Copper and Antimony Recovery from Electronic Waste by Hydrometallurgical and Electrochemical Techniques

Jose Angel Barragan, Carlos Ponce de León, Juan Roberto Alemán Castro, Aarón Peregrina-Lucano, Felipe Gómez-Zamudio, and Erika Roxana Larios-Durán*

ABSTRACT: A strategy for the efficient recovery of highly pure copper and antimony metals from electronic waste (e-waste) was implemented by the combination of hydrometallurgical and electrochemical processes. The focus is on copper recovery as the main component in the leached solution, whereas the antimony recovery process was established as a purification step in order to achieve a highly pure copper deposit. The strategy includes mechanical methods to reduce the size of the wasted printed circuit boards to enhance the efficiency of antimony and copper lixiviation via ferric chloride in acidic media (0.5 M HCl) followed by an electrowinning process. In order to establish the best parameters for copper electrowinning, the leached solution was characterized by cyclic voltammetry and cathodic polarization. Then, an electrochemical reactor with a rotating cylinder electrode was used to evaluate the copper concentration decay, the cathodic current efficiency, the specific energy consumption, and mass-transfer coefficient. Furthermore, antimony was recovered via precipitation by a pH modification in accordance with the Pourbaix diagram. Under this methodology, two valuable products from the e-waste were recovered: a 96 wt % pure copper deposit and 81 wt % pure antimony precipitate. The strategy for recovery of other metal ions, such as lead, present in the e-waste at high concentrations will be reported in further works.

1. INTRODUCTION

Rapid advances in electronic technologies has led to a large number of equipment being replaced periodically by new models resulting in an exponential accumulation of obsolete devices without an adequate decommissioning treatment. Around 50 million metric tons of waste was produced at the end of 2018. The main implications of e-waste accumulation are the environmental and human health risk due the hazardous materials contained in the printed circuit boards (PCBs). Waste printed circuit boards (WPCBs) represent 6% of the total weight of e-waste, and its main content is ferrous and non-ferrous metals, which can leak into the environment and cause pollution. Adequate decommissioning could convert this waste into source of income due to the high economic value of gold, palladium, silver, copper, among others metals.

Adequate recycling of the e-waste including WPCBs will prevent environmental pollution and the recovery and recycling of valuable metals. Several methods such as mechanical processes for size reduction, concentration via reverse flotation, froth flotation, and fluidization, have been proposed by governments and research institutions. Physical-mechanical processes are only a pretreatment for size reduction and concentration of metallic fractions followed by pyrometallurgical techniques or hydrometallurgical processes. The recovery of precious metals such as gold and palladium, copper, and rare earths through pyrolysis methods has the disadvantage of using high temperatures and only partial separation, whereby further processing and refining are required. Hydrometallurgical processes are preferred over pyrometallurgical because of their high selectivity and lower energy consumption.

In the case of copper, the common hydrometallurgical recovery method includes chemical leaching in sulphuric, nitric, or hydrochloric acids combined with different oxidants such as air, ferric chloride, ferric sulfate, or hydrogen peroxide. The leaching process in these acidic media has been extensively studied. Nevertheless, although leaching copper is currently a successful process, the applied techniques...
reactor has been deeply studied and used in many electrochemical analysis to establish the viability and in
Furthermore, the reactor adapts to different sizes, maintaining similar fluid flow and mass-transfer patterns. The RCE reactor has been deeply studied and used in many electrochemical processes; however, as far as the authors know, its application in a complex process dealing with a real multimetallic solution obtained from the leaching of e-waste has not been previously explored. The reactor was characterized by a synthetic copper solution at the same concentration of metal ions of the actual hydrometallurgical leaching process. The antimony is recovered from the leached solution by precipitation. Figures of merit such as conversion, current efficiency, specific energy consumption, and mass-transfer coefficient were determined. Two valuable products, highly pure metal copper and antimony salt were obtained; their purity was determined by energy-dispersive spectroscopy (EDS). The recovery of other metal ions in high concentration different from copper and antimony found in this paper will be reported in future works.

2. METHODOLOGY AND MATERIALS

2.1. Materials. The WPCBs treated in this work were obtained from a local collector in Guadalajara City, Mexico, and mainly included RAM memories and integrated chips circuits of different computer and phone models and manufactures.

