Electrodeposition for rapid recovery of cobalt (II) in industrial wastewater

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Abstract. Cobalt (II) recovery from wastewater opens the opportunity for sustainability and green process. Herein, cobalt (II) was recovered from the aqueous solution by electrochemical cell method, so-called electrodeposition. Cobalt electrodeposition from the solution was conducted in the electrochemical cell using a graphite anode and a stainless-steel cathode by varying current (0.25, 0.5, 0.75, 1 and 1.25 A), pH (2, 3, 4, 5, and 6), and cobalt concentration (10, 20, 30, and 50 ppm). The monitoring of all cobalt concentration changes was using ICP AES spectrophotometer. electrodeposition at various applied currents has been removed 99.81% of cobalt from the solution in 20 minutes. Prolonging electrodeposition up to 25 minutes has removed 100% cobalt in the solution. Electrodeposition was also found useful at acidic to neutral pH by removal efficiency 99.37% in 20 minutes of the process. Cobalt in various concentration solutions can be removed 99.54% by applying a current of 0.25 A for 20 minutes. The conclusion is that the cobalt recovery process from PTA plant wastewater is feasible to be further developed.

1. Introduction
Cobalt (II), a transition metal group member, has wide application as a catalyst in many industrial processes[1–3]. After the process, it can be released and will end in a wastewater stream [2]. The presence of cobalt (II) in waterbody harm both human and aquatic life [4]. Cobalt (II) is grouped as a toxic, non-biodegradable, carcinogenic and mutagenic pollutant [5–7]. Therefore, its concentration in water is strictly regulated. Cobalt ions and other heavy metal ions must be avoided to enter the anaerobic wastewater treatment plant because they also harm anaerobic microbial life.

Various heavy metal removal in wastewater methods are chemical precipitation, ion exchange, adsorption, membrane filtration, and electrochemical treatments [1,2,4,6]. In chemical precipitation, heavy metals are reacted with chemical precipitants, usually in basic condition, to produce precipitate [6]. The solid phase or sludge production and the need of large chemicals are the main drawbacks of this method [2]. The other heavy metal removal methods, such as ion exchange, adsorption, and membrane filtration, face several limitations that correlate to a fouling risk, incomplete removal, and high price operation [2,4,8].

Electrodeposition method is both practical and easy treatment for removing heavy metal from the solution. Electrodeposition is an electrochemical process by applying direct current to deposit chemical
species on an electrode. In addition, the electrodeposition method is reagentless, highly selective, low cost, and sludge less product [6]. In the electrodeposition process, oxidation occurs on the anode while reduction occurs on the cathode [9]. In the electrodeposition, heavy metal ion reduction usually occurs on the cathode to form a deposited layer of heavy metal [2]. Thus, the unwanted heavy metal ion in the solution can be removed. Since the heavy metal is reduced on the cathode, it can be automatically deposited on the surface. The electrodeposited heavy metal can be recovered and reused for catalytic application. Cobalt is one of the expensive heavy metals for catalyst applications. Thus, its recovery offers an advantage to open its sustainability process.

In this research, cobalt (II) will be electrodeposited simply by applying a DC power supply to provide electrical current. Wastewater was synthetically prepared by dissolving cobalt in water which contains 1 M KCl electrolyte. Electrodeposition was carried out in an electrochemical cell using stainless steel cathode and a pure graphite anode. Here in, the effect of applied current, pH solution and initial cobalt concentration toward the reaction rate were studied.

2. Methodology

2.1. Materials
Pure graphite plate was purchased from Pacseal, commercial stainless steel rod, cobalt (II) acetate ((CH₃COO)₂Co), potassium chloride (KCl), hydrochloride acid (HCl), and sodium hydroxide (NaOH) were purchased from Merck.

2.2. Methods

2.2.1. Electrodeposition of cobalt (II). Electrodeposition was conducted in a 100 mL beaker glass as an electrochemical cell. The cathode was a stainless steel rod of 10 cm and 0.5 cm in diameter. While the anode was a graphite plate 10 x 1 cm with 0.1 cm thickness. The two electrodes were 7 cm dipped in the electrolyte solution in the electrochemical cell. The distance between cathode and anode was kept 3 cm in all experiments. The electrochemical solutions were 100 mL of synthetic wastewater prepared by dissolving cobalt (II) in 1 M of KCl solution. The electrodeposition was carried out at various current from 0.25 – 1.25 A, various pH of the solution (2 – 6), and various of cobalt (II) concentration (10 – 50 ppm).

2.2.2. Inductively coupled plasma emission spectrophotometer (ICP-AES) measurement. Cobalt (II) solution concentration after electrodeposition was measured using ICP-AES (Shimadzu Sequential Plasma Spectrometer – 7510), at 228.6 nm.

3. Results and discussion
Cobalt (II) has a negative reduction potential standard (eq. 1), which needs external energy to form Cobalt (0). In this research, a DC power supply was used to provide current to perform an electrochemical reduction of cobalt(II) from synthetic wastewater solution. Herein, the electric field is the only driving force source for cobalt reduction. Positively cobalt ion is attracted to a negative electrode (cathode) and received two electrons, and be electrodeposited on the cathodes’ surface. Proton, H⁺ is also attracted to the cathode then being reduced to produced hydrogen gas [10]. The reduction of hydrogen is more easily than cobalt (II) due to its potential reduction standard. Herein, the bubble generation of hydrogen was observed on the stainless steel cathode during electrodeposition.

