Optimization of Castor Oil-Based Ion Selective Electrode (ISE) with Active Agent 1,10-Phenanthroline for Aqueous Pb\(^{2+}\) Analysis

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Abstract: This research has successfully fabricated ion selective electrode (ISE) for Pb\(^{2+}\) using castor oil (\textit{Ricinus communis} L.)-based polyurethane (PU) membrane with 1,10-phenanthroline as the active agent. The sensitivity of the Pb\(^{2+}\) ISE obtained is 27.25 mV/decade with a linear range of [Pb(NO\(_3\)]\(^2\)\(^{-}\) of \(10^{-10}\)–\(10^{-5}\) M and a coefficient of determination (R\(^2\)) of 0.959. The system response reaches stability after 25 s of measurement. The Pb\(^{2+}\) has a detection limit of \(10^{-10}\) M and gives a stable response at pH 7–8 with a 15-day lifetime. The investigation of the selectivity of the ISE was performed using the mixed solution method with log Kij values of <1. The selectivity order of Pb\(^{2+}\) ISE against the foreign ions is Ag\(^{2+}\) > Ca\(^{2+}\) > K\(^{+}\) > Mg\(^{2+}\) > Cu\(^{2+}\) > Fe\(^{3+}\) > Cr\(^{3+}\) > Zn\(^{2+}\) > Cd\(^{2+}\). The Pb\(^{2+}\) ISE shows acceptable reproducibility and repeatability with standard deviation values of 0.065 and 0.0079, respectively. Fourier transform infrared (FT-IR) spectra confirmed that 1,10-phenanthroline was responsible for the formation of the Pb\(^{2+}\) ion entrapment via complexation. Other characterizations (crystallinity, micro-surface morphology, and mechanical strength) suggest the degradation of the membrane structure integrity after the application. The analysis results of Pb levels using the Pb\(^{2+}\) ISE in artificial and wastewater samples were not significantly different from the atomic absorption spectroscopy (AAS) measurement.

Keywords: potentiometry; ISE; polyurethane; 1,10-phenanthroline; lead

1. Introduction

The consequence of improved living standards is followed by industrial growth, where increased pollution, particularly heavy metals, is expected. Lead (Pb) exposure could be harmful to the ecosystem and, more importantly, humans. This is owing to the fact that Pb could be bioaccumulated in bone tissue and damage neural functions deriving from its neurotoxicity [1]. Children have been found to be a higher risk group for Pb intoxication [2]. Toxicity of Pb is a serious problem because this metal is extensively used in industry, such as pipe [3] and paint manufacturers [4]. In addition, Pb is also used to increase the octane number of premium fuel [5]. Therefore, Pb should be analyzed on a routine basis to monitor the pollution level in order to prevent its deleterious effects. Based on the stated problem, a quick, cheap, sensitive, and accurate analysis of Pb is required.
Pb could be analyzed using conventional and instrumental methods. The instrumental method include ion selective electrode (ISE), which has been recognized for its high sensitivity because it could measure Pb content as low as $10^{-10}$ M concentration units [6]. Determination of Pb could also be carried out by spectrophotometry [7], atomic absorption spectrometry (AAS) [8], and X-ray fluorescence [9]. In general, methods requiring equipment such as UV-Vis spectrophotometer and AAS are complicated and could only be operated by skilled personnel. Besides, the analysis requires a long time, especially for the sample pre-treatment.

Potentiometry could be an alternative for Pb analysis, in which this method could measure low concentrations, have properties of being cheap and accurate, and does not require sample pre-treatment [10]. Parts of the equipment used for the Pb detection is ion selective electrode (ISE Pb$^{2+}$). The ISE consists of a matrix and active components (ionophore) that is responsible for ISE performance, such as the selectivity of the desired analyte [11]. This tool has been developed in the last few decades, but its development is slower compared to other electrometry methods such as voltammetry. This could be due to the limitation on the available active agents and compatible membrane in order to yield satisfying results. Various matrix and active agents have been employed to construct Pb$^{2+}$ ISE, such as glass multi-component chalcogenide (ChG), and GeSe2-PbSe-PbTe, respectively [12]. Furthermore, the use of polyaniline–titanium(IV)phosphate [13], polyvinyl chloride (PVC) membrane with active agent bovine serum albumin [14], and ether acridono [15] have also been reported. Another membrane used to construct Pb$^{2+}$ ISE is G-quadruplexba used with active agent AuNPs-DNA [16]. Pb$^{2+}$ ISE as reported in the foregoing cited literature, has a relatively narrow linear range suggesting the need for further investigation to improve the analytical performance of Pb$^{2+}$ ISE.

