

Examination of Carbon Paste Electrode/TiO₂ Nanocomposite as Electrochemical Sensor for Detecting Profenofos Pesticide

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Abstract—This study reports the preparation and performance of a smart material—a carbon paste electrode combined with TiO₂ semiconductor (CPE/TiO₂) as electrochemical sensor for detecting profenofos—a toxic organophosphates group insecticide widely used in agriculture. Such techniques as real samples tests and electrochemical tests were used to investigate the following parameters: a scan rate, an electrode response, a limit of detection (LoD), and repeatability. Based on the obtained results, the best mass composition of TiO₂ combined with CPE was found to be in a ratio of 1 : 1 : 5, with an anodic peak current (I_{pa}) of 150 μ A, an anodic peak potential (E_{pa}) of 0.87 V, and an optimal scan rate measurement of 0.5 V s⁻¹. The LoD based on a linearity curve with a value of 4.0×10^{-5} μ M was also observed, and a repeatability test against the working electrode was performed until the 30th day, using the Horwitz ratio of 0.16. A good electrochemical performance of the working electrode tested against a real sample showed the specifically detected profenofos with I_{pa} value of 7.0×10^{-5} μ M.

Keywords: electrochemical, sensor, carbon paste electrode, TiO₂, voltammetry, profenofos

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INTRODUCTION

Profenofos insecticide, a pesticide, a toxic organophosphate, is quite widely used in agriculture [1–3]. Profenofos works actively and efficiently in controlling insect pests and causes a significant inhibitory effect on the acetylcholinesterase enzyme in microorganisms [4, 5]. In nature, it is presented in low concentrations making it difficult to detect it, so a fast technique is needed to identify the existence of this pesticide. It is one of the persistent organic pollutants—chemical organic compounds that diminish resistance to environmental degradation and are difficult to detect because they are presented in low concentrations and also spread very quickly in the aquatic environment [6, 7]. Those poputants are pesticide compounds used in agriculture to eradicate plant pests. When farmers use them for pest control, they are injected into the plant, then they stick on the plant surface and fall into the ground [8, 9]. This condition is exacerbated when entering the rainy season, then

they will dissolve and can be carried by a water flow into a river [10–12], which can damage the aquatic environment. Those pesticide residues can also seriously affect food security and threaten human health [13–16]. As reported elsewhere, the people living in agricultural areas may be exposed to much higher levels of organophosphate pesticides than non-agricultural populations of Thailand during the dry and wet seasons ($p \leq .001$, 0.001 μ M) [17].

A common technique that has been applied to detect pesticide residues is chromatography [18–20]. In particular, gas chromatography [21–23], high performance liquid chromatography [24, 25], and gas chromatography-mass spectrometry [26]. Some other techniques are also being used by researchers such as applications of biosensors [27], of printed polymers [28], and fluorescence assays [29]. The last method is quite reliable but requires relatively expensive maintenance and procurement costs, the analysis is quite long, the analytical procedures are complicated and

can be done only with specific technical training [22, 23]. To overcome this shortcoming, sensors based on TiO₂ nanoparticles were developed using the voltammetry technique [30–32].

Voltammetry is an electrochemical technique based on the oxidation-reduction (redox) process on the electrode surface, which is widely used in chemical analyses [33–36]. In addition, the voltammetry method has advantages such as having high sensitivity, low detection limit, easy to use and simple preparation [37]. To apply voltammetry, an electrochemical cell with three electrodes such as working electrode, reference electrode, and counter electrode is needed [38, 39]. According to some previous studies by the authors, the effectiveness of graphite/carbon paste as a modifier into TiO₂ was quite high in detecting phenolic compounds [40–42]. So far, the electrochemical application is a promising method to determine organic compounds in the aquatic environment. The unique electronic structure in anatase TiO₂ has an energy band gap of approximately 3.2 eV, which plays its role as mobility of *n*-type charge carriers. In addition, the high resistivity and the Hall effect analyses also indicated the existence of an insulator-metal transition in a donor band in anatase TiO₂, expanding the applicability of these materials in a broader field, particularly, in nanoelectronics. These unique properties are amongst the key factors for an electrochemical sensor for highly physicochemical activities on the TiO₂ surface [43].

