Development of a Mercury Sensor using Voltammetry Techniques based on Waste Tire Carbon Electrodes Modified with Zinc Oxide Doped Ion Imprinted Polypyrrole (Pembangunan Penderia Merkuri menggunakan Teknik Voltammetri Berdasarkan Elektrod Karbon Tayar Sisa Diubah Suai dengan Zink Oksida Terdop Ion Polipirol Bercetak)

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ABSTRACT

Waste Tire Carbon (WTC) was chosen as the carbon source for fabricating the mercury sensor. Tires are inherently carbonrich (88%) and are considered elastomer blends. While WTC has been used as a sensor for mercury detection, the resulting sensitivity has been relatively low. Therefore, modifications to the working electrode are necessary to improve mercury detection. One such modification involves using nanoparticles, specifically zinc oxide (ZnO) doped with ion-imprinted polypyrrole (PPy). The modified WTC electrodes with ZnO and PPy were characterized using Fourier Transform Infrared (FT-IR) and Scanning Electron Microscopy (SEM). A 0.1 M KCl solution was used as the supporting electrolyte. The calibration curve was linear, with an R² of 0.9977, a concentration range of 0.01-8.00 ppm, a limit of detection (LoD) of 0.03 ppm, and a limit of quantification (LoQ) of 0.07 ppm, with %RSD below 2%. Selectivity tests were conducted to measure Hg²⁺ ions by adding the metal ions, namely Ag⁺ and Pb²⁺. The test results showed that the electrode had good selectivity, although there was a decrease in the peak current from 16 mA to 15,45 mA. These results indicate that the developed method is highly sensitive and selective to Hg concentrations.

Keywords: Electrode; mercury; polypyrrole; voltammetry; ZnO

ABSTRAK

Karbon Tayar Sisa (WTC) dipilih sebagai sumber karbon untuk fabrikasi elektrod kerja merkuri. Tayar sememangnya kaya dengan karbon (88%) dan dianggap sebagai campuran elastomer. Walaupun WTC telah digunakan sebagai penderia untuk pengesanan merkuri, sensitiviti yang terhasil adalah agak rendah. Oleh itu, pengubahsuaian pada elektrod kerja adalah perlu untuk meningkatkan pengesanan merkuri. Satu pengubahsuaian sedemikian melibatkan penggunaan zarah nano, khususnya zink oksida (ZnO) yang didopkan dengan polipirol bercetak ion (PPy). Elektrod WTC yang diubah suai dengan ZnO dan PPy telah dicirikan menggunakan Transformasi Fourier Inframerah (FT-IR) dan Mikroskopi Elektron Pengimbasan (SEM). Larutan KCl 0.1 M digunakan sebagai elektrolit penyokong. Keluk penentukuran adalah linear dengan nilai R² 0.9977, julat kepekatan 0.01-8.00 ppm, had pengesanan (LoD) 0.03 ppm dan had kuantifikasi (LoQ) 0.07 ppm dengan %RSD < 2%. Ujian selektiviti telah dijalankan untuk mengukur ion Hg²⁺ dengan menambahkan ion logam, iaitu Ag⁺ dan Pb²⁺. Keputusan ujian menunjukkan bahawa elektrod mempunyai selektiviti yang baik, walaupun terdapat penurunan arus puncak daripada 16 mA kepada 15.45 mA. Hasil ini menunjukkan bahawa kaedah yang dibangunkan mempunyai sensitiviti dan selektiviti terhadap kepekatan Hg. Keputusan ini menunjukkan bahawa kaedah yang dibangunkan adalah sangat sensitif dan selektiviti terhadap kepekatan Hg.

Kata kunci: Elektrod; merkuri; polipirol; voltammetri; ZnO

INTRODUCTION

Conductive polymers are widely utilized for various applications, including materials for various chemical sensors and biosensors (Bhattacharyya 2024). These polymers attract significant attention from researchers across different fields of science and technology due to their use in electrodes for energy storage (electrochemical batteries and capacitors), electric catalysts, biosensors, biofuel cells, and protective anti-corrosive gas separation membranes (Ramanavicius & Ramanavicius 2021). Conductive polymers can conduct electricity, for examples of conductive polymers include polyaniline (PANi), poly(3,4-ethylene dioxythiophene) (PEDOT), and polypyrrole (Ppy) (Ait-Touchente et al. 2020).

