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Optimization of Supporting Electrolytes for Enhanced Cu^{2+} Detection Using Silver-Modified Pencil Lead Electrodes

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Abstract

Cu^{2+} metal ion is a type of essential heavy metal that is needed in small amounts by living things, but in large quantities is toxic so it is harmful to organisms and the environment. This study aims to detect Cu^{2+} metal ions using pencil lead electrode modified with a thin layer of silver (Ag/PLE) through cyclic voltammetry method with potential scan of -0.5 V to +0.8 V. The results showed that the Ag/PLE electrode gave a better response than the ordinary PLE electrode, with a peak current value of 0.647 mA in 0.1 M $HClO_4$ supporting solution with 1 cycle electrodeposition. This modification increased the surface area and catalytic activity of the electrode. These findings offer a sensitive, simple, and cost-effective method for Cu^{2+} ion detection, which can be applied to environmental analysis.

Keywords : Cu^{2+}, cyclic voltammetry, silver thin layer, pencil lead electrode

Introduction

The rapid development of modern industry has both positive and negative impacts, especially on the environment. Negative impacts are often caused by industrial waste disposal (Muraya et al., 2018). Poorly managed waste can become pollutants that are difficult for organisms to absorb. These pollutants can be both organic and inorganic components, including heavy metals that contribute to environmental pollution.

One of the most commonly found heavy metals is copper (Cu). Copper is an essential heavy metal, which although toxic in large quantities, copper is needed by the body in small amounts, as is iron (Fe). Cu metal pollution into the environment is mostly caused by industrial activities such as the paint industry as antifouling, insecticide industry, and fungicides (Darmono, 2005). This can cause contamination in organisms such as humans. Excessive exposure to Cu^{2+} can cause various health problems in humans, including heavy metal poisoning that results in liver, kidney, and nervous system damage. Therefore, the regulation of the Minister of Health of the Republic of Indonesia number 492/MENKES/PER/IV/2010 has established that the critical limit of

Copper (Cu) content in water is 0.2 mg/L and according to WHO the threshold of Cu content in blood is 0.8-1.2 mg/kg.

Based on this, Cu^{2+} metal ion testing needs to be done. One method that can be used is the electrochemical method. Many techniques have been developed to detect copper including Atomic Absorption Spectrometry (AAS), UV-Vis Spectroscopy, and High Performance Liquid Chromatography (HPLC). Although these methods have a very high level of sensitivity, these methods have disadvantages, namely relatively long analysis times, expensive instrument devices and complicated preparations (Zhang et al., 2018) so that they are considered less practical in practice. Based on this, other methods need to be developed to overcome this problem. The emergence of electrochemical sensor methods has shown a good response and is very promising for analytical approaches because it offers a method that is sensitive, simpler and requires cheaper equipment (Sari et al., 2021).

Electrochemistry is a method based on electron transfer that occurs on electrically conductive media called electrodes. This electrochemical method provides a good and promising response because it offers a method that is sensitive, simple, and requires cheaper equipment (Sari et al., 2021). One of the electrochemical sensor methods that is good at detecting heavy metals is cyclic voltammetry. Cyclic voltammetry is an electroanalytical method that has been widely used to obtain information about electrochemical reactions in solution (J. Wang, 2001). The working principle of the cyclic voltammetry technique is to measure the current during a potential scan from the initial potential to the final potential and back again to the initial potential so that the cathodic and anodic currents can be measured.

Cyclic voltammetry provides rapid information about the redox reactions that occur in the analyte (Annu et al., 2020). In this study, a carbon-based electrode is used, namely Pencil Lead Electrode (PLE) which has good stability, low toxicity, is cheap and easily available. To improve the performance of the PLE, modifications are made to the electrode surface using silver (Ag). This modification is done to reduce excess potential in the electron transmission process so that the selectivity and sensitivity of the electrode becomes better (Sharifi Pour et al., 2022). Previous research has been conducted on the use of modified PLEs such as in the detection of Cu^{2+} ions with

PPS/CnP modification (Cantalapiedra et al., 2015) and detection (Pb, Cd, and Zn) with ERGseO-Bi-film modification (Pokpas et al., 2014).

