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Electroanalytical Performance of Graphene Paste Electrode Modified Al(III)-TiO_2 Nanocomposites in Fipronil Solution

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Abstract

The new composite material Al(III)-TiO_2 has been synthesized and applied as a modifier of graphene paste electrode for the determination of fipronil pesticide by cyclic voltammetry. The methods were to synthesis of Aluminum-Titanium dioxide (AT), preparation of graphene paste electrode with mass varied Al(III)-TiO_2 (GAT) (0.05 g, 0.1 g, 0.2 g), and fipronil electroanalytic respons. Addition of Al(III)-TiO_2 to the graphene paste electrode shows redox properties which are well characterized by a fast electron transfer process. Based on the results of measurements in a solution containing fipronil, it is known that fipronil is oxidized at a potential value of 0.26 V. Furthermore, the fipronil oxidation process on the GAT surface is influenced by diffusion control, this is powered by R^2 value 0.91 when plotted between peak oxidation currents (I_{pa}) vs. root scan rate. Other results show that measurement linearity is in the range 0.01 to 0.09 µg/L with a limit of detection (LOD) value of 0.0164 µg/L. Moreover, GAT shows good stability in the determination of fipronil with% RSD equal to 5%.

Keywords: Al(III), TiO_2, cyclic voltammetry, fipronil pesticide, graphene paste electrode

1. Introduction

Organic pesticides have been widely used in agriculture because they have high performance to eradicate pests, diseases, and weeds in plants. However, there are negative impacts caused to living things due to contamination of hazardous substances. One type of insecticide that is classified as Pollutant Organic Persistance (POPs) is Fipronil (Maulidiyah et al., 2019). Fipronil is a member of a group of phenyl pyrazole compounds (5-amino–1-[2,6-dichloro-4-(trifluoro-methyl)phenyl]-4 (trifluoromethyl) sulfinyl]-1H-pyra-zole-3-carbonitrile) (Wang et al., 2016). Fipronil is a insecticide that is designed for plants such as wheat, rice, cotton, sorghum, corn, and other grains. Excessive use of pesticides can cause residues from pesticides to be difficult to accumulate in the environment and body (Kim et al., 2019).

Electrochemical techniques have been reported as techniques with good sensitivity and selectivity for the determination of fipronil pesticide compounds (Nurdin et al., 2019a). The presence of fipronil in the environment is a serious concern due to its toxic nature (Tu et al., 2019), the slow degradation process (Stafford et al., 2018), and its impact on aquatic animals and marine invertebrates (Gunasekara et al., 2007; Guo et al., 2018). The results of a recent study reported that fipronil has a high affinity for human receptors which triggers nerve disorders (Gan et al., 2012; Kim et al., 2019; Ly et al., 2019). In addition, the degradation of fipronil will produce derivative compounds such as desulfinyl which are far more dangerous than fipronil molecules (Vasylieva et al., 2015).

In general, the detection of fipronil was carried out using a high-performance liquid chromatograph (HPLC), thin-layer chromatography (TLC) method, and gas chromatography-mass spectrometry (GC-MS) technique (Vílchez et al., 2001; Jimenez et al., 2008; Wang et al., 2014). Furthermore, some measurement techniques based electrochemical that are being developed includes amperometry (Pesavento et al., 2009), potentiometry (Prasad et al., 2007), voltammetry (Alizadeh 2009), and chronopotentiometric (Đurović et al., 2016). Simple tool preparation (Zhang et al., 2014), low cost of measurement (Ensafi et al., 2013), short measurement time (Janegitz et al., 2012), and good stability (Yang et al.,

2012) are the reasons why this technique continues to be developed for the determination of pesticide compounds. The performance of the voltammetry method is strongly influenced by the working electrode as the site of the oxidation reaction and reduction of the analyte molecule.

One of the working electrodes that have been developed is the graphene paste electrode. Graphene paste electrode is a working electrode in voltammetry. Graphene has excellent physical and chemical properties that can make it an electrical device and sensor. Graphene as a material with thin sheets of carbon atoms that form a regular hexagonal lattice has excellent electrical conductivity (Agusu et al., 2018). The excellent electrical conductivity of graphene makes it easy for the electron exchange between analyte molecules to be very efficient to be used as a base material for the working voltage of a voltammetry cell.

