

Parametric study for enhanced performance of Cu and Ni electrowinning

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Abstract. In this study, we performed an electrowinning process for effective removal of metals (Cu and Ni) in solution and their recovery as solid forms. A complete removal of Cu and Ni (1,000 mg/L) was observed during four times recycling test, indicating that our electrowinning system can ensure the efficient metal removal with high stability and durability. In addition, we investigated effect of operation parameters (i.e., concentration of boric acid only for Ni, variation of pH, concentration of electrolyte (H_2SO_4), and cell voltage) on the efficiency of metal removal (Cu and Ni) during the electrowinning. The addition of boric acid significantly enhanced removal efficiency of Ni as the concentration of boric acid increased up to 10 g/L. Compared to negligible pH effect (pH 1, 2, and 4) on the Cu removal, we observed the increase in removal efficiency of Ni as the pH increased from 1 to 4. The electrolyte concentration did not significantly influence the removal of Cu and Ni in this study. We also obtained great removal rates of Cu and Ni at 2.5 V and 4.0 V, which were much faster than those at lower voltages. Finally, almost 99% of each Cu and Ni (1,000 mg/L) was selectively removed from the mixture of metals by adjusting pH and addition of boric acid after the completion of Cu removal. The findings in this study can provide a fundamental knowledge about effect of important parameters on the efficiency of metal recovery during the electrowinning.

Keywords: electrowinning; extractive metallurgy; metal recovery; anode

1. Introduction

Industrial wastewater and sludge commonly contain different metals (e.g., copper (Cu), nickel (Ni), and zinc (Zn)), which can cause serious environmental pollutions when they are disposed to natural environments without proper treatment (Chang *et al.* 2007, Ghaee *et al.* 2016, Sharma and Agrawal 2005, Zhang *et al.* 2018). Recently, recovery of such metals from liquid and solid wastes has attracted an attention owing to limited amount of metallic resources in the Earth. Among the many metal recovery techniques, electrowinning (i.e., metal recovery process by electrodepositing of metals onto cathode) is one of methods commonly applied in metal plating industry.

A main drawback of electrowinning may be a relatively large operating cost caused by need of electricity supply. In order to overcome this problem, many researchers have investigated the development of efficient dimensionally stable anode (DSA) by examining the electric properties of various noble metals. For instance, iridium (Ir), ruthenium (Ru), tantalum (Ta), tin (Sn) and their combinations have been deposited on titanium (Ti) substrate in oxide forms to improve activity, stability, and energy efficiency of anodes (Zhang *et al.* 2017, Mussy *et al.* 2003). In addition, various important factors (e.g., working voltage, pH, electrolyte concentration, etc) should be optimized for the efficient operation of electrowinning. However, limited knowledge has been provided for the fabrication of effective anode and

its use for optimized operation of electrowinning.

In this study, we used a Ti/Ir-Ru anode (1:1 molar ratio) fabricated by spin coating technique, which can result in more uniformly coated layer of noble metals on the substrate surface than other techniques (e.g. dip-, spray-, and brush-coatings) (Hummelgård *et al.* 2013). This technique can allow to spread precursor solution on the surface of substrate using centrifugal force by controlling rotation speed and time. Firstly, the feasibility and durability of Ti/Ir-Ru anode was investigated by conducting recycling experiments for Cu and Ni electrowinning. In addition, the effect of various operation parameters such as pH, boric acid concentration, H_2SO_4 concentration, and cell voltage on the efficiency of Cu and Ni electrowinning was investigated.

