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Rapid and efficient removal of Ni(II) in water using constant-current electrolysis

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ABSTRACT

This study presents a constant-current electrolysis technique to remove Ni(II) efficiently from aqueous solution using an electrochemical cell. Three electrodes of aluminum, stainless steel, and graphite were used as cathodes, while rectangular graphite plates were the anode. The effects of solution pH values (0.3–7.0) and applied current density (I = 100–200 A/m^2) were investigated. Complete removal of Ni(II) ions was achieved within 12 min using a graphite cathode at pH 1.0 and I = 140 A/m^2, which had a current efficiency of 38%. Under the same conditions, more than 99% removal of Ni(II) was obtained from wastewater within 60 min of electrolysis time.

Keywords: Reduction; Electrochemical method; Wastewater; Toxic metals; Nickel

1. Introduction

Nickel (Ni) is considered as a strategic metal because of its toughness and high corrosion resistance, and therefore it is used in many industries including electroplating, production of stainless steel, batteries, and paint, mineral processing, and manufacturing [1–6]. Alloys of Ni are commonly used in industrial machinery and precision electronics. Because of extensive use of Ni in various industries, wastewater effluents contain nickel in the range of from tens to thousands of mg/L [7,8]. In electroplating, only 30–40% of metals in water are usually used and thus the remaining unused water contains high residual concentrations of Ni(II) [9]. Nickel and its compounds are toxic and may cause various health effects including dermatitis, dizziness, cyanosis, renal edema, and lung cancer [10,11]. According to the regulatory agencies worldwide, the release of Ni must be controlled to protect the environment and human health. It is thus imperative to develop effective methods to remove or recover Ni from water.

Removal of Ni is a challenging task and numerous treatment methods have been suggested, which include biological methods, ion exchange on either resin or zeolite, adsorption on red mud or activated carbon, microfiltration, chemical precipitation, and electrochemical techniques [8,12–17]. Electrochemical

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treatment methods seem promising as it is a relatively cleaner process involving the application of electrons and electrodes. The different methods comprise electrocoagulation, electrodialysis, electrodeionization, and electrodeposition [18–23]. These methods are able to remove >99% nickel, but generally require a long electrolysis time, ranging from several minutes to hours.

This paper aims to reduce the electrolysis time to less than 15 min for complete removal of Ni(II) ions in water by performing constant-current electrolysis in the laboratory and small pilot setups. In the electrolysis experiments, the effects of different cathodes (aluminum, steel, and graphite), pH, and applied current density on the removal of Ni(II) from water were examined. Elimination of Ni(II) was also demonstrated for a laboratory wastewater.

2. Experimental methods

All reagents were of analytical grade (Sigma Aldrich, Saint Lois, Missouri, USA and Carlo Erba Reagent, Reuil, France) and were used without any further purification. Solutions were prepared using deionized water that was obtained by passing double-distilled water through a 18 MΩ cm^{-1} Milli-Q water purification system (Billerica, Massachusetts, USA). Ni(II) solutions were prepared by dissolving a certain amount of solid nickel(II) sulfate in water to obtain a Ni(II) concentration of 979 mg/L. The pH of the separate aliquots of solution was adjusted to 0.3, 1.0, 3.0, and 7.0 by the dropwise addition of 10 M HCl. Dissolved organic carbon (DOC) was determined using a total organic carbon (TOC) analyzer (Shimadzu ASI-V, Japan). The TOC in the stimulated wastewater was determined to be 7.44 mg/L. Wastewater sample was also obtained from a university analytical laboratory in Thailand. The sample contained 1,281 mg/L Ni(II) and 1,830 mg/L DOC, and the pH was 0.3.

The experiments were carried out with electrodes, arranged in a two-compartment reactor setup (Fig. 1). The two compartments were separated from each other by an agar wall saturated with NaCl, which prevented intermixing of solutions without obstructing the migration of ions under the influence of the electric field. One of the compartments, called “cathodic”, contained wastewater at a desired pH while the other compartment, named “anodic”, had 1 M NaCl as an electrolyte. In this setup, two rectangular graphite plates served as the anode and two rectangular graphite or stainless steel or aluminum plates served as the cathode. The cathode surface area per solution volume (A/V) was 85 m^2/m^3. The source of the constant current was by DC power supply (GW Instek GRP-6060D, New Taipei City, Taiwan). A magnetic stirrer at 1,100 rpm was employed to ensure the uniform mixing of the solution.

