1   **Waste-to-energy bottom ash management:**

2   **Copper recovery by electrowinning**

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18 **ABSTRACT**

19 Municipal solid waste (MSW) incineration process generates 0.2 tons of bottom ash (BA)

20 per ton of waste. BA contains significant quantities of potentially harmful and/or value-

21 added metallic species such as Cu, which can be leached and discharged into the

22 environment unless they are conveniently managed. The reduction of metal content in

23 BA would allow its use in different applications (e.g., concrete pavement bases and

24 subbases), thus promoting circular economy schemes. In this work, the feasibility of Cu

25 recovery from BA has been studied for the first time by integrating solid-liquid (SL)

26 extraction and electrowinning (EW). First, the leaching of metallic elements from BA

27 was carried out using H_2SO_4. The resulting leachate, which contained Cu as well as Al,

28 P, Zn, Ca, Fe, Mg, Na, K and Mn as major elements, served as feed stream in the

29 electrochemical process. The EW parallel-plate cell operated in batch mode was

30 composed of one $Ti|IrO_2$ anode placed between two AISI 304 stainless-steel cathodes

31 (interelectrode distance of 2 cm). The operation parameters under investigation to achieve

32 the maximum electrochemical Cu recovery were: initial Cu^{2+} concentration (0.1-1 g/L),

33 pH (0.5-1.5), current density (100-300 A/m^2) and electrodeposition time (2-7 h). It was

34 possible to extract more than 98% of Cu from the leached stream by EW and to recover

35 almost 90% in the cathodes from a 1 g/L Cu solution at pH 1.5, operating at 200 A/m^2 for

36 5 h. Therefore, the integration of SL and EW processes offers an attractive alternative for

37 the valorization of BA from MSW. The recovered high-purity Cu could be used in several

38 high-tech sectors, such as batteries, fuel cells, electric traction motors, wind energy,

39 photovoltaics technology, robotics, drones, 3D printing and digital technologies, in good

40 agreement with current circular economy and waste-to-energy approaches.

41 *Keywords:* Circular economy; Electrodeposition; Metal recovery; Municipal solid waste;

42 Parallel-plate electrochemical reactor; Solid-liquid extraction

1. INTRODUCTION

The increase in the amount of municipal solid waste (MSW) generated by the rise in consumption goods has boosted global demand for technologies to address the recovery of energy and materials. In 2012, the production of this type of waste was approximately 1.3 billion tons, and it is expected to increase to 2.2 billion tons by 2025 [1,2]. The waste incineration, which is carried out in so-called "Waste-to-Energy (WtE)" plants, allows reducing its mass and volume by 70% and 90%, respectively [1,3]. Moreover, WtE plants are able to recover the energy generated in this process to produce electricity and/or heat. Although the incineration process depends on several factors, such as the characteristics of the MSW itself, the type of incinerator or the process efficiency, it can be established that approximately 80-85% of the incineration ash is bottom ash, which is equivalent to 16-35% of the initial mass of waste [1,3]. The other fraction of ash resulting from the incineration process is called fly ash. Approximately 230-280 kg of ash are generated per ton of incinerated MSW, being bottom ash the most abundant [4]. Since it contains the non-combustible fraction of waste, it mainly consists mainly of glass, ceramics, ferrous and non-ferrous metals (such as Cu, Zn, Al, Cr or Pb) and minerals [4–7], thus being crucial to implement strategies for its correct management.

The new high value-added applications in the field of MSW incineration require the recovery of hazardous contaminants from the mineral and metal fractions. This would fulfil the new circular economy approaches, in contrast to the typical current low value-added applications (e.g., use in building sites and pavements or, in the worst case, landfilling) [8–10]. Therefore, aiming to integrate the WtE technology as part of a circular economy scheme, it is mandatory to address the reuse of solid waste by extracting the metals for further recycling [9]. By doing this, the amount of wasted materials and energy would be drastically minimized [5].

68   Nonetheless, the amount of metal components that can be separated from the bottom ash

69   varies depending on the composition of the original waste. Ferrous materials account for

70   7-15 wt.% of bottom ash, whereas non-ferrous materials are present only in the range of

71   1-2 wt.% [5,11]. Additionally, it is estimated that the total amount of valuable metals,

72   such as zinc, copper and gold, in the bottom ashes of the European incinerators could

73   account for more than 600 million euro per year. For this reason, great concern about the

74   potential loss of value-added resources in incinerator ash has been growing in recent

75   years, which has promoted the treatment of such waste for metal recovery [12–14].

76   The first step to obtain a metal enriched solution from MSW bottom ash consists in

77   performing an acid leaching process [3,15,16]. Afterwards, different processes can be

78   used for metal recovery [6,17–19]. Among them, electrowinning (EW) is an electrolytic

79   technology that uses electricity to recover dissolved metals as a metal powder dispersed

80   in the solution or, ideally, a metal deposit adhered to the cathode surface [20,21]. To the

81   best of our knowledge, only one article has reported the recovery of copper from bottom

82   ash, although EW was not used to obtain the metal. In that work, Breitenstein et al. [12]

83   used froth flotation for copper recovery from bottom ash, achieving recoveries of around

84   50%. Other authors tried to recover copper from fly ashes by using similar techniques to

85   the ones proposed in the present work. For instance, Yang et al. [22] evaluated the

86   feasibility of lead and copper co-deposition, combining acid leaching of fly ash obtained

87   from MSW incineration with electrochemical treatment. The acid leaching of fly ash was

88   made at a liquid-solid ratio of 20:1 using a 0.5 M HNO_3 solution, yielding a liquid mixture

89   that revealed the extraction of 87.6% Cl, 59.4% Pb and 77.0% Cu. Thereafter, it was

90   possible to recover 25.7% Pb and 59.8% Cu by EW operating at 10 A. Finally, it is also

91   worth mentioning that other authors used EW for copper recovery from other kinds of

92   solutions, such as acid mine drainage or electronic waste [23–25].

93   Considering the aforementioned studies, in this work, the integration of two processes is

94   proposed for proper management of WtE bottom ash and the promotion of a circular

95   economy scheme: solid-liquid (SL) extraction followed by EW for the recovery of

96   copper. The performance of the EW process, based on the maximum Cu extraction and

97   recovery, was evaluated under different operation conditions to investigate the effect of

98   the initial Cu^{2+} concentration, the solution pH, current density and electrodeposition time.

99   **2. MATERIALS AND METHODS**

100   **2.1 Proposed process overview for copper recovery**

101   The treatment train consists in the integration of the SL extraction technique and the EW

102   process. For that, H_2SO_4 solution was used for leaching the metals contained in the bottom

103   ash (BA) produced from MSW incineration, thereby obtaining a liquid solution after

104   filtration. Then, the EW process was applied for metal electrodeposition, aiming to