Reaction on the cathode:

\[
\begin{align*}
\text{Co}^{2+}_{\text{(aq)}} + 2e^- \rightarrow \text{Co}_{\text{(s)}} & \quad E_{\text{SHE}} = -0.28 \text{ V} \\
\text{H}^+ + e^- \rightarrow \text{H}_2(g) & \quad E_{\text{SHE}} = 0
\end{align*}
\]
The synthetic wastewater was prepared in 1 M of KCl solution to provide a proper electrical conductivity during electrodeposition. The Cl\textsuperscript{-} anions are attracted to the anode and oxidized to form chlorine, Cl\textsubscript{2} gas (eq. 3). Another reaction on the anode is the oxidation of water to oxygen, O\textsubscript{2} gas (eq. 4)[11]. Water has a least positive potential reduction standard. Therefore, the oxidation of water will dominantly occur on the anode.

Reaction on the anode:

\[
\text{Cl}_2(\text{g}) + 2e^- \rightarrow \text{Cl}^{\text{aq}} \quad E_{\text{SHE}} = +1.36 \text{ V} \tag{3}
\]

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{H}_2\text{O}(\text{l}) \quad E_{\text{SHE}} = +1.23 \text{ V} \tag{4}
\]

3.1. Effect of the current
Cobalt concentration in the solution decreases almost linearly by time as the current applied (figure 1a). The lower current (0.25 – 0.75 A) promotes electrodeposition to follow kinetic at zero-order (table 1). While electrodeposition at higher applied current (>1 A) tends to follow the first order. Higher current means higher voltage improves the ion migration and performs faster cobalt reduction. The removal efficiency of cobalt (II) from synthetic wastewater solution are shown in figure 2b. About 99 % of cobalt can be eliminated from the solution after 20 minutes of electrodeposition at various applied currents.

![Image of Figure 1](image_url)

**Figure 1.** (a) Measured cobalt concentration, (b) histogram of cobalt removal efficiency after 5, 10, 15, 20, and 25 minutes electrodeposition at various applied currents.

| Current/A | Reaction Rate | $R^2$ | Order Reaction |
|-----------|---------------|-------|----------------|
| 0.25      | 1.0239        | 0.9967| 0              |
| 0.50      | 1.0062        | 0.995 | 0              |
| 0.75      | 0.9791        | 0.9824| 0              |
| 1.00      | 0.1447        | 0.9420| 1              |
| 1.25      | 0.1881        | 0.9218| 1              |
3.2. Effect of pH

Figure 2. (a) Cobalt concentration, (b) histogram of cobalt removal efficiency after 5, 10, 15, 20, and 25 minutes electrodeposition at 0.25 A in various pH of cobalt solution.

Figure 2a shows the variation of cobalt (II) concentration after 5, 10, 15, 20, and 25 minutes electrodeposition at various pH. pH correlates to the mobility of H⁺ and OH⁻ ions which play a major role in the electrodeposition process. The lower pH indicates a higher H⁺ concentration in the solution which stimulates faster cobalt (II) reaction. Hydrogen evolution on the cathode was also observed higher in the lower pH solution. Electrodeposition of cobalt (II) at pH range 2 – 6 follow kinetic at zero-order (table 2).

Table 2. Reaction rate equation of cobalt (II) electrodeposition.

| Current/A | Reaction Rate Equation | R²       | Reaction Order |
|-----------|------------------------|----------|----------------|
| 2         | y = -1.016x + 19.243   | 0.9875   | 0              |
| 3         | y = -1.0054x + 19.304  | 0.9921   | 0              |
| 4         | y = -1.0073x + 19.539  | 0.9955   | 0              |
| 5         | y = -0.9987x + 19.743  | 0.995    | 0              |
| 6         | y = -1.0144x + 20.174  | 0.9984   | 0              |

3.3. Effect of concentration

The electrodeposition of cobalt (II) from various initial concentrations of cobalt (II) containing synthetic wastewater is shown in figure 2a. Indeed, a higher initial concentration improves the electrolytic of the solution. Thus, the faster reaction rate of cobalt (II) concentration of 50 ppm, as shown in table 3. Figure 3b shows cobalt (II) removal efficiency from various initial cobalt (II) concentrations to reach 99% after 20 minutes of electrodeposition.
Figure 3. (a) Cobalt concentration and (b) histogram of cobalt removal efficiency after 5, 10, 15, 20, and 25 minutes electrodeposition at 0.25A in pH 6 solution by varying initial cobalt solution concentration.

Table 3. The reaction rate of cobalt (II) electrodeposition in various initial cobalt concentration.

| Current | Reaction Rate | R²     | Order     |
|---------|---------------|--------|-----------|
| 10      | 0.9675        | 0.9898 | Zero-order|
| 20      | 1.0146        | 0.9973 | Zero-order|
| 30      | 1.513         | 0.9745 | Zero-order|
| 40      | 2.0102        | 0.9973 | Zero-order|
| 50      | 2.4946        | 0.9984 | Zero-order|

4. Conclusion

The electrodeposition method has been successfully applied to remove and recover cobalt (II) from synthetic wastewater. The rate of cobalt (II) removals was affected by the applied current, pH of the solution, and initial cobalt (II) concentration. Removal efficiency of cobalt (II) reach 99% after 20 minutes electrodeposition.

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