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RESEARCH ARTICLE

# Copper recovery from waste printed circuit boards concentrated metal scraps by electrolysis

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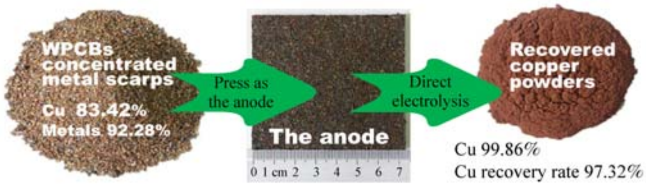
## HIGHLIGHTS

• WPCBs concentrated metal scraps were directly and successfully recycled by electrolysis.
• Factors that affect the electrolysis were discussed in detail.
• Copper recovery rate and copper purity are up to 97.32% and 99.86% respectively.

## GRAPHIC ABSTRACT

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## ABSTRACT

Copper recovery is the core of waste printed circuit boards (WPCBs) treatment. In this study, we proposed a feasible and efficient way to recover copper from WPCBs concentrated metal scraps by direct electrolysis and factors that affect copper recovery rate and purity, mainly $CuSO_4 \cdot 5H_2O$ concentration, NaCl concentration, $H_2SO_4$ concentration and current density, were discussed in detail. The results indicated that copper recovery rate increased first with the increase of $CuSO_4 \cdot 5H_2O$, NaCl, $H_2SO_4$ and current density and then decreased with further increasing these conditions. NaCl, $H_2SO_4$ and current density also showed a similar impact on copper purity, which also increased first and then decreased. Copper purity increased with the increase of $CuSO_4 \cdot 5H_2O$. When the concentration of $CuSO_4 \cdot 5H_2O$, NaCl and $H_2SO_4$ was respectively 90, 40 and 118 g/L and current density was 80 $mA/cm^2$, copper recovery rate and purity was up to 97.32% and 99.86%, respectively. Thus, electrolysis proposes a feasible and prospective approach for waste printed circuit boards recycle, even for e-waste, though more researches are needed for industrial application.



## 1 Introduction

Metal recovery from waste printed circuit boards (WPCBs) is a global issue that attracts lots attention from researchers and governors [1–3]. WPCBs of desk computers contain nearly 40% metals [4], such as Cu, Zn, Sn, Ag and Au. Therefore, the main purpose of WPCBs recycling is to recover valuable metals [5]. Copper recovery is the core of WPCBs recycling [6–8], since copper is the most abundant metal in WPCBs, approximately 20%, much higher than any other metals in the WPCBs. In addition, this number is also much higher than copper in its ore, about 0.6% [9].

There are many technologies for recovering copper from WPCBs, including pyrometallurgy [10–12], hydrometallurgy [13,14], mechanical separation [15], biohydrometallurgy [16], supercritical fluids [17]. Among these technologies, electrochemical process seems to be an effective way to recovery copper from WPCBs. For example, Kim et al. [5] reported that 97% copper was recovered from waste mobile phones using in situ electrogenerated chlorine. Xiu et al. [18] reported that 94% of copper was recovered from WPCBs by supercritical water oxidation combined with electrokinetic process.

In China, e-waste recycling is authorized to 109 e-waste recycling companies. For these companies, WPCBs are crushed and separated mechanically. Then WPCBs metal

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*Special Issue—Recycling Materials from WEEE (Responsible Editors: Jinhui Li & Eric David Williams) concentrated scraps are obtained [7,9,15,19–23]. However, researches on copper recovery from WPCBs concentrated metal scraps by direct electrolysis are limited. Thus, we collected WPCBs concentrated metal scraps from an authorized e-waste recycling company, conducted a series of electrolysis experiments and deeply discussed the factors that influence copper recovery rate and copper purity. The result may provide a further process for WPCBs concentrated metal scraps for these 109 authorized e-waste companies.

## 2 Materials and methods

### 2.1 Sample preparation

The concentrated WPCBs metal powders digested by $HNO_3$-HF-$H_2O_2$ system [19] and examined by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Scientific, iCAP 6500, Massachusetts, America). The results are presented in Table 1. It shows that the content of copper, tin and lead are 83.42%, 2.72% and 2.36% respectively.