105   maximize the copper recovery (see Figure 1).
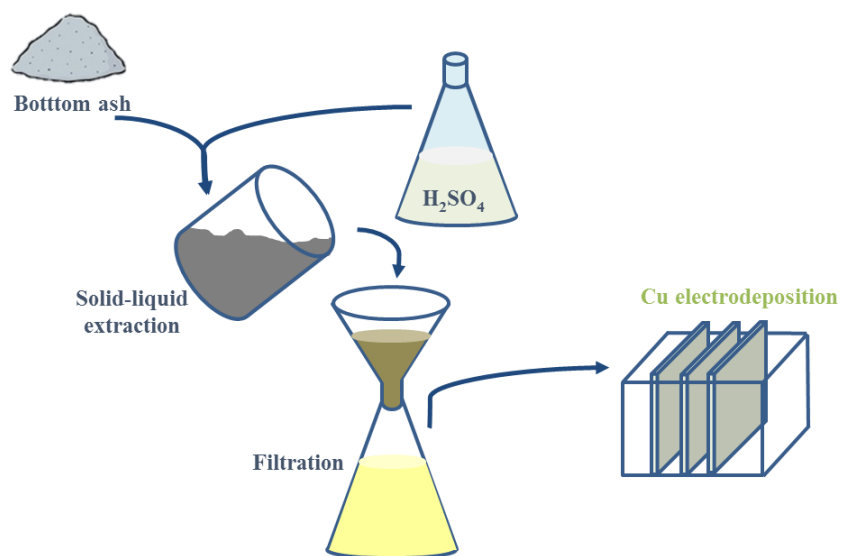
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107   *Figure 1. Scheme of the proposed integrated process for copper recovery: solid-liquid extraction followed*

108   *by electrowinning.*

109 **2.2 Reagents**

110 Concentrated sulphuric acid solution (95-97%, H_2SO_4) was used as the solvent for the

111 leaching process, whereas nitric acid (65%, HNO_3) was used to redissolve the metal

112 deposited on the cathodes after the EW treatment. Both acids were supplied by J.T. Baker.

113 Sodium hydroxide pellets (98%) were used to prepare an alkaline solution for pH

114 adjustment, and anhydrous copper sulphate (99-101%) was used for copper dosing into

115 the initial leachate in the tests planned to study the influence of the initial copper

116 concentration. Both chemicals were provided by AppliChem Panreac. In all cases

117 mentioned here, reagents were of analytical grade.

118 **2.3. Bottom ash from municipal solid wastes incineration**

119 The bottom ashes used in this work were provided by an energy recovery industry located

120 in Sant Adrià del Besòs (Barcelona, Spain). This is an integrated waste management plant

121 that actually includes two plants: The WtE section, managed by TERSA, and the

122 mechanical-biological treatment section, managed by Ecoparc del Mediterrani. The WtE

123 plant, operated by TERSA, manages and selects the MSW generated in the Barcelona

124 Metropolitan Area (AMB) [26].

125 Bottom ashes collected from the WtE plant were first homogenized, owing to the variety

126 of particle sizes and the presence of larger elements, such as glass or ceramic slag. The

127 larger particles, e.g., ferrous particles or glass, were removed manually, whereas moisture

128 from the samples was eliminated by drying the bottom ashes on the stove at 60 ºC for 24

129 h. Finally, the samples were grinded and sieved to obtain a particle size between 0.100

130 and 0.355 mm.

2.4. Solid-liquid extraction pre-treatment

To carry out the leaching process, a 1 M H_2SO_4 solution was mixed with the homogenized bottom ash, keeping a solid-liquid ratio of 0.05 (w/v), i.e. 50 g of bottom ash were mixed with 1 L of acid solution. The principal underlying mechanism in this process is the dissolution of main minerals in acidic medium. The SL extraction was conducted under magnetic stirring at 900 rpm and room temperature for 24 h, whereupon the resulting leachate was filtered by gravity with filter paper (30-50 μm). This last step was performed twice due to the high turbidity of the resulting dispersion.

2.5. Electrowinning for copper recovery

2.5.1 EW set-up

EW experimental tests were carried out in a polycarbonate electrodeposition tank equipped with a dimensionally stable anode (DSA) with dimensions of 12 cm × 12 cm × 3 cm, which consisted of a commercial Ti mesh coated with iridium dioxide (Ti|IrO$_2$), and two AISI 304 stainless-steel plates with the same dimensions as cathodes. The anode was placed between both cathodes, fixing an interelectrode distance of 2 cm by means of plastic slots that kept the three electrodes as parallel plates. For each cathode, only the side facing the anode was kept in contact with the solution, whereas the rear side was isolated with plastic tape. The immersed surface area of each cathode was 28 cm^2, giving rise to a total active cathode surface of 56 cm^2.

A 40 V N5746A power supply (Keysight Technologies, USA) was used to apply constant current to the electrodes. The positive pole was connected to the anode and the negative pole to the cathodes, in both cases using a busbar to make the connexion (see Figure 2). It must be noted that the experiments were carried out using 1 L of leachate, under constant stirring with a magnetic follower at 1200 rpm and at room temperature.
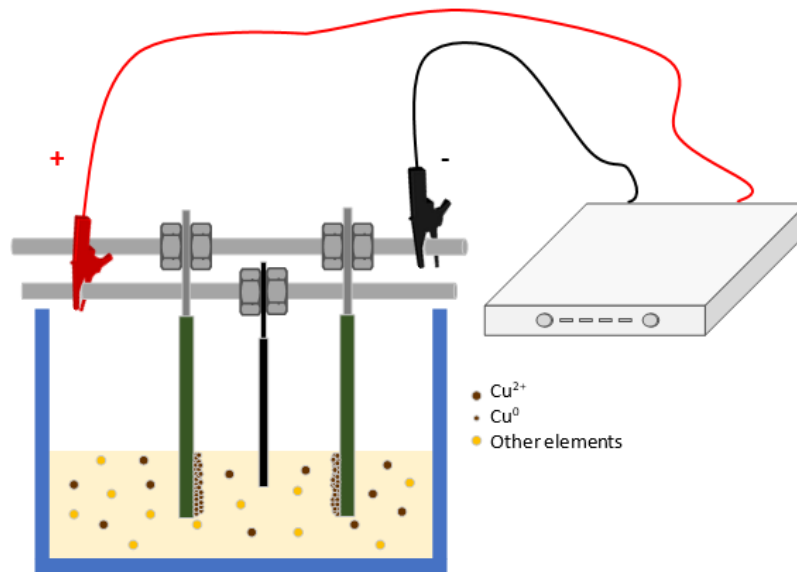
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156   *Figure 2. Sketch of the EW set-up.*

157   2.5.2 EW methodology

158   Before starting the EW process, the cathodes were submerged for 1 min into a 20%

159   sulphuric acid bath to increase the surface roughness, thus ensuring the adhesion of the

160   copper to be deposited. Subsequently, the cathodes were rinsed with water and dried

161   inside the stove until they were completely dry. In order to calculate the mass deposited

162   on the cathodes, both plates were weighted before each electrodeposition trial.

163   During the electrolytic trials, leachate samples were collected at regular time intervals

164   and analyzed by inductively coupled plasma (ICP) to determine the concentration of

165   copper and other elements present in the solution.

166   After each EW trial, the cathodes were introduced into the stove at 90 °C to remove

167   moisture and then weighted until achieving a constant mass value, which allowed the

168   calculation of the deposited metal mass. Afterwards, the mass deposited on the cathodes

169   was redissolved in 10 mL of HNO_3 (acid:water ratio 1:3 (v/v)), and the obtained solution

170   was also analyzed by ICP.

171   Finally, the cathodes were submerged again into the 20% sulphuric acid bath to perform

172   the next experiment.

