

Analysis of Hg(II) Metal by Voltammetric Method Using a Carbon Electrode Modified with EDTA from Used Tire Waste

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Abstract: Development of a carbon electrode sensor from used tire waste via pyrolysis, modified with ethylenediaminetetraacetic acid (EDTA) for mercury detection using the cyclic voltammetry (CV) method. EDTA plays a role in metal complexation due to its strong response to mercury metal. The FTIR results of the carbon electrode and EDTA show a C-N bond at a wavenumber of $1,217.08\text{ cm}^{-1}$, indicating the presence of EDTA. The SEM results reveal a clear difference between the unmodified carbon electrode and the EDTA-modified carbon electrode. The calibration graph is linear, with an R^2 value of 0.9961, a sensitivity of 0.3472, as well as LoD and LoQ values of 0.03 and 0.08 ppm, respectively. The correlation coefficient is less than 2%, and the %recovery is within the allowable error range. Mercury measurements in Sungai Mas water samples, Aceh Barat, using voltammetry and AAS, exceed the threshold set by Indonesian Government Regulation (PPRI) No. 22 of 2021. The t-test results for the two Hg measurement methods at a 5% significance level (α) show that $t_{\text{calculated}} < t_{\text{table}}$ ($0.083 < 2.571$). This indicates no significant difference between the voltammetry and AAS methods for measuring Hg concentrations in water.

Keywords: used tire waste; voltammetry; EDTA; mercury; cyclic voltammetry

■ INTRODUCTION

Gold mining by local communities is mostly conducted using traditional methods. The common process used by communities to obtain gold is amalgamation. Amalgamation is the process of mixing gold with mercury (Hg). This technique involves mixing gold ore with Hg using a trommel. However, this activity

has the potential to cause environmental contamination. Therefore, this study was conducted to analyze the potential Hg contamination resulting from gold mining activities in the rivers of the Sungai Mas area, Aceh Barat Regency, Aceh Province [1].

Hg is one of the heavy metals that is extremely dangerous whether in ion form or as an element in a solution. In nature, Hg is divided into three forms:

metallic Hg, organic Hg, and inorganic Hg. Hg is also known as a toxic metal with neurotoxic potential for both organisms and humans. As a heavy metal, Hg that enters aquatic environments is difficult to decompose. Hg can undergo various transformations in the environment, and Hg ions can be converted into one of the most toxic forms, methylmercury (MeHg), through abiotic and biotic pathways. They will subsequently accumulate through both bioaccumulation and biomagnification in the food chain. To determine the Hg pollution status in an aquatic environment, it is necessary to measure the Hg concentration using water as the medium of accumulation [2]. Analysis to detect Hg typically uses methods such as GC/MS, HPLC/ICP-MS, GF-AAS, and AAS but they require trained operators and are costly.

Voltammetry observes changes in current and potential. We chose voltammetric methods for this research because voltammetry offers good sensitivity, making it highly suitable for detecting heavy metals [3]. The basic principle of voltammetry is the measurement of current as a function of the applied potential when the indicator electrode (sensor) is polarized at a constant potential, allowing the analyte to undergo oxidation-reduction reactions [4]. Voltammetric methods have been researched for the detection of several heavy metals, such as Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} . Voltammetry uses three types of electrodes: the working electrode, the reference electrode, and the auxiliary electrode [5]. The electrode involved in measuring the analyte in voltammetry is the working electrode. The surface of the working electrode is where the electron transfer process occurs. Working electrodes can be made of materials, such as carbon, platinum, gold, silver, and Hg. Platinum and gold electrodes show good performance, but they are relatively expensive, and Hg is not recommended due to its toxic nature. Carbon-based electrodes are increasingly developed in voltammetric methods because they offer a wide potential range, low cost, and inertness [6].

Several studies have utilized various types of carbon electrodes to identify Hg. For example, graphite electrodes from pencils pre-treated with HNO_3 have been researched and are capable of detecting Hg in saliva at 5×10^{-3} ppm [7]. Carbon electrodes with the active substance 2-(5'-

bromo-2'-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) can detect Hg at 0.01 ppm [8]. Additionally, carbon electrodes with dithizone can detect Hg at 17×10^{-6} ppm [9]. These types of carbon electrodes need to be purchased and can be costly. Thus, there is a need for alternative carbon sources from waste materials in the environment.

Used tire waste worldwide exceeds 1.2 billion discarded each year, with at least 4 billion or more accumulated in landfills and dumps. One of the components of used tire waste is carbon. Carbon from used tires is underutilized. Research has explored its use as a carbon source through pyrolysis [10-11], and calcination [12]. This research aims to use carbon from waste tires to minimize environmental pollution. Carbon from waste tires is easy to form, durable, and provides a good detection limit of 0.0681 ppm by modifying the carbon electrode to enhance electron transfer and sensitivity using ethylenediaminetetraacetic acid (EDTA) [13].

EDTA is known as a chelating agent with the ability to form bonds with metal ions. This compound is also referred to as a chelate agent or chelating ligand. EDTA is highly stable, not easily decomposed, and serves as an effective chelating agent for metal ions by preventing precipitation. This study uses EDTA to modify carbon paste electrodes due to its strong response to Hg ions. The use of EDTA aims to enhance the current value and sensitivity of the electrode.

■ EXPERIMENTAL SECTION

Materials

Carbon material was obtained from used tires collected from a motorcycle tire replacement workshop in Gampong Pango Raya, Ulee Kareng District, Banda Aceh City. The samples for this study were river water from the Sungai Mas area, Aceh Barat Regency, Aceh Province, specifically from three villages: Desa Tutut, Desa Kajeung, and Desa Tungkop. Samples were collected at three sampling points, with each village having sampling points taken at the river surface and at a depth of 5 m from the surface. The materials used include liquefied petroleum gas (LPG, model: mini

portable), aluminum foil (Klinpak), copper wire (Eterna), paraffin (Gulf Wax), KCl (99%, E. Merck), HNO₃ (68%, E. Merck), Hg(II) (99.9%, E. Merck), Pb(II) (99.9%, E. Merck), Ag(I) (99.9%, E. Merck), K₄Fe(CN)₆ (99%, E. Merck), and EDTA (99%, E. Merck).

