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The Performance of Molecularly Imprinted Polymers (MIPs) - Modified Carbon Paste Electrode and Its Application in Detecting Phenol

Henry Setiyanto[1,*], *Sri Rahmadhani*[1], *Sukandar Sukandar*[2], *Vienna Saraswaty*[3],
Muhammad Ali Zulfikar[1], *Nandang Mufti*[4]

[1] Analytical Chemistry Research Group, Institut Teknologi Bandung, Bandung, Indonesia
[2] Waste and Air Management Research Group, Institut Teknologi Bandung, Bandung, Indonesia
[3] Research Unit for Clean Technology, Indonesian Institute of Sciences, Bandung, Indonesia
[4] Department of Physics, Universitas Negeri Malang, Malang, Indonesia
[*]E-mail: henry@chem.itb.ac.id

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Phenol is a very important chemical compound in life, especially in industry. Various methods of phenol analysis have been developed due to the harmful effect of phenol wastes that pollute the waters. A method employed to analyze phenol with simple instrumentation having good selectivity and sensitivity was a potentiometric method, which used a carbon paste electrode as the working electrode and was modified with a molecularly imprinted polymers (MIPs). The carbon paste electrode was electrochemically modified using a 15-cycle cyclic voltammetry technique at a potential range of -0.2 V – 1.0 V and scan rate of 100 mV/s with composition of the solution being 0.1 mM phenol: 0.2 mM aniline in a buffer solution having pH value of 9 and 0.1 M KCl as supporting electrolyte. Phenol was extracted from the polymer matrix electrochemically using 0.1 M HCl, thus expecting to form templates that can specifically recognize the molecule. The results showed that the phenolic content analysis, via a potentiometric method using MIPs-modified carbon paste electrode, had a linear range of 10^{-7} M – 10^{-1} M with a detection limit of 2.5×10^{-7} M. Besides, this electrode can respond to analytes within 60 – 70 s. The accuracy was determined based on the relative error value (% Er). The % Er obtained ranged from 1% to 3%, indicating that this method is quite accurate for the determination of phenol. The precision was identified with a good coefficient of variation, which was less than 2%. The effect of interference compounds was observed in the small selectivity coefficient ($K^{pot}_{A,B} < 1$), thus inferring that these electrodes have a higher selectivity towards phenol than other compounds contained in the sample. As a comparison, phenol measurements were carried out using the UV-Vis spectrophotometric method. Based on the percent recovery value and t-test, where t_{table} 4.30 > t_{exp} 1.12, it can be concluded that measurement with a potentiometric method using MIPs-modified carbon paste working electrode has no significant difference compared to the UV-Vis spectrophotometric method.

Keywords: electrochemistry, potentiometry, molecularly imprinted polymers (MIPs), polyaniline, phenol.

1. INTRODUCTION

Electroanalytical methods using chemical sensors such as conductometry, amperometry, voltammetry, and potentiometry have been prepared using different modified electrodes to improve the selectivity and sensitivity of the sensor [1-6]. One of the membrane electrodes that can be used as a sensor for sample analysis is a carbon paste electrode modified with a molecularly imprinted polymers (MIPs). Carbon paste electrodes have several advantages, such as ease of preparation, stability, good electrical conductor, low cost, and the use of inert chemical compounds; therefore, this type of electrode is widely used for electrochemical measurements, especially as a sensor electrode [7]. Modification of the electrode surface has been performed to form an electrochemical sensor that can improve its performance in detecting samples even in small quantities. Electrochemical sensors are strongly influenced by several factors, such as pH, concentration, and composition of the solution [8].

During the polymerization process via the electroanalytical method, the functional monomer reacts around the analytical molecule, and then the template is removed to form an imprinted polymer on the electrode surface [9]. MIPs-based sensors usually make the electrode more selective towards the target molecule, resistant to acids, bases and organic solvents, stable to temperature and low cost [10-11]. The MIPs modified electrode analyzes samples very efficiently because it has a template produced by electropolymerization, which has an active side that can specifically recognize molecules [12]. In addition to other electroanalytical methods, this method also improves the selectivity and sensitivity of the working electrode that is analyzed by potentiometric measurement [13]. In this research, a potentiometric method with MIPs-modified carbon paste electrode and copper wire (Cu) as a conductor was used. Electrochemical techniques, such as potentiometric and voltammetric methods with modified working electrodes, have been widely developed for the analysis of organic compounds, that is, phenol [14-18], because of its simple instrumentation, relatively fast response, low detection limit, wide measurement range, and good sensitivity. Unlike other transducing sensors, potentiometric sensors do not require template molecules to diffuse through the electrode membrane to increase the working potential, thereby reducing the electrode response time [6].