8

173   2.5.3 EW experimental design

174 Figure 2 illustrates the deposition of copper during the EW process. The dissolved Cu^{2+} in

175 the leachate is reduced to Cu(s) on the cathode, according to reaction (*1*):

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad (1)$$
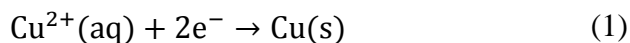
176 Such reduction occurs simultaneously to the water oxidation reaction (2) at the DSA

177 surface:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (2)$$
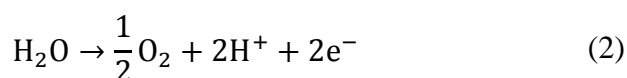
178 Hence, the global reaction (3) occurs inside the EW cell, assuming that copper is the main

179 deposited metal:

$$Cu^{2+}(aq) + H_2O \rightarrow Cu(s) + \frac{1}{2}O_2 + 2H^+ \qquad (3)$$
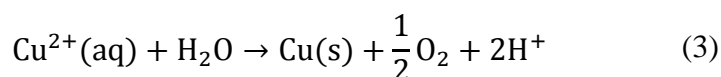
180 Several operation parameters can affect both the percentage of copper recovery and its

181 final quality: initial Cu^{2+} concentration, leachate pH, current density and

182 electrodeposition time. A suitable range has been selected for each one, as summarized

183 in Table 1.

184 *Table 1. Experimental design used.*

Experimental set	Current density (A/m^2)	Electrodeposition time (h)	Initial Cu^{2+} concentration (mg/L)	Leachate pH
A	100	2	100	0.3
	200			
	300			
B	200	7	100	0.3
	300			
C	200	5	100	0.5
			500	
			1000	
D	200	5	100	1.5
			500	
			1000	

185   Each experimental set was designed to study the effect of the abovementioned operation

186   parameters, aiming to obtain the maximum extraction percentage and copper recovery.

187   All experiments were carried out in triplicate to increase the accuracy of the results. Thus,

188   data are reported as: mean value ± standard deviation of triplicate determinations.

189   First of all, in set A, bottom ash leachate was used as the feed solution to test the effect

190   of current density (100, 200 and 300 A/m^2) in experiments that were prolonged for 2 h.

191   Subsequently, experiments of set B had a larger duration (7 h) to determine the optimal

192   residential time in the EW cell. Then, in sets C and D, the Cu^{2+} concentration and pH of

193   the bottom ash leachate were modified to study their effect on the overall performance.

194   For instance, the initial Cu^{2+} concentration was increased by adding anhydrous copper

195   sulphate, testing 100, 500 and 1000 mg Cu/L at two pH values (0.5 and 1.5), which were

196   adjusted by adding 1 M NaOH solution. A final experiment was performed with bottom

197   ash leachate at the optimized operation conditions.

198   **2.6. Data analysis**

199   To determine the optimal operation conditions, four figures of merit were determined

200   after each experiment: Concentration factor (Equation (*4*)), extraction percentage from

201   the leachate (Equation (*5*)), purity of each element deposited at the cathodes (Equation

202   (*6*)) and recovery percentage on the cathodes (Equation (*7*)).

$$CF = \frac{C_i}{C_0} \tag{4}$$

203   where CF is the concentration factor (dimensionless), C_i is the obtained concentration of

204   element "i" in the cathodes after the EW process (in mg/L) and C_0 is the initial

205   concentration of element "i" in the leachate (in mg/L).

$$\%E = \frac{C_0 - C_f}{C_0} \times 100 \tag{5}$$

206 where %E is the extraction percentage from the leachate and C_f is the final concentration

207 of each element in the leachate (in mg/L).

$$P_i = \frac{C_i}{\sum_{i=1}^{N} C_i} \times 100 \qquad (6)$$

208 where P_i is the purity of element "i" (in percentage).

$$\%R = \frac{m_c}{m_0} = \frac{V_m \cdot C_i}{V_{tank} \cdot C_0} \qquad (7)$$

209 where %R is the recovery percentage, m_c is the obtained mass in the cathodes (g), m_0 is

210 the initial mass in the leachate (g), V_m is the sample volume (L) and V_{tank} is the tank

211 volume (L).

2.7. Analytical methodology

213 First, X-ray diffraction (XRD) was employed for solid bottom ash characterization. In

214 this case, a D8 Advance XRD from Bruker was employed. The same instrument was also

215 employed to analyse the obtained solid after the solid-liquid extraction with H_2SO_4

216 solution. The Cu deposits obtained by EW were analysed using a PANalytical X'Pert

217 PRO MPD powder diffractometer.

218 The collected liquid samples (after solid-liquid extraction as well as during the EW

219 treatment) were analyzed by ICP combined with optical emission spectroscopy (ICP-

220 OES) or with mass spectrometry (ICP-MS). ICP-OES (5100 ICP-OES from Agilent

221 Technologies) was used to determine the concentrations of the elements in the mg/L

222 range, whereas ICP-MS (7800 ICP-MS from Agilent Technologies) was used to

223 determine the lowest concentrations in the μg/L range. Before ICP analyses, samples were

224 filtered at 0.22 μm and acidified with 2% HNO_3 solution. Furthermore, the solution pH

225 was determined by means of a GLP 22 pH-meter (Crison, Spain).

3. RESULTS AND DISCUSSION

3.1 Bottom ash characterization

Before carrying out the SL extraction and the EW treatment, an XRD analysis of the bottom ash powder was carried out (Figure 3).
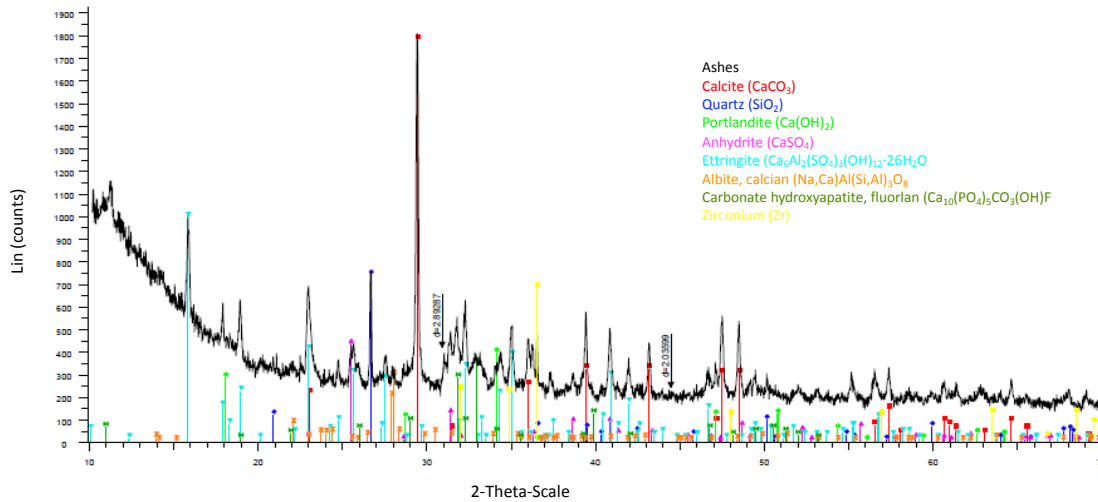
Figure 3. XRD analysis of original bottom ash.

As can be seen, the BA contained several crystalline compounds, mainly minerals such as calcite ($CaCO_3$), quartz (SiO_2), portlandite ($Ca(OH)_2$), anhydrite ($CaSO_4$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), albite-calcian ordered ($(Na,Ca)Al(Si,Al)_3O_8$) and carbonatehydroxyapatite-fluorian ($Ca_{10}(PO_4)_5CO_3(OH)F$), as well as zirconium (Zr).The diffractogram of the residual solid obtained upon acidic SL extraction is shown in Figure 4. As can be observed, its composition is much less complex, only being possible to identify highly insoluble compounds like. In contrast, carbonates, hydroxides and other metals and metallic compounds were completely solubilized at such low pH, which corroborates the suitable strategy to remove the value-added metals from the BA.

