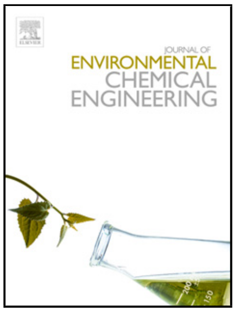

Copper recovery by cementing from waste solutions derived from the manufacturing/printing industry

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Copper recovery by cementing from waste solutions derived from the manufacturing/printing industry.

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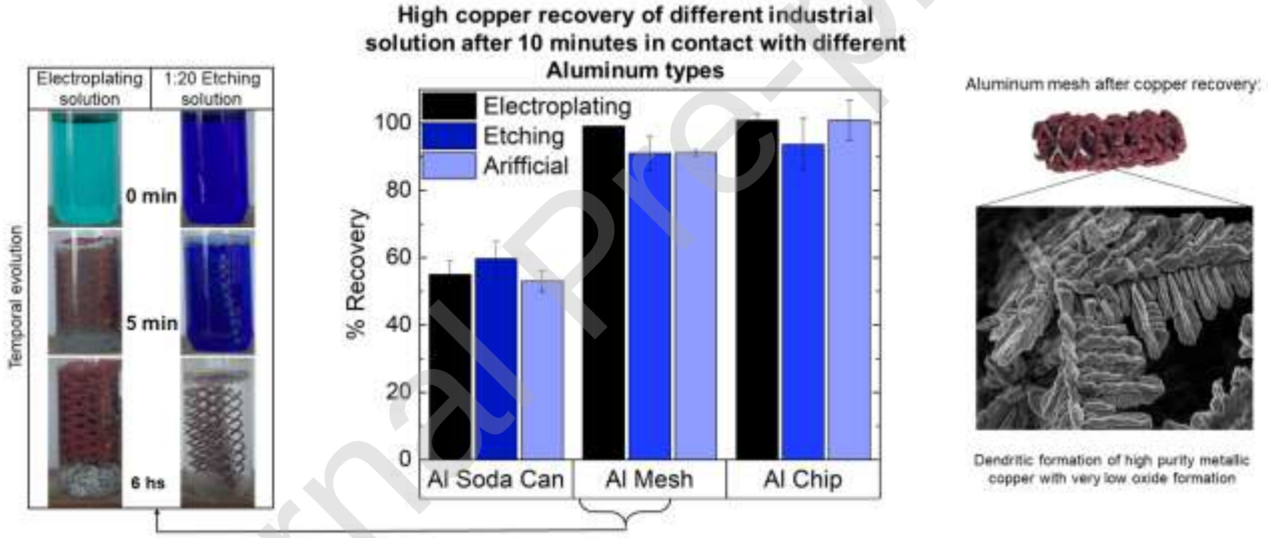
Graphical abstract



Highlights

- 90% Copper recovery from electroplating and etching real sample solutions.
- Recovery using aluminum from turning chips, soda cans or commercial meshes.
- Conditions for pure metallic copper without alloys or additives or chloride effects.
- Optimization of the treated volume and cementing agent mass ratio.
- Bases for the implementation of industrial copper recovery practices.

Abstract

We report the optimal conditions for copper recovery on a laboratory scale through a cementation process from industrial waste solutions. As cementing agent, aluminum was employed from different sources: discarding aluminum from soda cans and turning chip and commercial meshes. The percentage of recovery is highly dependent on the exposed area of aluminum and chloride additions. It was determined that the optimal chloride concentration should be equal to or greater than 100 mM and the ratio between mass of aluminum and volume of copper solution must be greater than (42+/-4) mg/mL for mesh or shavings to obtain recoveries up to 90%. For the case of aluminum from soda cans, this relation or the treatment time should be increased to reach the same relevant recoveries. As revealed by Scanning Electron Microscopy and X-Ray Diffraction experiments, the obtained copper is polycrystalline and dendritic, with low percentage of oxidized compounds. Under the conditions tested, the source of aluminum used does not seem to affect the quality of the product obtained. The conditions studied allow to scale the procedure and thus achieve the recovery of a metal of high economic value and reduce the environmental impact of industries such as the manufacture of printed circuits.

Keywords: copper recovery, cementation, electroplating solutions, etching solutions, X-Ray Diffraction, discarding aluminum

1. Introduction

Several aspects of human activity compromise the quality of the environment and especially have impacted natural sources of water. Today, electronic item consumption is faster than ever and contributes to the increase of the solid waste stream with an enormous environmental cost. The need for metal resources has driven many researchers to study different processes to recover heavy metal from electronic waste, wastewater and spent solutions [1–6].

Regarding primary metal resources conservation, the amount of solid waste generated, energy savings and prevention of environmental pollution, economic and environmental, and the advantages of metal recovery from E-waste are enormous [1]. These advantages could be applied to recover metals from other industrial sources such as the solutions generated during printed circuit boards (PCB) manufacture. These solutions contain significant concentrations of copper ions making them ideal sources of copper [7].

Copper, being a metal with high electrical and thermal conductivity, good malleability and ductility is considered one of the most important industrial metals [8,9]. It can be recycled and re-used countless times, and if it is in powder form or nanometer-sized, it reveals new properties [10,11]. These characteristics generate special interest in the recovery of copper.

Different techniques for removing copper from industrial solutions have been suggested such as neutralization, chemical precipitation, solvent extraction, flotation or adsorption on different adsorbents, or electrochemical [10,12–14]. However, these techniques present some drawbacks: ion exchange and carbon adsorption need regeneration, the high power consumption of electrowining and neutralization with sodium hydroxide generate new residues like mixed sludge [10]. Among these various treatment technologies, researchers are also studying cementation. It is a spontaneous electrochemical reduction of the metal ion to its elemental metallic state with the consequent oxidation of a sacrificial metal without applying energy [10]. This process is driven only by an electrochemical equilibrium becoming a low cost and ecofriendly process with a very high performance [10].

