



# Dismantling and electrochemical copper recovery from Waste Printed Circuit Boards in $\text{H}_2\text{SO}_4$ - $\text{CuSO}_4$ - $\text{NaCl}$ solutions

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## ABSTRACT

The worldwide growing of electrical and electronic equipment makes increasingly urgent to find environmentally friendly treatments for e-waste. In this paper, the attention has been focused on i) the eco-friendly dismantling of the electronic components from Waste Printed Circuit Boards and ii) recovering of pure metallic copper, which is the most abundant metal and one of the most valuable in Printed Circuit Boards. After an experimental optimization study, we found that a solution containing 0.5M  $\text{H}_2\text{SO}_4$ , 0.4M  $\text{CuSO}_4$ , and 4M  $\text{NaCl}$  can be successfully used to disassemble the electronic components from the boards by leaching of all exposed metals. Air was blown into the leaching solution in order to regenerate  $\text{Cu}^{2+}$  ions, which acts as the predominant oxidant species. The key role in dismantling/leaching process is played by  $\text{Cl}^-$  ion that stabilizes  $\text{Cu}^+$  through the chloro-complexes formation. The results show that, in this manner, the electronic components can be easier disassembled in undamaged state, allowing the efficient recycling and valorization of the contained materials. The feasibility to recover electrochemically the copper from the solution resulting from dismantling/leaching tests was verified through a preliminary cyclic voltammetry study aimed to investigate the copper electrodeposition in sulphate-chloride solutions in the presence of other metal ions such as  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ . A divided electrochemical cell operating in either galvanostatic or potentiostatic mode was employed to investigate simultaneous copper recovery and leaching solution regeneration. The results indicate that, in both modes, pure copper can be obtained after the removal of all surface impurities by dipping in acidic concentrated sodium chloride solution. The galvanostatic mode leads to deposit of higher quality, meanwhile the potentiostatic one determines a faster deposition and leaching solution regeneration.

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## 1. Introduction

The development of the technology in parallel to the urbanization and industrialization are leading to growing of the electrical and electronic equipment and, consequently, of e-waste. According to the most recent data, 44.7 million metric tonnes of e-waste were generated worldwide in 2016, an equivalent of almost 4500 Eiffel Towers and the amount of e-waste is expected to increase to 52.2 million metric tons by 2021 (Baldé et al., 2017). Printed Circuit Boards (PCBs) are essential components in almost all electrical and electronic devices. They have a very complex structure that contains a variety of hazardous organic substances, such as the brominated flame-retardants, and heavy metals (Pb, Cd, Hg, As, Cr, etc.) (Akcil et al., 2015; Bakhiyi et al., 2018; Chen et al., 2016; Khaliq et al., 2014).

Currently, the common techniques for e-waste recycling are based on physico-mechanical, pyrometallurgical and hydrometallurgical approaches (Kaya, 2018; Wang et al., 2017), but, unfortunately, a significant amount of electronic wastes collected for recycling in developed countries are illegally transferred to China, India or other devel-

oping countries where they are improperly treated (Ghosh et al., 2015; Ikhlayel, 2018; Wang and Xu, 2014). The development of recycling strategies is of paramount importance not only from an environmental point of view, but also because e-waste and, in particular, Waste Printed Circuit Boards (WPCBs), can be considered a valuable resource of secondary raw materials (Bizzo et al., 2014; Işıldar et al., 2018). For example, a computer circuit board contains typically 20% wt. of copper, a quantity much higher than the 0.6% of a copper ore (Chu et al., 2015).

The main electronic components (ECs), such as peripheral Component Interconnect (PCI) slots, D-sub, and Advanced Technology Attachment (ATA) connectors are soldered to the motherboard through a Pb-Sn alloy by pins in brass or bronze with a final finishing in gold or tin over nickel or copper (Mesquita et al., 2018). These ECs are constituted by a thermoplastic housing and are electrically connected. The external terminals (leads) of the integrated circuit are constituted typically of a Ni-Fe alloy base material, such as either Kovar (54Fe/29Ni/17Co) or Alloy 42 (58Fe/42Ni) (Kwon, 2007). D-sub connectors have an external metallic shell in Ni or Sn plated steel. Before the leaching experiments, the Ni-plated bronze-based screws were removed from the D-sub components to avoid the increase of the leaching time due to their high thickness. In a mother-

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board, other components are also present such as Lithium ion battery, Capacitors, etc. Usually, these types of ECs are disassembled just before starting any type of WPCBs recycling method and, separately, are sent to properly recovery processes.

In order to develop an effective process for recovering materials from WPCBs, the most investigated methodology is certainly the hydrometallurgical one, which mainly consists of leaching, purification, and recovery of metals (Iannicelli-Zubiani et al., 2017). Currently, leaching is conducted on pulverized WPCBs obtained after some pretreatments consisting in dismantling, grinding and separation of non-metallic fraction from the metallic one through either chemical or physical processes (Hadi et al., 2015).

Dismantling consists in the removal of ECs from the board in order to simplify the successive recovery of materials. Currently, the removal of ECs fixed to the board involves the heating of WPCBs to the temperature above the melting point of the solder. Such operation is not friendly owing to i) release of toxic gases, ii) high consumption of energy, and iii) damaging of some reusable components (Zhang et al., 2015). Besides, the current approach doesn't allow to recover copper, which is the main constituent of the pins used for the electrical connection of ECs to the board. In the current study, a chemical leaching method was investigated to dismantle ECs from WPCBs by dissolving all exposed metals. In particular, the attention was focused on specific ECs which are soldered to the board because other components, such as Li-ion battery, capacitors, Random-Access Memory (RAM) devices, Central Processing Unit (CPU) device, aluminum heat sinks are usually removed manually by applying small and non-destructive forces at the beginning of any recycling chain, and sent to properly treatment or recovery processes.

In recent years, a large number of papers have been published dealing with the leaching of copper from WPCBs due to its relevant abundance. Copper can be effectively leached out using acidic or ammoniac solutions. The last ones are largely preferred because have shown a greater selectivity towards copper (Alam et al., 2007; Koyama et al., 2006; Liu et al., 2009). Nevertheless, different acids have been used, mainly  $\text{H}_2\text{SO}_4$  for its easy regeneration and low cost, but also aqua regia,  $\text{HCl}$ , and  $\text{HNO}_3$  (Kinoshita et al., 2003; Mecucci and Scott, 2002; Veit et al., 2006). Generally, an oxidizing agent, such as  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$ , is added to the leaching solution to enhance dissolution process (Birlonga et al., 2013; Diaz et al., 2016; Fogarasi et al., 2013, 2015; Kim et al., 2011; Yazici and Deveci, 2014). Hydrogen peroxide is extensively used for its high redox potential (1.78 V vs. NHE) despite its high cost and consumption, especially at high temperature (Yazici and Deveci, 2014). Ferric ion represents a cheap alternative and can be easily regenerated (Cui and Anderson, 2016). The use of  $\text{Fe}^{3+}$  was tested by different authors achieving high dissolution rate for metals despite the drawback of contaminating the downstream solution, which can, however, be purified by goethite and jarosite precipitation before electrodeposition (Cui and Anderson, 2016).

