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The Performance of Organophosphate Pesticides Determination Using Biosensor Based on Small Device Potentiometer as a Transducer †

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Abstract: The need to control pesticide residues in foodstuffs in a fast and straightforward analysis for the field scale is required. Therefore, this research develops a transducer-based biosensor with a small device potentiometer (SDP) to produce a fast and accurate pesticide detection tool. The biosensor based on Au electrodes by immobilizing the acetylcholinesterase (AChE) enzyme coated membrane cellulose acetate (CA) 15% (*w*/*v*) cross-linked glutaraldehyde (GA) 25% (*v*/*v*) and SDP as a transducer that produces a potential value. The biosensor testing results on the organophosphate pesticide class, namely diazinon and profenofos, showed the sensitivity of 21.204 and 20.035 mV decade^{-1}, Limit of Detection (LoD) 10^{-7} mg L^{-1}, selectivity coefficient $-1 < K_{i,j} < 1$ and accuracy of 99.497 and 94.765%, respectively. The results showed that the biosensor connected to an SDP transducer had an excellent performance in determining the presence of organophosphate pesticides.

Keywords: small device potentiometer; biosensor; acetylcholinesterase; organophosphate; pesticide; diazinon and profenofos

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1. Introduction

Organophosphate pesticides are a group of pesticides that contain a phosphate group. The organophosphate pesticides in agricultural and plantation processing systems are widely used to tackle pests and diseases that attack plants, the leading cause of declining crop yields. However, the use of pesticides harms the health of living things and the balance of the environment [1,2]. Analysis of pesticide residues from crop yields is necessary to ensure food safety. One alternative method of pesticide analysis is a biosensor [3,4].

In recent decades, biosensors have become a popular research area capable of identifying pesticide residues and other chemicals. Biosensors are "self-standing devices" that record physical, chemical or biological changes, convert them into measurable signals from the sample and monitor the analyte of interest [5,6]. The sensor contains a recognition element that allows a selective response to a specific analyte or group of analytes, minimizing interference from other sample components. Another significant sensor component is a transducer or detection device that produces a signal [7].

Electrochemical biosensors are a subclass of chemical sensors that combine sensitivity—such as low detection limit—electrochemical transducers with the high specificity of biological recognition processes. These devices contain biological recognition elements (enzymes, proteins, antibodies, nucleic acids, cells, tissues or receptors) that selectively react with the

target analyte and generate an electrical signal related to the measured analyte concentration [5,8]. Enzyme-based electrochemical biosensors have advantages over conventional methods due to their excellent sensitivity, selectivity, mini size and fast response [5,9,10].

Maintaining the catalytic activity on the efficient immobilization of the acetylcholinesterase (AChE) enzyme is an essential consideration when developing electrochemical biosensors that can be used for practical applications. The highlight of the electrochemical biosensor is its unique ability to generate digital signals that can measure by converting the catalytic signal with the help of microfabricated electronics [3,11,12]. The electrochemical method using measurement tools is based on potentiometric [12], amperometric [13] or conductometric [14] biosensor. Potentiometric biosensors are suitable for measuring the response value of pesticide detection measurements [15].

Potentiometric biosensors are efficient for in-field analysis because they are more straightforward and ideal for real-time analysis [16]. The potentiometric detection system developed by Timur, S. and Telefoncu, A., 2004 [17], has the underlying principle of inhibition of AChE activity due to its properties in identifying organophosphate compounds. The enzyme was immobilized on the surface of the electrode with the help of a chitosan membrane [18]. Without a pre-concentration step, in both aqueous and organic media, detection of organophosphates without the requirement of trained personnel proved advantageous for the proposed portable biosensor. Pesticides were effectively detected in the range of 0.1–100 mM for parathion-methyl and methamidophos and 0.6–600 mM for Malathion [17]. However, in the presence of higher pesticide concentrations, only partial regeneration of the enzymatic activity was regenerated [15].