In order to understand the deposition mechanism, different metals and surfaces were tried, with or without surfactants, studying the kinetics and the morphology of the deposits. The results show that cementation occurs through a series of shorted electrochemical cells in which electrons are transferred from the cementation agent for reduction of Cu^{2+}. The formation of compact copper deposits inhibits dissolution of cementation agents thus decreasing copper cementation rate [15]. A less compact deposit or experimental conditions such as agitation can leave the cementation agent exposed and allow the reaction to continue [16]. Cementing agents are usually iron, zinc and aluminum, their standard electrode potentials are -0.44, -0.76 and -1.66 V, respectively. It is reported in [17] that iron, zinc and aluminum as cementation agents follow a first-order kinetics and different rates cementation are observed in each case. Having a large negative reduction potential, aluminum has served the precipitant metal of choice for different cementation systems such as gold [18,19], lead [20], mercury [21], platinum and palladium [22], and most of all, copper [8,18,23]:

$$3Cu^{2+} + 2Al = 3Cu + 2Al^{3+} \qquad E° = +2.00\ V\ (1)$$

By using aluminum as reductant, a useful solution of aluminum salt (sulfate, chloride, etc.) is obtained. These valuable products can compensate for the higher unit price of scrap aluminum over other agents. Aluminum swarf generated during machining and manufacturing can effectively be utilized in the cementation process [17]. However adherent oxide film that protects aluminum surface from environmental corrosion, causes slows reactions rates and side reactions, such as evolution of hydrogen gas [8,15,17]:

$$6H^{+} + 2Al = 3H_2 + 2Al^{3+} \qquad E°= +1.66\ V\ (2)$$

Mackinnon and Ingraham [18,24] found that small amounts of chloride ion activated the aluminum surface by dissolving its oxide film. They noticed that only 10 mg L-1 of chloride concentration could reduce the boundary layer increasing cementation rate constant and diffusion controlling resistance. Being small, mobile and active, chloride ions could easily be adsorbed on the oxide film of the aluminum surface [17]. Best results were obtained for solutions at pH = 2.5–3.2 and room temperature, recovering 60-70% within a few hours and 100% within a day [17].

Copper cementation is used for removing Cu^{2+} from electrowinning and electroplating solutions and to recover copper from leach solutions in [10]. The authors also explore the results obtained from cementation of ultrafine pure copper powders on iron chips from ammoniacal spent etching solutions. Although cementation is a very old hydrometallurgical process, the possibility of implementing the recovery of copper from waste material has not yet been specifically studied. Given the impact of heavy metals on the environment and the economic potential of copper recovery, it is critical to establish conditions that guarantee the quality of the obtained copper as a first step for new industrial applications.

In this work we explore the conditions of copper recovery from industrial solutions from electroplating and etching process. Both are from local printed circuit board manufacturing SMEs located in Buenos Aires, Argentina. The recovery was carried out by cementing reactions using discarded aluminum from turning shavings or soda cans. Commercial aluminum meshes were also included as standard geometry. First, we present the study of effects such as initial concentrations of copper and chlorides and type of aluminum in laboratory solutions, and then controlled recoveries in the industrial solutions. These results can be scaled to an industrial technology for copper recovery, minimizing at the same time the environmental impact of wastewater discard.

2. Materials and methods

2.1 Materials

Copper sulfate heptad-hydrated (Mallinckrodt, CAS 7758-98-7), sodium chloride (Carlo Erba, CAS# 7647-14-5), hydrochloric acid (CAS# 7647-01-0), sulfuric acid (CAS# 7664-93-9) were analytical grade reagents, and were used without further purification.

All solutions were prepared with deionized water (resistivity > 18 MΩ cm) obtained from a Millipore® system. The industrial copper solutions used were provided by local companies. The copper solutions for thickening of tracks (electroplating) contain the additive Cuprostar® (commercial additive based on 2-Chlorobenzaldehyde) and the solution for chemical etching is based on ammonium sulfate. The chemical composition of each solution samples are shown in Table I.

The aluminum used were of three sources, chips in the helical-form resulting from the discarding of machining of aluminum bars supplied by our institute turning workshop, commercial aluminum mesh and discarded soda cans. Examples of aluminum samples are shown in Figure 1.

2.2 Experimental conditions

Table I summarizes the experimental conditions used to prepare the samples for Scanning Electron Microscopy (SEM) and Powder X-Ray Diffraction (PXRD) analysis.

The three aluminum sources, soda can (A), mesh (B) and turning chip (C), were used for treating different types of copper solutions. Electroplating and etching solutions are from local SMEs that manufacture of printed circuit boards located in Buenos Aires, Argentina. Solution 1 corresponds to 1:4 dilution of electroplating industrial solution (copper sulfate 100 g/L, sulfuric acid 138 ml/L, hydrochloric acid 167 µl/L and additive Cuprostar® 6.67 ml/L) with the addition of 0.5 M NaCl, Solution 1* is the same as Solution 1 but prepared without the addition of additive. Both have pH value <1 and they were not modified. Solution 2 corresponds to 1:20 of etching industrial solutions with ammonium sulfate as etching agent (copper 120 g/L) previous acidification with hydrochloric acid 0.4 mL/L (until pH 1). Solutions 3 and 4 correspond to laboratory solutions from copper sulfate with NaCl 0.1 M (3) and NaCl 0.5M (4), pH 3.17 and 3.34 respectively. The complete composition of employed solution is presented in Table I. The industrial solutions were diluted in order to achieve a direct measurement of the copper concentration by visible spectroscopy before and after treatment. We decided to work with minimal pretreatments or additions to facilitate future industrial implementations. In the case of pH, its value was chosen within the acid range to avoid unwanted precipitation and the formation of complex species [12,13,17]. The initial copper and chloride concentrations were established from the results of the present study.

In order to study the chloride concentration effect and to optimize the operating conditions, NaCl was added in different concentration (0.01 M, 0.1 M, 0.5 M and 0.9 M) to copper sulfate ($CuSO_4$) 0.1 M. We also studied the effect of initial copper concentration using solutions of NaCl 0.5 M and varying $CuSO_4$ concentration (0.1 M, 0.2 M, 0.5 M and 0.75 M).

The samples prepared for SEM and DRX analysis and the optimization experiments were performed in plastic hemolysis tubes containing the aluminum and the corresponding copper solution. The reaction was ended by taking the supernatant in which the Cu^{2+} concentration was determined by an absorbance measurement. The thermostatic bath at 30 °C was maintained under orbital agitation at 65 rpm during the experiments.

2.3. Copper recovery tests and characterization

2.3.1 Visible spectrophotometric measurements

Visible spectroscopy is useful to measure copper concentration in aqueous solutions of Cu^{2+} before and after recovery treatment. In this case, the absorption spectra show a maximum at 815.58 nm. Calibration standards in the range of 1 mM to 125 mM copper sulfate were prepared without Cl^- additions and their absorption spectra between 400 and 1100 nm were measured using a 1 cm light path polystyrene cell and a modular Ocean Optics DT-Mini-2 spectrophotometer with a diode array detector connected to a PC and operated through Spectra Suite software.