Herein, the polyurethane (PU) membrane was used as a matrix, synthesized from castor oil (Ricinus communis L.), to construct the Pb$^{2+}$ ISE system. The castor oil-based PU was selected due to its possession of carbonyl and amine groups resulting in a negatively charged surface [17]. Another reported study suggests that the amine group of the PU could form covalent bonds with the active agent cerium (IV) phosphate [18]. In addition, PU has a hydrophobic property as reported previously [19]. This property is beneficial for its application involving aqueous media that could maintain the membrane stability (prevent swelling and leaching of active agent).

Based on its negatively charged surface property, castor oil-based PU membrane was selected as the matrix for cationic ISE such as Pb. The selectivity of the ISE toward Pb$^{2+}$ ions is expected to be achieved by optimizing the condition of the membrane that contains immobilized 1,10-phenanthroline. The 1,10-phenanthroline/PU membrane was immersed in Pb(NO$_3$)$_2$ solution to form the Pb-phenanthroline complex. The complex could form interface equilibrium on the membrane that produces interface potential that is correlated with the activity of Pb$^{2+}$ ions in the solution.

2. Materials and Methods

2.1. Materials

Materials used in this research included 1,10-phenanthroline, Pb(NO$_3$)$_2$, acetone, toluene diisocyanate (TDI), KCl, FeCl$_3$, NaNO$_3$, Cr(NO$_3$)$_3$, CuSO$_4$, ZnSO$_4$, Cd(NO$_3$)$_2$, Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$, Mg(NO$_3$)$_2$, KNO$_3$, Fe(NO$_3$)$_3$, FeCl$_3$, CH$_3$COOLi, and Ag wire. All the aforementioned chemicals were purchased from Merck with analytical grade quality. Commercial castor oil (Ricinus communis L.) was procured from PT. Rudang Jaya (Medan, Indonesia) with industrial grade quality and an agar was purchased from trademark Akos. A glue with the trademark UHU has been used as an adhesive to attach the PU membrane to the surface of the electrode body. The wastewater sample was collected from the area surrounding Industrial Area II in Medan, Indonesia.
2.2. Instruments

For the membrane characterization, instruments used herein included Scanning electron microscope (SEM) with a serial name Jeol Jsm 6360 LA (Tokyo, Japan), X-ray diffractometer (XRD)—Shimadzu XRD-700 Series (Kyoto, Japan), Fourier transform infrared (FT-IR) spectrometer—Shimadzu Prestige (Kyoto, Japan), and Universal Testing Machine HT8503 (Hung Ta Instrument Co., Ltd., Taichung, Taiwan). Moreover, during the analytical performance of the ISE Pb²⁺, we used potentiometer Orion model with a serial name Thermo Orion Scientific Star A2115 (Waltham, MA, USA) and atomic absorption spectroscopy (AAS)—Shimadzu AA-7000 (Kyoto, Japan). A hand-made Ag/AgCl reference electrode was also used.

2.3. Preparation of 1,10 Phenantrolin-Immobilized PU Membrane

Firstly, the membrane matrix was prepared by adding 1.75 g TDI into 3.5 g castor oil in a glass beaker, and then stirring for 3 min. Thereafter, 1,10-phenanthroline was added to the mixture with weight variation of 0, 1, 3, 5, 7, and 19 mg, stirred until homogenous and heated for 15 min at 45 °C. The next process involved sonicating the mixture while adding with 4 g of acetone. The solution was then casted on a glass plate and subsequently oven dried at 40 °C for 24 h.

2.4. Preparation of Ag/AgCl Reference Electrode

An Ag/AgCl reference electrode was prepared through electrolysis employing two Ag wires (d = 0.57 mm), performed in KCl 0.1 M solution for 30 s. The electrolysis lasted for 30 s until the black color was formed on the wire surface indicating the formation of Ag/AgCl.

2.5. Construction of Pb²⁺ Ions Selective Electrode (Pb²⁺ ISE)

Previously prepared membrane was cut into a round shape with a diameter of 0.57 mm and glued onto an electrode body surface. Then, the internal solution was poured which contained 0.1 M KCl and 0.3 M Pb(NO₃)₂. The ion selective electrode (ISE) was conditioned by soaking the electrode into a 0.1 M Pb(NO₃)₂ solution for 24 h. Prior to the analysis, the Pb²⁺ ISE surface was washed clean using distilled water. The measurement and optimization of the electrode were performed with 10⁻¹⁰⁻¹⁻¹ M Pb(NO₃)₂ standard solutions. The electrode and a schematic potentiometric cell are presented in Figure 1.

