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Membranes of Nata de Coco-Nanoparticles Fe_3O_4 For Diazinon Sensors

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ABSTRACT

Development of diazinon sensors using mixed membranes of nata de coco and Fe_3O_4 nanoparticles on the SPCE (screen printed carbon electrode) surface has been carried out potentiometrically. The sensor design was conducted by optimization of Fe_3O_4 nanoparticles added to the membrane by comparison of 50%, 67% and 75% (Fe_3O_4 nanoparticles in the Nata de Coco) while pH optimization was performed at pH 4-5 using acetate buffer and pH 6-7 using phosphate buffer. The diazinon sensor of the result has been tested at range concentration of 10^{-12} - 10^{-5} mol.L^{-1}. The results showed that the best sensor performance was used at a ratio of 67% Fe_3O_4 nanoparticles and at pH 5. The Nernst factor was 34.5 mV/decade, in the range concentration of 10^{-11} - $5x10^{-8}$ molL^{-1} with a response time of 140 seconds.

Keywords: diazinon, nanoparticles, Fe_3O_4, SPCE, potentiometry

INTRODUCTION

The Fe_3O_4 nanoparticles are super paramagnetic nanomaterials with low toxicity, and easy preparation stages [1-2], that have developed recently. The Fe_3O_4 nanoparticles have been widely applied in various sensors [3-5] and biosensor [6-8]. The nanometer-sized material has electrical and hydrophobic properties; thus, it is suitable to be used as contact material in ion selective electrodes [9]. The Fe_3O_4 nanoparticles have good conductivity of 800 μs/cm [10], and can absorb electromagnetic waves, suggesting its ability to promote the rapid electron transfer between the electrode and the active site of the reaction [6]. Among the nanomaterial types, Fe_3O_4 nanoparticles are widely used as contact materials in the sensor's manufacture as modified materials of working electrodes. The modified electrode using Fe_3O_4 nanoparticles has been applied in ascorbic acid measurements [11], determination of chlorite ions in aqueous media [12] and the determination of nitrite ions [13]. In this study, SPCE (screen printed carbon electrode) modification using Fe_3O_4 nanoparticles will be used to analyze diazinon. The diazinon sensors were fabricated using nata de coco - Fe_3O_4 nanoparticles. The membrane containing diazinon was coated on the surface of the SPCE *(screen printed electrode)* electrode. The readable signal is the potential difference between SPCE vs. Ag/AgCl.

Diazinon can undergo various reactions, thereby it can be analyzed electrochemically. Several research results on the successful diazinon sensor were applied, Motaharian *et. al* (2016) have reported the determination of diazinon by voltametry based on Molecularly Imprinted Polymer (MIP) [17]. Meanwhile, Wang *et. al* (2015) showed the potentiometric

determination of diazinon using the IrOX electrode as the working electrode and Ag/AgCl as the reference electrode [18].

Diazinon is an anti-cholinesterase organophosphate pesticide commonly used to eradicate insects in agriculture [14]. The maximum residual limit is 0.02 - 0.05 mg/kg in fruits and vegetables [15]. Acute exposure of diazinon into the body may inhibit the performance of cholinesterase enzymes in the central and peripheral nerves. The level of poisoning caused by the formulation of diazinon is characterized by headache, shortness of breath, sweating, nausea, vomiting, and diarrhea [16]. Molecular mass of diazinon is 304 g/mol, with water solubility of 20 mgL^{-1}[16]. Diazinon has an acid dissociation constant (pKa) of 2.6, indicated that in the acid state, diazinon is less stable in molecular condition. Dissociation of diazinon under acidic conditions was shown by Figure 1. In general, the organophosphate compounds including diazinon will undergo bond breaking to smaller phosphate subtituents under acidic conditions, or to larger phosphate substituents in an alkaline atmosphere [19]. However, in more acidic conditions, diazinon will experience a hydrolysis reaction [20]. Hence, this study uses pH above the pKa to avoid hydrolysis, which are pH 4.0, 5.0, 6.0, 7.0.