Instrumentation

The instruments used in this study include a ZIVE potentiostat ppi connected to a recorder and equipped with Smart Manager (SM) software, utilizing a three-electrode system (carbon electrode as the working electrode, Ag/AgCl electrode as the reference electrode, and Pt as the auxiliary electrode), a scanning electron microscope (SEM, JSM-6510LA), and a Fourier transform infrared (FTIR, Shimadzu XRD-7000).

Procedure

Pyrolysis of used tire waste

The pyrolysis process begins with cleaning the used tire waste, followed by air drying. The material is then cut into small fragments (1–3 cm in size) and weighed to obtain 50 g. The fragments are subsequently subjected to combustion using an LPG flame within a sealed furnace, ensuring the absence of oxygen contact for a duration of 2 h. The resulting carbon material is then ground for further use [11]. The carbon collected consists of soot deposited on the walls of the pyrolysis furnace. This soot is carefully gathered in a pre-weighed, aluminum foil-lined container to determine the yield. The collected soot is then characterized using SEM and FTIR. The pyrolysis process is presented in Fig. 1.

Preparation of carbon working electrode and modification with EDTA

A single copper wire, 10 cm in length, was prepared with one end stripped for 0.3 cm. Soot and paraffin in a 6:4 ratio were evenly mixed in a mortar and heated to form a paste. The paste was then molded into an insulator pipe (plastic) with a diameter matching the copper wire for a length of 0.5 cm. The stripped end of the copper wire was connected to the molded carbon paste. The other end of the wire was stripped to connect to the potentiostat instrument. The electrode was modified by immersing the carbon electrode in a 0.053 M EDTA solution for 24 h [14]. After immersion, the carbon electrode was rinsed

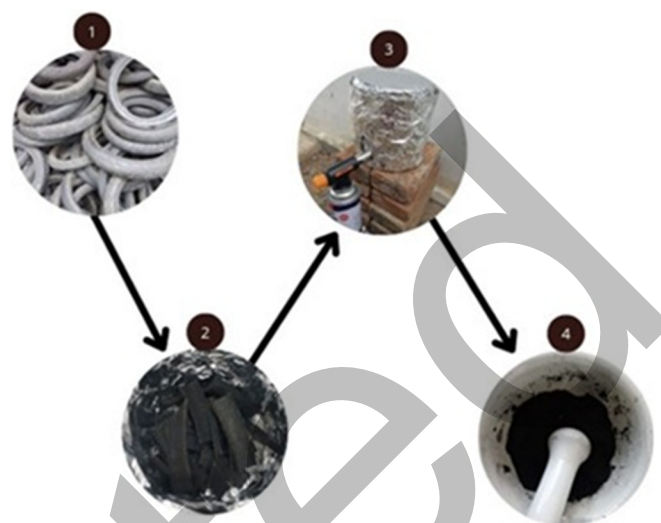


Fig 1. The pyrolysis process

with distilled water and dried, and then characterized using SEM and FTIR.

Testing the specific capacitance values of carbon electrode and EDTA-modified carbon electrode

The capacitance values were tested using the CV method. A 5 mM K₄[Fe(CN)₆] solution containing 0.1 M KCl, prepared to a volume of 25 mL, was placed into a sample container. The three electrodes (carbon electrode as the working electrode (sensor), Ag/AgCl electrode as the reference electrode, and graphite electrode as the auxiliary electrode) were positioned in the sample holder and immersed in the 0.1 M K₄[Fe(CN)₆] solution. The potentiostat was operated with CV parameters, at a scan rate of 10 mV/s over a potential range from –1 to 1 V for one cycle, to obtain the CV of the standard carbon electrode in the K₄[Fe(CN)₆] solution containing 0.1 M KCl. The same procedure was performed for the EDTA-modified carbon electrode, and the results of each electrode were compared [14].

Variation in scan rate

The EDTA-modified electrode was analyzed using a scan rate with a solution of Hg²⁺ at 2.5 ppm in 0.1 M KCl with a Tris-HCl buffer at pH 9. The scan rates ranged from 10 to 100 mV/s over a potential range from –1 to 1 V [15]. The resulting voltammograms were used to calculate the diffusion coefficient to determine the rate of mass transport at the electrode surface, employing the Randles-Sevcik in Eq. (1);

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C V^{1/2} \quad (1)$$

where I_p is the peak current, n is the number of electrons involved in the redox reaction, A is the electrode surface area (cm^2), D is the diffusion coefficient (cm^2/s), C is the analyte concentration (mol/cm^3), and V is the scan rate (V/s) [16].

Measurement of Hg(II) using modified electrodes

Measurements were conducted for Hg(II) with varying concentrations of 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, and 8 ppm. The purpose of this step was to establish the standard calibration curve for Hg(II) and to determine the limit of detection (LoD) and limit of quantitation (LoQ). The LoD was calculated using the Eq. (2);

$$\text{LoD} = \frac{3s}{m} \quad (2)$$

where 's' is the standard deviation of the blank and 'm' is the slope of the calibration curve. The LoQ was subsequently calculated using Eq. (3) [4].

$$\text{LoQ} = \frac{10s}{m} \quad (3)$$

Interfering ions

The EDTA-modified electrode was tested for selectivity in measuring Pb^{2+} and Ag^+ at a concentration of 1 ppm over a potential range from -1 V to 1 V, with a scan rate of 10 mV/s. The test involved mixing Hg^{2+} with other metal ions, specifically Pb^{2+} and Ag^+ , each at 1 ppm. Standard solutions of Hg^{2+} and Pb^{2+} , each at 1 ppm, were prepared, and similarly for Ag^+ . These solutions were mixed thoroughly to achieve homogeneity and were then analyzed using CV over the potential range from -1 to 1 V, with a scan rate of 10 mV/s [13].