In this study, for the first time, Cu^{2+} metal ions were detected using a Pencil Lead Electrode (PLE) modified with a thin layer of silver using the cyclic voltammetry method. Modification of the PLE electrode was carried out by electrodeposition of silver on the electrode surface. The electrode was modified because this thin layer of silver can expand the electrode surface and can increase its catalytic activity. This research provides an easy, sensitive, cost-effective, and fast method.

Method

Tools and materials

The tools used in this research are beakers, micro pipettes, measuring flasks, magnetic stirrers, spray bottles, 10 mL vials, 100 mL reagent bottles, Teflon tubes, e-DAQ potentiostat model EA163, platinum (Pt) auxiliary electrodes, Ag/AgCl reference electrodes, and the working electrode used a 0.9 mm *kokuyo lead refill pencil* (PLE) modified with a thin layer of silver. The materials used in this study include $Cu(NO_3)_2.3H_2O$, $AgNO_3$, $K_3[Fe(CN)_6]$, KNO_3, HNO_3, $HClO_4$, CH_3COOH, CH_3COONa, NaH_2PO4, Na_2HPO_4, Whatman paper, and distilled water.

Preparation of Pencil Lead Electrode with modified silver thin layer (Ag/PLE)

Cyclic voltammetry is an analytical technique that provides rapid information in characterizing the reactions that occur on the surface of the working electrode (Wang, 2006). In this study, the preparation of PLE modified with a thin layer of silver was carried out by electrodeposition method in a solution containing 5 mM AgNO3 and 0.1 M KNO3, the electrode potential was applied ranging from +1 V to -1 V with a scan rate of 100 mV/s for one cycle. The electrode is presented as a pencil tip electrode modified with a thin layer of silver.

Electrochemical measurement of non-modified (PLE) and modified (Ag/PLE) electrodes with Cu^{2+} using cyclic voltammetry method

Electrochemical measurements of unmodified (PLE) and modified (Ag/PLE) electrodes were carried out using the analyte $Cu(NO_3)_2$. $3H_2O$ 1 mM in supporting electrolyte solution $HClO_4$ 0.1 M using cyclic voltammetry method with scan rate 100 mV/s and scan potential +0.8 V to -0.5 V for 1 cycle.

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Comparison of PLE and Ag/PLE electrodes with variation of supporting electrolytes

Determination of the optimum supporting electrolyte was carried out by varying the supporting electrolyte, namely $HClO_4$ 0.1 M, HNO_3 0.1, phosphate buffer pH 7, and acetate buffer pH 4 each in a 1 mM Cu^{2+} test solution by applying a scan rate of 100 mV/s and scan potential of +0.8 V to -0.5 V for one cycle.

Result and Analysis

Preparation of Pencil Lead Electrode with modified silver thin layer (Ag/PLE)

Modification of the PLE electrode surface using a thin layer of silver was carried out by electrodeposition of 5 mM $AgNO_3$ in 0.1 M KNO_3 on the electrode surface for 1 cycle. Modification of PLE with a thin layer of silver was carried out by electrodeposition (Afifah & Sari, 2024). The purpose of this modification was to increase the sensitivity of the electrode surface (Phal et al., 2021). The advantage of modification by electrodeposition is that the process is easy, low cost, and has the same properties as pure metal from hardness and corrosion resistance (Pinate et al., 2021).

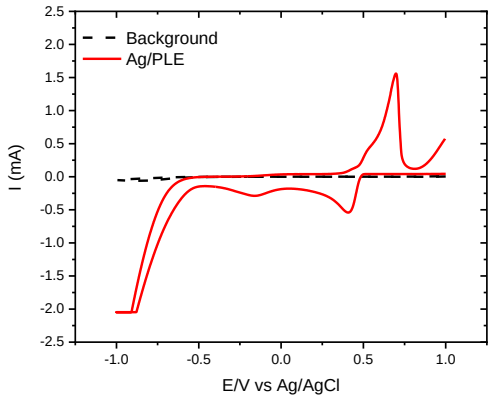

Figure 1. Cyclic voltammogram of modified PLE in 5 mM $AgNO_3$ and 0.1 M KNO_3 solution with scan rate of 100 mV/s