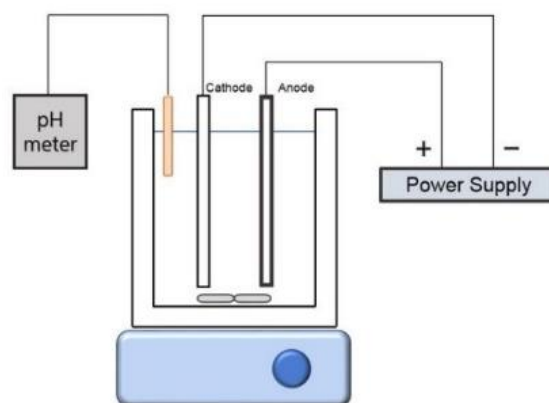


Fig. 1 Schematic diagram of electrowinning system used in this study

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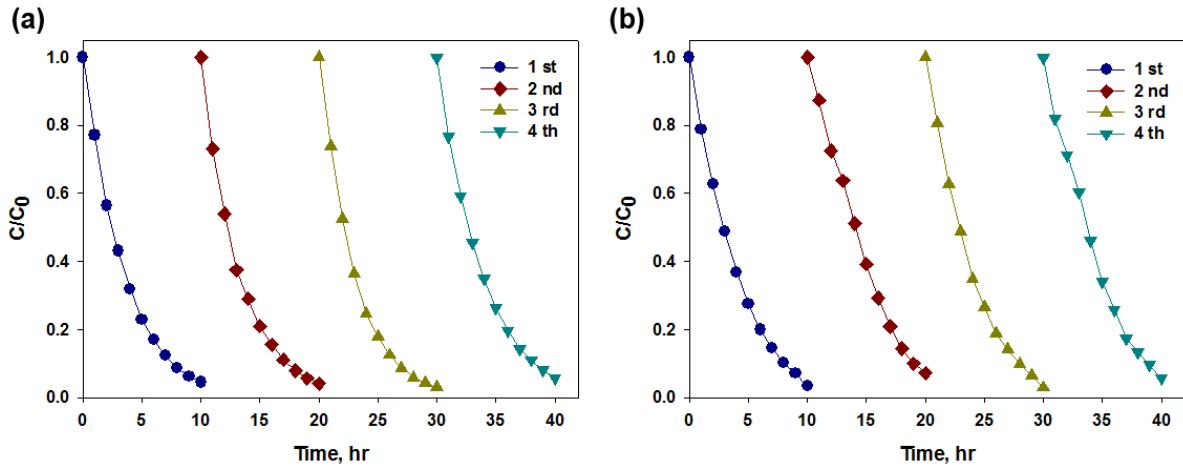


Fig. 2 Recycling tests of Ti/Ir-Ru anode for removal of (a) Cu and (b) Ni by electrowinning. For the Ni removal, 20 g/L of boric acid was added at pH 2

Table 1 Removal rate of Cu and Ni and the kinetic rate constant at each recycling test

	Removal rate (%)		k_1 (hr ⁻¹)		R^2	
	Cu	Ni	Cu	Ni	Cu	Ni
1 st	95.47	96.64	2.937e-1	2.653e-1	0.99	0.99
2 nd	95.86	92.80	3.144e-1	2.108e-1	0.99	0.98
3 rd	97.04	97.08	3.426e-1	2.725e-1	0.99	0.99
4 th	94.34	94.42	2.701e-1	2.259e-1	0.99	0.98

2. Experimental

2.1 Electrowinning system

A laboratory-scale electrowinning system was designed to investigate effect of operation parameters on removal/recovery of Cu and Ni (Fig. 1). A batch reactor (90×120×170 cm³) was used for recovery of metals by electrowinning process. For efficient electrowinning process, we fabricated a Ti/Ir-Ru anode (10×10×0.04 cm³) by spin coating technique. The details for fabrication method and characteristics of anode has been reported previously (Kim and Bae 2019). For the cathode, a commercial stainless-steel (SUS 304) electrode (10×10×0.04 cm³) was used in this study.

2.2 Electrowinning procedure

Unless stated otherwise, all experiments systematically investigated with 1,000 mg/L of metal (Cu or Ni) containing solutions prepared by dissolving CuSO₄·5H₂O or NiSO₄·6H₂O in 0.5 M H₂SO₄ solution prepared by Milli-Q water (Kang *et al.* 2014). For electrowinning of Cu and Ni, 1.5 V and 3.5 V of cell voltage was imposed by using a DC Power Supply (EX30-60) in mixing condition (200 rpm), respectively. Due to its difficulty of Ni removal, we applied higher cell voltage in Ni experiments than that of Cu (Li *et al.* 2011). At each sampling time, 10 mL of sample was collected to measure the concentration of metals by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo).