Modification of working electrodes is an important part of developing the technique. Modified working electrode carbon-nanotube (MWCNT)-glassy carbon electrodes (GCEs) (Montes et al., 2016), Graphite-polyurethane (GPU) composite electrode (Okumura et al., 2016), and ZnO@g-C_3N_4 modified glassy carbon electrode (Yin et al., 2019), and FeO.TiO_2-CPE (Nurdin et al., 2019a) have been reported to be able to detect fipronil compounds in different samples. Although the modification of the electrode shows high sensitivity with a low detection limit, electrode modification is still an interesting study in the past year. It aims to get accurate measurements on different matrices such as food, soil, and water.

In this work, we report the performance of Al(III)-TiO_2 nanocomposites as a new composite material in determining fipronil by cyclic voltammetry using graphene paste electrodes. In general, Al(III)-TiO_2 is reported to have high oxidation and reduction currents (Desireé et al., 2015; Murtada et al., 2018), but its application has not been reported as a composite material for the development of general voltammetry sensors and specifically pesticide detection sensors. Graphene paste electrodes were chosen in this work by considering several advantages such as easily updated and modified, cheap, and very low current interference. Previous research, we have specifically reported TiO_2 as an electrode composite to detect cypermethrin (Nurdin et al., 2019b) and phenol pesticides (Nurdin et al., 2019c).

2. Methodology

2.1. Materials

The materials used were titanium isopropoxide (TTIP, Sigma-Aldrich), aluminum isopropoxide (ATIP, Sigma-Aldrich), citric acid (powder of 98% purity, Sigma-Aldrich), graphene powder (Sigma-Aldrich), paraffin oil (Merck-Germany, d = 0.88 g cm^{-3}), TiO_2 degussa P25 (Merck-Germany), fipronil compounds (99%, Sigma-Aldrich, USA), hydrochloric acid (0.1 M, Sigma-Aldrich), sodium sulfate (Sigma-Aldrich), Cd(II) solution (Sigma-Aldrich), and Pb(II) solution (Sigma-Aldrich).

2.2. Preparation of GAT Electrode

Preparation of GAT electrodes begins by synthesizing composite Aluminum-Titanium dioxide (AT). The synthesis process was carried out using TTIP and ATIP as precursors. In summary, ATIP powder is dissolved in TTIP solution and added citric acid as a complexing agent. Then the mixture was heated for 3 hours at a temperature of 200 ^oC and continued with a temperature of 650^oC for 5 hours. The obtained composites were mixed with graphene powder and paraffin oil at a temperature of 80 ^oC with a composite mass varied between 0.05 g, 0.1 g, and 0.2 g. The formed paste has been homogenized.

Glass tubes with a diameter of 3 mm were used as a paste container and connect to copper wire to provide current during electrochemical measurements. For comparison, we used the Graphene-TiO_2 (GT) composite electrode whose preparation refers to the procedure reported by (Nurdin et al., 2019c). Graphene powder, paraffin oil, and TiO_2 degussa were simultaneously mixed with a ratio of 7: 3: 1, and homogenized at 80 ^oC.

2.3. Electroanalytical Response of Fipronil

The electroanalytic response of the fipronil compound was carried out by the voltammetry method using the DY2100B potentiostat with three electrode systems namely GAT as the working electrode, Ag/AgCl saturated in 3.0 M KCl as the reference electrode and platinum wire as auxiliary electrodes. For analytical purposes, fipronil compounds with concentrations of 0.1 µg/L were made by mixing them in a mixture of hydrochloric acid and sodium sulfate as

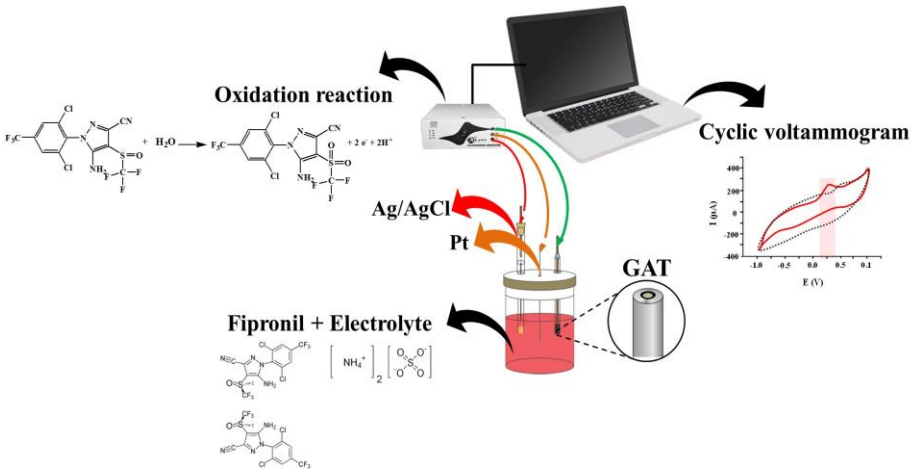

Figure 1. Scheme of the experimental

supporting electrolytes. The fipronil concentration was applied in 0.01, 0.03, 0.05, 0.07, and 0.09 µg/L to determine the linearity areas and LOD. We also determination the stability for 14 times. Scheme of the experimental shown in Figure 1.