Recently, the use of  $\text{Cu}^{2+}$  as an oxidizing agent for leaching of copper from WPCBs was tested to avoid the contamination from iron and reduce the costs compared to  $\text{H}_2\text{O}_2$  (Li et al., 2018; Ping et al., 2009; Yazici and Deveci, 2013, 2015). Yazici and Deveci (2015, 2013) investigated both  $\text{HCl-CuCl}_2\text{-NaCl}$  and  $\text{H}_2\text{SO}_4\text{-CuSO}_4\text{-NaCl}$  solutions for highly effective leaching of Cu, Fe, Ni and Ag. However, the  $\text{HCl-CuCl}_2\text{-NaCl}$  solution was found to be extremely corrosive and determining a difficult electrowinning of copper. The presence of NaCl in  $\text{H}_2\text{SO}_4/\text{CuSO}_4$  solutions is crucial because  $\text{Cl}^-$  acts as a ligand for the  $\text{Cu}^+$  ions resulting from  $\text{Cu}^{2+}$  reduction and hence, stabilizes the  $\text{Cu}^{2+}/\text{Cu}^+$  redox couple favoring metal oxidation.

In the present work, a new integrated hydro-electrometallurgical way for ECs dismantling and copper recovery from large size pieces or even entire WPCBs is presented. A  $\text{H}_2\text{SO}_4\text{-CuSO}_4\text{-NaCl}$  solution of experimentally optimized composition was used to leach out all exposed metals from WPCBs large samples ( $7\text{-}30\text{ cm}^2$ ) so as to disassemble the selected ECs. The present work evidences the possibility of i) recovering the ECs without damaging, ii) using a few aggressive and cheaper oxidant solution, and iii) conducting simultaneously dismantling and leaching, followed by copper recovery and leaching solution regeneration. A systematic study focused on the electrochemical characterization of the used leaching solution by cyclic voltammetry (CV) was also undertaken to identify the best operating conditions for copper recovery. Besides, in order to control the  $\text{Cu}^{2+}/\text{Cu}^+$  ratio before the copper recovery step, waste electric cables can be added to the used leaching solution, allowing the recycling of the copper wire scrap which is currently treated by melting and casting with consequent high consumption of energy (Randhawa et al., 2016).

## 2. Material and methods

The treatment of WPCBs investigated in the present work consists in two stages:

- ECs detachment and metal leaching;
- Electrochemical recovery of copper from the used dismantling/leaching solution.

The last one was investigated after an accurate CV study conducted initially on specifically prepared synthetic solutions and then on the solution resulting from dismantling/leaching tests.

### 2.1. Optimization of ECs detachment from WPCBs and metal leaching

Dismantling of ECs from WPCBs and metal leaching were performed using a solution of 0.5 M  $\text{H}_2\text{SO}_4$ , 0.4 M  $\text{CuSO}_4$ , and 4 M NaCl with a concentration ratio of chloride to copper ( $C_{\text{Cl}}/C_{\text{Cu}}$ ) of 10, in accordance with the literature which suggests a ratio higher than 8 (Herrerros et al., 2005). Air was continuously blown into the solution. Large motherboard pieces ( $7\text{-}30\text{ cm}^2$ ) on which characteristic ECs were soldered (ATA, D-sub connector, integrated circuit, PCI slot). These pieces were mounted at once and in the same reactor and were separated each other to avoid contact between metallic parts (Fig. S1).

Given the composition of ECs, the main base metals that were expected to find in the solution after dismantling and leaching of WPCBs were Pb, Sn, Fe, Zn, Cu, and Ni. According to the literature, the solid to liquid ratio was set at 1/11.5 (g/mL), while the duration of each leaching test at 12 h (Birlonga et al., 2013; Ping et al., 2009; Pinho et al., 2018; Yazici and Deveci, 2013).

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, PerkinElmer Optima 2100 DV) was employed to obtain the composition of leaching solution before and after its use. Before analysis of leaching solution, a calibration line was recorded for each metal by using properly standard solutions.

### 2.2. Cyclic voltammetry study

The feasibility of the electrochemical copper recovery was studied by cyclic voltammetry. Initially, copper deposition and dissolution were studied in a synthetic solution containing 4 M NaCl and 0.5 M  $\text{H}_2\text{SO}_4$  as a supporting electrolyte (SE) and 0.4 M of  $\text{CuSO}_4$  corre-

sponding to the optimised composition used for dismantling and leaching tests. Then, the modification of the voltammetric curves was investigated when Zn, Fe, Ni, Pb, and Sn were added to the copper solution, as shown in Table 1. Finally, CV of a real solution resulting from dismantling/leaching of WPCBs was performed.

The CV measurements were carried out using a multi-channel potentiostat model DXC240 (Datronix Computer, România), in a standard three-electrode cell with a glassy carbon (GC) disk of 3 mm diameter as a working electrode, a platinum wire as a counter electrode, and a silver/silver-chloride electrode in saturated KCl solution as a reference electrode ( $E^0 = 0.197 \text{ V vs. NHE}$ ). The working electrode was mechanically polished until a mirror-bright finishing (McCreery, 2008). For almost all tests, the electrode potential was linearly swept from +1 V to -0.7 V at 50 mV/s for three consecutive cycles.

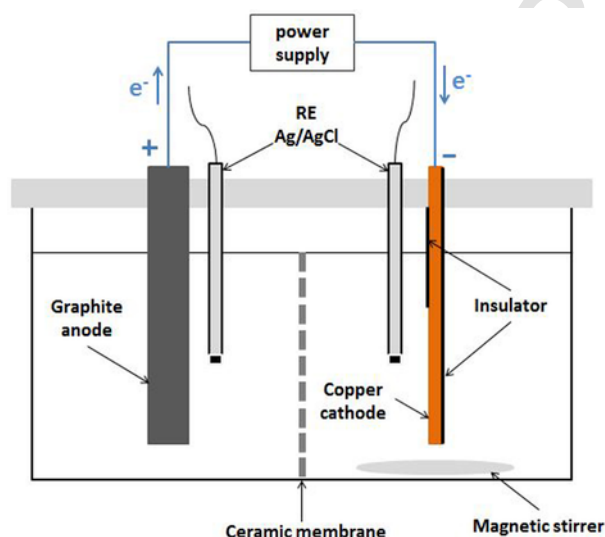
### 2.3. Copper recovery tests

A scheme of the electrochemical cell used for copper recovery tests is shown in Fig. 1. A 99.8% purity copper sheet and a graphite block (8 cm × 7 cm × 2 cm) were used as an anode and a cathode, respectively. The active area of the cathode was delimited with an insulating lacquer. The anodic and cathodic compartments were separated by a ceramic membrane, and both filled with solutions coming from

