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The Development of Diazinon Sensors using Polyvinyl Alcohol (PVA) Membrane CuO on Surface Screen Printed Carbon Electrode (SPCE) as A Receptor

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ABSTRACT

The development of Diazinon sensor has been studied using polyvinyl alcohol (PVA-CuO membrane on the surface of the screen-printed carbon electrode (SPCE) as a receptor. The membrane used consisted of polyvinyl alcohol (PVA) 5% (w/v), citric acid 5% (w/v), glutaraldehyde 4% (v/v), Diazinon solution 40 ppm (v/v), and CuO 5% (w/v). This study established the effect of Diazinon at 0.01,0.02 and 0.03 (w/w). besides, the concentration of CuO was 0.5 and 1 (w/w). Signal measurements were carried out in the concentration range of the Diazinon 10-12 - 10-5 M solution in Britton-Robinson buffer at pH 2 - 5. Besides, the influence of the electrolyte type was studied using HCl pH 4, 10-5 M KCl, pH
3 phosphate and phosphate-KCl pH 3 buffers. The results of the Diazinon sensor characterization showed that the highest sensitivity was obtained at 42 mV/decade with a response time of 180 seconds.

Keywords: Diazinon sensor; membrane; CuO

INTRODUCTION

Chemical sensors are devices that detect chemicals in an electrical quantity in the form of a signal. The components of the chemical sensor consist of receptors, transducers, and detectors, with the receptor functioning as a selective part of the analyte [1]. Various receptors in the sensor have been used are enzymes [2], DNA [3], antibodies [4], and membranes [5] [6]. However, the membranes are more widely used for chemical sensor applications, such as determination of disulfoton [7], methyl parathion [8], chlorpyrifos [9], and atrazine [10]. This is caused by the selective nature of the membrane receptors. This research applies a membrane receptor in Diazinon analysis.

Diazinon is a type of organophosphate insecticide used as a pest exterminator in vegetables and fruits [11]. Its maximum residual limit in agricultural products is 0.02 – 2 ppm [12]. Several reports on the determination of voltammetric of Diazinon have been carried out. For instance, Motaharian et al. used selective MIP (molecularly imprinted polymer) membrane receptor with methacrylate acid as a functional monomer. He also used ethylene glycol dimethacrylate as a cross reactant and a Diazinon template [13]. In addition, Boulanouar et al. conducted a membrane-based potentiation of Diazinon with a template in form of monochrotophos (MCP), methacrylic acid as functional monomers, and cross reactants as ethylene glycol dimethyl acrylate (EGDMA) [14].

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The composition of a membrane is produced to allow interaction with the analyte in solution by adding certain molecules [15]. The addition of molecules in membranes form templates due to interactions between added particles and polymers used in membranes [16]. The polymers widely used in the development of membranes include polyvinyl alcohol (PVA). This is due to PVA has good stability, it is polar and also has an -OH group which conduct electricity [17]. However, its polarity can be modified by the addition of glutaraldehyde cross reagent to minimize the swelling of the membrane [18]. In this study, the receptor uses PVA polymer, glutaraldehyde cross reactant, citrate acid catalyst and template of Diazinon.

The performance of sensors based on PVA membranes can be improved by the addition of materials such as CuO, an anti-ferromagnetic substance with super-thermal and high stability [19]. The research on the development of membranes with CuO modification was carried out by Li et al. using nicotinamide-CuO for dopamine determination [20]. Besides, Xie et al. developed a modification of CuO to graphene membranes for detecting Malathion [21]. Modification of CuO increases membrane conductivity by up to 60% [22], affecting the sensitivity of the sensor. This is due to the increases in electron transfer to the membrane, thereby accelerating their interaction with the electrode [23]. Also, it includes semiconductors with small resistance to maintain signals [24].

