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Model of Corncob Biochar Modified Carbon Paste Electrode for Nitrite Detection

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The ability of corncob biochar as a modifier of carbon paste electrodes for nitrite sensing was investigated and compared to unmodified carbon paste electrodes. Nitrite standard solutions in 0.1 M phosphate buffer solution (pH 7.0) were measured using cyclic voltammetry with a potential range of 0.1 to 1 V and a scan rate of 100 mV s^{-1}. The corncob biochar-modified carbon paste electrode provided better performance than the unmodified electrode, with an anodic peak of 20 mg L^{-1} nitrite appearing at a potential of 0.84 V, indicating nitrite oxidation. In contrast, the unmodified carbon paste electrode did not show any significant peak. To confirm that the observed peak is indeed the anodic peak of nitrite, we conducted measurements at different nitrite concentrations of 0, 20, and 50 mg L^{-1}. In the absence of nitrite, no significant peak was observed. However, in nitrite solutions, the anodic peak increased with higher concentrations of nitrite. Additionally, the corncob biochar-modified carbon paste electrode demonstrated good selectivity for nitrite detection, as cyclic voltammetric measurements of some interference components did not produce redox peaks in the potential range of nitrite oxidation. These findings suggest that corncob biochar has significant potential for the development of electrochemical nitrite sensors.

Keywords: Corncob biochar, Modified electrode, Electrochemical sensor, Nitrite.

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1. INTRODUCTION

Biochar is a porous, carbon-rich material with unique chemical and physical properties, resulting from the pyrolysis of biomass [1]. The properties of biochar are influenced by the type of biomass (cellulose, hemicellulose, lignin) and pyrolysis conditions [2]. Corn cobs are agricultural waste produced from corn plants. About 164 million tons are produced globally per year, but they are underutilized and poorly managed, causing environmental pollution [3]. Corn cob contains 29.6 % cellulose, 37.9 % hemicellulose, and 18.5 % lignin [4]. Considering the properties and the enormous production per year, corncob has a huge potential as a feedstock of biochar production.

Biochar's unique properties in terms of large surface area, high porosity, surface charge, and elemental content are very beneficial in various fields, such as the remediation of polluted environments, soil amendments, wastewater treatment, and electrochemical sensor [5]. Biochar produces a lower environmental footprint than other synthetic carbon materials, thus making the exploitation of biochar in chemical sensors development more intensive [6], As a modifier of carbon paste electrodes (CPE), biochar exhibits excellent results in detecting organic and inorganic compounds [7]. In this work, we modified the carbon paste electrode because of its simple manufacturing, produces low noise and residual current, and carries out good reproducibility and selectivity [8]. Biochars obtained from castor oil cake are used to modify CPE, it was applied for Pb^{2+} and Cd^{2+} determination under differential pulse adsorptive stripping voltammetry conditions resulting in a low limit of detection of 6.9×10^{-8} mol L^{-1} and 9.8×10^{-9} mol L^{-1} were found for Cd^{2+} and Pb^{2+}, respectively [9]. Another report shows, biochar modified CPE is better than unmodified CPE, resulting in a wide linear range from 1.0 to 3000 μmol L^{-1}, good repeatability and reproducibility, high sensitivity (11.06 μA L $mmol^{-1}$), and low limit of detection (30.9 nmol L^{-1}) of caffein acid [10].

The corncob biochar-modified carbon paste electrode (CPE/CB) performance was investigated in nitrite detection under cyclic voltammetry measurement. Nitrite is a pollutant that is harmful to the environment and highly toxic to humans [11]. WHO has set a maximum limit of 3 mg L^{-1} of nitrite in drinking water which is also included in the list of carcinogenic compounds. The European Union Scientific Committee on Food has set an acceptable daily intake of 0.06 mg kg^{-1} of nitrite for humans. Although it has marvelous sensitivity with detection limit up to 0.67 nM [12] and good selectivity, the existing methods used in determining nitrite content are considered quite difficult and expensive, such as, spectrophotometry [13], and fluorescence [12]. In addition, it is prone to errors that occur during sample preparation, and analysis [14]. Electrochemical methods are one of the most promising alternative methods to be developed because of the advantages of simple instrumentation, fast analysis, high sensitivity, and stability [15].

