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The effect of atrazine concentration on galvanic cell potential based on *molecularly imprinted polymers* (MIPS) and aluminium as contact electrode

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Abstract. Potentiometric sensors had been fabricated by employing the Atrazine MIPs as the working electrode; Aluminum (Al) as the electrode potential. A glass with diameter 3 mm and 6 mm as the vessels for chemical solution. The sensor target was a test solution of Atrazine with different concentration. The potential measured between the electrode contact and reference were increase by the rise of Atrazin concentration. The graph of potential cell versus logarithm of concentration revealed two slopes for Al contact. It implied that the potentiometric sensor was sensitive in the range of concentration 0.44-0.55 mM. Reevaluation of the sensor was conducted 3 months later by following the same procedure. Still, the graph showed a consistent curve that prove sensor stability.

1. Introduction

Molecular imprinting (MI) is a method to compose cavities in polymer based on target 'shape', in this case Atrazine molecules. Polymer produced by MI method (called MIP) had been applied as sensor to detect chemical and biological element [1-4], such as element within medicines and food [5-6].

Previous research had proved that MIP could be produced by a simple technique called cooling-heating procedure [7]. This method didn't require any Nitrogen flow into the pre-polymer solution as other researchers did [8-11]. The solution then been placed into a waterbath on zero Celcius temperature while radiated by UV light. The duration for this procedure was depend on the material in the research used.

Atrazine is a dangerous chemical element found usually in herbicide and had been Successfully detected by MIP sensor within water environment [12]. This potentiometric sensor had been used to measure the potential of galvanic cells. The potential scale would be depend on ionic activities inside chemical reaction of the cell.

This paper will present a potentiometric sensor based on MIP to target Atrazine utilized working electrode. The measurement showed that there are linear connection between potential of electrodes and solution concentration of Atrazine.

2. Methodology

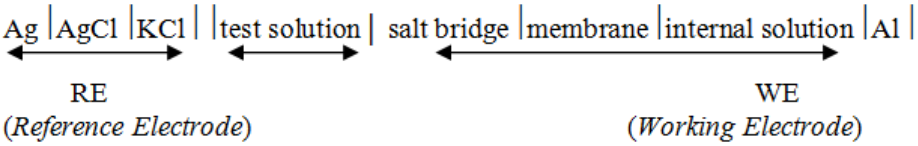
In this experiment, MIP membrane of Atrazine had been utilized as working electrode inside stainless-steel (SS) and *pyrex* glass vessels: one glass had diameter 3 mm (G1) and other 6 mm (G2). The membrane had been produced following these procedure: 0.025 gr of Atrazine (template) with 2.01 mL of Chloroform were mixed role as solvent solution. Then 0.059 mL of MAA (functional monomer), 0.525 mL of EDMA (as cross-linker) and 0.07 g of BPO (as initiator) were added into the solution while stirred for 15 minutes. Hereafter, this pre-polymer solution was placed into the vessels (SS, G1 and G2).

These vessels would be refrigerated for 1 hour before be heated in an oven for 150 minutes on 70^0C degree. Finally, template would be removed to compose cavities inside the polymer. Polymer was washed within solution of methanol /acetate acid by ratio 0.625 mL / 12.5 mL; solution of methanol/aquabidest by ratio 6.375 mL/12.5 mL; by methanol three times for 1 hour, 20 hour and 1 hour [13].

Membrane of MIP inside vessels functioned as working electrode was treated first by solution of Atrazine 1 mL 12.5 ppm, HCL 1 mL 0.03 M (pH=1.2) and KCl 1 mL 0.02 M for 16 hours, before covered by aluminium foil.

3. Results and Discussion

Experiment for MIP membrane was based on this following scheme:



Within test and internal solution, Atrazine was protonised inside acid condition (H^+ ion numbers increased). This H^+ ion was yield from hydrolysis process as seen in the following chemical reaction:

$$At + H^+ \rightleftarrows AtH^+ + H_2O \rightarrow AtOH + 2\,H^+$$

where At is Atrazine, AtH^+ is protonised single Atrazine, while $AtOH$ is Atrazine Hidrocide. H^+ ion from test solution will flow to internal solution (cathode) through the salt bridge since the internal solution more aqueous than test solution. Meanwhile, Cl^- anion will flow to anode. When Atrazine concentration is low, ions from Atrazine will occupy the cavities of MIP membrane so that its cell potential measured also low. The escalation of Atrazine concentration gradually will increase the ion activity of the working electrode. This will rise ions occupation inside membrane cavities and also its cell potential.