Testing of mercury sensor on river water samples

Water samples were collected from the Sungai Mas area in Aceh Barat Regency, Aceh Province, from three villages: Tutut (coordinates $4^\circ 31' 19.4''\text{N}$ $96^\circ 07' 22.0''\text{E}$), Kajeung (coordinates $4^\circ 31' 11.1''\text{N}$ $96^\circ 05' 37.5''\text{E}$), and Tungkop (coordinates $4^\circ 30' 56.0''\text{N}$ $96^\circ 06' 06.4''\text{E}$). The pH values of the water samples were 7.84, 7.95, and 7.70, respectively, and the temperatures were 25.4, 25.0, and 25.7 °C. Samples were taken at three sampling points in each village: at the river surface and at a depth of 5 m from the surface. The samples were stored in plastic containers

and preserved with HNO_3 . The river water samples were collected on Sunday, March 3rd 2024, at 15:00 GMT+7. The water samples were filtered using Whatman No. 1 filter paper to remove suspended particles. The pH of the water was adjusted to pH 9 by adding Tris-HCl buffer. Measurements for these samples were performed using the sensor with the CV method at the oxidation peak voltage [13].

RESULTS AND DISCUSSION

Pyrolysis of Used Tire Waste

The research began with the pyrolysis of used tire waste samples obtained from a tire repair shop in Gampong Pango Raya, Kecamatan Ulee Kareng, Banda Aceh City. The purpose of the pyrolysis was to separate the carbon material from the used tires. The pyrolysis process yielded 1.53 g (3.06%) of soot and 20.07 g (40.14%) of charcoal. Soot is a carbon particle produced from the non-stoichiometric combustion of carbon material, and it represents a fundamental nanostructure formed during the burning process [17]. This study selected soot as the material for sensor fabrication because, according to previous study [17], the nanometer size of soot allows the KCl solution to penetrate deeply into the electrode. The pyrolysis products were characterized using SEM and FTIR to examine the topography and structure of the carbon material.

SEM

SEM is a type of electron microscope capable of providing high-resolution images of the surface of a sample. SEM is typically used to observe very small objects at the nanometer scale [18]. The principle of SEM involves utilizing backscattered electrons from the surface of the sample and capturing images by detecting these electrons emitted from the object's surface. This study employs SEM to investigate any differences in the surface morphology of the electrode before modification with EDTA [19].

Fig. 2 shows the SEM images of the surface of the carbon electrode and the carbon electrode modified with EDTA at magnifications of 1000, 2500, and 5000 \times . Fig. 2(a), at 1000 \times magnification, does not clearly reveal the

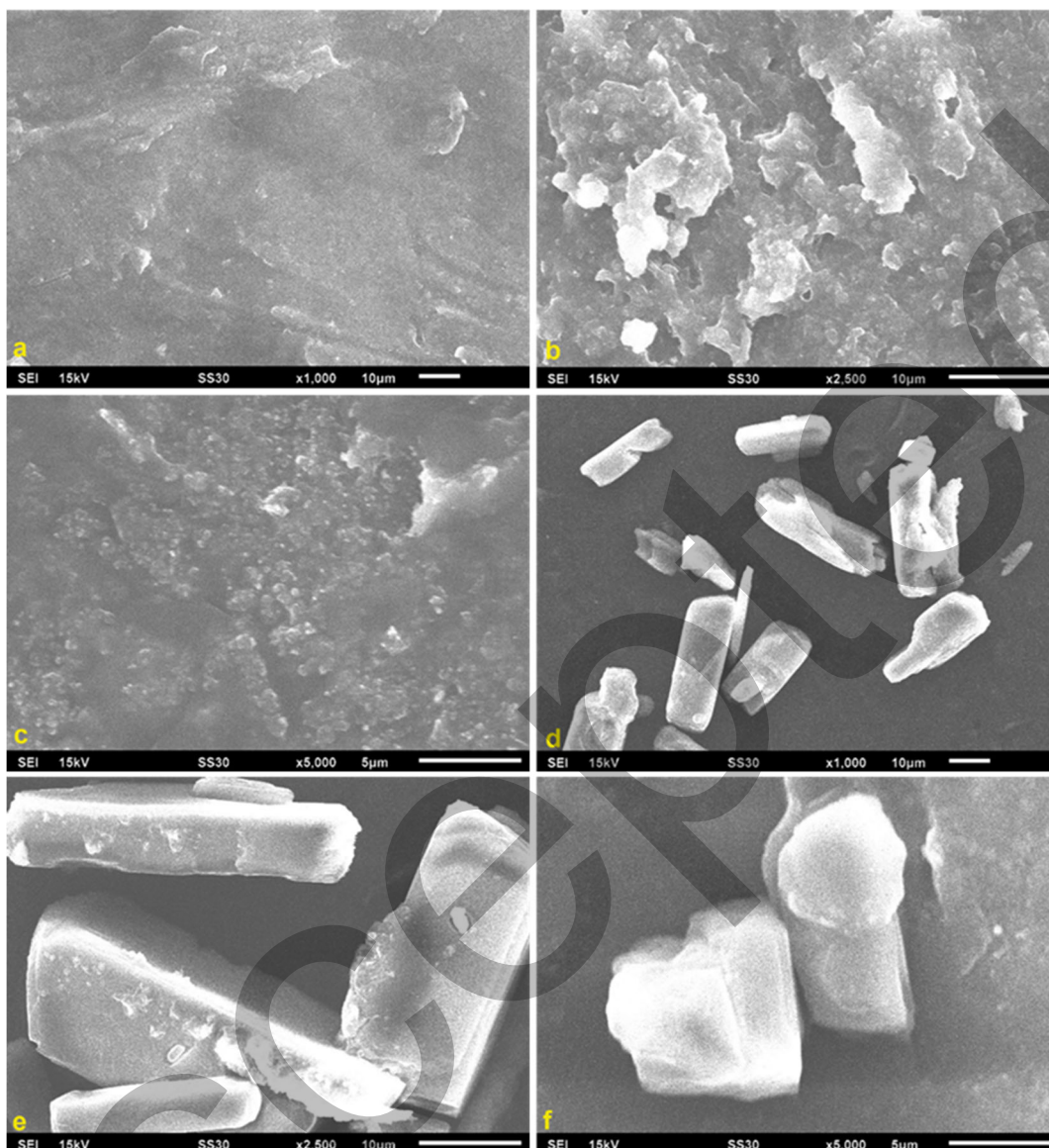


Fig 2. SEM Images of carbon electrode: (a) 1000 \times , (b) 2500 \times , and (c) 5000 \times magnification. SEM images of carbon electrode + EDTA: (d) 1000 \times , (e) 2500 \times , and (f) 5000 \times magnification

pores of the carbon. Fig. 2(b), at 2500 \times magnification, begins to show a porous, sponge-like appearance. Fig. 2(c), at 5000 \times magnification, clearly displays a highly porous sponge-like structure with numerous cavities ranging from approximately 1 to 10 μm , similar to findings reported by Yang [20]. Fig. 2(d), (e), and (f) illustrate the surface morphology of the electrode modified with EDTA, observed at various magnifications to assess whether EDTA binds to the carbon electrode. The presence of nearly octahedral crystals indicates the successful binding of EDTA to the electrode, consistent

with the previous research [21], confirming the effectiveness of the modification process.

