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Electroanalytical Measurement Using Carbon Paste Electrode Modified TiO_2/Ag-Li in Detection of Fipronil Compound

Muhammad Nurdin[1,a)], Thamrin Azis[1], Sitti Hadijah[1], La Ode Agus Salim[2], Akrajas Ali Umar[3] and Maulidiyah Maulidiyah[1]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Kendari, Indonesia*
[2]*Department of Chemistry, Faculty of Science and Technology, Institut Sains Teknologi dan Kesehatan 'Aisyiyah, Kendari, Indonesia*
[3]*Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, Bangi, Malaysia*

[a)] *Corresponding author: mnurdin06@yahoo.com*

Abstract. The development of electrochemical sensors has become a topic that has been studied by many researchers, especially in improving the performance of carbon paste electrodes. This study aims to determine the performance of CPE-TiO_2/Ag-Li in the determination of fipronil compounds by Cyclic Voltammetry (CV). The parameters electroanalytical are linearity, the limit of detection (LOD), lifetime, and real sample. The measurement of fipronil solution by CPE-TiO_2/Ag-Li for LOD and repeatability with the Horwitz Ratio (HR) value were 0.01 ppm and 0.11%, respectively. The optimum measurement stability of CPE-TiO_2/Ag-Li in the detection of fipronil compound was 10 days. The interfering compound test using $CuSO_4$ in analyte solution has a significant effect on fipronil analysis which was characterized by a decrease in peak oxidation current. The content of fipronil in the real sample obtained was 0.253 ppm. This research can potentially be used as an alternative pesticides control in agriculture in the future.

INTRODUCTION

Organic pesticides are frequently employed in agriculture because of their great efficacy in eradicating plant pests. However, the use of chemical pesticides impacts the accumulation of residues that take a long time to degrade, causing environmental pollution [1]. In addition, uncontrolled use can interfere with human health. One of the pesticides that are widely used by farmers is the fipronil pesticide. Fipronil belongs to the class of phenyl pyrazole insecticides and has an environmental threshold value of 10 μM [2]. The way fipronil works is to interfere with the central nervous system and digestive system of the target organism [3].

Many methods have been developed to determine fipronil pesticides, such as Raman microscopy [4], GC-MS [5], biosensors [6], and HPLC [7]. However, they have not been effective for detecting fipronil pesticides in low concentrations. Besides, the difficulty of sample preparation means that it takes a long time and requires a lot of reagent preparation. Techniques with low detection limit gains that are still a hot topic reported by researchers today are voltammetry analysis techniques. Several voltammetry techniques have been reported by modifying the working electrode, including carbon-nanotube (MWCNT)-glassy carbon electrodes (GCEs) [8], carbon paste electrode (CPE)-TiO_2 [9], Graphite-polyurethane (GPU) composite electrode [10], graphene paste electrode (GPE)-TiO_2 [11], ZnO@g-C_3N_4 modified glassy carbon electrode [12], and FeO.TiO_2-CPE [13].

The performance of the TiO_2 modified CPE showed an excellent electron transfer rate on the electrode surface, as previously reported [14]. TiO_2 has a large surface area, relatively good thermal stability, high adsorption properties, and has abundant adsorption sites for organic compounds [15–20]. In addition, TiO_2 has an economical price, chemical stability for a long time, good optical properties is non-toxic, and produces environmentally friendly reaction products

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[21–25]. Although CPE-TiO_2 modification has shown high sensitivity and low detection limit, modifying CPE-TiO_2 is still an interesting study to be improved. It aims to improve the accuracy of measurements on different samples such as soil, food, and water.

The peak current generated from CPE-TiO_2 is strongly influenced by modifier composition, deposition time, and electroanalytical parameters. The parameters electroanalytical are linearity, the limit of detection (LOD), lifetime, and real sample. The focus of this study, we report the performance of Lithium (Li) and Silver (Ag) modified CPE-TiO_2 for the detection of fipronil. We have previously described the surface properties of CPE-TiO_2/Ag-Li in detail [26].

