



REGULAR ARTICLE

Modification of the Gold Electrode with Nafion/WO₃ for Oxalate Ions Detection

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Gold electrode modification with nafion and WO₃ has been done for oxalate ion detection. The voltammogram of oxalate ion on the surface gold with and without modification showed a significant difference. This means that the modified gold electrode is sensitive to oxalate ions. The performance of the modified electrode in different pH (5, 7, and 12) in the KCl solution also has been studied using cyclic voltammetry. The range of the measurement is from -1.0 to +1.0 at a scan rate of 100 mV s⁻¹. The result showed that the optimum measurement pH is 12 with an anodic peak at 0.143 V and no reduction peak. The measurements of 0, 50, 100, 150, 200, and 250 mg L⁻¹ oxalic ion also have been conducted, showing a linear increase in current. The equation obtained is $y = 0.5426x + 0.9127$. In addition, the modified gold electrode showed good selectivity towards oxalate detection, as cyclic voltammetry measurements of some interference components did not produce redox peaks in the oxalate oxidation potential range. These findings indicate that gold electrodes modified with Nafion/WO₃ significantly affect the potential development of electrochemical oxalate sensors.

Keywords: Nafion, Modified electrode, Electrochemical sensor, Oxalate

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1. INTRODUCTION

Oxalic acid (OA) naturally exists in various plants, animals, and microorganisms. The number of OA that exceeds the threshold in the human body has an effect on human health. For example, OA can react with magnesium, potassium, and iron to form oxalate salts. Furthermore, oxalic acid can react with calcium from the blood to form calcium oxalate, which can lead to kidney stones or intrusion into the heart or nervous system [1, 2]. Considering the dangerous effects above, the US Department of Agriculture (USDA) recommends a certain limit of human OA daily intake [3].

One chemical that can combine with water to generate both soluble and insoluble salts is oxalate. Dietary oxalates are found in a variety of meals, however they are mostly found in plant-based foods [4]. It is important for several processes in plants, including calcium homeostasis, pH regulation, growth, development, and protection; photosynthesis; and heavy metal detoxification [5, 6]. Certain vegetables have extremely high oxalate content, including spinach, hard tofu, soymilk, potatoes, beets, raspberries, navy beans, almonds, and dates. Although there is no known maximum quantity of oxalate that can be found in the body, those following a low oxalate diet should keep their daily intake of oxalate to 40-50 mg [7].

Nafion has scientific interest since it is a biocompatible, ion-exchangeable, and discriminative polymer. In particular, Nafion's application as a membrane material is growing due to its exceptional resistance to chemical assault, even from potent oxidants at high temperatures [8]. Nafion is a perfluorinated sulfonated cation exchanger made composed of ethyl ether pendant groups with sulfonic cation exchange sites and a linear backbone of fluorocarbon chains. Nafion's facile production, superior electrical conductivity, and high partition coefficients of various redox chemicals have contributed to its growing popularity in recent years for the fabrication of modified electrodes [9]. Carbon paste electrodes (CPE), glassy carbon electrodes, carbon fiber microelectrodes, and mercury film electrodes have all been modified frequently using nafion [10]. In order to minimize interference with the analyte's diffusion to the electrode and to stop organic species' adsorption and desorption processes in biological fluids, a very thin layer of Nafion is sufficient [11].

Because electrochemical methods are among the most promising indispensable techniques to be developed, they surpass conventional methods for the determination of oxalic acid. These techniques include spectroscopy [12], chromatography [13], and enzymatic styles [14]. The advantages of electrochemical methods include simple instrumentation, fast procedure, good stability, and high

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perceptivity [15]. Even if a lot of electrochemical sensors have been created for OA discovery [16], it is still generally preferred to have a sensing platform with low preparation costs and excellent analytical performance, which includes high stability and high perceptivity [17]. The concentration of particular analytes in a sample can be described and measured using electrochemical sensors [18]. As a result, electrochemical sensors have drawn interest for many years because of their environmental safety, simplicity, and virtual perceptivity [19]. The sensor's surface can be altered using different materials to improve selectivity and strengthen the conductivity of the sensor to the analyte, producing a particular signal for a particular kind of molecule [20].