**Table 1**  
List of solutions used for cyclic voltammetry study<sup>a</sup>.

Solution number	CuSO <sub>4</sub> (mol/L)	ZnSO <sub>4</sub> (mol/L)	NiSO <sub>4</sub> (mol/L)	FeSO <sub>4</sub> (mol/L)	SnCl <sub>2</sub> (mol/L)	PbSO <sub>4</sub> (mol/L)
1	0.4	0	0	0	0	0
2	0.1	0.1	0	0	0	0
3	0.1	0	0.1	0	0	0
4	0.1	0	0	0.1	0	0
5	0.033	0	0	0	0	0
6	0.033	0	0	0	0.033	0
7	0.033	0	0	0	0	0.033
8	0	0	0	0	0	0.033
9	0	0	0	0	0.033	0.033
10	0	0	0	0	0.1	0.033

<sup>a</sup> All the solutions also contain 4 M NaCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte (SE).



**Fig. 1.** Schematic representation of the electrochemical cell used for copper recovery tests.

the leaching tests. The solution of the cathodic compartment was magnetically stirred, and before use the Cu<sup>2+</sup>/Cu<sup>+</sup> ratio was decreased in order to avoid excessive electrical charge consumption at cathode due to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. At this aim, 11.25 g/L of fine copper wires from waste cables were dissolved into the leaching solution.

The copper recovery was conducted in both galvanostatic and potentiostatic mode for 3 h. Different current densities, from 0.0238 to 0.050 A/cm<sup>2</sup>, and constant potentials in the interval from -0.25 to -0.35 V vs. Ag/AgCl, powered the cell. Despite the copper deposition is usually carried out in galvanostatic mode, here, the potentiostatic electrodeposition was also investigated. Indeed, as shown in the literature (Los et al., 2014), it is possible to get high quality deposits through a potential-controlled deposition determining much higher current densities than in current-controlled process.

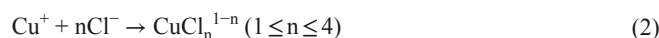
The morphology of cathodic deposits was investigated using a scanning electron microscope (SEM, model FEI QUANTA 200 FEG, FEI Company, USA) equipped with an X-ray energy dispersive spectrometer (EDS). Crystallographic structure was determined by XRD using an X-ray diffractometer model D-MAX 25600 HK (Rigaku Corporation, Japan). 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 analyzed by comparison with ICDD database (International Centre for Diffraction Data, 2007).

## 3. Results and discussion

In this study, leaching of metals from WPCBs and the copper recovery from the resulting solution were investigated separately even if in a possible real process, these two steps could occur simultaneously and continuously as schematized in Fig. S2. In particular, the solution leaving the leaching reactor is continuously adjusted in composition, in order to control the Cu<sup>2+</sup>/Cu<sup>+</sup> ratio and reduce the consumption of electrical charge at cathode, by addition of copper from e-waste (cables or WPCBs before sending them to the leaching reactor). Then, it is fed to the cathodic compartment where the recovery of pure copper occurs. The solution leaving the cathode is used to feed the anodic compartment where it is regenerated and re-circulated towards the leaching reactor.

### 3.1. Optimization of ECs detachment from WPCBs and metal leaching

The NaCl-H<sub>2</sub>SO<sub>4</sub>-CuSO<sub>4</sub> system was already used for successful leaching of the metals from WPCBs, but only after they were previously pulverized, while it was never used before to disassemble ECs (Ping et al., 2009; Yazici and Deveci, 2013). The reactions involved in the ECs detachment and simultaneous leaching of the exposed metallic parts are:



where reaction (1) shows that the dismantling and leaching process occurs by a cementation reaction driven by Cu<sup>2+</sup> ions in solution, while reaction (2) evidences the key role of Cl<sup>-</sup> in stabilizing Cu<sup>+</sup>. Also, the availability of Cu<sup>2+</sup> ions is of fundamental importance, therefore, it needs to restore those consumed in (1). A possible way consists in blowing air into the solution (Ping et al., 2009; Yazici and

Deveci, 2013) according to the following reaction:



Besides, it should be noted that, although oxygen contributes to maintain oxidizing conditions, its consumption induces pH increase. For this reason, the solution pH was monitored during the test and an increase from  $-0.2$  to  $+0.56$  was found after 12 h (Table S1). Thus, pH correction is necessary on longer time to avoid the precipitation of  $\text{Sn}^{2+}$  and  $\text{Fe}^{3+}$  when pH raises above 0.5 and 1, respectively (Cui and Anderson, 2016; Yazici and Deveci, 2015).

After dismantling/leaching process ECs are completely disassembled from the board (Fig. S3), therefore, may be sent to further treatment together with the remaining board, while plastic housings of PCI slot, ATA and D-sub connectors preserve their original structure. Therefore the materials of these components may be easier recycled without other treatments because totally metal free. Instead, integrated circuit, which still contains metals inside the external housing, may be sent to further treatments together with the remaining board.

The measured weight loss of WPCBs after 12 h of leaching was of about 24.8% (Table S2). The white colour layer on the soldering alloy surface (visible in Fig. S4a) indicates that Pb–Sn removal was lacking owing to its partial passivation by precipitation of lead sulphate.

Passivation occurrence of the soldering alloy due to  $\text{PbSO}_4$  precipitation is supported by the EDS analysis performed on these white areas (Fig. S5), confirming the presence of lead, whereas tin was almost completely dissolved. Indeed, the atomic fraction of lead (Pb/(Pn + Sn)) was of about 0.93 (Fig. S5). However, a complete removal of the soldering alloy was possible by alternating 12 h of leaching with 12 h of dipping in 4 M NaCl solution for two times. It was found that the amount of soldering alloy was decreasing over each washing up to complete dissolution (Fig. S4b). The action of concentrated NaCl solution in dissolving lead sulphate can be attributed to the formation of soluble lead chloro-complexes (Geidarov et al., 2009; Sinadinovic et al., 1997).

Concerning the initial concentration of  $\text{H}_2\text{SO}_4$  in the leaching solution, we have observed that (Fig. S6) connector and inserted pins remained on WPCB after treatment in 2 M  $\text{H}_2\text{SO}_4$ , whereas complete dissolution occurred in 0.5 M  $\text{H}_2\text{SO}_4$ . Thus, the optimal value corresponds to 0.5 M because higher concentration (1 and 2 M) reduced the metals dissolving rate, likely due to iron passivation and lead precipitation effects as reported in [Pedferri, 2018].

