Nickel removal from electroplating wastewater using electrocoagulation

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Abstract. Electrocoagulation processes for reducing nickel concentration in electroplating wastewater had been carried out in laboratory scale experiments. The experiments were conducted in a 500 mL batch reactor with dual electrodes: aluminum as the anode and copper as the cathode with electroplating wastewater at pH 7 and initial nickel concentration of 10.55 ppm. Parameters of electrocoagulation process such as removal efficiency, specific energy and produced precipitate were determined and assessed under various DC voltages (5, 7.5 and 10 V) and various operation time (30, 60 and 90 min) as variable of experiment. The results show that the optimum condition of electrocoagulation process was obtained at 5 VDC and for 76.5 min.

1. Introduction

The development of electroplating industry in Indonesia grows rapidly. Large amount of wastewater is produced daily by the electroplating industry and provide negative impact in environmental quality. Wastewater from electroplating industry usually contain heavy metals that may endanger living beings’ health and environment [1–4]. Moreover, the water pollution by heavy metals cause serious problems to human being due to bioaccumulation effects in aqueous environment [5].

Most of harmful elements in electroplating wastewater contain heavy metals such as nickel [1]. Nickel is the main pollutant in electroplating wastewater due to only 30-40% of nickel that can be utilized into product, while the rest is released into water body as wastewater effluent [1]. The Decree of the Minister of Environment Indonesia No. 5 in 2014 regulates the maximum nickel concentration in effluent released into water body must be less than 1 ppm [6]. For fulfilling the standard quality, the electroplating wastewater effluent must be treated by appropriate wastewater treatment technology. Various techniques for heavy metal removal from wastewater are available such as ion exchange, adsorption, filtration, coagulation and electrocoagulation as alternative solutions [1–5,7–15].

Electrocoagulation is an emerging technology in water and wastewater treatment that has been successful in dealing with organic and inorganic contaminants. It has gained immense attention due to its ease of distribution and moderate required amount of chemicals [4,7–11,13]. The technique involves dissolution of the sacrificial anodes that produce active metal hydroxide as strong coagulant. Then the removal of particles from wastewater proceed through destabilizing/neutralizing the repulsive forces that keep the contaminants suspended in water. When the repulsive forces are neutralized, the suspended contaminants will form large particles that can settle down for easier separation from wastewater. The success of this technology will depend on its ability to satisfy commercial criteria such as minimizing operational and maintenance costs as well as achieving profit on the investment made in the shortest
time possible. The major challenge that the technology is likely to encounter is that of high electricity consumption while treating the wastewater as it directly affects the operating costs [4,7–11,13]. Electrocoagulation process is influenced by operating parameters such as applied current density, electrodes material and configuration, type of electrical connection, pH and conductivity of the solution, and mixing state [4,7–11,13].

In this study, the influences of electrocoagulation process variables such as DC voltages and operation time were investigated in laboratory scale batch reactor. Effluent of an electroplating plant with typical high nickel concentration was used in the experiments. The optimum condition was expected to give a higher removal efficiency, lower specific energy and lower produced precipitate.

2. Materials and Method

2.1. Electroplating wastewater
The wastewater was collected from the effluent of an electroplating plant in Bandung City, West Java, Indonesia. The wastewater was characterized for pH, conductivity and nickel concentration (Table 1).

| Characteristics        | Value | Quality standard [6] |
|------------------------|-------|----------------------|
| Nickel concentration (ppm) | 10.523 | 1                    |
| TSS (ppm)              | 0.36  | 20                   |
| pH                     | 3.4   | 6-9                  |
| Conductivity (mS/cm)   | 16    | -                    |
| Color                  | Light green | -                |

Prior to experiment, the wastewater was filtered using a screen filter to remove suspended solids and the pH was adjusted to neutral condition by NaOH addition.

2.2. Electrocoagulation procedure
The setup of electrocoagulation equipment system is shown in Figure 1 and Figure 2. The electrocoagulation reactor was constructed from Pyrex a borosilicate glass beaker with 600 mL capacity, having dimensions of 90 mm outer diameter and 124 mm height. The total volume of wastewater in each experiment was approximately 500 mL. Aluminum (Al) plate was used as anode and copper (Cu) plates was used as cathode. Both plates have 45 mm height \times 75 \text{ mm} \times 3 \text{ mm} thickness in dimension and were arranged in monopolar configuration with the distance between plates was fixed at approximately 50 mm. The current was maintained constant by means of a precision DC power supply characterized by the ranges 0–6 A for current and 0–10 V for voltage.

