POTENTIOMETRIC SENSOR FOR ENDOSULFAN PESTICIDE BASED ON MOLECULARLY IMPRINTED POLYMER

Yohandri Bow[1)], Hairul[2)], Ibnu Hajar[3)]

[1,3)] *Chemical Engineering Department, Politeknik Negeri Sriwijaya, Palembang, 30139, Indonesia*
E-mail:yohandribow@gmail.com, ibnubaray@gmail.com

[2)] *Electrical Engineering Department, Politeknik Negeri Sriwijaya, Palembang, 30139, Indonesia*

Abstract**.** Molecularly imprinted polymers (MIP) is a technique to produce a polymer having cavities as a result of the removing of specific template. MIP endosulfan is MIP with endosulfan template, one of pesticide types. MIP can be applied to the electrodes. This study aimed to obtain optimum conditions of MIP endosulfan manufacture with cooling and heating methods, characterize MIP endosulfan using SEM, and test the performance of aluminum-carbon-based electrodes MIP endosulfan as a potentiometric sensor. Stages of generating electrodes of MIP endosulfan were MIP endosulfan generating, MIP endosulfan coating on the surface of the aluminum-carbon electrodes and electrode potentiometric testing. The obtained MIP endosulfan by washing and without washing were characterized using SEM. The results showed differences in the number of pores between MIP without and with washing. The test results of electrode performance indicated that MIP endosulfan-based aluminum-carbon electrode as sensor had detection limit of 0.02 mM, sensitive in the concentration range from 0.02 to 0.12 mM with Nernst factor> 0.059 V / decade and had good stability and repeatability.

Keywords: endosulfan, imprinted polymer, sensor, potentiometric

I. INTRODUCTION

Organochlorine pesticides are a group of chlorinated cyclodienes that are not only extremely toxic but also highly persistent organic pollutants (POPs). Although they play a vital role in crop production and protection, their widespread use has resulted in their bioaccumulation throughout the food chain and led to the contamination of various environments. The accumulation of organochlorines can have worst effects on human health and the environment, even though many of them are banned [1].

Endosulfan (6,7,8,9,10, 10-hexachloro- 1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-odioxa-thiepin-3-oxide) is one of the persistent organochlorine pesticides that is not banned worldwide and is consistently used in agriculture, viticulture and horticulture. The half-life of endosulfan in water depends on the amount of oxygen dissolved, turbidity, pH and other contaminants in the water; it varies from 3 days to 5 months. Endosulfan is an insecticide that acts a contact poison in a wide variety of insects and mite such as cabbage worm, and pests on fruits, vegetables, tobacco and cotton. Endosulfan can be easily absorbed into an organism through its stomach, lung and even through the skin and hence is an active contact hepatotoxin [2].

Molecularly imprinted polymer (MIP) is today a viable synthetic approach to design robust molecular recognition materials able to mimic natural recognition entities, such as antibodies and biological receptors. The design of synthetic materials, which are able to mimic the recognition processes found in nature, has become an important and active area of research making in recent years molecular imprinting one of the strategies followed to create materials with recognition ability comparable to the natural system. MIP is considered a versatile and promising technique which is able to recognize both biological and chemical molecules including amino acids and proteins, nucleotide derivatives, pollutants, drugs and food [3]. Further, application areas include: separation sciences and purification [4], chemical sensors [5], catalysis [6], drug delivery [7], biological antibodies and receptors system [8].

II. MATERIALS AND METHODS

The synthesis was initiated by inserting endosulfan as a template into a tube containing chloroform. Later, methacrylic acid (MAA) as a functional monomer, ethylene glycol dimethyl acrylate (EDMA) as a cross-linker, and benzoyl peroxide (BPO) as an initiator were added sequentially to make a pre-polymer solution. The pre-polymer solution was then stirred for 15 min, before it was out into a refrigerator at -5^{o}C for 60 min. After that, the cooled solution was heated at 70^{o}C for 150 min. Finally, the solid polymer product was formed in the solution. It was then filtered and crushed to obtain polymer particles. The resulting polymer particles were washed to remove the endosulfan template from them. As a result, cavities are left in the polymer particles and the polymer particles with cavities are known as endosulfan MIP particles. They can be used to identify a target that has physico-chemical properties similar to template.