The potentiometric method is based on the measurement of the potential that occurs between a pair of electrodes in the solution, which is a reference electrode and the working electrode. To produce good electrode performance, the electrode needs to be validated to improve the sensitivity of the sensor. Furthermore, for comparison, phenol was measured by the UV-Vis spectrophotometric method. This study is expected to provide its own advantages in analyzing phenol with precise and accurate results.

2. EXPERIMENTAL

2.1. Materials synthesis

In accordance with previous research [19], the fabrication of MIPs modified electrodes was prepared by placing the carbon paste electrode in a solution containing 0.2 mM aniline and 0.1 mM phenol. The carbon paste electrode was electropolymerized for 15 cycles by a cyclic voltammetric technique in a potential range of -0.2 V – 1.0 V at a scan rate of 100 mV/s. The removal of phenol in the polymer matrix was carried out by cyclic voltammetry in 0.1M HCl for 15 cycles in a potential range of -0.2 V - 1.0 V at a scan rate of 100 mV/s.

2.2. Electrochemical measurement

The response time was determined by measuring 10^{-5} M and 10^{-4} M phenol every 10 s to obtain a stable potential. The linear range was determined by measuring the potential of 10^{-8} M - 10^{-1} M phenol using an optimized electrode. The standard potential curve (mV) was plotted against the logarithm of phenol concentration in determining the linear equation to obtain the slope (Nernst factor). The range that gives a straight line and corresponds to the Nernst factor is the linear range. The detection limit was obtained by determining the intersection of the linear and nonlinear regression lines on the calibration curve of phenol.

Accuracy is usually related to the percentage relative error (% Er), which was determined by measuring 10^{-7} M - 10^{-1} M phenol. The % Er of each solution was then calculated using the following equation.

$$\%\ \mathrm{Er} = \frac{\text{obtained result} - \text{expected result}}{\text{expected result}} \times 100$$

Precision values were determined by measuring the potential of the phenol solution at concentrations of 10^{-5} M, 10^{-4} M and 10^{-3} M every three times. Then, the standard deviation (SD) and the coefficient of variation (CV) were calculated using the following equation.

$$\mathrm{CV} = \mathrm{RSD}\ (\text{in percent}) = \frac{\text{standard deviation}}{\text{average potential value}} \times 100\%$$

The selectivity of the electrode was known based on the selectivity coefficient value obtained by the Matched Potential Method (MPM). The selectivity coefficient was determined using the following equation:

$$\mathrm{K}_{\mathrm{A,B}}^{\mathrm{pot}} = \frac{\text{activity of primary compound}}{\text{activity of interfering compound}}$$

The determination of phenol concentration by means of the UV-Vis spectrophotometric method began with the determination of the maximum wavelength of phenol. Furthermore, the standard solution of phenol was prepared in the concentration of 10 ppm - 50 ppm in water. Then, the absorbance of the measured solution was plotted against the concentration of phenol standard solution. The obtained equation was used in determining the absorbance value of the sample so as to determine the concentration of phenol.

3. RESULTS AND DISCUSSION

Phenol was oxidized in the presence of one electron and one proton, resulting in a thermodynamically unstable phenoxy radical [20]. Stabilization of phenoxy radicals was accompanied by high potential hydrolysis, especially in the ortho- and para-positions. Phenol oxidation is always reversible in the entire pH range, which produces hydroquinone and catechol that are electroactive in non-alkaline solutions. These compounds will produce reversible oxidation at a lower potential [21].

Electrooxidation of aniline occurred at the anode, while polyaniline was coated on the surface of the carbon paste electrode. During the electropolymerization process, polyaniline interacted with phenol through hydrogen bonds between the N-H group of aniline and the O-H group of phenol, causing the trapping of template molecules in the polymer matrix as a result of electrooxidation. In addition, the interaction between the -NH group of aniline with π-electrons from benzene is also possible [22].