The corresponding calibration curve is reported in Figure 2, in which the absorption at 815.58 nm subtracting the absorption at 500 nm as base line is plotted versus the concentration of Cu^{2+} resulting $y = (0{,}0124 \pm 1e\text{-}4)\ [CuSO_4]\ 1/mM + (7e\text{-}3 \pm 4e\text{-}3)$ $R^2=0.99948$, LOD: 5.7 mM and LOQ: 11.1 mM [25]. Error bars correspond to standard deviation of three experiments and confidence bands are included in Figure 2. Industrial samples were diluted to be measured in this interval of concentrations, and no interference bands were observed, showing that this method is a suitable way to evaluate the treatment efficiency. The LOD determines that the limit to measure the percentage of copper recovery for solutions that initially contain 0.1 M is about 90%.

2.3.2 X-ray diffraction measurements

In order to study the structure of the obtained deposits Powder X-Ray Diffraction (PXRD) patterns of copper deposits were collected with a high resolution diffractometer (PANalytical Empyrean) in a Bragg-Brentano geometry (θ-θ). The experimental set was as following: Primary beam: Cu anode (K-Alpha1=1.5405980 Å), K-Alpha2 =1.5444260 Å. Beta-filter Nickel.

The data were collected from 20 to 100° 2θ, with 0.02626° step size, 3047 step and 22.44 sec. per step, continue scan, incident mask of 15 mm and slits of 1-2-9.1 mm.

2.3.3 Scanning Electron Microscopy SEM

The copper deposits morphology and size were observed by Scanning Electron Microscopy (SEM) using a FE-SEM Carl Zeiss NTS-SUPRA40 in secondary electron mode, at the Advanced Center for Microscopies (CMA, Universidad de Buenos Aires).

3. Results and discussion

Among the critical parameters that have been reported over time for the cementation process are the initial copper concentration, chloride concentration and the type of aluminum used. The main part of this work is to define the best conditions to recover copper from samples from the manufacture of printed circuits boards, especially the processes related to electrochemical thickening of tracks (electroplating) with solutions in sulfuric acid and those from chemical etching with ammoniacal solutions. Initially it is sought to establish the effect of initial copper concentration and chloride concentration that allows the process to be optimized using laboratory copper sulfate solutions with additions of sodium chloride. At this stage these samples were treated with aluminum meshes which provides high surface area and it is easy to cut reproducibly samples. Then we explored the behavior of the system employing discarding aluminum.

3.1 Cu^{2+} initial concentration effect

To study the effect of initial copper concentration we used solutions of NaCl 0.5 M and varied $CuSO_4$ concentration (0.1 M, 0.2 M, 0.5 M and 0.75 M). For this part of the study the experiments were carried out in a thermostatic bath at 30 ºC. This temperature allows us to avoid seasonal fluctuations in room temperature and is in accordance with previous results [8,17]. The experiments were performed in plastic hemolysis tubes containing approximately 0.05 g of mesh and 2 ml of the corresponding solution. The reaction was ended after 6 min by taking the supernatant in which the remnant Cu^{2+} concentration was determined by an absorbance measurement. The thermostatic bath was maintained under orbital agitation at 65 rpm during the experiments. Stirring is recommended to facilitate the homogenization of the solution and also to detach part of the deposit and facilitate the reactivity of the cementing agent.

In figure 3, the mass of copper reduced is calculated from the difference between initial and final copper concentration, which were obtained using the Lambert-Beer law from an absorbance measurement, divided by the atomic weight of copper and multiplied by the volume of solution used. Finally, this value is expressed by mass of aluminum employed as a reference.

As shown in Figure 3, the mass of copper reduced by gram of aluminum used increase linearly with the initial Cu^{2+} concentration (R^2=0,9999) indicating that, in this concentration range, the rate of reaction is independent of the concentration of Cu^{2+}. The absence of reaction inhibition at high concentration of copper avoids the need to prepare dilute solutions, which would reduce the treatment time and the water use, considering industrial applications.

3.2 Cl^- concentration effect

It was reported [18,24] that the addition of small amounts of chloride ion can activate the aluminum surface by dissolving its protective oxide film. In this work we choose sodium chloride (NaCl) as reactant for chloride additions. Sodium chloride is economically accessible, easy and safe to store and handle which would allow its use on an industrial scale.

The experimental conditions were the same as described in section 3.1, where NaCl was added in different concentration (0.01 M, 0.1 M, 0.5 M and 0.9 M) to copper sulfate $CuSO_4$ 0.1 M. The % recovery is calculated as a percentage between the initial and final concentration of copper in the treated solution. Each 2 ml of solution of initial copper concentration 0.1 M were treated using 0.05 g of mesh of aluminum, and the final concentration was determined after 6 minutes.

The Figure 4, in which % recovery is plotted versus the concentration of Cl^-, shows that the efficiency of recovery increases with the Cl^- concentration until approximate 100 mM, and then it seems to reach a *plateau*. This result shows that an excess of chloride does not significantly improve the performance of the reaction under the conditions tested but it seems to improve the appearance of the deposit (see section 3.4.2).

It is important to note that the optimum Cl^- concentration depends on the aluminum source, as shown in the inset of Figure 4, where the maximum % of copper recovery is obtained at 100 mM when using soda can. As the aluminum from soda cans was used in this study without pretreatment, it is assumed that the excess of chloride reacts with the paint or with the protective polymeric layer, slowing down the reaction of cementing.

3.3 Ratio between solution and mass of aluminum effect

As we mentioned, the aim of this work is to obtain the optimal conditions for the copper recovery. With this purpose we studied the sensitivity of the % recovery with the ratio mass of aluminum used/volume of copper solution. The % recovery was calculated as explained above. As shown in Figure 5, when this ratio decreases the *plateau* appears at lowers % recovery and when using a relation of 50 mg of Al mesh/1.2 mL of Cu^{2+} 0.1 mM the % of recovery was around the limiting value of 90%. (This value was determine from the calibrations curve employed to determine the copper concentration)

3.4 Al source and shape effect: Copper recovery tests

Regardless of the economic value of copper recovery, and that this is more commercially valuable than aluminum, the possibility of carrying out the process using discarded aluminum makes the cementing process much more promising. For this reason, we decided to test the recovery from a laboratory solution of copper sulfate and from the industrial solutions proposed, using aluminum discarded from turning works, from soda cans and to have regular reproducible aluminum pieces we also used commercial meshes. Samples conditions are summarized in Table I for solutions 1, 1*, 2 and 4.

In Figure 6 the % recovery has been determined using a ratio (42 ± 4) mg/mL mass of aluminum treated/volume of solution for 10 minutes. As expected, a greater relationship between the mass (exposed area) of the same type of aluminum and the volume of the solution to be treated, as well as the treatment time improve the process performance. This explains the differences between the results reported in figures 4 and 6, and the lower % recovery reach for soda cans. Soda cans present less surface exposed to the solutions than the other aluminum samples mostly due to the protective polymeric layer. We have achieved interesting recovery percentages with low process time in order to illustrate the effect of the different conditions. Adapting the process to industrial scale design is beyond the scope of this work but the comparison presented will be very useful for this purpose. However, we can conclude that typical additives used in electrowining/electroplating do not affect the percentage of copper recovery, and acidic conditions tend to favor recovery. In the next sections the composition of recovered copper is analyzed.