A control sensor was prepared in every case following the same procedure, but in the absence of template molecule. The control (or non-imprinted polymer-modified sensor) had at any time the same treatment as the imprinted sensor, to ensure that the effects observed are only due to the imprinting features and not to the subsequent treatments under-gone by the sensor.

III. RESULTS AND DISCUSSION

A. Optimum Condition for Generating Molecularly Imprinted Polymer

MIP was generated by mixing and stirring all the materials sequentially. At the initial compound, Methacrylic acid had higher ratio of mole compared to endosulfan aimed to form endosulfan mold surrounded by Methacrylic acid when reacted.

The polymerization process was considered complete when clear liquid heated at temperature of 70 ^{0}C turn into acrylic like the color methacrylic acid (MAA) attached to the vial. Generated MIP was then crushed to powder to produce MIP fine. Further washing was done to eliminate the remnants of the reactants in the polymerization process and eliminate endosulfan template.

Generating MIP was influenced by factors: the time of making the composition of generating MIP and the stirring. Based on data of optimum conditions experiments, MIP-generating optimum time was 150 minutes. Successfully Generating MIP required stable stirring. Unstable stirring caused failure. Besides that, the composition also affected the successful generation of MIP. Based on the experiment, the composition for the success of the MIP was by multiplying each material three times the original except endosulfan and benzoyl peroxide (BPO). The excess number of moles of MAA and EGDMA was made in order to form the endosulfan mold surrounded by the materials. BPO remained on the initial composition for BPO used only in small amounts as initiators or catalyst.

B. Characterization of MIP

MIP morphological characterization done by Scanning Electron Microscopy (SEM). By SEM, we could see the amount and the pore size of the electrode. Characteristics of the polymer surface were in Fig. 1.

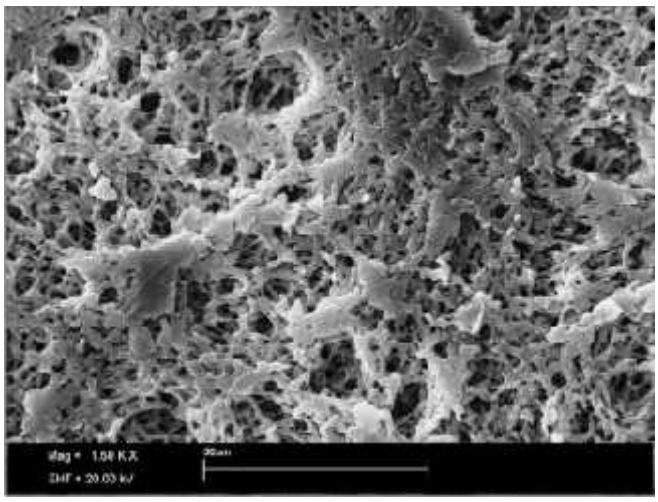

Fig.1 SEM image of MIP composite membrane by endosulfan template

Based on Figure 1, the MIP surface by washing had cleaner look than the MIP without washing. MIP surfaces were then analyzed for the number and size of the pore by using a software program in MatLab PoreDiz 2013. The obtained number and sizes were in Fig. 2.

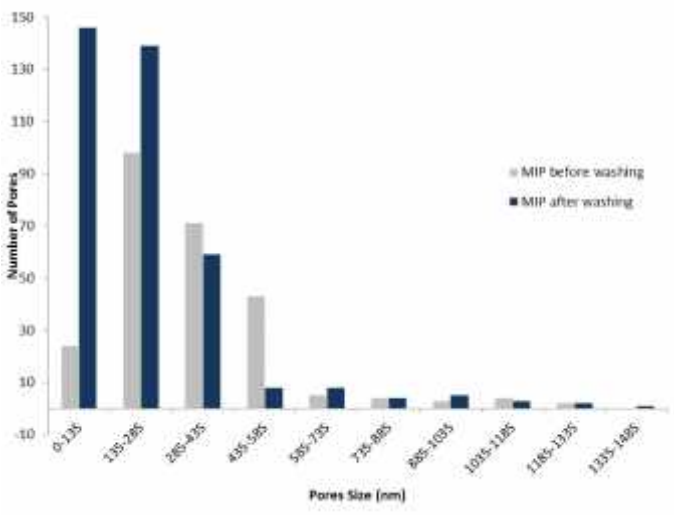

Fig. 2 Histogram of pore size distribution of MIP Endosulfan before washing and MIP Endosulfan after washing