3.1. Response time

Response time refers to the average time required for the electrode to reach a potential response within ±1 mV of the final equilibrium value after successively immersed in phenol [6, 9]. The response time measurements were carried out for 180 s, with the potential stabilized at 60 to 70 s, which was the response time of the electrode (Figure 1). This very short response time is effective when used for a large number of measurements.

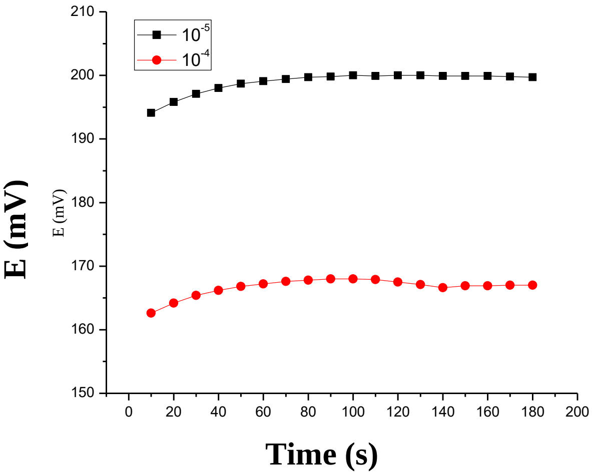

Figure 1. Response time of MIPs-modified carbon paste electrode

3.2. Measurement range, linearity and detection limit

The measurement range was determined to find the measurable concentration range of the analyte using the MIPs-modified carbon paste electrode that has been made. Measurements were carried out in phenol solution with a concentration of 10^{-8} M - 10^{-1} M in 0.1 M phosphate buffer (pH 9) and a 0.1 M KCl as supporting electrolyte. In a potentiometric measurement, the Nernstian factor was a vital consideration in knowing the best sensitivity. The measurement results of Nernst factor values are shown in Table 1 (slope). The potential curve of the MIPs-modified carbon paste electrode is shown in Figure 2. It can be seen from the figure that the plot obtained for MIPs-modified carbon paste electrode offers a linear response within a certain range of 10^{-7} M - 10^{-1} M.

Table 1. Measurement range of 1 mM phenol with MIPs-modified carbon paste electrode

Concentration (M)	Regression	Slope mV/decade	R^2
$10^{-8} – 10^{-1}$	25.817x + 109.15	25	0.9615
$10^{-7} – 10^{-1}$	28.843x + 100.07	28	0.9851
$10^{-6} – 10^{-1}$	30.597x + 95.393	30	0.9875
$10^{-7} – 10^{-2}$	28.760x + 100.51	28	0.9763
$10^{-6} – 10^{-2}$	31.350x + 91.880	31	0.9806

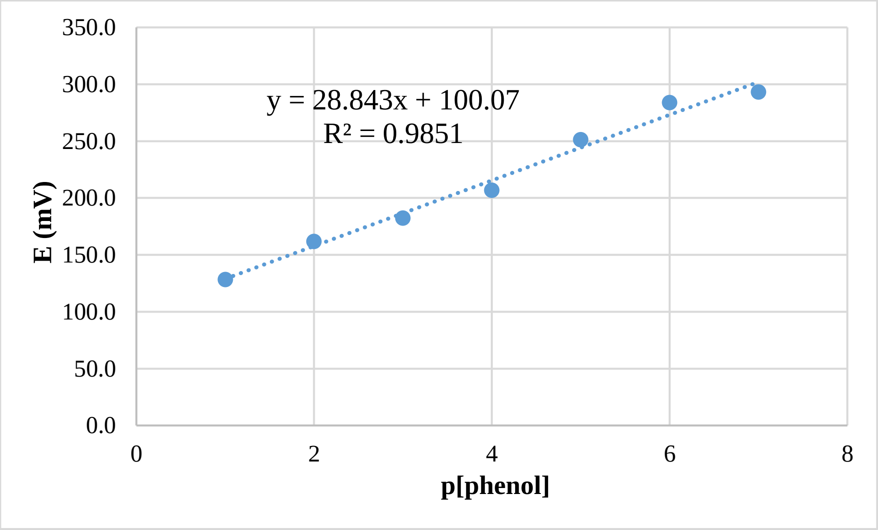

Figure 2. Calibration curve of phenol

The detection limit was determined to find out the minimum analyte concentration that can be measured with the MIPs-modified carbon paste electrode. The detection limit was calculated to be 2.5 x 10^{-7} M in accordance with Darmokoesoemo et al. [23]. A comparison of the detection limit values of some related studies can be seen in Table 2. A good result of this MIPs-based potentiometric sensor is due to the specific interaction between the phenol molecule and the template in the polymer membrane. Thus, it can be proved that MIPs is particularly effective in identifying target molecules [24-25].

