Desalination and Water Treatment
www.deswater.com
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doi: 10.5004/dwt.2011.2720

32 (2011) 345–350
August

Recovery of nickel with the addition of boric acid using an electrodeposition reactor

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Received 10 October 2010; Accepted in revised form 6 January 2011

ABSTRACT

Nickel pollution is usually caused by several industrial processes such as electroplating, plastics manufacturing, nickel–cadmium batteries, fertilizers, pigments, mining and metallurgy. The development of the effective and inexpensive methods is necessary for the removal and/or recovery of nickel. In this work, the electro-treatment of a high strength industrial lead frame nickel-plating wastewater ([Ni] = 1,600 mg/L) was studied through a newly designed electrodeposition reactor. The electrolyte was circulated rapidly past the anode and cathode at a higher flow rate, allowing for improvements in efficiency and recovery, and nickel electrodeposition on the surface of cathode. The results showed that increasing boric acid concentration could increase the efficiency of nickel removal. The pH decreased during the electro-treatment was due to the production of H^+ on the cathode surface. Therefore, the optimum pH periodically controlled was found to be 2.9±0.2, and the lower current density was accompanied with the higher current efficiency. This study successfully proposed a newly designed reactor to recover 99.9% nickel from simulated wastewater.

Keywords: Nickel-plating wastewater; Boric acid; Electrodeposition

1. Introduction

Nickel pollution can be caused by several industrial processes such as connecter, lead frame and tableware electroplating, plastics manufacturing, metal finishing, nickel–cadmium batteries, fertilizers, pigments, mining and metallurgical. It can approach 2–900 mg/L in plating rinse, which is known to be one of the major toxic pollutants [1–3]. The higher concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, e.g., nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema, and skin dermatitis [4]. It is also well known that high concentrated nickel would lead to deathly carcinogen [5]. Therefore, it is necessary to develop the effective and inexpensive methods for nickel removal and recovery.

The conventional methods for the removal of Ni(II) from wastewaters include chemical precipitation, activated carbon adsorption, and ion-exchange, etc. The chemical precipitation [6,7] is the most cost-effective technology but it produces a large volume of chemical sludge and needs further disposal. Adsorption by activated carbon or some low cost waste materials, such as hazelnut shell [8], walnut shell [9] and almond husk [10], usually generate the hazardous solid waste which is difficult to eliminate. Ion exchange has been widely ap-

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Presented at the Third International Conference on Challenges in Environmental Science & Engineering, CESE-2010
26 September – 1 October 2010, The Sebel, Cairns, Queensland, Australia

plied for removal of heavy metal ions from electroplating effluent due to its effective and easy operation [11,12]. However, ion-exchange resins must be regenerated by the additive chemical reagents (acid and alkali) as saturated, and a large number of impurities (including Co and Fe) may be retained in the resin bed [1,2]. This method also causes serious secondary pollution, and therefore, it is not suitable for high strength nickel-containing wastewater.

In recent years, a special nickel-iron alloy is widely used in lead frames [1]. The electronics industry accounts for approximately 6–8% of nickel consumption, which is a constantly growing share. Therefore, the treating technology for the wastewater contains a greater concentration of nickel, such as nickel streams or rinse water, must be on the premise of economical and advantageous thinking [14]. On the other hand, boric acid is an important component of a typical nickel plating bath and usually present in the rinse water and wastewater [13]. The effect of presence of boric acid on the electro-treatment is worthy to study. In this study, an industrial nickel plating wastewater of lead frame with high nickel concentration ([Ni] = 1,600 mg/L) was chosen as the target solution to be treated through a newly designed electrodeposition reactor [13]. The objective of this paper is to develop an efficient technology to recover the nickel content, and subsequently to remove Ni(II) to less than 1 mg L^{-1}. The effect of boric acid during the electrodeposition is also discussed.

