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Rahmi Wahyuni
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Padang, Indonesia, rahmiwahyuniz08@gmail.com

Trisna Kumala Sari
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Padang, Indonesia, trisna.kumala.s@fmipa.unp.ac.id

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RESEARCH ARTICLE

A Novel Electrochemical Sensor Based on A Pencil Graphite Electrode Modified MnO_2 for Detection of Pb^{2+} Metal Ion in Water Samples

Rahmi Wahyuni, Trisna Kumala Sari *

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Padang, Padang, Indonesia

ABSTRACT

This research aims to develop an ion Pb^{2+} sensor and determine the optimal conditions for testing Pb^{2+} ions using an MnO_2/PGE modified electrode with the voltammetric method. In this study, the Pencil Graphite Electrode (PGE) was modified using MnO_2 through drop-casting. Next, the optimization of the electrode was carried out by varying the supporting electrolyte type, voltammetric technique, and supporting electrolyte concentration. The results showed that the modified electrode (MnO_2/PGE) provided a better response for Pb^{2+} detection compared to the unmodified electrode (PGE). The optimal experimental conditions were found to be 0.1 M HCl as a supporting electrolyte, combined with the Square Wave Voltammetry (SWV) technique. The measurement of Pb^{2+} ions using MnO_2/PGE under optimum conditions yielded a correlation coefficient (R^2) of 0.9846 and a detection limit of 1.91 ppm, with an RSD value of ± 2.51%, indicating high sensitivity, selectivity, stability, and accuracy in the measurement of Pb^{2+} metal ions.

Keywords: Analytical chemistry, Heavy metal detection, Lead ion analysis, Modified electrode, Square wave voltammetry

Introduction

The levels of heavy metals in the water, especially lead (Pb), have increased due to the rising industrial activity around the water area.[1] Lead ions (Pb^{2+}) are heavy metals that are hazardous to health and the environment[2] because they are carcinogenic, cause gene mutations, are difficult to degrade, and have a high toxicity level.[3] Excessive exposure to heavy metal ions in humans can cause kidney and liver damage, digestive problems, and anemia[4]. The source of the Pb^{2+} metal ion pollutant comes from the combustion of fossil fuels, mining, paint and ceramic products, coal, mineral fertilizers, and battery production.[5] According to the World Health Organization (WHO), the provisional guideline for lead (Pb) in drinking water is 10μg/L (0.01mg/L), retained for practical reasons despite no longer being health-based, as even low-level exposure poses significant health risks.[6]

Generally, the testing of Pb (lead) metal ions is conducted using instruments such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Atomic Absorption Spectroscopy (AAS), and electrochemical methods.[7] An alternative method that can be used is the electrochemical method. This method provides high sensitivity, is inexpensive, and easy to apply for detecting heavy metals.[8] The voltammetric method is an electrochemical technique that will be used in this research, with the advantages of rapid analysis and the ability to measure low concentrations. In previous research, carbon-based electrodes were widely developed as sensors for determining Pb^{2+} metal ions, such as the rGO/g-C_3N_4 modified GCE,[9] the CPE modified lignin biopolymer,[10] and the SPCE modified

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* Corresponding author.
E-mail addresses: rahmiwahyuniz08@gmail.com (R. Wahyuni), trisna.kumala.s@fmipa.unp.ac.id (T. K. Sari).

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CuF/MWCNTs/SPCE.[11] In this study, the Pencil Graphite Electrode (PGE) is used as an electrode with the advantage of high conductivity,[12] being cheap, practical, easy to clean, and easy to modify.[13] In addition, the usage process is quick without complicated polishing procedures, and it has strong adsorption properties and low background current, as well as a wide potential range.[12] To improve the sensitivity, selectivity, and stability of electrode performance in electrochemical analysis, modifications to the electrode surface are necessary.[14] Modification of PGE in previous research includes: PGE modified with Bismuth-film,[15] PGE modified with gold thin film,[16] and PGE modified with silver thin films.[17] The modification made in this study uses manganese dioxide. MnO_2 is often used in catalysis and electrochemical sensor applications due to its high specific capacitance, good catalytic properties, non-toxicity, and affordability compared to nickel oxide, ruthenium oxide, cobalt oxide, and cerium oxide.[18] MnO_2 was chosen to modify the pencil graphite electrode (PGE) due to its good adsorption capacity for the target analyte, high surface area, and fast electron transfer kinetics.[19]

In this study, for the first time, research was conducted on an electrochemical sensor based on a MnO_2 modified pencil graphite electrode to detect Pb^{2+} metal ions in water samples. The modification of the PGE using manganese dioxide was carried out using the drop-casting method. The modification of PGE with MnO_2 using the drop-casting method offers significant advantages for electrochemical analysis. MnO_2 provides a high surface area and porous structure, which enhances the adsorption of target metal ions and facilitates electron transfer, leading to increased current response. This is in line with previous studies showing that electrochemical techniques are highly sensitive, cost-effective, and suitable for in-field applications due to their rapid response and miniaturization potential.[20]

Materials and methods

This research uses various chemicals, including $Pb(NO_3)_2$ (Smart-Lab, Surabaya, Indonesia), $K_3[Fe(CN)_6]$ (Pudak scientific, Bandung, Indonesia), KNO_3 (Merck, Darmstadt, Germany), HNO_3 (Merck, Darmstadt, Germany), $HClO_4$ (Merck, Darmstadt, Germany), HCl (Merck, Darmstadt, Germany), H_2SO_4 (Merck, Darmstadt, Germany), MnO_2 (Merck, Darmstadt, Germany), Whatman filter paper (Cytiva, Little Chalfont, UK), and aquades (locally prepared). The electrochemical measurement process uses the e-Daq potentiostat with a three-electrode system consisting of Ag/AgCl as the reference electrode, platinum wire as the auxiliary electrode, and Kokuyo Pencil Graphite Electrode (PGE) (0.9 mm, 2B) as the working electrode. Using Analytic Jena SPECORD 210 PLUS brand UV-Vis DRS for the characterization of MnO_2 dispersion as well as Using PerkinElmer/frountier Optica brand FTIR and using PanAlytical brand XRD which are useful in the characterization of electrode surfaces.