As for the initial  $\text{CuSO}_4$  concentration, it was found that a value of 0.4 M is adequate to provide enough  $\text{Cu}^{2+}$  ions in solution to sustain reaction (1), according to Herreros et al. (2005) who showed that the rate of copper dissolution was increasing with initial  $\text{Cu}^{2+}$  concentration. Consequently, chloride ions must be added into the bath to guarantee a  $C_{\text{Cl}}/C_{\text{Cu}}$  ratio higher than 8 (Herreros et al., 2005), which can be obtained by an initial NaCl concentration of 4 M. For low  $C_{\text{Cl}}/C_{\text{Cu}}$  ratios, the formation of chloro-complexes is limited with consequent poor stabilization of  $\text{Cu}^+$  ions. In fact, when NaCl concentration in the bath was lowered from 4 M to 1 M, abundant white precipitate of  $\text{CuCl}$  was formed according to the reaction:



As a consequence, a very low extraction of metals was found in the test with 1 M NaCl and in fact, after 12 h of dismantling/leaching process, many EC<sub>s</sub> components were still attached to the board. (Fig. S6). The measured weight loss of WPCBs was of about 8.9% (Table

S2), which is much lower than that found in 4 M NaCl in otherwise identical conditions. The final composition of leaching solution estimated by ICP-OES is reported in Table 2. As it was obvious to expect, after dismantling/leaching the solution is richer in copper (from 25.42 g/L of initial solution to 42.09 g/L of the final one) and furthermore contains Pb, Sn, Ni, Fe and Zn in smaller quantities.

### 3.2. Cyclic voltammetry study

At the end of the leaching tests using the 4 M NaCl-0.5 M  $\text{H}_2\text{SO}_4$ -0.4 M  $\text{CuSO}_4$  optimized system, the solution contains the ions of the oxidised/leached metals. Since copper is the predominant metal in WPCBs, the attention has been focused on its electrochemical recovery. Therefore, an electrochemical characterization of the solution at the end of the dismantling/leaching tests was conducted using the GC electrode. In order to correctly understand the cyclic voltammograms (CVs), initially, the fresh leaching solution was studied. Then, specifically prepared solutions containing ions of other metals such as Sn, Pb, Zn, Fe, and Ni were electrochemically characterized to evidence if interference effects exist.

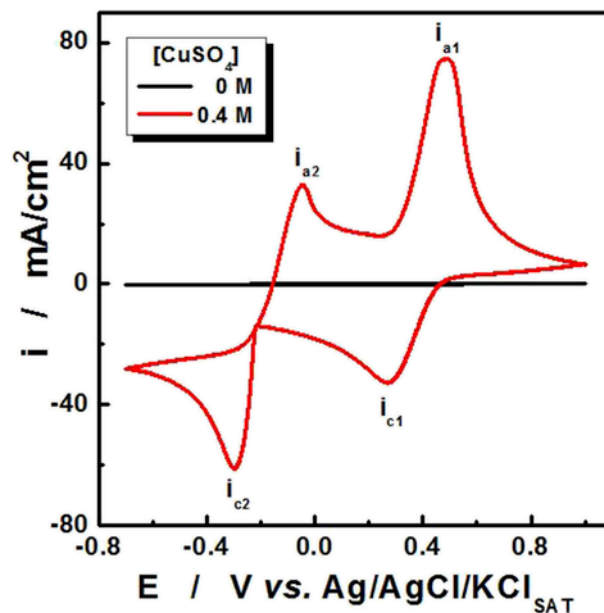
Fig. 2 shows that the cyclic voltammogram recorded on GC electrode in the SE solution (4 M NaCl + 0.5 M  $\text{H}_2\text{SO}_4$ ) is flat in the absence of copper, while there are two oxidation and reduction peaks when 0.4 M  $\text{CuSO}_4$  was added (sol. no. 1, Table 1). The peaks labelled  $i_{a1}$  and  $i_{c1}$  are associated to the quasi-reversible redox process:



**Table 2**  
The metal content of the leaching solution after dismantling process.

Concentration [mg/L]					
Zn	Cu	Pb	Ni	Fe	Sn
3472	42088 <sup>a</sup>	563.6	140.5	3350	1413

<sup>a</sup> Sum of the copper dissolved from WPCBs (16670 mg/L) and that present in the leaching solution as reagent (25418 mg/L).



**Fig. 2.** CVs recorded on GC electrode in SE solutions without and with addition of 0.4 M  $\text{CuSO}_4$ .



while  $i_{a2}$  and  $i_{c2}$  peaks are due to the Cu electrodeposition/electrodissolution process:



The reduction from  $\text{Cu}^+$  to  $\text{Cu}^0$  starts at about  $-0.23$  V, therefore, it is more negative than the equilibrium potential of the  $\text{Cu}^{2+}/\text{Cu}^0$  couple. Such an overvoltage is due to both stability of the chloro-complexes and deposition on a substrate different from copper (Grujicic and Pestic, 2002; Low et al., 2015).

The influence of Sn, Pb, Zn, Fe, and Ni ions on the copper CVs was specifically investigated. Using the solutions no. 2 and 3 of Table 1, it was found that zinc and nickel do not have any influence when

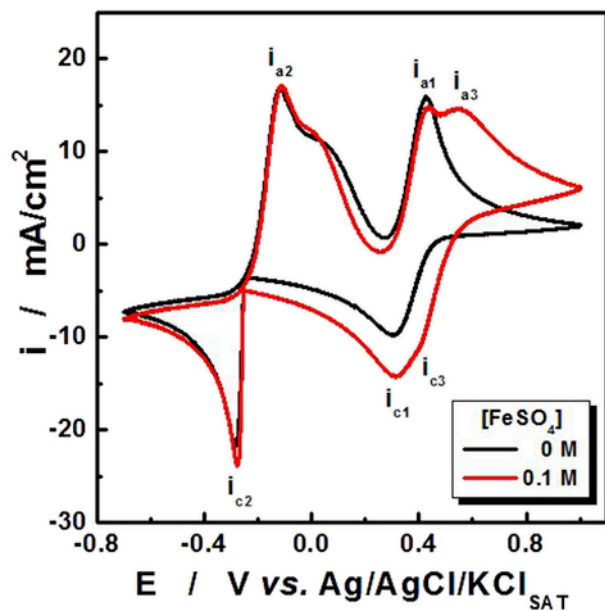


Fig. 3. CVs recorded on GC electrode in SE + 0.1 M  $\text{CuSO}_4$  solutions without and with addition of 0.1 M  $\text{FeSO}_4$ .

the potential is scanned within the range  $-0.7$ – $1$  V. As shown in Fig. 3, in the same interval of potential, the presence of 0.1 M  $\text{FeSO}_4$  in SE + 0.1 M  $\text{CuSO}_4$  solution (sol. no. 4, Table 2) determined the appearance of two new peaks ( $i_{a3}$  and  $i_{c3}$ ) corresponding to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  quasi-reversible redox couple.

