

Analysis of Nickel(II) in Water Medium using Electrochemical Techniques

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Abstract

Nickel (Ni) is a highly toxic heavy metal because nickel can accumulate and poison aquatic biotic components, therefore its levels must be determined with certainty. In this study, nickel metal measurements were made using the cyclic voltammetry method. Several measurement parameters, including voltage range, scan rate, and pH, were tested in this study to improve sensitivity and accuracy. This is done to achieve the best possible measurement conditions. The results show that the best conditions for detecting Ni ions are a voltage range of -0.75 V to -1.00 V, a scan rate of 250 mV/s, and a pH of 3. The validation test produced results in the range of 15 to 40 mM with a correlation coefficient of 0.99, detection and quantitation limits of 274.99 ppm and 916.66 ppm, respectively, and an RSD of 1.10%. As a comparison, Ni content was tested using AAS, and the Ni contents obtained by cyclic voltammetry and AAS methods were 1666.47 and 1676 ppm, respectively.

Keywords: nickel, cyclic voltammetry, pH, scan rate, voltage range

1. Introduction

Currently, nickel (Ni) is one of the heavy metals that is mostly produced by industry, household waste, and laboratory waste [1–3]. Nickel has a relatively high density, is toxic, and is harmful to the health of living things even at low concentrations [4]. The second largest Ni deposits of the earth rest in the sea. It is estimated that the sea (approximately eight billion tons), either dissolved in seawater or deposited in the seabed. Soils may contain nickel levels as low as 0.2 mg kg⁻¹ or as high as 450 mg kg⁻¹. In addition, Ni naturally occurs in several plants varying from 0.08 mg kg⁻¹ to 15.5 mg kg⁻¹ [5].

To determine the level of danger posed by Ni-polluted water, a threshold value must be established in accordance with applicable regulations. Therefore, we need an analytical method to detect metals at low concentration levels in water.

Several metal analysis methods exist, such as atomic absorption spectroscopy (AAS) [6,7], atomic emission spectroscopy (AES) [8], inductively coupled plasma-mass spectroscopy (ICP-MS) [9,10], and electrochemical methods [9,11,12]. The spectroscopic method cannot determine metal ion species or the levels of very small

metal ions in seawater in the range of 10⁻⁵ to 10⁻² mg/L, while sample matrices such as the salt content of seawater are quite high. Spectrographic and mass spectrographic techniques have high detection limits, high operating costs, and are challenging to directly apply (on-site). To achieve a detailed speciation analysis of a metal, it requires prior extraction, which can cause the chemical species of the metal to change easily during the extraction process, with the potential for sample contamination also increasing significantly [13].

The electrochemical analysis method appears as an alternative method with many benefits, including high sensitivity, a low detection limit on the g/L scale, ease of use, and simple sample preparation [14]. Several studies have also compared electrochemical analysis techniques to other metal analysis techniques, with the results indicating that the voltammetric method has a 95% confidence level for detecting Ni [9]. Other studies that used the differential pulse adsorptive cathodic stripping voltammetry technique found that it had a higher limit of detection (LOD) than other spectroscopic methods [15,16]. However, increasing the detection limit can improve electroanalysis sensitivity. Increasing the detection limit can be accomplished by experimenting with various

parameters such as voltage range, scan rate, and solution pH [17,18]. The resulting peak current depends on the parameters used. The greater the scan rate used, the easier it is for electron transfer to occur, resulting in a greater amount of current being used [19].

The formation of Ni(II) ions is also influenced by the pH of the solution. The pH of the solution influences the stability of the ions formed, as well as the concentration of the analyte towards the working electrode and the resulting peak current [20]. As a result, an electrochemical method was used in this study to determine the conditions for measuring Ni metal ions by examining the effect of variations in the voltage range, scan rate, and pH of the solution, as well as determining the concentration of nickel metal present in waste samples, so that it could be applied to various sample measurements. water in a heavy metal-contaminated environment.

2. Materials and Method

2.1 Materials

The potentiostat e-corder eDAQ 163 with eChem v2.1.0 software was used in this study for electrochemical measurements using a 3-electrode system by Metrohm with Pt wire as the working electrode, Pt wire as the counter electrode, and pH meters. The materials used included NiSO₄·6H₂O, concentrated HNO₃, HCl, NaOH, KCl (all materials were pro-analytical and purchased from Merck). The sample (Ni(II) content) of lab waste containing different cations was determined.