### 2.2 Electrolytic process

First, some conductive adhesive was blended with the concentrated metal scraps powders. After that, these mixtures was pressed by a hydraulic press (796YP-30T, KEQI, Tianjin, China) at 20 MPa to form plates (6 cm × 7 cm), which were further cut to small ones about 7 cm × 2 cm. These small pieces were used directly as the anode. The cathode was a copper sheet (7 cm × 2 cm) with a purity of 99.9%. A rectangular vessel (Fig. 1), 10 cm × 7 cm × 7 cm and divided into two compartments by a porous glass frits (thickness = 1 mm, pore size < 50 μm), was used as the electrochemical reactor. For each run, the electrodes were parallel to each other with a constant distance of 10 cm.

For a typical experiment, 100 mL electrolyte was used. The electrolyte was a mixture of copper sulfate pentahydrate ($CuSO_4\cdot 5H_2O$), sodium chloride (NaCl) and sulfuric acid ($H_2SO_4$). All the chemical reagents were of analytical grade unless otherwise mentioned. All the electrolytic experiments were conducted at room temperature. A constant current was supplied using a DC power supply (JPB-500, JIANGBO, Shenzhen, China). Four factors, $CuSO_4\cdot 5H_2O$, NaCl, $H_2SO_4$ and current density, were examined in detail. For quality control, the relative standard deviations of the triplicates were within the limits specified by a certified commercial laboratory and mean data values are presented in the Tables and Figures.

### 2.3 Characterization

After each experiment, the obtained copper powders were first filtrated, and then rinsed with distilled water and absolute ethyl alcohol (v/v 30%) for several times. After that, copper powders were dried at 50 °C for 24 h, weighed, digested and examined by ICP-OES. Copper recovery rate was calculated according the following equation:

$$\text{Copper recoveryrate} = \frac{M_1 + M_2 - M_3}{Mass\ of\ Cu\ in\ anode} \times 100\% \qquad (1)$$

where $M_1$ is the mass of Cu obtained at the cathode, g; $M_2$ is the mass of copper contained in electrolyte, g; $M_3$ is the mass of Cu in $CuSO_4\cdot 5H_2O$, g.

## 3 Results and discussion

### 3.1 Effect of $CuSO_4\cdot 5H_2O$

The effect of $CuSO_4\cdot 5H_2O$ on copper recovery rate and copper purity is presented in Fig. 2. It is obvious that copper recovery rate first increases as the increase of $CuSO_4\cdot 5H_2O$ concentration and then it decreases with further increasing $CuSO_4\cdot 5H_2O$ concentration, e. g., copper recovery rate increase from 68.74% to 97.32% as $CuSO_4\cdot 5H_2O$ concentration increases from zero to 50 g/L, and then it decreases to 84.21% when $CuSO_4\cdot 5H_2O$ concentration further increases to 90 g/L. While for copper purity, as shown in Fig. 2, it increases with $CuSO_4\cdot 5H_2O$ concentration in the whole investigated range, e.g., it increases from 92.56% to 99.86% when $CuSO_4\cdot 5H_2O$ concentration increases from zero to 90 g/L. At the beginning, the addition of $CuSO_4\cdot 5H_2O$ provides a resource of $Cu^{2+}$ ions for electrodepositing, thus favoring copper leaching from WPCBs concentrated scraps. Then copper recovery rate increases. However, when $CuSO_4\cdot 5H_2O$ increases to a certain value, $Cu^{2+}$ ions supplied by $CuSO_4\cdot 5H_2O$ would be enough or even exceeds the demand for electrodeposition. This means the electrodeposited copper is from $CuSO_4\cdot 5H_2O$ but not from the copper ions leached from WPCBs concentrated metal scarps. Moreover, the exceeded copper ions could also hinder its leaching. Therefore, a higher $CuSO_4\cdot 5H_2O$

**Table 1** Metals contained in WPCBs metal concentrated scraps

| Element | Cu | Sn | Pb | Al | Zn | Fe | Ba | Bi | Ni | Others |
|---|---|---|---|---|---|---|---|---|---|---|
| Content (%) | 83.42 | 2.72 | 2.36 | 1.96 | 0.96 | 0.23 | 0.48 | 0.11 | 0.039 | 7.721 |