Thus this paper reports a simple preparation of CPE/TiO₂ as working electrode used to detect profenofos. The preparation of CPE/TiO₂ is based on the graphite oxide mixed with liquid paraffin which has been easily modified and immobilized. In addition, the function of TiO₂ is to improve the CPE performance during electrochemical sensing [31, 44]. Generally, TiO₂ has been applied to transmit the supply of electrons and high electron signals to provide a considerable increase in the electrochemical activity of some organic compounds [45, 46]. The presence of TiO₂ is expected to improve the high-performance of a working electrode in detecting profenofos.

EXPERIMENTAL METHODS

Preparation of CPE/TiO₂ Composite used as Working Electrode

The TiO₂ powder (Degussa, P-25), was weighed to as much as 10 g, sifted with a 200 mesh, put into a porcelain cup, and then calcined at a temperature of 500°C for 3 h to obtain the TiO₂ anatase crystal. After that, graphite, liquid paraffin, and the TiO₂ anatase powder were mixed with the mass variations of TiO₂

anatase of (1 : 1 : 1), (1 : 1 : 5), and (1 : 1 : 10) w/w. This composition was improved according to the ratio of the graphite composition of 0.1 g (1 : 1 : 1), 0.01g (1 : 1 : 5), and 0.05 g (1 : 1 : 10). First graphite was crushed until smooth and sifted with a 200 mesh, then it was mixed with TiO₂ anatase in a watch glass containing paraffin oil. After that, it was heated to 80°C in order to make homogeneous and physical interactions occur with each material. Finally, it was stirred and inserted into the electrode body with a diameter of 3 mm while pressed to solidify, then the surface of the electrode was rubbed until smooth, flat, and shiny.

Electrochemical Tests

To observe the electrochemical behaviour of profenofos using CPE/TiO₂ electrode, the cyclic voltammetry was applied with a DY2100B potentiostat where the 15.0 mL electrochemical cell contained 1.0 M NaNO₃ and (10⁻⁶, 10⁻⁵, 10⁻⁴, 10⁻³, 10⁻², and 10⁻¹ μM) profenofos, and in which three electrodes such as CPE/TiO₂, Pt wire, and Ag/AgCl ones were inserted. Electrochemical sensing of profenofos was investigated using 0.1 M K₃[Fe(CN)₆] under a scanning rate of 0.1 Vs⁻¹ with a potential range of -0.8 to +2.0 V. Additionally, the scanning rate was evaluated against a 0.1 M NaNO₃ electrolyte solution containing 10⁻⁴ μM sample, and it was found to range from 0.02 to 0.5 Vs⁻¹ in the potential range of +0.8 to -0.8 V. The limit of detection (LoD) is determined respectively using the ratio 3σ/*b*, where *b* is the slope of the calibration curve and σ is the standard deviation value of three voltammograms.

RESULTS AND DISCUSSION

Synthesis and Characterization of Anatase TiO₂ Nanoparticles

The successfully synthesized TiO₂ anatase can be confirmed by using X-ray diffraction (XRD) (Fig. 1). The diffraction peaks 2θ show that the diffraction characteristics of the TiO₂ anatase crystals in the crystalline fields 101, 004, 200, 211, and 204 were in accordance with the Joint Committee on Powder Diffraction Standards card no. 21-1272 [47]. The crystal field 101 in the diffractogram had the highest intensity compared to other fields [48, 49]. This proves that the crystalline plane 101 (25.28) is dominant in TiO₂ with a CuK_α value of 8.04, this is why it was possible to assume the diameter of TiO₂ to be 9.41 Å = 0.941 nm [50]. Although the TiO₂ anatase has been formed 25.28 (101), there was a slight peak at 23.26, which indicated the formation of rutile phase, but it did not affect the anatase TiO₂ crystals [51]. This factor may occur due to distortion between TiO₂ particles during

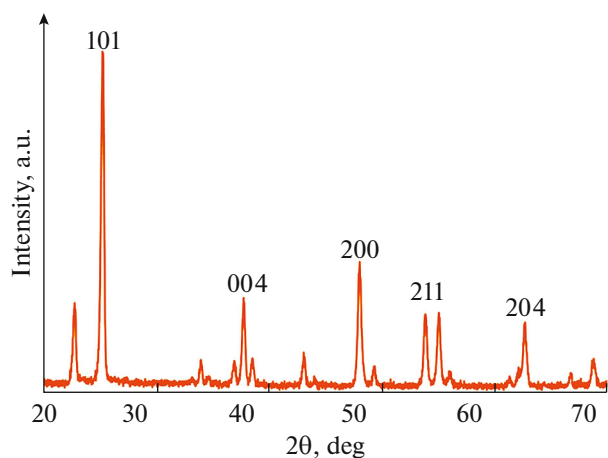


Fig. 1. XRD pattern of TiO₂ anatase prepared via sol-gel method.

the annealing process. According to the data in [52], the characteristic anatase of TiO₂ is 25.28 with the crystal plane 101.