FTIR

FTIR spectroscopy is a method used to detect molecular structures of compounds. The results from FTIR measurements are presented as spectra. This study employs FTIR to analyze the chemical components of activated carbon, identifying functional groups present in both the activated carbon and EDTA. It also aims to observe the differences in the spectra of the carbon

electrode compared to the EDTA-modified carbon electrode, both qualitatively and quantitatively (Fig. 3) [22].

Based on Fig. 3, several absorptions at the same wave numbers are observed in both the carbon electrode and the EDTA-modified carbon electrode. At a wavenumber of 3755 cm^{-1} , the presence of O–H groups is noted. Additionally, absorptions at wave numbers 2916, 2849, and 723 cm^{-1} indicate the stretching of C–H bonds, characteristic of alkanes, while the absorption at 1466 cm^{-1} signifies C–C vibrations in the aromatic ring. Furthermore, an absorption at 1709 cm^{-1} suggests the presence of C=O, an absorption at 1371 cm^{-1} indicates C–O bonds, and the absorption at 1579 cm^{-1} corresponds to C=C aromatic bonds in the structure of activated carbon. For the EDTA-modified carbon electrode, slight shifts are observed: C=O at 1693 cm^{-1} , C=C aromatic at 1572 cm^{-1} , and C–N at 1217 cm^{-1} , indicating the presence of EDTA. The FTIR analysis results indicate that the carbon electrode, as shown in Fig. 3, contains functional groups typical of activated carbon, including O–H, C=C aromatic, C–H, and C–O groups. These results are comparable to those reported in previous study [23] and are summarized in Table 1.

Preparation of Carbon Working Electrodes and Modification with EDTA, and Testing the Specific Capacitance Value of the Electrodes

The working electrode is prepared using a mixture of soot and paraffin in a 6:4 ratio and modified with a 0.053 M EDTA solution for 24 h. Scheme 1 illustrates the bonding process between the carbon electrode and EDTA. Fig. 4 shows the difference in the electrode surface

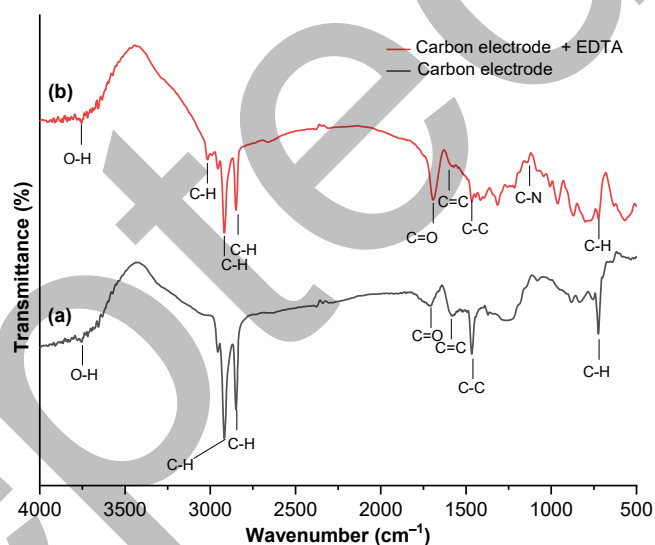
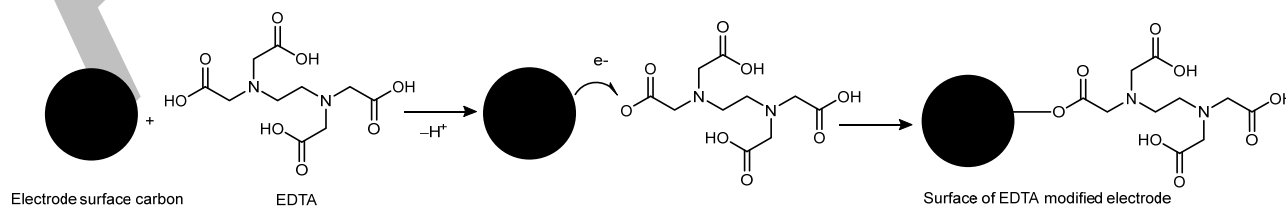


Fig 3. FTIR spectra (a) carbon electrode and (b) EDTA-modified carbon electrode

Table 1. Comparison of FTIR wavenumber

Carbon (cm ⁻¹)	Carbon + EDTA (cm ⁻¹)	Activated carbon from coconut shells (cm ⁻¹) [23]	Functional group (cm ⁻¹)
3755	3755	3426	O–H
2916	2916	2924	C–H
2849	2849	756	C–H
723	723	2376	C=O
1709	1694	1589	C–O
1371	1371	1589	C=C
1579	1571	1217	C–N



Scheme 1. Immobilization of the EDTA molecule

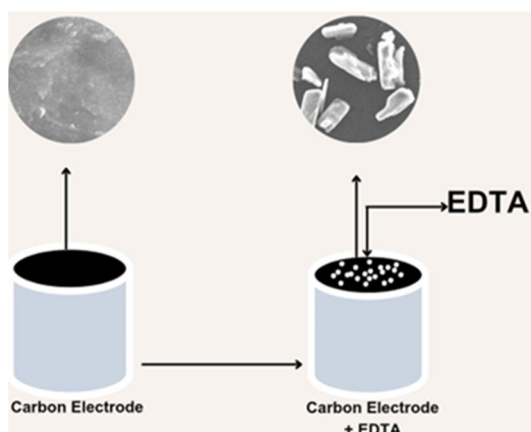


Fig 4. Surface of the electrode before and after modification with EDTA

before and after modification with EDTA. The use of EDTA in electrode modification is due to its stability, resistance to decomposition, and its effectiveness as a complexing agent for metal ions, which prevents precipitation and enhances the resulting current, as demonstrated in previous studies [13-14].