2.2 Methods

The purpose of this study was to determine the conditions for measuring Ni metal ions using cyclic voltammetry. Therefore, we studied the effect of the following parameters with 10 mM NiSO₄·6H₂O standard solution: the influence of variations in the voltage range, from -0.75 V, -1.25 V, -1.5 V to 0.75 V variations in the scan rate from 25 mV/s, 50 mV/s, 100 mV/s, 200 mV/s, and 250 mV/s, and variations in the pH of the solution from pH 3 to pH 8. To see the accuracy of the method, it is possible to determine the Ni(II) content in the lab waste and perform method validation by determining linearity, relative standard deviation, limit of detection, and limit of quantitation.

3. Results and Discussion

3.1 Voltage range test

Fig. 1 shows that the peaks of nickel metal ions appear best in the voltage range of -1.00 V to 0.75 V because they have one of the highest current peaks and are significant when compared to current peaks in other voltage ranges. This is due to the presence of nickel species formed at a voltage of -0.254 V in the voltage range, and the E value at

the peak of this Ni metal corresponds to the standard potential as shown in Eq. 1 [21]:

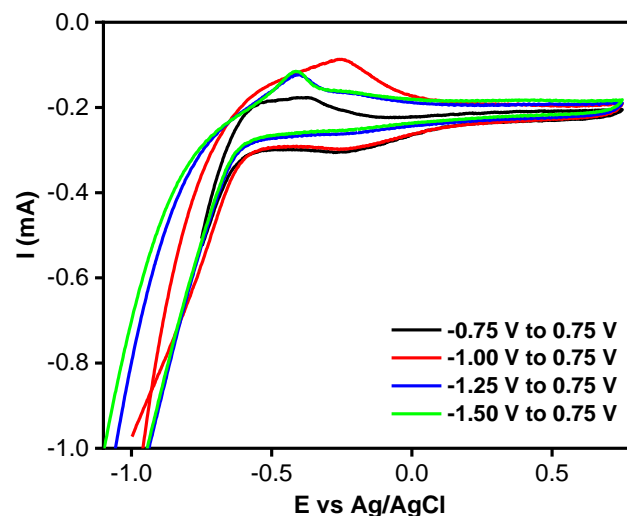
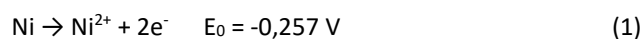


Figure 1. Cyclic voltammogram with different voltage range in 10 mM Ni solution.

Furthermore, other voltage ranges appear to produce less significant peaks where this voltage range does not indicate the formation of any nickel species at the potential standard (E_0), which corresponds to the formation of Ni metal peaks. As a result of the lower sensitivity in other voltage ranges, the peak current is found to be more sloping, with a small resulting current. As a result, the highest and most significant peak where the current generated is greatest is in the voltage range of -1.00 V to 0.75 V, so this voltage range is chosen for the analysis of Ni metal ions.

3.2 Scan rate test

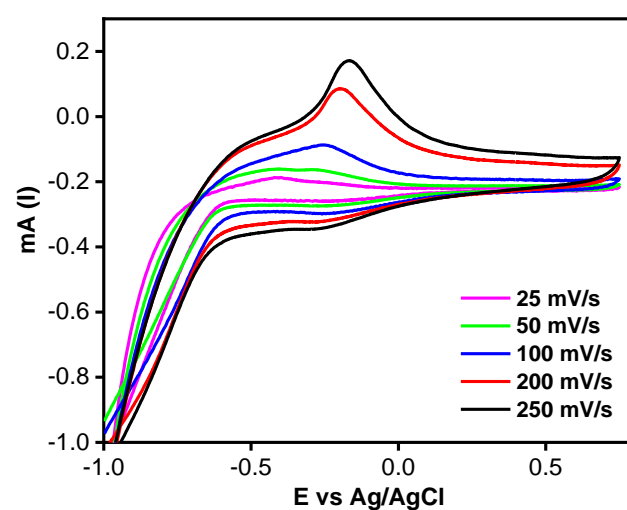


Figure 2. Cyclic voltammogram with different scan rate in 10 mM Ni solution.

The scan rate is related to the rate of electron transfer when a redox reaction occurs at the electrode surface (6). The scan rate variation test was carried out using the previously obtained voltage range, namely -1.00 to 0.75 V. The voltammogram results for various scan rate variations using cyclic voltammetry can be seen in Fig. 2.

The voltammogram shows that as the scan rate increases, so does the peak current. A high scan rate facilitates electron transfer, resulting in a greater amount of current being used, whereas a low scan rate impedes electron transfer to the electrode surface, resulting in a small current. As the scan rate increases, the cathodic peak current decreases while the anodic peak current increases [5]. A slow scan rate will cause the measured voltammogram curve to widen. If the scan rate is too high, the oxidation process is not optimized, and the resulting peak potential is not perfect.

