SELECTIVE AND EFFECTIVE RECOVERY OF COPPER FROM PRINTED CIRCUIT BOARD SCRAPS

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Received: 25 September 2017; Accepted for publication: 7 October 2017

ABSTRACT

Copper was recovered from printed circuit boards (PCB) scraps by the combined mechanical and electrochemical method using 7M nitric acid as leaching agent followed by metal electrodeposition electrolyzing leachate. The metal recovery selectivity and effectivity were investigated through determination of electrodeposition potentials based on anodic stripping voltammetry (ASV). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) techniques were also used to reveal the optimized electrolysis parameters. The influence of various process parameters such as current density, pH, and temperature on electrodeposition efficiency was examined. The high recovery efficiency, more than 90 %, was reached for copper electrodeposition from PCB leachate at cathodic current density of 20 mA/cm², pH=1 and temperature is 40 °C of the electrolyzer solution.

Keywords: printed circuit board, electrodeposition potential, copper deposition.

1. INTRODUCTION

Electronic waste (e-waste) contains significant amount of valuable metals such as gold, silver, copper, zinc, lead, and etc. [1]. At present, e-waste has been considered as a potential reusable resource for materials mining encompassing from the above listed popular metals to technologically vital and evidently exhausted rare earth elements [2]. Printed circuit board (PCB) scrap as a principal e-waste component, has been recovered for years to produce various metals, among which copper takes the first place. Nevertheless, copper commonly presents at high content in PCB and in e-wastes, its selective and efficient recovery is always considered a challenging issue due to simultaneous occurrence of other elements and substances hindering separation process. Nowadays, various methods have been applied to recover copper, but
Chemical leaching and electrochemical deposition have normally accepted as most efficient steps [3]. Especially, the electrochemical approach has widely been applied to separate copper in leachates, based on the different deposition potentials of occurred metals.

Through chemical treatment, Vijayaram R. et al. reported 8.5 - 92.7% efficiency of copper extraction, depending on used acid compositions [3]. Andrea M. and Keith S. [4] succeeded copper and lead separation in respective metal and oxide form, using nitric acid to dissolve PCB scraps, followed by electrolytic deposition step. Similarly, Kumar M. et al. even reached 98.3% efficiency of copper recovery from leachate, using 3 mM nitric acid under 800 rpm agitation and 60 °C heating [4]. Meanwhile, by using H₂SO₄ mixture, Nguyen T.T.H. et al. [5] and Weit H. M. [6] informed 82.1% and 98% efficiency for copper extraction, respectively.

To attain high copper separation selectivity, Sun Z. H. I. used ammonium-based recovery process with ammonium chloride leaching step and further electrodeposition [7]. Torres R. and Lapidus G. T. tried to separate copper from iron and lead in leachate by applying citrate solution [8]. Guimaraes Y. F. et al. conducted direct recovery of copper from PCB powder concentrate by a simultaneous electroleaching-electrodeposition process with approximately 50% copper came from solution [9]. Doche M. L. et al. recently performed an ultrasonic-assisted process for copper recovery using a cheap and safe ionic liquid as electrolyte for both electroleaching and electrodeposition. Under 20 kHz sonication, a leaching rate of copper reached 65 mg/h.cm² in choline chloride and ethylene glycol. In this medium, copper dissolves into Cu(I) complex form instead of Cu(II), leading to energetically more favourable of subsequent electroreduction [10].

In this paper, copper recovery process from PCB scraps are investigated based on the combined mechanical and electrochemical method using nitric acid as leaching agent followed by electrodeposition. A detailed electrochemical experiments were conducted to reveal conditions of selective and effective copper removal from leachate.

2. MATERIALS AND METHODS

2.1. Waste PCB recycling procedure

Waste PCB recycling procedure was conducted based on combined mechanical treatment and electrochemical deposition as described in literature [6] and preliminarily investigated in our previous work [11]. Some modification have been done in order to improve copper separation from PCB powder and to enhance the selectivity of metal deposition as seen in Figure 1. PCB scraps were collected from old TV set slumps and transferred to the mechanical treatment process after dismantling all active and passive components. The thoroughly rinsed scraps were cut into smaller pieces of 5 × 5 cm, followed by grinding to about 2 × 2 cm pieces and then by ball milling to powder under 1 × 1 cm size. Part of lead solder was eliminated by sieving with a minimal opening size of 0.2 mm. Iron filling was separated by magnetic device with average force of 6.0–6.5 G.

