Sol-gel TiO$_2$/Carbon Paste Electrode Nanocomposites for Electrochemical-assisted Sensing of Fipronil Pesticide

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ABSTRACT
The unique study of TiO$_2$ sol-gel modified carbon paste electrode (CPE) nanocomposites have been developed for electrochemical sensor detecting fipronil pesticide compound. We develop the easy synthesized TiO$_2$ via a sol-gel method and modified in CPE which applied electrochemical system as cyclic voltammetry (CV) because the concentration is proportional with current peaks. We discover the TiO$_2$ optimal mass used of 0.1 g which is compared with 0.7 g carbon and 0.3 mL paraffin. It has high-current anodic (I$_{pa}$) of 1.13×10$^{-3}$ μA and high-current cathodic (I$_{pc}$) -0.96×10$^{-3}$ μA in scan rate of 0.5 V/s. The limit of detection (LOD) of fipronil has been determined of 34.0×10$^{-5}$ μM in percent recovery of 0.8%. Its high-stability for lifetime TiO$_2$-CPE nanocomposites was expressed for 13 days which mean that can be used for detecting fipronil pesticide.

Keywords: Sol-Gel TiO$_2$, Carbon, Electrochemical, Sensor, Fipronil

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1. Introduction
Organic pesticide widely used in agriculture due to high-efficiency for the eradicate plant pests. various kinds of attention in utilization pesticide because of the contaminant effect against living things [1,2]. One of pesticide used in agriculture is fipronil which is categorized as persistent organic pollutants (POPs) waste [3]. POPs is phenol pollutant waste in low-concentration where accumulated in the aquatic environment and contacted with living things. In the future, the pesticide effect will be affecting metabolism human. Especially, fipronil can be contained in liver and kidney of the animal which consumed by a human. Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoro-methyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyra-zole-3-carbonitrile) that has upper limit threshold of 10 μM and lower of 0.1 μM [4]. Generally, it is used to control leaf pests such as Thrips sp. in chili plants, termite pest in palm oil, and Nilaparvata lugens pest attacking rice plant [5-7].

Need attention to detect fipronil pesticide using a new easy method for preparation, high-sensitivity, accuracy, and precise in low concentration. Several methods have been carried out to determine fipronil pesticide using biosensors [8], raman microscopy [9], Gas chromatography (GC) [10,11], and high-performance liquid chromatography (HPLC) [12,13], but these methods not effective for detecting fipronil pesticide in low concentration. In addition, the difficulty preparation sample caused a long time needed and many reagents preparation. So that, we attend to fabricate sensor device based titanium dioxide (TiO$_2$) because of its high-advantages in semiconductor and photocatalyst properties [14]. Especially in this study, we made TiO$_2$ nanoparticles using organometal solu-

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2.1 Preparation working electrode

The organometallic solution to produce TiO$_2$ is titanium tetra-isopropoxide (TTIP) which is mixed by ethanol 99%, acetylacetone, and acetate acid. These materials refluxed at a temperature of 80°C for 3 hours. Subsequently, sol TiO$_2$ was calcined at 500°C for 3 hours to form TiO$_2$ anatase crystal. This crystal is crushed by agate mortal and sieved to obtain smooth the TiO$_2$ nanoparticles [37]. Then, TiO$_2$ was varicated to obtain the mass optimization i.e. 0.01 g, 0.05 g, and 0.1 g. Then, it was mixed by 0.7 g carbon and 0.3 mL paraffin oil (d = 0.88 g cm$^{-3}$) followed heating at the temperature of 80°C to sticky between particles. Mobilization in wall glass, we rinse the probe glass by distilled water and acetone followed sonification for 15 minutes. Finally, the material was entered in probe glass with diameter 3 mm, connected by Cu wire as a conductor and also tip electrode was polished [2].

2.2 Determination of fipronil

Voltammetric detection of fipronil was conducted using a potentiostat (DY2100B-Digi.Ivy) with three electrodes system where the TiO$_2$-CPE nanocomposites as the working electrode. Meanwhile, a platinum (Pt) and Ag/AgCl wires were used as the counter and reference electrodes, respectively. The optimization response electrode determined by using K$_4$[Fe(CN)$_6$] that role for increasing a solution’s redox potential ($E^{\circ} \approx 436$ mV at pH 7). In addition, the sample tests under 1.0 M (NH$_4$)$_2$SO$_4$ electrolyte due to is a strong electrolyte, stability in osmotic effect, and dissolves 100% in aqueous solution. The fipronil concentration was applied in $10^{-6}$, $10^{-5}$, $10^{-4}$, $10^{-3}$, and $10^{-2}$ μM to determine the linearity areas and LOD. The real sample was tested by mixing electrolyte solution for identifying peak current characteristic fipronil in the real sample. We also determination of repeatability for 30 times and tested lifetime electrode for 23 days.