![Figure 1. Pb²⁺ ISE-based on PU membrane (a). A schematic diagram of potentiometric cell (b).](image)

2.6. Optimization of Pb²⁺ISE

2.6.1. Effect of 1,10-Phenanthroline Composition

The determination of optimum 1,10 phenanthroline weight was obtained based on the best sensitivity value with a broad linear range. The sensitivity of ISE was calculated from the slope at the linear region of the plots of the electrode potential (mV) and Pb(NO₃)₂ concentration.
2.6.2. Effect of Internal Solution Concentration

A membrane prepared with the optimum 1,10 phenanthroline composition was used to determine the effect of internal solutions consisting of KCl and Pb(NO₃)₂ against the ISE sensitivity and the width of linear range. The sensitivity was obtained based on the linear curve of the plot potential (mV) vs. Pb(NO₃)₂ concentration.

2.6.3. Effect of pH

An investigation on the effect of pH on Pb²⁺ ISE performance was conducted by measuring the potential against Pb(NO₃)₂ solution at pH 4—9 using phosphate buffer solution of 0.1 M.

2.7. Analytical Performance Analysis of Pb²⁺ ISE

2.7.1. Determination of Response Time

The response time of Pb²⁺ ISE was determined based on the minimum time required to yield constant potential (mV). It was performed on Pb(NO₃)₂ solutions of 10⁻¹₀—10⁻⁵ M. Potential was recorded after reaching a stable value indicated by a potential change in the range of ±0.1 mV to ±0.6 mV.

2.7.2. Repeatability Test

The repeatability test of the constructed Pb²⁺ ISE was performed by determining the ISE potential value measured repeatedly using the same ISE. Thereafter, the standard deviation (SD) was calculated for the obtained potential values.

2.7.3. Reproducibility Test

The reproducibility test was carried out on the potential response from ISE with optimum performance. The reproducibility value was obtained based on the SD of the sensitivity of 10 electrodes.

2.7.4. Selectivity Test for Pb²⁺ ISE

The selectivity of Pb²⁺ ISE was determined by using mixed solutions. The investigation was carried out with a Pb(NO₃)₂ concentration of 10⁻⁴ M following the introduction of Ca²⁺, Ag⁺, Fe³⁺, Cu²⁺, Mg²⁺, K⁺, Cr³⁺, Zn²⁺, and Cd²⁺ ions with the same concentrations.

2.7.5. Determination of Lifetime

The lifetime of Pb²⁺ ISE was determined by the deviation of the first-day sensitivity value compared with the measurement obtained on the following days. The test was carried out for 25 days with 5 day intervals.

2.8. Characterization of 1,10-Phenanthroline-Immobilized PU Membrane

To observe the effects of the characteristics of the 1,10-phenanthroline-immobilized PU membrane on the Pb²⁺ ISE analytical performance, we performed several analyses on the membrane sample before and after use for Pb²⁺ ion measurement at optimum conditions. These analyses included FT-IR to observe the functional groups, SEM—the surface morphology, and XRD—crystallinity, and tensile strength determination.

3. Results and Discussion

3.1. Pb²⁺ ISE Optimization

3.1.1. Effect of 1,10-Phenanthroline Weight

1,10-phenanthroline acts as an ionophore or active compound that is selective in the working system of Pb²⁺ ISE. 1,10-phenanthroline has a function to bind targeted ions from the solution. However, since 1,10-phenanthroline could also be used as a ligand to bind other cations, we designed the working system of ISE using Pb containing an internal solution. The same idea was employed by Papp et al. (2018) [20] in the making...
of Cu$^{2+}$ ISE using hydrophilic tripeptide as the active agent. In this present study, the ionophore 1,10-phenanthroline was immobilized into a PU membrane functioned as the sensor matrix. 1,10-phenanthroline is a ligand comprising a free electron pair on two N atoms which bind the cations. According to its binding mechanism, interaction between 1,10-phenanthroline and Pb$^{2+}$ ions was based on Coulomb force [21], highlighting that Coulomb attraction force interaction occurs on ions with different charges. The interaction between 1,10-phenanthroline and Pb$^{2+}$ has been illustrated and presented in Figure 2.