Reactions that occur in the Ag electrodeposition process:

Reduction : $Ag_{(aq)}^{+} + e^{-} \rightarrow Ag_{(s)}$

Oxidation : $Ag_{(s)} \rightarrow Ag_{(aq)} + e^{-}$

Based on the voltammogram above, the peak current (I_{pc}) and reduction potential (E_{pc}) measured are -0.5416 mA and 0.4080 V, while the oxidation peaks (I_{pa}) and (E_{pa}) are 1.5594 mA and 0.6980 V, respectively. These reduction and oxidation peaks

indicate the occurrence of a redox reaction process on the PLE surface, which confirmed the formation of a thin silver layer on the surface of the PLE working electrode. The cathodic peak results from the reduction of Ag^+ from the $AgNO_3$ solution to the electrode surface to Ag^0, which is then oxidized back to Ag^+ producing the anodic peak (Safavi et al., 2009). Thus, this working electrode can be referred to as silver thin layer modified PLE electrode (Ag/PLE).

Comparison of PLE and Ag/PLE response to Cu^{2+} Detection

Cyclic voltammetry analysis on $Cu(NO_3)_2$ test solution was measured by comparing PLE and Ag/PLE working electrodes in 0.1 M $HClO_4$ and 1 mM $Cu(NO_3)_2$ test solution with applied potential from 0.8 V to -0.5 V and scan rate of 100 mV/s.

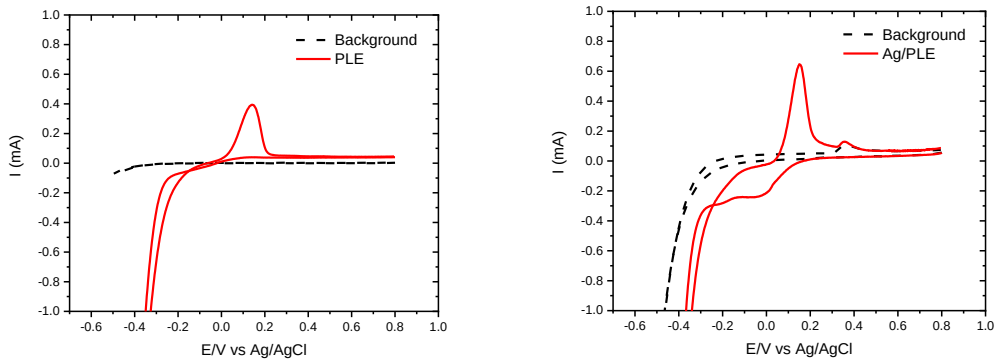

Figure 2. Cyclic voltammogram PLE (a) and Ag/PLE (b) of Cu^{2+} metal ion

The redox reaction that occurs at the electrode is :

$Cu(NO_3)_2 \rightarrow Cu^{2+} + 2NO^{3-}$

Reduction : $Cu^{2+} + e^- \rightarrow Cu$

Oxidation : $Cu \rightarrow Cu^{2+} + e^-$

Berdasarkan gambar voltamogram diatas elektroda PLE memiliki nilai arus (I_{pc}) dan potensial oksidasi (E_{pc}) yang terukur yaitu - 0.0865 mA dan – 0.1780 V, serta puncak oksidasi, I_{pa} dan E_{pa} adalah 0.2764 mA dan 0.1400 V. Sedangkan elektroda Ag/PLE memiliki nilai arus (I_{pc}) dan potensial oksidasi (E_{pc}) adalah - 0.242 mA dan – 0.0500 V, serta puncak oksidasi, I_{pa} dan E_{pa} adalah 0.647 mA dan 0.1500 V. The difference between the two electrodes gives a different current response. The Ag/PLE modified electrode provides a higher current response due to the larger surface area and electrocatalytic effect on the oxidation of Cu^{2+} metal ions (Pura et al., 2023).

