SYNTHESIS OF NANO-BENTONITE MODIFIED GRAPHENE OXIDE ELECTRODE FOR FORMALDEHYDE ANALYSIS BY CYCLIC VOLTAMMETRY

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Abstract

In this research, each graphene oxide and nano-bentonite was synthesized using the Improved Hummers method and the Sonochemical method for formaldehyde detection by cyclic voltammetry. Formaldehyde detection by cyclic voltammetry has several factors to accurately detect formaldehyde, such as electrode composition, the pH of the solution, the deposition time, and the scan rate. In this study, formaldehyde detection using nano-bentonite modified graphene oxide electrode has the optimum electrode composition in the ratio of graphene oxide: paraffin: nano-bentonite 3:2:5, pH of the optimum solution for detection of formaldehyde 4, 10-second deposition time and scan rate 100 mV/sec. Nano-bentonite modified graphene oxide electrode has a detection limit of up to 0.16856 ppm (0.005613 mM) with a recovery of 99.414%. This sensor was successfully applied for formaldehyde measurement in the actual sample and showed good selectivity, sensitivity, reproducibility, and precision.

Keywords: *cyclic voltammetry, formaldehyde, graphene oxide, nano-bentonite*

Introduction

Formaldehyde is a toxic and dangerous compound often used freely in food to extend the life of storage because it can kill bacteria, fungi, and even viruses. Some examples of products often contain formaldehyde, such as meatballs, tofu, wet noodles, and salted fish. Formaldehyde will accumulate in the body, and it can cause eye, nose, throat, and skin irritation at low concentrations. At high concentrations (large amounts of formaldehyde) can cause severe pain, vomiting, coma, and even death (Golden and Valentini, 2014).

Based on The Minister of Health Regulation of Indonesia Number 1168/MENKES/PER/X/1999, using formaldehyde as food additives are prohibited (Republik Indonesia, 1999). Many methods have been used to determine formaldehyde, such as high-performance liquid chromatography (HPLC) (Cui *et al.*, 2007), gas chromatography (GC), isotope dilution mass spectrometry (Prado *et al.*, 2008), fluorimetry (Zhang *et al.*, 2009), and spectrophotometry (McNary and Jackson, 2007). However, these methods require toxic reagents or are expensive and unsuitable for real-time measurements. Thus, operational development is needed to analyze formaldehyde using electrochemical techniques such as voltammetry.

Voltammetry measurements are usually carried out using three-electrode systems. The cell consists of the working, reference, and counter electrodes. The working electrode is the most important in voltammetry since it serves as the electrode at which the interest reaction occurs. The working electrode is the controlled parameter that causes the chemical species in the solution to be reduced or oxidized at its surface. One of

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the working electrodes that have high electron conductivity properties, fast electron transfer capability and a very large energy storage capacity is graphene oxide. Electrode with chemical modification can increase the rate of electron transfer on the electrode surface. The selection of an electrode modifier is very important because it can improve the performance of the working electrode.

This study uses nano-bentonite as a modifier of the graphene oxide electrode for formaldehyde analysis. Bentonite is a natural and predominantly montmorillonite clay with a high surface area, specific active sites and attractive adsorptive properties (Grim and Guven, 1978). Clay materials can play an important role as a parent host structure for inorganic and organic compounds owing to their intrinsic properties such as chemical and thermal stability, ion exchange and the presence on their interlayer surfaces of hydroxyl group active sites (Srinivasan, 2011).

This work aimed to develop a nano-bentonite modified graphene oxide electrode for formaldehyde analysis by cyclic voltammetry with a composition of graphene oxide: paraffin: nano-bentonite 3:2:5, 3:3:4, 3:4:3, 3:5:2, pH optimum 4, 10 s deposition time and scan rate 100 mV/s. Nano-bentonite modified graphene oxide electrode as a working electrode provides the best response in formaldehyde analysis by cyclic voltammetry. The sensor shows high sensitivity, selectivity, stable repeatability, and reproducibility. The nano-bentonite modified graphene oxide electrode has good detection limit for formaldehyde analysis and can be used commercially.