The grinded powder was then dissolved in 7M nitric acid at room temperature for 200 h, followed by filtration to separate leachate from residues containing H₂SnO₃ and other solid substances. The leached solution was then analyzed to reveal elemental contents and transferred for further electrochemical investigation.
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2.2. Analytical methods

2.2.1. Anodic stripping voltammetry

Anodic stripping voltammetry (ASV) is a rapid electroanalytical technique frequently used for qualitative and quantitative determination of metals including Au, Cd, Cr, Cu, Pb, Sn, Cu, Zn, etc. [12]. In this study, a Metrohm Autolab PGSTAT 30 with conventional three electrodes cell was used to conduct ASV investigation. A glassy carbon was used as working electrode (WE), while platinum and Ag/AgCl (3M KCl) were employed as counter electrode (CE) and reference electrode (RE), respectively.

The deposition potential of copper was determined in acetate buffer solution (pH 4.6) in a range of -0.8 to 0.5 V with scanning rate 50 mV/s. Based on defined deposition potential, an optimal deposition time was investigated, using the same Autolab system, to enhance the analytical selectivity of copper.

2.2.2. Determination of copper by standard addition method

To eliminate the influence of other elements occurred in leachate on analytical accuracy, method of standard addition was applied for copper analysis. An aliquot volume of standard leachate (with 1000 ppm Cu\textsuperscript{2+}) was added to 20.0 mL acetate buffer solution (pH 4.6) to form a mixed composition. The concentration of metal ion was then analyzed by ASV method with working glassy carbon electrode and optimal values of deposition potential defined in ASV previous experiment. The process was repeatedly performed for other aliquot volumes of
standard leachate ranging from 6 to 120 µL.

2.2.3. PCB dismantled quantification and elemental analysis

The PCB dismantled portion after a single step was checked and weighed by technical scales (±50 g). The leachate collected after PCB powder dissolution in 7M HNO₃ was separated from remained various residues by filtration, followed by elemental analysis using X-Ray Fluorescence (XRF) and Atomic absorption spectroscopy (AAS) techniques. These methods were applied as analytical tools for examination of copper content in aforementioned items 2.2.1 and 2.2.2.

The XRF analysis was conducted on Spectro Xapos XRF Spectrometer in CASE (Center of Analytical Services and Exprimentation). The analysis of copper was performed on FAAS spectrophotometer (Laboratory for Analytical Chemistry, University of Science, VNU-HCM).

2.3. Electrodeposition process

The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used to investigate the electrodeposition process of copper from PCB leachate and simulated solutions. The CV measurements was carried out using conventional three electrode cell, as similarly described in 2.2.1, was applied to inspect a priori electrolysis process of copper simulated leachate containing copper and lead nitrate solution. The experiment was conducted on Metrohm Autolab PGSTAT 30 potentiostat in a potential window ranging from -0.3 to 0.5 V at 50 mV/s scan rate.

The reduction and oxidation peaks during electrolysis and optimal current density were revealed by LSV technique on the BioLogic MPG2 (France) with ECLab software in a cell with Ag/AgCl reference electrode and platinized titanium grid counter electrode. Copper working electrode was prepared with surface area of 0.5 cm². The potential sweeping was processed at 50 mV/s scan rate and in the range of 0.3 to -0.8 V. As-prepared solutions containing Cu(NO₃)₂ (0.05 to 0.2M) and simulated leachate comprising of 0.2M Cu(NO₃)₂ and 0.03M Pb(NO₃)₂ in 1M HNO₃ mixture were used in above conducted experiments.

Electrodeposition was processed in an electrolyzer connected to GW Instek GPR-3510HD DC power supply with 20 cm² copper cathode and platinized titanium grid anode. The influence of current density, pH and temperature on current efficiency was examined. The efficiency of the electrolysis process was expressed via a percentage ratio between the data obtained by the experimental mass gain \( m_{exp} \) and the theoretical value \( m_{Far} \) calculated by Faraday equation.

3. RESULTS AND DISCUSSION

3.1. Metal composition of the PCB scrap

3.1.1. Mechanical treatment and separation

Alongside the various types of nonconductive plastic substrates, PCB scrap can contain numerous metals and alloys, including copper, lead, aluminum, steel, etc. in form of conductive tracks, pads or solder materials. Generally, the passive and active components such as capacitors, resistors are electrically connected to PCB by soldering. In mechanical treatment process, portions of dismantled steps were summarized and calculated as percentage to initial PCB scrap as shown in Table 1.
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Results show that greater portion of active and passive components in discarded TV set PCB, comprising 54.29% of initial scrap mass. PCB mass remained unchanged after grinding and ball milling. Due to magnetic separation, an amount of iron filling was removed and final PCB powder mass reduced to 36.57% of the initial scraps. The mechanical treatment with gradual decrease of scrap sizes favored the powder’s surface area, which increased contacts between PCB pieces and leaching solvent and finally, improved metal dissolution.

Table 1. Solid material distribution of PCB dismantled portions.

