

Curcumin Electropolymerization to Graphite Modification for Pb²⁺ Electrochemical Sensing

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ABSTRACT

Curcumin is an organic ligand that can be electrocatalytic. Curcumin can be coated on graphite electrodes to produce electrodes modified with curcumin (GPC). Curcumin acts as a ligand and forms complex compounds with metals. The modification process was carried out by electropolymerization. The electrochemical method characterized the electroactive area, electron transfer, and interaction between the electrode and Pb²⁺ metal ions. Functional groups and surface morphology were characterized using FTIR and SEM. Validation of analytical methods including linear range, sensitivity, limit of detection, limit of quantitation, precision, and accuracy. The interaction of the GPC electrode with Pb²⁺ follows the electrochemical adsorption process. The GPC electrode can identify the presence of Pb²⁺ metal ions with a range of 3.01-70.03 μM and 181-919.2 μM. The results of the analytical method validation include linear ranges of 3.125-67.400 μM and 179.334-919.5 μM; sensitivity of 3.3605 μA/μM; limit of detection of 6.07 μM; limit of quantitation of 18.39 μM; precision of 0.93%; and accuracy of 99%.

Keywords: curcumin, electropolymerization, graphite, Pb²⁺

1. INTRODUCTION

Environmental pollution is one of the factors causing environmental damage that will affect other living things. Many factors can cause ecological damage, one of which is caused by waste from industrial areas (Kurniawati et al., 2017). Industrial activities that are growing quite rapidly of course can also hurt the environment due to the presence of heavy metals contained in liquid waste discharged into the atmosphere, including ions of metals Pb²⁺, Hg²⁺, Cr³⁺, and Cd²⁺ (Khorasani et al., 2019).

One of the most common heavy metals with high toxicity is lead (Pb²⁺). Pb metal or commonly known as lead is one of the dangerous heavy metals. Water polluted with heavy metals can pose a health hazard. Lead that enters the human body will be adsorbed and accumulated in the body so that it can cause poisoning. Health problems caused by lead in the body include neurological disorders, impaired kidney function, reproductive system disorders, and nervous system disorders (Sullivan et al., 2013).

There are several methods of analyzing Pb²⁺ both conventionally and modernly analyzed Fe(II), Fe(III), Cr(VI), and Cr(III) in industrial wastewater using a combination method of UV-Vis spectrophotometry and atomic absorption spectrophotometry (AAS). The method of controlling the content of other heavy metal ions at low concentrations is to approach analytical methods that lead to sensors with high selectivity and sensitivity. Voltammetry is an appropriate method in metal sensors through electrochemical sensors (Pu et al., 2021).

Cyclic voltammetry is an electrochemical analysis technique with the advantages of simultaneous analyte measurement, low detection limits, low cost, simplicity, and practicality, making it suitable for analyzing Cd^{2+} , Pb^{2+} , and Cu^{2+} heavy metal ions (Sullivan et al., 2013). The working electrode significantly influences the performance of cyclic voltammetry. Graphite is a material with good electrical conductivity (10^4 S cm^{-1}), relatively high adsorption capacity, stability, heat resistance, minimal or no pretreatment, availability, low cost, and environmental friendliness (Chillawar et al., 2015). Despite these advantages, bare graphite electrodes still have low sensitivity due to high activation overpotential. Curcumin ($\text{C}_{21}\text{H}_{20}\text{O}_6$) possesses β -diketone groups and free electron pairs, which can act as ligands to form stable complexes with metal ions, making it a potential electrode modifier (Chillawar et al., 2015). The coating of curcumin on graphite electrodes can be achieved through electropolymerization, a technique for producing polymer films under the influence of an electric field, and this method has been successfully applied in the assembly of electrochemical sensors (Devadas et al., 2014). The presence of polycurcumin on graphite electrodes increases the number of active groups, which is expected to enhance the binding capacity for Pb^{2+} .

