Nickel recovery from precipitate of NCA lithium-ion battery leach liquor by using disodium ethylene diamine tetraacetate

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Abstract. The nickel cobalt aluminium oxides (NCA) type Li-ion battery is a type of battery currently used in electric vehicles. The UGM battery team has recycled this type of battery to obtain high purity lithium metal. Aside from lithium, the NCA battery contains high-value metals, nickel is one of them. This experiment aims to test the ease of nickel to chelate with disodium ethylene diamine tetraacetate (EDTA). The experiment was carried out by means of a triple neck flask for 4 hours. The samples were taken at certain minutes and then fitted using a pseudo homogeneous first-order reaction equation. The chelate formed was further processed through multilevel precipitation or electrodialysis to separate nickel. Based on the experiment, nickel formed chelates optimally at 60°C using 0.086 M EDTA with the reaction constant for nickel being 1.4819 min⁻¹. The Arrhenius constant and activation energy for nickel were 3.48×10¹¹min⁻¹ and 76,907 J/mole, respectively.

1. Introduction
Battery recycling is one of the crucial concerns in realizing the Government Regulation of the Republic of Indonesia Number 101 of 2014 about Management of Hazardous and Toxic Waste. Spent batteries contain valuable metals that may cause various harmful effects on the environment [1]. The most common battery used in several electronic devices such as laptops, smartphones, and electric vehicles is the lithium-ion (Li-ion) battery. Conventional Li-ion batteries are composed of a cathode, anode, separator, electrolyte, current collector (aluminium and copper foils), container, and sealing parts [2]. The substantial components of a Li-ion battery are cathode (35%), sealing (26%), and anode (18%) [3]. Li-ion battery cathodes use intercalated lithium compounds such as LiCoO₂ (LCO), LiFePO₄ (LFP), LiNi₀.₅Mn₀.₅O₂ (NMC), and LiNi₅₀Co₅₀Al₀.₅O₂ (NCA). Li-ion battery sales are expected to reach 200,000 MWh in 2025 [4].

Battery recycling can be carried out by applying the hydrometallurgical method using an acid leaching process. It can achieve high metal recovery with the low energy needed [5]. More than 50% of research in Li-ion battery recovery is conducted in the hydrometallurgical process [6]. Cobalt leaching usually uses both inorganic acids and organic acids. Inorganic acids such as HCl, H₂SO₄, and HNO₃, while organic acids are citric acid or oxalic acid [7]. University of Gadjah Mada (UGM) battery recycling team has succeeded in separating lithium from NCA through a leaching process by using H₂SO₄ 1 M and multilevel precipitation to separate lithium from NCA with a mixture of nickel and cobalt as a side product. In addition, the UGM researchers’ team has also recycled many other batteries using various methods [8–11].
Nickel and cobalt are two metals that have similar properties according to their adjacent positions on the periodic table of the elements. Therefore, the two metals are difficult to separate. This study aims to develop a suitable mathematical model for the nickel cobalt aluminium oxides (NCA) battery precipitate leaching process using the disodium ethylene diamine tetraacetate (Na$_2$EDTA). The use of Na$_2$EDTA in the chelation of nickel and cobalt contained in NCA battery precipitates has never been done before. Disodium EDTA is a chelating agent that can absorb various polyvalent cations. It is commonly used in research whereas it can usually reach efficient extraction of metals [12]. Ni-EDTA and Co-EDTA have different solubility constants in chelate therefore nickel and cobalt can be separated by using Na$_2$EDTA to form Ni-EDTA and Co-EDTA. The separation of nickel and cobalt in the presence of EDTA in mechanochemical approaches and electrodialysis methods show satisfactory results [13,14]. This study focuses on making a stable EDTA chelation for a nickel.

2. Mathematical model
The chelating reaction for Ni-EDTA from NCA’s second precipitate is formulated as in equation 1 [15].

$$\text{Ni}^{2+} + \text{H}_2\text{C}_{10}\text{H}_4\text{N}_2\text{O}_8^{2-} \rightarrow \text{NiC}_{10}\text{H}_4\text{N}_2\text{O}_8^{2-} + 2\text{H}^+$$

(1)

The kinetic of Ni curve using EDTA is fitted by a first-order reaction model that is formulated in equation 2.

$$\frac{dQ_i}{dt} = k_i(Q_i^0 - Q_i)$$

(2)

where $Q_i$ represents the amount of metal i that forms a chelate with EDTA in mg/L at time t, $Q_i^0$ represents the amount of metal i that forms a chelate with EDTA at equilibrium, and $k_i$ is the rate constant of the first-order reaction in min$^{-1}$. Integrating equation (2) for the initial condition $Q_i = 0$, and rearranging the solutions yields [16] as in equation 3.

$$Q_i = Q_i^0(1 - e^{-k_i t})$$

(3)

Arrhenius constant, A (min$^{-1}$), and activation energy, $E_A$ (J/mole), can be obtained using temperature and rate constant data from the experiment. Equation 4 shows the Arrhenius equation where R represents the universal gas constant (J/mole/K) while T is the temperature in Kelvin [17].

$$k_i = A_i \exp \left( \frac{-E_A}{RT} \right)$$

(4)

3. Materials and method
Raw material preparation started with the pre-treatment of NCA-type Li-ion battery precipitates. Pre-treatments were initiated by grinding the NCA precipitates by means of a mortar. This precipitated powder was then analyzed to determine the Co and Ni content. In addition, EDTA was dissolved by demineralized water so that the EDTA and Ni mole ratio was 1.

