

Analysis of Cobalt(II) and Nickel(II) in Water Medium using Voltammetry Techniques

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Received

11 March 2023

Received in revised form

26 April 2023

Accepted

8 May 2023

Published online

30 June 2023

DOI

<https://doi.org/10.56425/cma.v2i2.52>



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Abstract

Currently, the electrochemical method as one of the fast, accurate, and reliable techniques for detecting heavy metals such as Co and Ni has been widely developed. Cyclic voltammetry methodology was successfully employed for determination of trace cobalt (Co) and nickel (Ni). Co and Ni levels are studied because they can cause water pollution and can be toxic, and non-biodegradable which influences the health of living things. To obtain results with high accuracy, this study tested several electrochemical parameters. Based on the results processed, the CoNi level in the solution can be measured well in the voltage range, scan rate, and pH of the solution, respectively, at -1.00 V to 0.75 V, 250 mV/s, and pH 3 (Ni) and pH 7 (Co). This work have been validated and showed good results with correlation coefficients of Co and Ni. The detection limit and quantity limit for Co and Ni were 510.2 ppm and 723.5 ppm, respectively, with 274.99 ppm and 916.66 ppm. Co and Ni metal RSDs also showed good values (<5%). In this study, Co and Ni levels in lab waste obtained by the cyclic voltammetry method were 510.2 ppm and 1666.47 ppm, and the results obtained from atomic absorption spectroscopy (AAS) measurements of 510.7 ppm and 1676 ppm. The developed electrochemical systems based are giving new inputs to the existing devices or leading to the development of novel heavy metal detection tools with interest for applications in fields such as environmental, safety, security controls or other industries.

Keywords: cobalt, nickel, heavy metals, cyclic voltammetry

1. Introduction

The issue of heavy metals that pollute many waters is of particular concern because they can easily enter the food chain and endanger living things [1]. So, in this case, analysis of heavy metal levels is needed to determine the content and level of species that pollute the waters. Several method analyses that has been widely carried out such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrophotometry (ICP-AES) [2,3]. However, both methods are costly and less practical, unable to measure small levels of metal ions, and less efficient at the pre-concentration stage [4,5]. Currently, electrochemical methods such as voltammetry is presented as a promising alternative because having high sensitivity, low detection limits on the

µg/L scale (ppb), easy use, easy sample preparation, quick analysis, cheap infrastructure, and in the measurement of metal contamination in the sea, high salt content does not interfere with analysis [4,6,7]. The pre-concentration is also shorter, generally less than 1 minute [8].

Among various heavy metals, lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and arsenic (As) are highly toxic, especially nickel (Ni) and cobalt (Co) have a high amount of use compared to other metals so they are very susceptible to polluting waters. Co and Ni are also toxic, carcinogenic, and can affect the health of living things that are exposed [9]. However, increasing the detection limit can improve electroanalysis sensitivity. The use of electrochemical methods for the analysis of Ni and Co metals has challenges in determining the appropriate parameters for the analysis of metal levels studied.

Increasing the detection limit can be accomplished by experimenting with various parameters such as voltage range, scan rate, and pH solution. Therefore, in this study, the conditions for measuring Ni-Co metal ion levels were carried out by varying the range of potential, scan rate, and pH solution. Testing of metal ion levels using AAS is also carried out as a comparison of the measurement results.

2. Materials and Method

In this study, the cyclic voltammetry (CV) method which was controlled by potentiostat e-corder eDAQ 163 with a 3-electrode system, Pt as the working electrode, the Pt wire as the supporting electrode, and the Ag/AgCl (3 M KCl) as the reference electrode. The materials used include concentrated HNO_3 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, HCl, NaOH, KCl (all materials are pro-analysis), and chemical lab waste. 25 mM CoNi solution as a standard solution on measurement condition testing. Several parameters such as voltage range, scan rate, and pH are varied. Variations in voltage, scan rate and pH range respectively are at voltages from -0.75; -1.00, -1.25, and -1.50 V to 0.75 V; scan rates of 25, 50, 100, 200, and 250 mV/s, and pH of 3, 4, 5, 6, 7 and 8 are adjusted with the addition of HCl and NaOH. The manufacture of CoNi metal calibration curves to obtain line equations and relation was carried out by measuring standard solutions of Co 10, 15, 20, 25, and 30 mM and standard solutions of Ni 15, 20, 25, 30, and 40 mM each of which added 10 mL of KCl 300 mg/L solution.

