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Production of Working Electrodes Graphene Oxide For Phenol Analysis Voltammetrically

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***Abstract*—The working electrode in the voltammetry method is an electrode that responds to the current generated in a redox reaction. The working Electrode to response currents through the process of migration, convection and diffusion. Working electrodes can be made according to the needs for qualitative and quantitative analysis. Graphen oxide as working electrodes have been made, as phenol sensor samples, graphen oxide has been made by hammer methods. Graphen oxide working electrodes are characterized using IR, XRD, SEM. The copper wire cable as electrode body is made a 15 cm long 2mm diameter filled with 0.001mg graphen oxide which is then compacted until smooth. Graphene oxide electrodes have been used for the measurement of phenol by voltammetry compared to HPLC. Measurements applied to the concentration of 10 ppm phenol samples obtained by voltammetry recovery were obtained 97.4% and HPLC obtained 97.6%.**

Keywords—voltammetry, graphen oxide, phenol

I. INTRODUCTION

The voltammetry is a chemical electroanalysis method based on the reading of an electric current and potential changes. The plot of the change in potential and the resulting current is called a voltammogram. The generated voltammogram provides characteristic information for the analyzed sample both qualitatively and quantitatively. Qualitatively it can be seen from the oxidation and reduction potential which can be related to the standard oxidation reduction (E^0) of a compound, while quantitatively it can be seen from the current produced, the size of the current generated is directly proportional to the concentration of the sample (I = k [S]).

In the voltammetry method, there are three electrodes, namely the reference electrode (RE), auxiliary electrode (AE) and working electrode (WE). The reference electrode RE in the measurement means that the measured potential is a result relative to the reference electrode, usually Ag / AgCl. Auxiliary electrodes are electrodes that maintain the measured current is a voltaic current meaning the current produced is a redox reaction current, in other words the electrode which maintains the redox reaction during measurements is usually Pt. The working electrode is the electrode which responds to the sample according to its concentration, the working electrode is made as needed depending on the sample being analyzed. Organic samples usually use carbon paste electrodes, graphen oxide, whereas for inorganic samples usually use metal electrodes (Pt, Au).

The working of electrodes process responding to samples there are several ways including. Migration is the ion in the solution moves towards the electrode because of the electrostatic force from the electrode. Convection is the ion moves to the electrode due to mechanical processes in the solution such as stirring or flow. Diffusion is the ion moves to the electrode due to differences in the concentration of the surface of the electrode and the body of the solution. Briefly the movement of ions can be seen in the following figure.

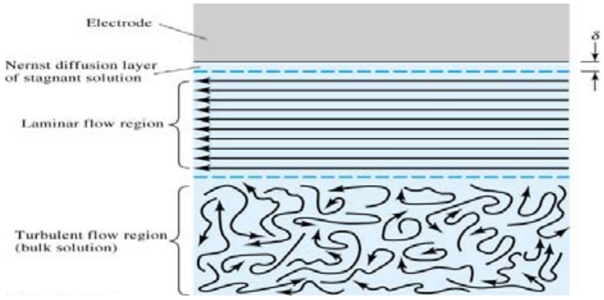

Fig. 1. The electrode process responds to the sample

The working electrode process responds to the sample read in the form of a current and is directly proportional to the concentration. The mass flux to the electrode is mathematically described by the Nernst-Planck equation for one dimension:

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x} - \frac{zFDC}{RT}\frac{\partial \phi(x,t)}{\partial x} + C(x,t)\ \ V(x,t) \qquad (1)$$

Mass flux (J) is directly proportional to the electric current generated

$$i = -nFAJ \qquad (2)$$

Based on Fick's law to I the speed of diffusion in this case flux is directly proportional to the concentration gradient.

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x}$$

Substitution Equation (3) into Equation (2)

$$i = nFAD\frac{\partial C(x,t)}{\partial x}$$

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The current and potential relationship caused by the mass transfer of a chemical reaction can be derived from the electron transfer caused by a reduction reaction.