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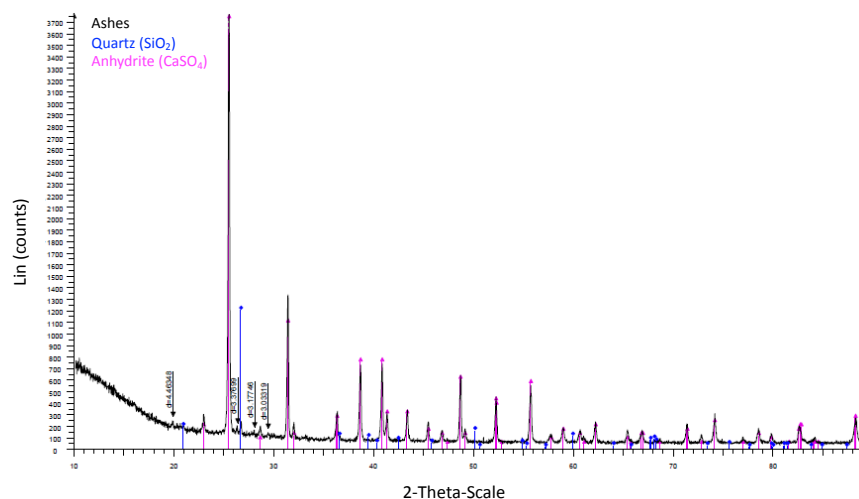
Figure 4. XRD analysis of the solid obtained after the SLextraction with H_2SO_4 solution.

3.2. Solid-liquid extraction of metals from bottom ash

Table 2 summarizes the composition of the solution obtained upon acidic leaching (final pH of 0.3) of the metals contained in the homogenized BA for 24 h.

Table 2. Composition of the leachate obtained after SL extraction.

Element	Concentration (mg/L)	Element	Concentration (mg/L)
Al	1791.46 ± 13.32	Ni	2.68 ± 0.01
P	854.90 ± 5.05	Cd	0.80 ± 0.01
Zn	832.64 ± 6.55	Nd	0.67 ± 0.01
Ca	679.11 ± 2.92	Ce	0.44 ± 0.01
Fe	622.52 ± 7.06	Gd	0.38 ± 0.01
Mg	545.76 ± 3.85	As	0.31 ± 0.02
Na	533.45 ± 2.64	Y	0.28 ± 0.01
K	221.01 ± 1.56	La	0.21 ± 0.01
Cu	98.49 ± 3.06	Pr	0.18 ± 0.01
Mn	19.45 ± 0.18	Ag	0.01 ± 0.01
Pb	4.55 ± 0.05	Hg	0.0042 ± 0.0004
Cr	4.47 ± 0.04	Au	0.0016 ± 0.0004

According to Table 2, major components of the leachate (> 10%) were Al, P, Zn, Ca, Fe, Mg, Na and K, which agrees with the disappearance of minerals containing some of these elements from the diffractogram shown in Fig. 3. The concentrations of heavy metals like
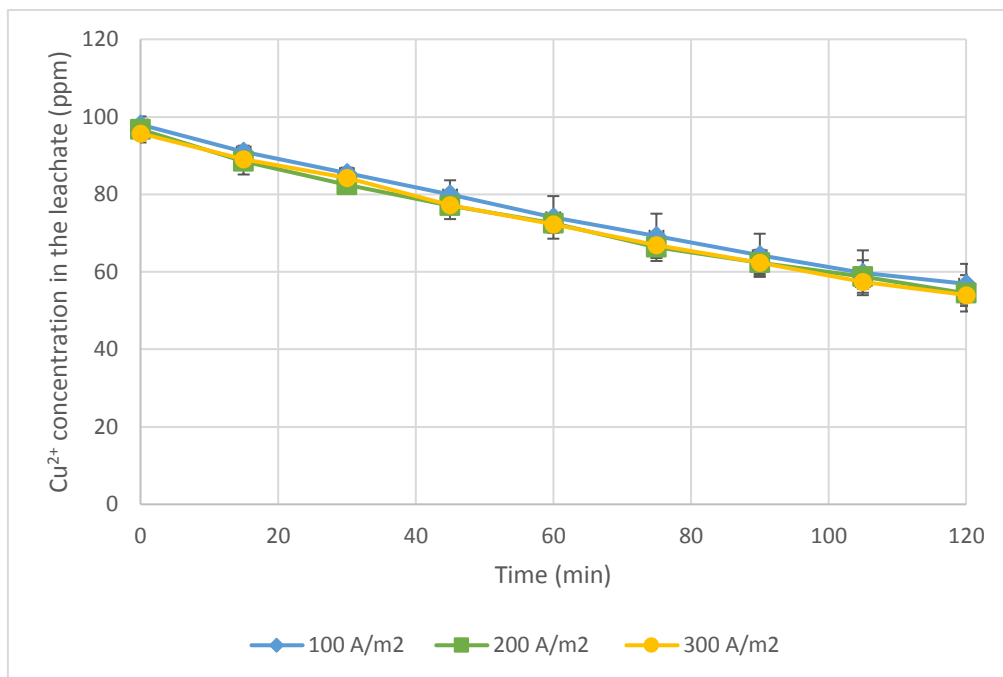
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250 Cd or Hg was low (< 1 mg/L), although Zn, Cu and Mn were abundant in the leachate

251 (around 830, 100 and 20 mg/L, respectively). At this point, it is worth mentioning that

252 Cu has the highest price in the market among them, thus existing a greater interest to try

253 to recover it from the leachate. The presence of other elements with high economic value,

254 such as rare earth elements, gold and silver was scarce, accounting for less than 1% of

255 the total composition.

256 It must be noted that the chemical composition of a leachate depends on the composition

257 of the original BA, which in turn is dependent on the type of incinerated MSW as well as

258 on the incineration conditions. The major components of BA used in this work were

259 calcium, sodium, aluminium, zinc, and iron (sorted from highest to lowest according to

260 mg element per g BA). These data agree with the concentration values of the elements in

261 the leachate (Table 2), verifying the correct extraction of the elements of interest. Indeed,

262 Bojinova et al. [27] carried out the leaching of BA with sulphuric acid, concluding that

263 this acid allowed large leaching of Al, although it was not selective for this element, since

264 Fe, Ca, Mg, Na, Mn, Cu and Zn were also dissolved simultaneously with the Al. In the

265 present work, Al was the element with the highest concentration in the leachate, even

266 though it was not the prevalent element in the original BA.

267 **3.3. Electrowinning treatment for copper recovery**

268   3.3.1. Effect of current density

269 Set A was designed to determine the optimal current density to obtain the maximum Cu

270 recovery. Figure 5 shows the copper concentration evolution during the EW treatment

271 performed at 100, 200 and 300 A/m^2 for 2 h, at pH=0.3

Figure 5. Time course of Cu^{2+} concentration in the leachate at different current densities.

As can be observed, the copper concentration decay profiles were very similar regardless of the applied current density, giving rise to a decrease from 100 to around 55 mg/L. Although the copper recovery could not be complete under the tested conditions, the important finding in this first set of electrolyses is that almost 50% of the metal could be deposited without carrying out a system optimization. On the other hand, the fact that a higher current density was not able to promote a larger copper recovery suggests that, at such low copper concentrations in the leachate (less than 100 mg/L since the beginning), the electrodeposition process is mass-transport controlled. The stirring employed was thus probably insufficient to induce a greater recovery as the current density became higher.