2. RESEARCH METHOD

To make graphite electrodes (GE), 30% silicone oil and 70% graphite powder were homogenized and mashed for approximately half an hour, or until the mixture was evenly moist. After smoothing it on tissue paper, the paste was pressed into the cavity of a 3 mm internal diameter Teflon tube. Electrical contact on the tube was made with copper wire tied at the end. After being deaerated with nitrogen for five minutes, 50 μM curcumin and 0.1 M BPS were electropolymerized at pH 7.0. Curcumin on the graphite electrode was electropolymerized using cyclic voltammetry at a potential of -1.0 to +1.0 V and a scan rate of 50 mVs⁻¹ for 24 cycles. Electropolymerization was performed using eQuadstat voltammetry (eDAQ Pty.Ltd., Australia) for electrochemical experiments, and Echem v2.1.0 software was used to operate it. Ag/AgCl as the comparison electrode, platinum electrode as the auxiliary electrode, and GE electrode as the working electrode.

Electrochemical characterization was carried out with $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ 1.0 mM in KCl 1.0 M current oxidation peak of the solution was carried out at a potential of -0.5 - +0.5 V with a wide variety of potential scan rates using a GPC electrode. Deposition time optimization was performed with 10 ml ABS pH 5.5 added with 100 μM Pb^{2+} using cyclic voltammetry technique using a GPC electrode at potential -1.0 - +1.0 V with various deposition time variations. pH optimization was also carried out with 10 μM of 10^{-2} M Pb^{2+} liquor at a potential of -1.0 - +1.0 V with various pH variations. Validation of the analytical method was carried out by measuring the oxidation peaks of standard solutions of metal ions at multiple concentrations, namely at concentrations of 0.30 μM - 953.21 μM using voltammetry set at a potential of -1.0 - +1.0 V with optimum deposition time, optimum pH, and optimum potential scan rate. FTIR and SEM were used to characterize the functional groups and surface morphology.

3. RESULTS AND ANALYSIS

3.1. Electrode Preparation Result

Graphite was chosen as the conductive material to supply the necessary electricity for electrical signal conduction in the sensor. Silicone oil was used as the non-conductive material to maintain mechanical consistency and resistance to the electrolytic working medium (Bojorge & Alhadef, 2011) (Bojorge dan Alhadef, 2011). The composition of graphite powder and silicone oil used in this study was 1.4 grams and 0.6 grams (7:3 w/w), a composition previously used in research for hydroquinone and catechol sensors (Chetankumar & Swamy, 2019) (Marwati, Trisunaryanti, et al., 2020). In this study, the graphite and silicone oil mixture formed a black paste that was easily molded into Teflon molds and did not easily break in liquid media.

3.2. Electropolymerization of Curcumin on GE Surface

The porous and rough surface of graphite allows curcumin to adhere strongly to the GE surface (Devadas et al., 2014) (Devadas *et al.*, 2014). This electropolymerization of curcumin increases the number of active groups on the GE surface, enhancing electron transfer activity as shown in Figure 1 by the increasing peak current response. The anodic peak current at -0.084 V represents the oxidation of curcumin, where the phenolic groups of curcumin are converted into phenolate ions. The reduction stage of curcumin, observed during the reverse scan at +0.07 V, corresponds to the removal of curcumin methoxy groups as methanol through hydrolysis, releasing an anion leading to the formation of highly reactive O-quinone compounds (Krishna Kumar et al., 2021). The oxidation peak shifts towards more positive and stable values after 24 scans, indicating that the polymerization saturation level has been achieved (Dey et al., 2021). This phenomenon has been reported by previous researchers for curcumin coating on graphite electrode surfaces (Krishna *et al.*, 2021), MnO₂-Graphene-Glassy carbon (Mejri et al., 2018), and glassy carbon (Devadas et al., 2014).