Preparation of MnO_2 dispersion

The MnO_2 dispersion was made at a concentration of 0.1 M by weighing 0.4347 grams of solid MnO_2 and then adding it to a beaker with H_2SO_4 p.a. at room temperature. The purpose of adding H_2SO_4 p.a. is to accelerate the dispersion of MnO_2. It was then poured into a 50 mL volumetric flask and diluted with distilled water up to the mark. Then it was sonicated for 15 minutes, the 0.1 M MnO_2 dispersion is ready to use.

Preparation of pencil graphite electrode with manganese dioxide modification (MnO_2/PGE)

The preparation of PGE using MnO_2 was done by drop-casting, which involves dropping 5 μL of MnO_2 0.1 M (8.7 mg/mL) onto the surface of PGE and then drying it for 1 hour at room temperature. Qualitatively, the success of the modification is indicated by the change in the color of the electrode surface, which originally had the characteristic gray color of graphite, turning deep black after the addition and drying of the MnO_2 solution. This electrode is represented as a Manganese Dioxide-Modified PGE (MnO_2/PGE).

Characterization of non-modified electrode (PGE) and modified electrode (MnO_2/PGE) with $K_3[Fe(CN)_6]$ using the cyclic voltammetry (CV) method

Electrochemical measurements of the PGE and MnO_2/PGE electrodes against a 2 mM $K_3[Fe(CN)_6]$ solution in a 0.1 M KNO_3 solution using the cyclic voltammetry method. The measurements were conducted by applying a scan rate of 100 mV/s, with a potential scan from +0.65 to –0.2 V.

Characterization of non-modified electrode (PGE) and modified electrode (MnO_2/PGE) with Pb^{2+} ions using cyclic voltammetry (CV) method

Electrochemical measurements of the PGE and MnO_2/PGE electrodes against a 1 mM Pb^{2+} ion

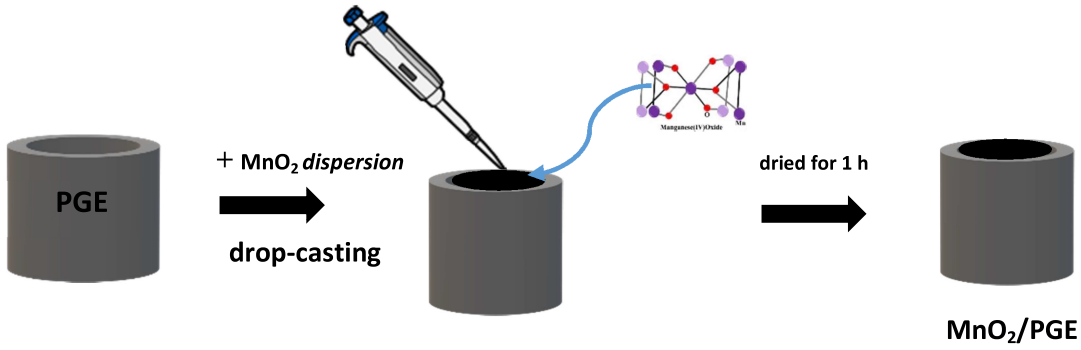

Fig. 1. Illustration of the modification of Pencil Graphite Electrode using manganese dioxide.

analytical solution in a supporting electrolyte solution using the cyclic voltammetry method. The measurements were conducted by applying a scan rate of 100 mV/s and a potential scan from 0 to –0.7 V.

Optimization of MnO_2/PGE electrode as a Pb(II) metal ion sensor.

Variations of supporting electrolytes

The measurement was conducted by varying the electrolyte solution in the electrochemical cell, namely HNO_3 0.1 M, $HClO_4$ 0.1 M, HCl 0.1 M, and H_2SO_4 0.1 M in a Pb^{2+} 1 mM test solution. The measurement was conducted using the CV method by setting the potential scan from 0 to –0.7 V and a scan rate of 100 mV/s.

Variations of voltammetric techniques (DPV, LSV, and SWV)

The measurements were conducted by varying the voltammetry technique models, namely: Differential Pulse Voltammetry (DPV), Linear Sweep Voltammetry (LSV), and Square Wave Voltammetry (SWV) in an optimum supporting electrolyte solution containing a 1 mM Pb^{2+} test solution. Then the potential scan was set from 0 V to –0.7 V and the scan rate to 100 mV/s.

Variation in the concentration of the supporting electrolyte solution

The measurements were conducted under optimal conditions of the supporting electrolyte and the voltammetry technique model by varying the concentration of the supporting electrolyte solution at optimal concentrations of 0.1 M; 0.01 M; 0.001 M, which were measured alternately in the Pb^{2+} 1 mM test solution. Then the potential scan was set from 0 V to –0.7 V, with a scan rate of 100 mV/s.

Results and discussion

Electrode modification using MnO_2 dispersion

The preparation of the MnO_2/PGE (Manganese Dioxide/Pencil Graphite Electrode) modified electrode is illustrated in Fig. 1.

The preparation of the MnO_2/PGE (Manganese Dioxide/Pencil Graphite Electrode) modified electrode begins with polishing the surface of the pencil graphite electrode (PGE) using filter paper. This step aims to remove impurities and expose the active surface of the electrode. Polishing facilitates better adhesion of the MnO_2 material to the electrode surface.

After polishing, the electrode is rinsed with distilled water to eliminate any remaining particles or contaminants. Then, 5 μL of 0.1 M MnO_2 dispersion is carefully applied onto the active surface of the PGE. MnO_2 serves as a modifying material with high electrocatalytic properties, which can enhance the performance of the electrode in detecting heavy metal ions.