2. EXPERIMENTAL SECTION

2.1 Reagent and Standard Solutions

Corncob biochar was gathered from the Indonesian Instruments Standardization Testing Center for Agricultural Environment. Graphite powder (C) and paraffin oil were purchased from Merck. Phosphate

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buffer pH 7.0 was prepared from di-Sodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), sodium dihydrogen phosphate monohydrate ($NaH_2PO_4{\cdot}H_2O$) purchased from Merck, and demineralized water. Nitrite (NO_2) standard solution was prepared from sodium nitrite ($NaNO_2$) purchased from Merck and demineralized water. The ascorbic acid ($C_6H_8O_6$) standard solution was prepared from solid ascorbic acid (Merck) and demineralized water. Lead (Pb) and Iron (Fe) standard solutions were purchased from Merck.

2.2 Washing Procedure and Characterization of Corncob Biochar

Biochar was washed at the ratios of biochar mass to volume of demineralized water (ratio *S*/*L*; *w*/*v*; 1/10). The solid/liquid mixture was stirred with a magnetic stirrer for 2 hours. The washed biochar particles were separated through the Whatman filter paper grade 42. The washed biochar was oven-dried at 55 °C for 24 hours to remove water and then characterized using SEM/EDS [16].

2.3 Preparation of Carbon Paste Electrode

For comparison, an unmodified carbon paste electrode (CPE) was prepared by mixing graphite powder and paraffin oil in a ratio of 7:3 (w/w). The modified carbon paste electrode with corncob biochar (CPE/CB) was prepared using a proportion of 30.0 % (w/w) of paraffin oil, 43.0 % (w/w) of graphite powder, and 27 % (w/w) of corncob biochar. The carbon pastes were macerated with pistil and mortar until complete homogenization of the components. After this, it was packed in a glass tube ($\Phi_{int} = 3.9$ mm), and the electrical contact was established by a silver wire ($\Phi_{int} = 1.0$ mm). The surface renovation was made by hand-polishing on filter paper [17].

2.4 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 with CPE and CPE/CB as the working electrode, Ag/AgCl electrode in saturated KCl solution as the reference electrode, and platinum wire as the counter electrode was chosen. To find out how the effect of biochar as a CPE modifier, CPE and CPE/CB measurements were carried out on a 20 mg L^{-1} nitrite standard solution in 0.1 M phosphate buffer pH 7 solution. Electrochemical measurements under cyclic voltammetry with a potential range of 0.1 to 1 V and a scan rate of 100 mV s^{-1} [18]. To investigate the selectivity of CPE/CB electrodes, cyclic voltammetry measurements were carried out on 20 mg L^{-1} standard solutions of Pb, Fe, and ascorbic acid at a potential range of 0.1 to 1 V and a scan rate of 100 mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1 Characterization of Corncob Biochar

The role and performance of biochar in different applications mainly rely on its physicochemical properties. SEM image shows that corncob biochar has a very porous surface structure (Fig. 1A), there are macropores with a diameter of 6 to 10 μm. The EDS spectrum showed that the highest biochar content is carbon (C) with 49.09 % weight. The other components are 31.90 % of oxygen (O), 6.41 % of silica (Si), 3.75 % of potassium (K), and some minor components.

