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Study of a Novel Electrochemical Method for Copper Recovery from Waste Printed Circuit Boards

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This study was carried out to recover copper from printed circuit boards of waste computers through an electrochemical process. To simplify the overall recovery process, large pieces of printed circuit boards were used instead of pulverized samples. In particular, these large pieces were directly used as an anode for copper electrorefining. For this purpose, electronic components and solder mask were initially removed from the boards. The electronic components can be treated separately to recover precious metals using various methods. The removal of solder mask was necessary to expose copper layers to the electrolytic solution and it was removed by a chemical treatment with sodium hydroxide. Electrolytic solution was a mixture of copper sulphate and sulphuric acid, and was maintained at 60°C during the process. The recovery of copper was conducted in an electrochemical cell where the anode was supplied by a constant current of 900 mA. The deposited copper was characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. Results show a uniform cathodic deposit of pure copper having a thickness of about 32.35 µm. The copper current efficiency was of 84% with a removal degree of copper from printed circuit board of about 46%.

1. Introduction

The rapid and continuous growth of the electronic market has led to an improvement of the people's style-life with the production of new goods that are always more accessible to everyone and have always shorter lifetime. This is causing an increase of both technological waste volume and global demand of raw materials for their construction. This is a key problem in view of the progressive natural resource depletion. According to the most reliable estimates, every year about 20-50 million tons (Ghosh et al., 2015) of e-waste are produced which will have negative impact on both environment and humans, if are sent to landfill without proper recycling. In the field of e-waste, great attention received printed circuit boards (PCBs) that currently constitute the 3% of the mass of e-waste globally generated (Luda, 2011). Usually, PCBs contain 40% of metals, 30% of organics and 30% of ceramics (Khaliq et al., 2014). The concentrations (w/w) of the various metals in the PCBs are higher or equal to those found in the mineral deposits, therefore PCBs are a valuable source of raw materials (Bizzo et al., 2014; Iannicelli Zubiani et al., 2015). For instance, typical copper concentration in a personal computer printed circuit board is around 20%, which is higher than that of a copper ore (0.6%) (Chu et al., 2015). When PCB is deprived of its electronic components, the precious metals content is practically zero and the metal present at higher concentration is copper that is used for making the conductive tracks on PCBs. The classical approach adopted to recover copper from waste PCBs is based on pyrometallurgical, hydrometallurgical or mechanical processes (Chu et al., 2015).

In recent years, many researchers have investigated a number of innovative approaches on copper recovery to provide a real answer to the increasing requirements of environmental legislation, including biochemical and electrochemical methods. Electrochemical processes have shown to be environmentally friendly because the main reagent is the electron that is clean (Fogarasi et al., 2013). Generally, electrolysis is an ideal process to recover copper due to its simple flowsheet, low energy consumption, high output and low environmental pollution (Wang et al., 2010).

Under this scenario, we present the preliminary results of an electrorefining process of copper in which printed circuit board, after removing the electronic components, works as an anode. In this way, electrochemical oxidation of copper occurs simultaneously with its cathodic deposition avoiding the grinding step of PCBs and simplifying the flowsheet of the overall recovery process. In addition, the proposed method allows to minimize the use of toxic solvents and the emission of gas.

2. Materials and methods

2.1 Chemical characterization of PCBs

A homogeneous powder obtained by mechanical grinding of PCBs was used for chemical characterization performed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 2100 DV). To have significant results from a statistical point of view, three PCBs coming from different models of waste computers were turned to dust to obtain a representative average chemical composition. According to the literature (Jianzhi et al., 2004; Silvas et al., 2015), an acid digestion was performed dissolving 100 mg of powder in 10 mL of aqua regia and subsequently making up to the mark with distilled water in a 100 mL flask and mixing. In this way, the concentrations of the analytes were reported in the linearity range of the calibration curve, which was built preparing appropriate multi-standard solutions. These latter were prepared on the basis of a preliminary Energy Dispersive X-Ray Spectroscopy (EDS) conducted on a pulverized sample of PCBs. The solid residue coming from filtering of leaching solution was also analysed by EDS, to confirm that all metals were dissolved in aqua regia. A further ICP-OES analysis was carried out on the powder of PCB after solder mask removal and on the electrolytic solution at the end of the electrochemical tests.