2.3 Electrowinning for parametric study

Prior to the parametric study, we repeated the Cu and Ni electrowinning at the same condition (2.0 V and 4.0 V of cell voltage, respectively) in order to confirm the feasibility and durability of Ti/Ir-Ru anode. In addition, the effect of pH (1, 2, and 4), H₂SO₄ concentration (0.1, 0.3, and 0.5 M), and cell voltage (Cu: 1.5, 2.0 and 2.5 V, Ni: 3.0, 3.5, and 4.0 V) on efficiency of electrowinning was carried out in this study. Industrial wastewater and leachate from metal sludge are commonly observed in acidic condition, thus we used H₂SO₄ as an electrolyte in this study. 10 M of NaOH solution was used to adjust and maintain the solution pH during the electrowinning of Cu and Ni, while 20 g/L of boric acid and NaOH (10 M) were used as buffer and pH maintenance during the electrowinning of Ni (Njau *et al.* 2000).

For the selective removal of Cu and Ni by electrowinning process, a mixture of Cu and Ni solution (1,000 mg/L each) was prepared in 0.5 M H₂SO₄ solution. We carried out a sequential 2-steps experiments; i) Cu removal at pH 0.4, then ii) Ni removal at pH 2 with 20 g/L boric acid. The voltages used for Cu and Ni were 2.0 and 4.0 V, respectively.

3. Results and discussion

3.1 Recycling test

Figure 2 shows the removal efficiency of Cu and Ni during four times electrowinning. Almost complete removal of metals was achieved within 10 h in all experiments. The removal kinetics of Cu and Ni was well fitted by a first-order kinetic model ($R^2 > 0.98$, Table 1). We observed very similar rate constant (k_1) during four electrowinning (Cu: 0.270–0.343 h⁻¹ and Ni: 0.211–0.273 h⁻¹, respectively). In addition, Fig. 3 shows that there was no significant change in appearance of Ti/Ir-Ru anode after electrowinning. The foregoing results indicates that Ti/Ir-Ru anode fabricated can be applied for the effective long-term electrowinning process.

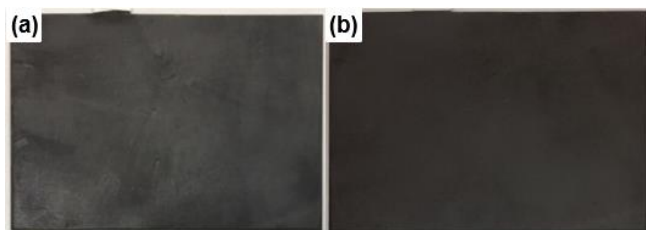


Fig. 3 Images of Ti/Ir-Ru anode (a) before and (b) after electrowinning process

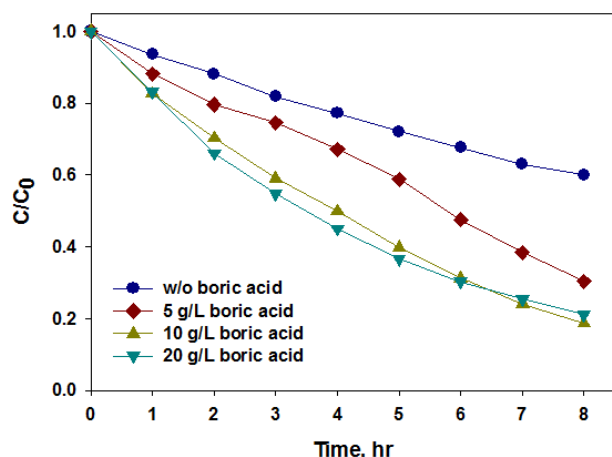


Fig. 4 Removal kinetics of Ni in different concentration of boric acid (0, 5, 10, and 20 g/L) at pH 2

3.2 Effect of operation parameters

3.2.1 Effect of boric acid on Ni electrowinning

The effect of boric acid was investigated for Ni removal by electrowinning process. Boric acid was used as an important additive to enhance Ni removal and pH buffering, which is relatively inexpensive without causing additional problems (Huang 1995). Figure 4 shows the removal of Ni by electrowinning at different concentrations (0, 5, 10, and 20 g/L) of boric acid. In the presence of boric acid, the removal efficiency of Ni gradually increased as the boric acid concentration increased up to 10 g/L, which is comparable with that of the absence. This is because boric acid can be absorbed on the cathode surface in form of nickel borate leading to the increase of cathode polarization and decrease of H_2 evolution (Lu *et al.* 2010). However, appropriate concentration of boric acid should be considered, since there was no change of removal rate for Ni more than 10 g/L of boric acid as previously reported (Lu *et al.* 2010).