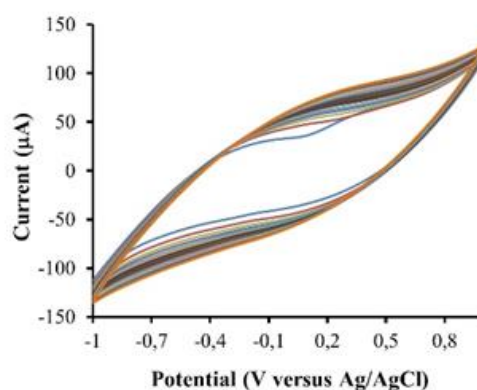


Figure 1. Cyclic Voltammogram of Curcumin Electropolymerization on GE over 24 Cycles

The mechanism of curcumin electropolymerization can be seen in Figure 2. Phenolic ions are formed from the enolic group of curcumin which participates in the initial oxidation process. The cathodic peak at +0.07 V represents the reduction of curcumin seen during the scan. By hydrolyzing curcumin, the methoxy group is lost to methanol, releasing the anion and producing the highly reactive O-quinone (Ziyatdinova et al., 2021).

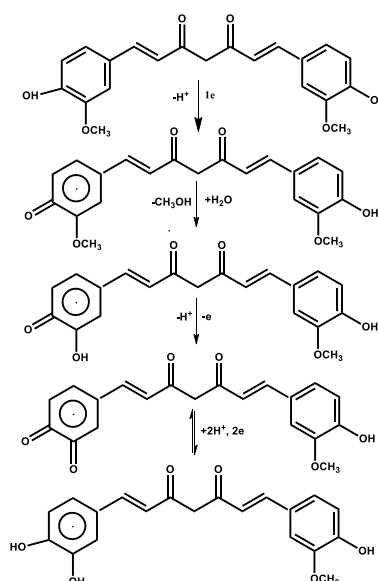


Figure 2. Electropolymerization of polycurcumin-modified electrodes and redox mechanism (Marwati et al., 2024)

3.2. A Feature of GPC

This characterization was carried out for the GE and GPC electrodes to compare by identifying the electron transfer rate with the cyclic voltammetry technique. Figure 3. presents the voltammograms of GE and GPC with a scan rate of 50 mVs^{-1} . The GE redox peak current response is smaller at peak separation ($-E_p$) at 0.336 V . In contrast, the GPC peak current response increases consistently at the same specific conditions and shows faster electron transfer kinetics compared to GE. Based on Figure 3, the ΔE_p of GPC is 0.260 V .

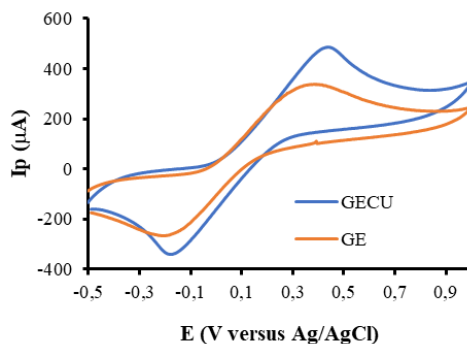


Figure 3. Voltammograms of GE and GPC at a solution of $1.0 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 1.0 M KCl with a scan rate of 50 mVs^{-1}

Electrochemical characterization was determined by identifying the electroactive area. The identification was done by measuring the oxidation peak current of $1.0 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ solution in 1.0 M KCl solution at various scan rate variations. The scanning rate was increased gradually at $25; 40; 50; 80; 100; 125;$ and 200 mVs^{-1} . Increasing the scan rate variation can increase the cathodic and anodic peak currents in GPC and the square root correlation of scan rate with peak current (I_p) can be seen in Figure 4.