The electrode is then left to dry at room temperature for one hour. This drying step is essential to ensure that the MnO_2 adheres firmly and forms a layer on the electrode surface. After the drying process, the MnO_2/PGE electrode is ready to be used in electrochemical analysis, specifically in this study for the detection of Pb^{2+} ions using voltammetric techniques.

Characterization of MnO_2 dispersion using UV-Vis DRS

The purpose of this characterization is to determine the optical properties, specifically to calculate the optical band gap energy (Eg) of the material. [21]

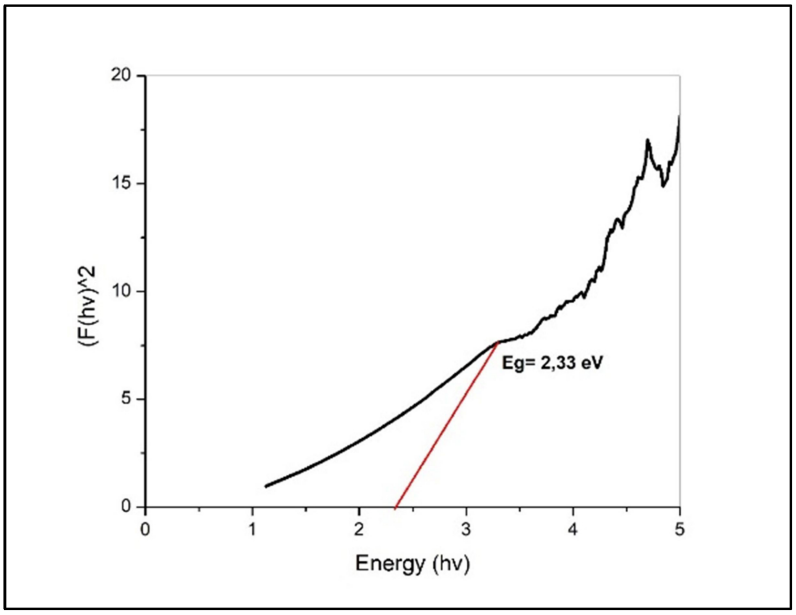

Fig. 2. Characterization results of MnO_2 dispersion using UV-Vis DRS.

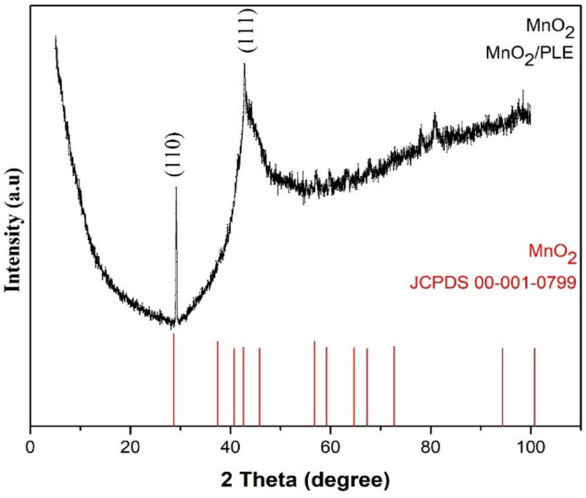

Fig. 3. Characterization results of MnO_2/PGE using XRD.

Based on Fig. 2, the band gap energy of dispersed MnO_2 is obtained as 2.33 eV. The band gap energy is in the range of 2.2–2.3 eV, which according to [22] is the band gap range of MnO_2.

Characterization of MnO_2/PGE using XRD

The characterization of the MnO_2/PGE surface was performed using XRD to confirm the presence of MnO_2 and verify the structure of its crystal phase. This analysis aims to ensure that MnO_2 is indeed deposited on the surface of the electrode.

Based on Fig. 3, the diffraction peaks of MnO_2 are detected at 2θ: 28.6° and 42.6°. The Miller indices for the MnO_2 diffraction peaks at $2\theta = 28.6°$ are (1,1,0), and for $2\theta = 42.6°$ are (2,0,0), in accordance with the standard diffraction pattern of ϵ- MnO_2 (JCPDS card 00-001-0799), which has a tetragonal structure. This indicates that MnO_2 has been effectively deposited on the surface of the PGE.

Next, the average crystal size is calculated using the Debye Scherrer equation, which is:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Note:

D = crystal size (nm)
K = crystal shape factor (0.9–1)
λ = wavelength of X-ray (0.15406 nm)
β = the value of Full Width at Half Maximum (FWHM) (rad)
θ = diffraction angle (degrees)

The result of the calculation based on the equation above yields an average crystal size D (nm) of 17.850 nm. [23]

Characterization of MnO_2/PGE using FTIR

FTIR is performed as a confirmation step that the active material (MnO_2) is indeed present on the electrode surface, with the aim of identifying the characteristic Mn–O chemical bonds and verifying the presence of MnO_2 on the electrode. [24]

Based on the FTIR characterization results of the PLE electrode modified with MnO_2 in Fig. 4,