The CVs recorded in the solutions #5, #6, #7 and presented in Fig. 4a and b reveal the appearance of a new pair of peaks ( $i_{c3}$  and  $i_{a3}$ ) attributable to the  $\text{Sn}^{2+}/\text{Sn}^0$  (Fig. 4a) and  $\text{Pb}^{2+}/\text{Pb}^0$  (Fig. 4b) electrodeposition/dissolution processes. These peaks indicate the almost simultaneous electrodeposition of tin or lead together with copper in both CVs marked in red in Fig. 4a and b. However, the same figures evidence that co-deposition of copper with tin or lead can be avoided by reducing the final cathodic potential ( $E_f$ ) from  $-0.8$  V to  $-0.5$  V, as shown by the CVs marked in green in Fig. 4a and b.

When  $\text{Pb}^{2+}$  and  $\text{Sn}^{2+}$  are both present in solution, their detection by CV is rather difficult because there is not a clear separation between the corresponding peaks. Reduction of  $\text{Pb}^{2+}$  to  $\text{Pb}^0$  starts approximately at the same potential of  $\text{Sn}^{2+}$  reduction to  $\text{Sn}^0$ . Fig. 5 shows that, comparing to the CV curve recorded in the solution containing only the SE + 33 mM  $\text{PbSO}_4$  (sol. #8), the addition of 33 mM  $\text{SnCl}_2$  (sol. #9) induced a weak increase of the  $i_{c1}$  reduction peak amplitude. Since the current peak located near  $-0.577$  V can be associated to the reduction reactions of both  $\text{Pb}^{2+}$  and  $\text{Sn}^{2+}$  to metallic Pb and Sn, respectively, we can assess that this weak increase is due to metals co-deposition. When the tin concentration was increased from 33 mM to 0.1 M (sol. #10), the CV curve shows an increase of both  $i_{c1}$  and  $i_{a1}$  peaks, and the appearance of a wave peak around  $+0.530$  V ( $i_{a2}$ ) due to the  $\text{Sn}^{2+}/\text{Sn}^{4+}$  irreversible oxidation.

All these data make possible to exhaustively characterize the solution resulting from the dismantling/leaching of the WPCB in order to establish the optimal operating parameters for the effective copper recovery (Mecucci et al., 2002; Reyes-Valderrama et al., 2017). Fig. 6 shows the CVs recorded in the fresh and used leaching solutions when the potential was scanned between  $-0.7$  V and 1 V. In both cases, the  $\text{Cu}^+/ \text{Cu}$  reduction peaks are located at  $-0.45$  V. Moreover, the copper electrodeposition process starts at quasi-identical potential values ( $-0.23$  and  $-0.24$  V). The higher reduction current density recorded in the solution resulting from the dismantling/leaching process is determined by the increased copper ion concentration due to the metal dissolution, as reported in Table 2. Besides, Fig. 6 shows

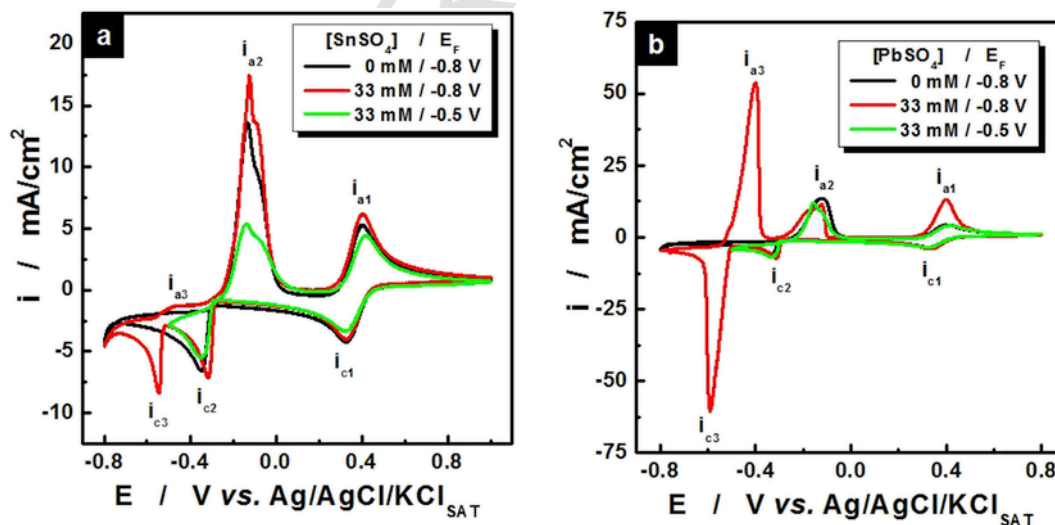


Fig. 4. CVs recorded on GC electrode polarized between  $+1$  or  $+0.8$  V and  $-0.8$  or  $-0.5$  V in SE + 33 mM  $\text{CuSO}_4$  solutions without and with addition of 33 mM  $\text{SnCl}_2$  (a) and 33 mM  $\text{PbSO}_4$  (b).

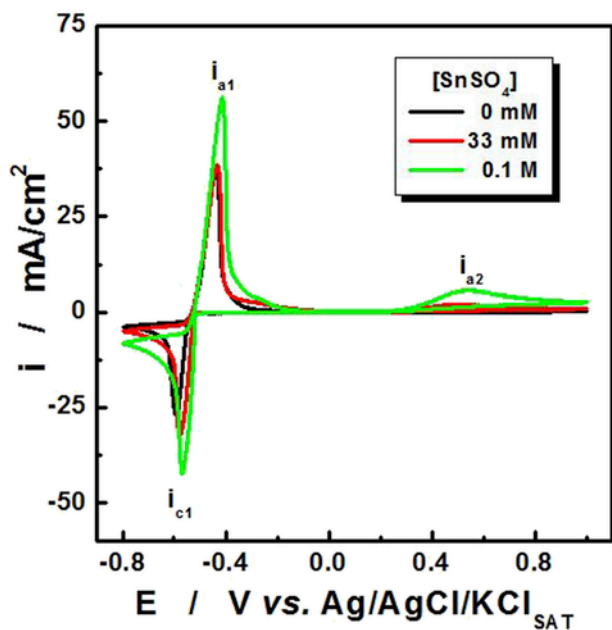


Fig. 5. CVs recorded on GC electrode in SE + 33 mM  $\text{PbSO}_4$  solutions without and with addition of 33 and 0.1 M  $\text{SnCl}_2$ .