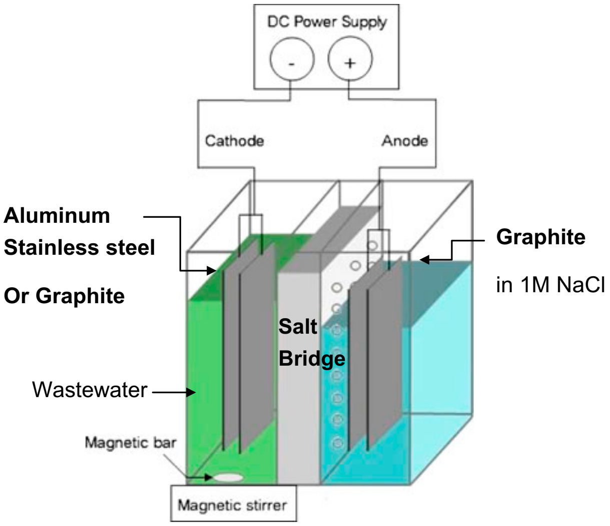

Fig. 1. Diagram of constant-current electrochemical cell.

Experiments were carried out by selecting a constant current, and samples were periodically withdrawn for evaluating the pH and determining the concentrations of Ni(II) ions. The quantification of Ni ions in the sample was carried out by atomic absorption spectrometry (Perkin Elmer AAnalyst 100, Waltham, Massachusetts, USA). A standard solution of Ni(II) was prepared from analytical grade $NiSO_4 \cdot 6H_2O$ (99% purity), obtained from Carlo Erba Reagent Spa (Reuil, France). The linear calibration curve was carried out in a range of 0–140 mg/L ($r^2 = 0.9928$). Each experiment was repeated three times and the measured parameters were expressed as a mean value of these three experiments (SD = 0.13–1.72).

3. Results and discussion

3.1. Effect and mechanism of nickel removal using different electrode materials

Initially, the influence of the cathode materials Ni(II) ion removal was tested using graphite, stainless steel, and aluminum sheets. For each cathode material, the results of Ni(II) concentration vs. electrolysis time at an initial pH of 0.3 are shown in Fig. 2(A). The removal of Ni(II) ions followed a similar pattern when graphite and stainless steel cathodes were used. The results using the aluminum cathode showed a different removal profile from the other cathodes (Fig. 2(A)). During this same experiment, the solution pH monitored the change in pH over time and is shown in Fig. 2(B). When graphite or stainless steel

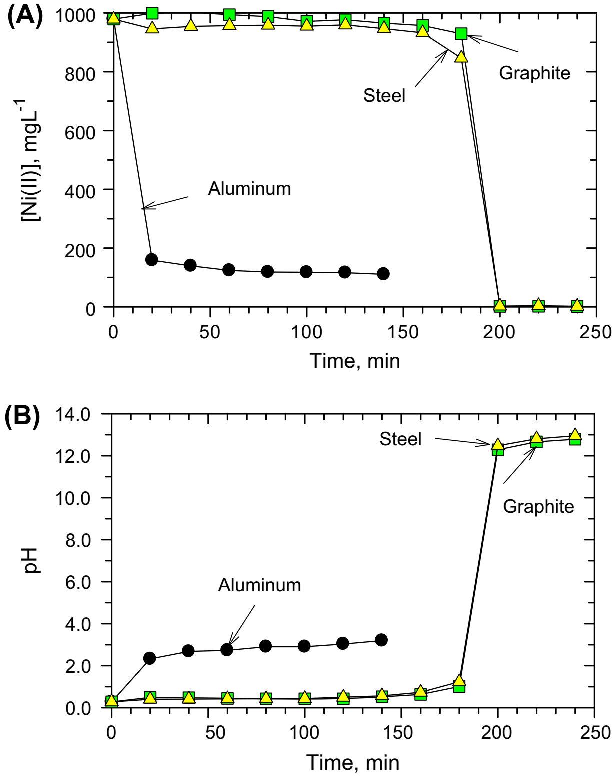

Fig. 2. Electrolysis as a function of time using different cathodes with initial pH 0.3. (A) Decay of concentration of Ni(II) and (B) change in pH.

cathodes were used, no significant changes in Ni(II) concentrations or pH values were observed in the first 180 min of electrolysis time. However, a rapid removal of Ni(II) ions after 180 min was observed and a complete removal was obtained at 200 min. The increase in pH occurred at the same time point as the removal of Ni(II) ions (Fig. 2(A) vs. (B)). In contrast, when the aluminum cathode was used, decrease in Ni(II) concentration was observed in the first 20 min of electrolysis time. The increase in pH with the aluminum cathode was the modest (Fig. 2B). Again, the decrease in the Ni(II) ion concentrations occurred at the same time as the increase in the pH of the solution.