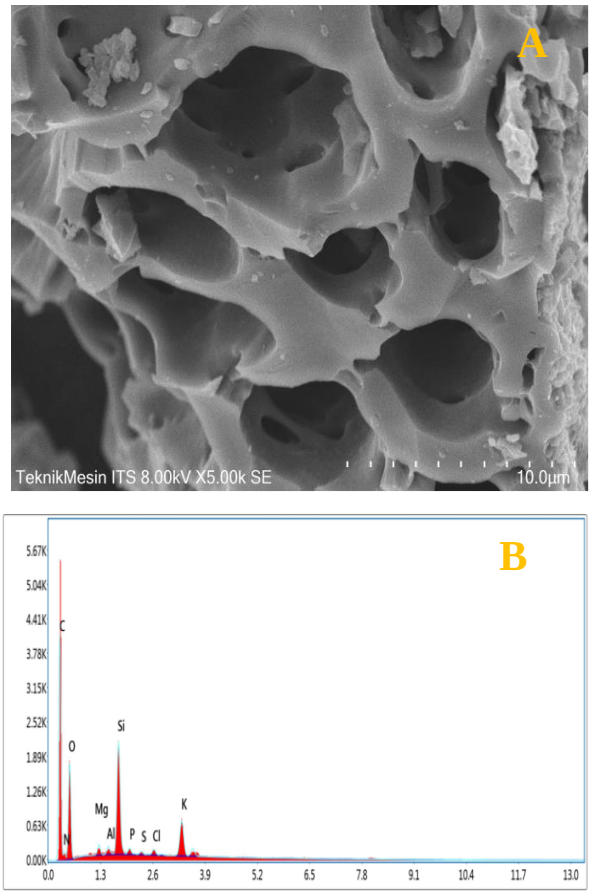

Fig. 1 – (A) SEM Image of corncob biochar (B) EDS spectrum of corncob biochar

3.2 Electrochemical Study of Corncob Biochar Modified CPE

Cyclic voltammetry measurements were carried out to verify the performance of corncob-modified carbon paste electrodes in nitrite censoring. CPE and CPE/CB electrodes were compared (Fig. 2A), and CPE did not show any significant current peak after measurement in standard nitrite solution at a potential range of 0.1 to 1 V indicating that electron transfer on the electrode surface is very slow. Meanwhile, the CPE/CB electrode showed an anodic peak at a potential of 0.84 V, which can be attributed to nitrite oxidation. This shows that biochar can induce an effective interaction between the electrode surface and nitrite ions, compared to unmodified CPE. Biochar has favorable properties for the detection of nitrite ions, such as the surface functional groups and cationic exchange capacity, which allows high adsorption of ions on its surface [19].

Fig. 2B shows the cyclic voltammograms of the CPE/CB in a solution without nitrites and the solutions containing 20 and 50 mg L^{-1} nitrite dissolved in 0.1M phosphate

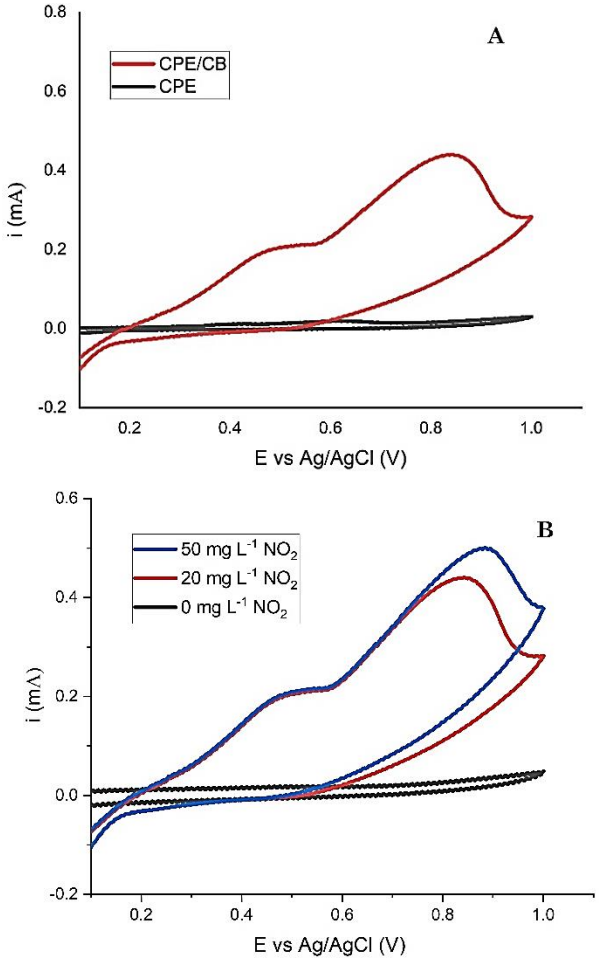

Fig. 2 – (A) CV curves of CPE and CPE/CB modified electrode in a 0.1 M phosphate buffer (PH = 7) solution containing 20 mg L^{-1} NO_2 at a scan rate of 100 mV s^{-1}, (B) CV Curve response of CPE/CB electrode in 0, 20 and 50 mg L^{-1} NO_2

buffer (pH = 7.0). The solution without nitrite did not show any significant current peaks. In a 20 mg L^{-1} nitrite solution, the anodic current (I_{pa}) was measured to be 0.44 mA at a potential of 0.84 V. When the nitrite concentration was raised to 50 mg L^{-1}, the I_{pa} increased to 0.50 mA at a potential of 0.88 V which could be defined as the oxidation peak of nitrite, where nitrite (NO_2^-) is oxidized to nitrate (NO_3^-), the corresponding transformation is shown in Eq. (1). Another study using a different working electrode also showed that the nitrite oxidation peak was detected in the potential range of about 0.8 to 0.9 V [15, 20]. The presence of an anodic peak at a concentration of 50 mg L^{-1} indicates that CPE/CB can detect nitrite up to a concentration of 50 mg L^{-1}, while the Fluorescence method commonly used in nitrite detection exhibits a detection range of 0.5-20 mg L^{-1} [12].