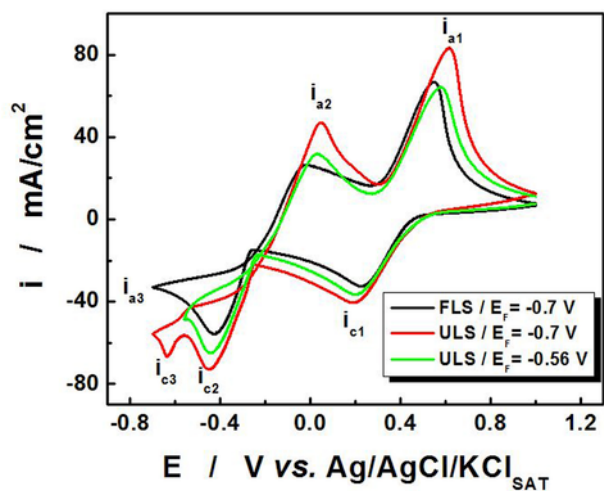


Fig. 6. CVs recorded on GC electrode polarized between  $-0.7$  or  $-0.56$  V and  $+1$  V in fresh (FLS) and used leaching solution (ULS).

an additional reduction peak located around  $-0.634$  V ( $i_{c3}$ ) with a corresponding oxidation peak ( $i_{a3}$ ) just visible. Both peaks can be due to the presence in the used leaching solution of either lead or tin, or, probably of both. However, it was checked that the unidentified species determining this couple of peaks does not influence the copper recovering. In particular, as shown also in Fig. 6, it has been found that lowering the final cathodic potential from  $-0.7$  V to  $-0.56$  V does not influence the  $\text{Cu}^{2+}/\text{Cu}$  reduction peak but avoid the co-deposition of tin and lead. Therefore, pure copper can be recovered if the cathodic potential was maintained in the interval from  $-0.23$  to  $-0.45$  V, approximately between the potential at which copper deposition starts and that of the cathodic peak for the  $\text{Cu}^{2+}/\text{Cu}$  couple.

### 3.3. Copper recovery tests

All above reported CV data showed the possibility to selectively recover metallic copper at high purity. To confirm these findings, specific tests were conducted in a divided electrochemical cell equipped with a graphite block and a pure copper sheet as an anode and a cathode, respectively. The solution resulting from the WPCBs dismantling/leaching tests was used as an electrolyte in both compartments of the cell in order to investigate the simultaneous copper recovery at the cathode and leaching solution regeneration at the anode. The electrochemical cell was powered in galvanostatic and potentiostatic mode for 3 h. In the last case, the potential was controlled between the cathode and  $\text{Ag}/\text{AgCl}$  reference electrode.

Fig. 7 shows a photo of copper deposits obtained in galvanostatic ( $-30$   $\text{mA}/\text{cm}^2$ ) and potentiostatic ( $-0.25$  V) mode. The deposits obtained in potentiostatic conditions appeared dendritic along the edges where the higher local current density and the edge effect favor the growth of dendrites as can be seen in Fig. 7. These results agree with the data reported in (Ibanez and Fatas, 2005; Nikolić et al., 2006). The average cathodic current density was about 60, 80 and 90  $\text{mA}/\text{cm}^2$  for cathodic applied potentials of  $-0.25$  V,  $-0.3$  V and  $-0.35$  V, respectively. For the galvanostatic electrodeposition experiments, the current density ranged between 23.8 and 50  $\text{mA}/\text{cm}^2$ . Therefore, the current density on the edges was higher in potentiostatic mode than in galvanostatic one. The dendritic structure is undesired because the copper deposit must be melted prior to any further working and, of course, this would be a severe disadvantage for technological application.

The obtained deposits were characterized by EDS and XRD analysis. The EDS spectrum example presented in Fig. 8a reveals that the as obtained deposit is not pure because it contains, in addition to Cu, elements such as Cl and O. The percentage compositions (at. %) of the deposits obtained in different operating conditions are shown in Table 3. The impurity existence is confirmed by XRD pattern shown in Fig. 8c that evidences the presence of both  $\text{CuCl}$  and  $\text{CuO}$  in addition to metallic copper. However, it was found that all impurities can be removed after immersion of the deposit, for about 10 min, in 4M  $\text{NaCl}$  adjusted at pH 1 by  $\text{HCl}$  addition. The EDS spectrum of Fig. 8b shows the disappearance of the peak due to Cl, while XRD of

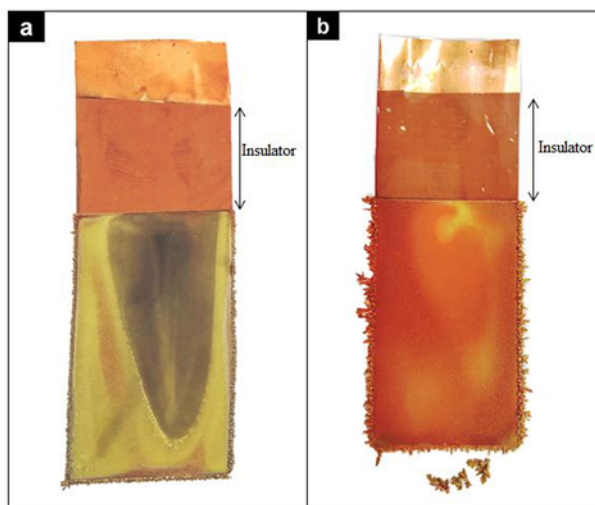


Fig. 7. Photos of copper deposits obtained in: a) galvanostatic ( $-30$   $\text{mA}/\text{cm}^2$ ) and b) potentiostatic ( $-0.25$  V) conditions.