The results of Fig. 2 may be described by considering the reactions at the cathode surface (Eq. (1)):

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \tag{1}$$

When voltage was applied, Ni(II) ions in the bulk solution were transported to the cathode surface due to attraction. At the cathode, Ni(II) ions were deposited and reacted with OH^- ions (Eq. (1)) to form $Ni(OH)_2$ (Eq. (2)), which caused removal of the ions from the solution (Fig. 2(A)):

$$Ni^{2+} + 2OH^- \rightleftharpoons Ni(OH)_2 \tag{2}$$

The minimal removal of Ni(II) ions before 180 min could be related to the neutralization of OH^- ions by the H_3O^+ ions in the highly acidic medium of the solution (i.e. pH 0.3) (Eq. (3)):

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \tag{3}$$

It appears that neutralization in the beginning of electrolysis caused a little variation in the pH of the solution. As concentrations of H_3O^+ ions decreased by the OH^- ions, the pH began to increase (see Fig. 2(B)). This prompted reaction (2) to decrease the concentration of Ni(II) ions in solution as observed experimentally (Fig. 2(A)). The precipitates of $Ni(OH)_2$ can be removed easily by filtration. With the aluminum cathode, Ni(II) ion removal was observed on a much shorter time scale compared to removal of Ni(II) ions using graphite or stainless steel cathodes (Fig. 2(A)). This may be related to the formation of Al(III) ions (Eq. (4)), which subsequently formed aluminum hydroxide ($Al(OH)_3$) flocs (Eq. (5)). These flocs served as an efficient coagulant in removing Ni(II) ions from the solution [9].

$$Al_2O_{3(s)} + OH^- + 3H_2O \rightleftharpoons 2Al^{3+} + 8OH^- \tag{4}$$

$$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3 \tag{5}$$

3.2. Effect of the initial pH conditions

The effect of the initial pH on Ni(II) removal was studied using a graphite cathode in order to avoid coagulation by amorphous aluminum hydroxides. In this study, the effect of four initial pH values (0.3, 1.0, 3.0, and 7.0) was investigated. The percentage removal of Ni(II) ions with electrolysis time is demonstrated in Fig. 3. After 20 min electrolysis, 99.85, 99.80 and 99.90% of Ni(II) were removed from the solution with the initial pH values of 1.0, 3.0, and 7.0, respectively. In the case of the lowest solution pH (pH 0.3), the Ni(II) removal reached to 99.71% after 200 min of electrolysis. As described above, the high acidity of the solution initially neutralized the hydroxide ions generated at the cathode (Eq. (1)), which were largely responsible for the removal of Ni(II) ions from the solution. This caused an increase in the electrolysis

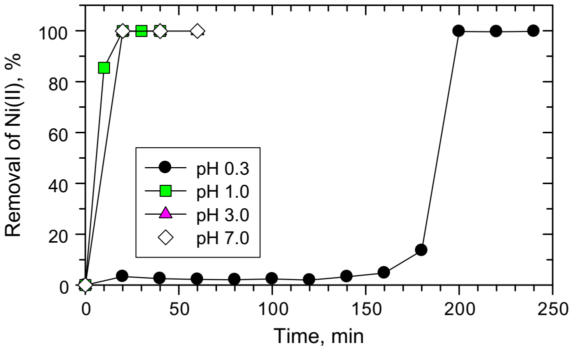

Fig. 3. Removal of Ni(II) at various initial pH using a graphite cathode.

time needed for the removal of Ni(II) ions from the low pH (0.3) solution compared to the other studied pH values. Overall, the results of Fig. 3 suggest that adjusting the initial pH of the solution helped shorten the electrolysis time and consequently improved current efficiency, which minimized energy consumption.

3.3. Effect of applied current density

The influence of the applied current density on the elimination of Ni(II) ions was examined by applying constant current densities of 100, 140, and 200 A/m^2 using the graphite cathode. The initial pH value of the solution was adjusted to 1.0. Fig. 4 shows the percentage of Ni(II) ion removal vs. electrolysis time. The results suggest that the applied current densities of 100, 140, and 200 A/m^2 yielded 99.90, 99.96, and 99.96% nickel(II) removal at 15, 12, and 9 min electrolysis time, respectively. This corresponded to 36.58, 37.89, and 30.50% current efficiencies at the applied currents of 100, 140, and 200 A/m^2, respectively.

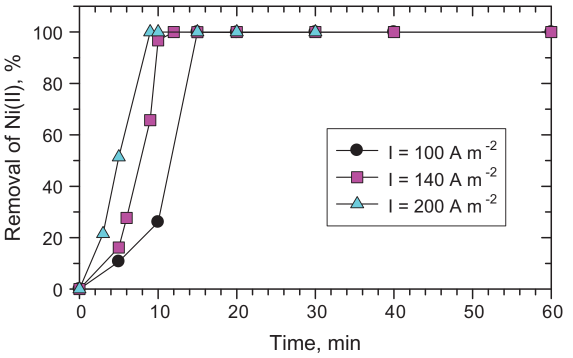

Fig. 4. Removal of Ni(II) at different applied current density (I).