MATERIAL AND METHODS

Materials

The research materials used were HCl, potassium ferricyanide, sodium nitrate, graphite, aquades, titanium isopropoxide (TTIP, 97%), paraffin oil (d = 0.88 g cm^{-3}), fipronil compound (99%), acetic acid, acetylacetonate, silver nitrate, ethanol (99%), and lithium nitrate obtained from Sigma-Aldrich.

Preparation of CPE-TiO2/Ag-Li

The synthesized TiO_2/Ag-Li was used from previously reported [26]. Graphite, paraffin oil, and TiO_2/Ag-Li powder were prepared using a mass ratio of 7:3:1. Graphite and TiO_2/Ag-Li powder were ground until smooth, sieved using 200 mesh stainless steel, and put into a watch glass containing liquid paraffin. Furthermore, heated to paraffin temperature at 80°C. The liquid is mixed and pushed into a 3 mm diameter electrode body to harden, after which the electrode surface is rubbed until it is flat, smooth, and glossy.

Validation Test of CPE-TiO2/Ag-Li to the Determination of Fipronil

- Determination of regional linearity and LOD was carried out using fipronil solution with a concentration range of 0.1 to 1 ppm in 1 M HCl electrolyte solution. Plots were made between concentration and current to obtain the linearity area of the current response [27].
- The precision test was carried out using the repeatability method. The repeatability of measurements is determined by the peak current having a Relative Standard Deviation (RSDR). If the Horwitz Ratio (HorRat) is less than 2, the measurement repeatability is considered satisfactory. HorRat value is the ratio of %PRSDR and %RSDR [28].
- The electrode lifetime determination test was carried out for 24 days and was carried out every 3 days. The electrode lifetime was determined by analyzing the voltammogram data from the measurement results until the 24 days.
- Real sample tests were carried out on pesticides containing the active ingredient fipronil. Measurements were made with two comparisons, namely real sample and real sample added with standard fipronil solution.

RESULTS AND DISCUSSION

Determination of Regional Linearity and LOD

The curve between the concentration of the fipronil solution and the I_{pa} value demonstrates regional linearity. The intercept obtained is 5.311 with a slope of 9.016, so that the linear equation y = 9.016x + 5.311 and the R^2 value obtained is 0.991 (Fig. 1). The purpose of this linear curve is to find a reasonable working range for the fipronil solution measurement's standard linearity [29]. The results of the average current measurement are 9.8 A, and the intercept standard deviation (SD) is 0.323. The LOD value calculated in the determination of fipronil is 0.01 ppm.

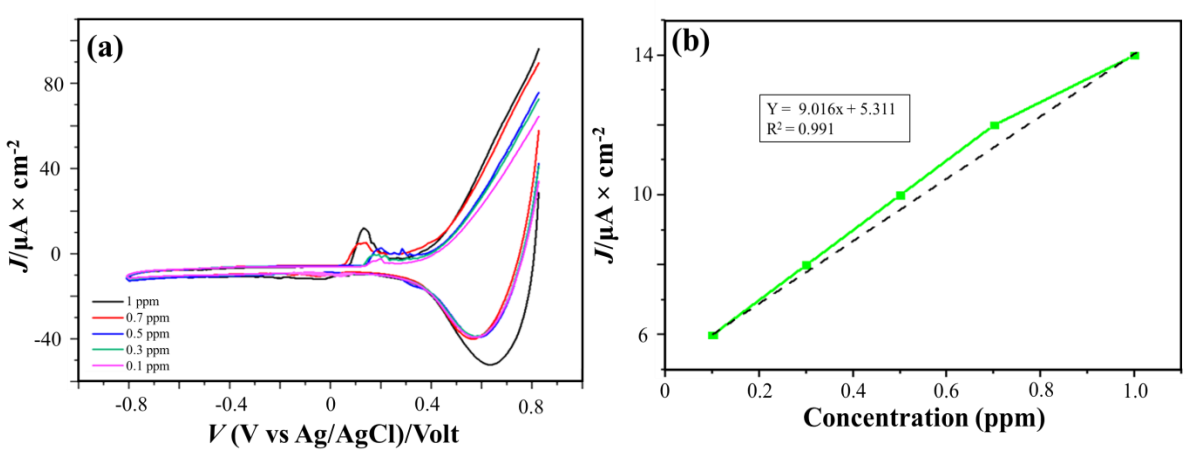

FIGURE 1. (a) CV voltammogram determination of fipronil compounds with various concentrations (0.1-1 ppm), and (b) voltammogram of oxidation vs. concentration range was used to create a linearity plot