This study aims to construct a novel, stable, and sensitive electrochemical sensor based on gold nanoparticles, Nafion, and Wolfram, which will be used to determine oxalate. The electrochemical actions of oxalate at our modified electrode will be investigated using Cyclic Voltammetry (CV) techniques.

2. EXPERIMENTAL SECTION

2.1 Reagent and Standard Solutions

Nafion (5 wt.%) analytical grade was bought from Sigma-Aldrich (St. Louis, MO, USA) – Tungsten Trioksida composite material was synthesized in the Chemistry Department of Institut Teknologi Sepuluh Nopember, Surabaya Indonesia. The gold wire was purchased from local market. Buffer pH 12 was homemade by mixing potassium chloride (KCl) with potassium hydroxide (KOH). Ammonium chloride (NH_4Cl), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), Lead Nitrat ($\text{Pb}(\text{NO}_3)_2$) 1000 ppm and Zinc Nitrate ($\text{Zn}(\text{NO}_3)_2$) solution 1000 ppm were purchased from Merck. All dilution is using demineralized water.

2.2 Preparation of Modified Electrode

Gold wire 5 cm long and 1 mm in diameter was cleaned using acetone, ethanol and water, respectively. Then, once again, it was cleaned with demineralized water in the ultrasonic bath for 20 minutes. The gold electrode is ready for further modification. A mixed 5% Nafion and WO_3 with a ratio of 1:1 was prepared at the watch glass. The mixture obtained was coated at the end of the gold wire by adding a small amount of ethanol absolute to the mixture to make an appropriate paste. The uncoated wire was completely covered using a shrinkage cable. The final product was denoted as Au/Nafion/ WO_3 electrode.

2.3 Electrochemical Procedure

The electrochemical measurements were carried out using an Autolab Potentiostat/Galvanostat model PGSTAT 128 N and controlled with software NOVA 2.1.6. Three-electrode working systems were chosen with Au/Nafion/ WO_3 as the working electrode, Ag/AgCl in

saturated KCl solution as the reference electrode, and platinum wire as the counter electrode. To improve the electrochemical sensing properties of the modified gold electrode for oxalate measurements were carried out on a 100 mg L^{-1} oxalate standard solution in 0.1 buffer KCl pH 12 solution. Electrochemical measurements under cyclic voltammetry with a potential range of -1.0 V to $+1.0 \text{ V}$ and a scan rate of 100 mV s^{-1} . To investigate the selectivity of Au/Nafion/ WO_3 electrodes, cyclic voltammetry measurements were carried out on 100 mg L^{-1} standard solutions of $(\text{Pb}(\text{NO}_3)_2)$, $(\text{Zn}(\text{NO}_3)_2)$, ammonium chloride and ascorbic acid at a potential range of 0.1 to 1 V and a scan rate

3. RESULTS AND DISCUSSION

Electrochemical Study of Nafion/ WO_3 Modified Gold Electrode

The solution of with and without oxalic acid was measured using a Nafion/ WO_3 modified gold electrode by cyclic voltammetry at buffer KCl pH 12. The oxalic acid concentration was 100 mg/L at a potential range measurement from -0.1 V to $+1.0 \text{ V}$ with a sweep rate of 100 mV s^{-1} . The results show that the voltammogram response is significantly different (Fig. 1). The response of the solution with oxalic acid is a little bit higher than the solution without oxalic acid. It means that the Nafion/ WO_3 modified gold electrode has potency to be oxalic sensor.