Fig. 2 showed that the number of pores of MIP endosulfan with washing were more than the MIP endosulfan without washing. The pore size of 0-285 nm were dominant. There were significant differences between MIP and MIP without washing at this size pore range. The number of pores in the range of 0-135 nm with washing amounted to 146 pores whereas without washing 24 pores. Same to the range of 135-285 nm pores where the number of pores by washing were 139 while without washing were 98. MIP endosulfan with washing had more pores because the generated endosulfan template was gone because of the washing process.

The washing process was repeated in order to produce completely clean MIP endosulfan as shown in Figure 2. The results of washing produced endosulfan specific cavity. Repeat washing was particularly useful when the MIP electrode applied to the electrode. The working principle of the electrode MIP was almost the same as lock and key theory on the enzyme and the substrate, only endosulfan molecules that filled the cavity resulting from the repeated washing process.

C. Sensor Performance Test

After testing the performance of the sensor by measuring the voltage (volts) on a standard solution with varying concentrations, linearity equation and Nernst factor were obtained.

Fig. 3 showed that the slope of the function E versus log concentration increased with increasing concentrations of the target value.

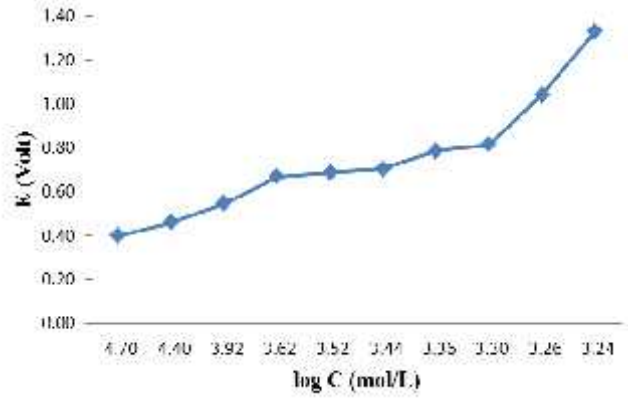

Fig. 3 Graph between MIP endosulfan potential to the target logarithm concentration on the aluminum sensor on the 1st day

Based on the graph, linear equation with three ranges of concentration was obtained. Based on the results of linear regression on the graph of potential E (volts) to the logarithm concentration, the obtained parameter values were as follows:

TABLE I
OBTAINED PARAMETERS FROM E (VOLT) POTENTIAL VS THE LOGARITHM OF THE CONCENTRATION AT THE 20TH DAY

Concentration Range (mM)	E = K + N (slope) Log C	Z	R^2
0.02 – 0.12	1.52 + 0.24 log C	0.241	0.969
0.24 – 0.44	2.82 + 0.61 log C	0.095	0.844
0.5 – 0.58	26.43 + 7.41 log C	0.00075	0.948

From the measurements performed in the concentration range from 0.02 to 0.58 mM obtained three N slope with a value of 0.24 in the concentration range from 0.02 to 0.12 mM, 0.61 in the concentration range from 0.24 to 0.44 mM, and 7.41 in the concentration range from 0.50 to 0.58 mM. These electrodes had good sensitivity in the concentration range from 0.02 to 0.12 mM as indicated by the linearity value closed to 1, $R^2 = 0.969$.

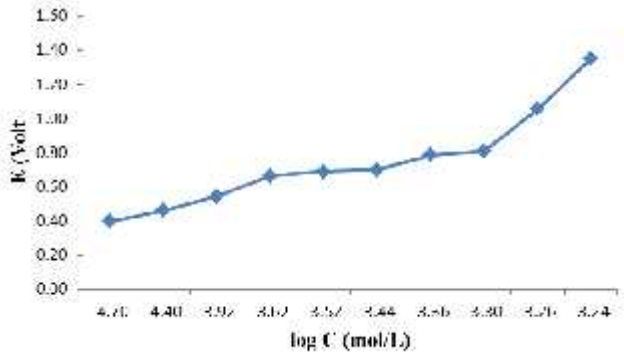

Fig. 4 Graph between MIP endosulfan potential to the target logarithm concentration on the aluminum sensor on the 4thday

From the measurements done on the fourth day in the concentration range from 0.02 to 0.58 mM N obtained three slope with a value of 0.24 in the concentration range from 0.02 to 0.12 mM, 0.55 in the concentration range of 0.24 - 0.44 mM, and 8.07 in the concentration range 0.50 to 0.58 mM. Measurement on the fourth day also showed sensor had good sensitivity in the concentration range from 0.02 to 0.12 mM with the linearity of $R^2 = 0.953$. A potentiometric said to have met the Nernst equation if Nernst factor 0.059/z or 0.059 V/ decade [9].