2. Materials and methods

2.1. Simulated wastewater characteristics

The source of plating wastewater containing nickel and boron collected are from a nickel-plating factory at Tao Yuen (Taiwan). The initial nickel concentration of simulated plating wastewater in this study was set at 1600 mg/L. The pH was conditioned from 1.6 to 4.5 using sulfuric acid and sodium hydroxide. The effects of boric acid additive were examined with 0, 0.125, 0.5, 4 g/L dosage, separately.

2.2. Chemicals and analytical method

All the reagents used for chemical precipitation were in industrial quality. Chemicals used to adjust solution pH, including sulfuric acid and sodium hydroxide, were of reagent grade. All the preparations and experiments were carried out at the room temperature. All samplings were filtered with TOYO 0.45 μm mixed cellulose ester filters before analysis.

The concentrations of Ni, Cu and Fe were measured with an atomic absorption spectrophotometer (GBC Sens AA). The chemical analyses were properly pretreated according to the instrument manufacturer's recommendations. TOC was determined through the total organic carbon analyzer (Sievers 900 Portable). The conductivity of the solutions was measured by the digital conductivity pro meter (WalkLAB, TRANS products, Singapore).

2.3. Reactor setup

2.3.1. Newly designed reactor (NDR)

Fig. 1a shows the newly designed reactor. The double electrode cell was setup with an inside diameter 4.3 cm, height 23 cm dimensionally stable anode (DSA, titanium coated alloy) net as anode, and a diameter 7.3 cm, height 24 cm stainless steel cylinder as cathode. The DSA anode used is titanium net coated with a thin layer of RuO_2/IrO_2. Each experiment was performed using 1.4 L solution in a 2 L acrylic electrolytic reactor in which the effective surface area of cathode was 527 cm^2. The cylindrical reactor operated at a constant current mode. Recycling pump was used for the mixing of the solution. Fig. 1c shows the profile of the newly designed reactor.

2.3.2. Traditional reactor (TR)

Fig. 1b shows the traditional reactor, in which the electrode cell was setup with 2 plates of 18 cm (L) × 17 cm (H) DSA net as anode and 1 plate of 18 cm (L) × 17 cm (H), height stainless steel as cathode. Each experiment was performed using 1.4 L solution. The acrylic electrolytic reactor was 2.4 L (20 cm (L) × 6 cm (W) × 20 cm (H)) where the effective cathode surface area was 432 cm^2. The reactor was also operated at a constant current mode. Recycling pump was also used for the mixing of the solution.

3. Results and discussion

3.1. Effect of boric acid

Our previous study has reported that the nickel could be highly recovered from 16,000 mg/L Ni^{2+} electrolysis through the optimum dosage of 8 g/L H_3BO_3 [13]. This study would further investigate the effect of boric acid concentrations. As shown in Fig. 2, the efficiency decreases with decreasing the boric acid concentration. Furthermore, at lower concentration (such as 0.5 g/L), undesirable green nickel hydroxide which affects the quality and nature of the electrodeposits was observed on the surface of the cathode (Fig. 3). More boric acid addition could retard the rate of pH variation at the cathode-solution interface, and therefore avoid the green nickel hydroxides formation. The limiting current density was then increased [14]. It has been also reported that the boric acid addition to the nickel solution can minimize the water splitting and the nickel hydroxide precipitation [15]. Thus, the 4 g/L of boric acid concentration was chosen in the following experiments.