Table 2. The comparison of detection limits by various method

Method	Detection limit (M)
UV-Vis [26]	3.70 x 10^{-8}
GC-MS [27]	1.03 x 10^{-9}
HPLC [28]	2.60 x 10^{-9}
Voltammetry [29]	3.80 x 10^{-7}
Potentiometry (current study)	2.40 x 10^{-7}

Phenol standard curves with the correct standard concentration or activity are quite difficult to make, so 0.1 M KCl was added to the solution as a supporting electrolyte. The addition of 0.1 M KCl was good in stabilizing the potential, so as to obtain a better regression value with better sensitivity. The supporting electrolyte solutions used should not react with analytes or interfere with the measurements, but can improve the performance of electrodes. The ionic strength regulating agent will have a constant ionic strength value if the solution is concentrated. Based on Figure 3, the sensitivity of the electrode is known to be much better with the addition of 0.1 M KCl.

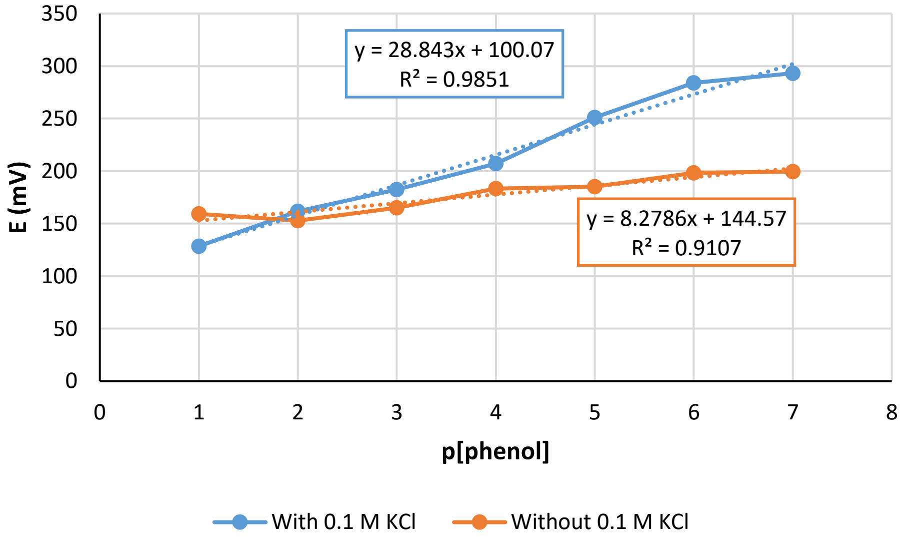

Figure 3. Effect of supporting electrolyte

3.3. Accuracy

The percentage relative error (% Er) is used as a parameter in determining the accuracy of a method. To obtain the value of % Er, the value of the concentration obtained was necessary by substituting the measured potential electrode into the linear regression equation of the standard curve. Errors in measurement were caused by several factors, including sampling error, method error, instrumental error, and personal error [30-31].

Table 3. Percentage relative error of phenol with MIPs-modified carbon paste electrode

Concentration (M)	E (mV)	%Er
10^{-7}	293	3.01
10^{-6}	284	1.42
10^{-5}	251	1.58
10^{-4}	207	2.96
10^{-3}	182	2.41
10^{-2}	161	1.72
10^{-1}	128	2.03

The magnitude of a method's relative error depends on the measurement accuracy of the signal. Based on Table 3, the % Er values obtained are known to range from 1% to 3%. Harvey [27] pointed out that if an experimental result is within 1% of the correct result, then the analytical method will be highly accurate. Methods resulting in relative errors between 1% and 5% are moderately accurate, but lowly accurate methods produce relative errors greater than 5%. Therefore, it can be said that the determination of phenol content with this method is quite accurate.