TABLE II
OBTAINED PARAMETERS FROM E (VOLT) POTENTIAL VS THE LOGARITHM OF THE CONCENTRATION AT THE 20TH DAY

Concentration Range (mM)	E = K + N (slope) Log C	Z	R^2
0.02 – 0.12	1.50 + 0.24 log C	0.241	0.953
0.24 – 0.44	2.60 + 0.55 log C	0.095	0.852
0.5 – 0.58	27.43 + 8.07 log C	0.00075	0.949

1) *Stability*: To determine the stability of the occurred measurement electrode, the measurement performed again four days after the first measurement. Measurement data were shown in Figure 5.

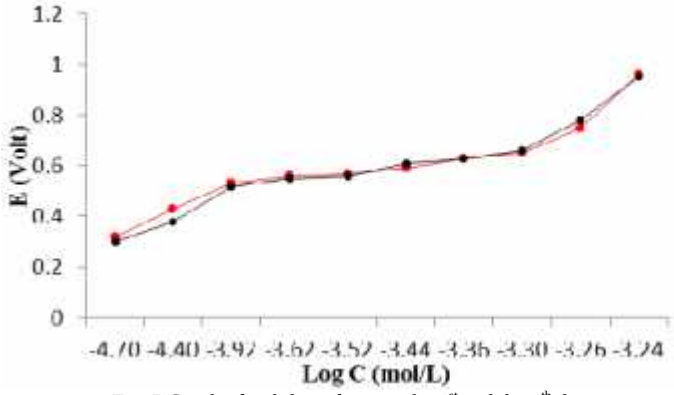

Fig. 5 Graph of stability of sensor the 1st and the 4th days

2) Limit of Detection: The limit of detection indicated the lowest concentration of analyte ions addressed by the electrodes as the lowest measurement limit. Based on the experiment, the detection limit of aluminium-carbon electrode was 0.02 mM. Electrodes responded well to a minimum level 0.02 mM concentration of endosulfan.

3) *Repeatability:* Good electrodes had good repeatability or reproducibility. Measurement data showed the repeatability of electrode as shown in Figure 6.

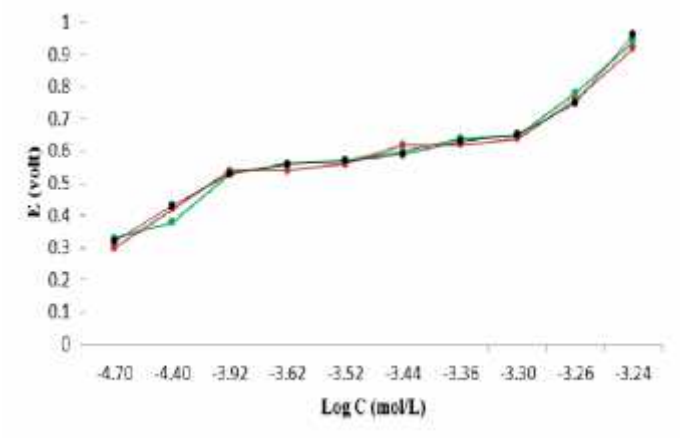

Fig. 6 Graph of repeatability of sensor for 1st day

Based on Figure 6, the three graphs coincided. This graph showed that measurement 1, 2, and 3 on the first day had identical measurement value. Based on the three measurements, electrodes had good repeatability. Good repeatability occurred when electrodes was measured on the 4th day as shown in Figure 7.