3.2. Effect of pH

To examine the effects of pH conditioned on the rate of

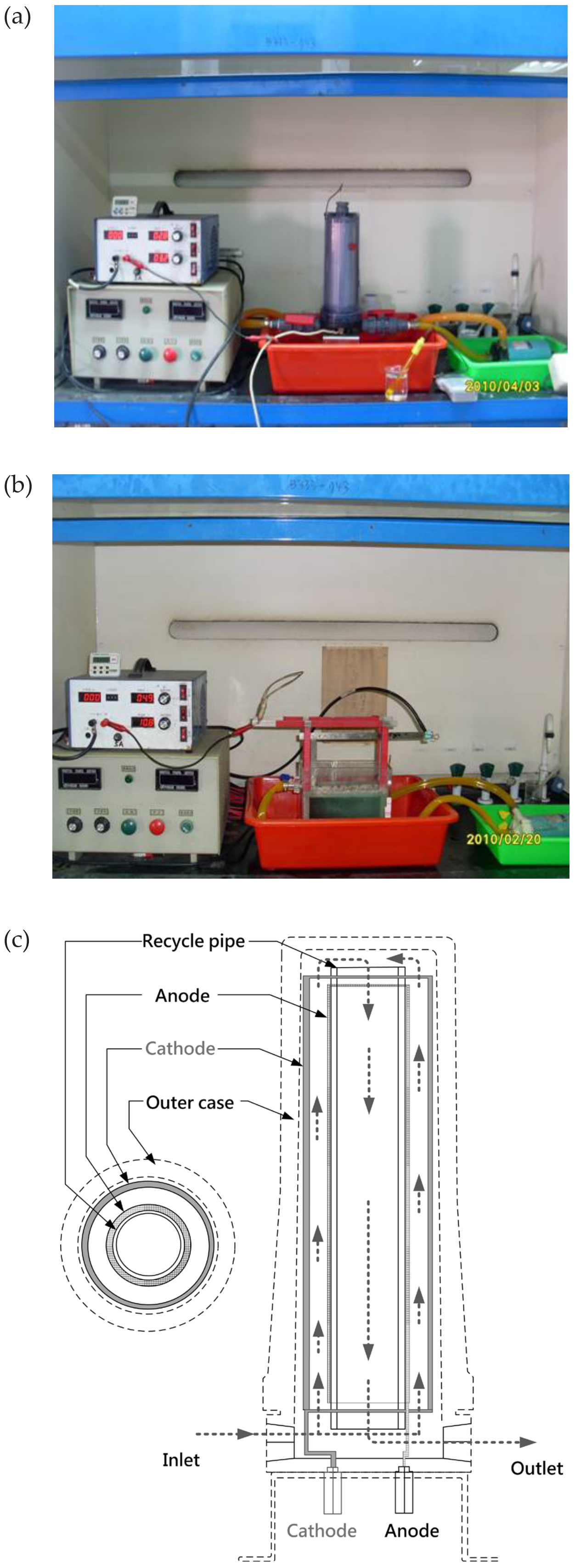

Fig. 1. Pictures of (a) NDR, (b) TR, and (c) the profile of NDR.

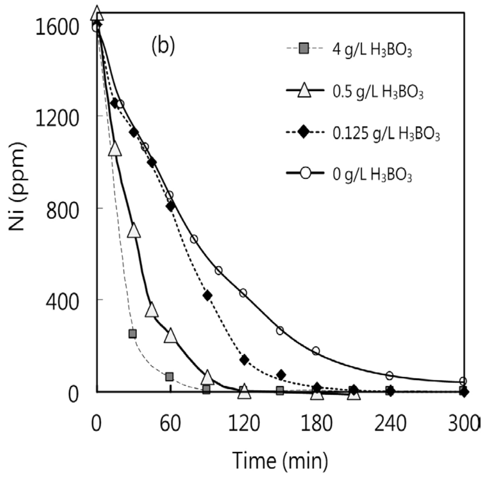

Fig. 2. Effect of boric acid concentrations on the nickel removal using NDR. Conditions: V = 1.4 L, current density = 2.0 A/dm^2 (current 10.6 A), pH = 2.2 ± 0.3.

Fig. 3. The photo of cathode after reaction. Conditions: [H_3BO_3] = 0.5 g/L, V = 1.4 L, current density = 2.0 A/dm^2 (current 10.6 A), pH = 2.2 ± 0.3.

nickel removal, the 1.4 L volume of the plating wastewater was treated with 2 A/dm^2 current density (10.6 A current applied) and the 4 g/L H_3BO_3 addition. As shown in Fig. 4, as the experiment carried out without pH control, the pH would vary from the initial 3.5 to 1.5. This observation is similar to the results reported in the literature [7]. The reactions on the electrode surfaces could be explained by Eqs. (1) and (2), in which H+ produced from the DSA anode increased the concentration of H+ ions in the solution. The nickel then electrochemically deposited onto the cathode. Another competing reaction occurred at the cathode was the hydrogen production ($2H^+ + 2e^- \rightarrow H_2$) which would decrease the H^+ concentration. The nickel formation on the cathode was therefore interfered. Hence,