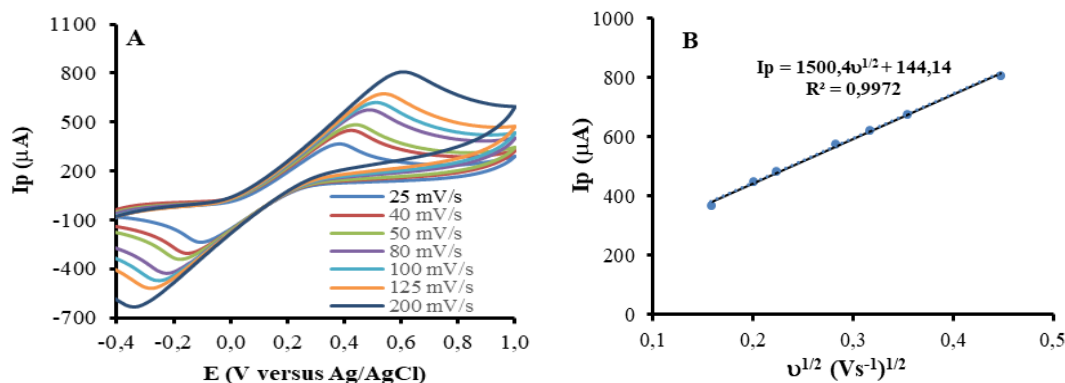


Figure 4. (A) Cyclic voltammogram of a solution of $1.0 \text{ mM } [\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 1.0 M KCl measured with GPC electrode at varying scan rate
(B) Linear correlation of I_p with square root of scan rate

Electrochemical characterization is determined by identifying the electroactive area. The electroactive area is one of the parameters that affect the sensitivity of the electrode (Guo et al., 2016). Figure 4(A) shows that the optimum current response occurs at the electropolymerized electrode with a potential scan rate of 200 mV s^{-1} . The magnitude of the potential scan rate affects the value of the potential difference between the oxidation and reduction peaks (ΔE) which will affect the speed of electron transfer (Marwati, Siswanta, et al., 2020). Figure 4(B) shows a linear curve between the square root of the scan rate and the peak current with an R^2 value of 0.9972 . From the correlation curve, $I_p = 1500.4v^{1/2} + 144.14$. Based on the Randles-Sevcik equation (equation 1) is obtained, then

the slope value in Figure 3(B) can be used to determine the electroactive area. The calculation results show that the electroactive area for GE is $0.43 \times 10^{-3} \text{ cm}^2$ and GPC is $2.004 \times 10^{-3} \text{ cm}^2$. The electroactive area of GPC is larger so the curcumin modified electrode is used for the next step of the research.

$$I_p = 2.699 \times 10^{-5} n^{3/2} D^{1/2} C_0 \nu^{1/2} \quad (1)$$

The characterization of functional groups with FTIR aims to confirm that the electropolymerization process of curcumin on the electrode surface has occurred and was successful. To facilitate the analysis, the GPC was chosen as the electrode to be characterized, illustrating the electropolymerization process of curcumin. The FTIR test results are shown in Figure 6. The FTIR analysis results indicate that the electropolymerization of curcumin leads to the formation of a sharper OH group absorption at 3448 cm^{-1} . The sharp absorption at 2924 cm^{-1} for GPC shows the C-H sp^3 stretching, demonstrating that the electropolymerization of curcumin results in the elongation of the carbon chain formed. The 1620 cm^{-1} absorption in GPC, which appears sharper and clearer, indicates aromatic C=C stretching, proving the presence of polycurcumin on the electrode. The $1095\text{--}1018 \text{ cm}^{-1}$ absorption, which only appears in the GPC spectra, represents moderate aromatic (aryl-O-CH₃) stretching, further supporting the presence of polycurcumin on the electrode.