The specific capacitance of the electrode, both before and after modification with EDTA, was measured using CV over a potential range of -1 to 1 V with a scan rate of 10 mV/s in a solution of $K_4Fe(CN)_6$ (containing 0.1 M KCl) and a pH 9 Tris-HCl buffer. The results showed a significant difference between the measurements before and after modification. The electrode modified with EDTA exhibited a higher current of 14.96 mA, compared to 14.67 mA for the electrode without EDTA modification, as shown in Fig. 5. This result indicates that EDTA forms complexes with metal ions, as EDTA is known as a chelating agent. The response to mercury ions is therefore much higher, and the results are consistent with previous research, which also reported higher current values for electrodes modified with EDTA compared to those without modification [13-14].

Effect of Scan Rate

In CV, the scan rate is used to observe electrochemical responses and understand the redox processes occurring at the electrode. The scan rate analysis was conducted for the electrode modified with EDTA using a 2.5 ppm Hg^{2+} solution in 0.1 M KCl with a Tris HCl buffer at pH 9, with scan rates ranging from 10

to 100 mV/s and a potential range from -1 to 1 V. The goal was to determine the optimal scan rate for analyzing Hg^{2+} ion concentration [15]. Fig. 6(a) demonstrates that the redox peak current increases significantly, with a slight shift in the peak position as the scan rate increases. Fig. 6(b) shows that at a scan rate of 10 mV/s, the oxidation and reduction peak areas are nearly equal, and the current is high. Therefore, a scan rate of 10 mV/s was selected for Hg^{2+} concentration analysis [13]. The diffusion coefficient of Hg^{2+} , obtained from the selected scan rate of 10 mV/s and calculated using Eq. (1), is $D = 6.96 \times 10^{-5}$ cm²/s. This diffusion coefficient is within the acceptable range of 10^{-5} to 10^{-6} cm²/s, and previous studies have reported a similar diffusion coefficient, $D = 7.43 \times 10^{-5}$ cm²/s, indicating that the results are consistent and acceptable [16].

Electrochemical Determination of Hg^{2+} Using EDTA-Modified Carbon Electrode

The EDTA-modified carbon electrode was subsequently used as the working electrode for measuring Hg^{2+} concentrations. The Hg^{2+} samples had known concentrations of 0.01 , 0.05 , 0.1 , 0.5 , 1 , 2 , 3 , 4 , 5 , 6 , 7 , and 8 ppm. This step aims to evaluate the success of the electrode modification by assessing the response of the modified electrode to the presence of Hg^{2+} . The measurement method was CV.

The CV response shows a continuous increase with

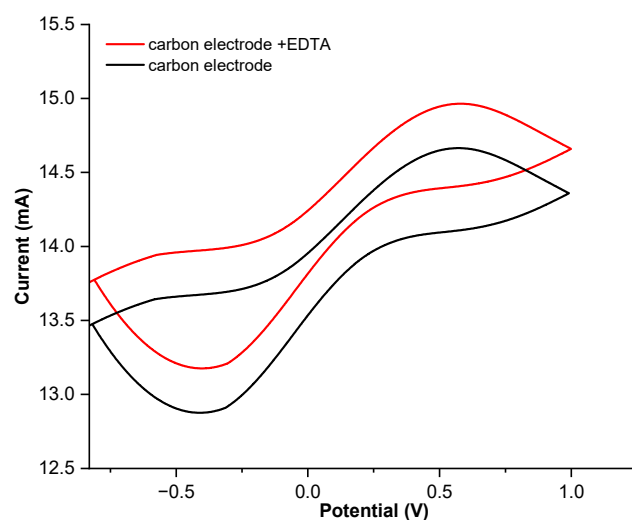


Fig 5. CV of carbon electrode and EDTA-modified carbon electrode in $K_4Fe(CN)_6$ solution (in 0.1 M KCl)

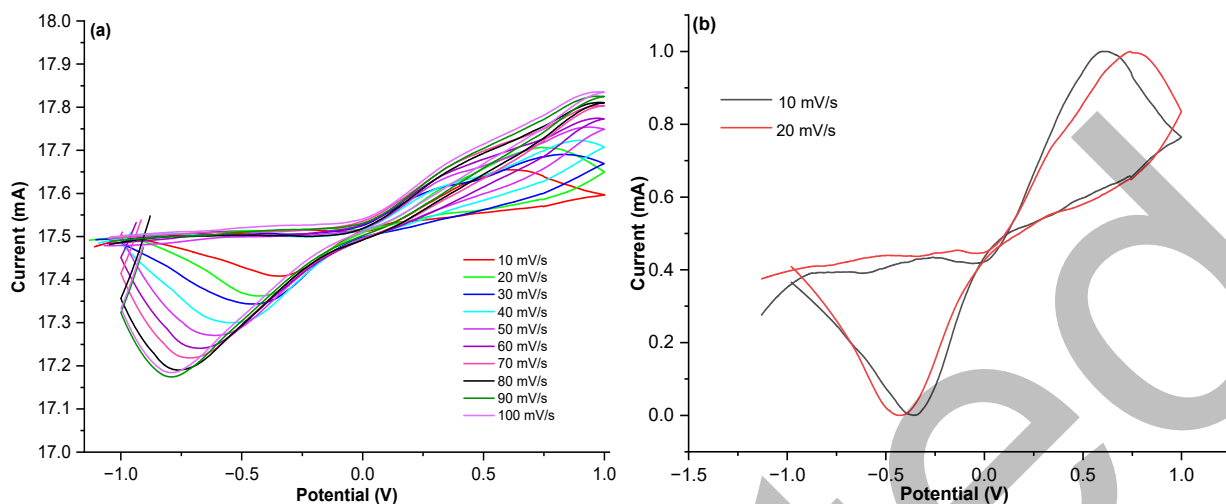


Fig 6. CV of carbon electrode + EDTA with a scan rate of (a) 10–100 mV/s and (b) 10 and 20 mV/s