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Effect of supporting electrolytes variation in Cu2+ ion detection

Cyclic voltammetry analysis on $Cu(NO_3)_2$ test solution was measured by comparing PLE and Ag/PLE working electrodes in 0.1 M $HClO_4$ and 1 mM $Cu(NO_3)_2$ test solution with applied potential from 0.8 V to -0.5 V and scan rate of 100 mV/s.

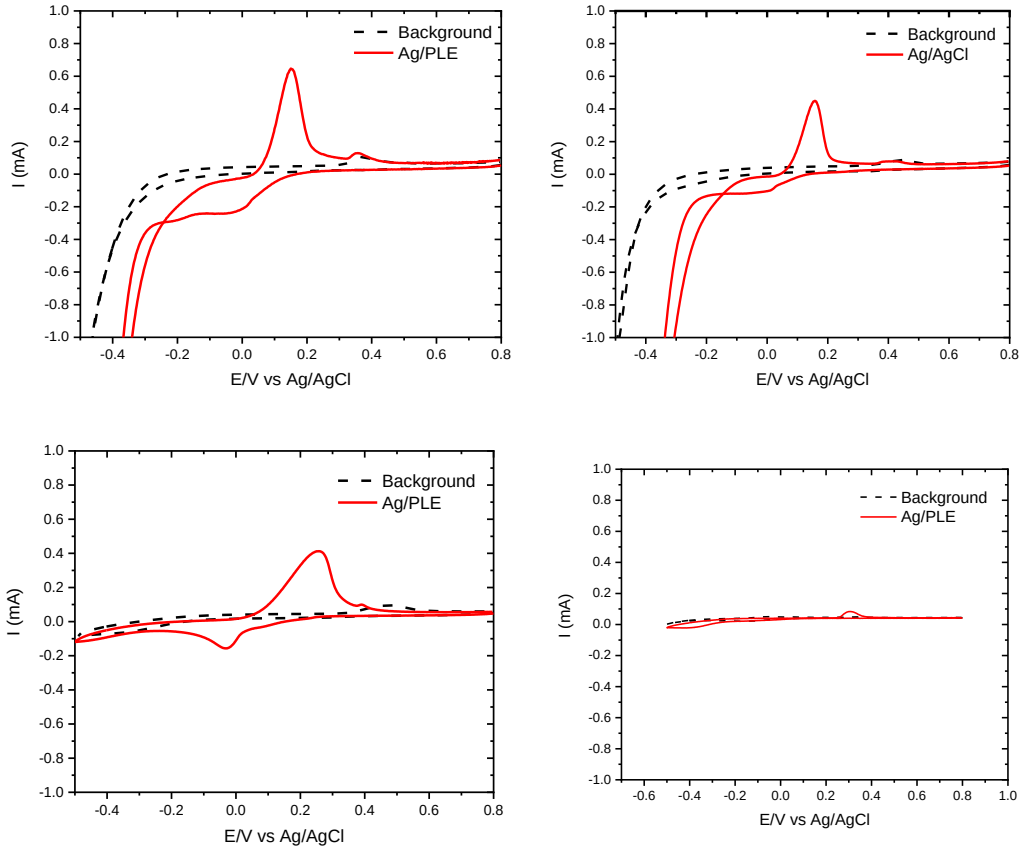

Figure 3. Cyclic voltammograms of Ag/PLE in various supporting electrolytes $HClO_4$ 0.1 M (a), HNO_3 0.1 M, (b) acetate buffer pH 4, (c) phosphate buffer pH 7 (d). Scan rate of 100 mV/s

Based on the voltammogram above, the optimum condition of Ag/PLE electrode in Cu2+ metal ion detection was obtained using 0.1 M HClO4 solution. The mobility ability of ions in conducting electric current affects the current response produced. HClO4 is a strong acid where it will be fully ionised into the solution. The higher the ability of the supporting electrolyte to ionise, the better its ability to conduct electric current (Angizi et al., 2023). Based on this, the most effective supporting electrolyte in the determination of Cu2+ ions is HClO4 0.1 M because it has the highest and strongest ionisation strength of 0.647 mA.