2.2. Mechanical Process. A wet mechanical process for size reduction and concentration of the samples was implemented by using a purpose-built ball miller of 95 dm³ volume. The flow diagram of this process is shown in Figure 1. The WPCBs were mixed in a 1:1 weight ratio with running tap water and grinded for 2 h. The content (branch A in Figure 1) was transferred to a 100 dm³ capacity tank for 48 h sedimentation. The sediment (branch C) was separated in two (branches D and E) with a 100-grid sieve, whereas the supernatant solution (branch B) was filtered with 15 µm pore filter paper. The water was returned to the initial point of the process (branch G), whereas the solids were dried at room temperature for 72 h and submitted to a leaching process (branch F). It should be noticed that concentration of copper and gold in branch F also corresponds to that in branch B (see Table 2). The treatment to the sediment (fractions D and E) will be published and discussed in a future investigation due the complexity of the high concentrations and variety of metals.

Table 1. Reported Processes for Cu Electrowinning from Multi-Metal Ions in Chloride Media

| metal recovered | metal ions in solution | metal recovery rate (%) | purity metal recovered (%) | reactor geometry used | reference |
|-----------------|------------------------|-------------------------|---------------------------|-----------------------|-----------|
| Cu              | Cu, Ag, Sn, Pb, Zn, Fe, Ni | Cu (45)                | Cu (>99)                  | three chamber electrochemical reactor | 34        |
| Cu, Te          | Cu, Te                 | Cu (95), Te (85)        | Cu (93.2), Te (98.3)      | emew cell             | 35        |
| Cu, Bi          | Cu, Bi, As, Sb, Pb     | Cu (97.8), Bi (97.8)    | Cu–Bi alloy (42–58), Bi (98) | emew cell             | 36        |
| Cu, Pb, Cd, Zn  | Cu, Pb, Cd, Zn         | not mentioned           | Cu, Pb, Cd, Zn > 99% mol | conventional three electrode cell | 37        |

Figure 1. Flow diagram of the mechanical process.
in this fraction. The metals in the solid material (branches A, B or C, D, and E.) were extracted by cupellation and the concentration of gold and copper was analyzed by atomic absorption spectrometry. In the following sections, only the recovery of copper is described, whereas the gold recovery process will be reported in a further paper.

### 2.3. Hydrometallurgical Process

The leaching experiments were performed with the dried solids in branch F in a 1 dm$^3$ glass reactor fitted with a propeller at room temperature. The leaching solution consisted of 0.5 mol dm$^{-3}$ hydrochloric acid (HCl) and 0.074 mol dm$^{-3}$ ferric chloride ($\text{FeCl}_3$) in distilled water$^{33}$ at a 1:10 solid/liquid (w/v) ratio stirred at 600 rpm for 24 h. The concentration of the metal ions in the leached solution was quantified by an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Elemental IRIS Intrepid IID).

### 2.4. Electrochemical Characterization

The leached solution was characterized by cyclic voltammetry. In order to identify the contribution of each metal ion, synthetic solutions of each ion at the concentrations found in the leached solution, were characterized separately. The cyclic voltammograms were performed in a typical three-electrode cell with a vitreous carbon working electrode of 0.05 cm$^2$ geometrical area and a platinum disc of 0.03 cm$^2$ as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode for all electrochemical characterizations and a computer-controlled potentiostat/galvanostat AUTOLAB model PGSTAT128N, fitted with the NOVA 2.0 software. The cyclic voltammograms started at the OCP value toward negative polarization curves were performed by using a copper rotating disk electrode (RDE) of 0.32 cm$^2$ geometrical area and a graphite rod of 0.42 cm$^2$ as the counter electrode. The experiments were performed in a 0.1 dm$^3$ cell containing the synthetic copper solution prepared in the laboratory with 0.5 mol dm$^{-3}$ HCl, 0.074 mol dm$^{-3}$ FeCl$_3$ and 1200 mg dm$^{-3}$ copper. The cathodic polarization curves were obtained at different rotation speeds $\omega$, between 100 $\leq \omega \leq 628$ s$^{-1}$ with a PINE rotor connected to the working electrode at a scan rate of 50 mV s$^{-1}$.