The determination of accuracy is determined by the obtained relative standard deviation (SRD) value. The determination of relative standard deviation is carried out by 8 repetitions ($n = 8$). Testing using a sample of laboratory waste solution is carried out using the voltage range, scan rate, and pH that have been obtained in testing the conditions for measuring CoNi levels in solution.

3. Results and Discussion

3.1 Measurement parameters condition analysis

Fig. 1a shows that the peak of the current is affected by the voltage range. The highest current obtained is in the voltage range of -1 V to 0.75 V. Range the Co-Ni mixture has a higher current response compared to other voltage ranges. The amount of metal that interacts with the electrode surface and is oxidized during cycling increases at this voltage [10].

Deconvolution current in Fig. 1b to determine the peak of the metal current analyzed. The results of the deconvolution of the current peak show that two peaks are legible. The readable current peak is likely to be the peak current of Co^{2+} and Ni^{2+} metal ions.

Fig. 2 shows the relationship of the scan rate to the peak of the current. The greater the scan rate, the higher

the peak current produced. This is due to the higher scan rate, the diffusion rate is greater than the reaction rate. Therefore, more electrolyte ions reach the electrode surface whereas very few ions participate in the charge transfer reaction. Therefore, the current at a higher scan rate will increase [11]. 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 [12].

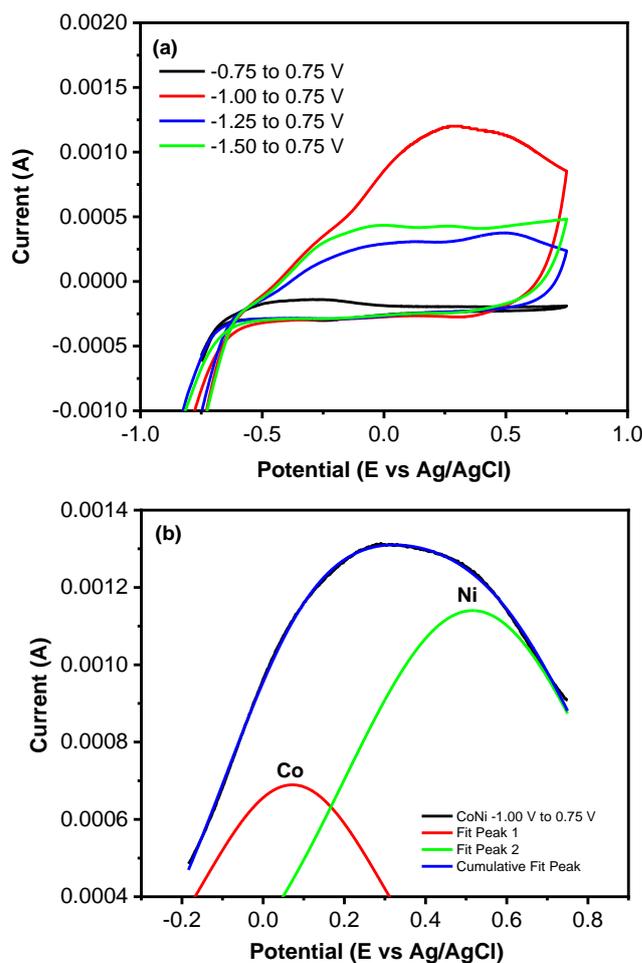


Figure 1. Cyclic voltammogram (a) with voltage range difference in 25 mM CoNi solution (b) deconvolution of CoNi peak at -1.00 to 0.75 V.

The voltammogram in Fig. 2b produces two peaks at different voltages. These peaks are thought to be Co and Ni peaks. And the two metals detected also experienced an increase in peak current as the scan rate increased. This is because the high scan rate will lower the diffusion layer and increase the faradic current [12]. Peak deconvolution of current is carried out to see that the peak current produced is the metal ion analyzed instead of other impurities. From the results of the deconvolution, two

peaks are produced which are the peaks of the current of Ni and Co metal ions. The shift in voltage towards positive with increasing scan rate also implies that voltage magnification is needed when the scan rate increases for the oxidation reaction to occur. In this case, 250 mV/s is the measurement condition of the best CoNi solution with the highest peak current value of the other scan rates.