From the previous data, the relevant figures of merit related to copper recovery were calculated in order to determine the optimal current density for carrying out subsequent studies. As can be seen in Figure 6a, similar copper extraction percentages were obtained at the three tested current densities, as readily deduced from the overlapped curves

15

288   presented in Figure 5. More precisely, the %E values were slightly higher at 200 and 300

289   A/m^2 (43.8 ± 2.9% and 43.6 ± 4.0%, respectively), as compared with the result obtained

290   at 100 A/m^2 (41.9 ± 5.9%).

a)   b)

c)   d)
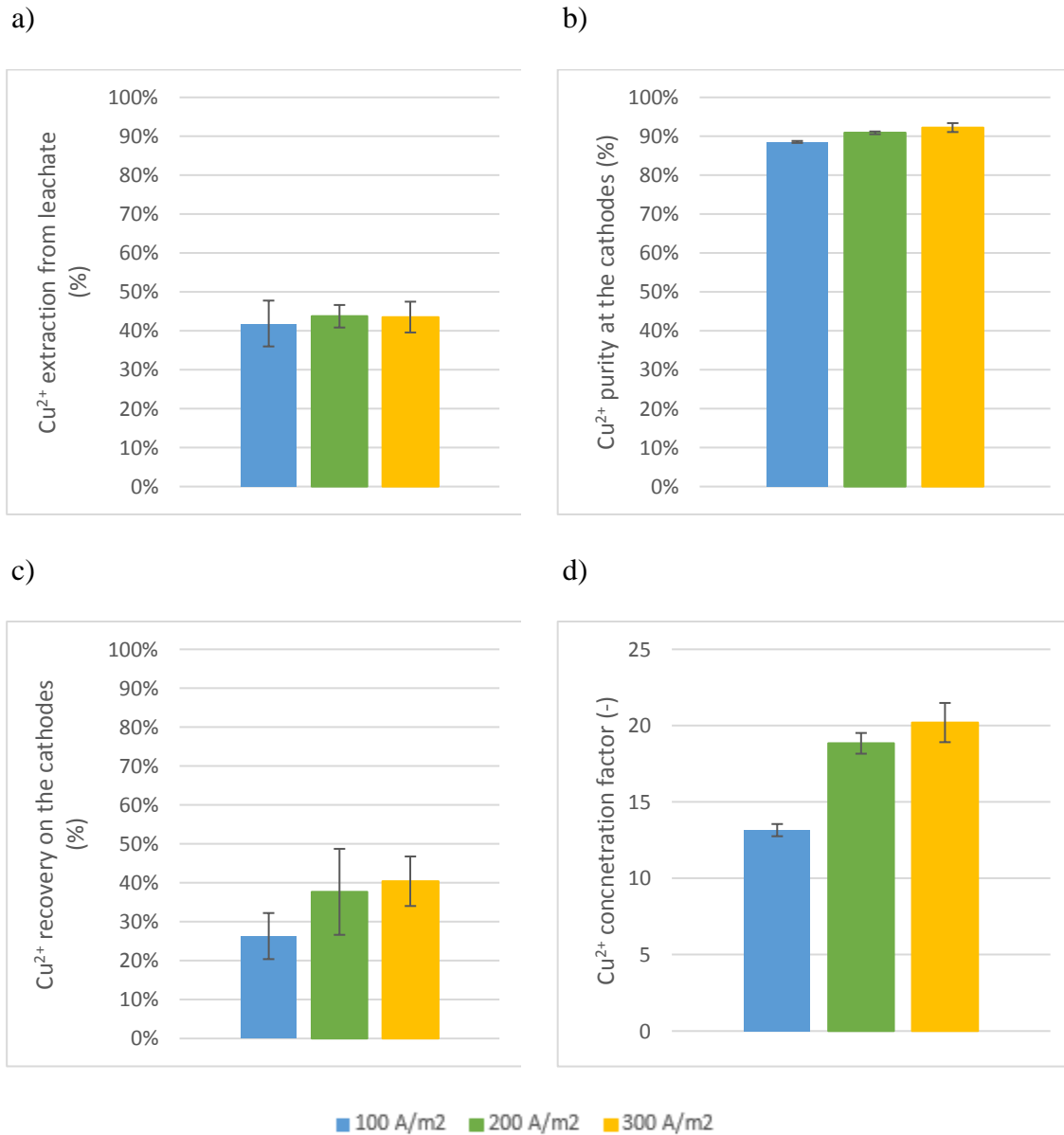
291   *Figure 6. Figures of merit for copper electrodeposition from the leachate: a) Extraction percentage, b)*

292   *purity, c) recovery percentage and d) concentration factor.*

293   Figure 6b shows that the copper purity was always very high, close to 90% or greater. In

294   fact, the purity gradually increased from 88% to 92% as the current density was risen

295   from the lowest to the highest value. This means that the deposition of the most noble

296   (i.e., Cu) amongst the most concentrated metals in the leachate is favoured at a larger

297   cathodic overpotential. Indeed, at 100 A/m^2, less concentrated metals can still be

298   transported to the cathode surface under the applied stirring conditions, whereas at 300

299   A/m^2, copper is more efficiently transported thanks to the greater concentration gradient,

300   ending in a relatively larger deposition.

301   Another interesting feature related to the influence of current density is revealed by the

302   recovery percentage values (Figure 6c), which became significantly greater, from 26.3 $\pm$

303   5.9% to 40.4 $\pm$ 6.4%, when the current density was increased from 100 to 300 A/m^2. This

304   trend is in disagreement with the quite constant %E values (around 43%) discussed in

305   Figure 6a. It can thus be hypothesized that copper reduction to form Cu(s) via reaction

306   (1) is given at the same rate in the range of 100-300 A/m^2, agreeing with a similar decay

307   of Cu^{2+} concentration in the leachate. However, at 100 A/m^2, Cu nuclei cannot grow

308   sufficiently and, as a result, the deposited powder is partially detached from the cathode

309   surface, thereby leading to a large discrepancy between %E and %R. Conversely, a higher

310   current density progressively favours the growth and adherence of the Cu crystals, so that

311   at 300 A/m^2 almost all the reduced copper is found on the cathode surface. In good

312   agreement with the trend shown in Figure 6c, a higher copper concentration factor (from

313   13.2 $\pm$ 0.4 to 20.2 $\pm$ 1.3) was obtained when current density was increased from 100 to

314   300 A/m^2, which corroborates the easier formation of an adherent electrodeposit as the

315   cathode overpotential becomes larger.

316   The results from the experimental set A allowed discarding the lowest current density of

317   100 A/m^2 for subsequent trials, since one of the goals of the study was to obtain stable

318   deposits on the cathode surface, which can only be achieved at higher current densities.

319   3.3.2. Effect of the electrodeposition time

320   The experimental set B was designed to determine the optimal electrodeposition time to

321   obtain the maximum Cu recovery, operating at 200 and 300 A/m^2 and pH=0.3. Figure 7

322   shows the copper concentration decays during the EW treatments at these two current