![Figure 2. Interaction between 1,10-phenanthroline and Pb$^{2+}$ forming phenanthroline-Pb complex.](image)

Ionophore composition causes the characteristics of the membrane indicated by the sensitivity of ISE membrane in determining the concentration of Pb$^{2+}$ ion (Table 1 and Figure 3). The sensitivity of Pb$^{2+}$ ISE was close to Nernstian for two valence ions and had the broadest linear range obtained by ISE membrane added with 5 mg 1,10-phenanthroline. On the contrary, the ISE membranes with 0, 1, and 3 mg 1,10-phenanthroline had low sensitivities and narrow linear ranges. This is ascribed to the insufficient number of ionophore causing the ISE sensitivity to be unable to reach the theoretical value. The ISE sensitivity experienced a deprivation for membranes with ionophore of >5 mg. Moreover, the addition of 1,10-phenanthroline could be affected by the hydrophobicity of the PU. The hydrophobic characteristic may be attributed to the binding of active agent, hence preventing the detachment of the active agent into the analyte solution and subsequently contributes to higher ion inter-surface mobility through the membrane due to more effective ion exchange capacity [22].

![Figure 3. Effect of amount 1,10-phenanthroline on sensitivity and linear range of Pb$^{2+}$ ISE.](image)
Table 1. Sensitivity and linear range profiles of Pb\(^{2+}\) ISE against the weight variation of 1,10-phenanthroline.

| 1,10-Phenanthroline (mg) | Sensitivity (mV/Decade) | Linear Range (M) | \(R^2\) |
|--------------------------|-------------------------|------------------|--------|
| 0                        | 8.19 ± 0.15             | \(10^{-10} - 10^{-8}\) | 0.966 ± 0.03 |
| 1                        | 18.45 ± 0.14            | \(10^{-10} - 10^{-6}\) | 0.962 ± 0.05 |
| 3                        | 20.58 ± 0.13            | \(10^{-10} - 10^{-6}\) | 0.976 ± 0.02 |
| 5                        | 26.46 ± 0.11            | \(10^{-10} - 10^{-6}\) | 0.985 ± 0.01 |
| 7                        | 5.71 ± 0.13             | \(10^{-7} - 10^{-5}\)  | 0.993 ± 0.01 |
| 10                       | 2.68 ± 0.03             | \(10^{-9} - 10^{-7}\)  | 0.935 ± 0.04 |

3.1.2. Effect of Internal Solution Concentration

The constructed Pb\(^{2+}\) ISE is a type of ISE that uses internal solution. A solution made from Pb(NO\(_3\))\(_2\) and KCl was used as the internal solution, functioned to stabilize the electrode performance. Determination of solution potential on ISE is likely affected by the ionic strength in the internal solution [23]. The data in Table 2 and Figure 4 show that the composition of Pb(NO\(_3\))\(_2\) and KCl affects the sensitivity and linear range of the Pb\(^{2+}\) ISE.

![Figure 4](image-url)  
**Figure 4.** Profile of Pb\(^{2+}\) ISE sensitivities and linear ranges on the variation of internal solution Pb(NO\(_3\))\(_2\) (a) and KCl (b).

The measurement results show that KCl concentration used as internal solution affects the sensitivity. The sensitivity of Pb\(^{2+}\) ISE is close to the Nenstian value obtained at [KCl] = 0.1 M, with a sensitivity of 25.57 mV/decade, at a Pb(NO\(_3\))\(_2\) concentration of \(10^{-10} - 10^{-6}\) M. Table 2 shows that ISE without the KCl has a low sensitivity. Nonetheless, the increase in the internal solution concentration also could cause the reduction in sensitivity.
3.1.3. Effect of pH

The effect of pH on the performance of Pb$^{2+}$ ISE was evaluated by measuring the solution potential of Pb(NO$_3$)$_2$ $10^{-4}$ M at pH 4–9, where the results are presented (Figure 5). As observed, ISE response is stable at pH 7—8. It is owing to the fact that at pH < 7, the Pb$^{2+}$ ionophore is deprotonated causing the disruption of its function to interact with the Pb$^{2+}$ ion analytes [24]. Meanwhile, when the pH level was increased to pH > 8, the sample solution becomes too basic, where the Pb$^{2+}$ is expected to precipitate [25]. Conversely, at low pH, the solution is rich in H$^+$ causing the protonation. In this situation, the active site of the membrane becomes less effective, indicated by a decrease in the potential value.

