

Removal of nickel ion from electroplating wastewater using double chamber electrodeposition cell (DCEC) reactor partitioned with water hyacinth (*Eichhornia crassipes*) leaves

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Abstract. Nickel is a heavy metal present in many types of industrial wastewater, and its contamination to the water bodies should be prevented. The objective of this research was to study the performance of Double Chamber Electrodeposition Cell (DCEC) for nickel ion removal. Water hyacinth (*Eichhornia crassipes*) leaves were used to separate the two chambers. The experiment was performed with synthetic electroplating wastewater in a batch system for 72 h. Changes of pH, electric current, and nickel ion concentration in the catholyte were monitored. An experiment with Single Chamber Electrodeposition Cell (SCEC) was also performed as comparison. After 72 h operation of DCEC, nickel ion concentration in the catholyte decreased from 2200 g.m^{-3} to 0.4 g.m^{-3} , equivalent to 99.98% removal. DCEC reactor performed better than the SCEC reactor that only achieved 59% removal. The results show that an almost-complete removal of nickel ion can be achieved with DCEC. Water hyacinth leaves can be used as low-cost alternatives for industrial membranes.

1. Introduction

Nickel is a heavy metal with broad industrial applications; more than half of global nickel production is used in stainless steel while electroplating accounts for 11% of total nickel processing [1]. The wastewater generated from nickel processing still contains a substantial amount of nickel that should be removed before the final discharge to the environment. Exposure to nickel may cause health problems including skin irritation, asthma, and conjunctivitis. High exposure of nickel e.g. in workplace has been linked to cancer [2,3].

Nickel ion can be removed from nickel-containing wastewater by several techniques: chemical precipitation, ion floatation, ion exchange, adsorption, membrane filtration, and electrochemical treatments [4,5]. Chemical precipitation is currently the most used treatment because the operation is simple and requires low capital cost. The drawback is the high volume generation of nickel-containing sludge that may still create environmental problem if not handled properly [4]. Electrochemical treatments enable recovery of nickel in the form of pure nickel, nickel compounds, or concentrated stream that can be reused in industrial processes [6–8]. The drawbacks of these treatments are the high energy consumption and possible fouling in the processes that use membranes [4].

Electrochemical treatments can be performed by electrodeposition, electrodialysis, electrodeionization, or combination of these processes [9]. Electrodeposition occurs based on the following reactions:

Cathodic reaction : $\text{Ni}^{2+}_{(\text{aq})} + 2 \text{e}^- \rightleftharpoons \text{Ni}_{(\text{s})}$

Anodic reaction : $\text{H}_2\text{O} \rightleftharpoons \frac{1}{2} \text{O}_{2(\text{g})} + 2 \text{H}^{+}_{(\text{aq})} + 2 \text{e}^-$



Competing reactions sometime occur in the cathode, for instance hydrogen gas ($H_{2(g)}$) formation and water hydrolysis. These reactions may influence nickel ion reduction on the cathode [10]. Membranes are sometimes used to separate the cathode and the anode, and optimize the reaction in each electrode. The use of membranes requires high capital cost and maintenance, therefore an alternative is envisaged.

Water hyacinth leaves were used in this experiment as the partition between the anode and the cathode chamber due to the similarities with industrial membrane's properties. The cell wall of water hyacinth leaves contains 20-25% cellulose, 35-40% hemicellulose, and 6-8% lignin [11]. Cellulose isolated from water hyacinth has been used to prepare cellulose diacetate, a membrane precursor, with comparable properties to commercial cellulose diacetate [12].

A previous study compared the performance of Single Chamber Electrodeposition Cell (SCEC) and Double Chamber Electrodeposition Cell (DCEC) partitioned with water hyacinth leaves [7]. During the 4 hr operation, DCEC had a higher current efficiency and a lower specific energy compared to SCEC. However, only 27% of nickel ion was removed from the initial concentration of 2402 g.m^{-3} to the final concentration of 1756 g.m^{-3} . The objective of this research was to study the nickel ion removal from DCEC partitioned with water hyacinth leaves during prolonged operation. An experiment with SCEC was also performed for comparison.

2. Experimental

2.1. Materials

Synthetic wastewater was prepared using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ dispersed in distilled water to the concentration of 2200 g-Ni.m^{-3} . All chemicals used were of analytical grade.

Water hyacinth leaves were obtained from Cikapundung River, Bandung, West Java, Indonesia. Prior to experiments, the leaves were rinsed with distilled water to remove dirt.