3. Results and Discussion

3.1. GAT Response in Fipronil Solution

Figure 2 shows the performance of the GAT electrode in detecting fipronil pesticides (solid line) in a solution containing a mixture of electrolytes supporting HCl and Na_2SO_4 of 0.1 M, respectively. Based on the figure, it can be seen that fipronil oxidizes at anodic potential (E_a) of 0.26 V with a current anodic peak (I_{pa}) of 262 µA. Compared to the Graphene-TiO_2 (GT) electrode (dot line), the performance of GAT in fipronil oxidation is much better, this is seen with the value of E_a fipronil in the GT of 0.57 V with a small value of the I_{pa} and a widening peak.

The results of previous studies reported that during the oxidation process, fipronil released 2 protons and electrons (Maulidiyah et al., 2019). The difference in the potential value of the two electrodes explains that the transfer of electrons between fipronil molecules and GAT electrodes is faster than GT. The combination of aluminum composite and TiO_2 (AT) has a significant influence on the performance of the electrode. Both cause the conductivity and surface area of the GT to increase (Munir et al., 2019; Xu et al., 2019). In addition, it also increases catalytic activity and the effectiveness of the electrode surface in fipronil oxidation. In general, the electroanalytic response of GAT in fipronil oxidation is much faster than MWCNT/GCEs (Montes et al., 2016), and GPU(Okumura et al., 2016).

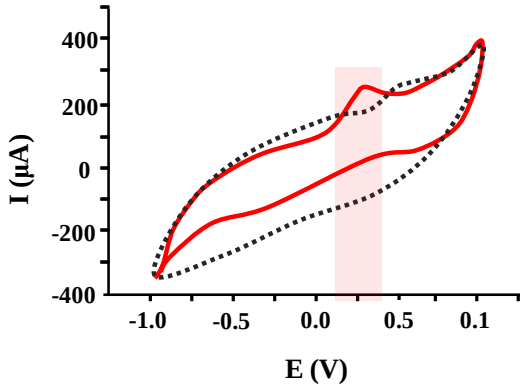

Figure 2. Voltammogram cyclic electrode GAT (solid line) and GT (dot line) in a solution of fipronil

The effect of AT modifier composition is also studied in this work. Like other modifiers, the mass of AT can affect the transfer of electrons and the resulting peak current on graphene paste electrode. Figure 3 shows that the addition of AT as much as 0.2 g (Figure 3c) causes electron transfer faster than the addition of AT at 0.05 g (Figure 3a), and AT at 0.1 g (Figure 3b). Addition of AT as much as 0.2 g causes a decrease in I_{pa} fipronil. Measurement during this work, a GAT electrode is used with an addition of AT of 0.2 g. The basic consideration is that the reduction in I_{pa} does not significantly change.

The difference in scan rate potential (20 mV/s, 50 mV/s, 100 mV/s, and 200 mV/s) in fipronil oxidation shows a linear relationship as shown in Figure 4. The fipronil oxidation current increases linearly with an increasing potential scan rate (Figure 4A). This linear

relationship results from GAT interactions with redox species during the formation of multiple electrical layers. The potential difference in scan rate does not cause a significant change in the value of E_a fipronil.

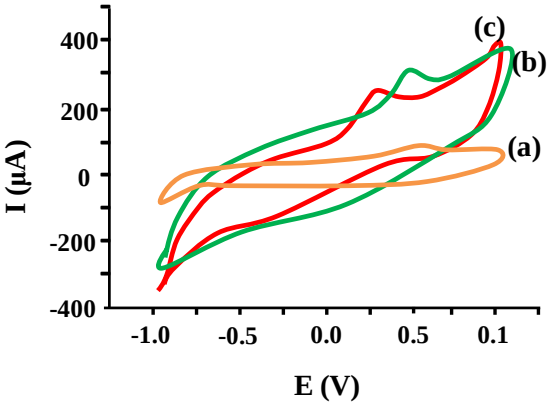

Figure 3. Voltammogram cyclic GAT response in a solution of fipronil with mass variation AT: (a) 0:05 g; (b) 0.1 g; (c) 0.2 g