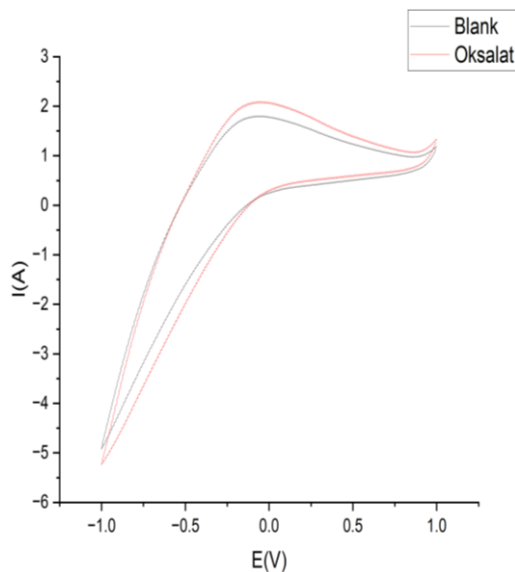


Fig. 1 – Voltammogram curves of 100 mg L^{-1} oxalic acid using Au/Nafion/ WO_3 modified electrode in a 0.1 M KCl buffer solution at pH = 12 with sweep rate of 100 mV s^{-1}

In this research, the effect of pH measurement on electrode performance was also studied (Fig. 2). pH greatly influences electrode performance because there are H^+ ions that can interfere with or accelerate the transfer of electrons at the oxidation-reduction process. The performance of the modified electrode depends on the pH conditions. We

evaluate the performance of the modified electrode at pH 5, 7 and 12. The optimum pH measurement was pH 12.

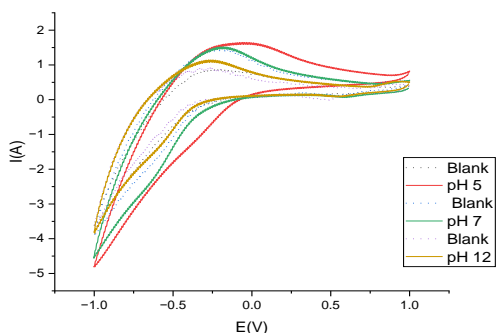


Fig. 2 – Voltammogram curves of 100 mg L⁻¹ oxalic acid using Au/Nafion/WO₃ modified electrode in a 0.1 M KCl buffer solution at various pH (5, 7 and 12) with sweep rate of 100 mV s⁻¹

Fig. 2 shows the cyclic voltammograms of oxalic acid on the Au/Nafion/WO₃ electrodes in various pH solutions. The pH 5 shows the highest increase in signal (high different current between with and without oxalic acid), but the electrode was severely damaged after one measurement. So we cannot use the electrode anymore, so we do not choose this pH condition. At pH 7, the voltammogram showed no significant difference between the blank and the oxalic acid measurement. It means the electrode is not sensitive to oxalic acid in this pH condition. But it is different when it sets the pH at 12. The voltammogram of oxalic acid and the blank is a significant difference. But the physical of the electrode remains stable. Thus, pH 12 was chosen as the optimum pH value for further measurement in this work. The potential oxidation peak is at 0.143 V with no reduction current.

The voltammogram of oxalic acid at various concentrations (50, 100, 150, 200 and 250 ppm) in a 0.1 M KCl at pH 12 with sweep rate of 100 mV s⁻¹ can be seen at Fig. 3.

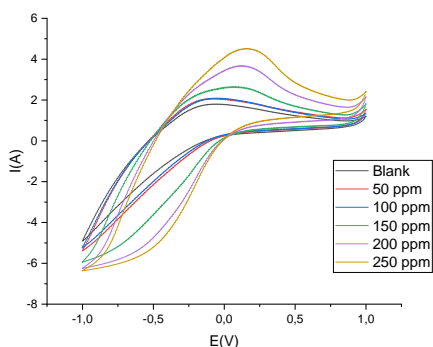


Fig. 3 – Voltammogram curves of oxalic acid using Au/Nafion/WO₃ modified electrode in a 0.1 M KCl buffer solution of pH 12 at various concentrations (50, 100, 150, 200 and 250) at a sweep rate of 100 mV s⁻¹

Fig 4 shows the calibration curve for oxalate acid in the range concentration of 50 ppm to 250 ppm, which was calculated from cyclic voltammogram calculation data.

The oxidation peak that appears at a potential of 0.143 V indicates that the gold electrode has a catalytic activity towards oxalate.

The regression gives linier equation $y = 0.5426x + 0.9127$ with *R*² value is *R*² = 0.8894.