Polypyrrole has five heterocyclic rings and a significant number of positive nitrogen atoms (Li et al. 2020). It is a stable polymer, easy to synthesize, and has higher conductivity than other conductive polymers (Kausar 2021). Polypyrrole can be used for heavy metal ion absorption, corrosion resistance, and specific proton doping/dedoping. It has many positive nitrogen atoms and is widely used for heavy metal ion adsorption (Pang, Arsad & Ahmadipour 2020).

One of the applications of conductive organic polymers derived from polypyrrole is in chemical sensors. Examples include polypyrrole-lignosulfonate (LSN) composites and chitosan modified with quaternary ammonium salts (CQAS) for Pb detection, sulfonated β -cyclodextrin-polypyrrole composites for dopamine detection, Cu(OH)₂-polypyrrole composites for non-enzymatic glucose detection, multiwalled carbon nanotube (MWCNT) composites for Pb and Cd detection, graphene oxide (GO)-polypyrrole composites for amoxicillin detection, and polypyrrole-ZnO composites for mercury detection (Ait-Touchente et al. 2020).

Chemical sensors using polypyrrole are easy to design and flexible, they can be formed into thin films interacting with analytes to produce output signals during transduction (Ramanavičius, Ramanavičiene & Malinauskas 2006). Electrochemical sensors are excellent alternatives due to their compact size, low cost, and ease of operation (Xu, Dai & Jin 2020). Many standard sensors are made from inorganic materials (solid chemicals) with strong metal bonds, making them non-biodegradable and causing new environmental problems. Furthermore, the increasing use of chemicals in industrial processes results in more waste.

Industrial waste comes from using chemicals such as textile dyeing, electroplating, fertilizer production, pesticide manufacturing, paper production, and pharmaceuticals. These processes generate heavy metals that can pollute the environment, especially water bodies. Technological and industrial advancements have positive impacts but also adverse effects on living organisms. One negative impact of increased industrialization is the rise of wastewater containing heavy metal ions such as Cr, Cd, Pb, As, and mercury (Hg) (Jin et al. 2020).

Mercury is an inorganic pollutant that poses various health and ecosystem issues. It is commonly found in large quantities in the environment through waste disposal from thermal power plants, cement production, chloralkali factories, and incinerators (hazardous waste, medical waste, regular waste). Additionally, small-scale gold mining using mercury leads to higher mercury pollution due to human activities. Mercury is used to extract gold from ore as a stable amalgam, which is then heated to evaporate mercury and isolate gold. Therefore, the West Aceh District River was chosen as the real sample to test the Hg^{2+} sensor in this study as shown in Figure 1. As known in Aceh Barat Regency, many people conduct traditional gold amalgamation processes and then dispose of the amalgamation wash waste into the river (Munandar & Alamsyah 2016). Exposure to mercury ions, even at low doses, can cause severe central nervous system issues and damage vital human organs. The World Health Organization (WHO) limits mercury to 1 µg/L (Ait-Touchente et al. 2020). This, mercury pollution needs to be detected before causing adverse health effects.

Several methods can be used for mercury detection, including HPLC (Li et al. 2019), AAS (Koesmawati et al. 2023), and ICP-MS (Jung et al. 2022). These methods are accurate, fast, and highly sensitive for low-concentration analytes. However, they require expensive instruments and trained operators. Therefore, a more straightforward, cost-effective, fast, accurate, and precise method, such as voltammetry, is needed for mercury ion detection.

Voltammetric techniques have been investigated for the detection of several heavy metals, such as Cd²⁺ (Sampari et al. 2020), Cu²⁺ (Bayindir 2019), Pb²⁺ (Xu, Dai & Jin 2020), and Hg^{2+} (Ait-Touchente et al. 2020). Each of these studies discussed various sensor modifications. In voltammetry, there are three types of electrodes: working/ indicator electrodes (sensors), comparison electrodes, and auxiliary electrodes. The sensor can act as a cathode or anode, depending on the type of electrode reaction. Sensor materials significantly affect the analysis results of the voltammetric techniques (Cheng et al. 2018). Some types of sensors, such as platinum-based (Kondo et al. 2018) and diamond-based sensors (Bogdanowicz et al. 2020), exhibit good performance, but both sensors are relatively expensive. Carbon-based sensors are currently widely developed using voltammetric techniques because they have several advantages, including a wide potential range, low background current, low price, inertness, and suitability for various types of sensors.