2.2. Experimental setup

The experiment was performed in a previously described setup [7]. A Double Chamber Electrodeposition Cell (DCEC) consisted of two conjoined cylindrical compartments partitioned with water hyacinth leaf, each having 500 ml working volume. The synthetic wastewater was placed in the compartment housing a copper plate cathode. The second compartment housed a graphite plate anode and $0.2 \text{ M H}_2\text{SO}_4$ was used as the anolyte. The experiment was performed in duplicate at $26.0 \pm 0.3^\circ\text{C}$, 5V DC input for 72 h. Nickel ion concentration, pH, conductivity, and electric current were measured over time.

In Single Chamber Electrodeposition Cell (SCEC), a cylindrical compartment (500 ml working volume) housed both the cathode and the anode. The experiment was performed at similar conditions as the experiment with DCEC.

2.3. Analysis

Nickel ion (Ni^{2+}) concentration in the solution was determined using Atomic Absorption Spectrophotometry (AAS). The absorbance was measured with Shimadzu AA 6501S (Japan) at 232 nm [13].

The pore size of water hyacinth leaves was measured using BET surface area analysis. Ion exchange capacity was measured using potentiometric titration [14].

2.4. Calculations

Reactor performance was measured by nickel ion removal (%), which was calculated based on initial nickel ion concentration ($C_0, \text{g.m}^{-3}$) and nickel ion concentration at time t (C_t):

$$\text{Removal} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Nickel ion removal may follow first order kinetic with removal rate constant k [15]:

$$\frac{dC_t}{dt} = -kC_t \quad (2)$$

Specific energy of removal (kWh.g-Ni^{-1}) is the amount of energy required to remove m g of nickel ion:

$$\text{Specific energy of removal} = \frac{V \cdot I \cdot t}{m} \quad (3)$$

V = applied voltage (V); I = measured electric current (A); t = time (h)

3. Result and discussion

3.1 Nickel ion removal

Nickel ion concentrations were measured over time, and the results are presented in Figure 1.

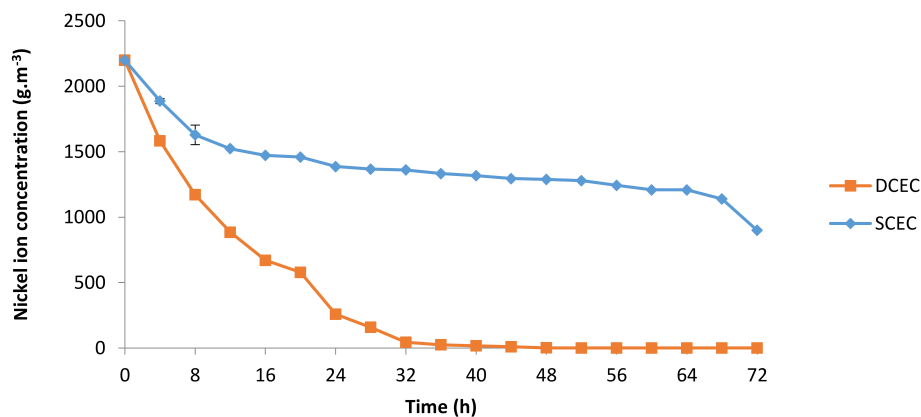


Figure 1. Nickel ion concentrations in Double Chamber Electrodeposition Cell (DCEC) and Single Chamber Electrodeposition Cell (SCEC).

Figure 1 shows that the nickel ion concentration in DCEC decreased rapidly between $t = 0$ (2200 g.m^{-3}) and $t = 32 \text{ h}$ (44 g.m^{-3}), and the final concentration at $t = 72 \text{ h}$ was 0.4 g.m^{-3} . This result showed the decrease of nickel ion concentration as 99.98% removal and therefore had met the Indonesian standard for liquid waste of 1 g.m^{-3} for metal plating industry [16]. DCEC performed better removal than SCEC, which still contained 900 g.m^{-3} nickel ion (59% removal) after 72 h.

Nickel ion removal in DCEC followed first order kinetic with removal rate constant $k = 0.12 \text{ h}^{-1}$ ($R^2 = 0.956$). On the other hand, nickel ion removal in SCEC only followed first order kinetic during the first 16 h with $k = 0.03 \text{ h}^{-1}$ ($R^2 = 0.907$). After $t = 16 \text{ h}$, nickel ion was removed from SCEC at the linear rate of $7 \text{ (g.m}^{-3}\text{).h}^{-1}$.