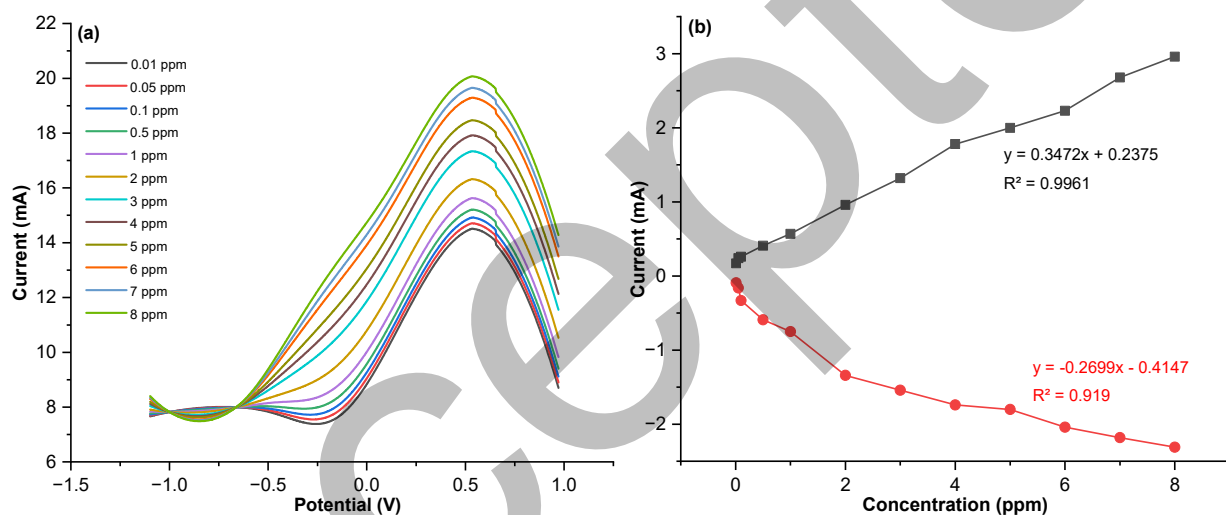
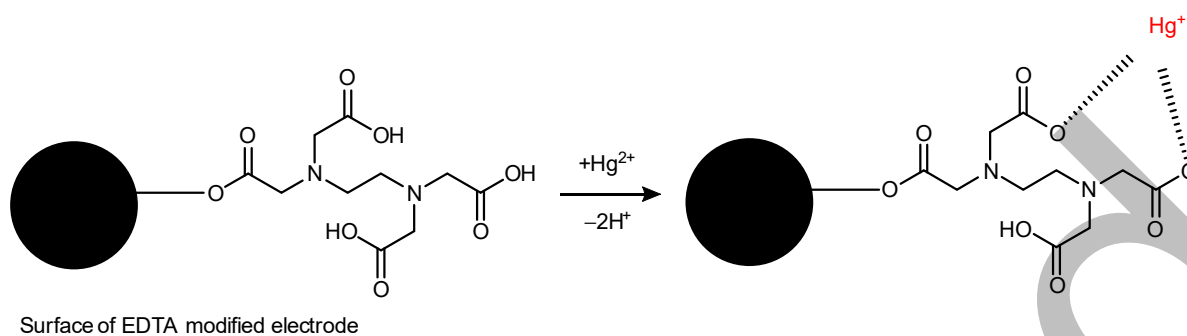


Fig 7. (a) CV method at Various Hg^{2+} concentrations in 0.1 M KCl, pH 9, using EDTA-modified carbon electrode (b) calibration curve of EDTA-modified carbon electrode with IpA and IpC

the rising concentration of Hg^{2+} (Fig. 7(a)). The calibration curve obtained (Fig. 7(b)) demonstrates a linear relationship between current and varying concentrations of Hg^{2+} using IpA. The calibration equation for IpA is $y = 0.3472x + 0.2375$ with an R^2 value of 0.9961, whereas the calibration equation for IpC is $y = -0.2699x - 0.4147$ with an R^2 value of 0.919. Based on the calibration curves for IpA and IpC, the IpA calibration curve was used in this study due to its higher R^2 value of 0.9961 compared to IpC. The recovery value obtained is 99–110%, which falls within the desired range according to previous study [24] with an acceptable error range of 80–120%. The

coefficient of variation is 1%, which is within the acceptable range of 2% [24]. The electrode stability is also excellent, as indicated by stable peak current values with repeated measurements over 3 cycles with the same sample, showing a coefficient of variation below 1%. LoD and LoQ was calculated using Eq. (2) and (3), respectively [25]. The results indicate that the LoD and LoQ values for the carbon-based Hg sensor from waste tire material are approximately 0.03 and 0.08 ppm, respectively. The proposed mechanism for mercury chelation by the EDTA-modified carbon electrode is shown in Scheme 2.



Scheme 2. Mechanism of mercury chelation by the EDTA-modified carbon electrode

Interfering Ions

The EDTA-modified electrode was tested for selectivity in measuring Hg^{2+} by adding other metal ions, Pb^{2+} and Ag^+ . The addition of other metal ions aimed to see if the resulting current would be affected before and after the addition of other metals. The standard solutions of Hg^{2+} , Pb^{2+} , and Ag^+ at 1 ppm were measured using CV over a potential range of -1 to 1 V, with a scan rate of 10 mV/s. Then, a mixture of Hg^{2+} (1 ppm) with Pb^{2+} (1 ppm) and a mixture of Hg^{2+} (1 ppm) with Ag^+ (1 ppm) were measured using CV under the same conditions. The peak currents for Hg^{2+} , Pb^{2+} , and Ag^+ at 1 ppm were 15.569 , 13.025 , and 12.778 mA, respectively. The peak current for the mixture of Hg^{2+} and Pb^{2+} at 1 ppm was 15.567 and 12.945 mA, showing a decrease in both metals; however, Hg^{2+} experienced a slight decrease of 0.002 mA and Pb^{2+} experienced a more significant decrease of 0.08 mA, as shown in Fig. 8(a). The peak current for the

mixture of Hg^{2+} and Ag^+ at 1 ppm was 15.566 and 12.763 mA. This mixture also showed a decrease in both metals; Hg^{2+} experienced a slight decrease of 0.003 mA, and Ag^+ experienced a more considerable decrease of 0.015 mA (Fig. 8(b)).