Furthermore, the Ni peak formed at a scan rate of 250 mV/s was at a voltage of -0.164 V, indicating the peak of nickel oxidation. With increasing scan rate there is a shift in voltage towards the oxidation peak in the positive direction. This indicates that as the scan rate increases a higher positive potential is required for the oxidation reaction to occur [22]. This causes electron transfer to be slow. As a result, the scan rate of 250 mV/s produces the highest peak where the generated current is greatest. For subsequent measurements of nickel metal ions, a scan rate of 250 mV/s was used.

3.3 pH test

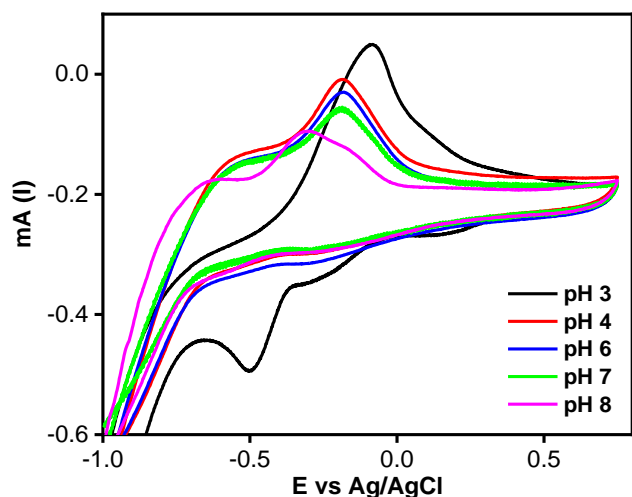


Figure 3. Cyclic voltammogram with different pH in 10 mM Ni solution, scan rate 250 mV/s.

pH is an indicator that can influence the voltammogram's peak because at the appropriate pH, Ni is protonated, allowing the nickel oxidation reaction to occur completely Ni [23]. The pH variation test was performed using the voltage range and scan rate obtained

from previous tests for the analysis of nickel metal ions. Fig. 3 shows the voltammogram results of various pH obtained by cyclic voltammetry.

Fig. 3 shows that the high peak current is affected by the pH conditions of the solution of Ni metal ions. At a pH variation of 3 to 8, the resulting peak current decreases. Under acidic conditions, such as at pH 3 and 4, nickel is protonated so that the nickel oxidation reaction can occur completely. However, at pH 3, the resulting current is greater than at pH 4. Moreover, the peak current decrease for pH levels higher than 3. This could be due to the presence of OH⁻ ions, which cause metal ions to form hydroxide and decrease the measured current [21]. As a result, the peak current decreases as the pH of the Ni(II) ion solution increases, and the highest oxidation peak is indicated by variations in pH 3, indicating that pH is the pH for the analysis of Ni metal ions using the cyclic voltammetry method.

3.4 Linear concentration range

From the results of the plot between the concentration of the solution and the peak current, a linear range is obtained, namely from 15 to 40 mM. In the linear range, the regression line equation is $y = 0.0069x - 0.05$. The increase in peak current is proportional to the increase in concentration, thus giving a linear response between concentration and peak current. The linear relationship between concentration and peak current is evidenced by the correlation coefficient value, which is close to one, namely 0.9994. According to previous studies based on ISO/IEC 1725, since the correlation coefficient value is close to or equal to 1, this method can be used to analyze Ni metal with good results [24].

3.5 Relative standard deviation (RSD)

The repeatability estimated in terms of the relative standard deviation (RSD%) for eight repetitive measurements with a reasonable time interval. In this study, the RSD was determined at a concentration of 15 mM Ni solution with the measurement conditions for the analysis of nickel metal ions that had been obtained and repeated eight times in a row. From the calculation results, the value of the RSD for the determination of Ni solution is 1.10%. A method with good precision is indicated by a RSD of less than 5% [25]. The RSD results showed good repetition.

3.6 Detection limits and quantitation limits (LOD and LOQ)

In this study, two methods were used to determine the detection limit. The first way is to measure metals with varying concentrations of 0.5 mM, 1 mM, and 5 mM. The goal of this method is to determine the concentration range in which the voltammogram is visible.

$$\text{LOD} = \frac{3 \times S(y/x)}{\text{slope}} \quad (2)$$

$$\text{LOQ} = \frac{10 \times S(y/x)}{\text{slope}} \quad (3)$$

Fig. 4 shows the voltammograms obtained for nickel metal ion concentrations of 0.5 mM, 1 mM, and 5 mM using the previously obtained measurement conditions. The voltammogram in Fig. 4 above shows that the peaks of metal ions are appears at concentration of 1 mM and 5 mM. According to calculations of LOD and LOQ as shown in Eq. 2 and 3, the detection limit for Ni(II) standard solution is 1.04 mM or 274.99 ppm. While the quantization limit is the smallest amount of analyte in the sample that is able to meet the criteria carefully and thoroughly with an analyte response that is 10 times greater than the response from the blank signal, The quantization limit of the calculation results is 3.48 mM, or equivalent to 916.66 ppm.