2.3 Characterization materials

The morphology of the nanocomposites was examined using a Scanning Electron Microscopy JEOL-JSM-6510LV. Meanwhile, the phase and crystallinity properties were characterized via X-ray diffraction spectroscopy (XRD) using Philips X-ray diffraction spectrometer with a CuKα irradiation ($\lambda=0.154$ nm) and scan rate as low as 2° min$^{-1}$.

3. Results and Discussion

3.1 Characterization of anatase TiO$_2$-CPE nanocomposites

The anatase TiO$_2$-CPE nanocomposites has been successfully prepared via sol-gel method. Due to
phase purity of anatase TiO$_2$ has a high-stability and electron transfer in the electrochemical system. Fig. 1 exhibits the XRD pattern of anatase TiO$_2$, there are at least 9 peaks spectrum characteristics based on JCPDS file no. 21-1272, namely 25°, 38°, 48°, 52°, 54°, 64°, 69°, 70°, and 76° with Bragg diffraction at the crystal field of (101), (004), (200), (105) (211), (204), and (215), respectively. These data have been compared with TiO$_2$ P25 standard [2].

We then observed the anatase TiO$_2$-CPE nanocomposites using SEM instrument. The unique microstructures were displayed that the anatase TiO$_2$ successfully incorporated in carbon matrix (Fig. 2). In same times, high-contacted a solid-state reaction by adding paraffin as attach agent. We can conclude the anatase TiO$_2$ nanocomposites were homogeneously distributed in the carbon paste matrix. The TiO$_2$ given shine characteristics caused the inducing of electron to make a high-atom number easy for emitting energy. We discover the approximate size of TiO$_2$ nanoparticles in this study is 2 μm (Fig. 2).

3.2 Mass optimization of anatase TiO$_2$-CPE

The mass optimization aims to synergistic the anatase TiO$_2$ combined with carbon paste which applied electrochemical system. The high current response observed based on CV by varying mass of 0.01 g, 0.05 g, and 0.1 g TiO$_2$ sol-gel mixed pristine carbon in 0.1M K$_3$[Fe(CN)$_6$] as an electrolyte solution under scan rate of 0.1 V/s. The K$_3$[Fe(CN)$_6$] as naturally for increased separation of cathodic and anodic peaks and reversible characteristic for redox reaction. As Fig. 3, we discover the mass optimum TiO$_2$ anatase of 0.1 g with oxidation peak the $I_p$ value of $1.13 \times 10^3$ μA, $E_{pa}$ value of 0.1 V with reduction peak of $I_p$ value of $-0.96 \times 10^3$ μA and $E_{pc}$ value of 0.34 V.

The high composition of anatase TiO$_2$ into the CPE matrix to increase performance the high TiO$_2$ concentration estabilized the optimum condition. Based on Fig. 3, the sample demonstrates an excellent electrochemical response with a high current peak. In addition, it can be remarked that the electron transfer process is extremely fast as indicated by a remarkably small difference in the redox potential. The electrode with a composition of 0.1 gram TiO$_2$ was the best electrode performance in electrochemical system causes the produce a maximum peak flow response when compared to other compositions. Finally, it is suitable to be used for measuring fipronil pesticide.

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**Fig. 1.** XRD pattern of anatase TiO$_2$ prepared via sol-gel method.

**Fig. 2.** The microscopic structure of material electrode, (A) Pristine carbon paste, and (B) TiO$_2$-carbon paste.
3.3 Electrochemical Response against Fipronil

This parameter was conducted to compare electrochemical response of fipronil which is containing electrolyte and without the fipronil solution. The electrochemical profile can be seen in Fig. 4. Based on the measurement (see Fig. 4) exhibit that the determination of the electrochemical response without the fipronil did not reveal peak response if it compared with adding fipronil causes the (NH$_4$)$_2$SO$_4$ electrolyte solution did not react with analytes, stable, and high-electron transfer [38]. We discover the high-current response for 0.1 μM fipronil containing electrolyte has a good oxidation response with $I_{pa}$ value of 31.4 μA and $E_{pa}$ value of -0.15 V. The $I_{pa}$ value was produced based on electrode measurement responded fipronil pesticide which is an oxidation reaction.

3.4 Optimization Scan Rate Test

The optimization the scan rate has been conducted by varying the of 0.05; 0.1; 0.2; and 0.5 V/s due to the faster scan rate in analyte measurements will be produced the high-current peak. The 1.0 μM fipronil shows the measurement rate has been increased when the high variation scan rate. This is due to the scan rate effect was reversibility concentration indirectly by measuring the apparent a standard rate constant for electron transfer from only cathodic (or anodic) polarization. In a few cases both cathodic and anodic [39]. Based on analyzed (Fig. 5), we obtain the optimum scan rate on 0.5 V/s with the $I_{pa}$ value of 31.7 μA and the $E_{pa}$ value of -0.15 V. The high scan rate has been produced proportional with the high scan rate.