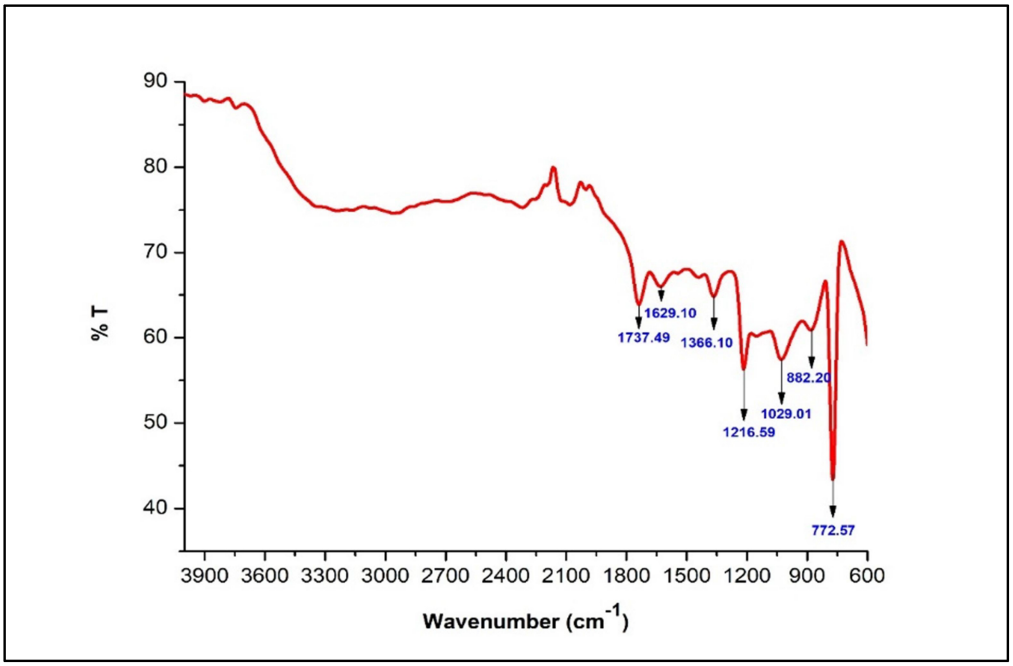

Fig. 4. Characterization results of MnO_2/PGE using FTIR.

absorption peaks were found at wave numbers 772.57 cm^{-1} and 882.20 cm^{-1}. Both peaks are within the range of 511–954 cm^{-1}, which according to[25] is a characteristic region for the vibration of the Mn–O bond in the MnO_2 structure. At the absorption peaks of 772.57 cm^{-1} and 882.20 cm^{-1}, they reflect the asymmetric stretching vibration of Mn–O in the octahedral [MnO_6] structure of MnO_2.[26] The presence of these peaks indicates that MnO_2 has successfully bound to the electrode surface and maintained the appropriate chemical structure.

Characterization of PGE and MnO_2/PGE electrodes towards $K_3[Fe(CN)_6]$

The cyclic voltammetry method can provide information in the form of the redox response of $[Fe(CN)_6)]^{-3/-4}$. The purpose of this characterization is to observe the performance of the PGE and MnO_2/PGE electrodes to see if both electrodes can respond well. Fig. 5 shows a comparison of the measurement results of PGE and MnO_2/PGE against $[Fe(CN)_6)]^{-3/-4}$.

The cyclic voltammetry (CV) on both electrodes is quasi-reversible for the redox $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (Ep_a–Ep_c) PGE at 0.274 V and MnO_2/PGE at 0.1009 V. The Ip_a value of PGE in this study was obtained as 12.151 mA and Ep_a 0.3315 V, Ip_c –15.071 mA and Ep_c 0.0575 V. Meanwhile, on MnO_2/PGE, the Ip_a obtained in this study was 20.1324 mA and Ep_a 0.2696 V, Ip_a –26.8546 mA, Ip_c 94.27, and Ep_c 0.1687 V. The effective surface area of the MnO_2/PGE electrode compared to the PGE

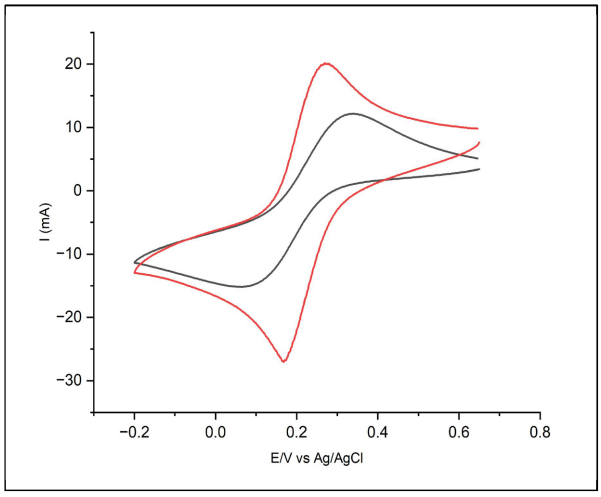

Fig. 5. Cyclic voltammogram obtained using the cyclic voltammetry (CV) in 2 mM $[Fe(CN)_6)]^{-3/-4}$ and 0.1 M KNO_3 at a scan rate of 100 mV/s by PGE (black) and MnO_2/PGE (red).

electrode was studied using cyclic voltammetry in 2 mM $K_3[Fe(CN)_6]$. The well-defined reduction and oxidation peaks were observed at +0.65 V to –0.2 V. MnO_2/PGE shows a high electroactive area based on the Randles-Servik equation:

$$I_p = 2,69 \times 10^5 AD^{1/2}n^{3/2}v^{3/2}C$$

Where Ip is the peak current, n is the number of electrons transferred (n = 1), A is the electrochemical surface area or effective surface area, D is the diffusion coefficient of $[Fe(CN)_6]^{3-}$ taken as

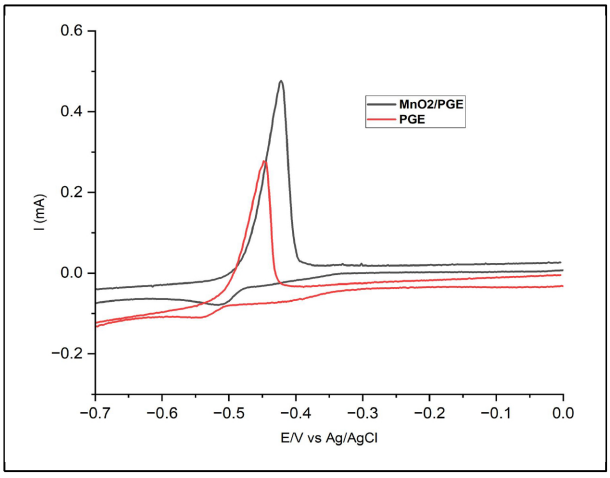

Fig. 6. Cyclic voltammogram obtained using the cyclic voltammetry (CV) method for Pb^{2+} 1 mM ions in 0.1 M HCl at a scan rate of 100 mV/s by PGE and MnO_2/PGE.