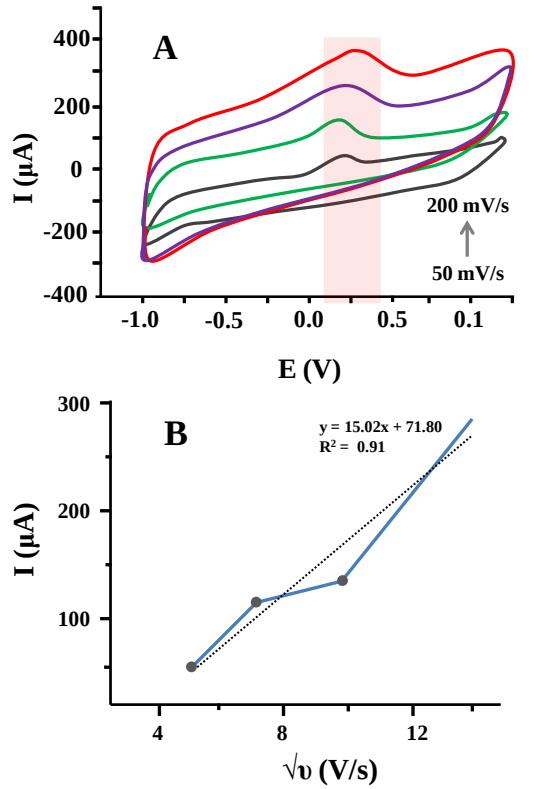

Figure 4. (A) Potential scan rate difference; (B) Interpolate the peak current vs. root scan rate. Linearity, detection limit, and GAT stability

In addition, based on the interpolation results of I_{pa} fipronil versus root scan rate (Figure 4B), it shows a linear nature for fipronil oxidation with a linearity constant (R^2) of 0.91. This result shows that electron transfer on the surface of the electrode is controlled by the diffusion. This diffusion process is the difference in concentration between the surface of the electrode and the body of the solution which causes the molecules to move to the surface of the electrode (Maulidiyah et al., 2019).

A high scan rate will cause the resulting diffusion layer to be thin so that the transfer of electrons on the electrode surface becomes easier and the peak current produced is also greater. Conversely, a small scan rate results in the thickness of the resulting diffusion layer, thus inhibiting the electron transfer process at the electrode surface and the resulting peak current is small (Nurdin et al., 2019b).

3.2. Linearity, Detection Limit, and GAT Stability

Linearity is the ability of the analytical method to produce a response that is directly proportional to the concentration of the analyte (Wibowo et al., 2017). The equation of a linear line is determined by making a plot between the resulting peak current (µA) and the concentration of the fipronil solution (µg/L). The detection limit of the measurement of fipronil pesticides is studied to find out the smallest amount of analyte in a sample that can still be detected and still gives a significant response compared to the blank. The GAT response in the fipronil analysis was also carried out with different fipronil concentrations ranges of 0.01 to 0.09 µg/L (Figure 5).

Figure 5A shows a voltammogram with an increase in I_{pa} that is linear with changes in the concentration of fipronil solution. The linear concentration of fipronil solution measurement from 0.01 to 0.09 µg/L obtained an Intercept of 70.75 with a slope of 325x to obtain a linear equation y = 325x + 70.75. The purpose of making this linear curve is to find out a good working range of standard linearity in fipronil measurements. The plot between Ipa vs concentration fipronil (Figure 5B) shows a linear regression equation with a linearity constant (R^2) of 0.96. The level of correlation between the correlation value R^2 with a range of 0.80-1.0 has a very strong linear relationship (Mursalim et al., 2017). The maximum residual limit (MRLs) of fipronil in environment ± 0.1 µg/L (Standard 2008). Based on the results of the analysis, it is known that the detection limit value for the fipronil measurement uses GAT of 0.0164 µg/L.