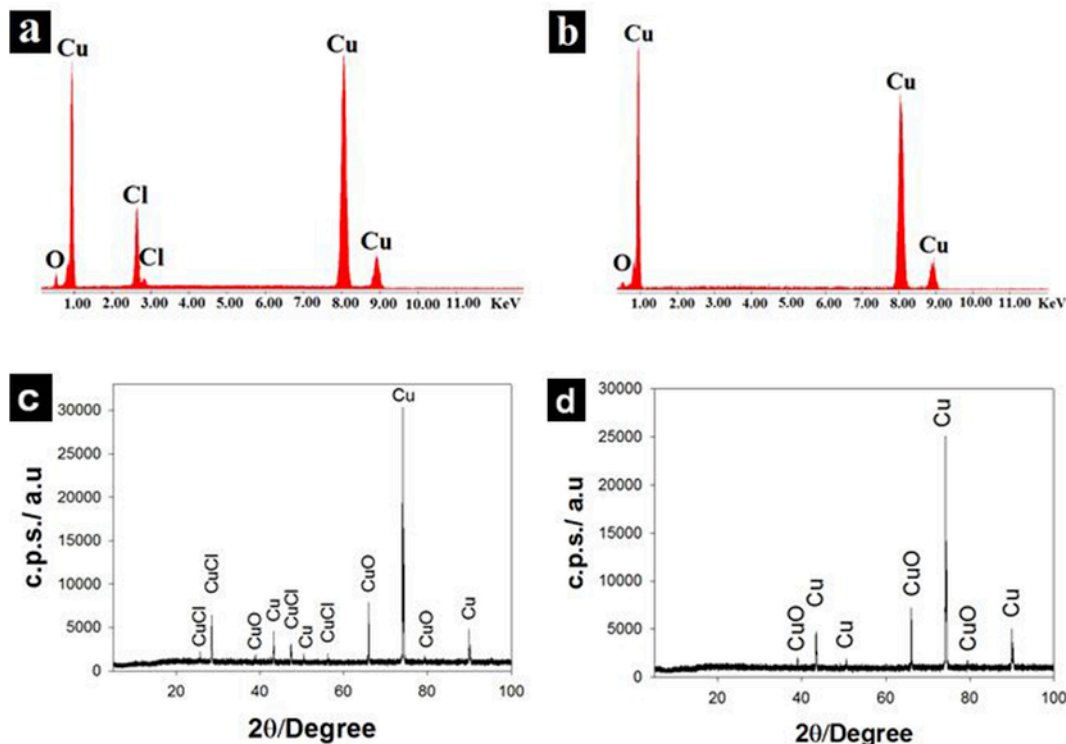


Fig. 8. EDS spectra (a, b) and diffraction patterns (c, d) of the Cu deposit obtained in galvanostatic mode at  $-23.8 \text{ mA/cm}^2$  before (a, c) and after (b, d) dipping in 4 M NaCl at pH 1.

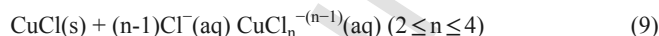
Table 3

Elemental composition (at. %) evaluated by EDS analysis of the copper deposits obtained by electrodeposition from the solution resulting from dismantling/leaching of WPCBs.

	Galvanostatic ( $\text{mA cm}^{-2}$ )				Potentiostatic (V vs. Ag/AgCl/KCl <sub>SAT</sub> )		
	-23.8	-30.0	-40.0	-50.0	-0.25	-0.3	-0.35
O (at. %)	15.4	32.4	31.0	31.4	28.6	34.8	40.5
Cl (at. %)	16.1	22.5	26.0	26.0	14.3	24.1	21.3
Cu (at. %)	68.5	45.1	43.0	42.6	57.1	41.1	38.2

Fig. 8d confirms the absence of CuCl, and the presence of CuO as a unique impurity.

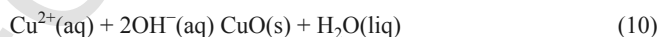
During the cathodic deposition, the concentration of  $\text{Cu}^+$  increases at the electrode/solution interface according to reaction (7) so that the concentration ratio of  $\text{Cl}^-$  to  $\text{Cu}^+$  is not enough to guarantee formation of chloro-complexes with consequent precipitation of a solid CuCl phase and its entrapment into the copper deposit. When the as obtained deposits are dipped in 4 M NaCl, soluble chloro-complexes are rapidly formed according to the reaction



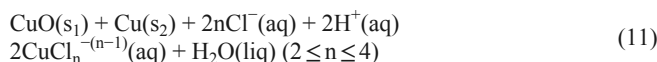
Consequently, dipping in 4 M NaCl for a few minutes was enough to purifying the deposit because solid CuCl is converted into soluble chloro-complexes.

Concerning the presence of CuO, it can be due to the oxidation of the extremely fine and reactive Cu micro-crystals with atmospheric oxygen during the drying step but, also to the pH raising at the elec-

trode/electrolyte interface owing to the parasitic reaction of hydrogen evolution, which can accompany copper deposition. Therefore, the following reaction can occur owing to the pH raising:



with consequent precipitation of cupric oxide as revealed by the XRD patterns of Fig. 8c. In principle, CuO might be dissolved on dipping the deposit in 4 M NaCl at pH 1. Likely, the acid-base reaction involving a solid phase is not very fast like the formation of the chloro-complexes, therefore, longer dipping time should need, with the risk of copper loss due to the following process:



After dipping in concentrated NaCl, the deposit turns from green to the typical color of electrodeposited copper (Fig. S8). The greenish color can be probably due to the presence of CuCl together with other impurities such as  $\text{CuCl}_2$ .

Table 4, in which the phases formed in different conditions are summarized, clearly evidences that the purity of the deposit is decaying as the deposition rate is increasing, i.e. when the applied current or potential were increasing (Aslin et al., 2017; Los et al., 2014). An exception to this trend is represented by the deposit obtained at  $-0.25 \text{ V}$ , which shows the highest purity together with that obtained at  $-23.8 \text{ mA/cm}^2$ , as also confirmed by the less greenish color of deposits obtained under these conditions (Fig. 7b). This finding suggests the possibility to operate at higher current density through a potential-controlled process making copper deposition and leaching solution regeneration faster.



**Table 4**  
Phases detected by XRD for different deposition conditions<sup>a</sup>.

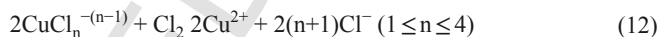
Galvanostatic (mA cm <sup>-2</sup> )				Potentiostatic (V vs. Ag/AgCl/KCl <sub>SAT</sub> )		
-23.8	-30.0	-40.0	-50.0	-0.25	-0.3	-0.35
Cu	Cu	Cu	Cu	Cu	Cu	Cu
CuO	CuO	CuO	CuO	CuO	CuO	CuO
CuCl	CuCl	CuCl	CuCl	CuCl	CuCl	CuCl
	Cu <sub>2</sub> O	Cu <sub>2</sub> O	Cu <sub>2</sub> O	Cu <sub>2</sub> O	Cu <sub>2</sub> O	Cu <sub>2</sub> O
	CuCl <sub>2</sub>	CuCl <sub>2</sub>	CuCl <sub>2</sub>	CuCl <sub>2</sub>	CuCl <sub>2</sub>	CuCl <sub>2</sub>
		Cu(OH) <sub>2</sub>	Cu(OH) <sub>2</sub>		Cu(OH) <sub>2</sub>	CuCl <sub>2</sub> ·3Cu(OH) <sub>2</sub>
					Cu <sub>3</sub> Cl <sub>4</sub> (OH) <sub>2</sub>	

<sup>a</sup> The ICDD cards used for identifying Cu, CuO, CuCl, Cu<sub>2</sub>O, CuCl<sub>2</sub>, Cu(OH)<sub>2</sub>, Cu<sub>3</sub>Cl<sub>4</sub>(OH)<sub>2</sub> and CuCl<sub>2</sub>·3Cu(OH)<sub>2</sub> were 03-1018, 03-0867, 09-0017, 03-0898, 34-0198, 03-0310, 23-0953 and 18-0439, respectively.