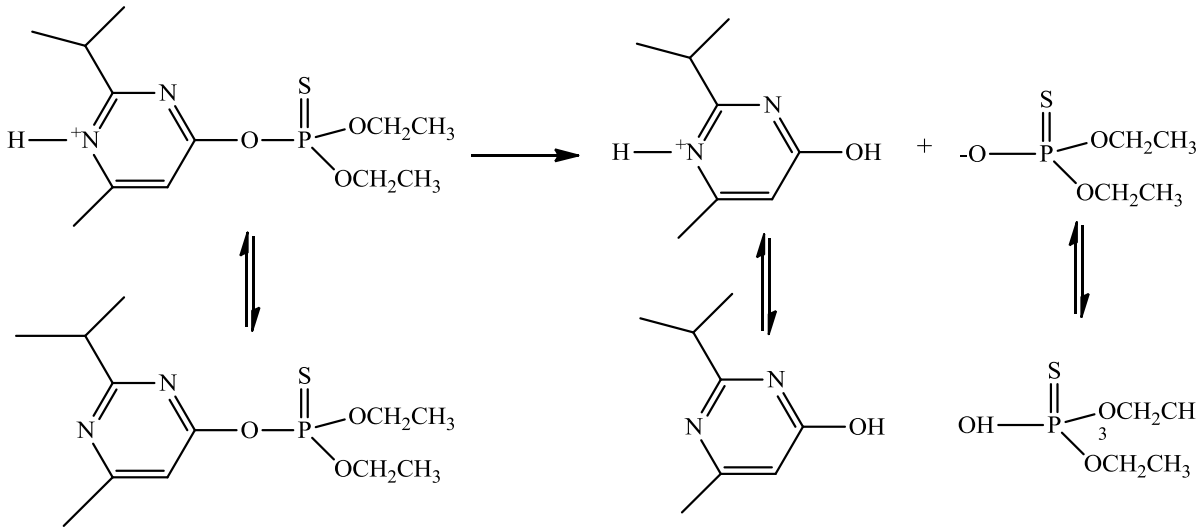

Figure 1. Acid catalysed aqueous hydrolysis of diazinon [20]

The parameter studied here is the amount of Fe_3O_4 nanoparticles in the nata de coco membranes that will be laminated on the SPCE surface. The sensor performance is indicated by the Nernst number, selectivity, detection limit, response time, concentration range and sensitivity [21]. The performance of the sensor is influenced by the composition, density and homogeneity of the active ingredient on the working electrode. Therefore, the paper shows the influence of Fe_3O_4 nanoparticles as a modifier for diazinon active ingredient in nata de coco membrane.

EXPERIMENT

Chemicals and instrumentation

The materials applied in this study are diazinon (600 EC), deionized water (Hidrobath), nata de coco (food grade) from a market in malang, potassium dihydrogen phosphate (Merck), dipotassium hydrogen phosphate (Merck), ammonium sulfate (Sigma Aldrich),

$FeSO_4.4H_2O$ (Sigma Aldrich), sodium hydroxide (Merck), $FeCl_3.6H_2O$ (Sigma-Aldrich), acetic acid 99% (Merck), sodium acetate (Merck).

The apparatus used in this study are Screen Printed Carbon Electrode (SPCE) BI 1302 (Quasense Inc), consisting of carbon as the working electrode and auxiliary electrode, Ag/AgCl as the reference electrode, pH meter (Trans Instruments Senz pH) with an accuracy of ± 0.2 pH, oven (Memmert), micropipette (Accumax pro), glassware, analytical balance (Mettler Toledo AL204), and potentiostat/galvanostat (Uniscan PG581) connected with computer and Scanning Electron Microscopy (SEM) FEI Inspect S50.

