

## **Effect of operation parameters on removal of Cu and Ni by electrowinning**

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### **ABSTRACT**

In this study, we fabricated a Ti/Ir-Ru anode by spin coating technique for effective recovery of metals (Cu and Ni) in electrowinning process. A complete removal of Cu (1000 mg/L) was observed during 4 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., variation of pH, concentration of electrolyte (H<sub>2</sub>SO<sub>4</sub>), and cell voltage) on the efficiency of metal removal (Cu and Ni) during the electrowinning. Compared to negligible pH effect (pH 1, 2, and 4) on the Cu removal, we observed 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 the complete removal of Cu in 5 h reaction at 2.5 V, which was much faster than those at 1.5 and 2.0 V. The findings in this study can provide a fundamental knowledge about effect of important parameters on the efficiency of metal recovery during the electrowinning process using by Ti/Ir-Ru and stainless-steel electrodes.

### **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 directly disposed to natural environments without pretreatment (Sharma 2005). 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 the real fields.

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 2017, Mussy 2003).

In this study, we first developed a Ti/Ir-Ru anode (1:1 molar ratio) by spin coating technique, which can fabricate more uniformly coated layer of noble metals on the substrate surface than other techniques (e.g. dip-, spray-, and brush-coatings) (Hummelgård 2013). Firstly, we investigated the feasibility and durability of Ti/Ir-Ru anode by conducting a recycling experiment for Cu electrowinning. In addition, the effect of various operation parameters such as pH, H<sub>2</sub>SO<sub>4</sub> concentration, and cell voltage on the efficiency of Cu and Ni electrowinning was investigated.

## 2. EXPERIMENTAL

### 2.1 Electrowinning system

The 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 cm<sup>3</sup>) was used for recovery of metals by electrowinning process. For efficient electrowinning process, we fabricated a novel Ti/Ir-Ru anode (10×10×0.04 cm<sup>3</sup>) by spin coating technique. The details for fabrication method and characteristics of anode has been reported previously (Kim 2018). For the cathode, a commercial stainless-steel (SUS 304) electrode (10×10×0.04 cm<sup>3</sup>) was used in this study.

### 2.2 Electrowinning procedure

Unless stated otherwise, all experiments were carried out with 1,000 mg/L of metal (Cu or Ni) containing solutions prepared by dissolving CuSO<sub>4</sub>·5H<sub>2</sub>O or NiSO<sub>4</sub>·6H<sub>2</sub>O in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. 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 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).

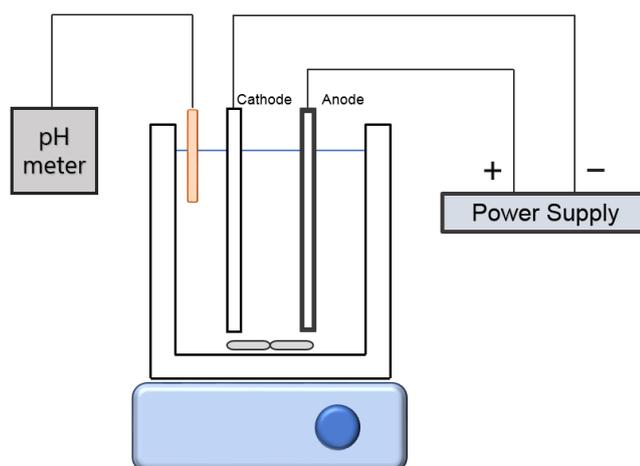


Fig. 1. Schematic diagram of electrowinning system used in this study.

### 3. RESULTS AND DISCUSSION

#### 3.1 Durability test

Prior to parametric study, we repeated the Cu electrowinning at the same condition in order to confirm the feasibility and durability of Ti/Ir-Ru anode. Fig. 2 shows the removal rate of Cu during four times electrowinning. Almost complete removal of Cu was achieved within 10 h in all the tests. The removal kinetics of Cu was well fitted by a first-order kinetic model ( $R^2 > 0.99$ , Table 1). We observed very similar rate constant ( $k_1$ ) during four electrowinning ( $2.70\text{--}3.43\text{ h}^{-1}$ ). In addition, Fig. 3 shows that there was no significant change in appearance of Ti/Ir-Ru anode after the Cu electrowinning. These indicate that Ti/Ir-Ru anode fabricated in this study can be applied for long-term electrowinning process.