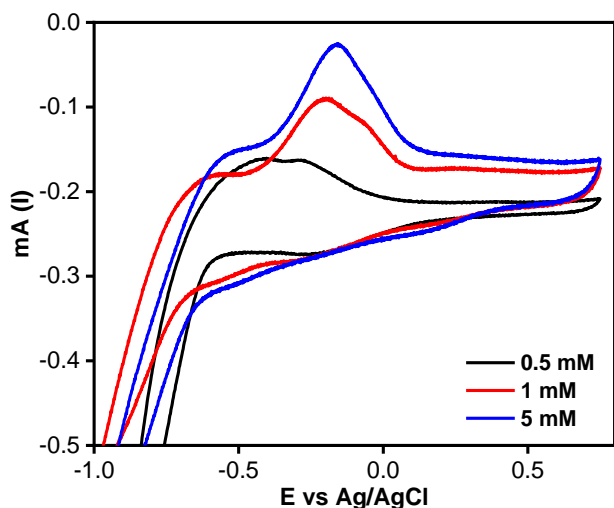


Figure 4. Cyclic voltammogram with different Ni concentrations with potential range -1.00 V to 0.75 V, scan rate 250 mV/s, and pH 3.

3.7 Determination of Ni(II) content in lab waste

The Ni(II) content of lab waste containing different cations was determined. Measurements were made at a voltage range of 0.75 V to -1.00 V, a scan rate of 250 mV/s, and pH 3. The voltammogram results for determining Ni levels using cyclic voltammetry can be seen in Fig. 5. A peak was found on the voltammogram at -0.156 V that could be assumed as an oxidation peak of Ni ions. The line equation is obtained shows the relationship between the standard concentration of Ni and the oxidation peak or $I_{pa} y = 0.0069x - 0.05$. From these calculations, the average concentration for 5 repetitions of Ni in the lab waste is 1666.47 ppm.

Furthermore, the Ni content of the samples obtained through voltammetry will be compared using the commonly used conventional method, namely AAS. The

AAS instrument can be used to determine the content of Ni metal at a wavelength of 232 nm.

Table 1. The Ni content of the sample by AAS.

No.	Sample	Concentration	Absorbance
1	Sample 1	1676 ppm	0.1542

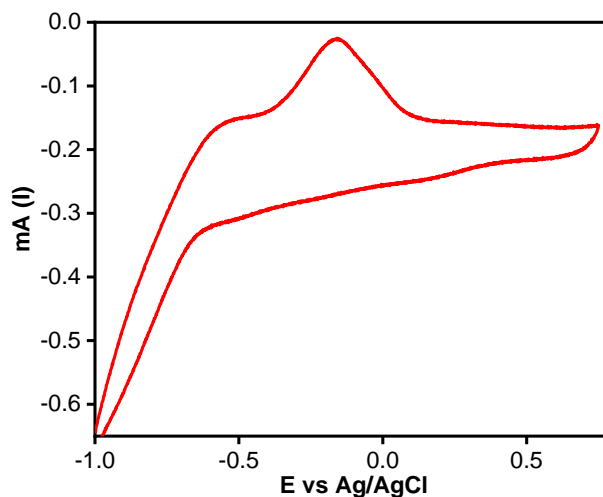


Figure 5. Cyclic voltammogram of waste sample.

According to Table 1, the results of testing for the content of Ni metal in the sample were calculated, and the concentration of Ni in the sample was 1676 ppm. As a result, electrochemical techniques have much higher accuracy in analyzing metals, with the nickel content obtained through voltammetric measurements in lab waste being 1666.47 ppm, which is close to the results obtained from AAS measurements, namely 1676 ppm.

4. Conclusion

Nickel metal of lab waste containing different cations can be determined using electrochemical techniques, namely cyclic voltammetry. Cyclic voltammetry have much higher accuracy in determined metals, with the nickel content obtained through voltammetric measurements in lab waste being 1666.47 ppm, which is close to the results obtained from AAS measurements, namely 1676 ppm. Measurement conditions that can produce high selectivity are in the voltage range of 0.75 V to -1.00 V, a scan rate of 250 mV/s, and pH 3.

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