The electrodes used in this study were screen-printed carbon electrode (SPCE), a decision attributed to their inert properties, low current used, and miniaturization [25]. It consists of a working and an Ag/AgCl comparative electrodes [25]. The PVA-CuO membrane is superimposed on the SPCE working electrode which acts as a transducer to produce signals. In the meantime, the signal formation mechanism work by dropping Diazinon solution on the working electrode and the comparison, interacting with the one in the membrane, producing a different potential. This is caused by the difference in concentration between Diazinon in the membrane and that in the solution [26]. The signal is produced from the membrane's latent difference between the working electrode with the comparative one, Ag/AgCl. Thereafter, the signal is transmitted by the transducer and read by the detector [1]. The performance of the Diazinon sensor can also be influenced by the pH of the solution and the electrolyte. Generally, the changes in pH affect the analyte measured [27]. Diazinon has a value of pKa 2.6 and therefore if pH increase, a lot in molecules form. Contrastingly, in pH conditions under pKa Diazinon charged molecules is easily undergone protonation [28]. This research studied the effect of pH at 2, 3, 4, and 5. The protonation reaction of Diazinon is as below.

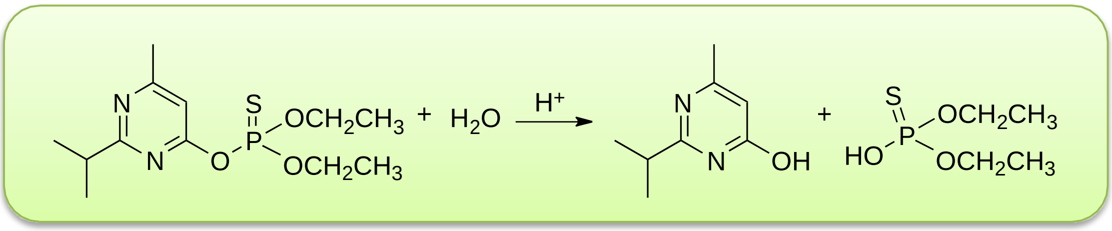

Figure 1. Diazinon protonation under acidic conditions [28]

Likewise, the other factor that influences the signal is the type of electrolyte from the solution, whose effect is related to the number of ions in the solution. The increase in electrolyte concentration affects the formation of electrical double layers that form on the surface of the membrane due to direct contact between the membrane and electrolyte solution consisting of diazinon and counter ion capable of producing capacitance [29]. The formation of capacitance on the membrane surface can reduce its potential difference, affecting the signal produced [30]. Therefore, the effect of the type of electrolyte was studied using HCl pH 4, Britton-Robinson buffer pH 3, phosphate buffer pH 3, and phosphate-KCl buffer pH 3.

EXPERIMENT

Chemicals and instrumentation

The materials used in this study were Diazinon (600 EC Diazinon), PVA (polyvinyl alcohol), glutaraldehyde 50% (Sigma-Aldrich), citric acid (CV. Kridatama), sodium hydroxide (Merck), cupric sulphate (Merck), acetic acid (Merck), boric acid (Merck), potassium hydrogen phosphate (Merck), and dipotassium hydrogen phosphate (Merck).

The apparatus used in this study were potentiometer SANWA, connector (Quasense Inc.), Screen Printed Carbon Electrode (SPCE), oven (Memmert), micropipette (Accumax Pro), and glassware.

Procedure

The PVA-CuO membrane was made by mixing PVA 5% (w/v) of volume 0.9 mL, citric acid 5% (w/v) 0.2 mL, glutaraldehyde 4% (v/v) 0.2 mL, and CuO suspension 5% (w/v) 66 µL with a Diazinon concentration added to the membrane of 0.01; 0.02; and 0.03% (w/w). The same method was carried out for CuO concentrations of 0.1; 0; 5; and 1% (w/w). The membrane was washed using ethanol for 1 hour at 100 rpm. Then the membrane is reheated at a temperature of 50°C for 30 minutes. The 0.1 gram of dried membrane was dissolved in hot water until homogeneous.