Mercury Sensor Testing on River Water Samples

Samples of river water from Desa Kajeng, Tutut, and Desa Tungkop, Aceh Barat Regency, Aceh Province,

Table 2. Determination of Hg^{2+} in river water samples

No	River water samples	Hg^{2+} concentration (ppm)
1	River water I-P	1.328
2	River water I-T	2.769
3	River water II-P	5.478
4	River water II-T	2.625
5	River water III-P	6.746
6	River water III-T	4.844

Note: River I = Kajeng, River II = Tungkop, River III = Tutut, P = Surface, and T = 5-m depth

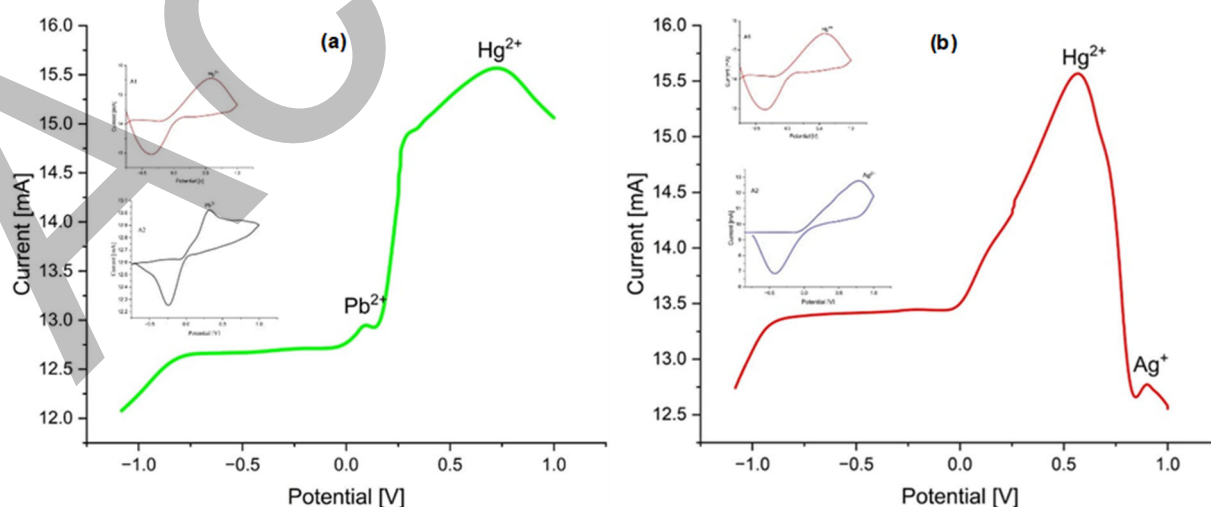


Fig 8. CV measurement of interfering ions between (a) Hg^{2+} and Pb^{2+} and (a) Hg^{2+} and Ag^+

Table 3. Comparison of CV and AAS methods for determining Hg²⁺ in river water samples

No.	Sample identification	Hg ²⁺ concentration with EDTA-based carbon sensor (ppm)	Standard deviation	Hg ²⁺ concentration with AAS (ppm)	Standard deviation
1.	River water I-P	1.328	0.000577	1.366	0.000577
2.	River water I-T	2.769	0.001	2.868	0.001
3.	River water II-P	5.478	0.001	5.420	0.000577
4.	River water II-T	2.625	0.001	2.613	0.000577
5.	River water III-P	6.746	0.001	6.895	0.000577
6.	River water III-T	4.844	0.000577	4.734	0.000577

were taken from the edges and at a depth of 5 m. The Hg concentration was measured using a carbon electrode modified with EDTA, employing the CV method at an oxidation peak voltage of 10 mV/s for half a cycle. The Hg concentration in the samples from Desa Kajeng, Tutut, and Desa Tungkop, obtained using the linear regression equation, can be seen in Table 2. Additionally, for comparison, water samples were also tested using AAS. The Hg concentrations in the river water samples from Desa Kajeng, Tutut, and Desa Tungkop, taken from the edges and at a depth of 5 m, are shown in Table 3. A t-test was then conducted between the two methods. The critical t-value was determined by setting a 95% confidence interval and a significance level (α) of 5% (0.05). The t-test results at a 5% significance level showed that $t_{\text{calculated}} < t_{\text{table}}$ ($0.083 < 2.571$), indicating no significant difference between the two methods for measuring Hg concentration in river water.

■ CONCLUSION

The pyrolysis of the used tire waste yielded 3.06% of soot and 40.14% of charcoal. FTIR and SEM results show that carbon modified with EDTA is effectively bonded within the electrode, as indicated by the presence of C–N groups and the nearly octahedral crystals suggesting the presence of EDTA. The EDTA-modified electrode has a higher oxidation peak value compared to the carbon electrode's in a K₄Fe(CN)₆ solution containing 0.1 M KCl. The electrochemical response of the EDTA-modified carbon electrode in water provides a LoD of 0.03 ppm, LoQ of 0.08 ppm, a correlation coefficient of < 2%, and %recovery within the acceptable error range. Comparison tests between the voltammetric and AAS methods show

that no significant difference between both methods for measuring Hg concentration in river water.

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■ CONFLICT OF INTEREST

The authors declare no conflicts of interest.

■ AUTHOR CONTRIBUTIONS

Sukoma conducted the research and wrote the manuscript. Khairi Suhud and Sagir Alva discussed the research findings and revised the manuscript. Julinawati, Eka Safitri, Mustanir, Syafrizal Fonna, Ahmad Kamal Arifin, Meri Dayanti, Fitri Dara and Muhammad Ihsan revised the manuscript.

■ REFERENCES

- [1] Bernadus, G.E., Polii, B., and Rorong, J.A., 2021, Dampak merkuri terhadap lingkungan perairan sekitar lokasi pertambangan di Kecamatan Loloda Kabupaten Halmahera Barat Provinsi Maluku Utara, *Agri-SosioEkonomi Unsrat*, 17 (2), 599–610.
- [2] Sapari, S., Abdul Razak, N.H., Hasbullah, S.A., Heng, L.Y., Chong, K.F., and Tan, L.L., 2020, A regenerable screen-printed voltammetric Hg(II) ion sensor based on tris-thiourea organic chelating ligand grafted graphene nanomaterial, *J. Electroanal. Chem.*, 878 (12), 114670.