Several previous studies have used various types of carbon electrodes to detect mercury in samples, such as carbon-screen-printed electrodes (C-SPEs) modified with gold particles (Some et al. 2016). This electrode can detect mercury up to a concentration of 1 μ g/L, but the C-SPE electrode has a very thin carbon layer, so care is required to keep the electrode surface undamaged during the modification process. Another study using graphite from

pencils pretreated with HNO₃ was able to detect mercury in saliva with a detection range of 5×10^{-9} to 1×10^{-7} (Kawde 2017). However, these electrodes have the major disadvantage of being fragile and thus, at risk of breaking during the measurement process. The weakness of the C-SPCE or pencil graphite indicates that other carbon sources may be considered.

Waste Tire Carbon (WTC) was recently chosen as a carbon source for electrode fabrication. Tires are rich in carbon (88%) and are considered elastomer blends. WTC was selected as a carbon source because it is easily obtained, eco-friendly, and underutilized. Baihaqi (2023) used WTC carbon electrodes for mercury sensors with cyclic voltammetry (CV), achieving a current of -0.0131 pA with a limit of detection (LoD) of 0.0681 ppm and a limit of quantitation (LoQ) of 0.229 ppm. The low current necessitated electrode modification. The electrode surface was modified using nanoparticles to form a nanostructured layer to improve the electrochemical sensor performance, including detection limits, sensitivity, and selectivity (Ait-Touchente et al. 2020). Zinc oxide (ZnO) was chosen as one such nanoparticle.

Ait-Touchente et al. (2020) combined the benefits of surface modification of gold electrodes with diazonium salts to grow ZnO nanorods with polypyrrole. This resulted in a limit of detection (LOD) of 1 pM, the lowest ever reported in the literature for gold electrode sensors, with a sensor sensitivity of $0.692 \pm 0.034 \,\mu\text{A.pM}^{-1}$.

This study will modify the surface of WTC electrodes with ZnO and ion-imprinted polypyrrole using L-cysteine as a chelating agent through an electropolymerization method, which has not been previously reported. L-cysteine was chosen as the chelating agent because of its high affinity for mercury ions. It contains -NH2, -COOH, and -SH functional groups, forming Hg-cysteine complexes Sistein (Ait-Touchente et al. 2020). The Hg sensor will be tested electrochemically to determine its specific capacitance using cyclic voltammetry (CV). The sensor's response to mercury and natural water samples will be tested using river water from Aceh Barat, Aceh Province. The results of mercury detection will be compared with measurements using Atomic Absorption Spectroscopy (AAS). Parameters to be tested include sensitivity, selectivity, limit of detection (LoD), limit of quantification (LoQ), water quality testing, and method comparison with a t-test (Siddiqui et al. 2019).

MATERIALS AND METHODS

The materials and samples used in this study include Liquified Petroleum Gas [(LPG) model: Mini Portable], aluminum foil (brand: Klinpak), copper wire (brand: Eterna), paraffin, 0.1 M KCl solution, pH 7 buffer, 0.1 M HNO₃ solution, pH 5.5 acetate buffer, standard mercury solution, zinc acetate dihydrate, NaOH, pyrrole, zinc nitrate hexahydrate, acetic acid, sodium acetate, L-cysteine (all chemicals from E.Merck), and ZnO nanoparticles (NRE lab).

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Pyrolysis of Waste Tire Carbon (WTC) The process begins with cleaning the WTC, air-drying, cutting it into small pieces (1-3 cm), and weighing 50 grams. The WTC is then burned using an LPG flame in a closed system (to avoid oxygen contact) for 1 h. The carbon material used is the soot formed on the walls of the pyrolysis furnace. The soot is collected in aluminum foil-lined containers and weighed to determine the yield. The soot is then characterized using Scanning Electron Microscopy (SEM).

Preparation of WTC Working Electrodes (Sensors) A single copper wire of 10 mm length with a 0.3 cm striped end is used to prepare the WTC working electrodes. WTC and paraffin are mixed in a 6:4 ratio, blended thoroughly in a mortar, and heated to form a paste. The paste is then molded with a plastic insulator pipe (same diameter as the copper wire, 0.5 cm length). The stripped end of the copper wire is contacted with the carbon paste, and the other end is stripped to connect with the potentiostat instrument. Before modification with ZnO and Ppy, the electrode surface is polished with tissue paper until a shiny and clean surface is obtained.