Screen-printed carbon electrode (SPCE) was coated with a composition of membranes made as much to 5 µL and dried 50°C for 1 hour. The characterization of Diazinon sensors was carried out with PVA-CuO membrane receptors using optimal Diazinon and CuO concentrations.

The PVA-CuO membrane was wrapped on the surface of the working electrode on the SPCE while the Ag/AgCl was used for comparison purpose. The SPCE was joined to the connector, the electrode indicator linked to the positive pole, while the comparative electrode was connected to the negative pole on the potentiometer. The measurement of the signal was carried out, dripping the test solution on both electrodes simultaneously and read the signal produced from the solution. The test solution used in measurements was 10^{-12} to 10^{-5} M.

RESULT AND DISCUSSION

Effect of diazinon concentration on membranes

The results showed that a relationship between the signal to -log[Diazinon] with a concentration range of Diazinon solution 10^{-12} to 10^{-5} M at pH 4 (Figure 2). The effect of the Diazinon concentration in the membrane was one of the important components in the sensor affecting the potential difference process at the electrode. Figure 2.a. shows the increase in Diazinon concentration in solution is inversely proportional to the signal at all electrodes. In the interim, the concentration of Diazinon 0% in the membrane produces a constant signal. Based on the curve in Figure 2.b, the Diazinon concentration can increase sensor sensitivity. The best sensitivity was produced at Diazinon 0.02% (w/w) in membranes at 15 mV/decade. However, the sensor sensitivity decreased with the increase in Diazinon concentration of more than 0.02% (w/w).

The addition of Diazinon to the membrane helps to distinguish it in the solution. The difference in the concentration of Diazinon in the membrane and in the solution produces potential difference which is read as a signal against the potential of Ag/AgCl. Therefore, when there is no addition of active compounds, Diazinon in the solution cannot detect the analyte, causing imbalance on the membrane surface thereby resulting in a constant readable signal [31]. The Diazinon concentration in the membrane is inversely proportional to the signal. This due to an increase in the Diazinon concentration which is directly proportional to the inner cell potential increases and thus the resulting signal decreases. Moreover, the addition of Diazinon with high concentrations can block the interaction between it in the membrane and that in the solution [32] and therefore the membrane potential difference is inhibited, causing a signal decrease.