Raw materials were analyzed by Energy Dispersive X-ray Spectroscopy (EDX) analysis to analyze the elemental composition of raw material samples with the EDX-8100 type (Shimadzu, Japan). In addition, to obtain more accurate analysis results, ICP-AES analysis (Inductively Coupled Plasma Atomic Emission Spectrometry) that used Optima 8300 type device (Perkin Elmer, USA) was utilized.

The reagent used for the leaching process was the disodium EDTA solution. The leaching process was carried out in a three-neck flask so that the solid-liquid ratio was 10g/L for 4 hours. The flask heated to 30°C, 60°C, and 90°C. The Na$_2$EDTA concentrations used were 0.086 M, 0.173 M, and 0.345 M. The stirring speed used was 400 rpm. The equipment used is presented in Fig. 1. The product samples were taken at 1, 3, 5, 10, 15, 30, 45, 60, 120, and 240 minutes. Product samples were analyzed using ICP-AES analysis to determine the nickel recovery from the leaching process using the Optima 8300 type device (Perkin Elmer, USA).
4. Results and discussion

4.1. EDX report for raw material
Table 1 shows the EDX report for NCA Li-ion second precipitate as raw material. Nickel was the major element in the precipitate (76.837%), while cobalt was only around 5.654%.

| Element | % (wt.) |
|---------|---------|
| Ni      | 76.837  |
| Co      | 5.654   |
| Others  | 17.509  |

Table 1. EDX report for NCA Li-ion precipitate.

Other elements contained in the precipitates tested were sulfur, calcium, phosphorus, and iron. These elements contributed 17.5% of the total elements.

4.2. Effect of changing the EDTA concentration
Figure 2 shows the recovery of nickel chelating with EDTA at various concentrations. The concentration variations that were used followed the moles of nickel contained in the raw material. The variations were 0.086 M, 0.173 M, and 0.345 M.

The test results showed that the three variations could take nickel up to 95.6%. According to Figure 2, the three variations formed almost the same amount of Ni-EDTA chelates. The concentration of 0.086 M can be considered as the optimum concentration used for further experiments.
4.3. Effect of changing the temperature

Figure 3 shows the nickel recovery in EDTA chelates at 30°C, 60°C, and 90°C. This experiment was carried out using 0.086 M EDTA for four hours.

![Figure 3. Nickel recovery in EDTA chelates at 30°C, 60°C, and 90°C](image)

The experimental results showed nickel recoveries for the three temperature variations were 77.66%, 95.55%, and 96.07%, respectively. The graph proves that the higher the temperature, the higher the formation of the metal-EDTA chelate. The increase in reaction temperature raised the number and chance of molecules collisions in the leaching medium and consequently increased the yield of metal extraction. The yield differences at 60°C and 90°C were not significant. In this experiment, 60°C was chosen as the optimum temperature for the formation of Ni-EDTA chelates.

4.4. Kinetics analysis

The kinetics model of nickel chelation with EDTA is needed for scale-up purposes so that it is easier to predict the chelating reaction in a plant scale. The reaction kinetics of the formation of Ni-EDTA chelate was fitted using equation 3. The curves which were modelled with an EDTA concentration of 0.086M for 240 minutes of leaching with three temperature variations (30°C, 60°C and 90°C) are shown in Figure 4. It shows that in a short time (less than 20 minutes), both 60°C and 90°C have reached their equilibriums. It means that the leaching has reached its maximum efficiency quickly. The differences between 60°C and 90°C were relatively small. The temperature of 60°C was decided as the optimum temperature of this experiment.

![Figure 4. Nickel concentration in EDTA chelates.](image)

Table 2 represents parameters such as reaction constant k, Q₀, and the Sum of Square Error (SSE) for nickel chelation with EDTA at temperatures of 30°C, 60°C, and 90°C. According to the Arrhenius equation, the rate of reaction constant increases following the temperature increase (except at 90°C). The value of Q₀ for a nickel at each temperature tended to be the same, approximately 1,505.83 mg/L.
Table 2. The reaction rate constant (k) in min\(^{-1}\), \(Q^0\) (mg/L), and the Sum of Square Error (SSE) of first-order reactions model for Ni chelation with EDTA at 30°C, 60°C, and 90°C.

| Temperature | Parameter | Amount   |
|-------------|-----------|----------|
| 30°C        | k         | 0.0095   |
|             | \(Q^0\)  | 1,609.20 |
|             | SSE       | 20,466.00 |
| 60°C        | k         | 1.4819   |
|             | \(Q^0\)  | 1,336.80 |
|             | SSE       | 194,070.00 |
| 90°C        | k         | 1.2746   |
|             | \(Q^0\)  | 1,571.50 |
|             | SSE       | 221,470.00 |

Table 3 shows the Arrhenius constant and activation energy for a nickel. The activation energy of nickel-EDTA according to Alpaslan’s experiment is 15,930 J/mole [18]. This difference is quite large because Alpaslan’s experiment used raw materials that have many impurities so that the controller of the leaching process was internal diffusion. In this experiment, the leaching process was reaction controlled. The Arrhenius constant for nickel-EDTA according to the experiment was \(3.48 \times 10^{11}\) min\(^{-1}\).

5. Conclusions
Based on the experiment, EDTA was suitable as a chelating agent for a nickel. For the s/l ratio of 10g/L, the chelating reaction occurred very short for less than 20 minutes at a high temperature. The optimum temperature for this experiment was 60°C using 0.086 M EDTA. The reaction rate constant for nickel of this reaction was 1.4819 min\(^{-1}\), whereas the Arrhenius constants and activation energy of nickel were \(3.48 \times 10^{11}\) min\(^{-1}\) and 76,907 J/mole.

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