It is important to mention that in addition to working with the diluted industrial solutions, as described in Table 1, tests have been carried out for undiluted industrial solutions such as electroplating solutions and for etching solutions in basic medium (without hydrochloric acid addition), adding 0.5 M in NaCl. In all cases, the optimum ratio is (42 ± 4) mg/mL mass of aluminum treated/volume of solution. The temporal evolution can be observer in Figure 7, which shows pictures of the experiments at 0, 5 minutes and 6 hours, from top to bottom, for 1:4 electroplating solution (Solution 1 from Table 1), 1:20 etching solution, undiluted electroplating solution and undiluted etching solution adding 0.5 M NaCl to all of them, from left to right. The concentrated solutions react very vigorously with emission of vapors and temperature increase, which should be analyzed in the case of being treated in these conditions on an industrial scale. In case 1:20 of the etching solution, although the treatment was possible, it was not easy to remove the copper from the aluminum mesh.

It is noteworthy that even without acidification of the medium, the PXDR analyses do not present evidence of cuprous oxide formation on the copper recovered from the etching solution (data not shown). This result requires a more detailed analysis, but it is in accordance with the objective of this work to recover high purity copper with the minimum of pretreatments.

3.4.1 X-ray diffraction measurements

The reddish copper deposits cemented at 30 °C and 65 rpm for the different conditions were collected, washed several times with distilled water, dried at room temperature and analyzed by PXRD.

As shown in Figure 8, the deposits are practically pure metallic copper, and there is no evidence for alloying. The peaks located at 43.3º, 50.5º, 74.1º are attributed to the (111), (200), (220) planes of metallic copper respectively. Hoverer, some oxidation may be occurring because samples A-1, A-4, B-1 and B-4 show six typical peaks located at 29.60°, 36.52°, 42.4°, 61.5°, 73.7° and 77.7° corresponding to the (110), (111), (200), (220), (311) and (222) planes of cuprous oxide, respectively [26–28] and http://rruff.geo.arizona.edu. This oxidization may be due to exposure of the deposit to the air, but also to the local increase in pH due to the reduction of protons, which occurs due to the side reaction in the cementation process. In sample C-1 there are peaks in the pattern that could be related to the accompanied aluminum powder probably coming from the turning chip during sample preparation.

Under the conditions tested, neither the source of aluminum used nor the presence of additives does not seem to affect the quality of the product obtained, even for etching solutions with hydrochloric acid additions.

In [17] the authors concluded the quality of cemented copper deteriorates when hydrochloric acid is used instead of sulfuric acid, since the cementation product is nantokite (CuCl) instead of pure copper. In our test conditions, no evidence of the formation of nantokite was found, despite the addition of chlorides as sodium chloride.

3.4.2 Scanning Electron Microscopy SEM

Figure 9 and 10 show SEM images of a copper obtained in the conditions of Table I (section 2.2): the different copper solutions (1, 2, 3 and 4) and aluminum source (A, B and C). In particular in Figure 10, SEM images of copper recovered from solutions with 0.1 M copper sulfate and sodium chloride 0.1 M (3) and 0.5 M (4) were presented. In all cases, the deposit consists of grains with a branched/dendritic shape, with approximately the same morphology and dimensions. For laboratory solution 3, the surface of the deposit is rougher, although the general aspect as to the dimensions of the branches remains. This result may be due to the presence of industrial additives in solutions 1 and 2, to the difference in pH or the concentration of chlorides. Regarding the latter, it is observed in figure 10 that the increase in the concentration of chlorides attenuates this effect.

4. Conclusions

Copper recovery by cementation process was studied in acidic medium for different industrial waste solutions such as electroplating and etching solutions. These solutions are discarded from printed circuits board manufacturing plans and the recovery is carried out by cementing reactions, using discarding aluminum. The aluminum comes from turning shavings, soda cans (only cut into strips for easy use) and commercial meshes.

In this work, the study of effects such as initial concentration of copper and chlorides, type of aluminum and the composition of the different solutions, allowed to establish the best recovery conditions in each case. Through techniques as Scanning Electron Microscopy and X-Ray Diffraction it was possible to identify a product of polycrystalline and dendritic copper, with low percentage of oxidized compounds.

The quality and general morphological characteristics of the product obtained were independent of the source of aluminum used or the presence of typical additives, working within acidic pH range and 0.5M of chloride. There are no significant differences in composition among copper obtained from the laboratory solutions of copper sulfate, from the industrial electroplating or from etching solutions, even using different types of aluminum as cementing agent.

Our results determine that for the optimal relation of (42+/-4) mg/mL between volume of solution and mass of aluminum it is necessary to add 0.5 M of chloride as sodium chloride, or for copper ammoniacal solutions with hydrochloric acid additions until the same relationship between copper and chloride concentrations. Under these conditions there was no evidence of copper chloride formation, and recoveries >90% could be obtained in 10 minutes.

We consider that these results will allow progress in the implementation of industrial copper recovery practices, especially for a growing industry such as circuit printing, reducing its environmental impact.

CRediT author statement

Cecilia Daniela Costa: Methodology, Investigation, Writing - Original Draft **Sonia Lustig:** Investigation, Writing - Original Draft, **María Verónica D'Angelo:** Investigation, Writing - Review & Editing, **Graciela Alicia González:** Conceptualization, Writing - Review & Editing

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Captions:

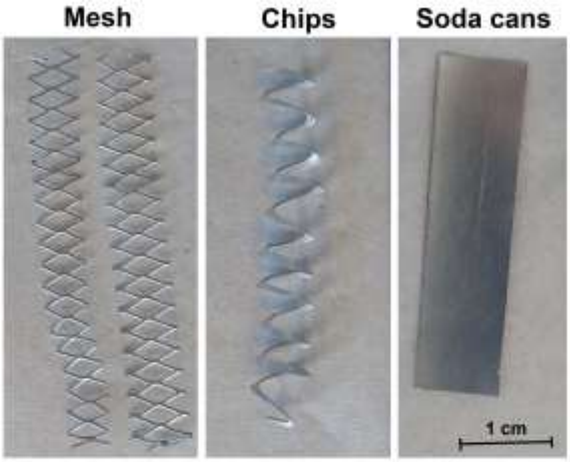


Figure1: The aluminum sources were of three types: commercial aluminum mesh, chips in the helical-form resulting from the discard of machining of aluminum bars supplied by our institute turning workshop and soda cans cut into pieces. Metric guide is included.