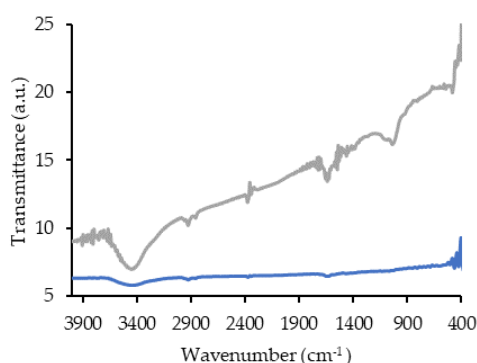


Figure 6. FTIR Spectra of GE (blue), and GPC (grey)

The surface morphology of GPC was analyzed using SEM at a magnification of 300 times, with GE used as a comparison. The surface morphology of each electrode is shown in Figure 7. The GPC surface exhibits a thicker and rougher coating compared to GE. The shiny appearance on both electrodes indicates the presence of silicone oil used as a paste-forming material.

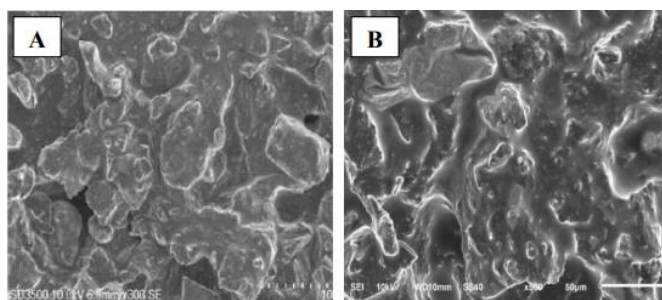


Figure 7. Surface Morphology: (A) GE and (B) GPC at 300x Magnification

3.3. Deposition Time and pH Optimization

To determine the optimum deposition time in the determination of Pb^{2+} sensor with GPC, cyclic voltammetry technique was performed using $100 \mu\text{M Pb}^{2+}$ solution in ABS pH 5.5 and GPC electrode at potential $-1.0 - +1.0 \text{ V}$. The deposition time variations were 30, 60, 90, 120, 150, 180, 200, and 220 seconds. Figure 8A. presents the correlation curve of deposition time with peak current.

Meanwhile, pH optimization was carried out by preparing 10 mL of ABS from each pH (3.5; 4.5; 5.5; 6; 7) added with 10 μM of 10^{-2} M Pb^{2+} liquor. Measurements were carried out using cyclic voltammetry technique using GPC electrodes at a potential of -1.0 - +1.0 V. The measurement process was carried out for each pH variation. The optimum deposition time that had been measured previously was 200 seconds. Correlation curve of pH with peak current is presented in Figure 8B.

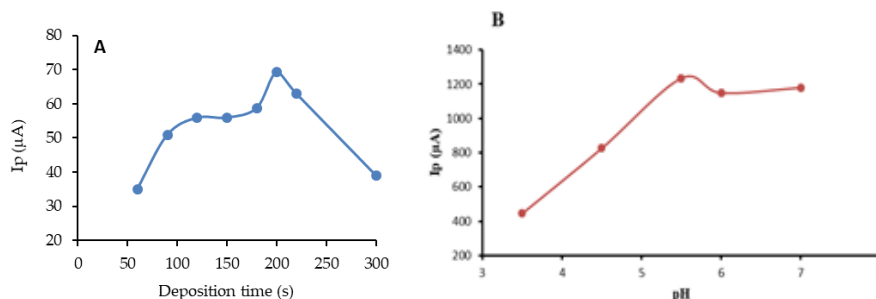


Figure 8. Correlation curve of (A) deposition time and (B) pH with peak current

3.5. Identification of GPC interactions with Pb^{2+}

The response of the Graphite Polycurcumin (GPC) can be seen by comparing the peak current detected between the GE electrode and the GPC. The solution used was 0.1 M ABS pH 5.5, added with 100 μM Pb^{2+} at a scan rate of 50 mVs^{-1} and a deposition time of 200 seconds. Figure 9 shows that GPC has a stronger sensitivity to Pb^{2+} compared to GE. The GE response is 380.24 μA while the GPC response is 1258.24 μA .