Repeatability Tests

The purpose of the repeatability method is to determine the repetition of measurements required under unchanged conditions to obtain the same result [30]. The SD value from the measurement results is 1.38 and the average peak current value is 12.28 A. %RSDr value is 0.11% while the %PRSDr value is 2%. Repeatability measurement is declared good if the HorRat value is less than 2 [28]. Based on the calculation results obtained HorRat value of 0.05. Based on the analysis results, CPE-TiO_2/Ag-Li was declared stable in analyzing fipronil. The repeatability test is a precision test that shows the degree of correspondence between individual test results and the average value if the procedure is repeated [31]. Figure 2 shows the results of the measurement repeatability test.

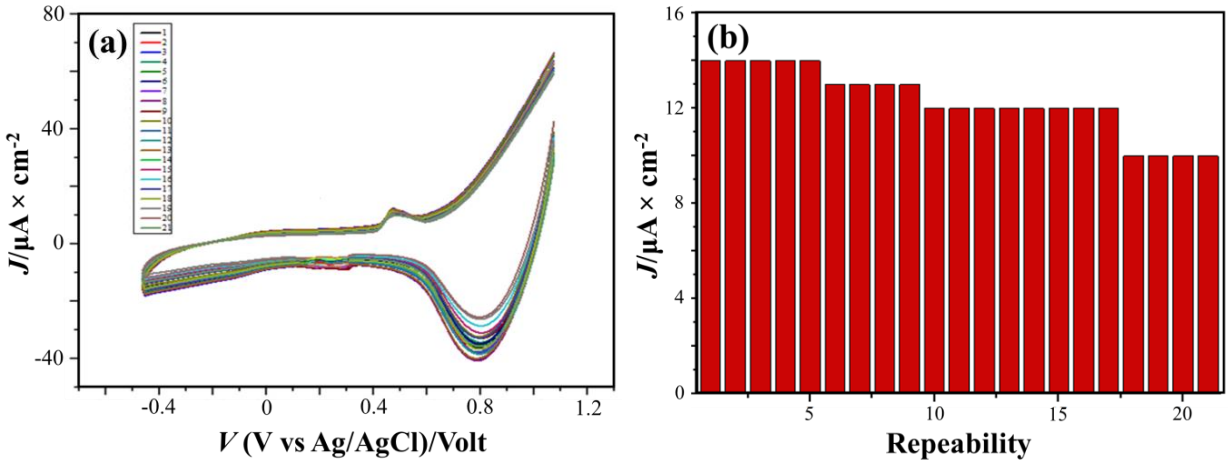

FIGURE 2. (a) Repeatability voltammogram, and (b) histogram of measurement repeatability

Lifetime Determination Test

Lifetime determination of electrode age is a test carried out to know the stability of electrode in the long term still suitable to determine fipronil compound [32]. Based on the measurement results (Figure 3), the electrode is still in a stable state, as evidenced by the peak current generated being higher and relatively constant over the first ten days. The resulting peak current decreases on the 11-27 days. The thickening of the diffusion layer on the working electrode's surface causes a sluggish electron transfer, resulting in a drop in peak current [33]. Because these electrodes are only utilized for a limited length of time, it is important to improve the electrode measurement's stability.