The morphology of the copper deposit formed at 23.8 mA cm<sup>-2</sup> and -0.25 V is shown in Fig. 9a-d after dipping in 4M NaCl at pH 1. Particles of various shape cover the surface forming a typical layer of electrodeposited copper already reported in the literature (Cocchiara et al., 2017; Fogarasi et al., 2014; Los et al., 2014). In potentiostatic mode (Fig. 9b, d), the average size of the grains is larger than that in galvanostatic mode (Fig. 9a, c). Normally, grain size decreases with the increase of the current density. However, some authors have reported that the addition of chloride into acidic sulfate solutions increases grain size of the electrodeposited copper (Shao and Zangari, 2009). It is likely that the concentration of chloride in proximity of the electrode surface increases with the current density leading to larger grains. The deposits obtained at 23.8 mA/cm<sup>2</sup> result more compact than that obtained at -0.25 V where crevices between the particles are observed (marked with red circle in Fig. 9d). Likely, this was due to a lower uniformity of the grain size.

The current efficiency of copper deposition was evaluated as a ratio of the deposited weight after the cleaning step to the expected one according to Faraday's law (see Eq. (8)). It has been found that the current efficiency was about 45% for deposition at 23.8 mA/cm<sup>2</sup> and 50% at -0.25 V. The low efficiency is due mainly to the competitive electron consuming reaction of Cu<sup>2+</sup> reduction to Cu<sup>+</sup>, and strong stability of chloro-complexes inhibiting the successive reduction step from Cu(I) to metallic Cu. To minimize this effect, the solution from leaching can be treated, without air blowing, with the addition of cop-

per from e-waste (cables or WPCBs pieces before sending them to the leaching reactor) prior to starting the deposition in order to consume Cu<sup>2+</sup> ions according to reactions (1) and (2). Besides, even iron (Fe<sup>3+</sup>/Fe<sup>2+</sup>) and tin (Sn<sup>4+</sup>/Sn<sup>2+</sup>) couples can contribute to the low current efficiency, according to the CV results. Another parameter that can contribute to diminishing the current efficiency is the chlorine evolution occurring at anodic potential more positive than 1.35 V. Chlorine can easily diffuse into cathode compartment where CuCl<sub>n</sub><sup>-(n-1)</sup> is oxidised to Cu<sup>2+</sup> according to:



therefore, Cu<sup>2+</sup> concentration increases in the catholyte and current efficiency diminishes. For all this, also the cell polarization must be controlled to avoid chlorine evolution.

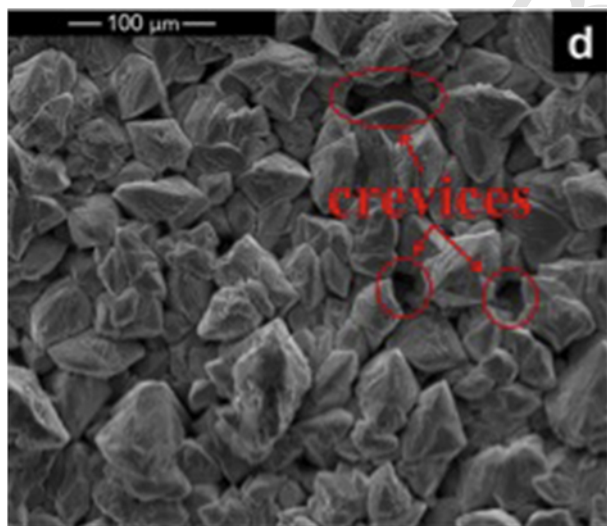
Finally, the energy consumption for copper deposition was 2.78 KWh/Kg for the test at 23.8 mA/cm<sup>2</sup> and 3.27 KWh/Kg for the test at -0.25 V. It is important to point out that a typical copper electro-winning consumes 3.45 KWh per Kg of deposited copper (Free, 2013).

According to these findings, it can be concluded that the better deposit in terms of purity and morphology is obtained in galvanostatic mode at a constant cathodic current of 23.8 mA/cm<sup>2</sup>, even if the current efficiency is a little below 50%. Since the possible causes of such a low current efficiency have been detected, more work is in progress for overcoming such drawbacks.

It must be also taken into account that the potentiostatic mode represents a promising solution from an industrial point of view because it allows to operate at higher current density and regenerate more rapidly the leaching solution that could be recycled. According to the present results, the principal disadvantages of operating in potentiostatic mode at a potential as low as -0.25 V are the purity and morphology of the deposit that presents distributed crevices and undesirable dendrites.

#### 4. Conclusion

On the whole, the results indicate that an efficient and eco-friendly dismantling/leaching process of WPCBs can be conducted using the NaCl-H<sub>2</sub>SO<sub>4</sub>-CuSO<sub>4</sub> system in the presence of blowing air for the in-situ regeneration of the oxidizing agent. The disassembled ECs maintain their structural integrity and, therefore, they can be easily separated and sent to recycle or further treatments. This is a key point because the current technologies use high temperatures and external actions (impact, shearing, vibration, etc.) for dismantling WPCBs with consequent i) damage of the components, ii) release of toxic substances, and iii) consume of energy. Simultaneously to dismantling, leaching of copper and other exposed metals occurs. There-



**Fig. 9.** SEM micrographs at different magnifications of the copper deposit dipped in 4M NaCl at pH 1. a), c) galvanostatic deposition at 23.8 mA/cm<sup>2</sup>; b), d) potentiostatic deposition at -0.25 V.



fore, copper, which is the most abundant and valuable metal, can be recovered at the cathode of an electrochemical cell fed with the solution coming from dismantling/leaching of WPCBs. The copper deposition can be conducted in either galvanostatic or potentiostatic mode. The current-controlled deposition permits to obtain a deposit of better quality in terms of purity and morphology. On the contrary, the potential-controlled deposition permits to work at higher current density so to shortening both the deposition time and leaching solution regeneration, but gives worse morphology and slightly lower purity. In all investigated operating conditions, the copper deposit contained some impurities, mainly of copper(I) chloride, which can be removed by dipping in concentrated NaCl solution slightly acidified with HCl without significant changes in the weight of deposits. Chemical analysis performed on the deposits after the cleaning confirmed that pure copper, with some minor CuO impurity, was obtained from the solution resulting after the dismantling of WPCBs and simultaneous leaching of exposed metals. More tests are in progress to improve the deposition current efficiency, recover also the other base metals from the used leaching solution and combine the leaching reactor with electrochemical cells for the simultaneous WPCBs dismantling/leaching and metals recovery.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2019.05.112>.

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