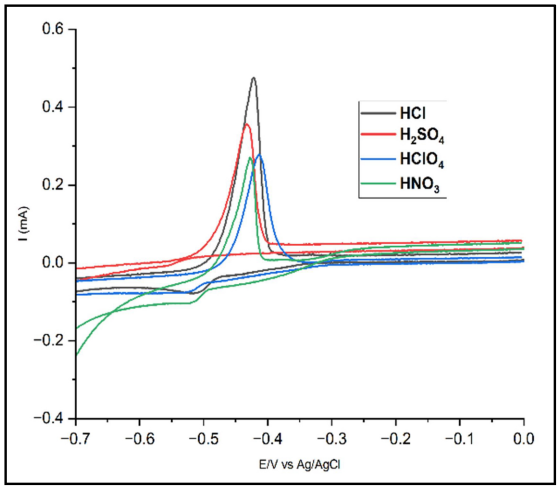

Fig. 7. Cyclic voltammogram obtained using the cyclic voltammetry (CV) method for Pb^{2+} 1 mM ions with variations of supporting electrolyte HCl 0.1 M; H_2SO_4 0.1 M; $HClO_4$ 0.1 M;HNO_3 0.1 M with a scan rate of 100 mV/s by MnO_2/PGE.

$6.057 \times 10–6\ cm^2s^{-1}$, v is the scan rate ($Vs^{-1}$). 0.1 V/s and C is the concentration (mol cm^{-3}). The surface area of PGE and MnO_2/PGE is 0.29 cm^2 and 0.88 cm^2, respectively, with a Faraday current of 96485.34 C mol^{-1}.

Based on Fig. 5, the resulting cyclic voltammogram shows that the performance of MnO_2/PGE is better than PGE against $K_3[Fe(CN)_6)]^{-3/-4}$, as seen from the higher surface area value and smaller ΔEp on MnO_2/PGE compared to PGE. This can occur because the use of manganese dioxide (MnO_2) to modify the electrode can enhance detection performance by expanding the active surface area. This allows more sites to participate in the electrochemical reaction, ultimately resulting in a higher current peak. [19]

The redox reaction that occurs in Fig. 5 is as follows.

i. Reduction: $[Fe(CN)_6)]^{-3} + e^- \rightarrow [Fe(CN)_6)]^{-4}$
ii. Oxidation: $[Fe(CN)_6)]^{-4} \rightarrow [Fe(CN)_6)]^{-3} + e^-$

Characterization of PGE and MnO_2/PGE towards Pb^{2+} ions

Characterization using cyclic voltammetry aims to obtain information on the reduction and oxidation potential of Pb^{2+} ions. Characterization was carried out using a 0.1 M HCl solution against 1 mM Pb^{2+} ions with a scanning potential from 0 to –0.7 V at a scan rate of 100 mV/s. The results of this characterization can be seen in Fig. 6.

Based on the voltammogram in Fig. 6, MnO_2/PGE shows better electrode performance compared to PGE in detecting Pb^{2+} metal ions. The oxidation peak of Pb^{2+} ions is detected at a potential of around –0.44 V on the PGE electrode, while on the MnO_2/PGE electrode, the peak appears at a potential of –0.42 V. This peak can be confirmed as the peak for Pb^{2+} because it aligns with previous research stating that the oxidation peak of Pb^{2+} ions usually appears within the potential range of –0.48 to –0.20 V. [27] The increase in detection current that occurs on the MnO_2/PGE electrode can be explained by the larger surface area of the electrode, [19] and the electrocatalytic effect of MnO_2 on Pb^{2+} metal ions. [28] The redox reaction that occurs is as follows.

$$\text{Reduction}: \quad Pb^{2+}_{(aq)} + 2e^- -> Pb_{(s)}$$

$$\text{Oxidation}: \quad Pb_{(s)} -> Pb^{2+}_{(aq)} + 2e^-$$

Optimization of MnO_2/PGE electrode as a Pb(II) metal ion sensor.

Variations in supporting electrolyte

This supporting electrolyte functions as a medium to balance the charge in the solution. Without sufficient electrolytes to achieve charge balance, the solution will experience resistance to charge transfer. Supporting electrolytes can be in the form of acidic, basic, or neutral solutions. [29] In this study, the variations of the supporting electrolyte used include 0.1 M $HClO_4$; 0.1 M HNO_3; 0.1 M HCl; and 0.1 M H_2SO_4, which have been mixed with a 1 mM Pb^{2+} solution. The scanning was conducted over a potential range from 0 V to –0.7 V with a scan rate of 100 mV/s. The results of this variation optimization can be seen in Fig. 7.

Supporting electrolyte plays a very important role in the mobility of ions to conduct electricity. This is due to the ionization ability of the supporting electrolyte solution; the better the ionization of a solution, the more effective its ability to conduct electric current. [30] Based on the cyclic voltammogram shown in Fig. 7, the 0.1 M HCl solution is the most

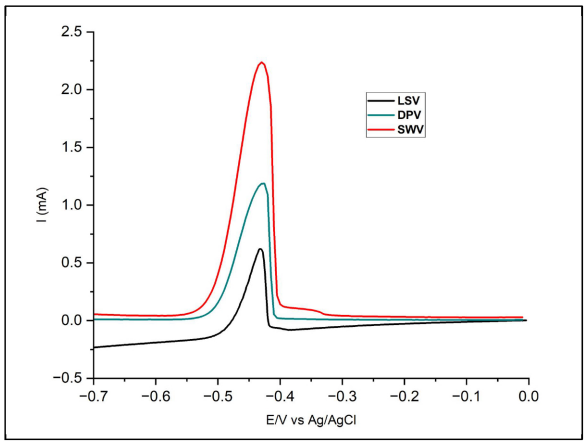

Fig. 8. Variation of voltammetric technique models in variation: SWV, LSV, and DPV in 1 mM Pb^{2+} ion solution with a scan rate of 100 mV/s.