Preparation of WTC-ZnO and WTC-ZnO-Ppy Electrodes The prepared WTC electrodes are modified by soaking in a 0.05 M ZnO solution for 24 h. The electrodes are then washed with distilled water and dried at room temperature, followed by testing with cyclic voltammetry (CV) (Hussain et al. 2022). The electrodes are characterized using SEM and FT-IR. The WTC-ZnO-PPy electrodes are prepared in two steps; a thin PPy layer is deposited by amperometry for 2 s at a potential of 1.05 V (vs Ag/AgCl) over 15 cycles in a KCl solution containing pure pyrrole (monomer) 10^{-2} M and solution L-cysteine 10^{-2} M (Ait-Touchente et al. 2020). The electrodes are characterized using SEM and FT-IR.

Specific Capacitance Testing of WTC-ZnO-Ppy Electrodes Capacitance values are tested using the CV method adapted from previous study with modification (Ran et al. 2022). A solution of 5 mM K [Fe(CN),] containing 0.1 M KCl is prepared, and 25 mL is placed in the sample holder. Three electrodes (WTC-ZnO-Ppy as the working electrode, Ag/AgCl as the reference electrode, and graphite as the counter electrode) are placed in the sample holder and immersed in the $K_4[Fe(CN)_6]$ 0.1 M solution. The potentiostat is operated with CV parameters at a scan rate of 10 mV/s, with a potential range of -1 to 1 V for 1 cycle to obtain cyclic voltammograms of the standard WTC-ZnO-Ppy electrode in the 5 mM $K_{4}[Fe(CN)_{6}]$ solution in 0.1 M KCl with pH of 9. For the soot-paraffin ratio experiments, different ratios (1:1, 2:1, and 6:4) were prepared and tested in a 0.1 M KCl solution at a scan rate of 10 mV/s. The cyclic voltammetry results were obtained under identical conditions to assess the effect of varying soot:paraffin ratios on the capacitance values (Ran et al. 2022).

*Measurement of Hg*²⁺ *Using Modified Electrodes* The electrochemical response of the sensor to mercury in water

is conducted using the CV method. Standard Hg solutions of HgCl₂ solutions with concentrations of 0.01-8 ppm are prepared, placed in sample holders, and measured using the sensor at the peak oxidation voltage. The calibration curve of the electrochemical response is used to determine the LoD and LoQ of the electrode, calculated using the formula LoD = 3 s/m, where 's' is the standard deviation of the average and 'm' is the slope of the calibration curve (Sapari et al. 2020; Siddiqui et al. 2019).

Interference Testing of Mercury Sensor The selectivity of the WTC-ZnO-Ppy electrode is tested with potential interfering metal ions. The CV method is used to test the selectivity of the WTC-ZnO-Ppy electrode. Standard mixtures of Hg, Pb, and Ag solutions are prepared, with Pb and Ag ion concentrations kept constant at 1 ppm and Hg concentrations at 1 ppm (Jerimiyas et al. 2018). The standard solutions are placed in sample holders, with sensors activated. Measurements are taken for each standard using the sensor with the cyclic voltammetry (CV) method at the peak oxidation voltage.

Testing of Mercury Sensor on River Water Samples The mercury sensor testing on river water samples is carried out as follows: the water samples are filtered using Whatman No.1 filter paper to remove suspended particles. The filtered samples are then measured using the sensor with the CV method at the peak oxidation voltage for half a cycle (Sapari et al. 2020).

RESULTS AND DISCUSSION

The study began with the pyrolysis of WTC samples to separate the carbon material. Pyrolysis was performed by burning 50 g of WTC using a Liquefied Petroleum Gas (LPG) flame for 1 h in a specially designed reactor. The resulting carbon material included 1.53 g of soot (3.06%) and 20.14 g of charcoal (40.14%). The produced soot is a fine, lightweight black powder that easily adheres to surfaces. Meanwhile, charcoal is the residue left from

combustion, characterized by its black color and hard, brittle texture. Soot consists of fine particles similar to dust produced from the combustion of WTC, which creates carbon particles with a basic nano-carbon structure formed during the burning process (Uttaravalli et al. 2022).