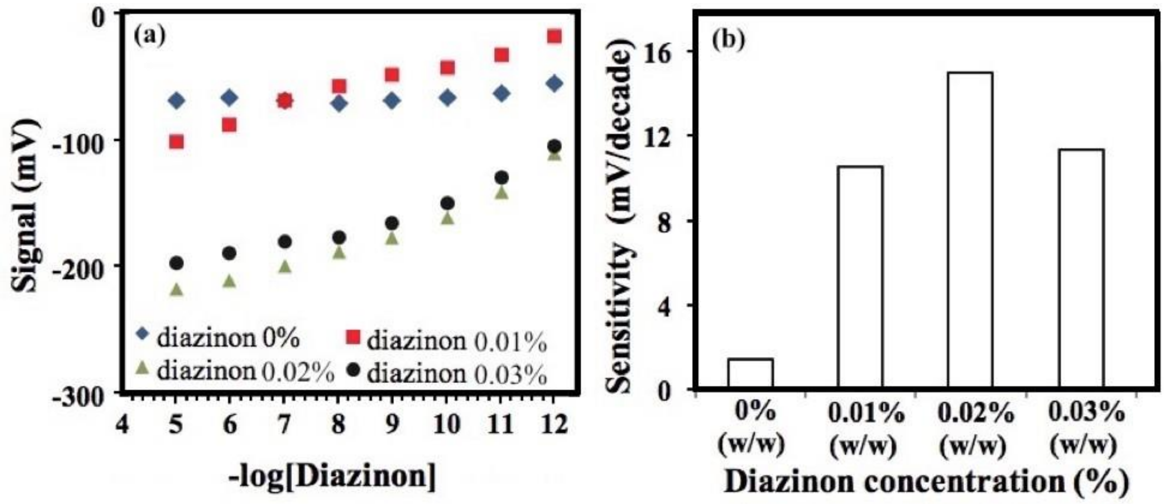

Figure 2. The results of sensor performance on the concentration of Diazinon active ingredients at membrane receptors (A) the effect of Diazinon concentration in membranes at concentrations of 0.01, 0.02 and 0.03% (w/w) (B) the effect of Diazinon 0 active ingredient concentration , 01; 0.02 and 0.03% (w/w) to the sensitivity of the Diazinon sensor.

The addition of Diazinon also affects the effectiveness of the sensor. The increase in sensitivity at 0.02% of the Diazinon active compounds in the membrane can be distributed evenly, such that when the solution is dropped on the surface, all Diazinon on the membrane can interact with the one in the solution by producing increased sensor friction [33]. However, the addition of Diazinon concentration which is too high with a fixed surface area results in an uneven distribution and increases the degree of irregularity in the membrane, thereby increasing the membrane resistivity [34]. This causes disruption of the interaction between Diazinon in the membrane and in the solution, resulting in decreased sensor sensitivity.

Effect of CuO concentration on diazinon sensor performance

The effect of CuO concentration on the signal is presented in Figure 3.a. On the curve, there is a relationship between the signal and the log [Diazinon]. From these results, the addition of the amount of CuO in the membrane was directly proportional to the increase in the signal. The highest signal was indicated by the addition of 0.1% CuO (w/w) concentration. The addition of CuO concentrations in the membrane also improve the performance of Diazinon sensors as indicated by an increase in sensitivity. However, the addition of CuO concentration in excess of 0.1% decreases the sensitivity of the Diazinon sensor. The best sensitivity was generated at 0.1% CuO concentration of 27 mV/decade.

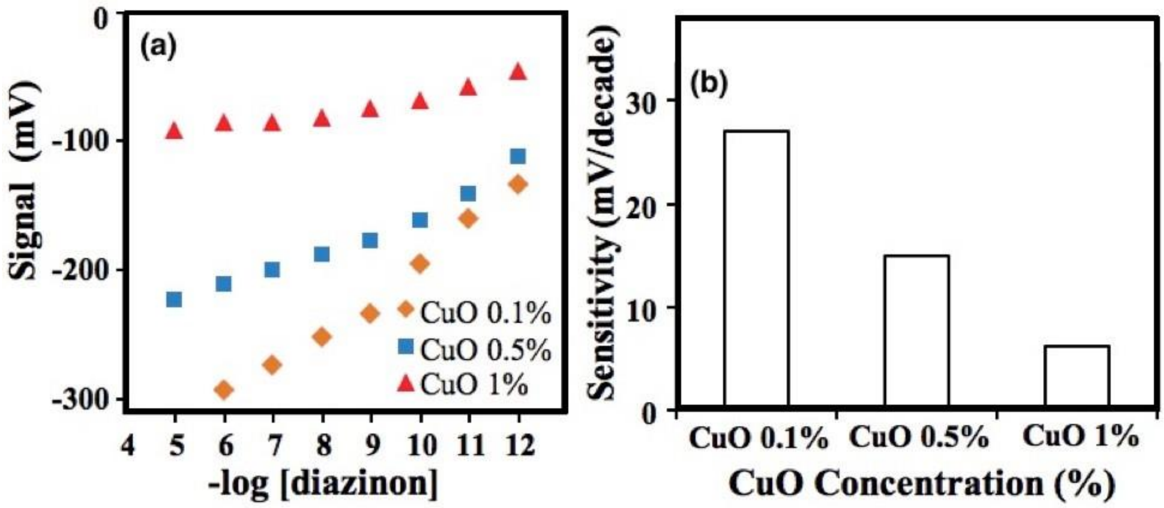

Figure 3. Results of sensor performance on CuO concentrations on membrane receptors (A), influence of CuO concentration in membranes 0.1, 0.5 and 1.0% (w/w) (B) the effect of CuO concentration of 0.1%; 0.5% and 1.0% (w/w) of the sensitivity of the Diazinon sensor.