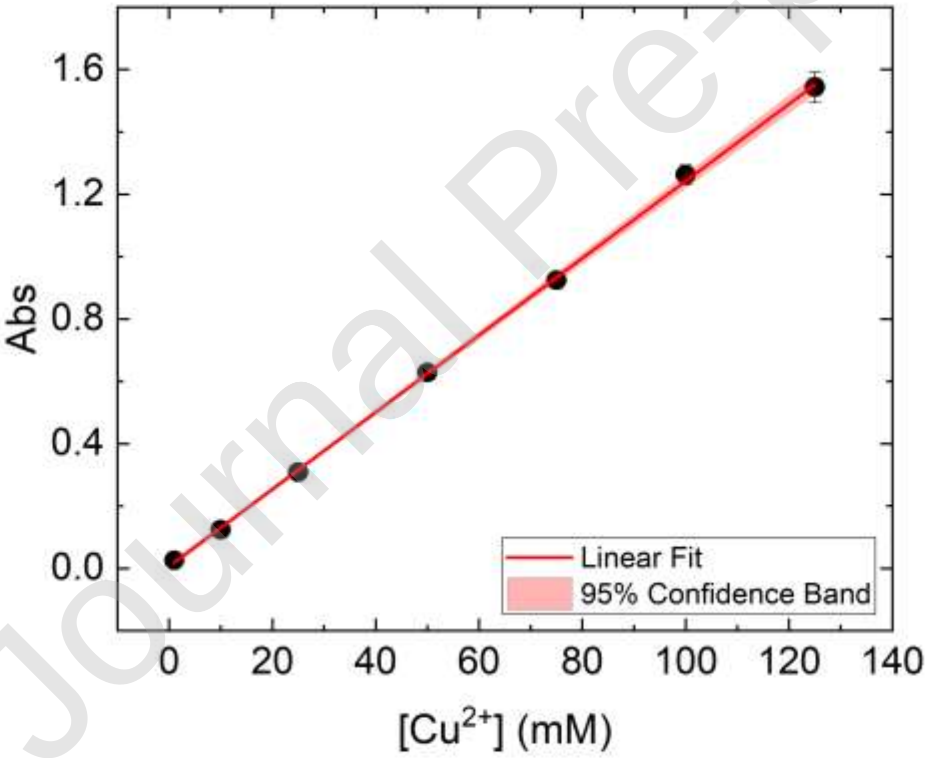


Figure 2: Calibration curve from visible absorbance measurements at 815.58 nm y = (0.0124 ± 1e-4) [CuSO4] 1/mM + (7e-3 ± 4e-3) R^2=0.99948 for aqueous solutions of copper sulfate from 0 to 120 mM. Error bars correspond to standard deviation of three experiments, confidence band at 95% are shown.

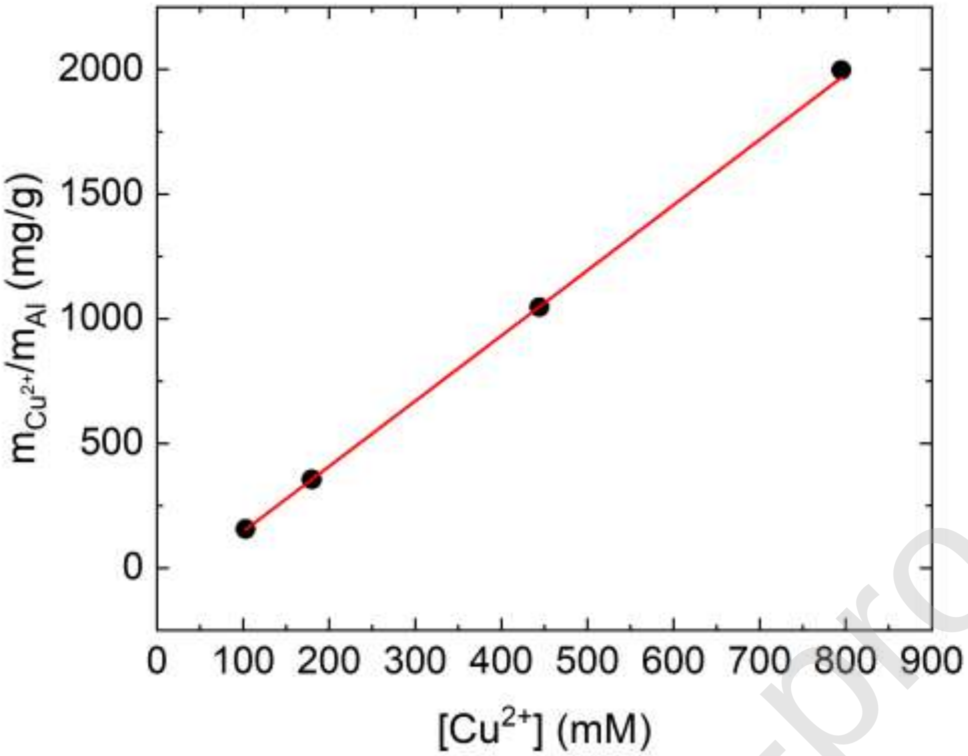
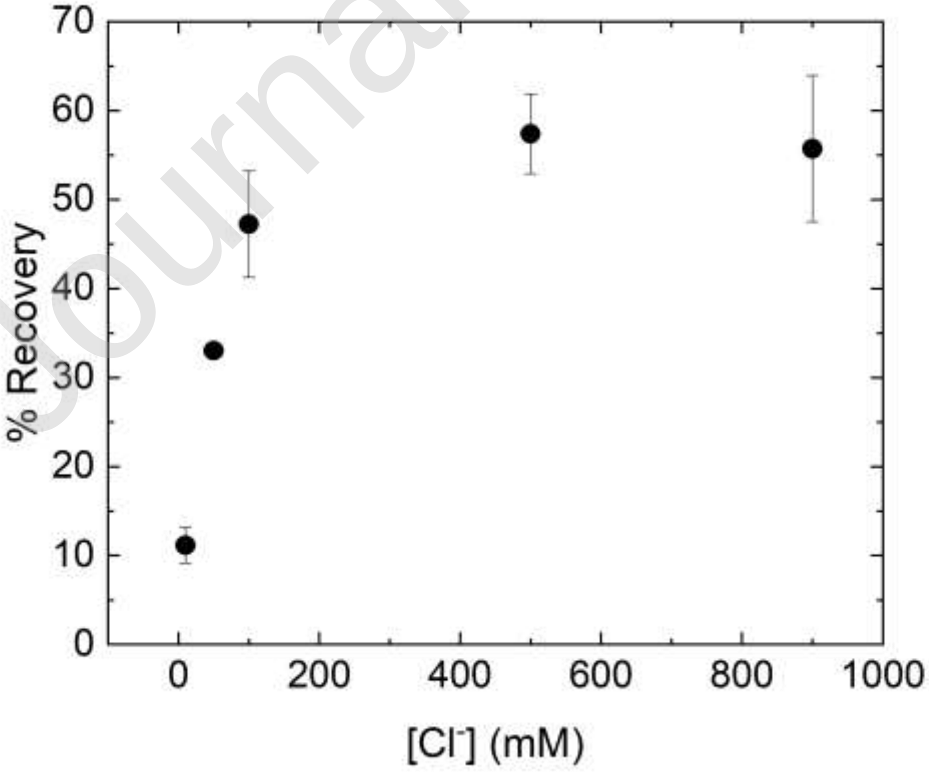