Carbon soot is used as a sensor material because it possesses good conductivity and stability and is inexpensive. Its nano size allows the KCl solution to easily penetrate the electrode's deepest parts (Uttaravalli et al. 2022). The obtained soot was then molded into working electrodes and characterized using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FT-IR).

SCANNING ELECTRON MICROSCOPY (SEM) AND FOURIER TRANSFORM INFRARED (FTIR)

This study utilized SEM to observe differences in surface morphology between unmodified WTC electrodes, WTC electrodes modified with zinc oxide (ZnO), and WTC-ZnO and polypyrrole (PPy). SEM images were taken at magnifications of 1,000x, 2,500x, and 5,000x (Figure 2).

Figure 2(A)-2(C) shows SEM images of the WTC electrodes before modification, showing a smooth and sturdy surface made from WTC soot bound with paraffin. This smooth and sturdy surface allows for further modifications on the WTC electrode. Figure 2(D)-2(E) shows SEM images of WTC electrodes modified with ZnO, highlighting the presence of ZnO nanoparticles that are aggregated and randomly distributed on the electrode surface. This indicates that the WTC electrode has been successfully modified with ZnO and is ready for further modification with polypyrrole. Figure 2(G)-2(I) displays SEM images of WTC-ZnO-PPy electrodes, showing a granular surface. The WTC-ZnO-PPy fuses effectively, resulting in a more cohesive, well-integrated surface due to the electropolymerization of polypyrrole, this is consistent with the findings of the previous study (Ait-Touchente et al. 2020).



FIGURE 1. Sampling maps



FIGURE 2. SEM images at 1,000x, 2,500x, and 5,000x magnification. (A-C) unmodified WTC electrodes, (D-F) ZnO-modified WTC electrodes, and (G-I) ZnO-PPy-modified WTC electrodes

The FT-IR spectra in Figure 3 show several absorption peaks at the same wavenumbers for all three types of modified electrodes. A broad peak at 3,755.50 cm⁻¹ indicates the presence of hydroxyl (O-H) groups. Peaks at 291.37 cm⁻ ¹, 2848.68 cm⁻¹, and 731.31 cm⁻¹ indicate C-H stretching, characteristic of alkane groups. A peak at 465.90 cm⁻¹ indicates C-C vibrations in aromatic rings. A broad peak at 1,708.93 cm⁻¹ indicates the presence of C=O groups, while peaks at 1,465.90 cm⁻¹ and 1,579 cm⁻¹ indicate C-O bonds and C=C bonds in aromatic rings, respectively, within the active carbon structure. For the ZnO-modified WTC electrodes, an absorption peak at 472.56 cm⁻¹ indicates the presence of Zn-O bonds, confirming the existence of ZnO nanoparticles on the electrode. The FT-IR spectrum of the WTC-ZnO-PPy electrodes shows a successful synthesis of polypyrrole, indicated by the stretching vibrations of C=C bonds at 1,681.93 cm⁻¹, characteristic of polypyrrole. This bond is not present in the spectra of unmodified WTC and ZnO-modified WTC electrodes.

ELECTRODE FABRICATION AND SPECIFIC CAPACITANCE TESTING

During the electrode manufacturing process, different ratios of carbon paste were tested, including 1:1, 2:1, and 6:4. The carbon paste with these ratios was easier to shape into electrodes and produced sturdier electrodes for further modification. However, the 7:3 carbon paste ratio proved more difficult to form into electrodes, resulting in more fragile and brittle electrodes that were prone to breaking during subsequent modifications. The WTC electrodes were sonicated at 50 m/s for 1 min in distilled water and then dried at room temperature to clean the working electrodes. Before use, the WTC electrodes were polished with sandpaper and Al₂O₃ to remove impurities.

The specific capacitance of the WTC electrodes was tested using the cyclic voltammetry (CV) method with an electrolyte solution of 0.1 M KCl and tris HCl buffer at pH 9. The voltammogram shows the capacitance values of the electrodes for different soot-to-paraffin ratios (Figure 4). A ratio of 6:4 provided higher currents compared to the 2:1 ratio, while the 1:1 ratio generated no current. Previous studies with a 2:1 ratio (Baihaqi et al. 2023) Reported a current of -0.8 pM. The current obtained in this study showed significant improvement over prior research.