Research Methods

Materials

Formaldehyde, ethanol, H_2SO_4, H_3PO_4, H_2O_2, and HCl were of analytical grade from E. Merck. Germany. Zn powder, demineralized water, 5000 ppm KCl solution, $C_6H_8O_7$ powder, $Na_3C_6H_5O_7.2H_2O$ powder, and Na-bentonite.

Instrumentation

Glass beaker, voltammetry instrument type 797 VA Computrace, analytical balance, copper cable, sandpaper, magnetic stirrer, pH meter, oven, furnace, centrifuge Hettich EBA-20, and ultrasonic Elmasonic S from Department Analytical Chemistry of State University of Surabaya laboratories.

Procedure

1) Synthesis of graphene oxide

   Graphene oxide was produced using an improved Hummers method from graphite pencil. In this method, 1 g of graphite was added to sulfuric acid and phosphoric acid (volume ratio 9:1), which was mixed and stirred for 6 hours. Then, 6 g of potassium permanganate added slowly into the solution. This mixture was stirred for 18 hours. To eliminate the excess $KMnO_4$, 1 ml of hydrogen peroxide was dropped slowly and stirred for several minutes. The precipitate was washed with demineralized water, HCl and ethanol in a centrifuge at 4000 rpm for 20 minutes. Precipitate was dried in an oven for 24 hours at 70 °C.

   To get graphene oxide, 0.1 g graphite oxide was added into 100 ml demineralized water. The solution was sonicated in an ultrasonic bath for 2 hours. After 2 hours, a reduction process with 37% HCl and Zn. Then, the precipitate was washed with demineralized water repeatedly and dried in the oven at 100^oC for 24 hours.

2) Synthesis of nano-bentonite

   The first step is the purification of the clay mineral. 20 g of bentonite stirred in a beaker containing 500 mL of 2 M sulfuric acid for 6 hours. Let it for overnight. Then, the clay suspension was washed with hot demineralized water, and the precipitate was dried in the oven at 100 °C for 3 hours. To make nano-bentonite, 0.18 g of 300 mesh activated bentonite was added into ethyl alcohol (ethanol 98% assay). The suspension was ultrasonically irradiated for 2 hours. Then, dried at 60 °C for 30 min for alcohol removal and finally calcined for 4 hours at 800 °C.

3) Preparation of working electrodes

The nano-bentonite modified graphene oxide electrode was prepared by thoroughly mixing graphene oxide and nano-bentonite with paraffin oil and about 0.1 g in a ratio of graphene oxide:paraffin:nano-bentonite 3:2:5, 3:3:4, 3:4:3, 3:5:2. A portion of the graphene oxide and nano-bentonite paste was filled firmly into insulator pipe (0.5 cm), and the opposite of copper wire was peeled (1.5 cm) to stabilize an electrical contact. The surface of the nano-bentonite modified graphene oxide electrode was polished on sandpaper to obtain a smooth surface before use.

Results and Discussion

Composition of nano-bentonite modified graphene oxide electrode

The composition of nano-bentonite modified graphene oxide electrode was made with various variations in the ratio between graphene oxide, paraffin oil, and nano-bentonite to determine optimum electrode composition for formaldehyde analysis by cyclic voltammetry. Measurements were recorded in electrochemical cells with a solution composition of 50 ppm formaldehyde, 5000 ppm KCl, and citrate buffer pH 4 in potential -2V to 1 V at 10s deposition time and 100 mV/s scan rate. The measurement results of voltammetry are processed using *Origin Pro 8.5*, as shown in Figure 1. The anodic and cathodic peaks show the mechanism of formaldehyde oxidation and reduction process. A formaldehyde redox reaction is shown in Equation (1).