Chemical structure of Atrazine as shown in Figure 1. The left side is Atrazine structure before hydrolysis while the right side is after hydrolysis happened.

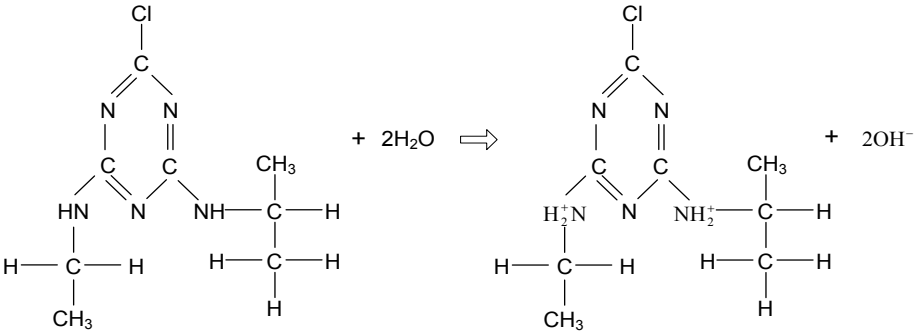


Figure 1. Chemical structure of Atrazine in hydrolysis process.

Data of potential measured within working electrode is showed in Table 1. Based on the table, a graph of potential versus logarithm of target concentration was obtained for Aluminium as contact electrode.

Tabel 1. Potential measured with Aluminium as contact electrode.

Concentration C (10^{-3}mol/L)	**Potential (Volt)**		
	SS (6 mm)	**G1** (6 mm)	**G2** (3 mm)
0.01	0.35	0.49	0.47
0.02	0.45	0.57	0.48
0.11	0.51	0.6	0.52
0.22	0.57	0.65	0.55
0.33	0.60	0.76	0.68
0.44	0.67	0.82	0.74
0.51	0.81	0.85	0.90
0.55	0.93	0.92	0.97

The potential (E) curve was calculated using Equation 1:

$$E = K \pm N \log a_{atrazin}$$

Where K is equilibrium constant, $N = \frac{RT}{zF}$ (z = atomic number), while a was calculated using Equation 2.

$$a_i = \gamma_i c_i$$

a_i is analyte activity, γ_i is activity coefficient of analyte and c_i is analyte i concentration. By the aquoues concentration of the solution (below 10^{-3} M) effect the γ_i value around 1 so that activity value can be assumed as concentration itself. From here, E curve versus log C can be plotted for the test solution.

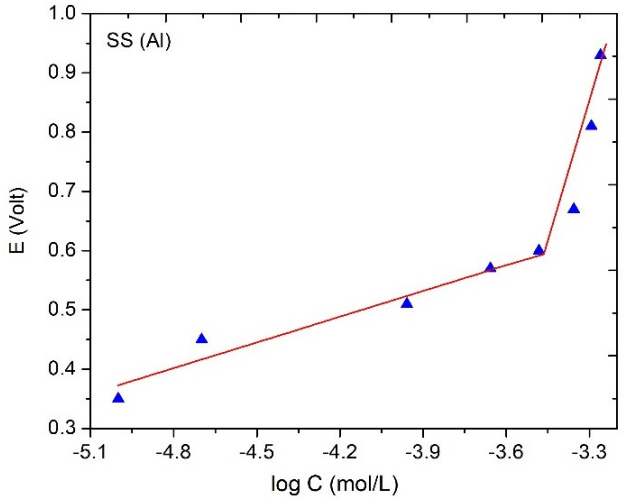


Figure 2. Curve of MIP Atrazine potential versus log C (target concentration) within stainless-steel vessel using Aluminium as contact electrode

Figure 2 reveal the relation between MIP Atrazine potential and target concentration in log scale. Concentration of test solution in range 0.01-0.55 mM had lower slope than concentration in range 0.33-0.55 mM. These two slopes had been reported also for Nerstian plot type for solution with high acidity (Agostino, 2006). These slope have a good meaning for sensor characteristic where the slope within range 0.33-0.55 mM is more sensitive than other. Statistical test affirmed this conclusion by $R^2 > 0.85$.

The same procedure had been conducted for different vessel of pyrex glass (6 mm). The result also similar with previous vessel where two slopes of potential curve obtained: 0.1 within range 0,01-0.22

mM and 0.65 within range 0.33-0.55 mM. The curve also stated that best sensor sensitivity is within range of target concentration 0.33-0.55 mM by R^2>0.89.