Preparation of Fe_3O_4 Magnetic Nanoparticle

The procedure of making Fe_3O_4 nanoparticles is the result of modification of the study Ghandoor *et. al* (2012) [22]. In brief, $FeSO_4.4H_2O$ (1.12 g) and $(NH_4)_2SO_4$ (0.66 g) were dissolved in 20 mL deionized water. Both solutions were mixed and stirred with a magnetic stirrer at 80°C until homogeneous and formed $(NH_4)_2Fe(SO_4)_2$. Then, solution of $FeCl_3.6H_2O$ (2.7 g in 20 mL deionized water) was added. The mixture was stirred to homogeneous and kept constant at 80°C. NaOH 1.6 g was dissolved in deionized water 50 mL. The NaOH solution was heated at 100°C.. Solution $(NH_4)_2Fe(SO_4)_2$ and $FeCl_3$ added to NaOH solution were stirred for 90°C minutes until black sediment was formed. The precipitate was wash using deionized water to pH 7 and free Cl^-. The precipitate was separated by centrifugation. The centrifugation product was dried in an oven at 100°C for 90 minutes to remove water content.

Sensor Preparations

Nata de coco 100 g was washed and added with 50 mL water, then it was blended until smooth and than filtered off. A 5 g filtered nata de coco, was added with 100 mL of buffer (pH 4-5 acetate buffer and phosphate buffer pH 6-7). The nata de coco was then refined to a suspension, and pipetted with a micro pipette 0.5-10 µm.

Fe_3O_4 nanoparticles (0.05, 0.1 and 0.15 g) were inserted in a separated container, added with 1 mL of 40 ppm diazinon solution, and stirred for 24 hours. Then, the solution was mixed with 1 mL of nata de coco (to get 50%, 67%, 75% concentrations), and the solution was kept stirred for 24 hours. A 2.5 µL mixture of nata de coco, Fe_3O_4 nanoparticles and diazinon were coated on the SPCE surface, the coating was performed 4 times. The modified SPCE was dried in an oven at 50^0C for 1 hour. The modified electrode was sterilized in a desiccator for 24 hours before they are used.

RESULT AND DISCUSSION

The Influence of Fe_3O_4 Nanoparticles

The effect of Fe_3O_4 nanoparticles on cell potential can be seen in Figure 2, the curve of the relationship between -log [diazinon] to cell potential. Figure 2 shows that the potential value is inversely proportional to log [diazinon], indicating that diazinon is measured as a cation, the concentration of diazinon solution is between 10^{-5}-10^{-12} $molL^{-1}$.

Based on Figure 2, it can be seen that Fe_3O_4 nanoparticles can increase the cell potential, but the increase in cell potential is not proportional to the percentage of Fe_3O_4 nanoparticles. The cell potential of the electrode containing 67% and 75% of Fe_3O_4 nanoparticles, produce cell potential that is not significantly different. This probably is due to the amount of diazinon in the electrodes (sensors) driven by Fe_3O_4 nanoparticles. An increase in the addition of Fe_3O_4 nanoparticles will only increase the magnetic properties and

decrease the conductivity value [5,23]. In addition to being influenced by the percentage of Fe_3O_4 nanoparticles, the cell potential is also influenced by diazinon concentrations.

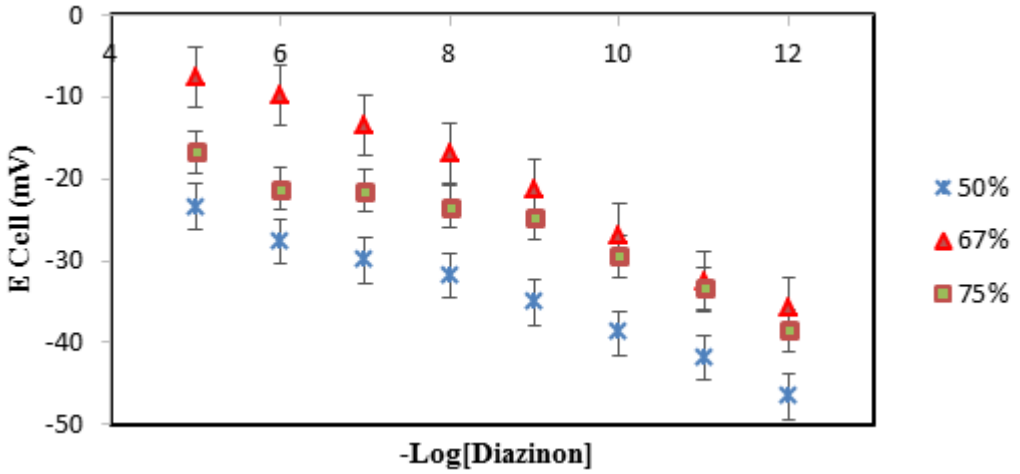

Figure 2. The relationship between cell potential to -log [Diazinon], composition of Fe_3O_4 nanoparticles added in the membrane