323   densities for 7 h.
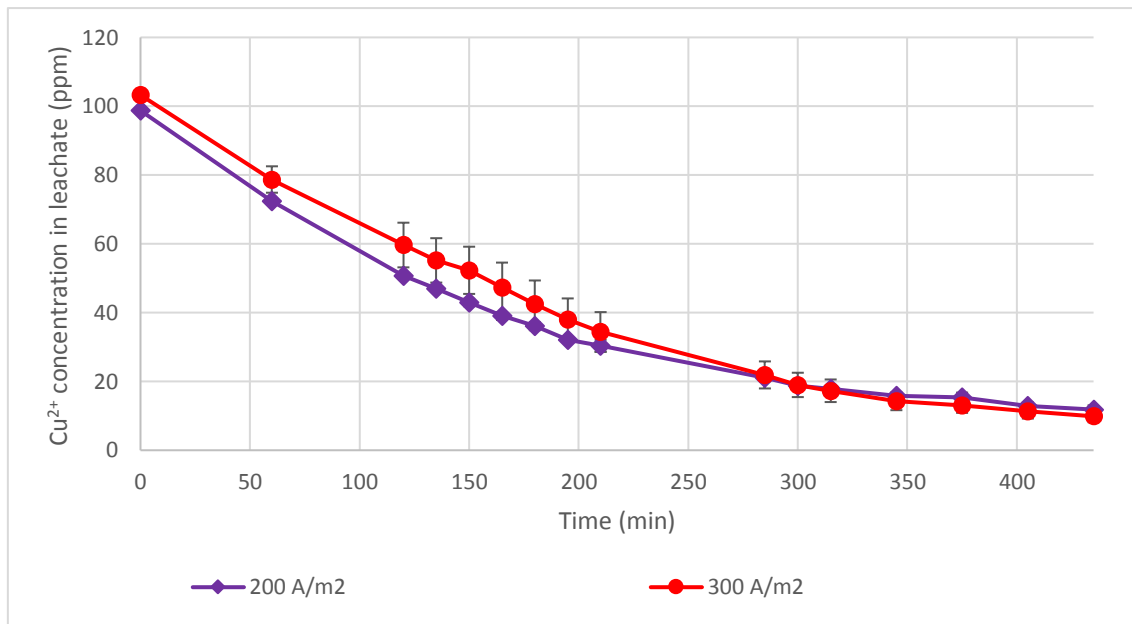
325   *Figure 7. Time course of Cu^{2+} concentration in the leachate at different current densities.*

326   Very similar profiles were obtained in both cases throughout the whole electrolysis,

327   giving rise to a decrease in the metal concentration from around 100 to ca. 10 mg/L. More

328   in detail, it can be seen that, at 300 A/m^2, the copper concentration attained at the end was

329   slightly lower despite starting from a higher initial metal content. In addition, it should be

330   noted that during the first 3 h of the experiments, almost 70% of the total copper was

331   already removed, whereas the metal extraction from the 5th hour (i.e., 300 min of

332   electrolysis) until the end of the experiment only represents a 9% of the copper extraction.

333   This means that the rate of copper deposition was significantly reduced from the 5th hour,

334   reducing its extraction rate from the leachate. Again, this can be attributed to the limited

335   mass transport due to the stirring conditions, but also to the very low copper concentration

18

336   remaining in solution at that time. For this reason, 5 h (~80% Cu extraction) was selected

337   as the optimal electrodeposition time.

338   Also for set B, the relevant figures of merit were calculated to determine the optimal

339   current density to operate for 5 h. Table 3 shows a similar but slightly higher copper

340   extraction at 300 A/m^2 (90.4 vs 88%), which can be explained by the larger cathode

341   overpotential. In both cases, the high %E agrees with the semi-noble character of Cu.

342   However, the maximum purity of around 98% was achieved at 200 A/m^2. This agrees

343   with Schlesinger et al. [28], who pointed out that the application of an excessively high

344   current density could favour the formation of dirty deposits, thus affecting to the purity

345   of copper if not handled properly. The effect of current density differs from that described

346   in Figure 6b, which is due to the high Cu extraction at 5 h, which eases the deposition of

347   other less noble metals whose transport to the cathode was very limited while the Cu^{2+}

348   concentration was still high during the first hours.

349

350   *Table 3. Calculated figures of merit for experimental set B, at 5 h of operation.*

	Current density (A/m^2)	
	200	**300**
Cu extraction from leachate (%)	88.0 ± 1.2	90.4 ± 5.6
Cu purity at the cathodes (%)	97.8 ± 0.9	92.5 ± 0.2
Cu recovery on the cathodes (%)	69.1 ± 4.0	63.0 ± 3.7
Cu concentration factor (-)	34.6 ± 1.6	31.5 ± 11.8

351   Owing to such high %E at 5 h, the parasitic cathodic H$_2$ evolution became intense at 200

352   and 300 A/m^2 in such acidic medium once the Cu^{2+} content was low enough. For this

353   reason, the recovery percentage was lower than 70% (Table 3), considerably far from the

354   ~90% of extracted copper. The comparison between %E and %R, at high current density,

355   is thus quite different from that shown in Figure 6, which again corroborates that a highly

356 efficient copper recovery (out of the scope of the present work) would require the

357 maintenance of a high copper concentration in solution (i.e., electrochemical reactor

358 operated in continuous mode) and suitable mass transport conditions (i.e., use of flow

359 cells and porous electrodes, or a rotating cylinder electrode reactor [29]).

360 In good agreement with the recovery percentage values, the concentration factor was

361 higher at 200 A/m^2. Therefore, aiming to operate for long time looking for a high %R,

362 which in turn magnifies the competition between H_2 evolution and Cu deposition, this

363 current density was selected for subsequent trials.

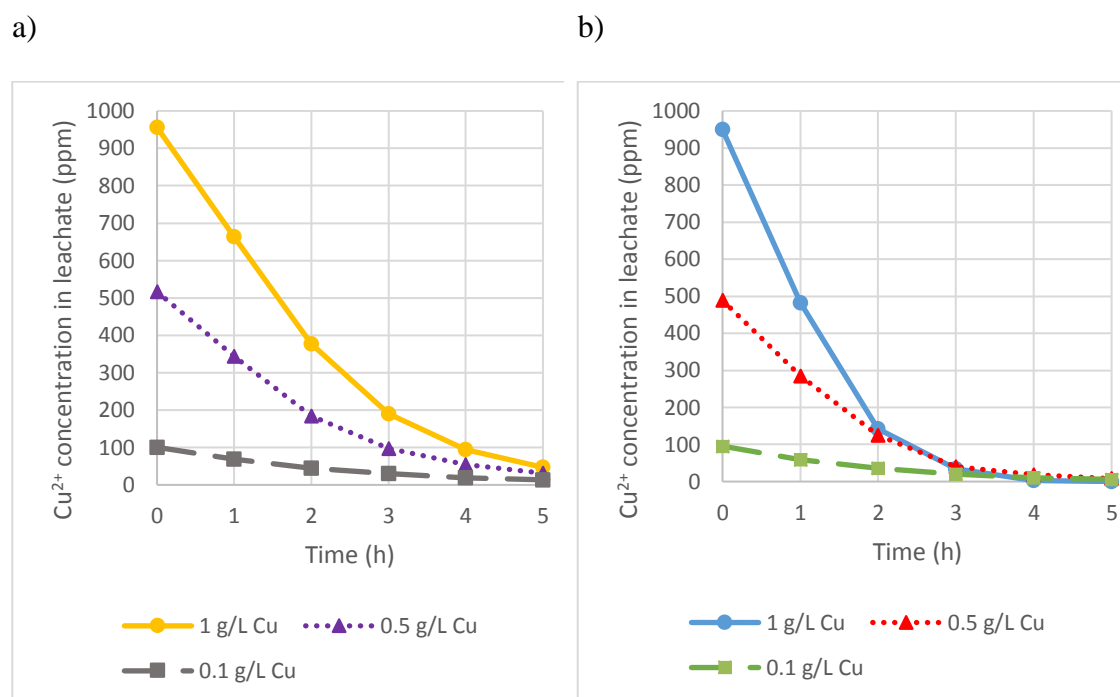364   3.3.3. Effect of initial copper concentration and solution pH

365 The experimental sets C and D were designed to determine the optimal initial copper

366 concentration and pH of the leachate to obtain the maximum Cu recovery percentage

367 when working at 200 A/m^2 for 5 h. The copper concentration profiles during the EW

368 treatment of leachates containing 100, 500 and 1000 mg Cu^{2+}/L at pH 0.5 and 1.5 are

369 plotted in Figure 88, being possible to observe two relevant findings.