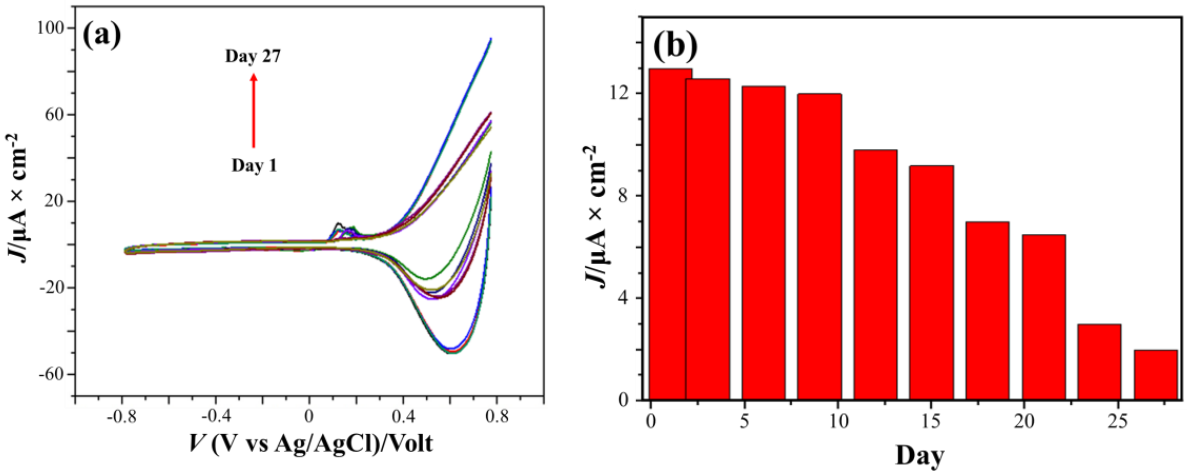

FIGURE 3. (a) Lifetime determination voltammogram, and (b) electrochemical stability histogram

Real Sample Test

Real sample testing aims to determine the ability of CPE-TiO_2/Ag-Li in analyzing fipronil to real samples. Previous studies demonstrated the ability of modified CPE to detect fipronil samples in real samples [29]. The voltammogram shows that the real sample did not identify a peak current of fipronil; it is caused there are many other chemicals in the real sample (Figure 4). Based on the I_{pa} value data from the fipronil solution in the real sample obtained, then the concentration value was determined using the regression equation y = 9.016x + 5.311. The calculation results show that the oxidation current of 7.6 A is equivalent to 0.253 ppm. These results are relatively lower than the concentration of the standard solution of fipronil used in the real sample test. These results indicate that CPE-TiO_2/Ag-Li has not provided an accurate response in determining fipronil in real samples.

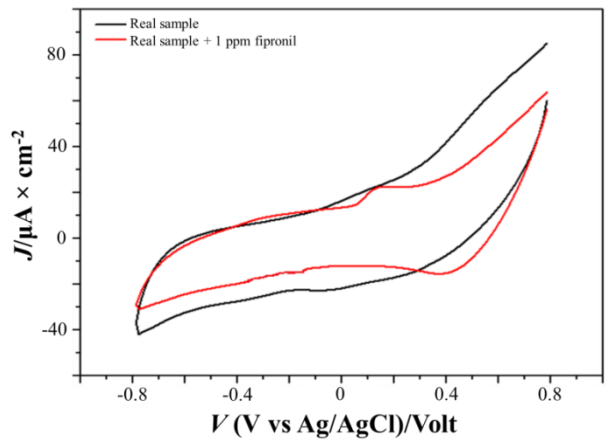

FIGURE 4. Real sample voltamograms

CONCLUSION

A validation test of CPE-TiO_2/Ag-Li to determine of fipronil compound has been successfully carried out. The LOD obtained from the measurement of the CPE-TiO_2/Ag-Li in the fipronil solution was 0.01 ppm, and the repeatability performance is 0.11% with a HorRat value of 0.05. The low %RSD value indicates that the precision level of the CPE-TiO_2/Ag-Li is good. The optimum measurement stability of CPE-TiO_2/Ag-Li in analyzing fipronil solution was 10 days. The content of fipronil in the real sample was 0.253 ppm; however, it has not provided an accurate response.

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