2.2 Electrorefining process

Before undergoing the electrorefining process, a pre-treatment of PCB was necessary to disassemble electronic components by heating above the melting point of the solder. Disassembled components can be subjected to a different treatment for the recovery of precious metals and for the isolation of hazardous components. Then, PCB was cut in pieces of 10x10 cm and every piece was chemically treated to remove the solder mask and so expose copper metal to the electrolytic solution. For this purpose, the best chemical reagent was sodium hydroxide (NaOH) (Adhapure at al., 2014; Jadhav and Hocheng, 2015). Therefore, PCB's pieces were dipped in 10M NaOH for 24 hours, washed with distilled water to remove any trace of NaOH, and then mounted as an anode for the electrorefining process. Two flat plates (10x10 cm) of pure copper were used as cathodes. Both cathode plates were coated on one side with an insulating resin to guarantee that only one side, the one opposite to the anode, worked. The electrolyte was a mixture of copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sulfuric acid (H_2SO_4) with concentrations of 0.7 M and 2 M respectively (Pletcher and Walsh, 2012). No other chemicals or additives were employed. All the chemical reagents were of analytical grade. A cylindrical vessel was used as electrochemical reactor within which both faces of the anode were opposite and parallel to copper electrodes with a distance of 3 cm. This parallel-plate electrode design is similar to that used in industrial electrolytic refining of copper (Pletcher and Walsh, 2012). Electrolyte temperature was monitored and maintained at 60°C with an external bath of ethylene glycol that was used as heating fluid. A constant current of 900 mA was supplied using a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273). The cathode plates were weighed before and after tests to record the increase of weight and calculate the current efficiency of copper by the following equation:

$$\eta_{Cu}=\frac{W_e}{W_t} \qquad (1)$$

where W_e is the experimental weight of copper deposited on the cathode and Wt is the theoretical weight of deposited copper calculated with Faraday's law:

$$W_t=\frac{M_{Cu} I\, t}{z_{Cu} F} \qquad (2)$$

where M_{Cu} is the molar mass of copper; I the applied current; t the time of the electrochemical refining; z_{Cu} the valence of copper; F the Faraday's constant.

Copper recovered on the cathode was removed by a simple peeling, washed with distilled water and allowed to air dry. Then it was chemically and morphologically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The morphology was investigated using a scanning electron microscopy (SEM, FEI mod.: QUANTA 200 FEG) equipped with an X-ray energy dispersive spectrometer. EDS analysis was carried also on the solid residue found in the bottom of electrochemical reactor. A further characterization was investigated by XRD analysis, (Rigaku, D-MAX 25600

HK). All X-ray analyses were conducted in the 2ϑ range from 5° to 100° using the Cu Kα radiation (λ=1.54 Å). Diffraction patterns were analysed by comparison with ICDD database (ICDD, 2007).

3. Results and discussion

A preliminary EDS analysis was carried out on the powder obtained from three different disassembled PCBs. The chemical elements found in descending order of concentration were: C, O, Br, Cu, Si, Ca, Sn, Pb and other metals in trace such as Fe, Al, Zn, Ni, Ba and Au. In fact, removed the electronic components, the remaining board consists of organics, ceramics and base metals. As it can be seen, copper was the most abundant metal followed by tin and lead. For a more accurate determination of metal concentrations, an ICP analysis was carried out and the results were presented in Table 1. The metal present at higher percentage composition was copper again. In comparison with the literature (Chu et al., 2015), the quantities of tin and lead found were greater, likely due to an excessive solder residue coming from the disassembly step. A small dissolution of tin and lead in NaOH was detected by ICP analysis performed on the powder of printed circuit board after chemical treatment. The hypothesis to change chemical reagent will be considered in the future perspective to recover also Pb and Sn from electrolytic solution.

Table 1: Major metals contained in PCBs powders

Elements	Percentage composition (wt.%)
Cu	63.39
Sn	21.48
Pb	12.29
Fe	0.23
Al	0.23
Ba	0.21
Zn	0.1
Ni	0.04
Others	0.03

The chemical characterization was relevant to understand what metal was better to recover from disassembled PCBs. In particular, copper was found to be the most precious metal present and the most abundant among those detected. In the light of the most current scientific publications, it was chosen to adopt an electrochemical method for copper recovery. The electrochemical tests of copper electrorefining were carried out using large pieces of PCBs, previously thermally and chemically treated, as working electrode with a constant current of 900 mA. Cell voltage remained constant at a value of about 0.15 V during the first hour, then increased suddenly to 1.8-2 V remaining constant until the end. The sudden increase of potential could be attributed to the increase of the overvoltages associated to the copper dissolution. The potential value measured during the experiment was higher if compared to that of the industrial process (Pletcher and Walsh, 2012). As well known, in an electrorefining process, the cathode reaction is the reverse of that one at the anode, therefore the cell voltage is exclusively due to voltage drop. The overvoltages, likely due to the insulating nature of the support material of PCBs, were significant since the beginning of the process but they became more important with the passage of time.