Based on the XRD pattern, anatase TiO₂ has been prepared through a thermal annealing process. Subsequently, the mass variations of TiO₂ were determined, which would be combined with CPE to provide a highly sensitive electrochemical behaviour of profenofos. Figure 2a shows a typical microstructure of TiO₂ with a smooth surface morphology of TiO₂ anatase, with the estimate grains size of $\pm 2.0 \mu\text{m}$. Specifically, scanning electron microscopy images of TiO₂ have

shown white glowing colour when exposed to a high electron energy. Figure 2b demonstrates the combination of TiO₂ and CPE differences in the material colour. An even distribution of TiO₂ on the graphite surface of the carbon paste is helpful in expanding the electrode surface, thus giving the effect of a faster electron transfer process, which results in an increase in the peak current in the measurement process compared to carbon paste without modifications [53].

Electrochemical Behavior of CPE/TiO₂

Electrochemical characterization was carried out as the initial stage of electrode measurements to observe the electrodes performance with the effect of adding a TiO₂ modifier to graphite. Measurements were made in a solution of 0.1 M K₃[Fe(CN)₆] which acts as a test solution with variations of the scan rate speed. The results in Fig. 3 indicated that the presence of TiO₂ in carbon paste has a significant effect with an increase in the peak oxidation current and a reduction compared to those of the carbon paste without modification.

The voltammograms using CPE/TiO₂ showed that the anodic peak current reflects the oxidation reaction that occurs in the surface of the working electrodes (Fig. 3a). From these data, it was found that the composition of 0.05 g TiO₂ produced higher I_{pa} values than other compositions (Fig. 3b). The peak flow occurred due to an increase in the total transfer of electrons from profenofos mediated by TiO₂ nanoparticles. A