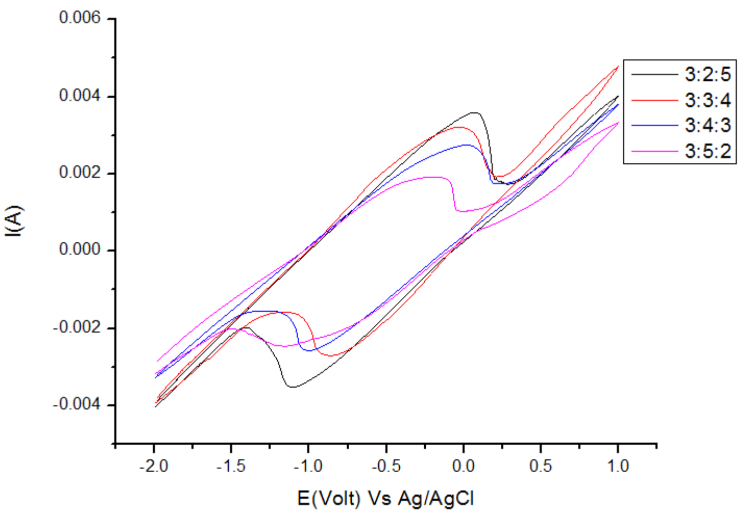

Figure 1. Cyclic voltammogram of 50 ppm formaldehyde using nano-betonite modified graphene oxide electrode at the different composition

$$HCOH\ (aq) + H_2O\ (aq) \leftrightarrow CO_2(g) + 4H^+ + 4e^- \quad (1)$$

As shown in Figure 1, the nano-bentonite modified graphene oxide electrode signal is increased with an increasing amount of nano-bentonite because a characteristic of a Graphene oxide and nano-bentonite are conductors while paraffin is an insulator. The presence of more nano-bentonite will result in more binding sites for formaldehyde cations on the electrode surface. Thus, a graphene oxide: paraffin: nano-bentonite electrode composition of 3:2:5 was selected as an optimal condition with Ipa value 0.00360295542 A and lowest Ipc value -0.00352249637. Ipa and Ipc values of different compositions are shown in Table 1

Table 1. Ip_a and Ip_c values of nano-bentonite modified graphene oxide electrode composition

Graphene Oxide:Paraffin:Nano-Bentonite	Ip_a (A)	Ip_c (A)
3:2:5	0.00360295542	-0.00352249637
3:3:4	0.00295387017	-0.00214949202
3:4:3	0.00275530132	-0.00255297533
3:5:2	0.00229624432	-0.00276777939

Calibration curve

Determination of formaldehyde concentrations in food samples was done using a standard calibration method using standard solutions of 10–50 ppm. Measurements were recorded with solution composition of 10-50 ppm formaldehyde, 5000 ppm KCl, and pH 4 of citrate buffers in potential -2 V to 1 V at 10 s deposition time and 100 mV/s scan rate. The measurement results of voltammetry are processed using *Origin Pro 8.5*, as shown in Figure 2.

Under all the optimized experiment conditions, the cathodic peak current obtained from cyclic voltammograms of formaldehyde on the nano-bentonite modified graphene oxide electrode was proportional to the formaldehyde concentration in concentration ranges of 10 to 50 ppm (Figure 2).

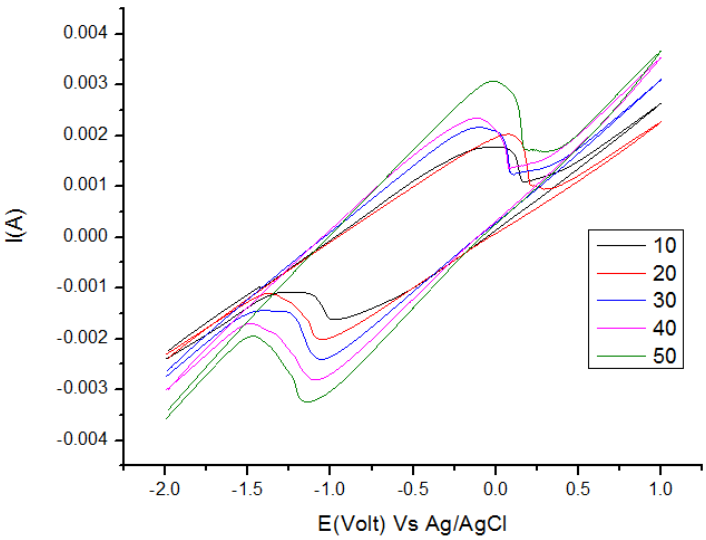

Figure 2. Voltammogram of formaldehyde 10–50 ppm in citrate buffer pH 4 with 10 s of deposition time and 100 mV/s of scan rate

Cyclic voltammograms were recorded for calibration graph construction on the nano-bentonite modified graphene oxide electrode under the optimum conditions described above using the standard calibration method presented in Figure 3.