Figure 3: Influence of initial copper concentration: mass of copper recovered per gram of aluminum exposed to treatment versus initial concentration of copper in aqueous solution. For 2 ml of solution 0.5 M sodium chloride and initial copper sulfate concentration 0.1 M, 0.2 M, 0.5 M and 0.75 M were employed 0.05 g of aluminum mesh, and the final concentration was determined after 6 minutes of treatment at 30 ºC and 65 rpm. Trend line is plotted in red.



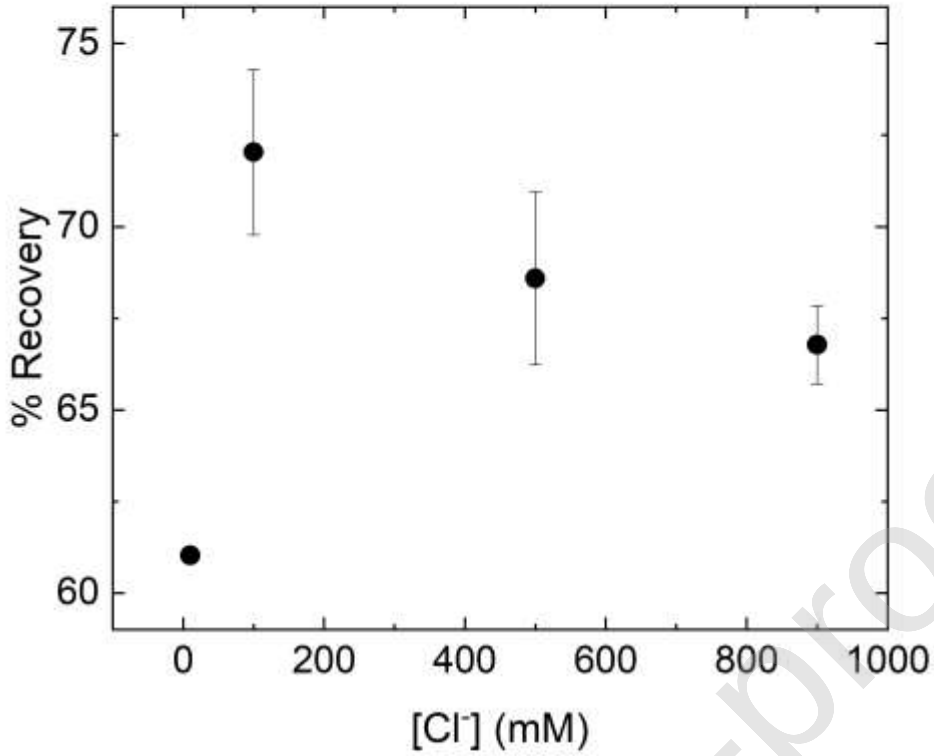


Figure 4: Copper recovery percentage is plotted versus the concentration of Cl$^-$. For 2 ml of solution of initial copper concentration 0.1 M were employed 0.05 g of mesh of aluminum, and the final concentration was determined after 6 minutes of treatment at 30 ºC and 65 rpm. Inset: Copper recovery percentage is plotted versus the concentration of Cl$^-$. For 2 ml of solution of initial copper concentration 0.1M were employed 0.1 g of soda can, and the final concentration was determined after 6 minutes of treatment at 30 ºC and 65 rpm.

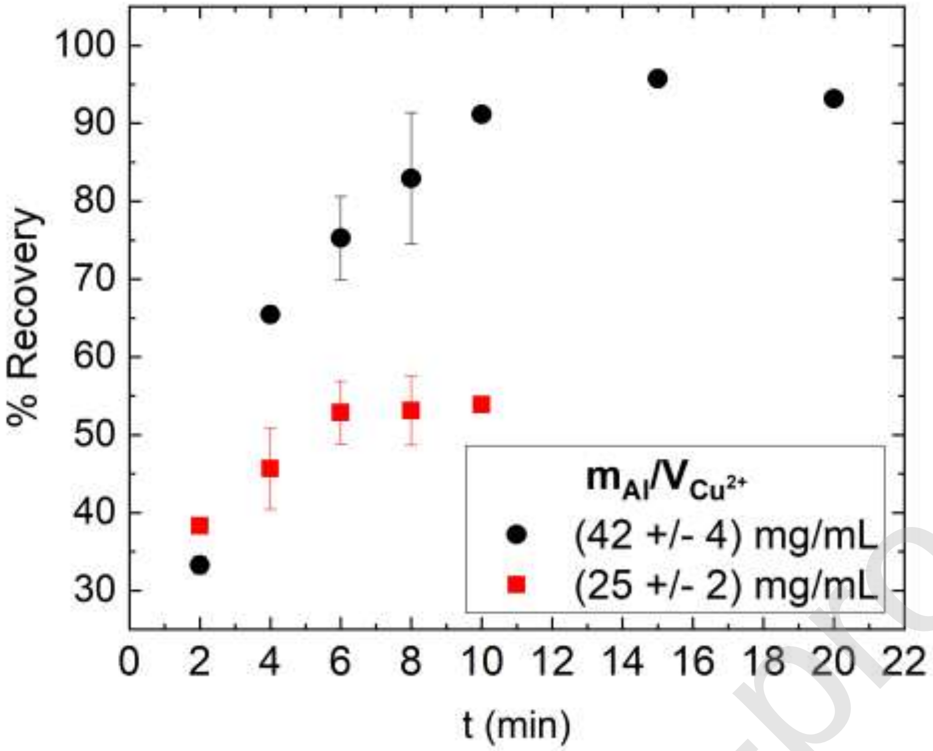


Figure 5: Copper recovery percentage is plotted versus time of treatment. For 2 mL (red squares) and for 1.2 mL (black circles) of solutions of initial copper concentration 0.1 M were employed 0.05 g of aluminum mesh at 30 ºC and 65 rpm.