$$O + ne^- \rightleftharpoons R$$

The reaction of the product formation in the form of reduction (R) is a reaction order I so that

the reaction speed

$$V_f = k_f \, C_O(0,t)$$

The speed of the reverse direction reaction is also the reaction order to I

$$V_b = k_b \, C_R(0,t)$$

With kf and kb the reaction speed constants depend on the potential applied following the following equation:

$$k_f = k^0 e^{-\frac{\alpha nF(E-E^0)}{RT}} \qquad (5)$$

$$k_b = k^0 e^{\frac{(1-\alpha)nF(E-E^0)}{RT}} \qquad (6)$$

k0 heterogeneous standard speed constants and α transfer coefficients. Positive and negative potential corresponds to the speed of oxidation and reduction, so the overall potential in a redox reaction is:

$$V_{net} = V_f - V_b = k_f C_0(0,t) - k_b C_R(0,t) \qquad (7)$$

The resulting current corresponds to Vf and Vb

$$i_f = nFAV_f$$

$$i_b = nFAV_b$$

Likewise the total current generated in the reaction

$$i_{net} = i_f - i_b = nFA[k_f C_0(0,t) - k_b C_R(0,t)] \qquad (8)$$

Substitution Equation (5), (6) into Equation (8)

$$i = nFAk^0 \left\{ C_O(0,t)\, e^{-\frac{\alpha nF(E-E^0)}{RT}} - C_R(0,t)\, e^{\frac{(1-\alpha)nF(E-E^0)}{RT}} \right\}$$

(9)

From Equation (9) we see the relationship between currents and potential for redox reactions. Equation (9) is known as the Butler-Volmer equation. If the reaction reaches an equilibrium where in, i = 0 then the equation becomes

$$0 = nFAk^0 \left\{ C_O(0,t)\, e^{-\frac{\alpha nF(E_{eq}-E^0)}{RT}} - C_R(0,t)\, e^{\frac{(1-\alpha)nF(E_{eq}-E^0)}{RT}} \right\}$$

(10)

Equation (10) can be arranged into

$$\frac{C_O(0,t)}{C_R(0,t)} = e^{\frac{nF(E_{eq}-E^0)}{RT}}$$

(11)

Equation (11) can be written which is a potential response by the working electrode in a redox reaction.

$$E_{eq} = E^0 + \frac{RT}{nF} \ln \frac{C_O(0,t)}{C_R(0,t)}$$

(12)

The current generated follows equation (4)

$$i = n\ F\ D\ A\ \frac{\partial c}{\partial x}$$

n: number of electrons involved in the reaction
F: faraday number (96500 C / eq)
A: electrode surface area (cm^2)
D: diffuse coefficient (cm^2/ sec)
∂C / ∂x: concentration gradient between the surface of the electrode and the body of the solution

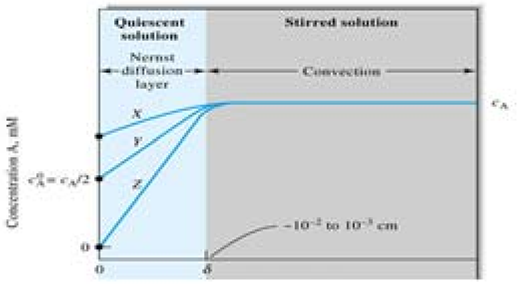

Fig. 2. Gradient concentration (∂C / ∂x) between the surface of the electrode and the body of the solution

$\frac{dc_A}{dx} = \frac{c_A - c_A^0}{\delta}$ so equation (4) can be written

$$i = nFDA\frac{c_A - c_A^0}{\delta} \qquad (13)$$

if $k_A = \frac{nFDA}{\delta}$ then equation (4) can be simplified to be

$$i = k_A(C_A - C_A^0) \qquad (14)$$

Equation (14) is the current measured on the surface of the electrode from the oxidation form

$$i = k_{ox}([Ox] - [Ox]_0) \qquad (15)$$

Cathode diffusion current $i_{do} = k_{ox}[Ox]$ so that equation (15) can be written

$$i = i_{do} - k_{ox}[Ox]_0$$

$$k_{ox}[Ox]_0 = i_{do} - i$$

$$[Ox]_0 = \frac{i_{do} - i}{k_{ox}} \qquad (16)$$

Analogous to the oxidation form, the reduction form is related to the current

$$i = k_{red}([Red]_0 - [Red]) \qquad (17)$$

Because the reduction form in the body of the solution is very small [Red] ≪ $[Red]_0$ then equation (17) can be simplified $i = k_{red}\,[Red]_0$ so

$$[Red]_0 = \frac{i}{k_{red}} \qquad (18)$$

substitution equation (16), (18) into equation (12)

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]_o}{[Red]_o}$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{\frac{i_{do} - i}{k_{ox}}}{\frac{i}{k_{red}}} \qquad (19)$$

Equation (19) can be arranged into

$$E = E^0 + \frac{RT}{nF} ln \frac{k_{red}}{k_{ox}} + \frac{RT}{nF} ln \frac{t_{da}-t}{t} \qquad (20)$$

If $t = \frac{t_{da}}{2}$ then $E = E_{\frac{1}{2}} = E^0 + \frac{RT}{nF} ln \frac{k_{red}}{k_{ox}}$ so that equation (20) can be written

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} ln \frac{t_{da}-t}{t} \qquad (21)$$

In the same way a potential relationship to the anode diffusion current can be written

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} ln \frac{t}{t_{da}-t} \qquad (22)$$

The equation is the basis for the calculation of the voltammetry method, while the working electrodes that have been made include graphen oxide working electrodes and their application for phenol analysis.