![Figure 5. Potential curve (mV) measured on different pH levels (pH 4–9).](image)

### Table 2. Sensitivity of the electrode depending on the internal standard component variation.

| Standart Solution Compositions | Sensitivitas (mV/Decade) | Linear Range (M) | R$^2$  |
|-------------------------------|--------------------------|------------------|-------|
| Pb(NO$_3$)$_2$ (M) | KCl (M) |  | |
| 0 | 0 | 15.24 ± 0.13 | $10^{-10}$–$10^{-8}$ | 0.987 ± 0.01 |
| 0.1 | 0.1 | 25.57 ± 0.002 | $10^{-10}$–$10^{-6}$ | 0.950 ± 0.05 |
| 0.3 | 0.3 | 19.73 ± 0.16 | $10^{-10}$–$10^{-7}$ | 0.978 ± 0.001 |
| 0.5 | 0.5 | 15.40 ± 0.05 | $10^{-10}$–$10^{-7}$ | 0.975 ± 0.02 |
| 0.7 | 0.7 | 7.142 ± 0.01 | $10^{-10}$–$10^{-8}$ | 0.970 ± 0.02 |
| 0 | 0 | 9.20 ± 0.1 | $10^{-10}$–$10^{-8}$ | 0.960 ± 0.02 |
| 0.1 | 0.1 | 25.13 ± 0.03 | $10^{-10}$–$10^{-6}$ | 0.990 ± 0.01 |
| 0.3 | 0.1 | 27.25 ± 0.14 | $10^{-10}$–$10^{-5}$ | 0.991 ± 0.004 |
| 0.5 | 0.1 | 8.62 ± 0.06 | $10^{-10}$–$10^{-7}$ | 0.973 ± 0.04 |
| 0.7 | 0.1 | 2.23 ± 0.10 | $10^{-10}$–$10^{-8}$ | 0.962 ± 0.01 |

3.1.4. Effect of TISAB Solution

The potential determination using ISE is dependent on the solution ionic strength. In this regard, a total ionic strength adjuster buffer (TISAB) acts to maintain the stability of the ionic strength in the solution. On the other hand, TISAB could also contribute to the results obtained from the measurement of the potential. Herein, NaNO$_3$ $10^{-4}$ M was selected as the TISAB, mixed into each concentration of Pb$^{2+}$ with a concentration range from $10^{-10}$ to $10^{-1}$ M. The results of the investigation on the influence of TISAB are presented in Figure 6 and Table 3. By incorporating TISAB into the analyte solution, a wider linear range was obtained which could be ascribed to its role in stabilizing the ionic strength at low concentrations.
Table 3. TISAB solution comparison profile and without TISAB.

| Parameters                      | With TISAB            | Without TISAB         |
|--------------------------------|-----------------------|-----------------------|
| Sensitivity (mV/Decade)        | 24.04 ± 0.11          | 27.44 ± 0.11          |
| Linearity range (M)            | 10^{-10}−10^{-7}      | 10^{-10}−10^{-5}      |
| R²                            | 0.950 ± 0.002         | 0.953 ± 0.001         |

![Figure 6. Effect of TISAB on the sensitivity and linearity range of ISE Pb^{2+}.
](image)

3.2. Performance Characteristics of Pb^{2+} ISE

3.2.1. Profiles of Sensitivity, Linear Range, and LOD of Pb^{2+} ISE

The responses Pb^{2+} ISE on the variation of Pb(NO_3)_2 concentration with the previously documented optimum conditions are presented in Figure 7. The linear range was obtained at Pb(NO_3)_2 concentration ranged from 10^{-10} to 10^{-5} M with an acceptable coefficient of determination value of 0.970. As can be seen from the curve, a lower concentration of Pb^{2+} ion causes lower potential (mV). This corresponds to the Nernst equation for cations as shown in the equation below:

\[ E_{cell} = E_0 + \frac{0.05916}{n} \log[A] \]

![Figure 7. Response profile of Pb^{2+} ISE on varied concentrations of Pb(NO_3)_2.
](image)
The determination of the LOD of Pb²⁺ ISE was carried out by measuring the potential of blank solution (in this regard the solution was NaNO₃ 10⁻⁴ M. The LOD obtained was 10⁻¹⁰ M calculated using the equation expressed below:

\[- \log(LOD) = \frac{Y_{LOD} - \text{intercept}}{\text{slope}}\]