The experimental range and levels of independent process variable were DC voltage (5, 7.5 and 10 V) and operation time (30, 60 and 90 min), as shown in Table 2. The wastewater was agitated with a magnetic stirrer at 200 rpm during electrocoagulation. Electrodes were sanded and washed with dilute HCl between experiments.

To follow the progress of the treatment, samples of 10 mL were taken from the electrocoagulation cell at the end of the experiment. The samples were then filtered (0.45 \mu m) to eliminate sludge formed during electrolysis. The filtrate from each experiment were analyzed using ICP-OES instrument (Agilent 240FS AA) for determining the residual nickel concentration. The produced precipitate and electrode consumption were analyzed using gravimetric method [16]. The pH reduction and the specific energy consumption were also analyzed during each process.
1. Power supply
2. Cathode, Cu
3. Anode, Al
4. Beaker glass
5. Electroplating wastewater
6. Magnetic bar
7. Magnetic stirrer

**Figure 1.** Schematic of electrocoagulation equipment system.

**Figure 2.** Electrocoagulation apparatus. A rectifier (1) acted as an AC-to-DC converter and an electric voltage controller; a coagulation reactor (2) served as a wastewater treatment plant; an AVOmeter (3) acted as an electric current meter and connecting wires of such devices.

| Process variable          | Range and Value |
|---------------------------|-----------------|
| DC voltage (V)            | Low | Middle | High |
|                           | 5   | 7.5    | 10   |
| Operation time (min)      | 30  | 60     | 90   |

**Table 2.** Experimental range and levels of independent process variable.

2.3. *Calculations*

Nickel removal efficiency (%) was calculated based on initial nickel concentration \(C_0\), ppm and residual nickel concentration \(C_r\):

\[
Removal = \frac{C_0 - C_r}{C_0} \times 100\%
\]  

The high electricity consumption while treating the wastewater with electrocoagulation process is a major challenge and directly affects the operating costs, thus the electrical energy consumption is a very important economical parameter. The electrical energy consumption was calculated using the following equation:

\[
E = \frac{U \cdot I \cdot t}{V}
\]

where \(E\) was the energy consumption (kWh/m³), \(U\) was the applied voltage (V), \(I\) was the current intensity (A), \(t\) was the electrocoagulation time (h) and \(V\) was the volume of the treated wastewater (L).
The amount of electrode dissolved was calculated theoretically by using Faraday's law:

\[ C = \frac{I \cdot t \cdot M}{Z \cdot F \cdot V} \]  

where \( C \) was the aluminum concentration in the electrolytic cell (g/L), \( I \) was the current intensity (A), \( t \) was the electrocoagulation time (s), \( M \) was the molecular weight of the anode (g/mol), \( Z \) was the chemical equivalence, \( F \) was the Faraday constant (96500 C/mol) and \( V \) was the volume of the treated wastewater (L) [9].

3. Results and Discussion

Electrocoagulation process was carried out to determine the effect of variations in voltage and time on the concentration of nickel (Figure 3).

![Figure 3. Chart of voltage and electrocoagulation time toward Ni\textsuperscript{2+} concentration.](image)

Analysis results of Ni\textsuperscript{2+} concentration in the samples shows a reduction that was not significant (Figure 3). Overall, the concentration of Ni\textsuperscript{2+} of 10,522.70 ppm in the initial sample decreased until it reached the smallest concentration was of 8,965.15 ppm at 5 V for 90 min.

Pahlevi et al [4] suggested that decrease levels could be caused by the formation of precipitate and floating floculants which indicated the movement of Ni\textsuperscript{2+} ions with an orbit helix-shaped around the electrode plate, so there was a tendency of Ni\textsuperscript{2+} ions to adhere into the whole electrode plate (cathode). The graph above also indicates the reduction of nickel levels that were influenced by the supply of Al\textsuperscript{3+} cations into the wastewater. This was caused by the more Al\textsuperscript{3+} cations supplied so more cations that could absorb or bind pollutants (in this case was a heavy metal compounds named nickel). With a large of anode’s weight (Al) scraped would influence into reduction of nickel content in wastewater [8,9].

Figure 4 shows the nickel removal from the wastewater. Nickel removal by electrocoagulation in this study was not obtained perfectly, where the maximum reduction of nickel content only reached 14.8% at 5 V for 90 min. Relationships with reduction of nickel concentration are shown in Figure 4. The amount of precipitate formed, changes in pH, and the amount of the anode scraped would also indicate a decrease of the dissolved nickel in electroplating waste.