During metal electrodeposition on the cathode, the involved mechanisms are diffusion, convection, and migration of metal ions and electrons toward the cathode surface, followed by electron adsorption to form adatom, and diffusion of the adatom to form crystal [10]. Without partition between the anode and the cathode chambers, hydrogen ions (H^+) that were formed in the anode were transferred onto cathode and formed $\text{H}_{2(\text{g})}$ that reduced the mass transfer toward the cathode surface. The transfer of H^+ still occurs when sulfonated membranes are used as partition, since these membranes are capable of proton transfer [17]. The main functional groups in water hyacinth leaves are C=O , CH_3 , and -COOH [12], and our results suggest that water hyacinth leaves were able to prevent H^+ transfer from anode to cathode. Furthermore, a high nickel ion concentration in the cathode chamber also optimized the mass transfer.

Water hyacinth leaves used in the experiments had surface pore sizes of 2-50 nm, ion exchanger capacity of 0.64 meq.g^{-1} , and conductivity of 0.13 mS.cm^{-1} . Conductivity and current in DCEC were higher than SCEC, and relatively constant throughout the experiment. The differences in conductivity were only 2% or less (Figure 2a), confirming that water hyacinth leaves had a good conducting property as expected.

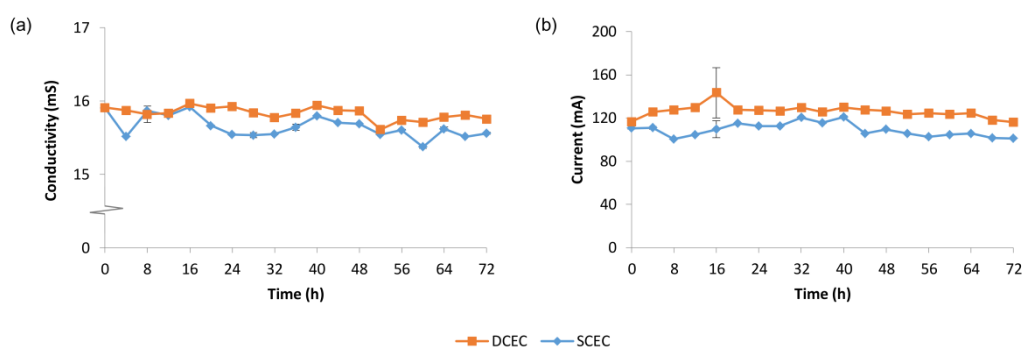


Figure 2. Conductivity (a) and current (b) in DCEC and SCEC.

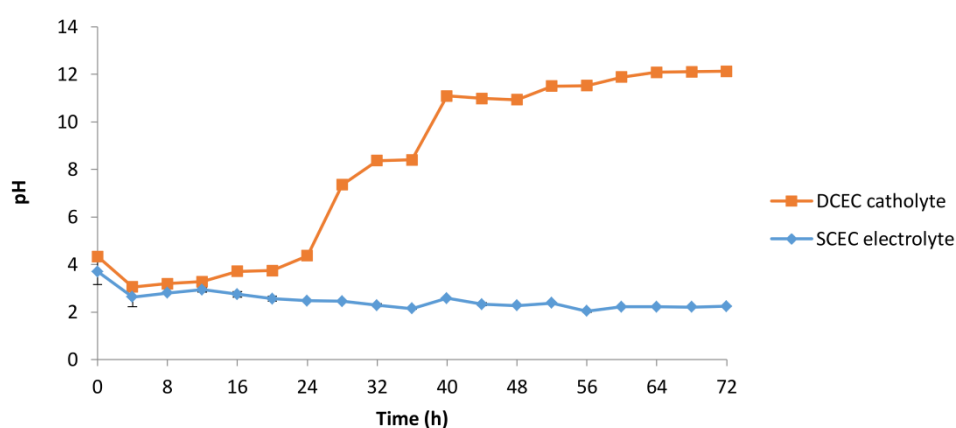


Figure 3. pH changes in DCEC and SCEC.

Compared to conductivity, the differences in current were more evident. This suggests that compared to SCEC, the reactions occurred more efficiently in both chambers of DCEC, therefore enabled a higher electron transfer rate.

Figure 3 shows that between $t = 0$ and $t = 24$ h, the pH in the cathode chamber of DCEC was around 4. The pH started to increase after $t = 24$ h and reached 12 at the end of the reaction. At $t = 24$ h, 88% nickel ion removal was already achieved and the competing reaction that hydrolyze water into $H_{2(g)}$ and hydroxide ion (OH^-) started to occur. The increase in OH^- concentration occurred faster as nickel ion concentration decreased, and consequently the pH increased. Since the optimum pH for nickel ion precipitation is 10–11 [18], the increase of pH particularly between $t = 24$ h and $t = 48$ h increased the deposition of nickel ion and consequently its removal from wastewater.