MODIFICATION OF WORKING ELECTRODES WITH ZINC OXIDE (ZnO) AND POLYPYRROLE (PpY)

The prepared WTC carbon electrodes were modified by soaking them in a 0.05 M ZnO solution for 24 h. The soaked electrodes were washed with distilled water, dried at room temperature, and tested using CV. The ZnO-modified WTC electrodes were further modified with a 0.1 M pyrrole solution and L-cysteine dissolved in 0.1 M KCl as a dopant. Electropolymerization was then performed using CV with a scan rate of 10 mV/s.

The WTC carbon electrodes, both before and after modification, were measured using CV within a potential range of -1 V to 1 V at a scan rate of 10 mV/s in a 0.1 M KCl solution with tris HCl buffer at pH 9. Figure 5 shows the differences in measurements before and after modification, with the obtained current increasing significantly. The unmodified WTC electrodes had a current of 13.59 mA, the WTC-ZnO electrodes had a current of 14.1 mA, and the WTC-ZnO-Ppy electrodes had the highest current of 15 mA. This indicates that the WTC-ZnO-Ppy-based sensor can capture more Hg^{2+} ions due to the addition of ZnO nanoparticles on the electrode surface (Ait-Touchente et al. 2020).

The general mechanism of polypyrrole in capturing Hg²⁺ showed that the PPy polymer reacts with mercury species resulting from dissociation or/and de-protonation as follows:



Both modified and unmodified WTC carbon electrodes were tested using a 5 mM $K_4Fe(CN)_6$ solution in 0.1 M KCl with a pH of 9. Measurements were conducted CV at a potential range of -1 V to 1 V and a scan rate of 10 mV/s. The results shown in Figure 6 indicate that the conductivity characteristics of the electrodes were maintained both before and after modification (Ait-Touchente et al. 2020).

EFFECT OF SCAN RATE

The effect of scan rate in CV was analyzed to observe the electrochemical response and understand the redox processes occurring in the electrode. The WTC-ZnO-PPy electrode was tested in a 2.5 ppm Hg solution in 0.1 M KCl



FIGURE 3. FT-IR spectrum. (A) WTC electrode, (B) ZnO-modified WTC electrode, and (C) ZnO-PPy-modified WTC electrode



FIGURE 4. Cyclic voltammogram (CV) of WTC electrodes with different soot: Paraffin ratios (1:1, 2:1, 6:4) in 0.1 M KCl solution at a scan rate of 10 mV/s



FIGURE 5. Cyclic voltammogram of electrodes before and after modification using CV method in 0.1 M KCl solution at a scan rate of 10 mV/s



FIGURE 6. Cyclic voltammogram of WTC carbon electrode and WTC-ZnO-Ppy in K_4 Fe(CN)₆ solution with 0.1 M KCl



FIGURE 7. Cyclic voltammogram of WTC-ZnO-Ppy carbon electrode at scan rates from 10 to 50 mV/s

with tris HCl buffer at pH 9, using scan rates from 10 mV/s to 50 mV/s, within a potential range of -1 V to 1 V (Ait-Touchente et al. 2020). The results are shown in Figure 7. At a scan rate of 10 mV/s, the peak areas for oxidation and reduction are almost equal. Additionally, as the scan rate increases, the system current increases significantly, increasing the area around the CV curve. Consequently, the composite material exhibits high current release capability, making the 10 mV/s scan rate optimal for Hg²⁺ analysis. This finding aligns with research by Hussain et al. (2022), which showed that varying the scan rate from 10-100 mV/s resulted in the highest current at 10 mV/s, with the current decreasing at higher scan rates.

CURRENT SENSOR RESPONSE TO MERCURY

The current response of the sensor to mercury in water was evaluated using the CV method with standard Hg solutions at concentrations ranging from 0.01 to 8.00 ppm in 0.1 M KCl solution, repeated three times. The electrochemical voltammograms of the standard Hg solutions are shown in Figure 8.

Based on the current response, a calibration curve of standard Hg concentration (0.01-8.00 ppm) vs. IpA was created to obtain the linear regression equation, which will be used to determine the Hg concentration in river water samples. The calibration curve is shown in Figure 9(A). The CV response showed a continuous increase with rising Hg²⁺ concentrations. Based on Figure 9, the IpA data provided a more linear curve, and the linear regression equation for IpA was y = 0.5112x + 0.2884 with an R² value of 0.9977. The linear regression for IpC was y = -0.4205x - 0.7913 with an R² value of 0.8522. Therefore, the IpA calibration curve was used in this study due to its better R² value than the IpC calibration curve.