3.2.2. Response Time

Response time is an essential parameter to determine the time required to reach the stable potential. By doing so, the data obtained would be more precise and accurate. Based on Figure 8, the response of the Pb²⁺ ion sensor reaches the stability after the 25th second and lasted until the 60th second. The measurements on the 25th second revealed the potential values of around 170, 190, 210, 230, 250, and 273 mV when the concentrations were set at 10⁻¹⁰, 10⁻⁹, 10⁻⁸, 10⁻⁷, 10⁻⁶, and 10⁻⁵ M, respectively. Thereafter, the values tend to be fluctuating with changes occurring no more than 0.1 mV. Thus, 60 s were obtained for the rest of the studies because the potential values were considered to be constant. At concentration of 10⁻¹⁰–10⁻⁵ M, the estimated potential resulted in a drift <0.9 mV/second. It suggests the ISE is sufficiently good and appropriate for the criteria by the International Union of Pure and Applied Chemistry (IUPAC), where change potential occurring within the measurement should be 1 mV/min [26].

![Figure 8. Response time profile of Pb²⁺ ISE using different analyte concentrations.](image)

Figure 8 also shows that all concentrations tested required the same time to reach the equilibrium on the membrane surface. It can be concluded that the ability of ion immobilization is equal across all tested concentrations. Constant potential would be reached when the Pb²⁺ ion exchange in the analyte equals to the Pb²⁺ ions in the membrane inter-surface. The concentration is correlated with the generated potential. Hence, the higher the concentration of the analyte, the higher the potential obtained. It could be attributed to the higher occurrence of ion exchange.

3.2.3. Repeatability of ISE

Repeatability of Pb²⁺ ISE was tested aiming to reveal the closeness of the potential measurement value performed with repetition using the same condition. In this test, the potential of Pb²⁺ ISE was measured using standard solution Pb(NO₃)₂ of 10⁻¹⁰–10⁻⁵ M for 5 measuring series, in which the results are presented (Table 4). The test results of the repeated measurement show similar Pb²⁺ ISE sensitivity, proven by STDV of <5%. This low deviation suggests the feasibility of using the system for analytical purposes [27].
Table 4. Repeatability of Pb\textsuperscript{2+} ISE with linear range Pb(NO\textsubscript{3})\textsubscript{2} solutions of 10\textsuperscript{−10}−10\textsuperscript{−5} M.

| [Pb(NO\textsubscript{3})\textsubscript{2}] | Repeatability |
|--------------------------------|--------------|
| Sensitivity (mV/decade) | I | II | III | IV | V |
| 26.819 ± 0.001 | 26.28 ± 0.003 | 27.28 ± 0.004 | 26.04 ± 0.01 | 25.38 ± 0.02 |
| 0.994 ± 5.6 × 10\textsuperscript{−5} | 0.941 ± 3 × 10\textsuperscript{−4} | 0.94 ± 5.8 × 10\textsuperscript{−5} | 0.978 ± 1 × 10\textsuperscript{−4} | 0.991 ± 5.8 × 10\textsuperscript{−5} |

3.2.4. Reproducibility of the ISE

Reproducibility is an investigation performed to observed the deviation occurring between each cathode constructed using the same condition [28]. The analyte used was Pb(NO\textsubscript{3})\textsubscript{2} of 10\textsuperscript{−10}−10\textsuperscript{−5} M, where results from this investigation are presented in Table 5. The sensitivity of Pb\textsuperscript{2+} ISE had a deviation standard of less than 5%. However, indeed, the potentials resulting by one electrode with another are different, probably because the homogeneity of the membrane surface deviated from one another. Nonetheless, all of the 10 tested electrodes have the same ability of responding to the Pb\textsuperscript{2+} presence in the solution.

Table 5. Reproducibility of Pb\textsuperscript{2+} ISE with linear range of 10\textsuperscript{−10}−10\textsuperscript{−5} M.

| Parameter | Electrode Reproducibility |
|-----------|---------------------------|
| Sensitivity (mV/Decade) | I | II | III | IV | V | VI | VII | VIII | IX | X |
| 25.29 ± 0.01 | 24.95 ± 0.02 | 25.42 ± 0.01 | 24.64 ± 0.03 | 24.65 ± 0.03 | 24.65 ± 0.34 | 25.04 ± 0.02 | 24.58 ± 0.08 | 24.26 ± 0.03 | 24.64 ± 0.07 |
| 0.987 ± 5.77 × 10\textsuperscript{−5} | 0.986 ± 5.77 × 10\textsuperscript{−5} | 0.991 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} | 0.992 ± 5.77 × 10\textsuperscript{−5} |