<table>
<thead>
<tr>
<th>Mechanical treatment step</th>
<th>PCB scrap mass (kg)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial PCB mass</td>
<td>3.50</td>
<td>100.0</td>
</tr>
<tr>
<td>PCB after components dismantling and cutting to 5 x 5 (cm) pieces</td>
<td>1.60</td>
<td>45.71</td>
</tr>
<tr>
<td>PCB scraps after grinding to 2 x 1 (cm) pieces</td>
<td>1.50</td>
<td>42.85</td>
</tr>
<tr>
<td>PCB powder after ball milling to &lt;1 x 1 (cm) pieces</td>
<td>1.50</td>
<td>42.85</td>
</tr>
<tr>
<td>PCB powder after magnetic separation of iron filling (&lt;1 x 1 cm)</td>
<td>1.28</td>
<td>36.57</td>
</tr>
<tr>
<td>Iron filling</td>
<td>0.15</td>
<td>0.040</td>
</tr>
</tbody>
</table>

3.1.2. Leachate analysis

As reported in our previous work [11], the metallic composition of PCB scraps after dissolution in nitric acid contained a great number of elements comprising metallic and nonmetallic origin. However, the main constituents of leachate revealed by XRF analysis are presented in Table 2, showed prevailing occurrence of copper and lead in PCB scraps.

Table 2. Principal metal ions in PCB leachate (%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ba</th>
<th>K</th>
<th>Zr</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>5.552</td>
<td>2.596</td>
<td>0.05287</td>
<td>0.0260</td>
<td>0.0244</td>
<td>0.020</td>
<td>0.0132</td>
</tr>
<tr>
<td>Element</td>
<td>Mo</td>
<td>Sn</td>
<td>Bi</td>
<td>Fe</td>
<td>Te</td>
<td>Sr</td>
<td>In</td>
</tr>
<tr>
<td>Content</td>
<td>0.0110</td>
<td>0.01349</td>
<td>0.01048</td>
<td>0.0086</td>
<td>&lt; 0.0047</td>
<td>0.00248</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

High contents of copper and lead in discarded PCB were anticipated results of analysis, due to exclusive technological role of copper in applied conductive traits and of lead in used tin-lead solder. However, tin in form of H₂SnO₃ precipitation was preliminarily removed by filtration of leachate and a minute quantity (0.01349%) detected by XRF analysis. Data in Table 1 also showed insignificant contents of remained elements, each of which not exceeded 0.06%. Thereby, the selective recovery of copper from leachate could practically be attained by elimination of lead codeposition during treatment. As an advanced method commonly used in practice, an electrochemical approach was chosen for further investigation.
ASV technique was used to determine optimal deposition time for standard copper solution with its dependence on current signal with data presented in Figure 2.

Figure 2. Dependence of ASV current signal on deposition time.

In whole studied deposition time duration from 10 to 120 s, a linear dependence was revealed for a range of 40 to 80 s. A linear equation with $R^2=0.9937$ was processed by regression analysis. Thus, this time range with stable current signal was selected for analytical procedure to determine copper in the solution mixed with other elements. Usually, a fixed value of 50 s of the range was used for further steps.

Based on ASV technique, copper concentration was determined using the standard addition method and the recorded results are depicted in Figure 3.

Figure 3. Standard addition plot of copper in a solution prepared by mixing 0.2M Cu(NO$_3$)$_2$/0.03M Pb(NO$_3$)$_2$ in 1M HNO$_3$.

A linear equation: $y = 2.3391x + 8.8215$, representing a relationship between current signal and Cu$^{2+}$ concentration, was developed with $R^2 = 0.9996$. From this dependence, an equation between the determined copper concentration $C_{Cu}$ and ASV current signal $I_d$ was established with $k$ is a slope:

\[
y = kC_{Cu} + b\]
Using this equation, copper in the leachate solution was determined and the received value was equal to: 12.57 ppm, comparable with value checked by FAAS method 12.05 ppm with error limited to 4.31 %.

3.2. Feature of copper electrodeposition

To define the electrochemical characteristics of codeposition process, CV scanning was applied with the cyclic voltammogram depicted in Figure 4. This voltammogram registered for the mixed 0.2 M copper and 0.03 M lead nitrate solution. In the investigated potential range, two oxidation reactions are occurred on anodic branch and respectively, two typical peaks are clearly revealed at -0.25 V and -0.47 V on cathodic branch, standing for reactions of lead and copper cations reduction:

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu} \\
\text{Pb}^{2+} + 2e^- & \rightarrow \text{Pb}
\end{align*}
\]

Figure 4. Cyclic voltammogram recorded for mixed copper and lead solution (Ag/AgCl).