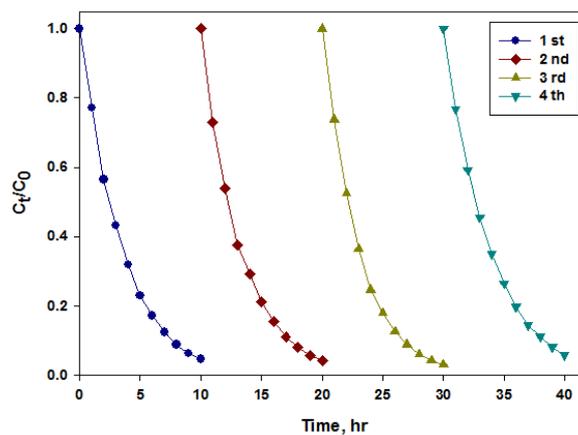


Fig. 2. Recycling tests of Ti/Ir-Ru anode for Cu removal by electrowinning process

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

	Removal rate (%)	$k_1$ ( $\text{hr}^{-1}$ )	$R^2$
1 st	95.47	2.937e-1	0.99
2 nd	95.86	3.144e-1	0.99
3 rd	97.04	3.426e-1	0.99
4 th	94.34	2.701e-1	0.99

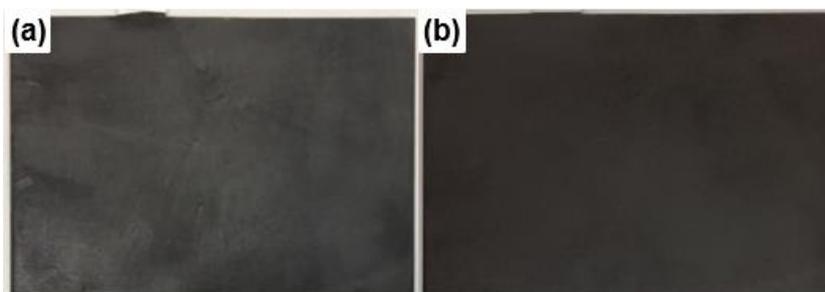


Fig. 3. Images of Ti/Ir-Ru anode (a) before and (b) after electrowinning process

### 3.2 Effect of operation parameters

#### 3.2.1 Effect of pH

In order to evaluate the effect of pH on efficiency of electrowinning, we carried out the experiments at different pH values (pH 1, 2, and 4) in 0.5 M  $H_2SO_4$  solution. Industrial wastewater and leachate from metal sludge are commonly observed in acidic condition, thus we used  $H_2SO_4$  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 while 10 g/L of boric acid and NaOH (10 M) were used as buffer and pH maintenance during the electrowinning of Ni (Njau 2000). For the Cu electrowinning, we could not observe any significant change at different pHs (Fig. 4a). On the other hand, a remarkable change was observed at each pH for Ni removal by electrowinning process (Fig. 4b). Almost no removal of Ni was observed at pH 1 in 6 h reaction, whereas approximately 85% and 65% of Ni were removed at pH 2 and 4, respectively. This may be because Ni known as the most electropositive metal requires high reductive condition to be removed by electrowinning (Giannopoulou 2007).