In order to identify the kinetic and mass-transfer control zones of the electrodeposition of copper ions, cathodic polarization curves were performed by using a copper rotating disk electrode (RDE) of 0.32 cm$^2$ geometrical area as the working electrode and a graphite rod of 0.42 cm$^2$ as the counter electrode. The experiments were performed in a 0.1 dm$^3$ cell containing the synthetic copper solution prepared in the laboratory with 0.5 mol dm$^{-3}$ HCl, 0.074 mol dm$^{-3}$ FeCl$_3$ and 1200 mg dm$^{-3}$ copper. The cathodic polarization curves were obtained at different rotation speeds $f$, between 100 $\leq f \leq 600$ rpm corresponding to the angular velocities between 10.5 $\leq \omega \leq 62.8$ s$^{-1}$ with a PINE rotor connected to the working electrode at a scan rate of 50 mV s$^{-1}$.

### 2.5. Antimony Recovery and Electrolyte Purification

The Pourbaix diagrams for antimony were constructed with HSC Chemistry 6.0 software to identify the predominance of the Sb species as a function of $E$ (V) and pH in order to have a thermodynamic understanding of antimony chemistry for its recovery. Based on the Pourbaix diagrams, the pH of the solution was modified from an initial value of 0.5–2.4 by adding 99.99 wt % pure NaOH crystals, and a precipitate was obtained from this procedure. The volume of the leached solution was 1100 cm$^3$ and 26 g of NaOH crystals were required to reach the final pH. Using NaOH crystals instead of a saturated NaOH solution avoids diluting the copper ions in the leached solution. The precipitate was analyzed by EDS (Bruker), whereas the final solution was analyzed by ICP-OES to determine the concentration of copper and antimony ions after this process.

#### 2.6. RCE Electrochemical Reactor

An in-house design RCE electrochemical reactor was used for recovering copper ions from the leached solution by electrolysis. The reactor container was built up with the Nylamid polymer. An electrolytic grade copper cylinder of 3.8 cm diameter and 10 cm length was the cathode, whereas a graphite hollow cylinder with an inner diameter of 8 and 10 cm length was the anode. The geometrical areas of the cathode and anode exposed to the electrolyte were 120 and 251 cm$^2$, respectively. The rotation rate of the cathode was 50 rpm corresponding to a Reynolds number ($Re$) of 15120. The Reynolds number is defined as $Re = ud/\nu$, where $d$ is the RCE diameter in cm, $u$ the RCE angular velocity in cm s$^{-1}$, and $\nu$ the electrolyte kinematic viscosity in cm$^2$ s$^{-1}$.

#### 2.7. Cu Recovery in RCE Electrochemical Reactor

A constant electrode potential of $\sim$0.45 V versus SCE was applied to the RCE electrochemical reactor for 2400 s. Samples of 1 cm$^3$ were taken every 8 min in order to follow the copper concentration. After the electrolysis, the copper deposited on the cylinder was scraped with care to avoid damaging the electrode surface and the composition was analyzed by EDS (Bruker).

The electrochemical reactor was evaluated in terms of conversion, current efficiency, and specific energy consumption. These parameters were calculated according to the following equations:

- **conversion:** $X(t) = 1 - \frac{c_t}{c_0}$ (1)
- **Current efficiency:** $\frac{8nF\Delta CV_R}{\int_0^t I(t)dt}$ (2)
- **specific energy consumption:** $E_s = \frac{\int_0^t I(t)dt}{V_0c_0X(t)M}$ (3)

where $c_t$ and $c_0$ are the concentration of copper ions at $t > 0$ and at $t = 0$, respectively, in mol cm$^{-3}$, $n$ is the number of electrons transferred (equiv mol$^{-1}$), $F$ the Faraday constant, $V_R$ the reaction volume in cm$^3$, $I$ the current in amperes, $E_{cell}$ the cell voltage in volts, and $M$ the molecular weight of the reactant ion in g mol$^{-1}$.