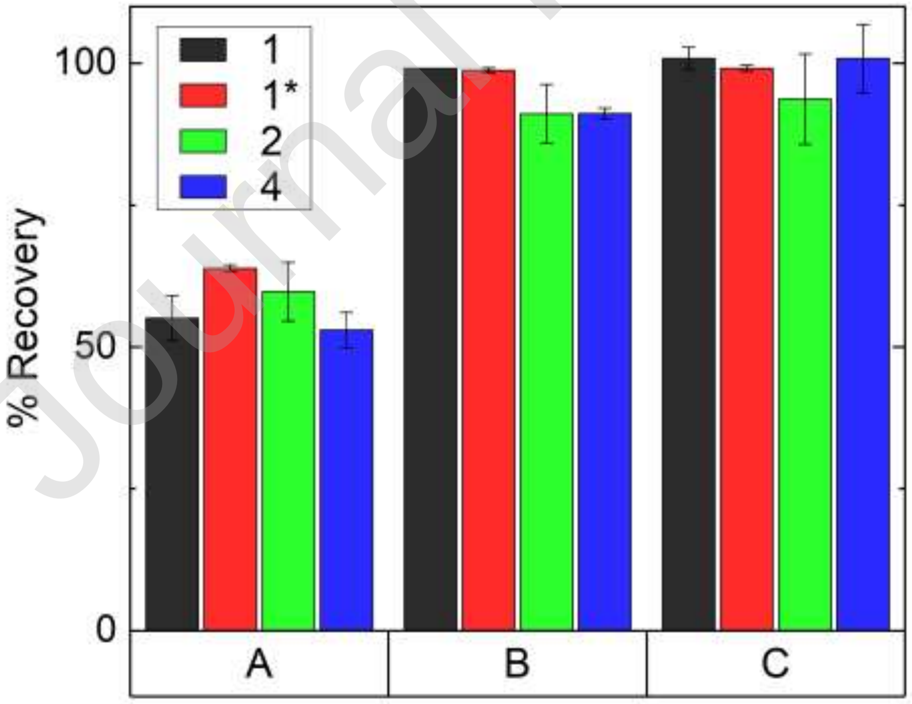


Figure 6: Copper recovery percentage for Solutions 1, 1*, 2 and 4, from Table I and different aluminum source A, B and C. For 1.2 ml of solution of initial copper concentration 0.1 M were employed 0.05 g

of sample of aluminum, and the final concentration was determined after 10 minutes of treatment at 30 ºC and 65 rpm. Black bars correspond to electroplating solutions with additive, red bars correspond to electroplating solutions without additive, green bars correspond to etching solutions and blue bars correspond to laboratory solutions.

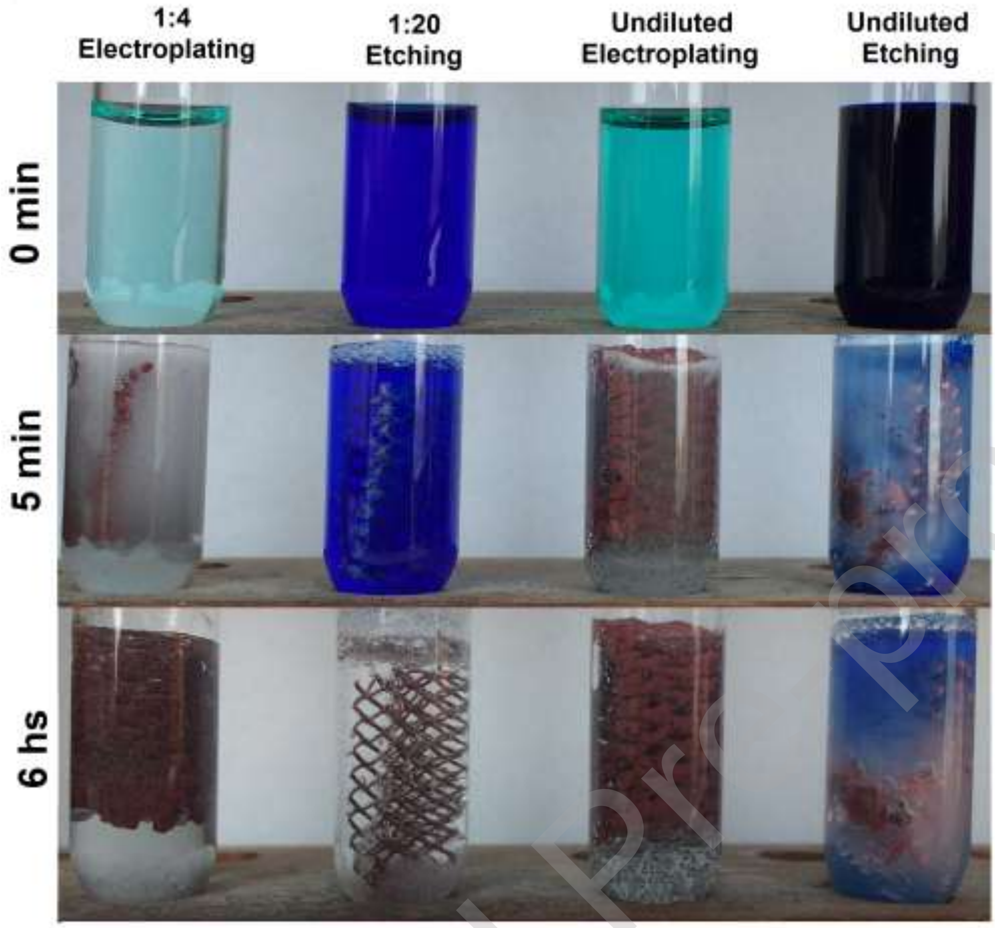


Figure 7: The temporal evolution of the experiments at 0, 5 minutes and 6 hours, from top to bottom, for 1:4 electroplating solution (Solution 1 from Table 1), 1:20 etching solution, undiluted electroplating solution and undiluted etching solution adding 0.5 M NaCl to all of them, from left to right.