3.2.5. Selectivity of ISE

One of important parameters, selectivity coefficient (K\textsubscript{ij}), was also determined in this present study, where the data are presented in Table 6. K\textsubscript{ij} depicts the ability of ISE in responding to the primary ion of interest as opposed to other foreign ions [29]. Herein, the K\textsubscript{ij} values were measured based on the mixed solution method at [Pb(NO\textsubscript{3})\textsubscript{2}] of 10\textsuperscript{−4} M. The foreign cations used included K\textsuperscript{+}, Co\textsuperscript{2+}, Cr\textsuperscript{2+}, Zn\textsuperscript{2+}, Ag\textsuperscript{2+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, and Fe\textsuperscript{3+}. The test is important since the amine group from PU also has an affinity with other competing ions [30].

Table 6. Selectivity coefficient of the Pb\textsuperscript{2+} ISE against various foreign ions.

| Foreign Ions | Log K\textsubscript{ij} |
|--------------|------------------------|
| Ag\textsuperscript{2+} | −6.14 ± 0.0002 |
| Ca\textsuperscript{2+} | −6.68 ± 0.02 |
| K\textsuperscript{+} | −7.18 ± 0.002 |
| Mg\textsuperscript{2+} | −7.26 ± 0.005 |
| Cu\textsuperscript{2+} | −7.31 ± 0.005 |
| Fe\textsuperscript{3+} | −7.92 ± 0.007 |
| Cr\textsuperscript{3+} | −8.48 ± 0.002 |
| Zn\textsuperscript{2+} | −8.49 ± 0.02 |
| Cd\textsuperscript{2+} | −8.73 ± 0.004 |

3.2.6. Lifetime

The determination of the lifetime aimed to evaluate the stability of the ISE response across a variation of time. The results indicate that the Pb\textsuperscript{2+} ISE has a stability over 4 days of evaluation, where no significant sensitivity reduction occurred (Figure 9). The decrease in the sensitivity of 8.29% and 23.09% occurred on day-5 and -11, respectively. This reduced trend of the sensitivity probably continues after the next following days. This is ascribed to the loss of available active agent on the electrode surface owing to the
membrane swelling and eventually caused leaching. This is yet unproven, since more investigation on the interaction between the PU membrane and 1,10-phenanthroline is required. Sensitivity of Pb2+ ISE < 25 mV/decade suggest that the system did not meet the two-valence standards [31]. A similar phenomenon was also obtained on PVC-based Pb2+ ISE from a previously published report [32].

![Figure 9. Lifetime of Pb2+ ISE.](image1)

3.3. Characteristics of the 1,10 Phenanthroline-Immobilized PU Membrane before and after the Pb2+ Measurement

3.3.1. FT-IR

FT-IR profiles of the 1,10-phenanthroline-immobilized PU membranes before and after Pb2+ analysis are presented (Figure 10). A broad spectral band at 3372 cm⁻¹ is assigned to the stretching vibrational band of N-H, which is formed due to the condensation of O-H from the castor oil and N=C=O from the TDI. In a previous study, the bending vibration of aromatic C-N should appear at around 1408 cm⁻¹ [33]. Nonetheless, in this present study, the foregoing spectral peak was observed at 1236 cm⁻¹, which indicates its disturbed vibration probably due to the interaction between 1,10-phenanthroline and the PU membrane. After Pb2+ ISE use, a further shift to the right of this spectral peak could be observed from 1236 to 1198 cm⁻¹. A previous study suggested this kind of wavenumber shifting could be attributed to the complex interaction with metals [34]. This is corroborated by the appearance of a spectral peak at 1318 cm⁻¹, assigned as ligand N-metal Pb bending vibration [35].

![Figure 10. FT-IR spectra of 1,10-phenanthroline-immobilized PU membranes before and after use for Pb2+ analysis.](image2)
3.3.2. SEM

SEM images of the 1,10-phenanthroline-immobilized PU membranes before and after use for Pb\(^{2+}\) analysis, observed under 5000× magnification, are presented (Figure 11). The surface morphology of both membranes appeared relatively smooth and dense, suggesting the proper variation of castor oil and TDI compositions used during the preparation [36,37]. After the analysis, the crack-like structure is more pronounced on the membrane surface. Similarly, the crack-like structure was observed on the used membrane by a previously reported study [38]. Explanation of this could be attributed to the Pb\(^{2+}\) binding that disturbs the integration of membrane structure [39]. Another explanation is the possibility of membrane swelling that also could result in membrane disintegration.