The two cathode plates were weighed both before and after test and the overall increase of weight was 7.62 g. Using Eq (1) for a time of eight and a half hours, the current efficiency of copper was 84%, which was low for an electrorefining process, usually 90-97% (Pletcher and Walsh, 2012). It was evident that some eddy reactions had consumed charge for processes different from copper deposition. To have a better idea of what happened at the cathode, a chemical and morphological characterization was made on the deposit. This latter was in the form of compact foil easily peelable from metallic support for analysis by scanning electron microscopy. Figure 1a shows the morphology of the deposit and indicates similar structures to those found in the literature for electrodeposited copper (Fogarasi et al., 2014; Alfantazi et al., 2003). Figure 1b shows the cross section of copper foil. The thickness of the Cu layer is uniform along the entire section analysed with a value of about 32.35 µm. The purity of the deposit was determined by energy dispersive spectroscopy. Figure 1c shows EDS spectrum where the only presence of copper can be seen. Carbon peak is due to the conductive tape used to fix the sample in the stub while the peak of oxygen is due to the presence of partially oxidized copper, as will be shown more clearly later in the text. The copper deposit was also characterized by XRD as shown in Figure 2. Copper (ICDD card number 04-0836) is the main phase but some diffraction peaks of CuO (ICDD card number 02-1041) were also identified.

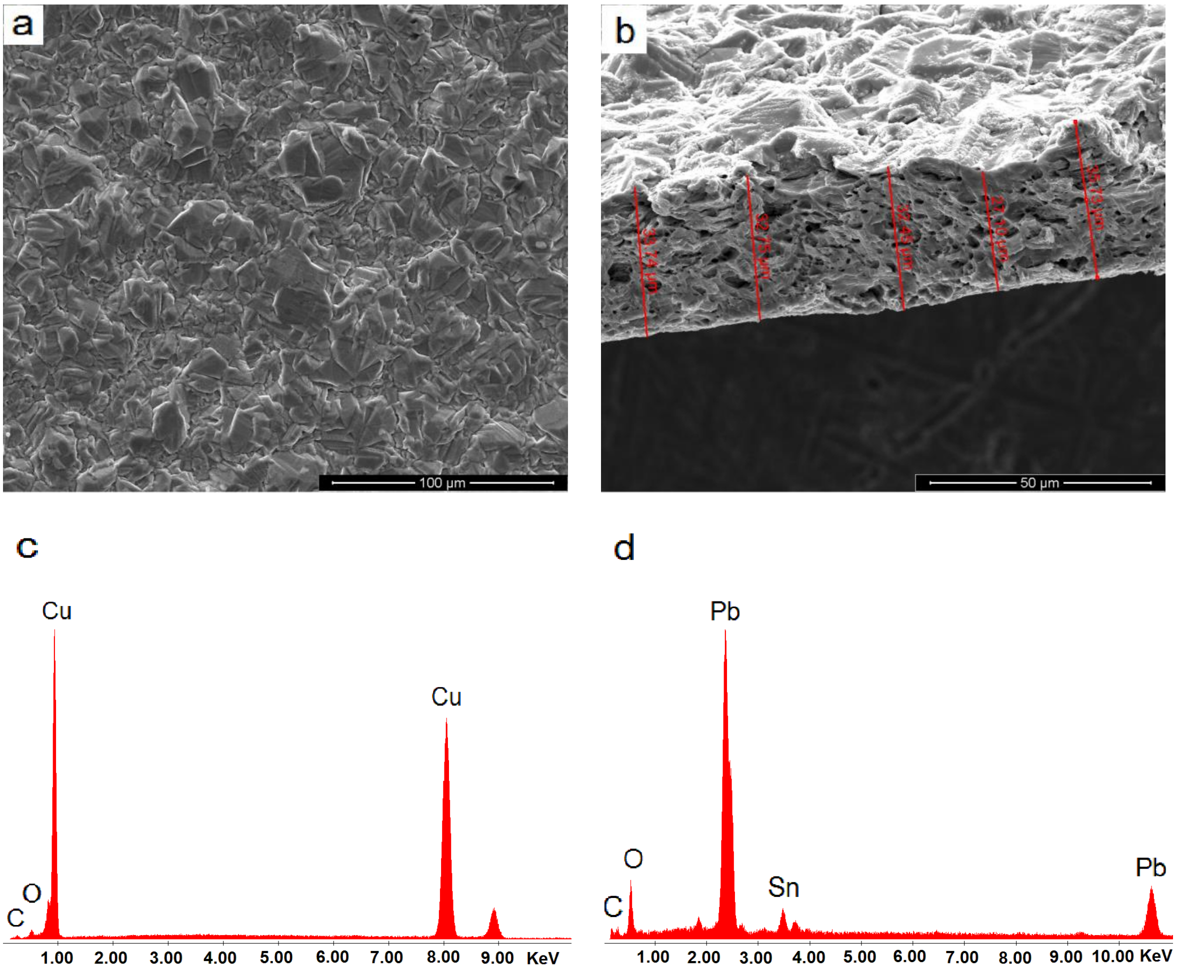

Figure 1: SEM images at different magnification of copper deposit top view (a) and cross section (b). EDS spectra of copper deposit (c) and solid residue recovered at the bottom tank at the end of the electrorefining process (d)