3.4. Precision

Precision is the closeness between the analysis result values on the same analyte. When a sample is analyzed multiple times, the individual results are rarely the same. The closer the agreement between the individual analyses, the more precise the results will be. Precision is determined by knowing the coefficient of variation, which is a percentage of the relative standard deviation (RSD) [30]. Measurements were made using the same solution three times of measurements at each concentration. The calculated data can be seen in Table 4. The reproducibility criteria for assay components are within < 2% [32-33]. Based on the data in Table 4 below, it is known that the coefficient of variation value of this potentiometric method is very good because it is within the allowable range.

Table 4. The value of standard deviation and coefficient of variation

Concentration (M)	E (mV)	Standard deviation	Coefficient of variation
10^{-5}	162	1.35	0.83
10^{-4}	119	1.30	1.09
10^{-3}	95	2.05	2.15

3.5. Selectivity

MIPs-modified carbon paste electrodes should respond specifically to molecules, but sometimes they can respond to other molecules in the solution. This may occur if the molecules are physically or chemically similar to the compound being measured. The presence of other components besides the analyte in the sample can affect the measured potential. A selectivity test was performed to determine the electrode's ability to provide a specific response to the analyte, which was expressed in terms of potentiometric selectivity coefficients ($K_{A.B}^{pot}$) [34] and evaluated by the MPM (Matched Potential Method) that has been recommended by IUPAC [35].

This method is widely applied because it has several advantages, such as not being influenced by changes in the potential of the two solutions because possible changes in the interfering solution will be measured. In addition, this method can also be applied to the solution that does not obtain the Nernst factor [36-37]. One of the industrial wastes containing large amounts of phenol is medical waste. In this study, the selection of these interfering compounds was based on the amount of the compound in drugs, so there is a possibility that these compounds will mix with phenol, especially in wastewater.

Table 5. Potentiometric selectivity coefficient values

Interfering	$\mathbf{K_{A.B}^{pot}}$
KCl	0.03
$CaCl_2$	0.18
$ZnSO_4$	0.18
$MgSO_4$	0.01
NaCl	0.25

The selectivity coefficient, $K_{A.B}^{pot}$, was obtained by comparing the activity ratio of the primary compound (A) with that of the interfering compound (B) [9]. The value of $K_{A.B}^{pot}$ can be grouped into 3 categories. If $K_{A.B}^{pot} = 0$, then other compounds will not interfere. When $K_{A.B}^{pot} < 1$, the electrode is selective against compound A compared to compound B. If $K_{A.B}^{pot} > 1$, then the electrode has a higher selectivity for compound B than compound A [38]. From the measurement, the selectivity coefficients are known to be less than 1. This result confirms that these compounds do not interfere with the detection of phenol. Therefore, this MIPs-modified potentiometric sensor can be used for the analysis of phenol even though there is a disturbing compound in the sample.

3.6. Comparison method

Phenol was also measured by UV-Vis spectrophotometry as a comparison with the potentiometric method. The percent recovery in Table 6 provides information that those two methods are not much different. Furthermore, statistical tests can also be performed to compare both methods [31].

Table 6. Percent recovery of 10^{-3}M phenol

Methods	**% Recovery**		
	Sample 1	**Sample 2**	**Sample3**
Potentiometry	85,82	109,94	116,72
Spectrophotometry UV-Vis	98,61	102,42	97,45

To begin with, the study must determine whether the variances of the two analyses are significantly different. The critical value for F (0.05, 2, 2) is 39.00. Since Fexp is 44.10, which is greater than F (0.05, 2, 2), the null hypothesis (H_0: $s_A^2 = s_B^2$) is rejected, while the alternative hypothesis (H_A: $s_A^2 \neq s_B^2$), in which the variances are significantly different, is accepted.

The mean values obtained by the two analysts were compared using a two-tailed *t*-test. The null and alternative hypotheses are: H_0: $\overline{X_A} = \overline{X_B}$ H_A: $\overline{X_A} \neq \overline{X_B}$

The critical value for t (0.05, 5) is 4.30. Since the calculated value of t is 1.12, which is less than t (0.05, 5), the null hypothesis is retained, and there is no evidence that the two sets of phenols are significantly different at the chosen significance level.

4. CONCLUSIONS

This MIPs-based potentiometric sensor electrode has a wide measurement range, a small detection limit, and a fast response time. Its accuracy, precision and selectivity prove that this electrode can detect more specific samples with good sensitivity and reproducibility. It is also not significantly different when compared with the UV-Vis spectrophotometric method.

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