- [3] Jin Mei, C., and Alang Ahmad, S.A., 2021, A review on the determination heavy metals ions using calixarene-based electrochemical sensors, *Arabian J. Chem.*, 14 (9), 103303.
- [4] Siddiqui, S., Nafady, A., El-Sagher, H.M., Al-Saeedi, S.I., Alsalmeh, A.M., Sirajuddin, S., Talpur, F.N., Sherazi, S.T.H., Kalhor, M.S., Shah, M.R., Shaikh, T., Arain, M., and Bhargava, S.K., 2019, Sub-ppt level voltammetric sensor for Hg^{2+} detection based on nafion stabilized l-cysteine-capped Au-Ag core-shell nanoparticles, *J. Solid State Electrochem.*, 23 (7), 2073–2083.
- [5] Bayindir, S., 2019, A simple rhodanine-based fluorescent sensor for mercury and copper: The recognition of Hg^{2+} in aqueous solution, and $\text{Hg}^{2+}/\text{Cu}^{2+}$ in organic solvent, *J. Photochem. Photobiol.*, A, 372, 235–244.
- [6] Cheng, Y., Hao, Z., Hao, C., Deng, Y., Li, X., Li, K., and Zhao, Y., 2019, A review of modification of carbon electrode material in capacitive deionization, *RSC Adv.*, 9 (42), 24401–24419.
- [7] Kawde, A.N., 2017, Trace determination of $\text{Hg}(\text{II})$ in human saliva using disposable electrochemically pretreated graphite pencil electrode surfaces, *Acta Chim. Slov.*, 64 (2), 267–275.
- [8] Mahamane, A., Despas, C., Adamou, R., and Walcarius, A., 2022, Carbon paste electrode modified with 5-Br-PADAP as a new electrochemical sensor for the detection of inorganic mercury(II), *J. Mater. Environ. Sci.*, 13 (1), 54–69.
- [9] Zhu, W., Tang, J., and Huang, L., 2019, Ultra-sensitive electrochemical determination of mercury ions based on the dithizone modified electrode, *Int. J. Electrochem. Sci.*, 15 (1), 168–176.
- [10] Bowles, A.J., Nievas, A., and Fowler, G.D., 2023, Consecutive recovery of recovered carbon black and limonene from waste tires by thermal pyrolysis in a rotary kiln, *Sustainable Chem. Pharm.*, 32, 100972.
- [11] Ding, K., Zhou, L., Qu, R., Zhang, D., Chen, J., He, X., Wang, L., Wang, H., and Dou, H., 2020, Honeycomb-shaped carbon particles prepared from bicycle waste tires for anodes in lithium-ion batteries, *Mater. Chem. Phys.*, 251, 123202.
- [12] Baihaqi, B., Suhud, K., Alva, S., Safitri, E., Julinawati, J., Ginting, B., Fonna, S., Arifin, A.K., Zulnazri, Z., and Islami, N., 2023, Fabrication of mercury (Hg) sensor based on Tire Waste (TW) carbon electrode and voltammetry technique, *SINERGI*, 27 (3), 415–422.
- [13] Moutcine, A., and Chtaini, A., 2018, Electrochemical determination of trace mercury in water sample using EDTA-CPE modified electrode, *Sens. Bio-Sens. Res.*, 17, 30–35.
- [14] Touzara, S., Amlil, A., Ennachte, M., Smaini, M.A., and Chtaini, A., 2020, Development of carbon paste electrode/EDTA/polymer sensor for heavy metals detection, *Anal. Bioanal. Electrochem.*, 12 (5), 644–652.
- [15] Saenchoopa, A., Klangphukhie, S., Somsub, R., Talodthaisong, C., Patramanon, R., Daduang, J., Daduang, S., and Kulchat, S., 2021, A disposable electrochemical biosensor based on screen-printed carbon electrodes modified with silver nanowires/HPMC/chitosan/urease for the detection of mercury(II) in water, *Biosensors*, 11 (10), 351.
- [16] Al-wadei, M.J., Bakheit, A.H., Abdel-Aziz, A.A.M., and Wani, T.A., 2021, Betaxolol: A comprehensive profile, *Profiles Drug Subst., Excipients, Relat. Methodol.*, 46, 91–136.
- [17] Bharj, R.S., Bharj, J., and Vasistha, V., 2018, “Thermodynamics of Carbon Nanotubes and Soot Formation” in *Air Pollution and Control*, Eds. Sharma, N., Agarwal, A.K., Eastwood, P., Gupta, T., and Singh, A.P., Springer Singapore, Singapore, 143–151.
- [18] Mohammed, A., and Abdullah, A., 2018, Scanning Electron Microscopy (SEM): A review, *Proceedings of 2018 International Conference on Hydraulics and Pneumatics - HERVEX*, Băile Govora, Romania, 7–9 November 2018, 77–85.
- [19] Vasanthi Sridharan, N., and Mandal, B.K., 2022, Simultaneous quantitation of lead and cadmium on an EDTA reduced graphene oxide-modified glassy

- carbon electrode, *ACS Omega*, 7, 45469–45480.
- [20] Yang, Z., 2024, Voltammetry for quantitative determination of trace mercury ions in water via acetylene black modified carbon paste electrode, *Alexandria Eng. J.*, 87, 107–113.
- [21] Kasapoğlu, N., Baykal, A., Toprak, M.S., Köseoğlu, Y., and Bayrakdar, H., 2007, Synthesis and characterization of NiFe₂O₄ nano-octahedrons by EDTA-assisted hydrothermal method, *Turk. J. Chem.*, 31, 659–666.
- [22] Gong, Y., Chen, X., and Wu, W., 2024, Application of Fourier transform infrared (FTIR) spectroscopy in sample preparation: Material characterization and mechanism investigation, *Adv. Sample Prep.*, 11, 100122.
- [23] Tiwow, A.V., Rampe, J.M., Rampe, H.L., and Apita, A., 2021, Pola inframerah arang tempurung kelapa hasil pemurnian menggunakan asam, *Chem. Prog.*, 14 (2), 116–123.
- [24] Harvey, D., 2000, *Modern Analytical Chemistry*, McGraw-Hill, New York, US.
- [25] Taleuzzaman, M., 2018, Limit of blank (LOB), limit of detection (LOD), and limit of quantification (LOQ), *Org. Med. Chem. Int. J.*, 7 (5), 127–131.