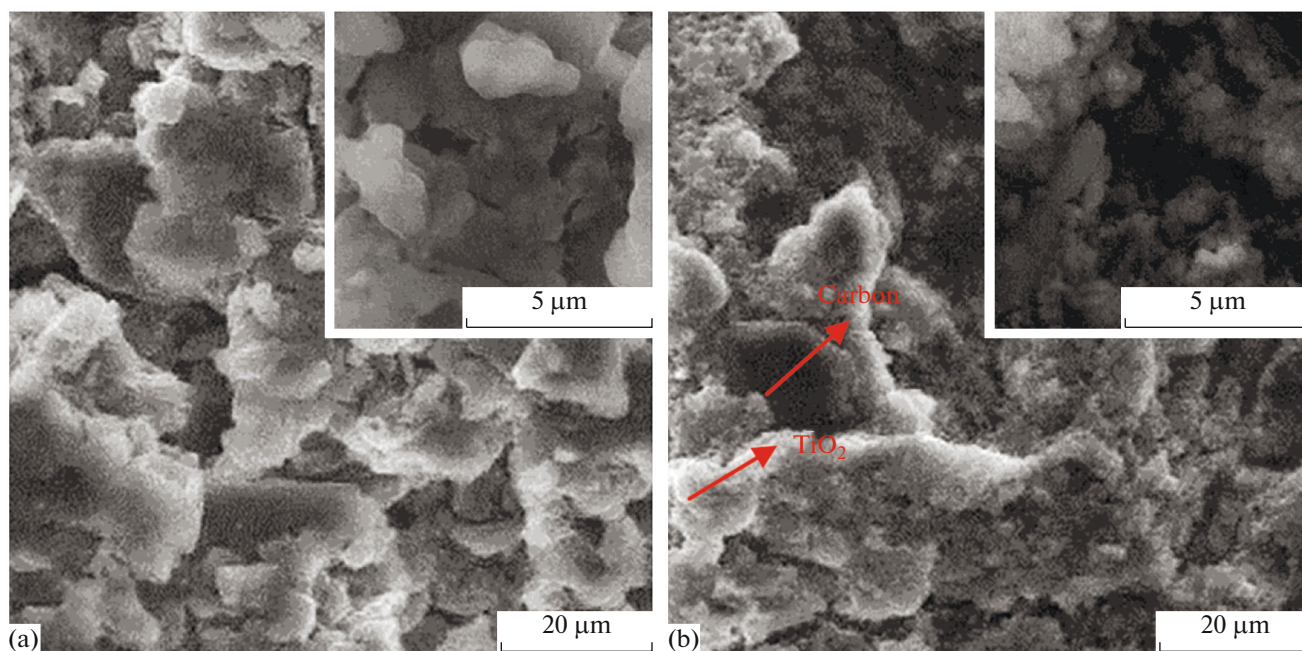


Fig. 2. Microscopic structures of: (a) TiO₂ and (b) anatase CPE/TiO₂.