II. METHODOLOGY

A. Material

Zinc powder, potassium permanganate, hydrochloric acid 37% pa, hydrogen peroxide 30%, sulfuric acid 96% v /v pa, phosphoric acid 85% v / v pa, aquademineral water, ethanol 96% v / v pa, disodium hydrogen phosphate pa (Na2HPO4), sodium dihydrogen phosphate dehydration (NaH_2PO_4 • $2H_2O$), potassium chloride (Merck) and phenol.

B. Electrode Making

Faber-castel 2B graphite pencils and paraffin oil (Merck) were used to prepare carbon paste. Graphene oxide synthesis: Graphene oxide is made by the hummer method and characterized (FTIR, XRD and SEM). For the reduction of graphene oxide, a suspension in pure water (50 mg / 50 mL) was added 0.6 g of zinc powder with 20 mL of 37% hydrochloric acid. After stirring for 1 hour, the solution is cooled, then, centrifuged and the precipitate is washed with water and then dried at 60 ° C in the oven for 24 hours. as a 15 cm long electrode body 2 mm in diameter is filled with 0.001mg graphen oxide which is then compacted until smooth.

III. RESULTS AND DISCUSSION

Electrochemical phenol measurements with the voltammetry method were performed using 797 VA Computrace. The electrodes used are Ag /AgCl electrodes (KCl, Sat.) as comparison electrodes, platinum electrodes as auxiliary electrodes and graphene oxide electrodes as working electrodes. Graphen oxide electrodes are made by mixing graphen powder plus liquid paraffin by comparison (5: 5; 4: 6; 3: 7; 2,5: 7,5; 2: 8) then to determine the best electrode in response to 5 ppm phenol as for The resulting voltogram can be seen in the following figure:

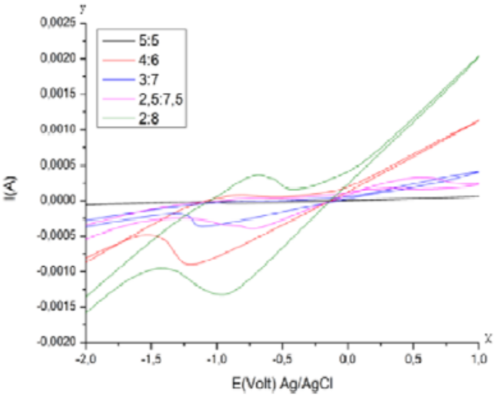

Fig. 3. 5 ppm phenol voltammogram with graphen oxide working electrodes relative to Ag / AgCl comparison electrodes.

Based on the results of a voltammogram, it can be seen that the ratio of 2: 8 is the best electrode with Ipa and Ipc respectively 0.0011614 A and -0.0013271, then the best deposition time and scan rate are determined.

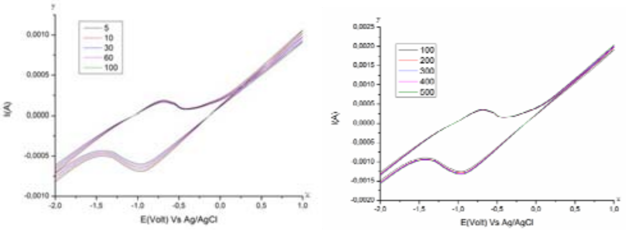

Fig. 4. (A. deposition time B. scan rate) of the 5ppm phenol relative Ag / AgCl electrode

Based on the voltammogram, the best deposition time is 5 seconds, Ipa 0,000189A (figure 4 A) and scan rate of 500 mV / second Ipa 0,000363 (figure 4B). The voltammogram for determining pH can be seen in the following figure:

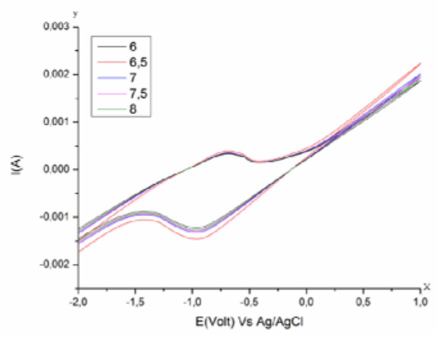

Fig. 5. 5ppm phenol voltammogram with pH variations

Based on the voltammogram it is seen that pH 6.5 gives the highest Ipa of 0,000399A. So that in the analysis of phenol samples used a deposition time of 5 seconds, a scan rate of 500mV /sec and a pH of 6.5. As for the application of phenol analysis, a series of standard phenol solutions (5,10,15, 20, 25) ppm are made with the following voltammogram results.