Table 1. Effect of Fe_3O_4 on diazinon sensor performance

Fe_3O_4 (% w/w)	Sensor constant (K, mV)	R^2
50	132.9	0.862
67	140.4	0.972
75	95.50	0.815

Table 1, shows that the nanoparticles number has a relationship with the value of K. Refers to the equation (1.1):

$$K = E_{asy} - \frac{0.0592}{n} \log a_2 \qquad (1.1)$$

E_{asy} is an asymmetric potential caused by an asymmetrical membrane between the outer and the inner membrane, thus the readable cell potential can be more positive or more negative [21]. Based on this, it is known that the addition of nanoparticles has an effect on E_{asy} and diazinon activity equal to K. It is proven by the increase of potential value of cell in Figure 2. The increase in K price occurs in the ratio of 50% and 67%, whereas in the 75% ratio the resulting price of K decreases. It shows an increase in the number of Fe_3O_4 nanoparticles added to the membrane resulting in a decrease in K value,. This is in accordance with the results of the study Yavuz et al., 2008 stating that the electrical conductivity decreased significantly as the addition of Fe_3O_4 increased. This is because the load carrier of the composite already has no gaps that can be passed so that the electrons will not move freely [23]. Based on the results of measurement the best value of K is obtained at a ratio of 67% and is directly proportional to the coefficient correlation.

Sensor Characterization

Evaluation of the diazinon sensor was performed using acetate buffer (pH 4-5) and phosphate buffer (pH 6-7) at concentration range of test solution of 10^{-12}, 10^{-11}, 10^{-10}, 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5} mol.L^{-1}. The result of measuring effect of pH on sensor performance is presented in Table 2.

Table 2. The relationship between pH to Nernst factor

pH	Nernst (mV/decade)	R^2
4	4.2	0.986
5	14.4	0.972
6	7.6	0.977
7	4.4	0.803

Table 2, shows that the effect of pH range used towards the sensor sensitivity did not differ significantly. It is likely influenced by the dissociation of diazinon contained in the membrane. Diazinon has a conjugated structure of the pyrimidine ring which causes the diazinon compound to be more stable. Thus, in a neutral condition, diazinon will be difficult to change into ions. Absence of formed ions caused no equilibrium occurrence in the working electrode, thereby decreasing the sensitivity of the sensor. Lower Nernst factors are obtained at range pH of 6.0-7.0 due to the molecular form of diazinon. The solutions contain another ion such as $H_2PO_4^-$, HPO_4^{2-}, K^+, and H^+ instead of diazinon molecule because of the use of phosphate buffer at pH 6.0-7.0. The disrupting ions present in the solution makes it possible to achieve equilibrium with similar ions present in the membrane, therefore it can be measured by the sensor.

The ion presented in the solution includes Na^+, CH_3COO^- and H^+ in addition to diazinon molecule by using acetate buffer pH 4-5 . The best sensor sensitivity is obtained at pH 5 as the highest Nernst factor. It shows that at pH 5, diazinon has dissociated to form an equilibrium in the working electrode. Meanwhile, the sensor sensitivity decreases at pH 4, theoretically diazinon ion will be more easily formed at pH 4 than pH 5, but the Nernst factor obtained in this study is just the opposite. In a more acidic condition, the membrane of nata de coco will be susceptible to swelling, thus the active ingredients and Fe_3O_4 nanoparticles present in the membranes becomes non-uniform. It affects the sensitivity towards sensor performance. However, the highest correlation coefficient was obtained at pH 4. Thus, it can be concluded that the pH of the diazinon affects the performance of the diazinon sensor.