![Figure 11. SEM images of the 1,10-phenanthroline-immobilized PU membranes before (a) and after use for Pb\(^{2+}\) analysis (b).](image)

3.3.3. XRD

XRD patterns generated from the analysis of 1,10 phenanthroline-immobilized PU membranes before and after use for Pb\(^{2+}\) determination are presented in Figure 12. A clear crystallinity modification occurred after the membrane was exposed with Pb\(^{2+}\) solution and could be observed at a 2\(\theta\) range of 5°–15°. Attenuation of crystalline peaks in the used membrane was observable throughout the diffractogram, indicating the effect of Pb\(^{2+}\) complexation on the membrane structure which subsequently reduced its crystallinity. The crystallinity values of the membrane before and after use for the determination of Pb\(^{2+}\) were 99.87% and 88.16%, respectively. The precedence of this case has been reported [40]. Furthermore, in the used membrane, a new small crystalline peak appeared at 2\(\theta\) = 16°C, which could be assigned to the Pb\(^{2+}\)–1,10-phenanthroline complex [41,42].

![Figure 12. Diffractogram of 1,10-phenanthroline-immobilized PU membranes before and after use for Pb\(^{2+}\) analysis.](image)
3.3.4. Mechanical Properties

Mechanical profiles of 1,10-phenanthroline-immobilized PU membranes before and after use for Pb\(_{2+}\) analysis, as depicted by elongation (%) versus tensile strength (MPa), are presented (Figure 13). Mechanical properties could reveal the effect of the membrane use as Pb\(_{2+}\) ISE on its structure. Herein, a reduction in mechanical properties of the membrane was observed. A similar phenomenon has been reported by other research groups [43]. This finding corroborates the previous ones regarding the loss of membrane structure integrity after incorporating Pb\(_{2+}\) through complexation. However, the possible role of membrane swelling should not be ruled out. Overall, this analysis along with the previous ones (SEM and XRD) suggest the membrane degradation after use for Pb\(_{2+}\) analysis. This is the downside of the membrane being unable to be reused.

![Mechanical profile 1,10-phenanthroline-immobilized PU membranes before and after used for Pb\(_{2+}\) analysis.](image)

3.4. Investigation on Real Sample

The optimized Pb\(_{2+}\) ISE was tested for its performance on two artificial wastewater samples ([Pb\(_{2+}\)] = 6.8 and 7.6 mg/L) and a real sample. The real sample collected the wastewater effluent from the Medan Industrial Area, North Sumatra, Indonesia. The aim was to identify the accuracy of Pb\(_{2+}\) ISE for Pb\(_{2+}\) ion detection as compared with the standard method. The standard method used for the validation herein was atomic absorption spectroscopy (AAS). The results of this validation are presented in Table 7. By comparing the data obtained from Pb\(_{2+}\) ISE with those obtained from AAS, we obtained the results of the t-test calculation on three repetitions of measurements and show that there was no significant difference between the Pb measurements of ISE and AAS. Such value range suggests the good analytical performance of this proposed method which is close to the AAS method.

| Sample                  | Pb(NO\(_{3}\))\(_{2}\) (mg/L) | Pb\(_{2+}\) ISE | AAS  | t-Measure | T Table |
|-------------------------|-------------------------------|----------------|------|-----------|---------|
| Real wastewater         | 2.4 ± 0.09                    | 2 ± 0.062      | 0.133| 4.32      |
| 7.6                     | 7.6 ± 0.05                    | 7.2 ± 0.03     | 0.131|           |
| 6.8                     | 6.8 ± 0.04                    | 6.6 ± 0.04     | 0.146|           |

Note. AAS = atomic absorption spectroscopy.

4. Conclusions

The Pb\(_{2+}\) ISE constructed herein was based on PU membrane and 1,10-phenanthroline, and was successfully developed with very good selectivity and analytical performance against the working parameters of ISE. The analytical method developed had excellent...
accuracy and good correlation in determining the Pb$^{2+}$ ions from the analyte solution. FT-IR analysis proved that the 1,10-phenanthroline has a primary role in Pb$^{2+}$ ion complexation during the analysis. The downside of this membrane is the degradation of its structure integrity following its usage as Pb$^{2+}$ ESI. Application in the real sample suggests our newly proposed method could be used to determine Pb$^{2+}$ in wastewater.

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