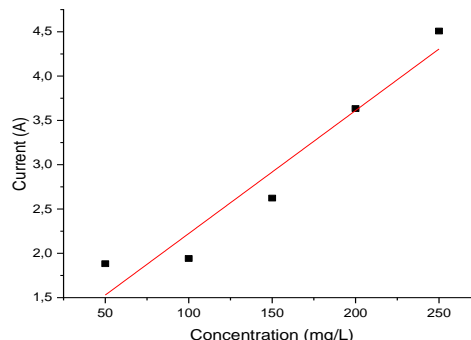


Fig. 4 – Calibration curve of oxalic acid in the range 50 – 250 ppm

Au/Nafion/WO₃ electrodes were studied in the presence of interferences such as ascorbic acid, Zn²⁺, Pb²⁺, and NH⁴⁺. The voltammogram is presented in Fig. 5. The result shows that the potential oxidation of oxalic acid is at different potential against the interferences. Thus, the proposed electrode Au/Nafion/WO₃ can be used as an electrochemical sensor which has excellent selectivity in oxalate detection.

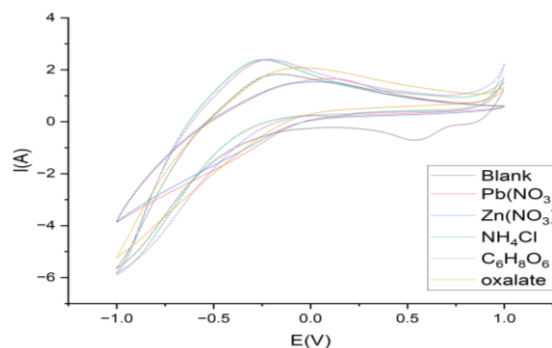


Fig. 5 – Voltammogram curves of 100 mg L⁻¹ oxalic acid using Au/Nafion/WO₃ modified electrode in a 0.1 M KCl buffer solution of pH 12 at various interferences with a sweep rate of 100 mV s⁻¹

4. CONCLUSION

In this work, the modification electrode Au/Nafion/WO₃ sensor was successfully carried out. The best selectivity was obtained when the measurement was performed in pH 12. The modified Au electrode using Nafion and WO₃ has better detection limits to detect oxalate ions. Nafion/WO₃ system is used as a new and veritable effective strategy to construct electrodes. The modified electrode has been shown to be effective for the electrocatalytic oxidation of oxalate. The results showed that the method was simple and sensitive enough for the determination of oxalate with good precision, accuracy, and selectivity.

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Модифікація золотого електрода з Nafion/WO₃ для виявлення оксалат-іонів

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Для виявлення оксалат-іонів була проведена модифікація золотого електрода за допомогою нафіону та WO₃. Вольтамперограма оксалат-іона на поверхні золота з модифікацією та без модифікації показала значну різницю. Це означає, що модифікований золотий електрод чутливий до іонів оксалату. Ефективність модифікованого електрода при різних значеннях pH (5, 7 і 12) у розчині KCl також була вивчена за допомогою циклічної вольтамперометрії. Діапазон вимірювань становить від -1,0 до +1,0 при швидкості сканування 100 мВ с⁻¹. Результат показав, що оптимальний pH вимірювання становить 12 з анодним піком при 0,143 В і без піку відновлення. Також були проведені вимірювання 0, 50, 100, 150, 200 і 250 мг л⁻¹ іонів щавлевої кислоти, що показало лінійне збільшення струму. Отримане рівняння $y = 0,5426x + 0,9127$. Крім того, модифікований золотий електрод продемонстрував хорошу селективність щодо виявлення оксалату, оскільки циклічні вольтамперометричні вимірювання деяких компонентів перешкод не дали окисно-відновних піків у діапазоні потенціалу окиснення оксалату. Ці висновки показують, що золоті електроди, модифіковані Nafion/WO₃, значно впливають на потенційну розробку електрохімічних оксалатних датчиків.

Ключові слова: Nafion, Модифікований електрод, Електрохімічний сенсор, Оксалат.