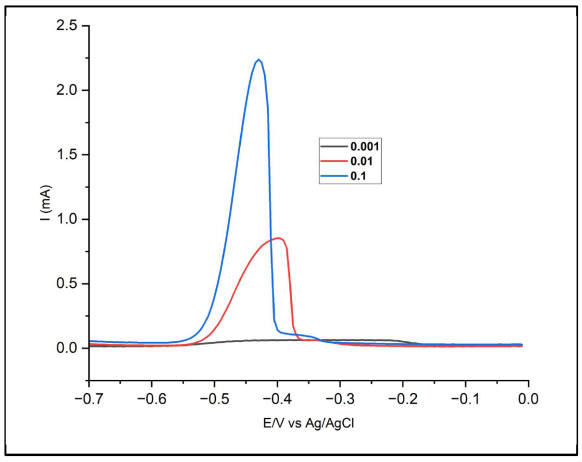

Fig. 9. SWV voltammogram with varying concentrations of supporting electrolyte in 1 mM Pb^{2+} ion solution with a scan rate of 100 mV/s.

optimal supporting electrolyte for detecting Pb^{2+} ions, with a recorded current of 0.4764 mA at a potential of –0.422 V. This is likely influenced by the diffusion rate in HCl, which is better compared to HNO_3, H_2SO_4, and $HClO_4$.[31]

Variations of voltammetry techniques (DPV, LSV, and SWV)

The goal of varying voltammetry technique models is to find the most sensitive method for detecting and measuring the concentration of a specific analyte. In this study, three voltammetry techniques were used: Linear Sweep Voltammetry (LSV), Differential Pulse Voltammetry (DPV), and Square Wave Voltammetry (SWV). The measurement results can be seen in Fig. 8.

Based on the voltammogram obtained in Fig. 8, the Square Wave Voltammetry (SWV) technique produced the highest current peak, which was 2.238 mA, while the Differential Pulse Voltammetry (DPV) technique showed a lower current of 1.187 mA. Meanwhile, the Linear Sweep Voltammetry (LSV) technique showed 0.622 mA. This indicates that SWV is the most sensitive voltammetry method compared to the others in detecting and measuring the concentration of Pb^{2+} ions used in this study.

The advantages of SWV are, first, that SWV applies a more efficient measurement method, where the current is measured at the end of each pulse, thereby reducing interference from non-Faradaic currents. In addition, the shorter measurement time in SWV also contributes to reducing the charging current. SWV also provides a better response on the electrodes used and functions more effectively in ionic liquids, which supports the oxidation reaction process.[32]

Variation in the concentration of the supporting electrolyte solution

The variation in the concentration of the supporting electrolyte is related to the strength of ion mobility in conducting electric current. In this study, variations in the concentration of the supporting electrolyte were conducted on a 1 mM Pb^{2+} solution in HCl solution with concentration variations of 0.1 M; 0.01 M; 0.001 M. The measurement was conducted using the SWV method at a scan potential of 0 V to –0.7 V with a scan rate of 100 mV/s. The results of this measurement are shown in Fig. 9.

Based on the voltammogram obtained in Fig. 9, 0.1 M HCl solution is the most optimal condition for detecting Pb^{2+} ions. This is evident from the highest current response, which reached 2.238 mA. Meanwhile, at a concentration of 0.01 M HCl, the current obtained was 0.852 mA, and at a concentration of 0.001 M HCl, the current decreased to 0.060 mA. This is because the higher the concentration of the supporting electrolyte, the higher the conductivity.[29]

Calibration curve

The calibration curve is created to evaluate the extent of linearity of the analytical method used. In this study, the calibration curve was performed using the SWV method under optimal conditions. In Fig. 10, it shows the voltammogram and the linearity of Pb^{2+} measurement at several concentrations. This data shows that the higher the concentration of heavy metals accumulated on the electrode surface, the greater the measured oxidation current.[33] As concentration rises, more electroactive analyte ions are reduced or deposited at the working electrode as a

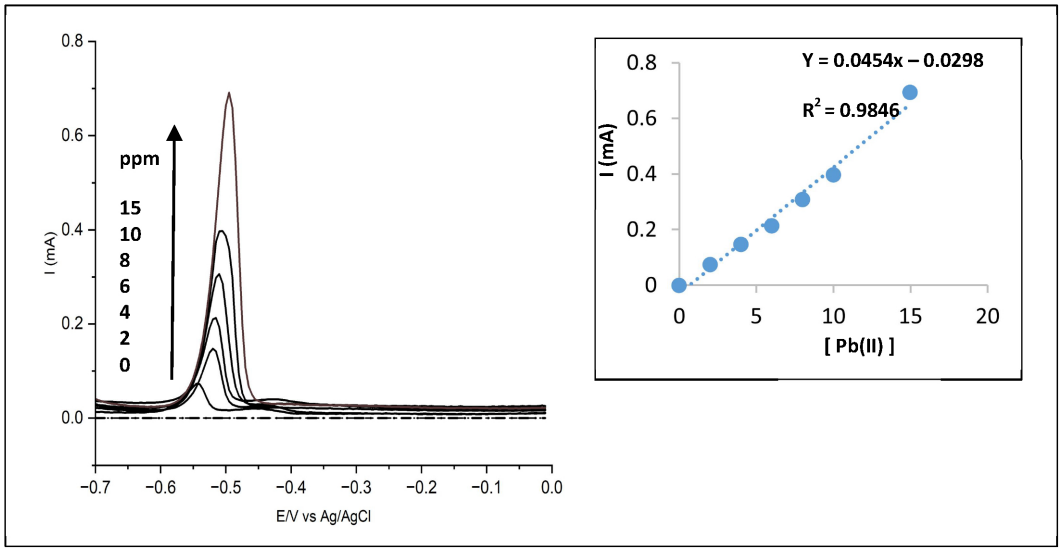

Fig. 10. SWV responses on MnO_2/PGE in 0.1 M HCl with varying concentrations of Pb^{2+} metal ions. The inset is the calibration curve.