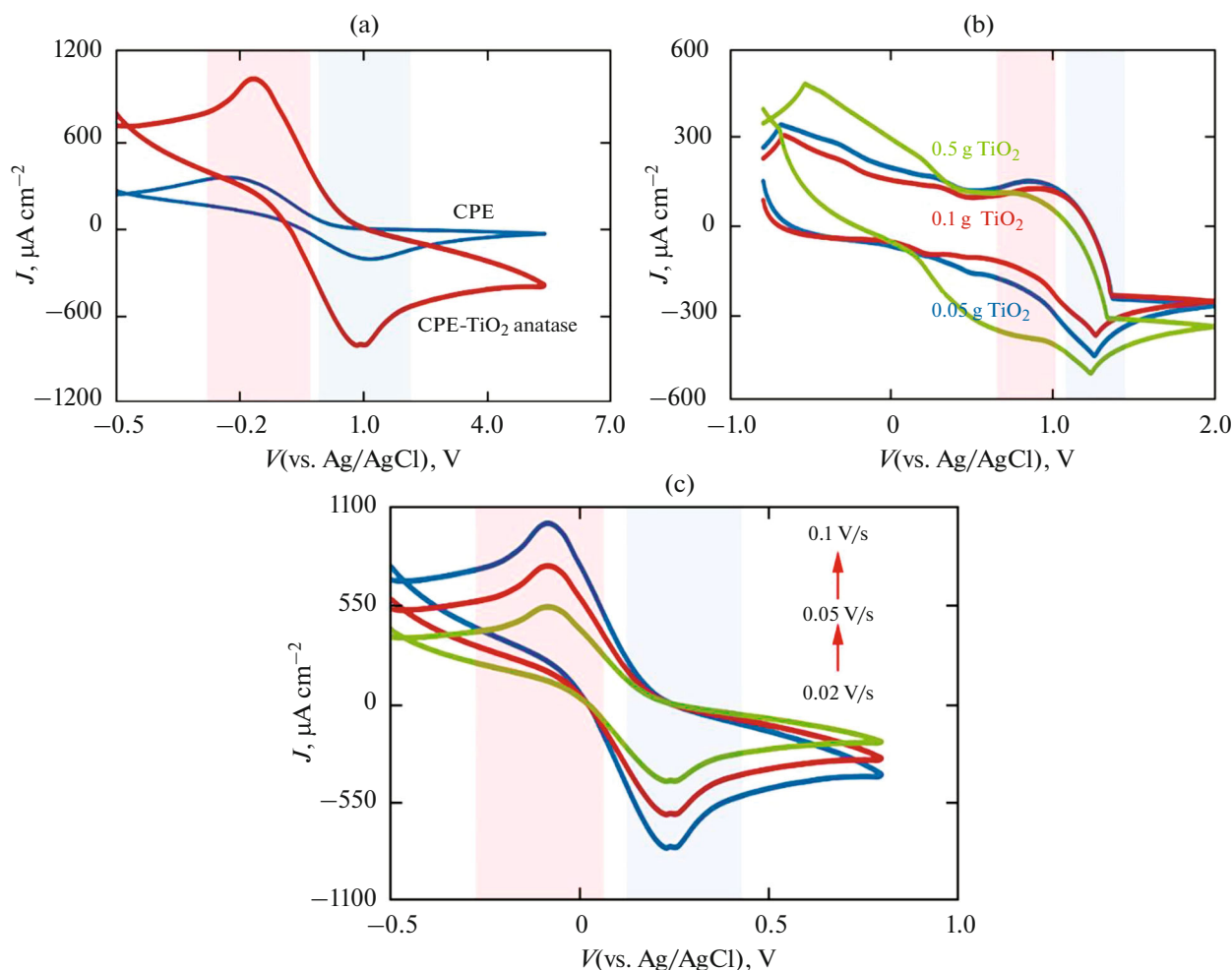


Fig. 3. Cyclic voltammogram of working electrodes: (a) comparison of performance of CPE and CPE/TiO₂ anatase with scan rate 0.1 V s^{-1} , (b) optimization of TiO₂ mass modified in CPE, and (c) scan rate test of CPE/TiO₂ anatase.

decrease in the peak current was caused by a higher concentration of TiO₂ nanoparticles covering graphite so as to reduce the conductivity on the electrode surface [54]. A high scanning rate produces a thin diffusion layer, making electron transfer to the electrode surface easier and causing an increase in the peak current. Figure 3c shows the best scanning speed to be 0.1 V s^{-1} .

NaNO₃ Electrolyte Test of Profenofos

Figure 4a demonstrates that the best scan rate was indicated on 0.5 V s^{-1} under $0.1 \mu\text{M}$ profenofos containing 1.0 M NaNO_3 of the electrolyte solution. The I_{pa} has been obtained with the variation potential in a range of -0.8 to 2.0 V . A high scan rate was produced as response from the electron transfer effect by the electrolyte besides a diffusion layer formed was thinning so that the transfer of electrons on the working electrode on the surface was going well. From the data,

scan rate measurement of 0.5 V s^{-1} obtained an I_{pa} value of $656 \mu\text{A}$ and E_{pa} value of 0.62 V . Also the differences of the redox current against NaNO₃ were observed in the electrolyte solution compared with those without $0.1 \mu\text{M}$ of profenofos. These unique properties exhibit a high electrochemical response produced by mixing the electrolyte solution with profenofos. Meanwhile without adding a real sample, the peak current was not reflected because of the redox responses when the studied pesticide interacted with CPE/TiO₂ nanoparticles (Fig. 4b).

Determination of Regional Linearity and Limit of Detection

The linear concentration range of profenofos was determined by varying a series of its solutions with concentrations of 10^{-6} , 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , and $10^{-1} \mu\text{M}$ in 1.0 M NaNO_3 solution as electrolyte (Fig. 5a).

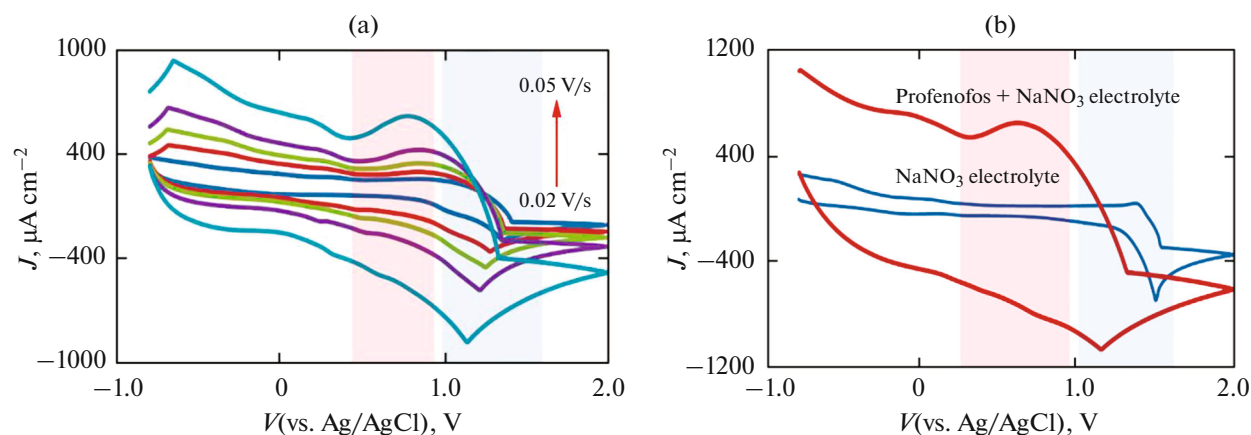


Fig. 4. (a) Scan rate voltamogram of 1.0 M NaNO₃ + 0.1 μM profenofos and (b) cyclic voltammograms of 1.0 M NaNO₃ of 0.1 M profenofos $v = 0.5 \text{ V s}^{-1}$ electrolyte CPE/TiO₂. In both: in its absence (blue line) and in its presence (red line).