### 3. RESULTS AND DISCUSSION

#### 3.1. Mechanical Process

Figure 1 shows the flow diagram of the experimental conditions during the process, whereas

### Table 2. Copper and Gold Concentration at Each Branch Depicted in the Flow Diagram for the Mechanical Process

| branch | Au (wt %) | Cu (wt %) |
|--------|-----------|-----------|
| A      | 0.05      | 32.57     |
| B, F   | 0.02      | 1.60      |
| C      | 0.24      | 58.53     |
| D      | 0.01      | 65.19     |
| E      | 0.66      | 46.30     |

#### Table 3. Metal Ion Concentration in the Leached Solution Characterized by ICP-OES from Branch H in Figure 1

| metal ion | concentration (mg dm$^{-3}$) | metal ion | concentration (mg dm$^{-3}$) |
|-----------|------------------------------|-----------|------------------------------|
| Cu        | 1200                         | W         | 4.62                         |
| Au        | 1.8                          | Pd        | 0.38                         |
| Sb        | 430                          | Ag        | 1.43                         |
| Ni        | 80                           | Ti        | 1.78                         |
| Pb        | 400                          | Ba        | 13.87                        |

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Table 2 presents the gold and copper content as solid metal concentrations (wt %) obtained at each step. After the sedimentation process, the concentrations of gold and copper in the branch C were 4.8 and 1.8 times higher than the initial values in branch A, respectively [0.24 wt % Au and 58.53 wt % Cu in branch C, whereas previously in branch A, they were 0.05 wt % Au and 32.57 wt % Cu]. Low concentrations of metals, as those obtained in the solids at the supernatant solution, branch B, also F, [0.02 wt % Au, 1.6 wt % Cu] are suitable for the leaching process and the electrochemical recovery. High concentrations, as those obtained in branches D [0.01 wt % Au, 65.19 wt % Cu] and E [0.66 wt % Au, 46.3 wt % Cu] are more complex to deal with. Future research will be needed to discuss the treatment of these branches (D and E), and the results will be published in future papers. The focus of this study is on the leaching process, branch F (the metal concentrations at branch F corresponds to those in branch B), and the copper electrochemical recovery, branch H.

3.2. Hydrometallurgical Process. Table 3 shows the concentration of the different metal ions present in solution after the leaching process, branch H in Figure 1. The highest concentration corresponds to copper ions and one of the lowest to gold ions, which is in accordance with the e-waste characterization reported in Section 3.1. In addition, other metals ions were identified at this point even though in lower concentrations than copper. The concentrations of antimony, nickel, and lead would require a complete electrochemical characterization in order to identify and avoid interferences in

Figure 2. Electrochemical characterization by cyclic voltammetry of leached and synthetic solutions. (a) Black line corresponds to the leaching solution, red and blue lines correspond to the synthetic copper solution and leached solution with 1200 mg dm$^{-3}$ of copper, respectively; cyclic voltammetry of (b) 430 mg dm$^{-3}$ antimony; (c) 80 mg dm$^{-3}$ nickel, and (d) 400 mg dm$^{-3}$ lead. All solutions with 0.5 mol dm$^{-3}$ HCl, 0.074 mol dm$^{-3}$ FeCl$_3$, and the corresponding ion concentration at a scan rate of 50 mV s$^{-1}$ on vitreous carbon with a surface area of 0.05 cm$^2$.

Figure 3. Cathodic polarization curves at different angular velocities in a copper RDE with a geometric area of 0.32 cm$^2$ for a synthetic solution with 0.5 mol dm$^{-3}$ HCl, 0.074 mol dm$^{-3}$ FeCl$_3$, and 1200 mg dm$^{-3}$ Cu (0.0189 mol dm$^{-3}$) at a scan rate of 50 mV s$^{-1}$.

Figure 4. Pourbaix diagrams constructed with HSC Chemistry 6.0 software at the corresponding concentrations of antimony and chloride ions (Sb 0.0035 mol dm$^{-3}$, Cu 0.0189 mol dm$^{-3}$, Pb 0.002 mol dm$^{-3}$, Ni 0.0014 mol dm$^{-3}$, Fe 0.07 mol dm$^{-3}$, Cl 0.57 mol dm$^{-3}$).
3. Electrochemical Characterization. Figure 2a shows a typical cyclic voltammetry response of several solutions; the blue line was obtained with the leached solution, branch H. The red line corresponds to the voltammetry response of the synthetic solution with 1200 mg dm$^{-3}$ copper, and the black line represents the voltammetry for the leaching solution before the leaching process. Figure 2b–d depict the cyclic voltammetry for synthetic solutions for antimony, nickel, and lead ions, respectively, at the same concentration as those of the leached solution, branch H, cited in Table 3.