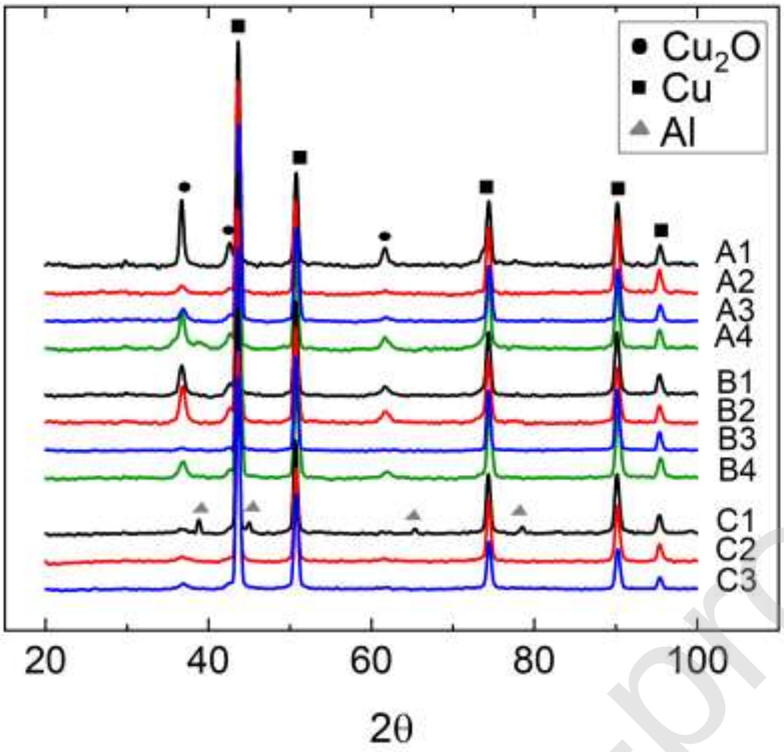


Figure 8: XRD diffractograms of copper recovered for the different copper solutions (1, 2, 3 and 4) and aluminum source (A, B and C) listed in Table I.

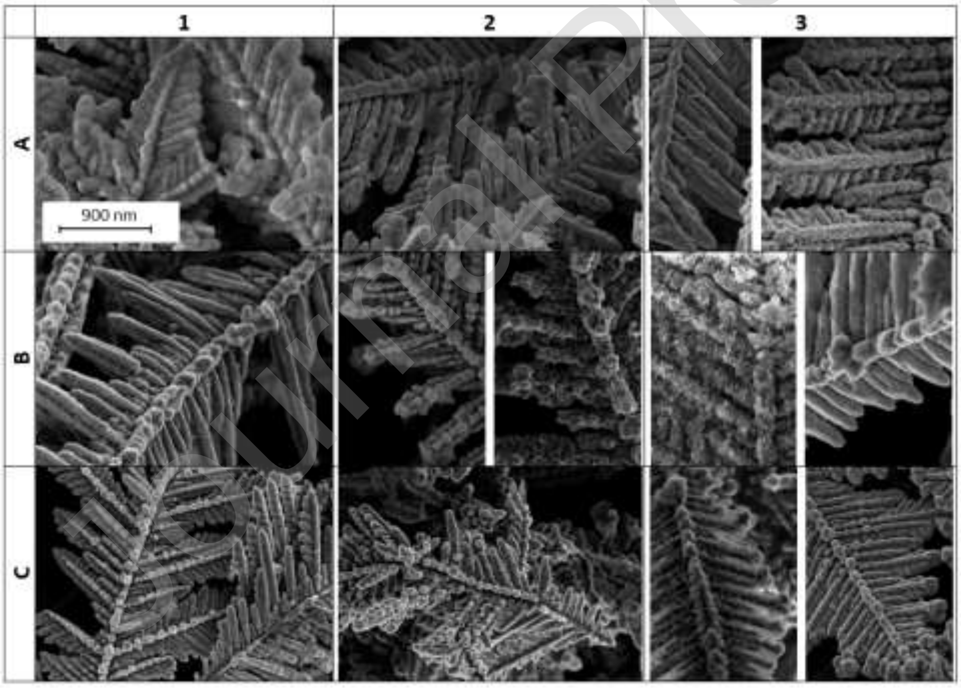


Figure 9. SEM images of copper recovered for the different copper solutions (1, 2, and 3) and aluminum source (A, B and C) listed in Table I.

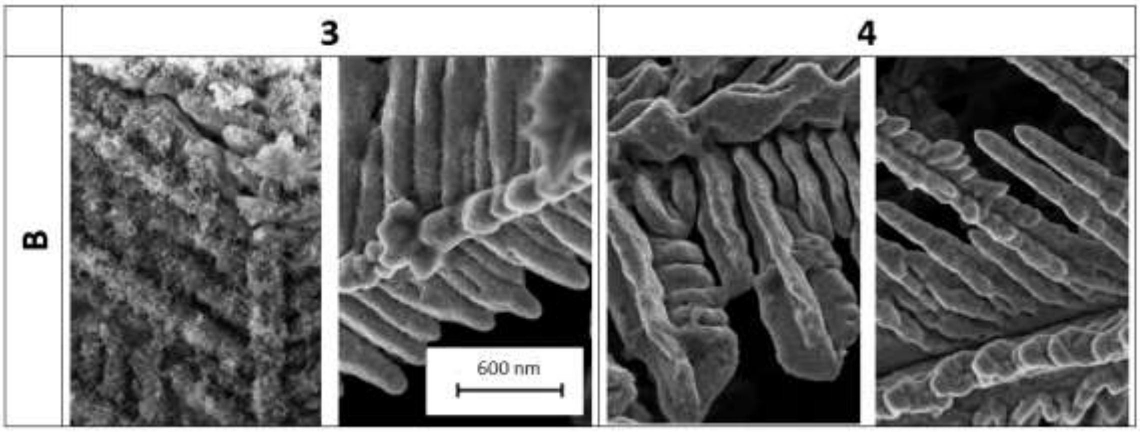


Figure 10: SEM images of copper recovered from solutions with 0.1 M copper sulfate and sodium chloride 0.1 M (3) and 0.5 M (4), samples B-3 and B-4 respectively, using mesh of aluminum as cementation agent.

Table I: Experimental solutions used to prepare the samples with the different sources of aluminum.

			Aluminum shape		
			Soda Can	Mesh	Turning Chip
Copper solutions	Description	Name	A	B	C
	1:4 electroplating industrial solutions with Cuprostar® additive + 0.5 M NaCl, pH<1	1	A-1	B-1	C-1
	1:4 electroplating industrial solutions without Cuprostar® additive + 0.5 M NaCl, pH<1	1*	A-1´	B-1´	C-1´
	1:20 etching industrial solutions (ammonium sulfate as etching agent) + 0.44M HCl, pH 1	2	A-2	B-2	C-2
	0.1 M $CuSO_4$ + 0.1 M NaCl, pH 3.17	3	A-3	B-3	C-3
	0.1 M $CuSO_4$ + 0.5 M NaCl, pH 3.34	4	A-4	B-4	C-4