Sensor performance is also influenced by CuO concentrations in membrane. The increase in CuO concentration in it is directly proportional to the signal increase. This is because the area occupied by CuO can increase the interaction between Diazinon in membranes with that in the ocean [35]. In addition, the increase in CuO concentration can stabilize the signal because it is a p-type semiconductor with a hole. Where the solution is dropped on the working electrode, it fills the hole with H^+ from the acidic Diazinon test solution. Consequently, the resistance decreases, producing a signal which continues to upsurge [24].

Addition of CuO concentrations in the membrane can increase sensitivity. This is caused by the ability of Cu to easily transfer electrons. This means without the addition of CuO the electrons pass through a large gap, whereas with it, the gap will be filled by Cu, accelerating electron transfer [36]. The electron transfer speed affects the haste of the signal to the transducer, increasing sensitivity. Sensor sensitivity decreases with increasing CuO concentration because the substance cover the surface or pores of the membrane [37]. The abundance of CuO on the membrane surface can affect the sulphur group of Diazinon binding Cu to form a barrier, causing obstruction of the interaction between Diazinon in the membrane and Diazinon in solution. The signal is slower towards the transducer due to decreased sensor sensitivity [38].

Effect of pH and electrolyte type on the performance of diazinon sensors

The signal response that is influenced by pH in the Briton-Robinson buffer can be seen in Figure 4. From figure 4.A, it is evident that pH affects the signal. These results indicate that the highest signal was obtained at pH 3, while the lowest signal was at pH 2. Figure 4.B shows the relationship of sensitivity to the pH of the solution. The best sensitivity was recorded at pH 3 of 28 mV/decade.

The molecular shape of diazinon is affected by pH value. Diazinon will be protonated at the N group become –NH + at pH 2 to form a positively charged molecule. Whereas at pH 3, diazinon will be protonated (50%) at one of N ring. Therefore diazinon were detected in the form of negatively charged molecules [28]. As a result of the form of negatively charged molecule caused the signal is inversely proportional to the concentration of the analyte. in addition, the pKa of diazinon is 2.6, thus diazinon is negatively charged at 3, 4, and 5 pH conditions [43].