In SCEC, the pH decreased from 4 at the beginning of the reaction until 2.2 after 72 h. At low pH, more H^+ are available for reduction reaction at the cathode, competing with nickel ion reduction and therefore lowering the efficiency of nickel ion removal at the cathode.

After 72 h, the difference between initial and final concentration showed that 1.1 g of nickel ion was removed from synthetic wastewater in DCEC. However, based on the initial and final weight of the cathode, it was observed that only 0.7 g nickel ion was deposited on the cathode or equivalent to 67% of the removed nickel ion. This discrepancy suggests that around one third of the nickel ion was adsorbed by water hyacinth leaf. The ability of water hyacinth leaves to adsorb heavy metals has been documented previously [19–21]. Therefore, water hyacinth leaves increased nickel ion removal through two mechanisms: preventing H^+ transfer and nickel ion adsorption.

3.2 Energy consumption

The hourly energy consumption in DCEC was relatively constant at 0.0005 kWh. As the energy increase was in a higher order compared to the increase of removed nickel ion, the overall specific energy of removal almost linearly proportional to energy consumption. For 72 h of operation, the total specific energy of removal was 0.041 kWh.g-Ni⁻¹.

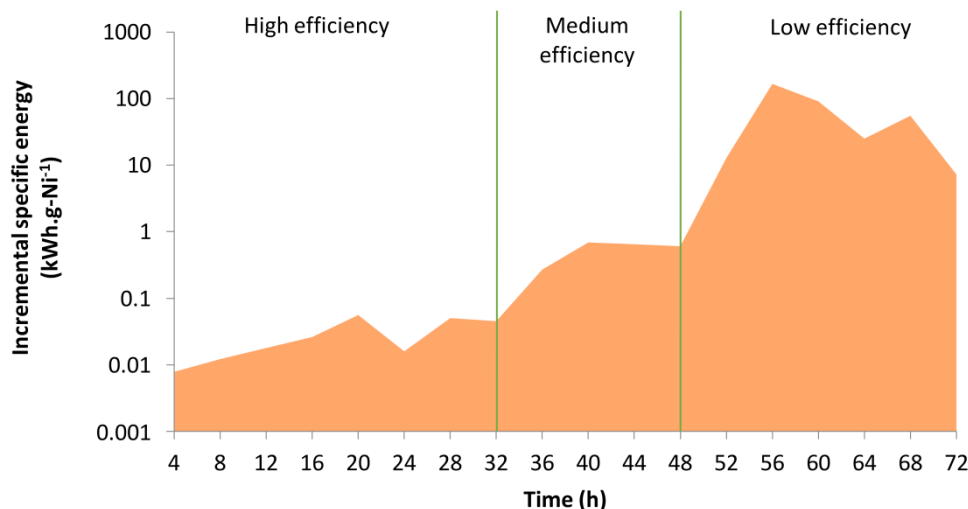


Figure 4. Incremental specific energy of removal in DCEC.

Figure 4 shows the required energy per g of removed nickel ion for every 4 h period. Between $t = 0$ and $t = 32$ h when nickel ion concentration was still higher than 40 g.m⁻³ (Figure 1), the specific energy of removal was less than 0.1 kWh.g-Ni⁻¹. To reduce nickel ion concentration from 44 g.m⁻³ ($t = 32$ h) to 1.5 g.m⁻³ ($t = 48$ h), 0.3-0.7 kWh.g-Ni⁻¹ (0.5 kWh.g-Ni⁻¹ on average) was required. The least efficient removal occurred after $t = 48$ h to reduce nickel ion concentration from 1.5 to 0.4 g.m⁻³. On average 30 kWh.kg-Ni⁻¹ was required, more than 1000 times the energy requirement before $t = 32$ h. It is suggested that if a complete removal is not expected, 48 h operation can be applied. However, if the aim is to meet the effluent standard of 1 g.m⁻³ [16], it might be more energy-efficient to combine DCEC with a polishing step e.g. adsorption or membrane filtration [5,22], that can remove nickel ion at low concentration.

4. Conclusion

The results show that nickel ion can almost be completely removed from artificial wastewater using a DCEC reactor partitioned with water hyacinth leaves. The prevention of hydrogen gas attachment on the cathode, high pH in the cathode chamber, and adsorption of nickel ion by water hyacinth leaves contribute to this high removal. This also shows that water hyacinth leaves can be low-cost alternatives for industrial membranes.

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