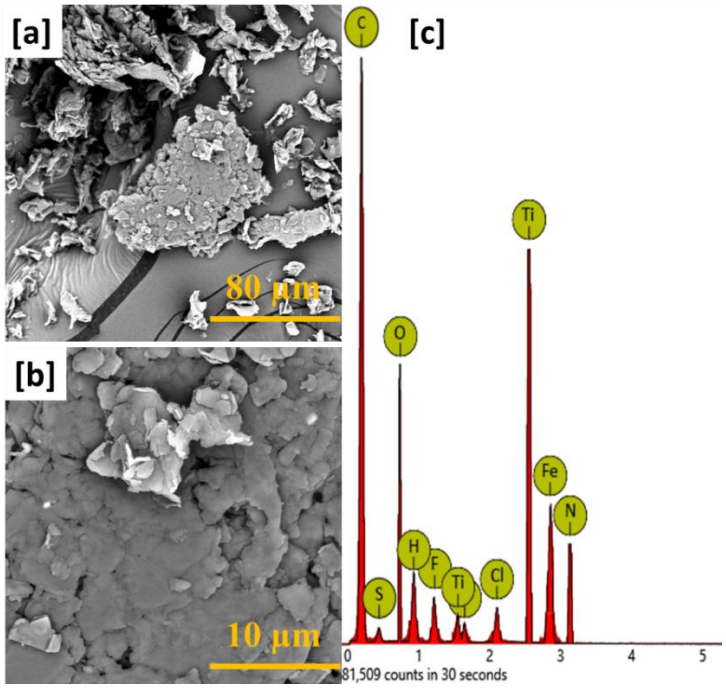

Figure 3. Microstructure of GPE/$FeO.TiO_2$@MIP composite analyzed by SEM–EDX, **(a)** magnification of 1000 times; **(b)** magnification of 3000 times; **(c)** EDX spectra of GPE/$FeO.TiO_2$@MIP composite.

The results of SEM characterization are shown in Figure 3. It can be seen that the GPE/$FeO.TiO_2$@MIP composite with magnifications of 1000 and 3000 times has a finer and

denser porous morphology. The even distribution of PANi on the surface of GPE/FeO.TiO_2 electrodes can result in a larger surface area, thereby increasing diffusion current and significantly improving the electrode's sensitivity and responsiveness [25,26]. Furthermore, the EDX analysis (Figure 3c) results indicate the EPG/FeO.TiO_2-MIP composite contains the elements C, Ti, O, Fe, N, H, F, Cl, and S with the respective percentages of 65.83%, 15.36%, 8.24%, 4.35%, 4.02%, 1.37%, 0.73%, 0.08%, and 0.02%. The elements come from graphene (C), ilmenite (Ti, O, and Fe), aniline (C, N, and H), and fipronil (C, O, N, H, F, Cl, and S).

3.2. Electrochemical and characterization GPE/FeO.TiO_2@MIP electrode.

The electropolymerization process was conducted in a 10 mM aniline solution containing 1 M $MgSO_4$ supporting electrolyte with a potential range of 0.8-1.2 V, scan rate 0.5 V/s, and 10 consecutive cyclic scans [27]. Figure 4 indicates the current response of cyclic voltammograms in the electropolymerization process. The imprinting of GPE/FeO.TiO_2@MIP electrode clearly peaks at 0.45 V, indicating the oxidation peak of fipronil, while peaks at 0.2 V represent the reduction peak of aniline. When the number of cyclic scans increases (until 10 cyclic scans), the current peak oxidation-reduction decreases (Figure 4A). As we can see, after removing the template from the MIP film, the current response of fipronil decreases (until 5 cyclic scans) (Figure 4B). These indicated that the fipronil has been removed from the PANi matrix.