Characterization of a diazinon sensor was carried out with a sensor of 67% Fe_3O_4 nanoparticles at pH 5. The concentrations of the solution used were $5x10^{-8}$, 10^{-8}, $5x10^{-9}$, 10^{-9}, $5x10^{-10}$, 10^{-10}, $5x10^{-11}$, 10^{-11} $molL^{-1}$. Characterization of the diazinon sensor includes linear concentration range, response time (Figure.4), and Nernst factor. The results showed that the response time of the sensor was not influenced by the concentration of diazinon because the diazinon concentration was very low. The sensor response time is 140 seconds with a 34 mV / decade Nernst factor.

The diazinon sensor has been applied directly to detect the residual diazinon in spinach and cabbage (The sample comes from markets in Malang, Indonesia). Vegetable spinach and cabbage is a type of vegetables widely consumed by the people of Indonesia [24]. Sample used 1 gram, repetition done three times in different day, the result found that the residue of diazinon in spinach is 9.4 ± 0.3 ppb while in cabbage 0.25 ± 0.3 ppb. The results shown that the levels of diazinon residue were below the SNI (Indonesia national standard)-set threshold of 0.02-0.5 ppm [15]. Referring to research prayoga, Indrajid et al (2014), the determination of diazinon concentrations by conductometric for spinach 1,5 ppm while for cabbage <LOD (concentration of residu in 5 gram samples (ppm)) [25]. This shows that the diazinon sensor is able to detect a very low diazinon concentration. This is proven by% RSD obtained at 18.9% for cabbage and 3.5% for spinach.

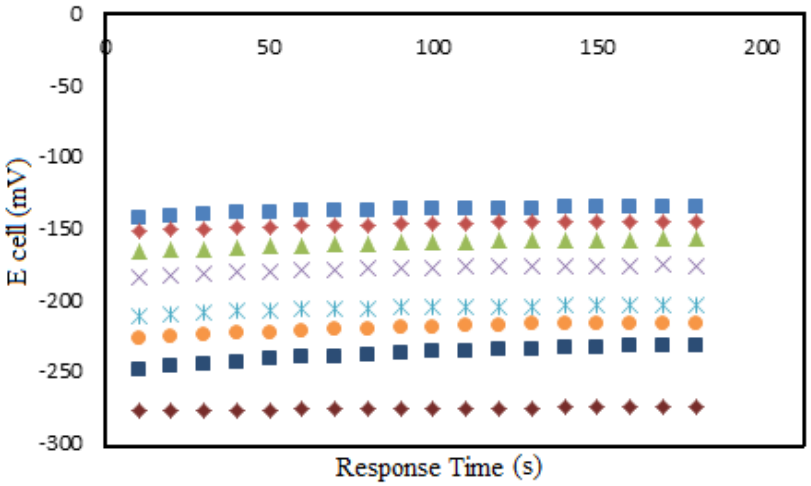

Figure 3. The relationship between time to the cell potential (■)$5x10^{-8}$ $molL^{-1}$, (◆)10^{-8}, $molL^{-1}$ (▲)$5x10^{-9}$ $molL^{-1}$, (×)10^{-9} $molL^{-1}$, (✳)$5x10^{-10}$ $molL^{-1}$, (●)10^{-10} $molL^{-1}$, (■)$5x10^{-11}$$molL^{-1}$, (◆)$10^{-11}$ $molL^{-1}$

Table 2. Sensor Characterization

Parameters	Result
pH	5
Nernst Factor	34 mV/decade
R^2	0,980
Concentration Range	$5 \times 10^{-8} - 1 \times 10^{-11}$$molL^{-1}$
Response time	140 s

CONCLUSION

Based on this research, it can be concluded that the nanoparticles Fe_3O_4 can be used as recognition elements for the fabrication of a sensitive and selective potentiometry sensor for the determination of diazinon pesticide. The best sensor performance was obtained using 67% Fe_3O_4 nanoparticles at pH 5, with Nernst factor of 34 mV/decade with a response time of 140 s in the $5x10^{-8}$ to 10^{-11} $molL^{-1}$ concentration range.

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