3.2.2 Effect of pH

For the Cu electrowinning, we could not observe any significant change at different pHs (Fig. 5a). On the other hand, a remarkable change was observed at each pH for Ni removal by electrowinning process (Fig. 5b). Almost no removal of Ni was observed at pH 1 in 6 h reaction, whereas approximately 65% and 85% of Ni were removed at pH 2 and 4, respectively. This may be because Ni known

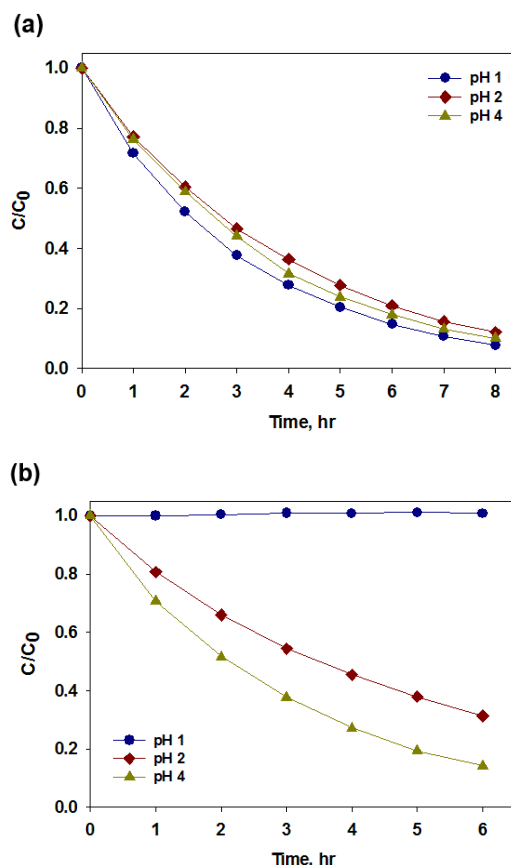


Fig. 5 Removal kinetics of (a) Cu and (b) Ni removal at different pHs

as the most electropositive metal which requires high reduction potential condition (i.e., higher pH values) to be removed by electrowinning (Giannopoulou and Panias 2007).

3.2.3 Effect of H_2SO_4 concentration

Figure 6 shows the effect of H_2SO_4 concentration on the removal of Cu and Ni by electrowinning. Compared to Cu case operating without pH control (pH 0.5–1) owing to no significant difference in the range of pH from 1 to 4, the pH value for Ni electrowinning was maintained at pH 2 using boric acid and NaOH for a proper removal of Ni as shown in Fig. 5b. Although the H_2SO_4 concentration was different during the electrowinning of Cu and Ni, we obtained no significant effect of H_2SO_4 concentration. It has been also reported that the variation of H_2SO_4 (30–150 g/L) did not show significant effect on current efficiency or power consumption (Panda and Das 2001). However, the main drawback of increasing H_2SO_4 concentration in the electrolyte may be the increase of viscosity and decrease of diffusion of ions to the cathode surface (Owais 2009). Therefore, application of relatively low H_2SO_4 concentration may be relevant during electrowinning.

3.2.4 Effect of cell voltage

Effect of cell voltage on the efficiency of Cu and Ni electrowinning was investigated at three different voltages