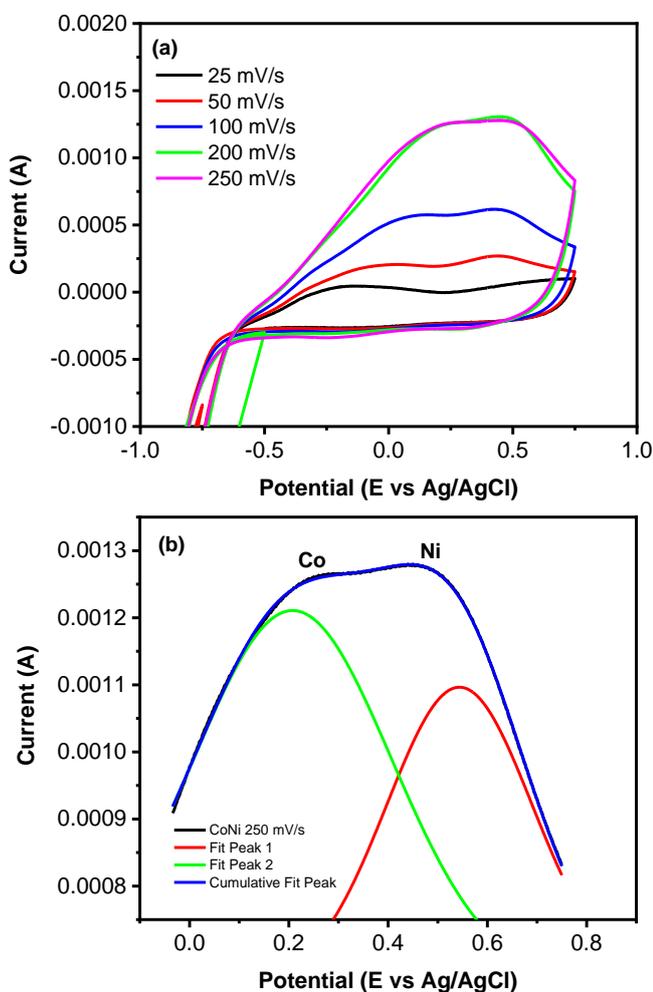


Figure 2. Cyclic voltammogram (a) with different scan rate in 25 mM CoNi solution (b) deconvolution of CoNi peak at 250 mV/s.

Fig. 3a shows the effect of pH on peak current (I_p). From pH 3 to 7 there is a decrease in peak current so that the highest peak current is obtained, namely pH 3. At pH 3, the CoNi solution is well protonated so that the oxidation reaction for Co and Ni metals occurs perfectly. At pH 4-7, the peak current is low because there are still excess protons that can compete with Ni^{2+} and Co^{2+} ions forming another complex. Conversely, at a pH greater than pH 3 there is a decrease in the peak current value due to the presence of H^+ ions, as well as OH^- ions that cause metal ions to form their hydroxides so that the measured current will decrease for that pH 3 was chosen as the measurement condition in the next analysis [14]. On the deconvolution

chart, there are two peaks that appear, respectively, namely the metal peaks Co and Ni. The peak of the metal Ni lies at a more positive voltage according to previous research [15].

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 [19]. Peak current of Co, on the other hand, decreases as the pH rises above 7. Previous research has shown that pH 7 is the best pH for Co analysis [20].