result of rising diffusion currents, which causes the current response to rise as well.[34]

This is consistent with Fig. 10, which shows that as the concentration of Pb^{2+} ions increases, the detected current also increases. Based on the data, the regression equation y = 0.0454x–0.0298 was obtained with a correlation coefficient (R^2) of the calibration curve being 0.9846 and an LOD value of 1.91 ppm.

The limit of detection (LOD) was calculated based on the linear regression equation of the calibration curve, Y = 0.0454x–0.0298, with a standard deviation (S) of 0.028955. The LOD was determined using the formula:

$$\mathrm{LOD} = \frac{3 \times S}{M}$$

where M is the slope of the calibration curve (0.0454). From this calculation, the LOD obtained was 1.91 ppm, indicating good sensitivity of the modified electrode for Pb^{2+} detection at low concentrations.

The use of manganese dioxide (MnO_2) as a modification material on pencil graphite electrodes (PGE) has been proven to significantly enhance the detection performance of Pb^{2+}. MnO_2 has good electrocatalytic properties and a porous structure that allows for an increase in the active surface area of the electrode. A larger surface area provides more active sites for adsorption and electron transfer, resulting in a higher current peak during the detection of Pb^{2+}. Additionally, MnO_2 is capable of selectively interacting with heavy metal ions such as Pb^{2+} through ion exchange and complexation mechanisms, which also enhance the sensitivity and selectivity of the sensor.

Compared to other modified materials such as graphene oxide, CNT, or gold nanoparticles, MnO_2 offers a more economical and environmentally friendly approach without requiring complex synthesis processes. Thus, the advantages of MnO_2/PGE lie not only in its good electrochemical performance but the PGE itself is low-cost, and disposable because the price is cheap yet reusable through simple polishing with filter paper and rinsing with distilled water, and can be easily re-modified with MnO_2, making it a potential alternative for practical and applicable Pb^{2+} detection.

Selectivity, reproducibility, and sample tests

– Selectivity Test

Selectivity is one of the main characteristics of specific ion electrodes to verify the possibility of reliable measurements in the target sample. The selectivity test for Pb^{2+} metal ions was conducted under optimal conditions in a 0.1 M HCl solution using the SWV technique model, applying a scan potential from 0 V to –0.7 V with a scan rate of 100 mV/s. The test results can be seen in the following Fig. 11.

Based on the voltammogram in Fig. 11, the measurement results show that in the selectivity test for Pb^{2+} ions, the addition of other metals such as Fe^{3+}, Zn^{2+}, Cr^{6+}, and Ni^{2+} does not cause significant changes. This indicates that the MnO_2/PGE electrode is selective in determining Pb^{2+} metal ions.

– Reproducibility Test

This reproducibility test was conducted under optimal conditions in a 0.1 M HCl solution using the SWV technique model by applying a scan potential from

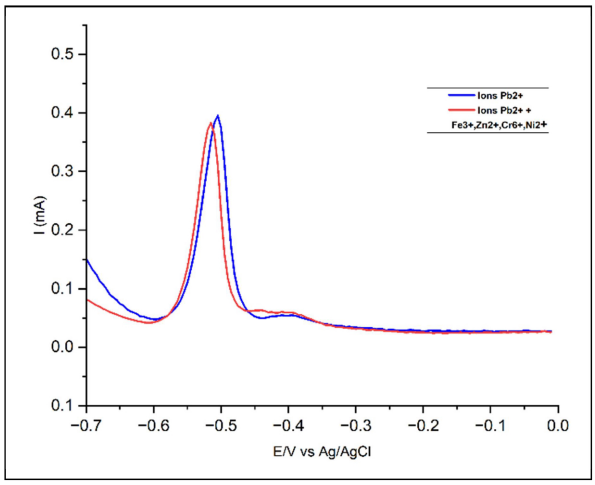

Fig. 11. SWV voltammogram of the selectivity test of the Pb^{2+} test solution with other metal ion solutions Fe^{3+}, Zn^{2+}, Cr^{6+}, Ni^{2+} at the same concentration (5 ppm) and with the same electrode in a 0.1 M HCl solution with a scan rate of 100 mV/s.

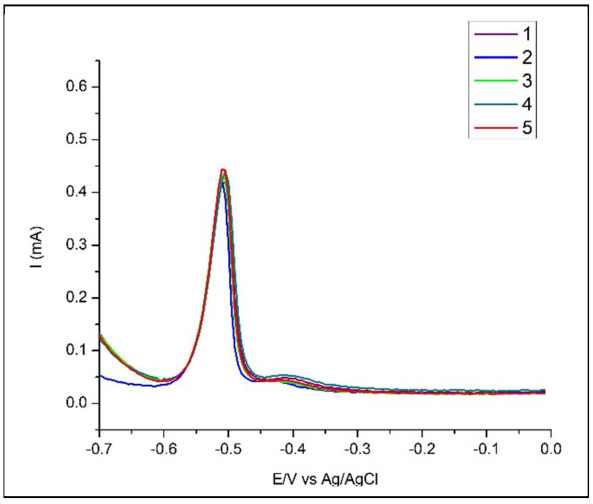

Fig. 12. SWV voltammogram of reproducibility test in 5 measurements of 5 ppm Pb^{2+} test solution in 0.1 M HCl solution with a scan rate of 100 mV/s.