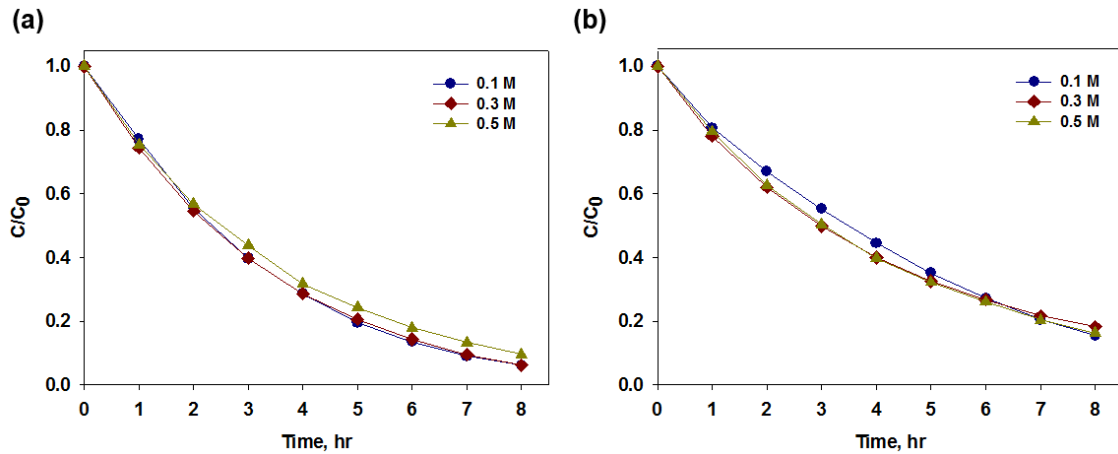


Fig. 6 Removal kinetics of (a) Cu and (b) Ni removal at different concentration of H_2SO_4

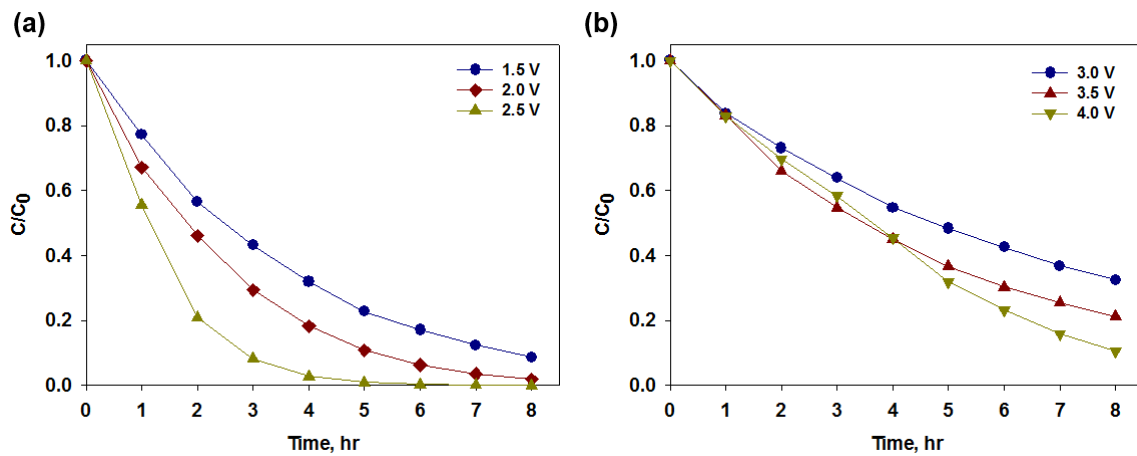


Fig. 7 Removal kinetics of Cu and Ni at 1.5 ~ 4.0 V

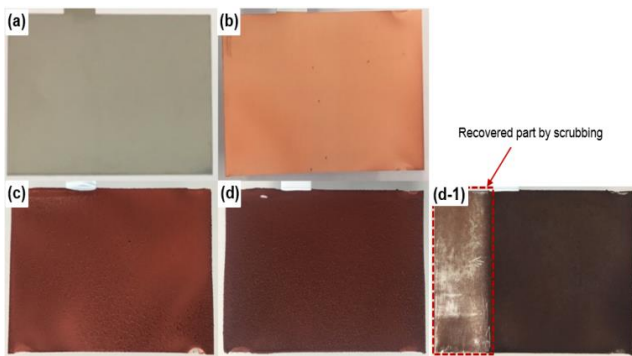


Fig. 8 Surface images of cathode (a) before and after Cu electrowinning at (b) 1.5 V (c) 2.0 V (d) 2.5 V (d-1) 2.5 V and partially recovered

(Fig. 7). We observed the removal efficiency of both metals continuously increased as the cell voltage increased (99% and 90% in 8 h-reaction). This indicates that increasing working voltage can enhance the removal kinetics of Cu and Ni because of the enhanced electron transfer from the cell into the anode, which can result in electrowinning (i.e., more metal ions are attracted to the cathode) in the given time. Fig. 8b shows that Cu was electrodeposited on the initial cathode (Fig. 8a) at 1.5 V of cell voltage. In contrast,

powder form of copper was deposited more on the cathode as the cell voltage increased (Fig. 8c and 8d), which can be recovered easily by scrubbing process (Fig. 8 (d-1)). In addition, the colour of Cu deposited on the cathode tended to darken as the cell voltage increased, probably attributed to oxidation of Cu(0) to CuO_2 (Giannopoulou and Panias 2007). In the case of Ni, the cathodic deposits were formed at all cell voltages and some greenish nickel hydroxide deposits were observed on the cathode surface at 4.0 V (Fig. 9) (Njau *et al.* 2000). This indicates that the working voltage should be optimized during the electrowinning for mixture of Cu and Ni. It is preferable to impose high voltage only for fast removal kinetics of metals, but low voltage is required to recover high purity metals.