The linear concentration of a profenofos standard solution was measured with concentration variations of 10^{-6} – 10^{-4} μM (Fig. 5b). The data range for the LoD has been selected between 10^{-6} to 10^{-4} because the working electrode still was detecting profenofos even in low concentrations. The LoD selected based on the limit quantitatively data obtained was used in order to detect the sample in an aquatic environment. Based on the calculation, the LoD measurement of profenofos was 4×10^{-5} μM (Table 1). The linear curve is helpful in determining a good area standard linearity in the measurement of profenofos [38]. This concentration range has a linear correlation between the concentration of profenofos and the produced current with an R^2 value of 0.9697. This is based on the data from [55] which state that the level of the correla-

tion value R^2 with a range of 0.80–1.0 has a very strong linear relationship.

Repeatability Tests

In order to determine the stability of CPE/TiO₂, repeatability measurements were carried out as many as 30 times against 10^{-4} μM profenofos solution. The aim was to determine the necessary repetitions of measurements under unchanging conditions so as to obtain the same results [60], calculating the value of the Horwitz Ratio (*HorRat*) [61]. The *HorRat* value is the ratio between $\%RSD_R$ and $\%PRSD_R$ from the peak current of the standard solution measurement. The measurement of repeatability is good if the *HorRat* value is less than 2, and the $\%RSD_R$ value obtained is lower than the $\%PRSD_R$ [62]. Based on the data

Table 1. Comparison of detection results of profenofos with various working electrodes

Working electrode	Method	Linearity range, μM	LoD, μM	References
Molecularly imprinted polymers doped Au (MIP/Au)	Quartz crystal microbalances	10^{-8} – 10^{-5} and 10^{-5} – 10^{-3}	2.0×10^{-7}	[28]
Molecularly imprinted polymers doped Au (MIP/Au)	Quartz crystal microbalances	10–1000	0.38	[56]
Tyr/PtNPs/graphene/glassy-carbon-electrode (GCE)	Amperometric	3×10^{-3} – 3×10^{-2}	2.0×10^{-3}	[57]
AuNPs@PANI/ graphite screen-printed electrode	Differential pulse voltammetry) on deoxyribonucleic acid aptasensor	0.1–10	0.27	[58]
CNTs@SiO ₂ -MIP/GCE	Amperometric	0.01–200	2.0×10^{-3}	[59]
CPE-TiO ₂	Cyclic voltammetry	10^{-6} – 10^{-4}	4.0×10^{-5}	This work