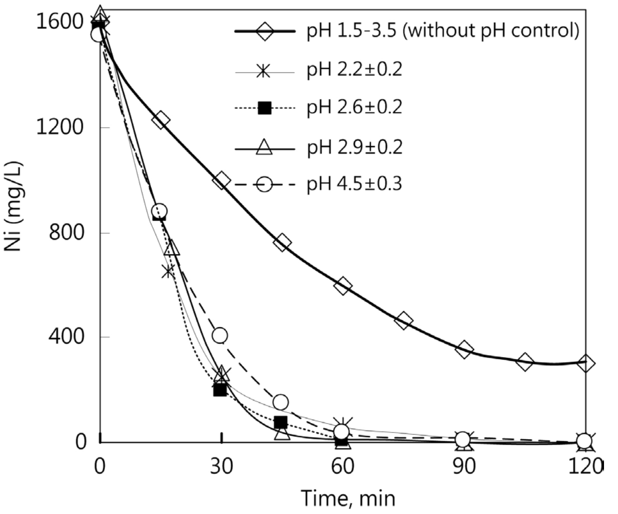

Fig. 4. Nickel concentration as a function of reaction time at different pH using NDR. Conditions: Conditions: [H_3BO_3] = 4 g/L, V = 1.4 L, current density = 2 A/dm^2.

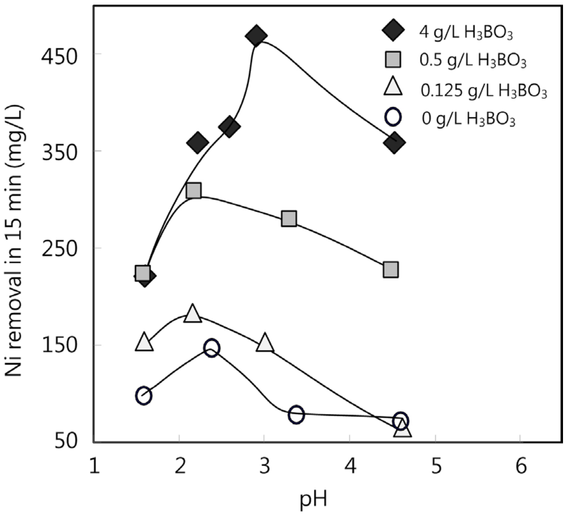

Fig. 5. The removal amount of nickel reaction with pH at different boric acid concentrations. Conditions: V = 1.4 L, current density = 2 A/dm^2.

the solution pH is an important factor for the nickel removal through the electrodeposition.

Anode:

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e^- \quad (1)$$

Cathode:

$$Ni^{2+} + 2e^- \rightarrow Ni(s) \quad (2)$$

The solution pH was monitored and conditioned at 2.2–2.9 by sulfuric acid and sodium hydroxide, periodically. As indicated in Fig. 4, due to the competing reactions between the hydrogen production ($2H^+ + 2e^- \rightarrow H_2$) and the electrochemical deposition of nickel ($Ni^{2+} + 2e^- \rightarrow Ni(s)$) occurring at the cathode, the electrochemical deposition of nickel could dominate if pH was controlled appropriately. However, at higher pH, the nickel removal rate becomes slower. Although the interference of H+ concentration could be inhibited by the addition of sodium hydroxide, the $Ni(OH)_2$ might precipitate simultaneously resulting in a low current efficiency for nickel deposition at higher pH values [16,17] , as shown in Table 1. Accordingly, the optimum pH for the removal of nickel from industrial nickel plating wastewater of lead frame is pH = 2.9 ± 0.2. Fig. 5 shows the nickel removal in 15 min reaction with pH at different boric acid concentrations. Obviously, the optimum condition for the nickel removal was 4 g/L boric acid addition and pH 2.9.