The CV curves in Figure 2a show that the reduction and oxidation processes of the leaching solution, black line, are minimal compared to the redox characteristics of the leached solution, branch H. The synthetic copper solution, red line, presents a slightly visible reduction process in the potential range of 0.3 to 0.1 V versus SCE related to the reduction of copper from Cu(II) to Cu(I) and a process associated to the reduction of Cu(I) to Cu(0) at potentials between -0.25 and -0.5 V versus SCE. In addition, the synthetic copper solution, red line, presents two oxidation processes attributed to the Cu(0) to Cu(I) and Cu(I) to Cu(II) oxidations in the intervals of -0.25 to -0.1 and 0.1 to 0.25 V versus SCE, respectively.
two oxidation signals are observed, the comparison with the synthetic copper solution, red line. First copper and antimony, respectively. 0.5 and 0.75 V versus SCE associated to the reduction of ff
leached solution, blue line, presents some di oxidation is observed at around 0.7 V versus SCE. The process takes place at around 0.25 V versus SCE; whereas its response of a synthetic solution of nickel ions, the reduction versus SCE and from

This phenomenon is in good agreement with the literature for the reduction process of copper ions in chloride media, where copper reduction takes place in two single-electron transfer steps because Cu(I) is stabilized by chloride ions. The same redox signals are observed for the leached solution, Figure 2a blue line; however, some differences are evident: first, two reduction signals are presented, a wider reduction peak from −0.3 to −0.75 V versus SCE which overlaps with another one that shows a small shoulder from −0.5 to −0.4 V versus SCE. This behavior can be indeed associated to the reduction signal of copper, but also to the reduction processes of lead and antimony ions, which are observed between −0.5 and −0.8 V versus SCE and from −0.3 to −0.5 V versus SCE, respectively, as is clearly shown in Figure 2b.d. The oxidation process in the leached solution, blue line, presents some differences in comparison with the synthetic copper solution, red line. First of all, two oxidation signals are observed, the first one in the range of −0.25 to −0.1 V versus SCE and the other between 0.5 and 0.75 V versus SCE associated to the reduction of copper and antimony, respectively.

On the other hand, Figure 2c shows the voltammetric response of a synthetic solution of nickel ions, the reduction process takes place at around 0.25 V versus SCE; whereas its oxidation is observed at around 0.7 V versus SCE. The electrochemical response of nickel ions is not observed in the voltammetry response of the leached solution, Figure 2a blue line, because nickel ions are presented at 80 mg dm−3, which is lower than copper, lead, and antimony concentration as shown in Table 3. This conclusion is in good agreement with the results summarized in Table 3; the ions at the highest concentrations are the ones that have the greatest current response in their reduction/oxidation processes and overlap the electrochemical responses from the ions at lower concentrations. The metal ions in the second column of Table 3 were not analyzed because they do not interfere significantly with the quality of copper deposition, and they are not of strong economic interest at those low concentrations, although from the environmental perspective, it will be necessary to remove them. Future research will be needed to increase their concentration and subsequent recuperation.

From the potential reduction ranges for copper and antimony presented above, a highly pure copper deposit is not possible to achieve in the presence of antimony. This is in accordance with the thermodynamic data available from the literature; for these reasons, a purification process to remove and recover antimony ion was implemented as described in Section 2.5. The recovery of Pb ions will be discussed in future work.

### 3.4. Determination of Electrolysis Potential for Cu Electrowinning.

The optimal electrode potential at which copper ions deposit on a copper bulk electrode was determined by the polarization curves shown in Figure 3, which represent the RDE experiments of a synthetic solution with 1200 mg dm−3 copper (0.018 mol dm−3). This solution emulates the copper concentration in the real leached solution. Looking at the current—potential curves in Figure 3, the potential range of copper deposition depends on the rotation rate. At 100 rpm, the reduction process occurs in the interval of −0.36 > E < −1.0 V versus SCE. As can be observed, in this polarization interval, the process is controlled by mass transfer; however, the polarization interval diminishes as the rotation rate increases, reaching an interval between −0.5 > E < −0.8 V versus SCE at the highest rotation speed of 600 rpm. In all cases, the hydrogen evolution reaction occurs at more negative polarization potentials, which should be avoided in order to reach high current efficiencies.