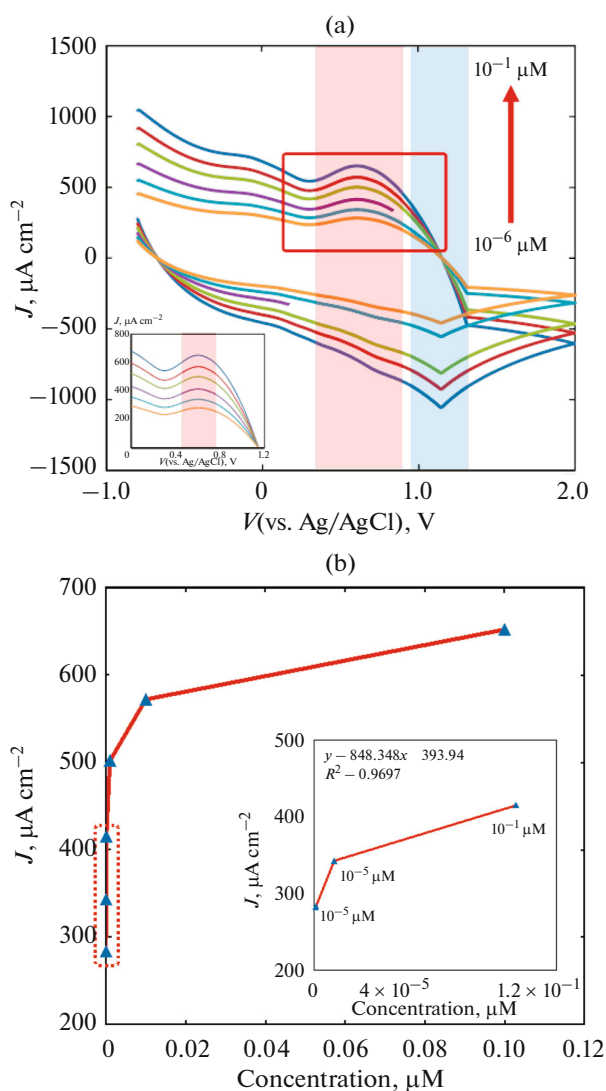


Fig. 5. Cyclic voltammograms of profenofos with various concentrations (10^{-6} – 10^{-1} μM) and (b) linear concentration graph of profenofos based on I_{pa} value.

obtained, CPE/TiO₂ can be said to be stable in analyzing profenofos. The results of repeated measurements can be seen in Fig. 6.

Electrode Life Time Determination

The lifetime of the electrode was measured by using CPE/TiO₂ towards a 10^{-4} μM profenofos solution for 20 days with a once daily measurement period. The measurement results are shown in Figs. 7a, 7b.

Based on the measurement results (Fig. 7), from the first day to the 10th day, the electrode was still in a stable condition, which is characterized by the resulting peak currents either higher or relatively the same. Meanwhile, from the 11th to the 20th days, the resulting peak current decreased. The occurrence of a decrease in the peak current because the use of the electrode carried out continuously can cause thickening of the diffusion layer on the working electrode surface so that the electron transfer takes place slowly, and the resulting peak current decreases in the electrode response. It can also cause the electrode to decay and be unstable at room temperature after being stored for a long time [63].

Real Sample Test

The real sample test aims to determine the ability of CPE/TiO₂ in analyzing profenofos in a real sample (Wanggu river–Southeast Sulawesi, Indonesia) compared with a 10^{-4} μM profenofos solution. The measurement results are shown in Fig. 8. It is evident that a peak current appeared in the real sample, which indicates the existence of profenofos even though there are differences in the peak currents and the peak potentials between the real sample and the profenofos test solution. The real sample had a lower peak current

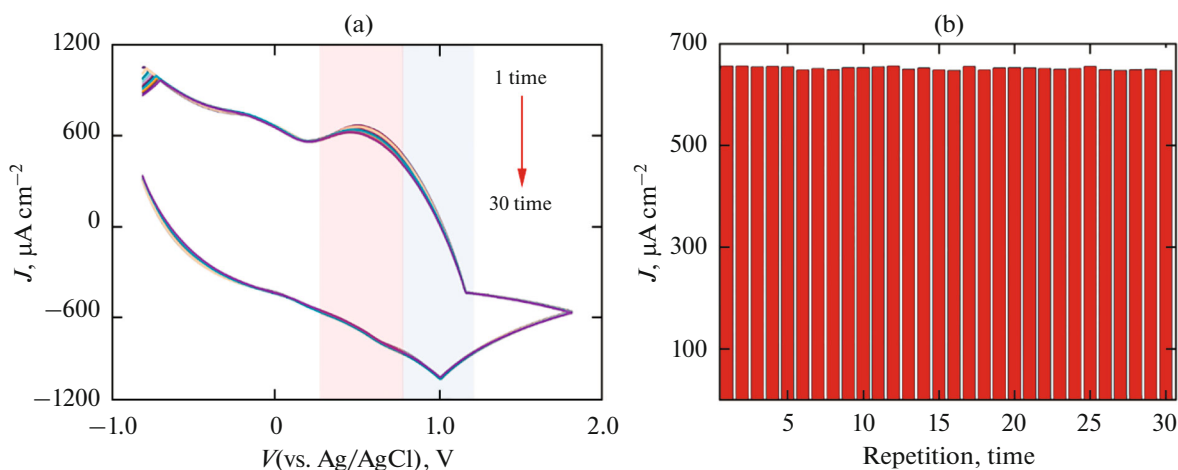


Fig. 6. (a) Repeatability test voltammogram and (b) electrochemical stability histogram showing peak current densities during repeated measurements.