INTERFERING IONS

The selectivity of the WTC-ZnO-Ppy-based mercury sensor was tested against the measurement of Hg^{2+} by adding other metal ions, specifically Ag^+ and Pb^{2+} . Ag^+ was chosen due to its smaller ionic radius than Hg^{2+} , while Pb^{2+} was selected due to its larger ionic radius than Hg^{2+} (Ait-Touchente et al. 2020). The test was conducted in two ways: first, measuring Ag^{2+} and Pb^{2+} ions in 0.1 M KCl solution at a concentration of 1 ppm for each ion without mercury; second, measuring with the addition of 0.5 ppm Hg^{2+} in each solution, stirred until homogeneous, and measured using CV at a potential range of -1 V to 1 V, with a scan rate of 10 mV/s. The results of the interference measurements are shown in Figure 10.

The testing showed that the sensor selectively detected Hg^{2+} . Figure 10 demonstrates ion competition, as Hg^{2+} had a peak current of 16 mA, which decreased to 15.45 mA after adding Ag^+ and Pb^{2+} ions at the same concentration of 1 ppm. Quantitatively, the sensor had clear selectivity for Hg^{2+} ions.

LINEARITY AND LINEAR RANGE

Linearity was assessed by plotting the measured IpA values (y-axis) against the standard solution concentrations (x-axis) and calculating the coefficient of determination (R²). The linear regression equation for Hg²⁺ within the 0.01-8.00 ppm range was IpA y = 0.5112x + 0.2884 with an R² value of 0.9977. An analytical method is considered linear within a specific concentration range if the R² value obtained is greater than 0.995. Thus, it can be concluded that the analysis of Hg²⁺ using the WTC carbon electrode modified with ZnO and polypyrrole showed good linearity in the range of 0.01-8.00 ppm (Hussain et al. 2022).

ACCURACY

The accuracy determination is based on the recovery value, which indicates the closeness of the measured value to the actual concentration. The concentration range of Hg^{2+} used with the WTC-ZnO-Ppy carbon electrode was 0.01 - 8.00 ppm. Based on the recovery percentage calculation, the accuracy is within the allowable error range of 80-120% for metals (Harvey 2009), indicating that the method used has high accuracy.

PRECISION

The precision of the WTC-ZnO-Ppy carbon electrode was calculated from the current obtained using the CV method with standard mercury solutions at varying concentrations from 0.01-8.00 ppm, repeated three times. The relative standard deviation (RSD) values obtained are shown in Table 1.

Based on Table 1, the precision values range from 0.03% to 0.76%, below 2%. A method is considered to have good precision if the RSD value is less than 2% (Harvey 2009). The RSD values in this precision test meet the requirements because, according to the literature, a method provides good repeatability if the %RSD $\leq 2\%$. The deviations observed are within the allowed range, indicating that the method used has good repeatability in analysis. The smaller the %RSD value obtained, the more accurate the analysis performed.

LIMIT OF DETECTION (LoD) AND LIMIT OF QUANTITY (LoQ)

The sensitivity of an analytical method can be expressed in terms of the limit of detection. The Limit of Detection (LoD) is calculated using the equation 3.3 SD/b, where SD is the standard deviation of the Hg^{2+} concentration measurements, and b is the slope of the calibration curve equation. The measured detection limit for Hg^{2+} is 0.0257 ppm or 0.03 ppm. The limit of quantification also indicates the sensitivity of the analytical method used. The LoQ is calculated using the equation 10 SD/b; the result is 0.07 ppm.



FIGURE 8. Anodic peak current (IpA) voltammograms of standard Hg solutions at concentrations of 0.01-8.00 ppm in 0.1 M KCl (n=3)





FIGURE 10. IpA peak of Hg^{2+} peak current response with the addition of Ag^+ and Pb^{2+} in 0.1 M KCl at pH 9 with a scan rate of 10 mV/s

TABLE 1. Precision calculation for WTC-ZnO-Ppy carbon electrode

	Concentration (ppm)(n=3)	Standard deviation (SD)	%RSD
1	0.5	6.0.10-4	1.1.10-2
2	2.0	1.0.10-2	7.6.10-2
3	3.0	6.0.10-4	3.0.10-2