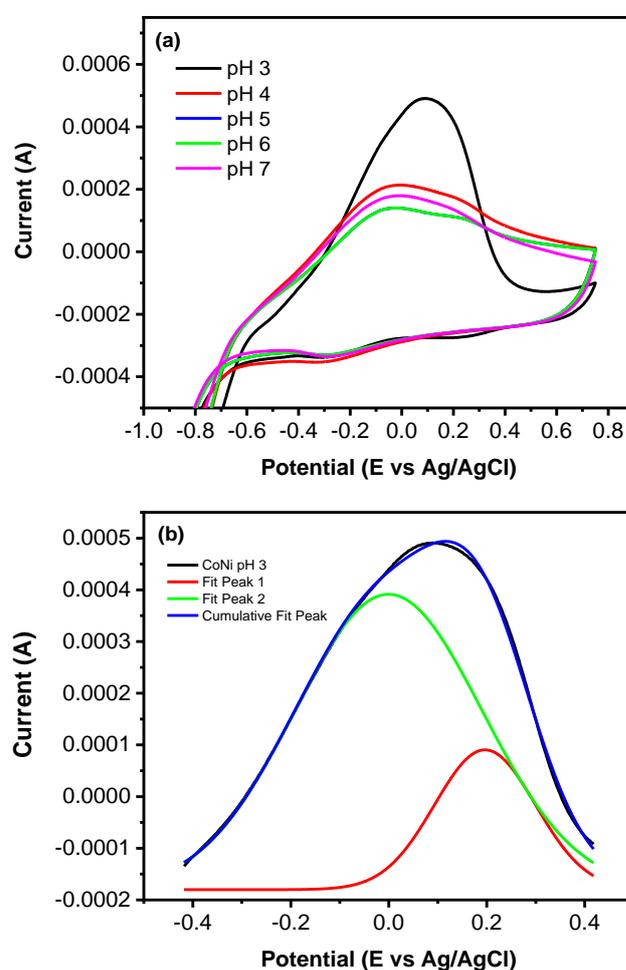
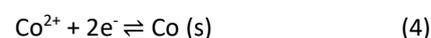


Figure 3. Cyclic voltammogram (a) with a difference in pH range in a 25 mM CoNi solution (b) deconvolution of CoNi peak at pH 3.

The reaction that occurs is shown in Eq. 1– 4.



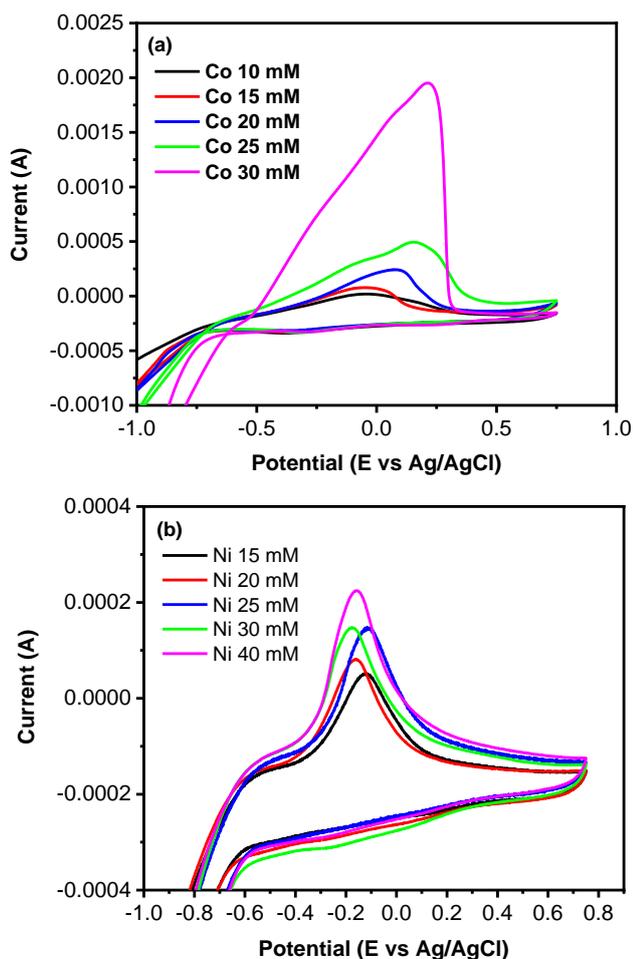


Figure 4. Cyclic voltammogram variations in concentration on (a) Co with a potential of 0.75 V to -1.5 V; scan rate 200 mV/s and pH 7, (b) Ni with a potential of 0.75 V to -1.00 V; scan rate 250 mV/s; pH 3.

3.2 Validation of measurements and applications to lab waste

Table 1. The relationship between current and concentration.