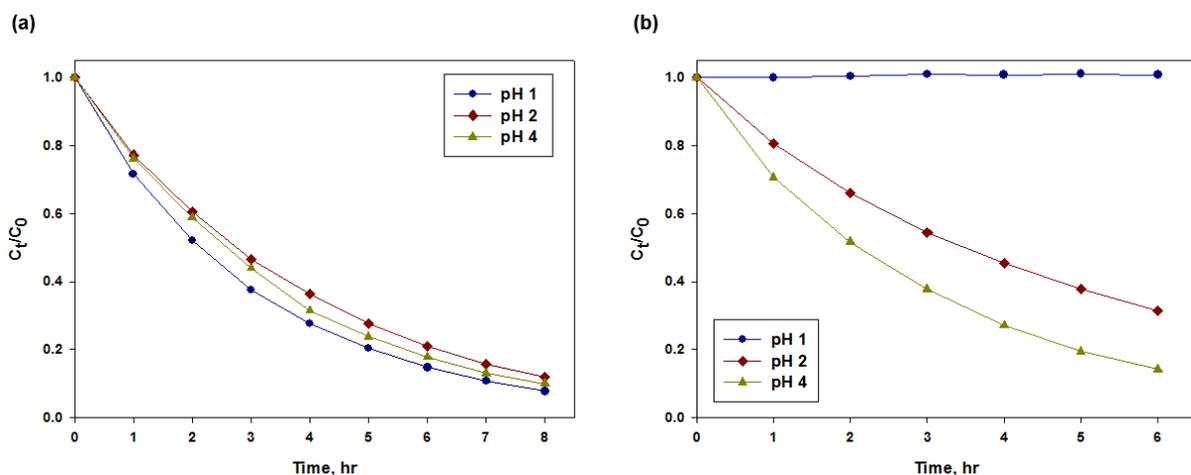


Fig. 4. Removal kinetics of (a) Cu and (b) Ni removal at different pHs by electrowinning.

#### 3.2.2 Effect of $H_2SO_4$ concentration

Effect of  $H_2SO_4$  concentration was investigated at different concentration of  $H_2SO_4$  (Fig. 5). 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 kinetics of Ni as shown in Fig. 4b. 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 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 Cu electrowinning.

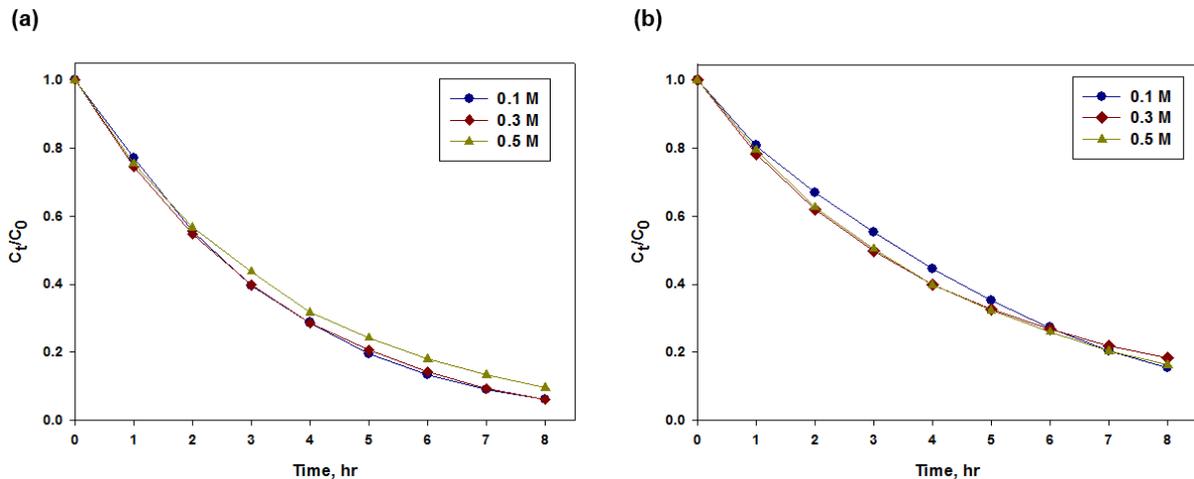


Fig. 5. Removal kinetics of (a) Cu and (b) Ni removal by electrowinning at 1.5 V and 3.5 V, respectively.

### 3.2.3 Effect of cell voltage

Effect of cell voltage on the efficiency of Cu electrowinning was investigated at three different voltages (i.e., 1.5, 2.0, and 2.5 V) (Fig. 6). We observed the complete Cu removal in 5 h reaction at 2.5 V, while the removal efficiency continuously decreased as the cell voltage decreased (99% and 91% in 8 h reaction at 2.0 and 1.5 V, respectively). This indicates that Increasing working voltage can enhance the removal kinetics of Cu because of the enhanced electron transfer from the cell into the anode, which can result in faster electrowinning (i.e., more Cu ions are attracted to the cathode) in the given time. Fig. 7b shows that Cu was electrodeposited on the cathode as non-recoverable form 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. 7c and 7d), which can be recovered easily by scrubbing (Fig. 7 (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<sub>2</sub> (Giannopoulou 2007). This indicates that both low and high cell voltage are not suitable, thus needs to find out the optimal voltage during Cu electrowinning process.