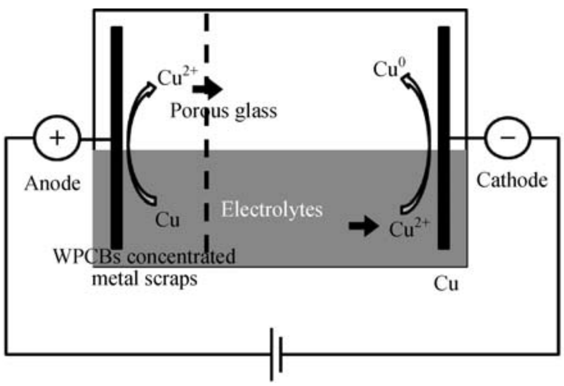


**Fig. 1** Schematic of experimental set-up

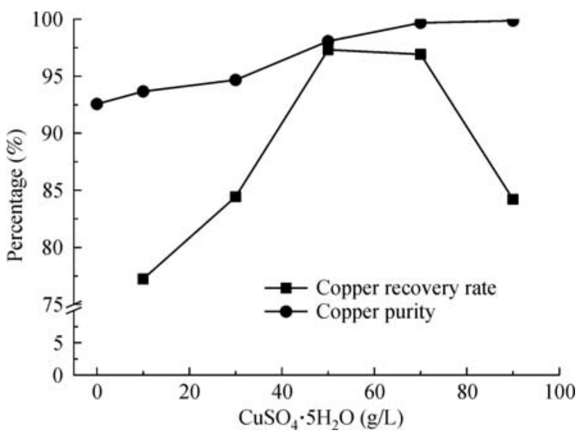


**Fig. 2** Effect of $CuSO_4 \cdot 5H_2O$ on copper recovery rate and purity

would lead to a decrease for copper recovery rate. Obviously, copper purity would increase with $CuSO_4 \cdot 5H_2O$ concentration since as the increase of $CuSO_4 \cdot 5H_2O$, this process turns to be copper powders electrodeposition from $CuSO_4 \cdot 5H_2O$ and other metal ions leached from WPCBs can be ignored.

## 3.2 Effect of NaCl

Figure 3 shows the effect of NaCl concentration on copper purity and copper recovery rate. It can be seen that the purity varies slightly, which first increases from 97.41% to 98.06% and then decreases from 98.06% to 95.76% when NaCl concentration increases from 0 to 40 g/L and then to 80 g/L. Copper recovery rate presents a similar trend as copper purity, which increases from 90.48% to 97.32% and then decreases to 89.33% when NaCl concentration increases from zero to 40 g/L and then to 80 g/L. Previous studies reported that $Cl^-$ introduced by NaCl could increase the current efficiency [24], thus increasing the recovery rate and purity. However, too much $Cl^-$ would lead to hydrogen evolution and other impurities may appear [25],

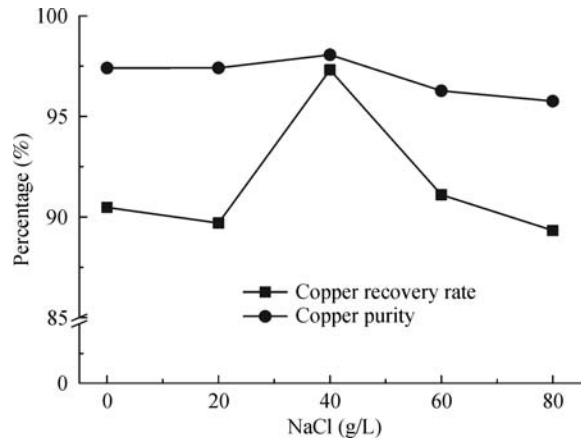


**Fig. 3** Effect of NaCl on copper recovery rate and purity

leading to the decrease of copper recovery rate and purity.

## 3.3 Effect of $H_2SO_4$

Figure 4 shows the effect of $H_2SO_4$ on copper recovery rate and copper purity. As shown in Fig. 4, copper recovery rate first increases from 75.95% to 97.32% when $H_2SO_4$ concentration increases from 39 g/L to 118 g/L, and then it decreases to 82.79% with further increasing $H_2SO_4$ concentration to 196 g/L. Meanwhile, copper purity also shows a similar trend though its variation is not as significant as copper recovery rate. The increase of $H_2SO_4$ concentration could facilitate the anodic oxidation and of course increase the conductivity, thus increasing copper recovery rate and purity. While at a relatively higher concentration, hydrogen evolution would be dominant and therefore reduces the recovery rate and purity [26].