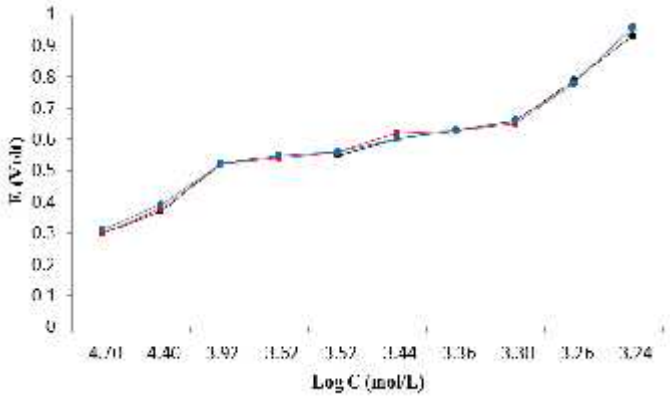

Fig. 7 Graph of repeatability of sensor for 4th day

IV. Conclusions

Based on MIP characterization using SEM, it was concluded that the pore size range 0-285 nm. There were significant differences regarding the number of pores and the MIP endosulfan with and without washing.

The results of performance tests based electrode MIP endosulfan as a sensor indicated that the electrode had good sensitivity in the concentration range from 0.02 to 0.12 mM with a value of linearity (R^2) of more than 0.98. These electrodes also had good stability and repeatability and were capable of measuring the concentration of endosulfan until the concentration of 0.02 mM. The result of measurement indicated that cell potential response was not Nernstian but upper Nernstian.

Acknowledgment

The authors would like express great gratitude to Ministry of Research, Technology and Higher Education that had funded this research and State Polytechnic of Sriwijaya that had facilitated this research.

References

[1] H. Saikh, N. Memon, M.I. Bhanger, S.M. Nizamani and A. Denizli, Core-shell molecularly imprinted polymer-based solid-phase microextraction fiber for ultra trace analysis of endosulfan I and II in real aqueous matrix through gas chromatography-micro electron capture detector, *Journal of Chromatography A*, 1337, pp. 179-187. 2014.

[2] G. Vasapollo, R. D. Sole, L. Mergola, M. R. Lazzoi, A. Scardino, S. Scorrano and G. Mele., Molecularly imprinted polymers: Present and future prospective, *Int. J. Mol. Sci*. 12. Pp. 5908-5945. 2011.

[3] Kanchan Singh, Akmal Pasha, B.E. Amitha Rani. Preparation of Molecularly Imprinted Polymers for Heptachlor: An Organochlorine Pesticide. Chronicles of Young Scientists, Vol. 4(1). p. 46-50. 2013. doi: 10.4103/2229-5186.108806.

[4] Abdul Latif Ahmad, Nuur Fahanis Che Lah and Siew Chun Low. Molecular Imprinted Polymer for Atrazine Detection Sensor: Preliminary Study. Chemical Engineering Transactions. Vol. 45. p. 1483-1488. 2015. doi: 10.3303/CET1545248.

[5] Maricely Janette Uria Toro, Luiz Diego Marestoni and Maria Del Pilar Taboada Sotomayor. A New Biomimetic Sensor Based on Molecularly Imprinted Polymers for Highly Sensitive and Selective Determination of Hexazinone Herbicide. Sensors and Actuators B 208. p. 299-306. 2015.

[6] Jianshe Tang and Li Xiang. Development of a Probe Based on Quantum Dots Embedded with Molecularly Imprinted Polymers to Detect Parathion. Pol. J. Environ. Stud. Vol. 25, No. 2. p. 787-793. 2016. doi: 10.15244/pjoes/60888.

[7] Fabrizio Ruggieri, Luca Lozzi, Angelo Antonio and Sandro Santucci. Development of Molecularly Imprinted Polymeric Nanofibers by Electrospinning and Applications to Pesticide Adsorption: Sample Preparation. Journal Separation Science. February 2015. doi: 10.1002/jssc.201500033.

[8] Singh, *et al. Molecular Imprinting for Heptachlor*. Cronicles of Young Scientists. Vol. 4, Issue 1 Jan-Jun. p. 46-50. 2013.

[9] Vishnuvardhan, Varada, *et al. Imprinted Polymer Inclusion Membrane Based Potentiometric for Determination and Quantification of Diethyl Chlorophosphate in Natural Waters.* American Journal of Analytical Chemistry, 2, p. 376-382, 2011.