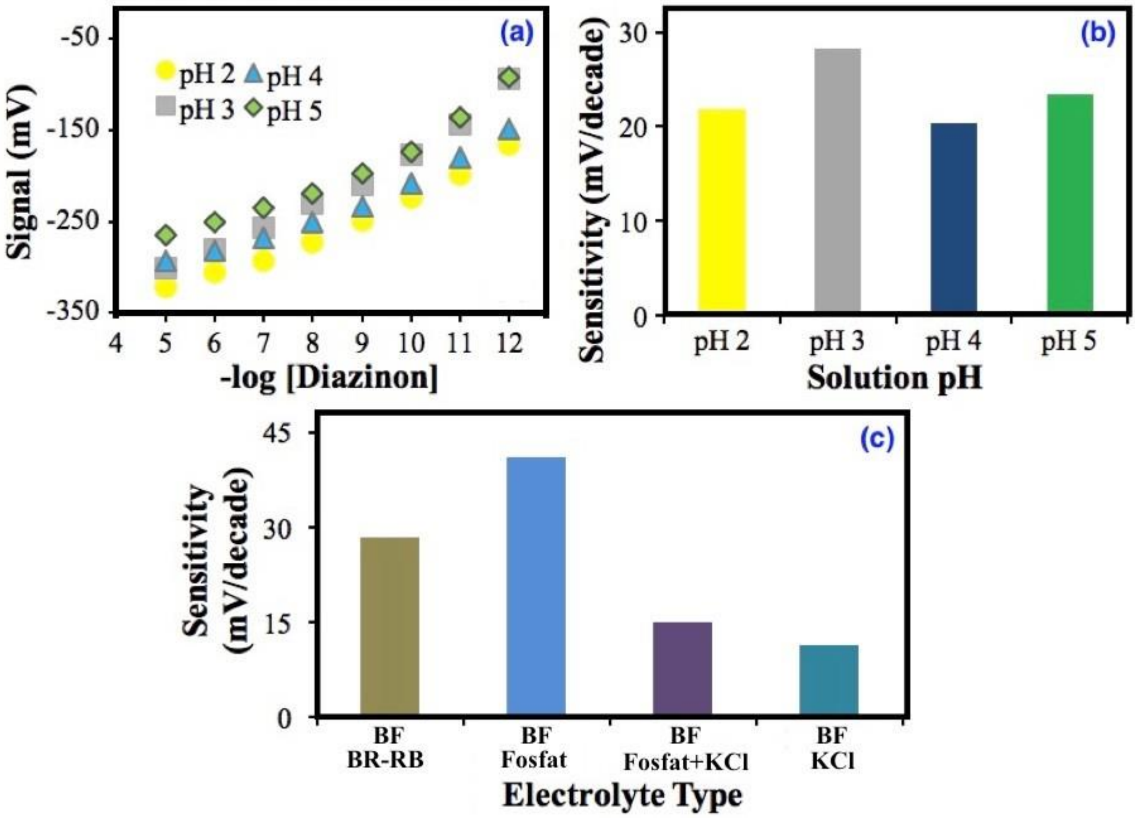

Figure 4. The results of sensor performance on pH effect (a) curve of the signal relationship to –log [Diazinon] on variations of pH, (b) Effect of pH variation on Diazinon sensor sensitivity, and (c) Effect of electrolyte type on Diazinon sensor sensitivity.

The solution under conditions close to base exacly at pH 4 affects the ions movement in the solution caused the decreased of conductivity [40]. If the conductivity decreases, the speed of the signal towards the transducer the sensitivity of the sensor Diazinon is lowered at pH 4. However, in conditions that are too acidic the sensitivity decreases due to the formation of the complex salt between Cu and acid characterized by new colour changes during mixing. This complex can cause deposits on the surface of the membrane, resulting in reduce d interaction between Diazinon inside and outside the membrane [41].

Diazinon sensor signal is also influenced by the type of electrolyte producing capacitance that affects the signal. The effect of KCl on Diazinon signals is seen in the magnitude of the signal produced. KCl is classified as a strong electrolyte because the ions in solution can move freely, sending a larger signal [42]. In addition, KCl can also control the potential well where its presence can maintain signal stability from Ag/AgCl electrodes, making the electrodes respond to both Cl^- ions in the solution. The signal decrease in the britton-robinson buffer is influenced by the ion strength of acetate of 1.76 x 10^{-5} phosphate, 7.52x10^{-3} and borate 7.3 x 10^{-5}. The increase in ion strength is directly proportional to the capacitance and the use of Britton-Robinson buffer. It is possible to form electric double on the membrane surface which causes a capacitance that can reduce its potential, resulting to a smaller signal [43]. The lowest signal is produced by a phosphate buffer. This is caused by a phosphate cushion which is a weak electrolyte with smaller conductivity, resulting in a small sensor signal. However, the highest sensitivity obtained in phosphate buffer is caused by the ions possessed by phosphate buffer that is more stable in solution and can increase the interaction between Diazinon in the solution and on the membrane, and thus the signal can be transmitted to the transducer stably and produce the best sensor sensitivity [44].

CONCLUSION

From the study, it can be concluded that the best sensor performance is produced at a concentration of Diazinon 0.02% (w/w) and CuO concentration of 0.1% (w/w) in pH 3. The characterization of Diazinon sensors produces a sensitivity of 42 mV/decade in phosphate buffer.

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