The combination of potentiometric-based AChE enzyme biosensors as transducers with analytical techniques has been widely reported in the literature as a suitable method. In this work, we report the development of a small device potentiometric (SDP) based biosensor as a transducer for the determination of pesticide organophosphates, based on the AChE enzyme immobilized on cellulose acetate (CA) and glutaraldehyde (GA) membrane-coated Au electrodes.

2. Materials and Methods

2.1. Meterials

Acetylcholinesterase (AChE, from electrophorus, Sigma-Aldrich, St. Louis, MO, USA, 1.17 mg with activity 425.94 units per mg (EC. 3.1.1.7)) in 9 mL PBS pH 8 and 1 mL KCl 10^{-1} M, cellulose acetate (CA, from Sigma-Aldrich, St. Louis, MO, USA, 15% v/v in acetone), glutaraldehyde (GA, from Sigma-Aldrich, St. Louis, MO, USA, 25% in H_2O), potassium chloride (KCl, from Merck, Darmstadt, Germany, 10^{-1} M in H_2O) and acetone (C_3H_6O, from Sigma-Aldrich, St. Louis, MO, USA, $\geq$99.5%). Phosphate buffer solutions (PBS) with values of pH 8.0 were prepared by mixing standard stock solutions of 0.2 M Na_2HPO_4 (99% purity) and 0.2 M NaH_2PO_4 (99% purity). Standard solution of acetylthiocholine chloride (ATCl, A5626 from Sigma-Aldrich, St. Louis, MO, USA) substrate with concentrations of 10^{-1}, 10^{-2} and 10^{-3} M in PBS solution. The pesticides used in the OP group are diazinon and profenofos was purchased from Merck, Darmstadt, Germany, as inhibitors, each made in concentrations of 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mg L^{-1} in 5 mL ethanol (C_5H_6O, from Sigma-Aldrich, St. Louis, MO, USA, 99.8%) and H_2O.

2.2. Apparatus

The potentiometer is used as an experimental tool for measuring the potential value of analyte detection [19]. The working electrodes used are Au and a platinum (Pt) as a cathode of the electrolysis process and an Ag/AgCl as a reference electrode.

2.3. Electrolysis of Ag/AgCl

Reference electrodes of Ag/AgCl were carried out by electrolyzing Ag wire (anode) and Pt wire (cathode) in 0.1 M KCl solution for $\pm$20 min. The length of time electrolysis

will affect the thickness of AgCl on Ag wire, where the more extended the electrolysis process, the thicker it will be to a certain extent, and vice versa. Next, the Ag/AgCl wire that has been formed is then dried in the open air. Finally, Ag/AgCl wire that has been dried at room temperature is inserted into the electrode body as a comparison electrode for Ag/AgCl [20].

2.4. Preparation of Au Electrode Biosensor

The Au electrode tip was immersed in a 15% CA membrane solution. The CA membrane formed was rinsed with distilled water and then dipped in 25% GA solution for 6 h. Furthermore, the electrode was rinsed with distilled water and PB solutions pH 8, then an electrode membrane (Em) was formed. Then, Em was immersed in the AChE enzyme for 2 × 24 h at 4 °C. Before measuring the response to the biosensor, the components in the measurement, such as standard electrodes, coated wire type working electrodes, ATCl substrate and inhibitor solution, need to be left at room temperature for about 2 h until components are stable and produce a good response [20].

2.5. Measurement of the Potential Value Biosensor

Measurement of the potential value of the enzymatic biosensor electrodes with the pesticide inhibitors diazinon and profenofos in concentrations of 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mg L^{-1} using a potentiometer. Em was immersed in PBS pH 8.0 for 10 min and then used ME to measure the potential value of 10^{-3} M ATCl substrate to obtain a constant value. The Em was removed and rinsed with distilled water, and then Em was immersed in a pesticide solution for 30 min, then removed and rinsed with PB solution pH 8.0 before being dipped again into the ATCl substrate solution. Furthermore, it made observations to obtain a constant potential value.