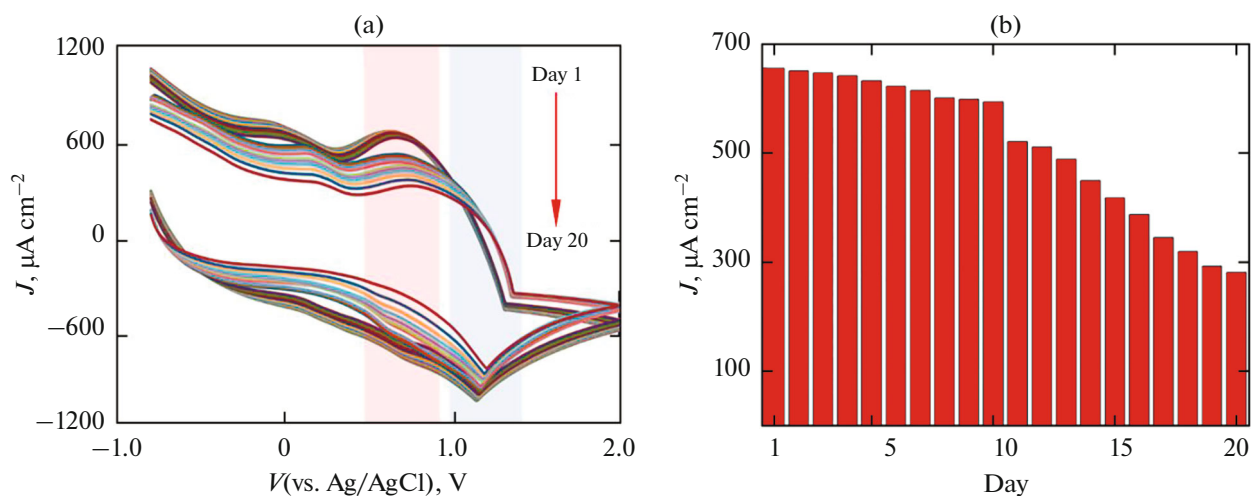


Fig. 7. (a) Lifetime determination voltamogram and (b) electrochemical stability histogram showing peak current densities during lifetime measurements.

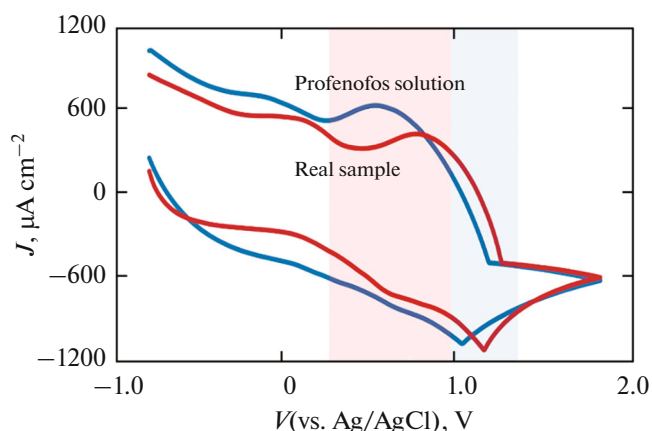


Fig. 8. Real sample voltamograms.

than that of the profenofos test solution and an increasingly positive shift in the potential range. With 450 μA plotted into a linear curve, the real sample concentrations of profenofos was $6.6 \times 10^{-5} \mu\text{M}$. A decrease in the flow of the real sample was smaller than in the profenofos test solution. As to, the potential range shift, it was due to the fact that the commercial pesticides contained other compounds in them so that they can influence the measurements, and the detected current was the peak current of profenofos under the influence of other compounds in the sample.

CONCLUSIONS

Based on the obtained results, good performance of CPE/TiO₂ as an electrochemical sensor for detecting profenofos can be stated. The best mass composition of TiO₂ combined with CPE is in a ratio of 1 : 1 :

5 (0.05 g), with an anodic peak current (I_{pa}) of 150 μA , an anodic peak potential (E_{pa}) of 0.87 V, and an optimal scan rate of 0.5 V s^{-1} . Also it was observed that the LoD based on a linearity curve with a value of $4.0 \times 10^{-5} \mu\text{M}$ and a repeatability test against the working electrode until the 30th day was best with the *HorRat* of 0.16. A good electro-chemical performance of the working electrode was tested against a real sample was confirmed by the specifically detected profenofos pesticide with I_{pa} value of $7.0 \times 10^{-5} \mu\text{M}$.

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