The electrolysis potential at which reduction of copper is a mass transfer control process on the RCE electrochemical
reactor potential was selected at −0.45 V versus SCE and 50 rpm. This polarization potential will avoid the deposition of other metal ions with a more negative reduction potential than −0.45 V versus SCE, such as lead ions. If more metals are present in the leached solution, a purification process will be required to avoid their electroreduction on the RCE at the polarization potential close or more positive than −0.45 V versus SCE.

3.5. Antimony Recovery and Electrolyte Purification. Figure 4 shows the E versus pH diagram for antimony in aqueous media in the presence of chloride ions. According to the diagram, at the pH of the leached solution, corresponding to 0.5, antimony is stable as an SbO$^+$ complex and at a pH higher than 1, the SbO$^+$ complex will precipitate as Sb$_2$O$_3$(s). The chloride ions do not interfere with the stability of Sb species under this experimental condition.

In order to ensure the precipitation of SbO$^+$ to Sb$_2$O$_3$(s), the pH value of the leached solution was changed from its original value of 0.5 to 2.4 by adding 99.99 wt % pure NaOH crystals to avoid the copper ions dilution. The precipitated salt was value of 0.5 to 2.4 by adding 99.99 wt % pure NaOH crystals to avoid the copper ions dilution. The precipitated salt was analyzed by EDS. Figure 5 shows the precipitate obtained by this procedure and the results of the analysis, which indicate that the predominant element in the sample is antimony, however a slight signal corresponds to copper. The quantitative results of this analysis report a concentration corresponding to 81 wt % Sb$_2$O$_3$(s). On the other hand, an analysis by ICP-OES reveals that after changing the pH, the final Cu and Sb ion concentrations in the leached solution was 1060 and 6.38 mg dm$^{-3}$, respectively. The increment in the pH value is an adequate methodology to purify the leached solution, reaching 98.5% depletion of antimony by precipitation. The Cu ions concentration determined by the ICP-OES analysis of the leached solution corresponds to the concentration fed to the RCE reactor.

3.6. Copper Recovery and Performance Analysis of the RCE Electrochemical Reactor. The RCE electrochemical reactor was operated for 2400 s at −0.45 V versus SCE as selected from Figure 3. During the electrolysis, the concentration of copper decreased as a function of time as shown in Figure 6a from 1060 mg dm$^{-3}$ (16 × 10$^{-3}$ mol dm$^{-3}$) to 110 mg dm$^{-3}$ (1.73 × 10$^{-3}$ mol dm$^{-3}$) after 2400 s.

The performance parameters of the RCE reactor were determined using eqs 1−3. Figure 6d shows that up to 90% conversion was achieved in 2400 s. Figure 6c,b) show the current efficiency and the specific energy consumption, respectively, for the deposition of metallic copper onto the RCE. Both parameters maintained almost constant values during the first 800 s; this behavior is due to the high concentration of copper, which is the main reaction over other secondary reactions. At higher times, the value of the current efficiency decreases almost linearly to a final value of 73%, which is still acceptable if compared with values reported in the literature. For example, the current efficiency for nickel recovery in a RCE electrochemical reactor from emulated industrial discharges, started at low concentrations (i.e., 200 mg dm$^{-3}$), was 60% and was still an economically viable benefit. Opposite behavior was observed for the specific energy consumption, which increases with time after 900 s to a final value of 1.75 kW h kg$^{-1}$ at 2400 s. The changes observed in Figure 6c,b are associated to the depletion of copper ions as a function of time (as is shown in Figure 6a). As expected, the current efficiency decreases, and the specific energy increases when the copper concentration in the solution decays more than 50% of the initial value. At low concentrations, secondary reactions such as hydrogen evolution take place. For instance, in the case of the global current efficiencies, the values in this work are higher than those previously reported by Fogarasi et al., who achieved a global cathodic current efficiency of 63.84% in 240 min in a flow cell, operating at 4 mA cm$^{-2}$ and a flow rate of 200 mL min$^{-1}$ with static electrodes and a similar leaching system for copper recovery. The differences in the energetics values reported are associated to the electrochemical reactor configurations and operation mode, besides that the RCE diminishes considerably the operation time. On the other hand, the specific energy consumption values reported in this study are lower than those reported by Haccarui et al., where 2.33 kW h kg$^{-1}$ was achieved in 2 h of electrochemical processing for copper recovery at 40 °C from e-waste and also with static electrodes, where the agitation of the system was promoted with a magnetic stirring bar in order to improve the mass transport phenomena. Therefore, it is noticeable that the use of the RCE electrochemical reactor improves the process efficiency and reduces the operation time when compared with static electrodes. In addition, it should be highlighted that under these working conditions, the current efficiency values are not too different when compared to values reported for silver recovery by Arredondo et al., where the current efficiency is up to 90% before the 95% of silver-ion recovery is achieved in electrolysis time of 90 min in a RCE electrochemical reactor.