2.6. The performance Test of Biosensor

2.6.1. Sensitivity

The sensitivity value (Nernst factor) is determined using a graph of the relationship between the potential value and –log of inhibitor concentration. Then, we can see the linear equation from the chart to obtain the sensitivity range of the diazinon and profenofos pesticide electrode.

2.6.2. Limit of Detection (LoD)

LoD is the lowest limit of analyte concentration that can be measured by the instrument, which is statistically different from the blank. Determination of LoD was carried out by analyzing the potential response of a series of standard solutions of various pesticide concentrations of 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} mg L^{-1}. The analysis results obtained a linear equation of the calibration curve, y = ax + b, then the measurement of the potential value of the blank. The equation for the value of y at the detection limit is based on equation of Christian et al. (2014) [21]. They suggest calculation for the LoD = 3 × (SD/S) based on the response's standard deviation, SD, and the slope or sensitivity, S, of the calibration curve at levels approaching the limit.

2.6.3. Selectivity

Selectivity is expressed as the degree of bias of the primary analyte analysis data with interference compared to the analyte analysis data without interference [21]. The sample analysis used a concentration of 10^{-5}, 10^{-4} and 10^{-3} mg L^{-1}. Measuring the potential value using a potentiometer and calculating the selectivity coefficient ($K_{i,j}$). The value of the electrode selectivity calculated based on the Nicolsky–Eisenman equation [22]. The potential of an ion-selective electrode in the presence of an interfering ion follows an equation:

$$E_{ISE} = k + \frac{S}{z} log\left(a_i + \sum_{j \neq i} K_{i,j}\, a_j^{z_i z_j}\right)$$

where ***S*** is the slope (theoretically 2.303RT/F) and ***k*** is the ion charge including all contributions independent of activities ***a*** and ***z*** is the ion charge. The subscript ***i*** stands for the primary pesticides and subscript ***j*** stands for the interfering pesticides.

2.6.4. Accuracy

Determination of the accuracy value is obtained by calculating the % recovery, where the sample used is mustard greens with the addition of inhibitor concentrations of 10^{-4}, 10^{-3} and 10^{-2} mg L^{-1}. Measurement of potential value using a potentiometer and calculated % recovery based on the equation of Christian et al. (2014) [21].

3. Results and Discussions

As shown in Figure 1, an analysis of the performance of the biosensor on the pesticide diazinon and profenofos using a small device potentiometric (SDP)-based biosensor as a transducer was carried out. SDP-based biosensor performance tests, including sensitivity, LoD, selectivity and accuracy, are essential parameters in biosensors.

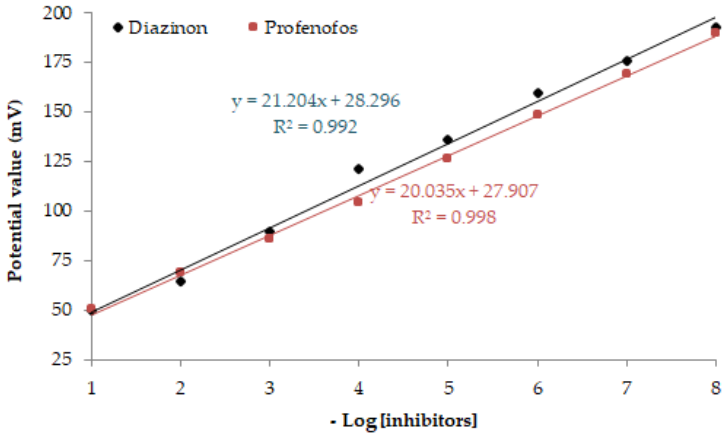

Figure 1. Graph of the relationship of −log [inhibitors] with the potential value of biosensor-based SDP.