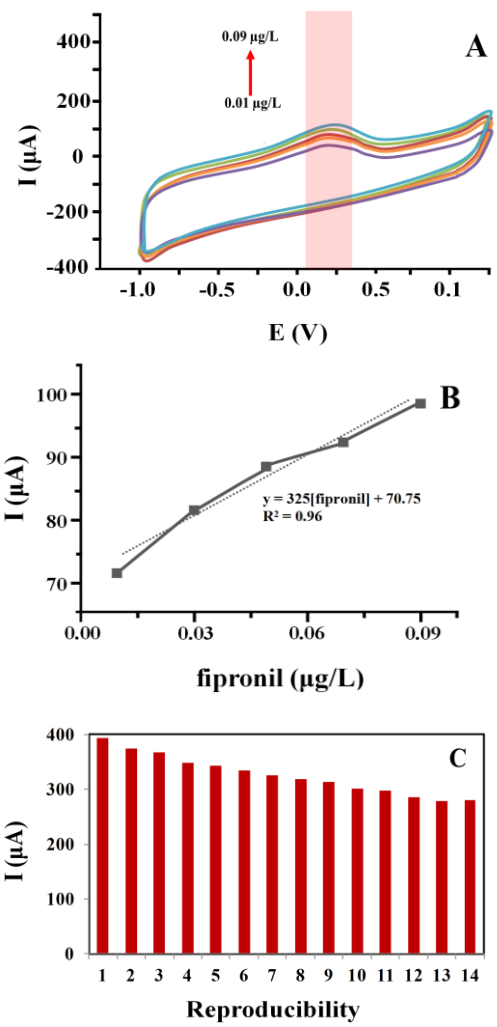

Figure 5. (A) Voltammogram linearity area fipronil 0.01 to 0.09 µg/L; (B) fipronil linearity curve; (C) reproducibility measurements

Table 1. Comparison of detection results of fipronil from various working electrodes

Working electrode	Method	LOD (µg/L)	References
MWCNT/GCEs	Amperometric	1.88	(Montes et al., 2016)
Graphite-polyurethane (GPU)	SWVS	0.80	(Okumura et al., 2016)
ZnO@g-C_3N_4/GCE	Electrochemiluminescence (ECL)	0.65	(Yin et al., 2019)
FeO.TiO_2-CPE	Cyclic voltammetry (CV)	1.04	Nurdin et al., 2019a)
Al(III)-TiO_2/Graphene	Cyclic voltammetry (CV)	0.0164	This work

In addition, GAT also shows good stability (Figure 5C) in detection of fipronil with% RSD of 5% (Yuan-Yuan et al., 2015). Several comparisons of electrochemical techniques in detecting fipronil with the use of electrodes and different modifiers are shown in Table 1.

3.3. Effect of Disturbing Ions

The electrode selectivity used needs to be known before the stage application on the environment. One way to determine the level of selectivity is to add disturbing ions to the fipronil solution to determine the effectiveness of the electrodes in detecting pesticide compounds in the presence of other compounds or ions in the same analyte.

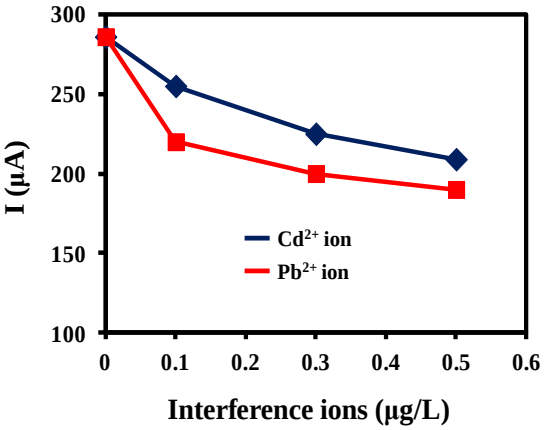

Figure 6. GAT response with the presence of heavy metal interference ions

Figure 6 shows the effect of confounding ions on the electroanalytical GAT response in the fipronil analysis. The interfering ions tested are heavy metal ions such as Cd^{2+} and Pb^{2+} with different ion concentrations. The result shows that the GAT response to fipronil anodic currents has decreased. However, based on the calculation of the standard deviation carried out, the decline can still be tolerated.

4. Conclusion

The electroanalytic response of the GAT electrode in a solution containing fipronil has been studied in this work. GAT synthesis was carried out using the sol-gel method with the presence of TTIP and ATIP as precursors. During the testing process, we observed that fipronil was oxidized at anodic potential of 0.26 V. This potential was recorded on the use of fipronil solution with a concentration of 0.1 µg / L in a mixture of electrolytes supporting

HCl and Na_2SO_4 with a concentration of 0.1 M respectively. The addition of Al (III) -TiO_2 nanocomposite by 0.2 g causes faster electron transfer at the GAT surface. The resulting detection limit of 0.0164 µg/L shows the sensitivity of measurement with good stability. In addition, the presence of disturbing ions in the form of metal ions Cd^{2+} and Pb^{2+} does not have a significant effect on the anodic current and potential of fipronil.

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