3.3. *Effect of current density*

The current density is preferably between 1 and 3 A/dm^2 based on geometric area [18]. Fig. 6a shows the results of plating wastewater treated at different current density (0.25–3.0 A/dm^2). The pH was controlled at 2.6 ± 0.2, and the reaction was kept for 30 min. The rate of nickel removal efficiency (mg/A.h) increases as the current density ranged from 0.09–1 A/dm^2, but decreases from 1.5 to 3 A/dm^2. The undesirable $Ni(OH)_2$ was proposed to be significantly produced due to the over current. Therefore, the optimum current density is 1 A/dm^2 (5.3 A), while the removal of nickel could reach 556 mg/A·h. Fig. 6b

Table 1
Nickel concentration at different pH and reaction time

	pH = 2.2 ± 0.2		pH = 2.6 ± 0.2		pH = 2.9 ± 0.2		pH = 4.5 ± 0.3	
Time (min)	[Ni] (mg/L)	Ni,r (%)	[Ni] (mg/L)	Ni,r (%)	[Ni] (mg/L)	Ni,r (%)	[Ni] (mg/L)	Ni,r (%)
0	1592	—	1571	—	1640	—	1550	—
30	246	84.5	197	87.5	266	83.8	403	74.0
60	60.5	96.2	8.42	99.5	0.30	>99.9	37.3	97.6
90	4.13	99.7	4.00	99.7	0.09	>99.9	4.60	99.7
120	0.80	>99.9	0.70	>99.9	0.05	>99.9	2.60	99.8

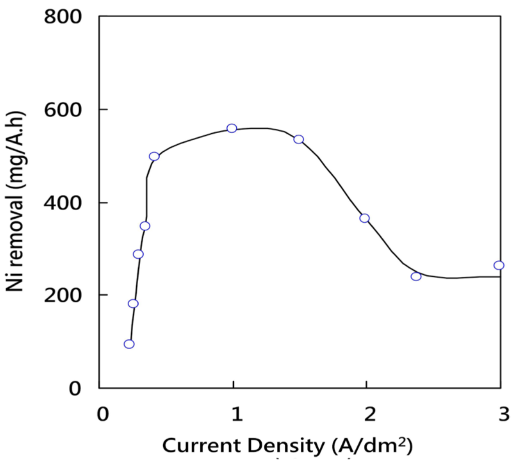

Fig. 6a. Effect of current density on the removal of nickel. Conditions: [H_3BO_3] = 4 g/L, V = 1.4 L, pH = 2.6 ± 0.2.

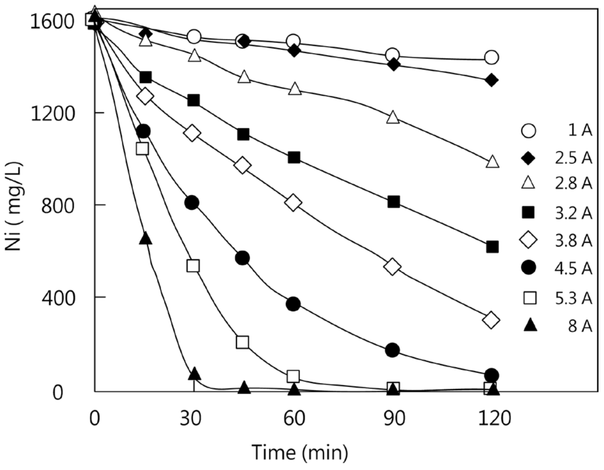

Fig. 6b. Effect of current on the removal of nickel. Conditions: [H_3BO_3] = 4 g/L, V = 1.4 L, pH = 2.6 ± 0.2.

shows the results of plating wastewater treated at different current density (0.09–3.0 A/dm^2) as a function of reaction time. The pH was controlled at 2.6 ± 0.2, while the removal increased with increasing current applied.