The sensitivity, or Nernst factor, is one of the general parameters of biosensor performance testing, using SDP as a transducer indicated by the slope resulting from the calibration of the electrode potential response to the analyte's activity. Analysis using potentiometric is based on the potential change in each variation of ion concentration [16]. The feasibility of a tool used in detecting an analyte is seen from how much sensitivity is in the measurement process. So, in this study, the Nernst factor value was determined to see how well the sensitivity of the tool and the measurement range of an electrode was suitable for use as a pesticide detection tool. The results of the measurement of the potential value of the biosensor performance are presented in Table 1.

Figure 1 shows the sensitivity of the performance of SDP-based biosensors to the detection of pesticide diazinon and profenofos of 21.204 and 20.035 mV $decade^{-1}$, respectively. The sensitivity is the slope value of the linear regression equation from the graph of the relationship −log [inhibitor], with the potential value measured using a potentiometer. The value of the Nernst factor is more ideal if it is close to the value of 29.6 mV $decade^{-1}$ [23].

The characteristics of a biosensor are also determined by its ability to detect the concentration of an analyte. The smaller the concentration that can be seen, the better the biosensor features. Limit of Detection (LoD) is the minor analyte concentration that gives a sufficiently large signal and can be distinguished from the signal obtained from the blank with a 99% confidence level [15]. The optimum performance of a biosensor can be determined by its ability to detect the concentration of an analyte. The LoD was determined using the standard deviation of the intercept and the slope of the calibration line. Table 1 shows the LoD value of the SDP-based biosensor as a transducer, which is 10^{-7} mg L^{-1} instead of 10^{-8} mg L^{-1}, because the potential at that concentration is close to the potential

blank value. So, the smaller the concentration that can be detected, the better the biosensor characteristics [24].

Table 1. Measurement of potential value, sensitivity value and LoD of biosensor.

Substrate Concentration (M)	Inhibitor Concentration (mg L^{-1})	Potential Value	
		Diazinon	Profenofos
10^{-3}	10^{-1}	50	50.7
	10^{-2}	64.8	69.3
	10^{-3}	89.5	86.1
	10^{-4}	121.1	104.2
	10^{-5}	135.7	126.5
	10^{-6}	159.9	148.7
	10^{-7}	175.8	169.4
	10^{-8}	192.9	189.6
Potential value of substrate (mV)		199.8	195.7
Potential value of blank (mV)		199.1	196,3
Potential value of 10^{-8} mg L^{-1} (mV)		195.5	194.6
Sensitivity (mV $decade^{-1}$)		21.204	21.035
Linear regression equation (R^2)		0.992	0.998
LoD (mg L^{-1})		10^{-7}	10^{-7}

The selectivity is carried out to determine the method's ability to measure the presence of pesticides carefully and thoroughly in interfering components. The ideal biosensor is expected to only respond to the primary analyte to be detected with selectivity coefficient $-1 < K_{i,j} < 1$. If the electrode is highly selective towards ***i*** rather than ion ***j***, $K_{i,j} < 1$. Conversely, if the electrode is highly selective towards ***j***, ion ***i***, $K_{i,j} > 1$. Variations in the value of $K_{i,j}$ depend on the electrode's response and the component environment in solution. The selectivity coefficient value obtained is smaller than 1 (Table 2). Based on the overall value received, the range of low concentrations of interfering components is still within tolerance. The average selectivity coefficient value received still meets the specified selectivity value standard, greater than −1 and more minor than +1, except for the primary analyte analysis data, diazinon 10^{-5} mg L^{-1} and profenofos interfering 10^{-5} mg L^{-1}, then the average selective electrode for pesticide detection compared to interfering compounds [25,26].