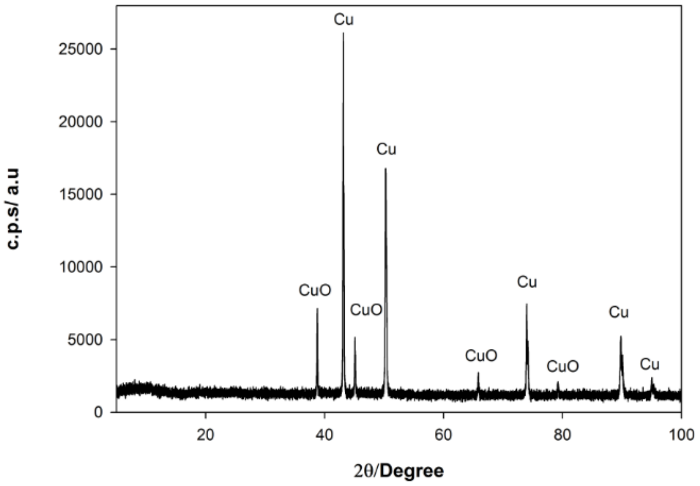

Figure 2: Diffraction pattern of the copper deposit

It’s well know that copper is easily oxidized in the environment but in this case its formation could be of different nature. In fact, according to the literature (Gao et al., 2002), the change of pH determined by some undesired reactions could have an important role in the copper oxide formation. In particular, hydrogen evolution and oxygen reduction reactions could increase the pH close to the cathode determining the formation of copper hydroxide, which, however, is dehydrated to generate the more stable copper oxide. This hypothesis would be consistent with the result of low efficiency found and with the absence of metallic impurity at the cathodes. Therefore, the cathodic reactions likely occurring at cathode were

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O \qquad (E°=1.23\ V/NHE) \tag{3}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad (E°=0.34\ V/NHE) \tag{4}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (E°=0\ V/NHE) \tag{5}$$

Oxygen reduction was the most favoured reaction but the static conditions imposed inside the vessel limited the amount of oxygen in solution. In an ideal operation of the electrochemical cell, the reaction of hydrogen evolution couldn’t take place because less noble of the redox couple Cu/Cu^{2+} but, owing to the overvoltages, the cell voltage could be high enough to activate the reduction of hydrogen. Electrochemical deposition of other metals less noble of copper (Pb, Sn, Zn etc.) was excluded taking into account the high purity of copper obtained. Therefore, the low efficiency obtained was mainly determined by hydrogen evolution reaction. At the end of the test, the anode was dismantled, washed with distilled water, pulverized and then dissolved in aqua regia to perform an ICP analysis. Results show a removal degree of copper from PCBs of about 46% compared to the initial value. Encouraging findings were obtained from the chemical analysis of both electrolytic solution and solid residue found on the bottom tank. Figure 1d shows EDS analysis of the solid residue. The EDS spectrum shows only the presence of two metallic elements, lead and tin, with tin traces compared to lead. ICP analysis carried out on the electrolytic solution gave consistent results showing a negligible concentration of lead in solution compared to that of tin. Therefore, tin was relatively stable in $CuSO_4$-H_2SO_4 solution remaining dissolved in the electrolyte while lead formed the solid precipitate found on the bottom of the vessel. The trend showed from these results, suggests the possibility of an easy separation of lead and tin that can be recovered in addition to copper.

4. Conclusions

The chemical characterization of the pulverized samples of PCBs guided us towards developing a method to recover copper, which is the metal most abundant and at higher added value. The advantages coming from the proposed method, an electrolytic refining of copper directly using waste PCB as an anode, include the possibility to use any type of PCB (flexible process) without knowing the exact composition of the input materials. Besides, the leaching and recovery steps can occur simultaneously and in the same apparatus with a global simplification of the recovery process. A key issue was also the reduced environmental impact of the process. In fact, electrolytic solution can be recycled after a purification step to remove the metal impurities accumulated, as in the industrial process of copper electrorefining. Pure copper was obtained with a current efficiency of 84% and with a copper removal from the PCB of 46%. Further works will be conducted to optimize the process, in particular, the main goals will be to improve the current efficiency without sacrificing the high purity of the deposits, and the dissolution of copper. Besides, it will be scrutinized the possibility to recover also tin and lead, because, after a complete removal of metals from waste PCB, the remaining board could be easily recycled.

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