The similar voltammograms with redox reversible couple process for copper and lead are recorded in [13]. Theoretically, lead can also electrodeposited from strongly acidic solutions with a cathodic efficiency approaching 100 % as revealed on CV scans. However, in practical conditions, due to slow electrolysis in aerated mixed solutions, metallic copper is cathodically deposited and lead dioxide is anodically formed as reported in [11] and [14]. Based on these results, a selective copper reduction could be reached if cathodic reaction is conducted in a range of its deposition potential. Analyzing the voltammetric response, a selective deposition of copper without interfering of lead or other metals can be achieved at deposition around -0.35 V.
LSV technique was used to define the cathodic current density for copper from single copper nitrate and mixed copper-lead nitrate solutions. Results of the experiment with single copper nitrate solution were summarized in Table 3. Table 3 shows a directly proportional ratio between cathodic current density and copper concentration in single nitrate solution. At defined deposition potential, a fixed quantity of copper can be discharged on cathode; however, high current density can hinder the copper adhesion to surface due to intensive formation of metallic copper particles on cathode.

In a mixture of 0.2 M Cu(NO₃)₂ and 0.03 M Pb(NO₃)₂ the average value of cathodic current density presented is 28.23 mA/cm², slightly lower than data recorded for single 0.2 M Cu(NO₃)₂ solution. That means, the mixed solution has lower conductivity, which can substantially influences on the deposition process, causing higher energy consumption and slower recovery rate during electrolysis.

Table 3. Relation of cathodic current density (Dc) and Cu(NO₃)₂ concentrations.

<table>
<thead>
<tr>
<th>[Cu(NO₃)₂] (M)</th>
<th>0.05</th>
<th>0.10</th>
<th>0.15</th>
<th>0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dc (mA/cm²)</td>
<td>16.45</td>
<td>22.60</td>
<td>32.13</td>
<td>41.78</td>
</tr>
</tbody>
</table>

The average Dc value received for PCB leachate was measured as 15.77 mA/cm², what estimated less than a half of the value recorded for mixed Cu(NO₃)₂/Pb(NO₃)₂ solution. This result demonstrates significantly lower cathodic current density achieved at similar electrolysis conditions. This low cathodic current density attained for real PCB leachate requires more detailed investigation of copper deposition and its influenced process parameters such as temperature, pH to enhance the rapid electrolysis and to reach high current efficiency.

3.3. Process parameters and copper deposition efficiency

Electrolysis was applied to real PCB leachate with cathodic current densities Dc varying from 10 to 40 mA/cm² and deposition efficiencies CE were calculated as described in 2.3. Relation between CE and Dc are depicted in Figure 5.

![Figure 5. Relation between electrodeposition efficiency and cathodic current density.](image-url)
The deposition efficiency is gradually decreased with increase of current density, falling from 99.64 % at 10 mA/cm² to 52.42 % at 40 mA/cm². Theoretically, copper cathodically discharged with nearly 100 % efficiency, thereby, these decrease can be explained by insufficient adhesion of the particles on surface and following their sedimentation and further dissolution in electrolyzer. A reasonable range of cathodic current densities for 90 % or higher efficiencies can be accepted from 20 to 10 mA/cm². The value of 20 mA/cm² was selected for further study to maintain high rate of copper deposition.

The leachate pH is another parameter considered to copper recovery with opposing role: to enhance the solution conductivity favouring electrolysis and to accelerate the cathode corrosion and product dissolution. Both actions reflect the possible influence on copper deposition efficiency. Results of copper deposition efficiency obtained by electrolysis at 20 mA/cm² and different pH values are presented in Table 4.

Table 4. Dependence of copper deposition efficiency and solution pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>1.0</th>
<th>2.0</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency (%)</td>
<td>91.66</td>
<td>90.64</td>
<td>88.33</td>
</tr>
</tbody>
</table>

However, data demonstrated in Table 4 prove that in the studied range, pH has slight influence on deposition efficiency with inconsiderably varying values from 88.33 % to 91.66 % for respective pH decrease from 3.0 to 1.0. For this reason, a practicable pH can be maintained about 1.0 during leachate electrolysis.

Finally, the influence of the electrolysis temperature on deposition efficiency was also examined and the summarized results are demonstrated in Table 5. Deposition of copper via reaction (1) and its dissolution in strong nitric acid are also expressed as opposing effect with electrolysis temperature. An optimal temperature for highest copper recovery efficiency was found at 40 °C.

Table 5. Dependence of copper deposition efficiency and temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency (%)</td>
<td>89.83</td>
<td>97.16</td>
<td>96.43</td>
<td>80.52</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Copper can be effectively and selectively recovered from waste PCB scrap by the combined mechanical and electrochemical method using nitric acid as leaching agent, followed by electrodeposition. The various steps of mechanical treatment allow formation of fine solid powder containing mainly nonmetallic substances and metallic copper and lead. These metallic constituents are effectively transformed into leachate by 7M nitric acid. A value of 90 % and higher efficiency for copper deposition can be achieved by electrolysing a PCB leachate with cathodic current density of 20 mA/cm² at 40 °C and pH = 1.0.

REFERENCES