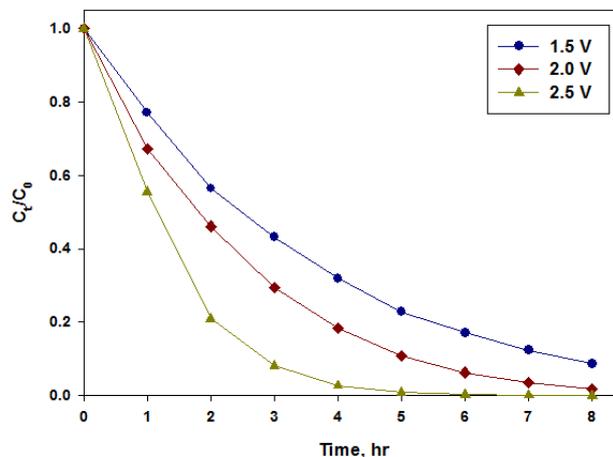


Fig. 6 Removal kinetics of Cu at 1.5, 2.0, and 2.5 V of cell voltages.

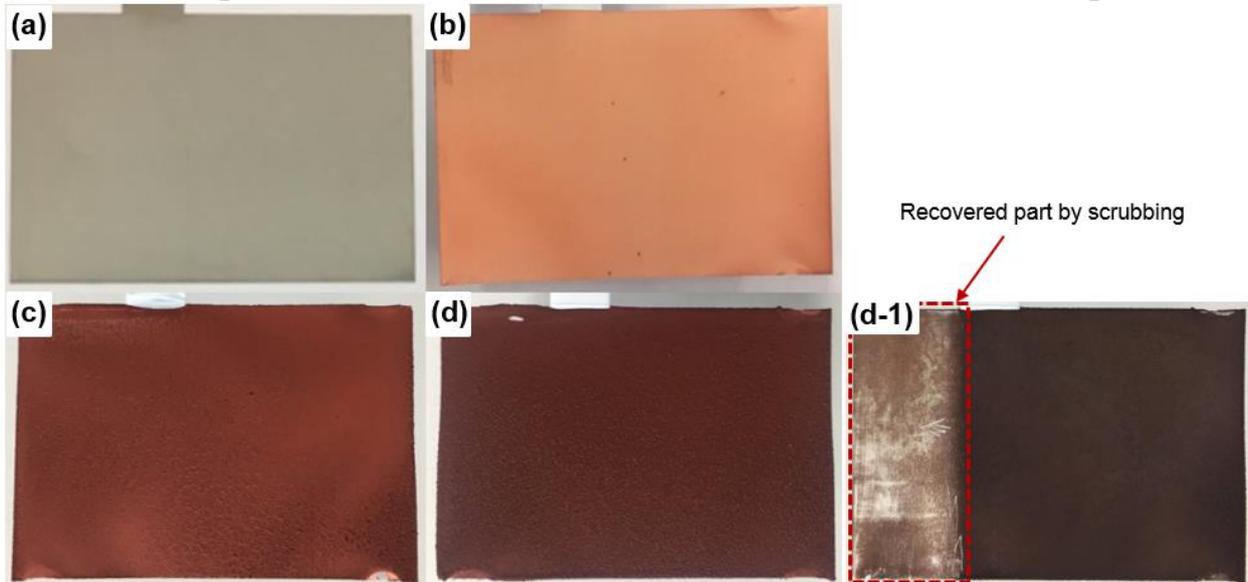


Fig. 7. Surface images of cathode (a) before electrowinning, after electrowinning at (b) 1.5 V (c) 2.0 V (d) 2.5 V (d-1) 2.5 V and partially recovered.

#### 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 and our electrowinning system. 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 from 85 % to 0 % as pH changed 4 to 1 due to the different reduction condition at each pH. In addition, removal kinetics of Cu increased as the cell voltage increased, leading to the formation of different Cu phase on the cathode surface depending on the applied cell voltages. The results obtained from this study can provide fundamental knowledge for the effect of pH,  $H_2SO_4$  concentration, applied cell voltage on metal recovery by electrowinning process.

#### Acknowledgments

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