The oxidation reactions at the anode occurred as follows [18]:

\[ 2H_2O(l) \rightarrow 4H_\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{(aq)}}}}}}}}}}}}+ O_2(g) + 4e^- \]
\[ Al(s) \rightarrow Al^{3+}(aq) + 3e^- \]
Figure 4. Chart of Ni^{2+} removal in electrocoagulation process.

At the cathode, the Al^{3+} ions were not reduced because of $E^{\text{red}} \text{Al}^{3+} < E^{\text{red}} \text{H}_2\text{O}$, so there would be a reduction reaction of water that produced H$_2$ gas and hydroxide ions.

$$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow 2\text{OH}^- \text{(aq)} + \text{H}_2\text{(g)}$$

The metal ions would be reduced to their metal and present on the electrode surface.

$$\text{Cu}^{2+} \text{(aq)} + 2\text{e}^- \rightarrow \text{Cu(s)}$$

Based on the above reaction Al^{3+} ions would be released from the plate electrode (anode). The Al^{3+} ion would react with the hydroxide ions from the cathode to form Al(OH)$_3$ precipitate according to the following reaction:

$$\text{Al}^{3+} \text{(aq)} + 3\text{OH}^- \text{(aq)} \rightarrow \text{Al(OH)}_3\text{(s)}$$

As shown in above reactions, during electrocoagulation, Al(OH)$_3$ was produced by the aluminum anode and the hydroxide ions (OH⁻) derived from the H$_2$O molecules. The free OH⁻ also would form metal hydroxide compounds ((M(OH)$_x$) that were insoluble in water [8,9]. In addition, Al(OH)$_3$ as a coagulant would further absorb the existing pollutants into their molecular cavities to form a complex metal oxide compound (MAI$_2$O$_4$) and insoluble in water [17].

As also shown in above reactions, O$_2$ gas and H$_2$ gas would be produced in the anode and cathode, respectively. Al(OH)$_3$ then formed flocs that interacted with the gas bubbles to generate low-density flocs that would move to the surface [8,9]. The flocks formed will have a relatively small size so that the flock will increase its size along with the electrocoagulation process time [9]. This matter plays a role in lifting the contaminant of the solution onto the surface of the reactor, which is usually called the flotation process.

The amount of precipitate formed in the electrocoagulation process is shown in Figure 5. The precipitate was a mixture of various compounds, consisted of Ni$^{2+}$ that was coagulated by Al(OH)$_3$. The maximum precipitate weight of this process, 0.185 g, was generated at 5 V and 90 min. This maximum precipitate weight corresponded to the decrease in dissolved nickel content, which also reached the optimum point at 5 V and 90 min.

Figure 6 shows the pH value of the solution at the end of the experiment. There was a decrease in the pH value of the solution from the initial pH 7. Usually the variation of the voltage does not significantly affect the final pH of the experiment, whereas the experimental time greatly affects the final pH of the experiment. In our experiment, a significant decrease of pH occurred in almost every experimental variation, where the initial pH of waste (7) decreased to pH 4-5. The reaction that occurred in the anode caused the increase of H$^+$ ions. Furthermore, metal ions in the solution would bind the OH$^-$ ions. Therefore, there was an excess of H$^+$ ions and the pH of decreased.
**Figure 5.** Influence of electrocoagulation parameters on precipitation.

**Figure 6.** Final pH on electrocoagulation process.

**Figure 7.** Weight of scraped anode on electrocoagulation process.
The magnitude of the eroded anode was affected by the voltage and electrocoagulation time as shown in Figure 7. The total mass of reduced aluminum anode reached a maximum of 0.076 g at 5 V and 90 min. The pH changes in the electrocoagulation process also influenced the amount of eroded Al and the formation of Al(OH)$_3$ precipitate which indicated a decrease in dissolved nickel content therein.

Specific energy is the energy required per kg of nickel removed from the solution. The smaller the specific energy, the smaller the energy used to decrease the dissolved nickel content. This would affect the cost efficiency of the process.

![Figure 8. Specific energy for electrocoagulation process.](image)

Figure 8 shows the specific energy required for each voltage and time variation. The smallest specific energy was achieved at 7.5 V and 30 min, which means that the process at these conditions would bear minimum cost with specific results. There was a difference between the optimum point of specific energy with decreased levels of nickel and the precipitate produced in the electrocoagulation process.

4. Conclusion
The research concluded that the percentage of reduction of dissolved nickel concentration in the sample by electrocoagulation reached 14.8% from 10,553.70 ppm to 8,965.15 ppm. It is indicated that the electrocoagulation process can be used to reduce dissolved nickel. However, the experimental results in this study have not succeeded in reducing the concentration of soluble nickel until reaches the quality standard as stated in the regulation of Environment Minister No. 5 year 2014.

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