## 3.4 Effect of current density

Current density is a key factor to recover copper from WPCBs metal concentrated scraps when there are plenty of

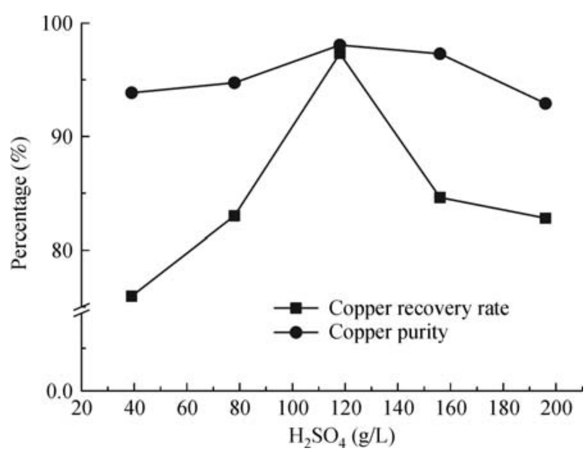


**Fig. 4** Effect of $H_2SO_4$ on copper recovery rate and purity

copper ions in the electrolyte. Figure 5 shows the effect of current density on copper recovery rate and copper purity. Almost the same as Figs. 3 and 4, copper recovery rate and copper purity also increases first from 78.83% and 93.86% to 97.31% and 98.07% when current density increases from 40 mA/cm$^2$ to 80 mA/cm$^2$, and then they decrease to 84.69% and 92.91% with further increasing current density to 120 mA/cm$^2$. At certain lower current density, its increase means more electrons, and then more ions that are copper could be reduced to metallic copper. Thus copper recovery rate and copper purity would increase. However, a much higher current density also means a much higher cell voltage, which would intensify hydrogen evolution and other side reactions. Therefore, copper recovery rate and copper purity would decrease.

The increase of current density is beneficial to anodic oxidation. While under a higher current density, the side reactions increase. With the increase of current density, voltage loss caused by the resistance of each contact and conductor of electrolytic cell increases. At the same time, the overvoltage of cathode increase, which is in favor to separate $H^+$ out on cathode and lead to waste electric energy.

## 4 Conclusions

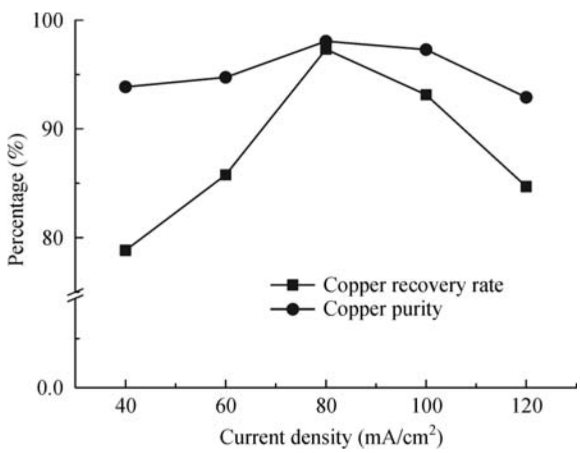


**Fig. 5** Effect of current density on copper recovery rate and purity

In this study, electrolysis was directly and successfully applied in WPCBs metal concentrated scraps to recovery copper powders. Copper purity increases with the increase of $CuSO_4 \cdot 5H_2O$, while copper recovery rate first increases and then decreases with the increase of $CuSO_4 \cdot 5H_2O$. NaCl, $H_2SO_4$ and current density show a similar effect on both copper recovery rate and copper purity, which increase first and then decrease. Copper recovery rate and copper purity reaches to 97.32% and 99.86% when the concentration of $CuSO_4 \cdot 5H_2O$, NaCl and $H_2SO_4$ were 90, 40 and 118 g/L and the current density was 80 mA/cm$^2$. This process proposes a prospective approach for WPCBs recycling, or even e-waste reutilization. However, more researches are needed for industrial application.

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