370 First, the copper electrodeposition was significantly improved at higher pH in the studied

371 very acidic range. In fact, at each initial Cu^{2+} concentration, the differences between

372 concentrations attained at each pH were greater during the first 2 h of electrolysis. This

373 is particularly evident at a progressively greater initial Cu^{2+} concentration. For example,

374 at an initial content of 1000 mg Cu^{2+}/L, the metal concentration was reduced to 380 ppm

375 at pH 0.5 and to 125 ppm at pH 1.5. This means that an excessively acid medium causes

376 a less efficient recovery, which can be attributed to the parasitic H_2 evolution.

377

378

379

a)   b)

380   *Figure 8. Time course of Cu^{2+} concentration in the leachate at different initial copper concentrations and*

381   *at a) pH 0.5 and b) pH 1.5.*

382   *In these cases, copper extraction percentage from leachate, copper recovery percentage*

383   *and also the concentration factor were calculated to determine the optimal conditions for*

384   *Cu recovery (Table 4).Table 4. Calculated figures of merit for experimental sets C and D, at 5 h of*

385   *operation.*

386

		Initial Cu^{2+} concentration (mg/L)		
		100	**500**	**1000**
Cu extraction (%)		86.4%	93.9%	95.1%
Cu recovery (%)	**pH = 0.5**	87.7%	90.2%	84.2%
Cu concentration factor (-)		43.8 ± 5.7	45.1 ± 1.4	42.5 ± 6.1
Cu extraction (%)		93.8%	98.4%	100.0%
Cu recovery (%)	**pH = 1.5**	92.7%	88.6%	98.1%
Cu concentration factor (-)		46.4 ± 4.7	44.3 ± 11.2	49.0 ± 2.8

391   As summarized in Table 4, the extraction percentage increased substantially when

392   increasing the initial Cu^{2+} concentration from 100 to 1000 mg/L. In fact, it is particularly

393   noticeable the 100% of extraction reached at pH 1.5 when operating at the highest Cu^{2+}

394   content. Certainly, these conditions limit the H$_2$ evolution and enhance the mass transport

395   of Cu^{2+} thanks to the much larger concentration gradient. Therefore, the presence of a

396   larger amount of metal in the leachate is desirable, which opens the door to improve the

397   Cu recovery by finding better conditions in the BA production and the subsequent metal

398   leaching step. These results were in accordance with those of Peng et al. [30], who

399   concluded that the lack of Cu ions near the cathode stimulates the generation of hydrogen

400   gas bubbles that reduces the electrodeposition efficiency.

401   Regarding the Cu recovery percentage, at pH 0.5, similar and insufficient values were

402   obtained at the three Cu^{2+} concentrations. However, Table 4 makes in evidence the much

403   better results obtained at pH 1.5, being feasible to recover more than 98% of Cu at the

404   cathode starting with 1000 mg/L. From this, a leachate with ~1000 mg Cu^{2+}/L at pH 1.5

405   was selected as optimal for EW.

406   3.3.4. Copper recovery under optimal operation conditions

407   Based on the results commented so far, the best conditions for copper removal from

408   bottom ashes by EW are: leachate containing 1 g/L Cu^{2+} at pH 1.5, operating at a current

409   density of 200 A/m^2 for 5 h. Therefore, a final experiment was designed to validate the

410   EW technology under such optimal conditions by real bottom ashes. First, the evolution

411   of the concentration of Cu^{2+} and the other elements in the leachate over time was

412   determined, as depicted in Figure 9.

413   As can be seen, copper was the main element removed from the leachate during the EW

414   treatment, whereas the concentration of other elements remained quite constant during

415   the whole trial. In fact, the performance regarding the copper extraction was very high,

416   reducing the Cu^{2+} concentration (~ 800 mg/L) down to around 13 mg/L (i.e., ca. 98.3%

417   of extraction percentage). This demonstrates the high effectiveness as well as the high

418   selectivity of the EW process. Figure S1 shows a FESEM image of the deposit, which

419   was obtained as a rough film (Figure S2) of high purity (Figure S3).

420 To avoid misunderstanding, please note that the high sodium concentration (over 12000

421 mg/L) and the substantial decrease of the initial Cu^{2+} concentration (the expected 1000

422 mg/L decayed to 800 mg/L) were due to NaOH solution addition required for the pH

423 adjustment to 1.5.

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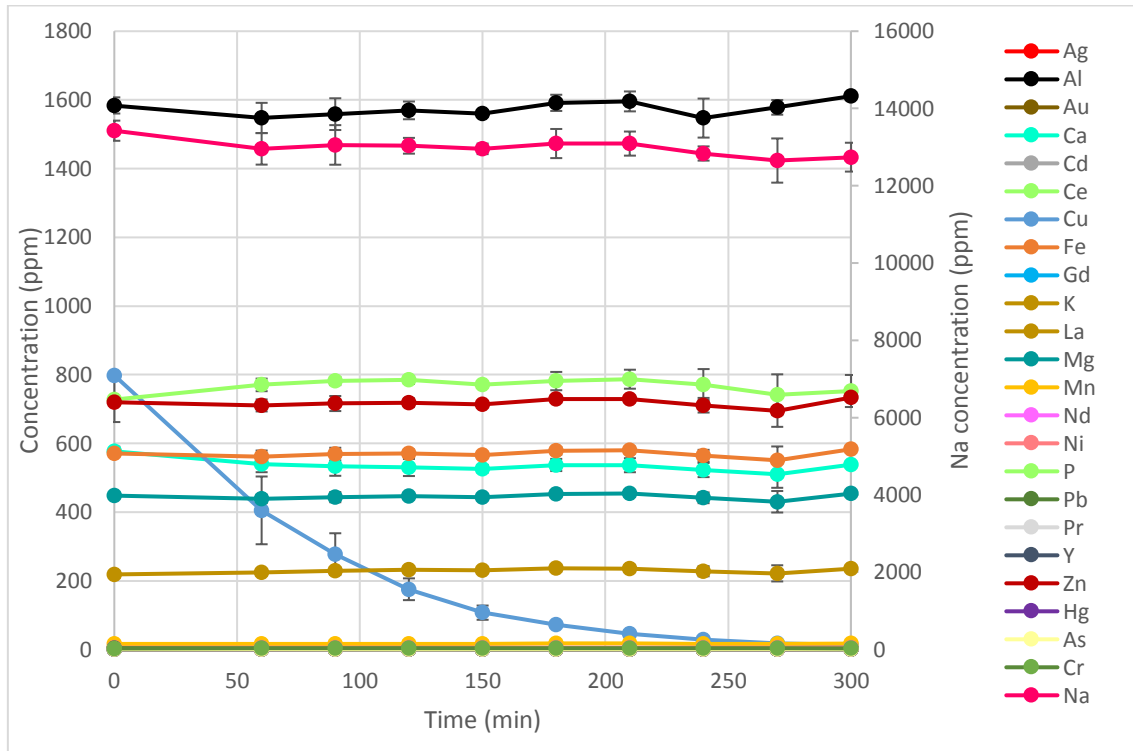
Figure 9. Time course of the concentration of all the elements in the leachate pH 1.5, operating at 200 A/m².

427 Despite the Cu extraction selectivity in the EW treatment, note that Cd and Pb were also

428 deposited on the cathodes. This cannot be observed in Figure 9 due to their low initial

429 concentrations, but it is summarized in Table 5, along with the calculated figures of merit

430 for the three elements.