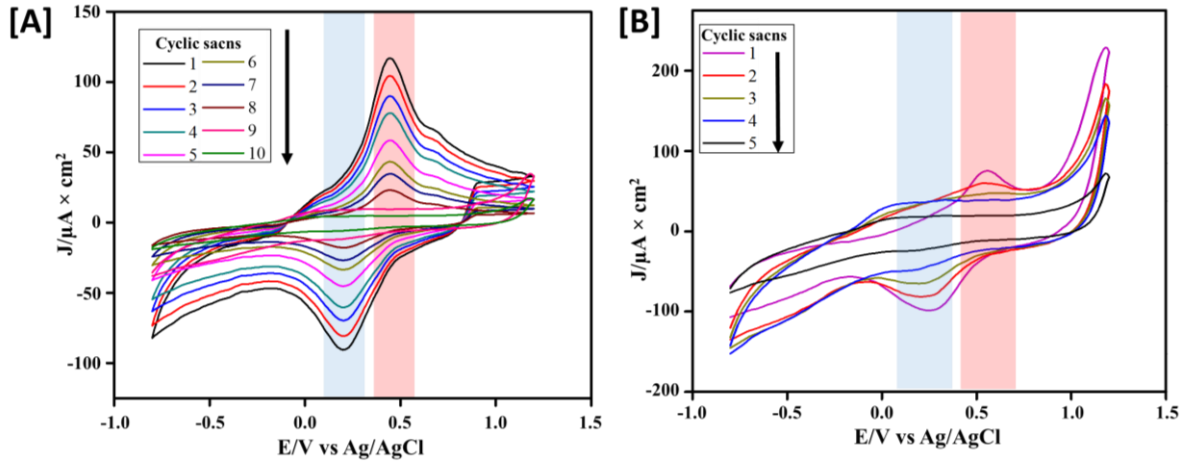

Figure 4. Cyclic voltammograms of GPE/FeO.TiO_2@MIP electrode **(A)** electropolymerization process; **(B)** removal of fipronil template in an electrolyte solution containing 1 M $MgSO_4$, in the potential range of -0.8 to 1.2 V at a scan rate of 0.5 V/s.

3.3. Effect of supporting electrolyte.

Based on Figure 5, it can be seen that there is a significant difference in current between the $MgSO_4$ solution, aniline, and fipronil. It is observed that the electrolyte solution $MgSO_4$ does not produce a peak current. The supporting electrolyte solution is considered good if it is stable and does not react with the analyte. In aniline solution, it produces a cathodic peak current (Ipc) of -54 µA at a potential of 0.2 V. Meanwhile, in fipronil solution, it produces an anodic peak current (Ipa) of 120 µA at a potential of 0.45 V, indicating that the current formed in GPE/FeO.TiO_2@MIP electrode is the current from fipronil.

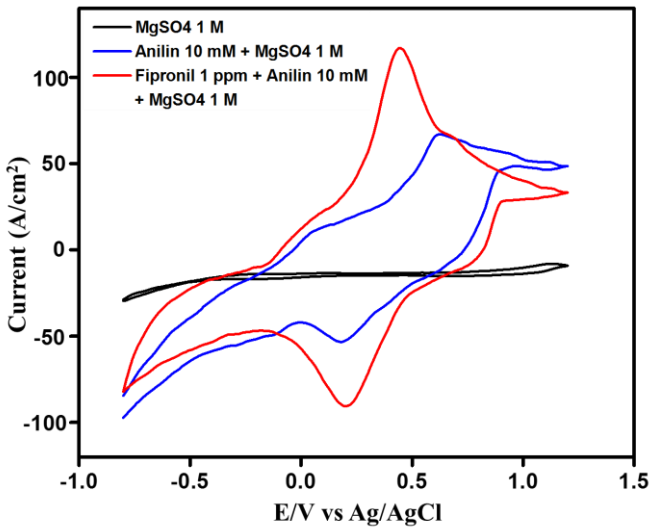

Figure 5. Cyclic voltammogram of aniline and fipronil in an aqueous solution of $MgSO_4$.