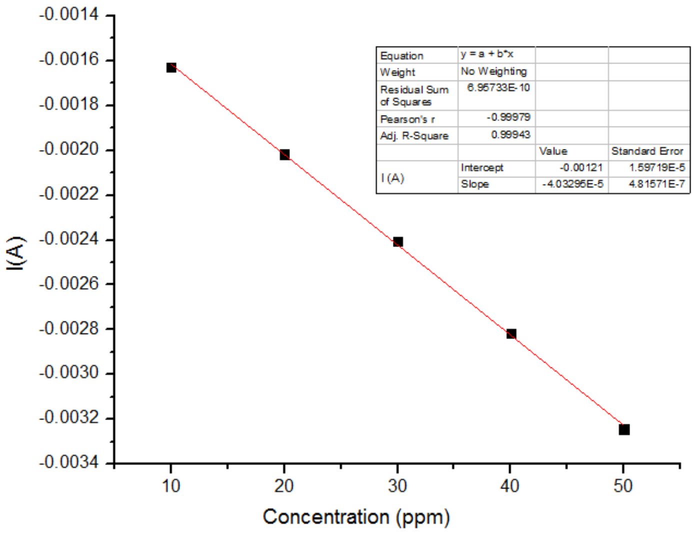

Figure 3. Graph of the relationship between formaldehyde 10–50 ppm with a cathodic peak current (Ip_c)

Recovery and limit detection

Recovery was performed to test the accuracy of formaldehyde identification using the nano-bentonite modified graphene oxide electrode. Recovery was processed to measure formaldehyde standard solution as computed in Equation (2). The results of recovery using nano-bentonite modified graphene oxide electrode with a ratio of 3:2:5 for formaldehyde analysis by cyclic voltammetry are shown in Table 2.

The result of formaldehyde analysis showed a very good recovery of 99.414%.

The calibration plots of cathodic peak current vs concentration increased linearly in the range of 10–50 ppm for formaldehyde. The linear regression equations are $y = (-4.03295 \times 10^{-5})\, x - 0.00121\ (R^2 = 0.99943)$. The analytical parameters are summarized in Table 3, where the limits of detection (LOD) were computed as Equation (3), where m is the slope of the calibration curves, and Sd is the standard deviation of three measurements of currents peak for the formaldehyde solution.

$$\text{Recovery (\%)} = \frac{\text{experimental concentration}}{\text{theoretical concentration}} \times 100\% \qquad (2)$$

Table 2. Recovery result of nano-bentonite modified graphene oxide electrode composition

Theoretical Concentration (ppm)	Experimental Concentration (ppm)	Recovery (%)
20	19.9696	99.848
30	29.6617	98.872
40	39.8099	99.524

$$\text{LOD} = \frac{3\ \text{Sd}}{\text{m}} \times 100\% \qquad (3)$$

The proposed method presented an excellent detection limit of 0.001658 ppm (0.005613 mM). Therefore, this sensor offers very low detection limit for quantifying formaldehyde. Also, the simplicity of the electrode preparation is the main advantage of this method for determining formaldehyde. The comparison of several parameters of formaldehyde at some working electrodes is listed in Table 3. It can be seen from the table that the detection limits obtained in this study are comparable with values reported by other research groups for the electrocatalytic oxidation of formaldehyde on the surface of chemically modified electrodes by other mediators.

Table 3. Comparison of some of the analytical parameters of the different working electrodes for formaldehyde determination

Electrode	Limit of Detection (mM)	Reference
Pd-graphene	3.15×10^{-6}	(Qiao *et al.*, 2013)
Novel ionic liquid/carbon nanotube paste electrode	9.5×10^{-4}	(Zarei *et al.*, 2018)
Nano-bentonite modified graphene oxide	5.613×10^{-3}	This research

Conclusions

In this study, the nano-bentonite modified graphene oxide electrode was used for the determination of formaldehyde. The cyclic voltammetry investigations showed effective electrocatalytic activity. High sensitivity and selectivity, a very low detection limit (0.16856 ppm or 0.005613 mM), and reproducibility of the voltammetric responses make the proposed modified electrode very useful for accurate determination of formaldehyde with recovery of 99.414%.

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