$$NO_2^- + H_2O \rightarrow 2H^+ + NO_3^- + 2e^- \quad (1)$$

The selectivity of the developed CPE/CB sensor was investigated in the presence of some components such as ascorbic acid, Pb^{2+}, Fe^{2+}, and NO_3^- at a potential of 0.1 to 1 V. From the obtained cyclic voltammogram (Fig. 3), we can assume that these components did not interfere with the nitrite response, only nitrite shows the anodic peak at a potential range of 0.8 to 0.9 V. Thus, the proposed electrode CPE/CB can be used as an electrochemical sensor which has excellent selectivity in nitrite detection.

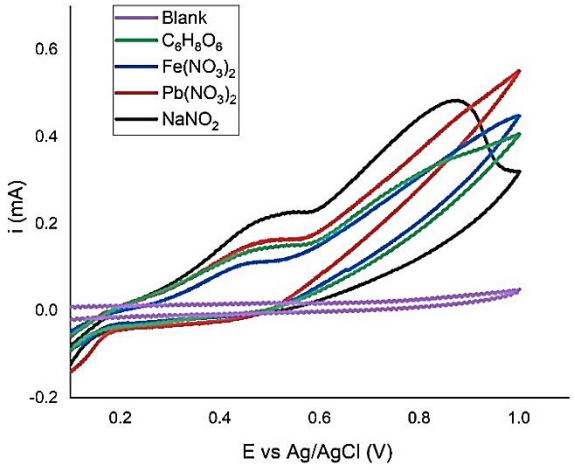

Fig. 3 – CV Curve of CPE/CB electrode in 20 mg L^{-1} of NO_2 solution and 20 mg L^{-1} of various interferences in 0.1 M phosphate buffer, pH 7.0, scan rate 100 mV s^{-1}

4. CONCLUSION

The performance test of the corncob biochar-modified carbon paste electrode has been carried out under cyclic voltammetry. The experimental results show that corncob biochar has a great ability to improve the performance of CPE. The modified electrode CPE/CB provides preferred results over the unmodified CPE in nitrite detection. The CPE/CB voltammogram shows an anodic peak at a potential range of 0.8 to 0.9 V, while CPE does not exhibit a significant current peak. CPE/CB also has good selectivity in nitrite detection, proved by measuring some interference components which give no redox peaks in the nitrite oxidation potential range. So, the CPE/CB electrode has enormous potential to be developed in nitrite electrochemical sensors, and further measurement is needed.

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Модель модифікованого вугільною пастою електрода з біовугілля для виявлення нітритів

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Досліджено здатність біовугілля кукурудзяного початку як модифікатора електродів із вугільної пасти для визначення нітриту та порівняно з немодифікованими електродами з вугільної пасти. Стандартні розчини нітриту в 0,1 М фосфатному буферному розчині (pH 7,0) вимірювали за допомогою циклічної вольтамперометрії з діапазоном потенціалів від 0,1 до 1 В і швидкістю сканування 100 мВ $с^{-1}$. Електрод забезпечив кращі характеристики, ніж немодифікований електрод з анодним піком 20 мг $л^{-1}$ нітриту при потенціалі 0,84 В, що вказує на окислення нітриту. Навпаки, електрод з немодифікованої вугільної пасти не показав жодного значного піку. Для підтвердження того, що спостережуваний пік справді є анодним піком нітриту, були проведені вимірювання при різних концентраціях нітриту 0, 20 і 50 мг/л. За відсутності нітриту істотного піку не спостерігалося. Однак у розчинах нітритів анодний пік зростає з більш високими концентраціями нітритів. Крім того, електрод з вугільної пасти, модифікований біовугіллям кукурудзяного початку, має хорошу селективність для виявлення нітритів, оскільки циклічні вольтамперометричні вимірювання деяких компонентів не дали окисно-відновних піків у потенційному діапазоні окислення нітритів. Зроблено висновок проте, що на основі біовугілля можуть бути розроблені електрохімічні датчики контролю нітритів.

Ключові слова: Біовугілля, Модифікований електрод, Електрохімічний сенсор, Нітрит.

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