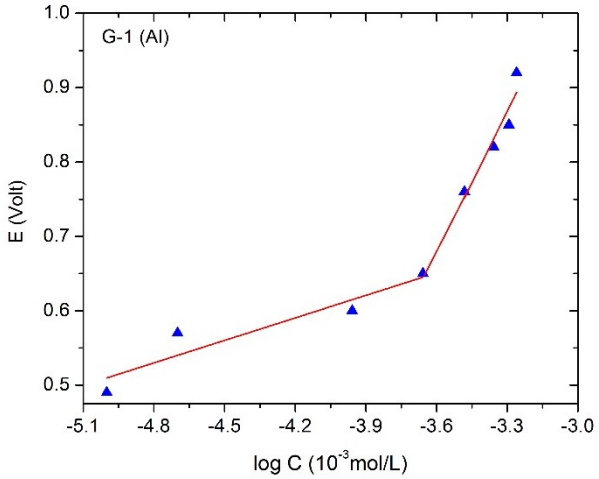


Figure 3. Curve of MIP Atrazine potential versus log C (target concentration) within glass (6mm) vessel using Aluminium as contact electrode

When glass diameter of vessel was changed to 3 mm, the slope value obtained are 0.06 within range 0.01-0.22 mM and 1.29 within range 0.33-0.55 mM. Stastistical test also confirmed this result by R^2 = 0.86.

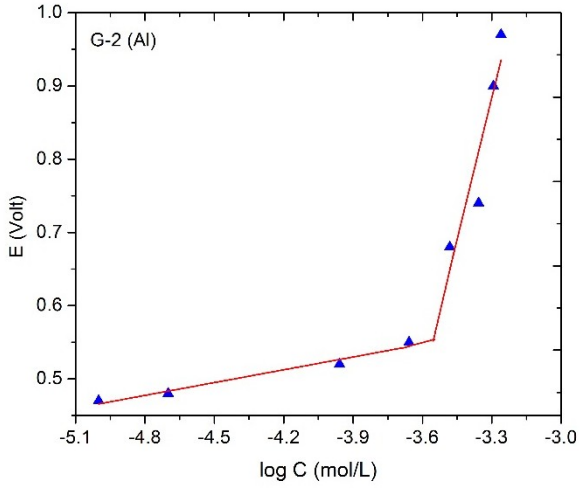


Figure 4. Curve of MIP Atrazine potential versus log C (target concentration) within glass (3mm) vessel using Aluminium as contact electrode

Figure 4 show that measured potential was rising along the escalation of target concentration. This phenomena tell us that cavities of the MIP membrane Successfully detect the Atrazine ion from the test solution. Linear regression of the curve bring us to the values in Table 2.

Tabel 2 Parameter obtained from potential curve using Aluminium contact electrode.

Vessels	Concentration Range	E = K + S log C	Z	R^2
Stainless-steel	0.01 - 0.22	E = 1.12 + 0.15 log C	0.4	0.93
	0.33 - 0.55	E = 5.45 + 1.4 log C	0.04	0.85
Glass (6 mm)	0.01 - 0.22	E = 1.03 + 0.1 log C	0.6	0.89
	0.33 - 0.55	E = 3.01 + 0.65 log C	0.09	0.90
Glass (3 mm)	0.01 - 0.22	E = 0.07 + 0.06 log C	0.98	0.97
	0.33 - 0.55	E = 5.17 + 1.29 log C	0.05	0.86

Theoretically, Nersnt factor for n=1 is 0.059 Volt/decade. Based on table 2 can be seen that for all z values within range 0.33-0.55 mM had the closest values with Nersntian than range 0.01-0.22 mM. Electrode sensitivity was higher in range 0.33-0.55 mM since the concentration of Atrazine rised gradually which effected the H^+ ion numbers. This would absolutely rise the cell potential measured in the experiment.

4. Conclusion

Based on performance test using galvanic cell (potentiometric test) revealed that there was a linear connection between electrode potential (E) and solution concentration of Atrazine. All vessels (stainless-steel and glass) gave the same result of potential measurement. The best range of potential measurement were in concentration of Atrazine 0.33-0.55 mM. The curve showed sensor had a good sensitivity along those range. Therefore, MIP of Atrazine produced in this research could be employed as an active sensor material.

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