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In HNO3 the peak current produced is 0.450 mA, although it is a strong acid but it has a weaker acid strength than HClO4 so that the peak current produced is lower than HClO4 In acetate buffer the peak current produced is lower at 0.392 mA, this occurs because the complexing properties of acetate ions with metals play a role in reducing the peak of the voltammogram. Acetate can form a weak complex with Cu^{2+} ions, although this weak complex can reduce the availability of free ions to undergo reduction at the electrode. This results in lower current peaks compared to HClO4 and HNO3 (Yomthiangthae et al., 2020). In phosphate buffer, a good volamogram peak is not produced, this occurs because phosphate ions can interact with metal ions to form complex compounds, this is characterised by the formation of a precipitate in the solution. This can interfere with the measurement process so that a good current peak is not produced (Honeychurch, 2019).

Cycle electrodeposition variation in Cu^{2+} ion detection

Electrodeposition cycle variations were measured in test solutions of 1 mM $Cu(NO_3)_2$. $3H_2O$ and the optimum supporting electrolyte obtained which is $HClO_4$ 0.1 M with variations of 1 cycle, 3 cycles, 5 cycles, and 10 cycles using Ag/PLE electrodes with scan potential from 0.8 to -0.5 V and scan rate of 100 mV/s.

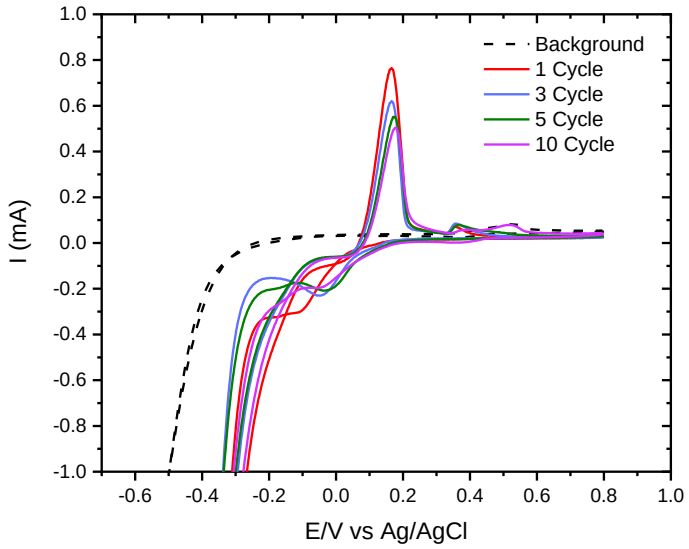

Figure 4. Cyclic voltammograms of Ag/PLE in various cycle electrodeposition 1 cycle (a), 3 cycle, (b) 5 cycle, (c) cycle (d). Scan rate of 100 mV/s

Based on the voltammogram image, it can be seen that the variation of 1 cycle electrodeposition gives the best results compared to other cycle variations, whereas the cycle of Ag electrodeposition increases on the surface of the PLE electrode, the peak current produced decreases. The 1 cycle electrodeposition variation results in a thin layer of silver on the PLE surface while the 3, 5, and 10 cycles cause the formation of a thicker silver layer as more cycles are applied to the electrode surface (Nguyen & Lee, 2017)

Conclution

This study shows that the modification of Pencil Lead Electrode (PLE) with a thin layer of silver significantly increases the selectivity and sensitivity of the electrode in detecting Cu^{2+} metal ions due to the electrocatalytic effect and larger surface area. This can increase the peak current with the peak current generated by PLE is 0.3947 mA and Ag/PLE is 0.6470 mA. The Ag/PLE electrode was tested based on the effect of supporting electrolyte variation and electrodeposition cycle which showed optimum results in cyclic voltammetry measurement of Cu^{2+} in 0.1 M $HClO_4$ supporting electrolyte solution with 1 electrodeposition cycle. This method offers a more rapid, sensitive, and economical approach compared to other analytical techniques that are more complex and expensive. The invention has potential application in environmental monitoring for heavy metal detection.

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