0 V to –0.7 V with a scan rate of 100 mV/s. The test results can be seen in Fig. 12.

Based on the voltammogram in Fig. 12, the Pb^{2+} test solution was measured 5 times at the same concentration of 5 ppm using the same electrode, resulting in a %RSD value of 2.51%. This indicates high reproducibilityof the modified electrode used in this study with an RSD below 4.5%.[35] The electrode can be reused simply by polishing its surface on filter paper, rinsing it with deionized water (aquadest), and drying it. After this simple treatment, the electrode is ready for re-modification and subsequent use. For further applications, the electrode can be easily renewed or replaced due to its low cost, making it suitable for both single-use and short-term repeated use scenarios.

Table 1. Recoveries of Pb(II) from spiked water samples (n = 3).

Sample	Found/ mgL^{-}	Spiked/ mgL^{-}	Recovery[a],%	RSD,%
Tap Water (UNP)	N.D.	5 ppm	101.9	2.91
Mineral water	N.D.	5 ppm	100.8	4.02

a. The mean of three replicate determinations.
N.D: No detected.

– Determination of Pb(II) metal ions in water samples

To demonstrate the performance of the MnO_2/PGE electrode for environmental samples, tap water (from the laboratory of the Universitas Negeri Padang) and packaged mineral water were chosen as representative water samples. The samples were measured using the SWV method in a 0.1 M HCl solution of 50 μL. The result showed that Pb(II) was not detected in these samples using the SWV method. Then, 5 ppm Pb(II) was added to the samples, and the obtained concentration was determined using the calibration curve method. The recovery of Pb(II) in these samples was calculated as the average of three repetitions, summarized in Table 1. Recovery ranging from 100.8% to 101.9% indicates that the developed MnO_2/PGE electrode can be used as an effective working electrode for SWV of Pb(II) ions in water samples.

The method testing was conducted using tap water and mineral water samples because both are the most commonly used types of water in daily life, and are thus considered to represent real conditions that are practically relevant. Both types of water have relatively good clarity and low levels of interfering ions, making them suitable for the initial stage of evaluating the method's effectiveness.

Conclusion

Electrochemical analysis using PGE and MnO_2/PGE on Pb^{2+} ions shows that the response from MnO_2/PGE is superior compared to PGE. The increase in the peak current for the detection of Pb^{2+} ions is caused by the electrocatalytic effect of manganese dioxide, which also serves to expand the electrode surface. The optimum conditions for testing Pb^{2+} ions with MnO_2/PGE were obtained using a 0.1 M HCl supporting electrolyte with the Square Wave Voltammetry (SWV) technique. On the Pb^{2+} calibration curve, a correlation coefficient (R^2) value of 0.9846 was obtained with an LOD value reaching 1.91 ppm and an RSD value of ±2.51%, indicating high sensitivity, selectivity, stability, and accuracy in

the measurement of Pb^{2+} metal ions. Furthermore, the MnO_2-modified PGE electrode shows potential for application in the detection of other heavy metal ions. The electrocatalytic properties of MnO_2 and the versatility of the PGE platform make it a promising candidate for broader applications.

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Author's declaration

- Conflicts of Interest: None.
- We hereby confirm:
  All the Figures and Tables in the manuscript are ours. Any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No human studies are present in the manuscript
- No animal studies are present in the manuscript
- Ethical Clearance: The project was approved by the local ethical committee at Universitas Negeri Padang, Indonesia.

Authors' contribution statement

R.W.: Conducted the research, performed data collection and analysis, and drafted the manuscript. T.K.S.: Supervised the research, contributed to data interpretation, and reviewed and edited the manuscript. Both authors have read and approved the final version of the manuscript and agree to be accountable for the integrity and accuracy of the work.

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مستشعر كهربائي كيميائي قائم على قطب الجرافيت بالقلم الرصاص المعدل بـ MnO_2 للكشف عن أيونات المعادن Pb^{2+} في عينات الماء

رحمي وهيوني، تريسنا كومالا ساري

قسم الكيمياء، كلية الرياضيات والعلوم الطبيعية، جامعة بادانج الحكومية، بادانج، إندونيسيا.

الخلاصة

تهدف هذه الدراسة إلى تطوير مستشعر أيون Pb^{2+} وتحديد الظروف المثلى لاختبار أيونات Pb^{2+} باستخدام قطب كهربائي معدل بـ MnO_2/PGE بطريقة الفولطامتري. في هذه الدراسة، تم تعديل قطب الجرافيت الرصاصي (PGE) باستخدام MnO_2 من خلال طريقة السكب بالتنقيط. بعد ذلك، تم تحسين الإلكترود من خلال تغيير نوع الإلكتروليت الداعم، وتقنية الفولتمترية، وتركيز الإلكتروليت الداعم. أظهرت النتائج أن القطب المعدل (MnO_2/PGE) قدم استجابة أفضل لاكتشاف Pb^{2+} مقارنة بالقطب غير المعدل (PGE). تم العثور على أن الظروف التجريبية المثلى هي 0.1 M HCl كإلكتروليت داعم، مع تقنية الفولطائية الموجية المربعة (SWV). قياس أيونات Pb^{2+} باستخدام MnO_2/PGE تحت الظروف المثلى أسفر عن معامل ارتباط (R2) قدره 0.9846 وحد كشف قدره 1.91 جزء في المليون، مع قيمة RSD ± 2.51% ، مما يشير إلى حساسية عالية، انتقائية، استقرار، ودقة في قياس أيونات المعدن Pb^{2+}.

الكلمات المفتاحية: الكيمياء التحليلية، الكشف عن المعادن الثقيلة، تحليل أيون الرصاص، قطب معدل، قياس الفولتية بالموجة المربعة.