The data collected in Table 2 are from Fig. 6b. After reaction for 60 min, the nickel removal efficiency could reach 87.1, 99.97, and 99.99 % for 1.0, 1.5, and 3.0 A/dm^2, respectively. As compared with the results have been reported [18,19], the newly designed reactor in this study could operate at higher current density (3.0 A/dm^2) and treat the higher initial nickel concentration (1,600 mg/L), and finally obtain higher removal efficiency of wastewater to be discharged (0.536 mg-Ni/L).

3.4. Comparison between NDR and TR

To compare the NDR and TR, the 1.4 L plating wastewater was treated at current 8 A in both reactors. As illustrated in Fig. 7a, the nickel removal of both reactors was rapid at the beginning of the process and slowed down as the treatment progresses. On the other hand, the rate of nickel removal of NDR was higher than that of TR.

Fig. 7b shows the relation between the removal efficiency of nickel and current density using NDR and TR. The removal efficiency of nickel using NDR was similar to that using TR at low current density (< 1 A/dm2). At higher current density, however, the efficiency using NDR was much better than that using TR. This result indicated that the better mass transport occurred in NDR and led to the better electrodeposition at high current density.

4. Conclusions

The NDR can operate at high current density (1–3 A/m^2) and obtain high nickel removal efficiency (>99.9%). Boric acid concentration significantly affects the removal efficiency of nickel. Moreover, the optimum pH range for the removal of nickel from simulated industrial nickel plating wastewater is pH = 2.2–2.9. As Comparing with the TR, NDR proves better mass transport and shows greater ability of electrodeposition at high current density. Through this study, the simulated wastewater of 1,600 mg-Ni/L can be treated to meet the effluent standard of 1 mg-Ni/L by NDR.

Table 2
Nickel concentration at different current density

	1.0 A/dm^2		1.5 A/dm^2		3.0 A/dm^2	
Time (min)	[Ni] (mg/L)	Ni,r (%)	[Ni] (mg/L)	Ni,r(%)	[Ni](mg/L)	Ni,r(%)
0	1588	—	1588	—-	1550	—
30	535	66.3	70	95.6	72.6	95.6
60	58.85	87.1	0.461	99.97	1.67	99.9
90	3.56	99.78	0.158	99.99	0.78	99.9
120	0.924	99.94	0.076	99.99	0.536	99.9

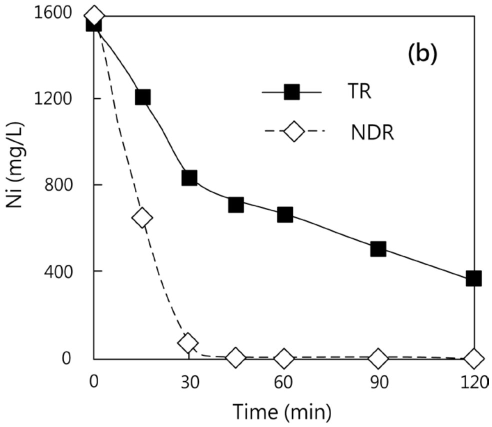

Fig. 7a. Nickel concentration as a function of reaction time using NDR and TR. Conditions: [H_3BO_3] = 4 g/L, *V* = 1.4 L, pH = 2.6 ± 0.2, current = 8 A.

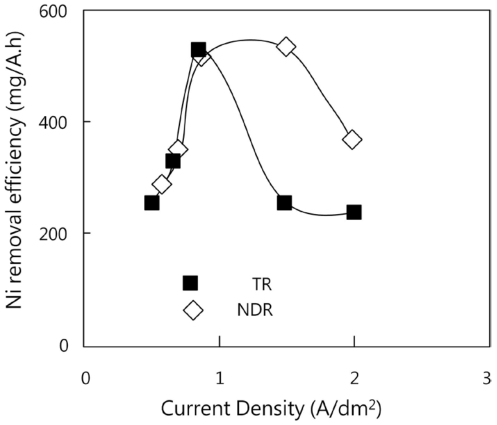

Fig. 7b. Removal efficiency of nickel at different current density using NDR and TR. Conditions used: [H_3BO_3] = 4 g/L, *V* = 1.4 L, pH = 2.6 ± 0.2, current = 8 A.

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