3.3 Selective removal of Cu and Ni

In order to investigate the possibility of selective removal of Cu and Ni by electrowinning process, we conducted additional sequential experiments as shown Fig. 10. Almost 99% of Cu was firstly removed in 10 h-operation and deposited on the cathode surface, while Ni was not removed at all. After complete removal of Cu, the

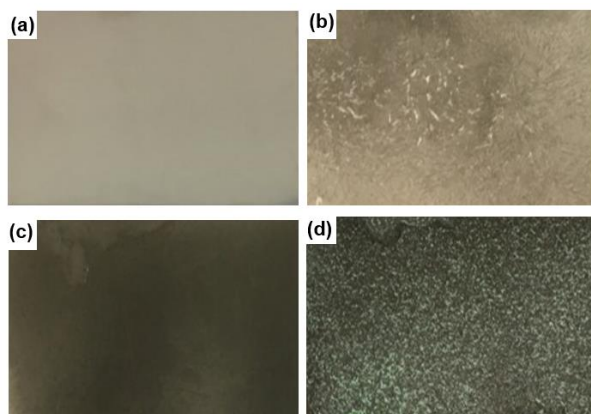


Fig. 9 Surface images of cathode (a) before and after Ni electrowinning at (b) 3.0 V (c) 3.5 V (d) 4.0 V

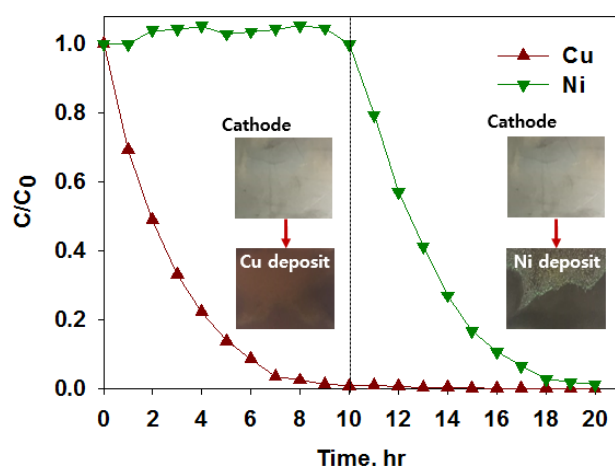


Fig. 10 Selective removal of Cu and Ni by electrowinning

solution pH was adjusted to pH 2 using 10 M NaOH and 20 g/L of boric acid was added for Ni removal. The first cathode deposited by Cu was changed to fresh one and 4.0 V was applied. As a result, the complete removal rate of Ni was also achieved in the next reaction in 10 h. Because the reduction potential of Ni ($\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}^0$, $E^\circ = -0.27$ V) is much lower than that of Cu ($\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}^0$, $E^\circ = +0.34$ V), we need to impose higher cell voltage for removal of Ni by electrowinning (Vegliò *et al.* 2003)

4. Conclusions

In this study, we investigated effect of operation parameters on electrowinning of Cu and Ni by working with a Ti/Ir-Ru anode fabricated by spin coating technique and a commercial cathode (SUS 304). The results from recycling test showed the stability and durability of Ti/Ir-Ru anode during the electrowinning process. The change of H_2SO_4 concentration had no influence on removal of both Cu and Ni. Compared to Ni case showing almost no effect of pH on Cu removal, the removal rate of Ni significantly decreased as pH changed 4 to 1 owing to lowering the reduction potential of solution. In the Ni electrowinning, the

addition of boric acid significantly influences on removal rate of Ni. In addition, removal kinetics of Cu and Ni increased as the cell voltage increased, leading to the formation of different metal phase on the cathode surface depending on the applied cell voltages. Finally, the technical feasibility of selective removal of Cu and Ni from the mixed solution was proved through adjustment of pH and addition of boric acid for the Ni removal. The results obtained from this study can apply to the enhanced performance of electrowinning for mixed Cu and Ni plating wastewater.

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