3.4. Removal of Ni(II) from wastewater

Since the highest current efficiency was obtained when 140 A/m^2 current density was applied. The removal of Ni(II) ions from a sample wastewater was sought using an optimized condition of 140 A/m^2 current density with a graphite cathode. The wastewater sample had 1,281 mg/L Ni(II) ions at pH 0.3. Before electrolysis, the pH was raised to 1.0 by adding concentrated NaOH (5 M). Fig. 5 shows the removal of Ni (II) as a function of electrolysis time. Almost complete removal of Ni(II) ions was achieved in 60 min. Comparatively, for a solution that had DOC of 7.44 mg/L, the electrolysis time for removal of Ni(II) occurred in 12 min (see Section 3.3). This suggests that organic species presented in the wastewater played a role in postponing removal of Ni(II) ions from the wastewater.

3.5. Comparison with other studies

The removal efficiency of Ni(II) ions in the present study is compared with other studies in Table 1. The electrochemical cell used in this study was able to achieve Ni(II) removal in a shorter time than other systems. A sample in our study, which had low levels of DOC, showed removal of Ni(II) in 12 min. However, other studies containing much lower amount of initial concentrations of Ni(II) required much longer electrolysis times (≥35 min) (Table 1). For example, the electrolysis time for a wastewater containing 100 mg/L initial Ni(II) was 35 min [8]. Our study had more than ten times this initial Ni(II) level initially, but 100% removal was achieved in 60 min. The DOC levels were not available in most of the known literature, therefore, a comparison of the results examining the effect of the DOC was not possible.

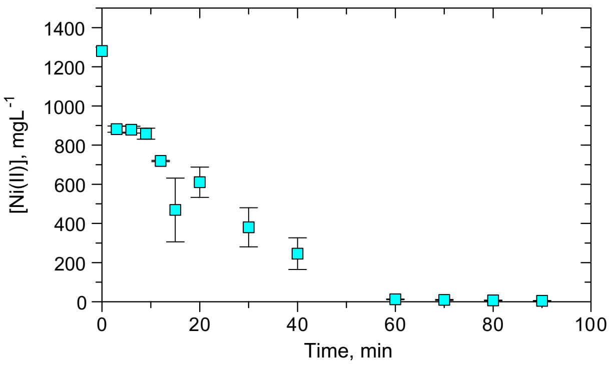

Fig. 5. Removal of Ni(II) in wastewater.

Table 1
A comparison of multiple studies of electrochemical treatment for Ni^{2+}

Method	Anode	Cathode	Initial [Ni(II)], mg/L	Initial pH	Conditions	Electrolysis time	Removal efficiency (%)	Energy consumption (kW h/kg Ni removed)
Our work	Graphite	Graphite	979	1.0	140 A/m^2	12–60 min	100	16–63
Electrocoagulation [18]	Stainless steel	Stainless steel	282	6.0	90 A/m^2	120 min	100	60
Electrodialysis [19]	Pt oxide coated Ti	Stainless steel	11.7	N/A	400 A/m^2	480 min	69	N/A
Electrodeionization [8,20,21]	Platinized titanium	Graphite powder	100	4.0	30 A/m^2	35 min	100	N/A
	Platinum	Platinum	4.8	2–3	80 A/m^2	480 min	40	N/A
	Platinum	Platinum	56	2.65	5 V	24 h	100	N/A
Electrodeposition [22,23]	Graphite RDE	Platinum foil	27,200	3.0–4.0	100–500 A/m^2	N/A	N/A	N/A
	Activated Ti	Metal granules	2,000	5.5	325 A/m^2	120 min	90	4.2

Note: N/A—not available.

The consumption of energy for various systems is reported in Table 1. They were calculated using Eq. (6):

$$\text{Energy consumption} = \frac{I \times E \times t}{\text{g of Ni removed}} \tag{6}$$

where I is the current in ampere, E is the voltage (v), and t is an electrolysis time in hour. In some studies, the electrolysis time (t) were not available and the energy consumption could not be calculated. Using the electrolysis time of 120 min, the electrodeposition method consumed an energy of 4.2 kW h/g Ni, which had much lower energy than the energy consumed in the electrocoagulation method (60 kW h/g Ni). In our study, the energy consumption was similar to the electrocoagulation method. Also, the energy consumption used to remove Ni(II) ions with our method was low for the solution that had low levels of DOC (16 kW h/g Ni).

4. Conclusions

The removal efficiency varied with the material of the cathode. The aluminum cathode was effective in removing Ni(II) ions at a shorter time than the stainless steel or graphite cathodes. The removal improved with increasing pH. The optimal condition was at 140 A/m^2 applied current density at pH 1.0. Ni(II) at ~1,000 mg/L could be removed rapidly (<15 min), however, wastewater containing organic compounds could influence the electrolysis time required for removal. The results suggest that high values of DOC in wastewater could prolong the time required for complete removal of Ni(II) beyond 15 min.

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