TESTING WTC-ZnO-PpY CARBON ELECTRODES ON REAL RIVER WATER SAMPLES

The proposed method needs to be evaluated using real samples to assess the sensitivity and selectivity of the developed method for detecting Hg^{2+} ions. The evaluation was conducted by testing the WTC-ZnO-Ppy carbon electrodes on river water samples from the Sungai Mas area in Aceh Barat Regency, Aceh Province, collected from six different points: Desa Kajeng, Desa Tungkop, and Tutut, at both the surface and 5 m depth. Measurements were repeated three times using CV within a potential range of -1.00 to 1.00 V and a scan rate of 10 mV/s.

According to Appendix IV of the Government Regulation of the Republic of Indonesia (PPRI) No. 22 of 2021 on 'Implementation of Environmental Protection and Management', the river water samples must comply with the quality standards for class 2 river water. This class of water can be used for infrastructure, water recreation, freshwater fish farming, livestock, irrigation, and other uses requiring similar water quality. Samples from Rivers I, II, and III, both from the edges and the middle, exceeded the allowable quality standards and were contaminated with mercury. The maximum permissible concentration of Hg^{2+} for class 2 river water is 0.001 mg/L (ppm). The Hg sensor based on WTC-ZnO-Ppy carbon could detect Hg^{2+} in the river water samples.

The water samples were also compared using Atomic Absorption Spectrophotometry (AAS) at the Environmental Quality Testing Laboratory, Department of Chemical Engineering, Faculty of Engineering, Universitas Syiah Kuala. According to Test Result Sheet Number: 036/JTL-USK/LTPKL/2024, the Hg concentrations in the samples from River I, II, and III at the edges and middle were as follows: 1.366 ppm; 2.868 ppm; 5.420 ppm; 2.613 ppm; 6.895 ppm; and 4.734 ppm, respectively. The Hg concentrations in the samples measured using the WTC-ZnO-Ppy carbon Hg sensor and AAS are shown in Table 2.

The Hg²⁺ concentration data in water samples measured using the voltammetry method with the

No.	Sample identification	Hg concentration with WTC-ZnO-Ppy carbon-based sensor (ppm)	Hg concentration with AAS (ppm)
1	River I-S	1.364	1.366
2	River I-D	2.866	2.868
3	River II- S	5.410	5.420
4	River II- D	2.611	2.613
5	River III- S	6.894	6.895
6	River III- D	4.733	4.734

TABLE 2. Hg concentrations in river water samples measured using WTC-ZnO-Ppy carbon-based Hg sensor and AAS

River I = Kajeng, River II = Tungkop, River III = Tutut, S = Surface level, and D = 5 meters depth

WTC-ZnO-Ppy carbon-based Hg sensor and AAS in Table 2 were further analyzed using a t-test to compare the means of the two measurement methods. The t_{table} value was obtained by determining a 95% confidence interval with a significance level (α) of 5% (0.05). The t-test result showed that $t_{calculated} < t_{table}$ (2.121 < 2.570), indicating no significant difference between the two methods for measuring Hg concentration in river water. This result demonstrates that the WTC-ZnO-Ppy carbon-based Hg sensor is almost as effective as AAS in detecting Hg in river water samples. From a practical standpoint, the voltammetry method allows for direct Hg detection at the sampling location, whereas AAS cannot be operated directly on-site. Additionally, the cost of Hg analysis using the voltammetry method is relatively cheaper than AAS.

CONCLUSION

The WTC carbon working electrode modified with ZnO and polypyrrole can be used as an electrode for mercury detection. The currents obtained for the WTC-ZnO and WTC-ZnO-Ppy carbon electrodes were 14.1 mA and 15 mA, respectively. The electrochemical response of the WTC-ZnO-Ppy electrode had an optimal scan rate of 10 mV/s, a calibration curve for IpA of y = 0.5112x + 0.2884 with an R2 value of 0.9977, a concentration range of 0.01 ppm to 8 ppm, a recovery rate of 97-110% within the allowable error range, a coefficient of variation less than 2%, a LoD of 0.03 ppm, and a LoQ of 0.07 ppm. The current response of the WTC-ZnO-Ppy electrode using the cyclic voltammetry technique can detect mercury in river water, and there was no significant difference in mercury measurement between the voltammetry method and AAS.

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