3.4. Effect of scan rate.

The scan rate is critical in many electrochemical measurements, particularly cyclic voltammetry (CV). The effect of the scan rate can be significant on the electrochemical behavior of a system under investigation. Figure 6 (a) exhibits the cyclic voltammogram of the prepared electrode at diverse scan rates. It's visible that as the potential scan rate increases from 0.02 to 0.50 V/s, there is a noticeable rise in the oxidation peak current—additionally, the peak possible shifts towards the positive direction. The peak current exhibits a linear increase in relation to the scan rate and can be described by the regression equation 1, with a correlation coefficient of 0.97 (Figure 6b).

$$Ipa\ (\mu A) = 174.23x\ +\ 10.726\ v\ (V/s) \qquad (1)$$

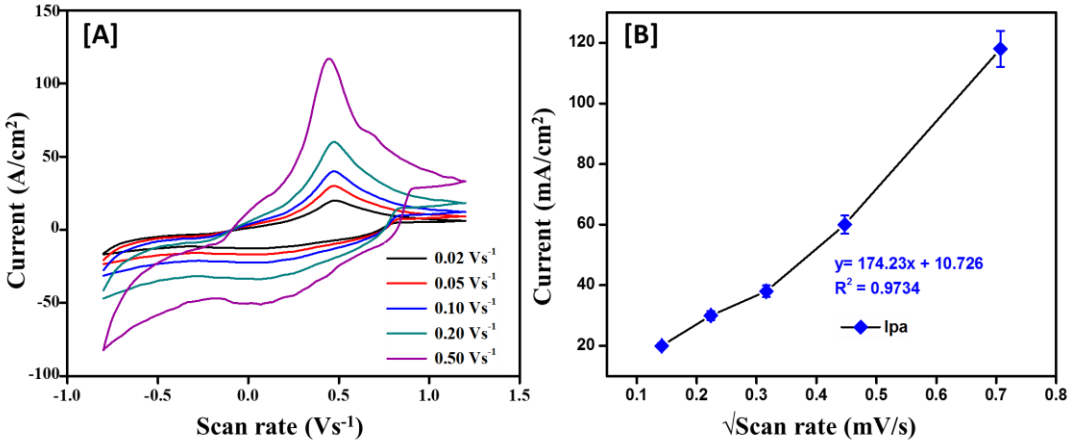

Figure 6. (A) Effect of scan rate variations on fipronil peak current; **(B)** Plot of root scan rate ($\upsilon^{1/2}$) vs peak current.

3.5. Interference ion test and repeatability.

Interference ion examines are conducted to determine whether the presence of other ions in the electrolyte solution can interfere with the measurement of the target ion. The effect of the presence of Cu (II) as interfering ions on the detection of fipronil was studied under the optimum condition. It's visible that the existence of Cu (II) ions causes the oxidation peak to decrease (Figure 7). Cu ions can form complexes with fipronil, which can affect the redox behavior of fipronil and, consequently, oxidation peak decrease [28]. The complex formation

can occur through the interaction of Cu ions with the sulfur and nitrogen atoms present in the fipronil's chemical structure. The formation of the Cu-fipronil complex can alter the electrochemical behavior of fipronil and, thus, interfere with the analyte measurements.

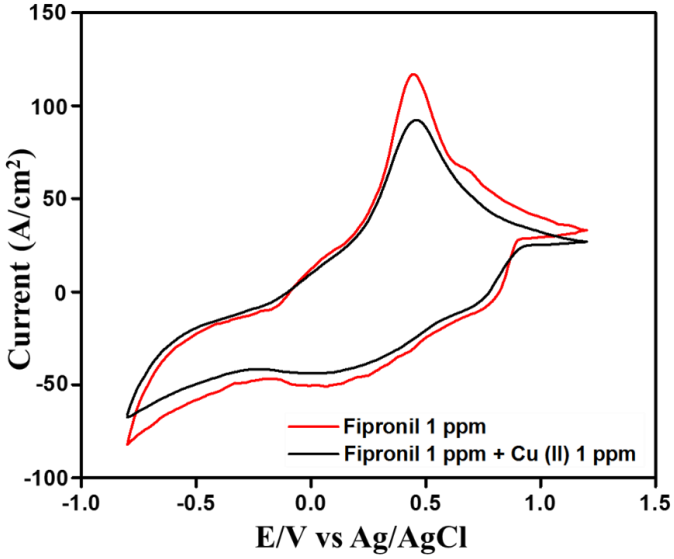

Figure 7. Cyclic voltammogram of GPE/FeO.TiO_2@MIP in the presence of interfering ions.