3.5 Determination of Linearity and Limit of Detection (LOD)

The linearity of fipronil has been determined by plotting the variation concentration (10$^{-6}$, 10$^{-5}$, 10$^{-4}$, 10$^{-3}$, 10$^{-2}$, and 10$^{-1}$ μM) which is containing 1.0 M (NH$_4$)$_2$SO$_4$ as electrolyte between $I_{pa}$ value which produced from CV profile. Fig. 6 exhibits that the
high concentration causes a high CV response. This phenomenon because of increasing fipronil concentration makes the increase ions produced to interact on the electrode surface. Based on the curve, the cathodic (reduction) potential not significantly produced because the (NH₄)₂SO₄ electrolyte containing fipronil only giving the oxidation response onto the working electrode (see Fig. 4). The TiO₂-CPE nanocomposites play a role for oxidation process sensing and high transfer electron in the electrochemical system. We then plot the linear line equation between Ipₐ value with concentration to obtain the linearity area from the working electrode by the range of electrode performance detecting fipronil compound in low concentrations from 10⁻⁶, 10⁻⁵, and 10⁻⁴ μM. The unique performance is identified as the LOD in low concentration which is cannot be analyzed by high-instrumentation. The higher concentration proportional with increase in anodic current [40,41]. High concentration causes more fipronil ions to accumulate on the electrode surface so that the current result is also higher. We discover the determination of LOD value was 34.0×10⁻⁵ μM by multiplying 3 with standard deviation divided by the value of the slope. This phenomenon to obtain the lowest quantity of fipronil concentration that can be identified from the working electrode.

4. Real Sample Test

We testing the TiO₂-CPE nanocomposites for sensing against the real sample which is commercial pesticide in society. This due to we attempt comparing the real sample with the sample treatment 1.0 μM fipronil which aims to how are this electrode can be determining fipronil compound at the real sample. Based on this experiment, the oxidation peak has been obtained from the real sample with Ipₐ value of 120 μA and an Epₐ value of -0.1 V. Meanwhile, the 1.0 μM fipronil also shows the low oxidation peak of
fipronil. We can determine the real sample concentration by comparing the \( I_{pa} \) value of the real sample with the 0.1 M fipronil (\( I_{pa} \) value = 49.1 \( \mu \)A) so that we obtain the real sample concentration of 0.25 \( \mu \)M. Based on this experiment, we concluded that the TiO\(_2\)-CPE nanocomposites have a high-performance for sensing fipronil pesticide compound under low concentration.

4.1 Electrode Repeat Test

The repeatability test was conducted to exhibit the working electrode performance against the consistency of measurement. This treatment the TiO\(_2\)-CPE nanocomposites has been tested by using 1.0 \( \mu \)M fipronil containing 1.0 M (NH\(_4\))\(_2\)SO\(_4\) as the electrolyte. Fig. 8 depicts the results of repeatability working electrode that the high-performance of TiO\(_2\)-CPE stability for 30 times tested. The rate electrons transfer were stabilized on the electrode surface and oxidizing the fipronil compound. Based on this study (Fig. 8), we obtain the \( I_{pa} \) value of 27.4 \( \mu \)A and calculating the standard of deviation (SD) of 2.512 and Relative Standard Deviation (RSD) is 0.8%. We declare that the TiO\(_2\)-CPE nanocomposites has stabilized due to the Horwitz value is obtained less than 2%.

4.2 Electrode lifetime Determination

Especially, we explore a lifetime of TiO\(_2\)-CPE to obtain the high-performance electrode for 23 days. The lifetime test performance has been carried out by using the same solution on the repeatability test. Extension lifetime electrode enforced for clarifying TiO\(_2\)-CPE to sensitivity against fipronil. Fig. 9 exhibits that the optimum performance electrode from 1 until 13 days relatively stable, while the 14 until 23 days the low-performance electrode. This condition that the longer electrode used causes thickening diffusion on the electron transfer system and limiting peak current. In addition, it has saturated on electrode pores causes the current diffusion. Meanwhile, if it will be enhanced the TiO\(_2\)-CPE nanocomposites should be annealing to remove the organic compound on the electrode surface.

Fig. 8. Repeatability test of TiO\(_2\)-CPE nanocomposites (A) Cyclic voltammetry of repetition, (B) Stability histogram peak current density during a repeated measurement.

Fig. 9. lifetime test of TiO\(_2\)-CPE nanocomposites, (A) Cyclic voltammetry profile of lifetime measurement, (B) Histogram peak current density during a life time measurement.
5. Conclusions

The performance of anatase TiO$_2$-CPE nanocomposites in voltammetric technique for examining the fipronil pesticide exhibits that the best composition of anatase TiO$_2$ as a modifier on CPE with a composition of 0.1 gram. In addition, the voltammogram data shows an Ip value of $1.13 \times 10^3$ μA, Ep value of 0.1 V with reduction peak of Ip value of -0.96×10$^3$ μA and Ep value of 0.34 V. The LOD has been determined of 0.8% so that the anatase TiO$_2$ electrode system also shows a percent recovery (% RSD) of 0.25 μM, so that this electrode is feasible to be applied to the environment.

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