Accuracy is a measure that shows the degree of closeness of the analysis results to the actual analyte content. Accuracy is expressed as the % recovery of the added analyte. In general, the acceptance criteria for accuracy (% recovery) are 80–110% [27]. Accuracy analysis is carried out using the recovery method by sample spiking or standard addition to the sample to be analyzed. The method is carried out by adding a certain amount of analyte with a certain concentration to the analyzed sample. The data in Table 3 show that the average % recovery of the SDP-based biosensor as a transducer has an accuracy rate of 99.497 and 94.765% for diazinon and profenofos pesticide detection, respectively. The percent recovery value obtained is in accordance with the required standard. See Supplementary Materials for details.

Table 2. Selectivity of biosensor-based SDP.

[Diazinon] (mg L^{-1})	[Profenofos] (mg L^{-1})	Potential Value (mV)				Selectivity	
		Diazinon		Profenofos			
		a_i (1)	a_j (1)	a_i (2)	a_j (2)	$K_{i,j}$ (1)	$K_{i,j}$ (2)
10^{-5}	0	160	0	126.5	0	0	0
	10^{-9}		159.5		127.9	−0.24	0.64
	10^{-8}		158.9		126.1	−0.53	−0.19
	10^{-7}		158.6		125.9	−0.67	−0.29
	10^{-6}		158.1		124.7	−0.91	−0.87
	10^{-5}		157.4		124.5	−1.26	−0.96
10^{-4}	0	131.1	0	104.2	0	0	0
	10^{-9}		130.5		106.3	−0.29	0.96
	10^{-8}		130.1		105.7	−0.48	0.68
	10^{-7}		129.8		104.8	−0.63	0.27
	10^{-6}		129.5		103.3	−0.77	−0.43
	10^{-5}		129.1		102.2	−0.97	−0.97
10^{-3}	0	90	0	80.1	0	0	0
	10^{-9}		89.8		82.2	−0.1	0.95
	10^{-8}		89		81.9	−0.49	0.81
	10^{-7}		88.7		80.5	−0.63	0.17
	10^{-6}		88.2		79.6	−0.88	−0.25
	10^{-5}		88		78.1	−0.98	−0.98

a_i is the concentration of primary pesticides, a_j is the concentration of interfering pesticides, $K_{i,j}$ is the selectivity coefficient, $_{(1)}$ for diazinon pesticide and $_{(2)}$ for profenofos pesticide.

Table 3. Accuracy of biosensor-based SDP.

$[C'_A]$	$[C_A]$	$[C_F]$	Potential Value (mV)						Accuracy, % Recovery	
			Diazinon			Profenofos			Diazinon	Profenofos
			$[C'_A]$	$[C_A]$	$[C_F]$	$[C'_A]$	$[C_A]$	$[C_F]$		
10^{-2}	10^{-3}	10^{-2}	64.8	131.1	79.1	80.4	118.6	76.9	79.123	76.899
10^{-3}		10^{-3}	90.0		84.8	118.6		99.2	84.790	99.232
10^{-4}		10^{-4}	131.1		107.7	130.8		108.2	107.690	108.165
Mean of % Recovery									99.497	94.765

C'_A is the concentration of pesticides added, CA is the concentration of the sample, CF is the total concentration of the sample obtained from the measurement.

4. Conclusions

Based on the results and data obtained from the study of SDP-based biosensors as transducers in the detection of organophosphate pesticides, the sensitivity was 21.204 and 20.035 mV decade^{-1}, LoD 10^{-7} mg L^{-1}, selectivity coefficient $-1 < K_{i,j} < 1$ and accuracy of 99.497 and 94.765%. Thus, potentiometric biosensors with CA and GA membranes immobilized by AChE enzymes have good sensitivity, selectivity and accuracy in detecting the presence of organophosphate pesticides in a sample and LoD from tiny biosensors are effective for detecting at low scale and concentration.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/CSAC2021-10604/s1, presentation materials at the 1st International Electronic Conference on Chemical Sensors and Analytical Chemistry, 1–15 July 2021.

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