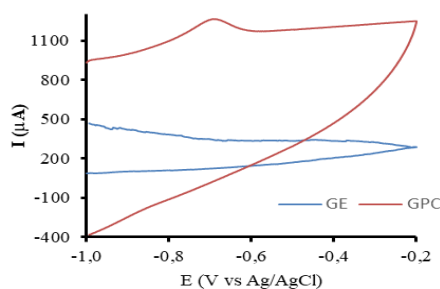


Figure 9. Cyclic voltammogram of 100 μM Pb^{2+} in ABS (pH 5.5) with GE and GPC

The scan rate variation treatment was performed using 100 μM Pb^{2+} standard solution in ABS pH 5.5. Measurements were carried out using cyclic voltammetry technique at -1.0 - +1.0 V potential at various potential scan rate variations (20; 25; 40; 50; 80; 100; 125; 200 mVs^{-1}). Figure 9. shows the effect of scan rate on the current generated. Figure 9. shows that the higher sensitivity of GPC is due to the number of active sites in Pb^{2+} binding. Peak separation is very visible in GPC, this indicates that modification with polycurcumin successfully accelerates electron transfer and increases the number of active binding sites so that it is more sensitive to the presence of Pb^{2+} metal (Devadas *et al*, 2014).

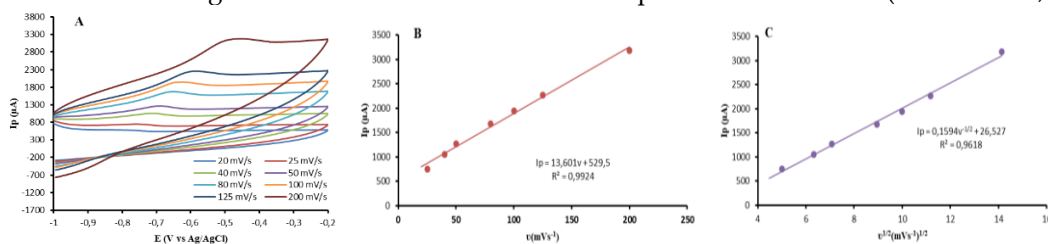


Figure 10. (A) Voltammogram of 100 μM Pb^{2+} in ABS pH 5.5 with varying scan rate; (B) Correlation of peak current with scan rate (C) Correlation of peak current with square root of scan rate

Figure 10(A) shows that the peak current at the scan rate increases as the scan rate increases. The peak current increased significantly at a scan rate of 200 mVs^{-1} with a peak current read at $3179.8 \mu\text{A}$. From the treatment of scan rate variation can provide information about the interaction between Pb^{2+} with GPC. The experimental results on the GPC follow the Randles-Sevcik equation which is shown from the linear equation of the peak current correlation graph with the scan rate in Figure 10(B), $I_p = 13,601v + 529,5 (\mu\text{A}, \text{mVs}^{-1}, R^2 = 0,9924)$. While Figure 10(C) shows the regression equation of the correlation between the peak current and the square root of the scan rate, $I_p = 0,1594v^{1/2} + 26,527 (\mu\text{A}, (\text{mVs}^{-1})^{1/2}, R^2 = 0,9618)$. Figure 5(B) has a higher coefficient of determination (R^2) than Figure 10(C), meaning that the peak current read is more linear with the scan rate than the square root of the scan rate. Therefore, the interaction of the GPC electrode with Pb^{2+} is indicated to be dominated by the electrochemical process of adsorption (Elgrishi et al., 2018).

3.6. Validation of Pb^{2+} Concentration Measurement with GPC

Validation was carried out by measuring the peak oxidation current of standard solutions of metal ions at various concentration variations, namely at concentrations of $0.3 \mu\text{M} - 953.21 \mu\text{M}$. Measurements were carried out by cyclic voltammetry technique using electrode modification as GPC working electrode. Voltammetry was set at $-1.0 - +1.0 \text{ V}$ potential with optimum deposition time (200s), optimum pH (5.5), and optimum potential scan rate (50 mVs^{-1}). Figure 11 presents the results of the voltammogram of Pb^{2+} concentration variation and the correlation graph between Pb^{2+} concentration and peak current.