Using the data from Figure 6a, it is possible to evaluate the specific mass-transfer coefficient for copper ions at the RCE reactor by evaluating the parameters in eq 4 for a simple batch reactor and assuming a first-order kinetic reaction

$$\ln \frac{c_t}{c_0} = -k_{ma}a t$$

where $c_0$ and $c_t$ are the copper concentrations in mol cm$^{-3}$, at time 0 and $t$, respectively; $k_{ma}$ is the mass transport coefficient in cm s$^{-1}$, $a$ is the specific surface area in cm$^{-1}$, and $t$ is the electrolysis time in s.$^{46}$

The graphical analysis of eq 4, shown in Figure 7, suggests a specific mass-transfer coefficient, $k_{ma}$, of 8.66 × 10$^{-4}$ s$^{-1}$, which is similar to 6.39 × 10$^{-3}$ s$^{-1}$ reported by de Oca et al.$^{42}$ for Cu(II) ions reduction onto a 304-type stainless-steel RCE in acidic media, 1.0 M H$_2$SO$_4$ and 15.7 mM Cu(II), which suggest that the process is mass transport-controlled over the charge-transport phenomena. The mass transport value calculated could be useful to determine the Sherwood number (Sh) for subsequent scale up and optimization of the process.

Figure 8a shows the EDS results of the copper deposited. The main signals are related to copper, which corresponds to a purity of 96 wt %. The lower signals correspond to oxygen and chloride, which comes from the copper oxidation after the process and from the electrolyte composition, respectively. It is worth noting that the EDS result does not shows the presence of impurities of Pb, Sb, and Fe in the leached solution. This suggests that the methodology for purifying the electrolyte and choosing the reactor operation potential were adequately established. Figure 8b,c shows the RCE used in the electrochemical reactor before and after copper recovery, respectively.

4. CONCLUSIONS

A process for the successful recovery of copper from e-waste by using both hydrometallurgical and electrochemical techniques was developed. A simple intermediate purification step, which
allows the recovery of antimony, through variation of pH, was presented. The electrochemical characterization was the main objective to achieve copper recovery and allowed establishing the parameters for the selective copper electrowinning onto the RCE.

The RCE configuration proves to be an efficient technology for metal-ion recovery from e-waste. The process achieved high-performance parameters, reaching 73% in the total cathodic current efficiency and 1.8 kWh kg⁻¹ Cu for the specific energy consumption after 2400 s. The specific mass-transport coefficient was evaluated as well, reporting an efficient value of 8.66 × 10⁻⁴ s⁻¹.

The methodology proposed in this work allows recovery of not only metallic copper at high purity, but also an 81 wt % Sb₂O₃(s) salt, that is two commercially valuable products.

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### NOMENCLATURE

#### Abbreviation
- OCP: open-circuit potential, V
- RAM: random access memories
- RCE: rotating cylinder electrode
- RDE: rotating disk electrode
- SCE: saturated calomel electrode
- WPCBs: waste printed circuit boards

#### Symbols
- $E_\text{cell}$: cell potential, V
- $E$: specific energy consumption, kWh kg⁻¹
- $F$: Faraday constant, C mol⁻¹
- $f$: Frequency, rpm
- $k_{\text{m,a}}$: specific mass transfer coefficient, s⁻¹
- $M$: molecular weight, g mol⁻¹
- $V_s$: volume of solution in the electrochemical reactor, cm³
- $X(t)$: conversion at time t, dimensionless

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