Repeatability refers to the ability of the electrode to provide consistent results under the same experimental conditions. The repeatability of GPE/FeO.TiO_2@MIP electrodes were evaluated using fipronil solution 1 ppm containing supporting electrolyte $MgSO_4$ 1 M (Figure 8). A series of frequentative CV evaluations of one electrode showed a relative standard deviation (RSD %) value of 1.8 % for 20 measurements designating outstanding reproducibility.

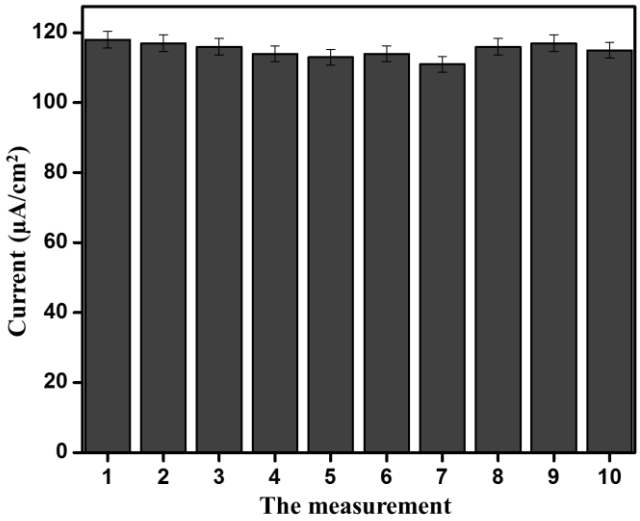

Figure 8. Histogram of repeatability detection of fipronil in the presence of Cu^{2+} ion interfering.

3.6. Limit of detection.

The detection limit is the smallest analyte concentration that can still be detected by the electrode. Determining the detection limit is necessary to know the minimum concentration that can still provide a current signal in GPE/FeO.TiO_2@MIP electrode. The detection limit is determined through the linear equation of the calibration curve within the fipronil concentration range of 0.1-1 ppm. The linearity curve of fipronil detection is shown in Figure 8. Based on the

calculation results, the detection limit for EPG/FeO is as follows: TiO_2-MIP in determining fipronil is 0.19 ppm.

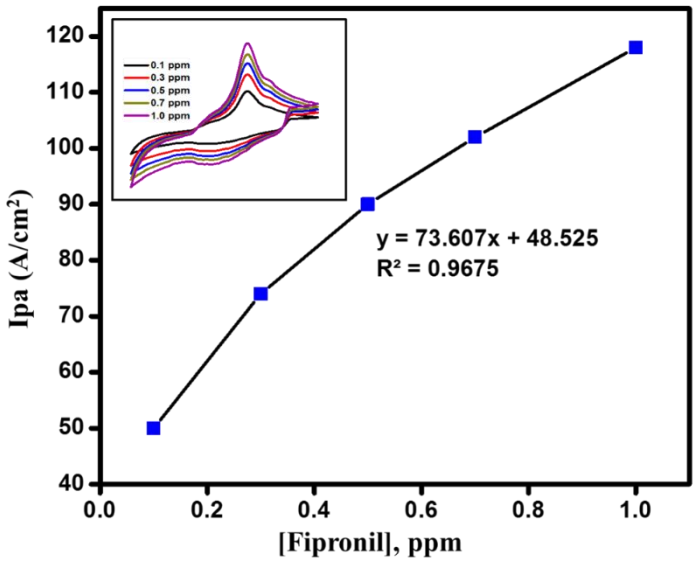

Figure 9. Plot of fipronil concentration vs. Ipa (insert image: cyclic voltammogram of the anodic peak current at various concentrations).

4. Conclusions

In summary, the GPE/FeO.TiO_2@MIP electrode, highly sensitive for the detection of fipronil, was successfully prepared. In this case, the molecularly imprinted PANi polymer via electropolymerization process using the cyclic voltammetry technique is employed as a recognition element. Moreover, SEM analysis confirmed the existence of PANi, which is evenly distributed on the surface of GPE/FeO.TiO_2 electrode. The developed electrode indicated good sensitivity, high stability, and low detection limit. The electrochemical sensor also produces high sensitivity due to the MIP layer from the electrode.

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Conflicts of Interest

The authors declare no conflict of interest.

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