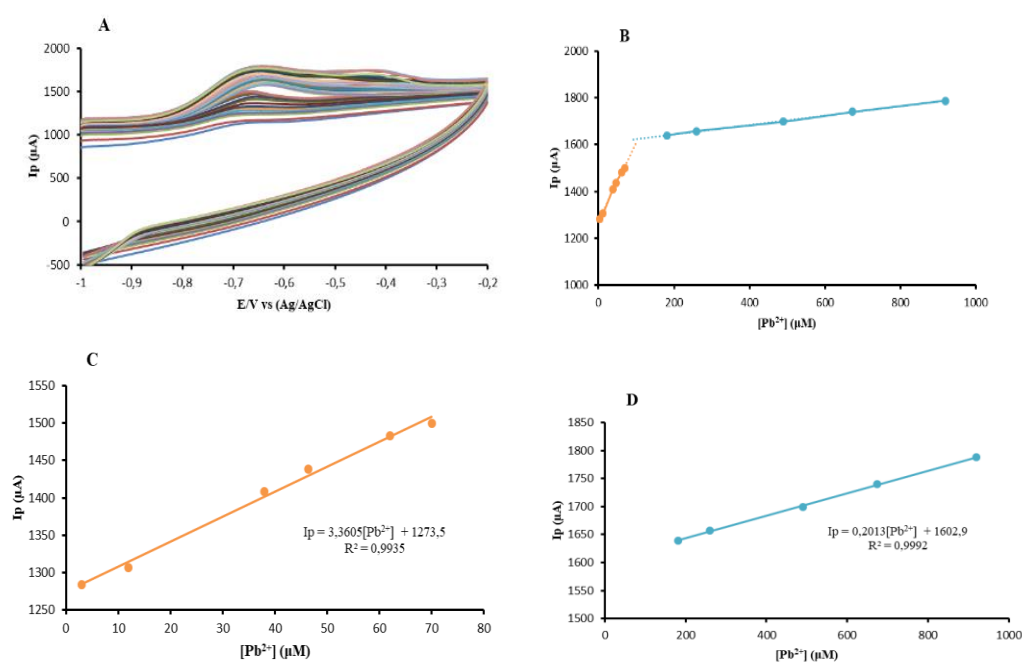


Figure 11. (A) Voltammograms of Pb^{2+} at various concentrations ($0.3 \mu\text{M} - 953.21 \mu\text{M}$) in ABS pH 5.5 by GPC at a scan rate of 50 mVs^{-1} (B) Correlation of Pb^{2+} concentration with peak current in the range of $3.01-919.2 \mu\text{M}$, (C) $3.01-70.03 \mu\text{M}$, and (D) $181-919.2 \mu\text{M}$

The results of method validation in the measurement of Pb^{2+} with GPC can be written in Table 1.

Table 1. Comparison data between acceptance criteria and validation results of Pb²⁺ analysis method with GPC by voltammetry

Validation Parameter	Measured Value	Value	Criteria for Acceptance
Linearity	R ²	0,9992	✓
Linear range	[Pb ²⁺]	3,125 – 67,400 μM 179,334 - 919,5 μM	✓
Sensitivity	<i>gradient</i>	3,3605 μA/μM	✓
Akuration	<i>%Recovery</i>	99%	✓
Precision	<i>%RSD</i>	0,93%	✓
LoD	LoD	6,07μM	✓
LoQ	LoQ	18,39μM	✓

CONCLUSION

Based on this research, it can be concluded that kukumin can be used as a modification for graphite electrodes by improving the response to be better. This modification enhances electron transfer quality, increases the electroactive surface area, and produces impressive analytical results for Pb²⁺. The process of metal ion identification electropolymerization showed positive results and was sensitive and easy to perform. The research method is well validated so that it can be developed for metal ion sensor applications.

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