Co (mM)	Current (mA)
10	-0.21
15	0.28
20	0.74
25	1.21
30	1.75
Ni (mM)	Current (mA)
15	0.05
20	0.09
25	0.12
30	0.16
40	0.23

The creation of the calibration curve is carried out using the measurement conditions that have been obtained in the previous stage, namely using a voltage range of 0.75 V

to -1.5 V, a scan rate of 200 mV/s, a pH of 7 for Co metal and a tension range of 0.75 V to -1.00 V, a scan rate of 250 mV/s, pH 3 for Ni metal. Based on the data shown in Fig. 4 and Table 1, it can be seen that the current increases and shifts along with the increase in the concentration of Co-Ni, this is due to the increasing concentration of Co-Ni ions, more and more Co-Ni metals will be observed on the electrode surface [14]. A relationship is made between current and concentration so that a standard Co-Ni calibration curve is obtained with the equation $y = 0.097x - 1.186$ with R^2 of 0.9992 and 0.9994, respectively. This shows that the single metal ion Co-Ni can be detected well because it has a correlation coefficient value close to 1 or equal to 1 [17]. Therefore, the measurement conditions that have been obtained in this study can be used to analyze Co and Ni metals with good results. Co and Ni level testing was performed using AAS as a comparison of the measurement results.

Table 2. Measurement of Co(II) solution 10 mM and Ni(II) 15 mM.

Repetition	I_{pa} Co (mA)	I_{pa} Ni (mA)
1	0.0280	0.0527
2	0.0282	0.0529
3	0.0279	0.0536
4	0.0281	0.0533
5	0.0284	0.0521
6	0.0276	0.0519
7	0.0280	0.0525
8	0.0277	0.0531
Average	0.02799	0.052773
Standard deviation	0.000286	0.000582
RSD	0.009949%	1.10%

The resulting curve on the measurement of single metal ions Co^{2+} and Ni^{2+} using AAS also shows a linear increase in current with R^2 of 0.9988 and 0.9953. Based on the obtained R^2 value, it shows that a single metal ion of cobalt can be detected well using AAS. From successive calculations of 2.30 mM and 1.04 mM or equivalent to 510.2 ppm and 274.99 ppm. The value indicates that for cobalt with concentrations smaller than 510.2 ppm and nickel smaller than 274.99 ppm, the rated peak current is indistinguishable from the response of the blank solution. Determination of Co and Ni metal content using AAS instruments was tested at wavelengths of 580 nm and 232.1 nm using Co and Ni metal cathode lamps. The straight-line equation obtained is used to calculate the concentration of the sample because there is a linear relationship between concentration (C) and absorbance (A). Based on the data, the concentration values of Co and Ni in the sample were 510.70 mg/L and 274.99 mg/L. As shown in Table 2, measurements of relative standard

deviation in a solution of Co 10 mM and Ni 15 mM were also carried out. The average current values for Co and Ni metals are 0.000286 and 0.000582 mA, with RSD (Relative Standard Deviation) values of 0.9% Co metal and 1.10% Ni metal. This value indicates a good level of precision because it has an RSD value of <5% [16]. Furthermore, the detection limit of Co(II) and Ni(II) standard solutions based on the results of successive calculations of 2.30 mM and 1.04 mM or equivalent to 510.2 ppm and 274.99 ppm and the quantization limit for cobalt metal is 2.57 mM or equivalent to 723.5 ppm. As for nickel metal, it is 3.48 mM or equivalent to 916.66 ppm.

4. Conclusion

Based on the results of the research obtained, it can be concluded that the measurement conditions for CoNi metal analysis using electrochemistry are at a voltage of 0.75 V to -1.5 V, a scan rate of 200 mV/s, a pH of 7 for Co metal and a tension range of 0.75 V to -1.00 V, a scan rate of 250 mV/s, pH 3 for Ni metal. The obtained parameter values have been proven to be usable for CoNi metal analysis on testing samples of mixed solutions using the cyclic voltammetry method. From the measurement results, the concentration values of Co and Ni are close to the value of the AAS measurement results. Each Co and Ni levels in the lab waste obtained by the cyclic voltammetry method were 510.2 ppm and 1666.47 ppm which corresponded to the results obtained from AAS measurements of 510.7 ppm and 1676 ppm. On the validation of measurements, it shows that the measurement conditions using the cyclic voltammetry method for CoNi metal analysis show good results.

Acknowledgment

This work was supported by DRTPM Kemendikbudristek under PTKN scheme 2022.

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