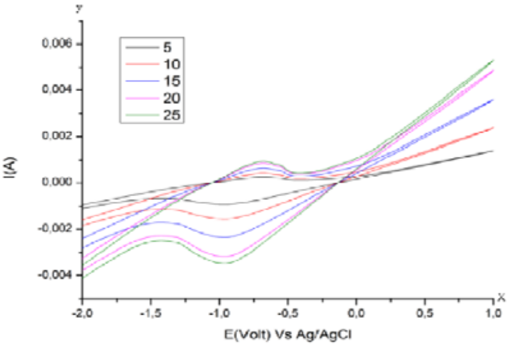

Fig. 6. Standard phenol voltammogram relative to Ag / AgCl electrodes

Based on the above voltammogram data can be taken between the concentrations and currents produced according to the following table:

TABLE 1. STANDAR PHENOL CONCENTRATION AND FLOW DATA

Fenol Concentration (ppm)	*Ipa (A)*
5	0,000251
10	0,000425
15	0,000647
20	0,000868
25	0,000984

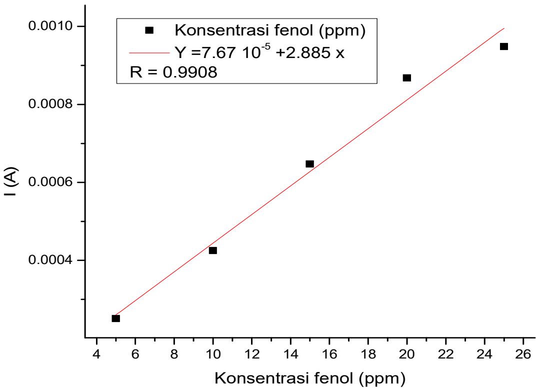

Fig. 7. Standard graph of phenol current versus concentrations

The measurement results using the voltammetry method with graphen oxide working electrodes compared with chromatographic measurements. The measurements using standard HPLC (Hewlet Packart) and phenol samples are the same as the developer of acetonitrile flow rate of 1mL / min, UV detector, column RP18, pressure 68 psi obtained data such as table 2.

TABLE II. VARIATIONS IN PHENOL CONCENTRATION AND PEAK AREA

Phenol concentration (ppm)	*Time of retention (menit)*	*Peak area (mAU)*
5	2,716	149.408
10	2,758	162.232
15	2,740	181.345
20	2,741	194.651
25	2,732	216.701

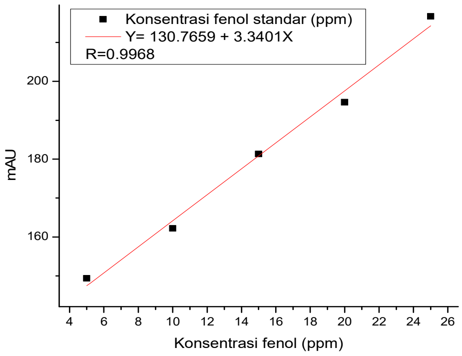

Fig. 8. Standard graph of phenol concentration versus peak area

Based on the standard graph in figure (7) Y = 7.67 10-5 + 2.88 10-6 x and figure (8) Y = 130, 76 + 3,3401 x will be compared to the results of the reconstruction of a 10 ppm sample concentration measured by voltammetry with graphen oxide electrodes compared with HPLC.

TABLE III. VALIDATION OF MEASUREMENT RESULTS WITH GRAPHEN OXIDE ELECTRODES BY VOLTAMMETRY COMPARED TO HPLC

Phenol contentration (ppm)	***Ipa (A)***	***Peak area (mAU)***	***Measurement concentration (ppm)***	***Recovery (%)***
10	0,000105		9,74	97,4
10		163,359	9,76	97,6

IV. CONCLUSION

Work electrodes can be made according to the needs of the analysis qualitatively and quantitatively. Grapen oxide working electrode application that has been made for phenol analysts then validated by HPLC obtained 97.4% and 97.6% recoferi respectively statistically it can be said that the oxide grapen electrode is valid for phenol measurement.

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