431 *Table 5. Cu, Cd and Pb extraction percentage, concentration factor and recovery percentage.*

Element	Extraction from the leachate (%)	Concentration factor (-)	Recovery on the cathodes (%)
Cu	98.3 ± 0.1	44.6 ± 4.4	89.2 ± 0.2
Cd	95.2 ± 0.3	35.2 ± 2.2	70.5 ± 0.2
Pb	79.3 ± 2.3	34.6 ± 2.9	69.2 ± 1.5

432 According to Table 5, Cu was the element with highest %E and %R from the leachate,

433 although Cd and Pb were also extracted from the solution and partially deposited onto the

434 cathode. In the case of Cd, some authors have demonstrated the feasibility of Cd electro-

435 recovery from Ni-Cd spent batteries, with high current efficiency in acidic medium using

436 steel cathode thanks to the mediation of adsorbed hydrogen [31]. The high %E for Pb,

437 accompanied by a modest cathodic recovery percentage, can be attributed to the Pb^{2+}

438 leaching from the BA followed by the precipitation of very insoluble $PbSO_4$ (Kps =

439 1.6×10^{-8} at 25 ºC). Nevertheless, the impact on electrodeposition of these two elements

440 was not critical for copper recovery, since their initial concentrations were less than 1 mg

441 Cd/L and less than 4 mg Pb/L. Furthermore, the composition of the deposit found on the

442 cathodes at the end of the trial was also analysed (Figure 10). The deposited mass mainly

443 corresponded to copper (around 92%), although the large amount of sodium added to the

444 leachate for pH adjustment to 1.5 reduced the Cu purity, since around 5% of sodium was

445 also deposited. The third most abundant element (2%) was calcium, in agreement with its

446 relatively high initial content (ca. 700 mg/L).
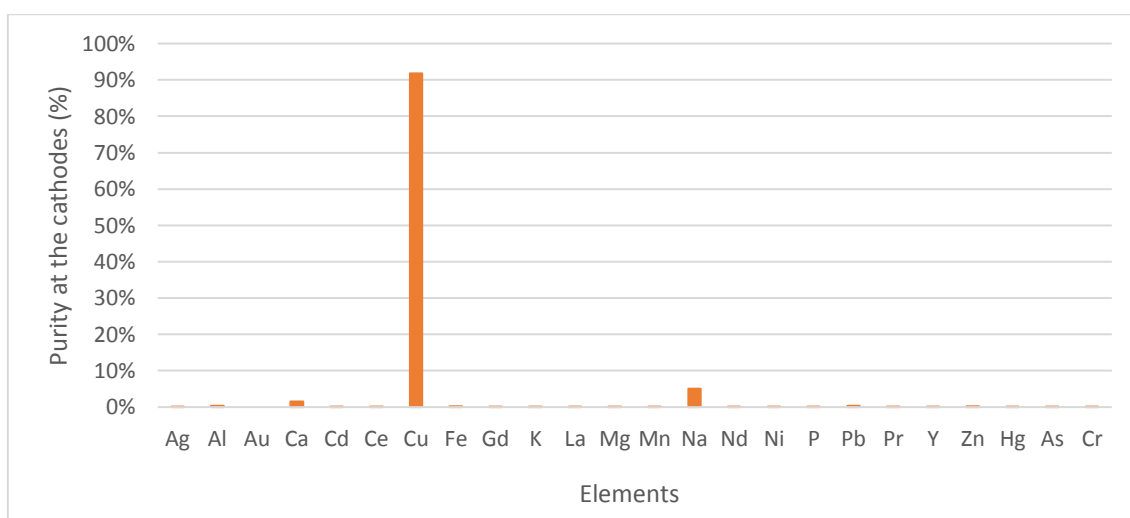
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448 *Figure 10. Mass percentage of each element in the cathodic electrodeposit obtained under optimal EW*

449 *conditions: ~1 g Cu/L, pH 1.5, operating at 200 A/m² for 5 h.*

3.4. Comparison of copper extraction techniques

450

451 As demonstrated in this work, copper extraction from BA by EW is feasible. However,

452 other techniques could be used for the same purpose, such as electrodialysis (ED) or

453 solvent extraction. For completeness sake, a bibliographic survey has been done, aiming

454 to compare the electrochemical technique employed here with other methods previously

455 reported for Cu recovery. Table 6 summarises the experimental conditions, the copper

456 origin and the extraction percentage obtained in this work, as well as the same data

457 published elsewhere.

458 Worth mentioning, only one study was found in the literature regarding the Cu recovery

459 from bottom ashes, although the authors did not use EW. In that case, froth flotation was

460 addressed, achieving 50% Cu recovery with Cu grade of ca. 5%.

461 *Table 6. Comparison of copper extraction percentages obtained by different techniques.*

Copper origin	Experimental conditions					Extraction (%)	Ref.
	pH (medium)	Initial Cu^{2+} concentration	Time	T (ºC)	Technique		
Bottom ashes	1.5 (H_2SO_4)	1000 mg/L	5 h	room	EW (200 A/m^2) after SL extraction pre-treatment	98.3	This work
Printed circuit boards (PCB) waste	2.0 (H_2SO_4)	290.37 mg/g PCB	3 h	-	Bioleaching and EW	75.8	[23]
Electronic waste (e-waste)	- (HCl)	1200 mg/L	40 min	room	EW after hydrometallurgical processes	81.9	[24]
Acid mine drainage (AMD)	- (H_2SO_4)	25 - 45 g/L	4 h	40	EW after high- pressure oxidative leaching and solvent extraction	95.0 (current efficiency)	[25]
Chromated copper arsenate-treated wood	1.3 (H_2SO_4)	306 mg/L	90 min	25	Electrolytic deposition after a chemical precipitation pre-treatment	99.0	[32]
Fly ashes	1.3 (HNO_3)	43.5 mg/L	6 h	23	Electrodeposition (154 A/m^2) after nitric acid lixiviation	79.9	[33]
Alkaline leaching with highly selective ammoniacal complexing agents	9.0 (cupric tetramine)	0.01 - 0.1 mol/L	3 h	20	Electro-electrodialysis (EED)	~89.0	[34]

26

Similar to a copper EW electrolyte	- (H₂SO₄)	9000 mg/L	24 h	25	5 compartments ED (250 A/m²)	96.6	[35]
Fly ashes	3.9 (H₂O)	2.2 mg/g ash	15 d	-	ED for metal removal (8 A/m²)	90.0	[36]
Fly ashes	5.0-6.0 (NaCl)	1.43 mg/g ash	3 h	25	Carrier-in-pulp method, with Fe powder as the carrier for metal extraction	95.6	[37]
Fly ashes	2.0 (HCl)	24.3 mg/L	1-5 min	20	Liquid-liquid (LL) extraction (LIX860N-I) combined with SL pre-treatment	> 90.0	[38]
AMD	1.2 (H₂SO₄)	5250 mg/L	15 min	25	Solvent extraction before electrochemical recovery	96.0	[39]

462

463 As summarized in Table 6, several authors have studied copper extraction and recovery by

464 EW [23–25], electrodeposition [32,33], ED-based technologies [34–36] and extraction

465 techniques [37–39].

466 For instance, copper recovery by EW from electronic wastes has been previously studied

467 by Baniasadi et al. [23] and Barragan et al. [24], since copper is the most abundant metal

468 in electronic wastes (20% w/w of PCBs). In both cases, moderate extraction values were

469 achieved: 75.8 and 81.9% in the former study and the latter, respectively. In the first case,

470 bioleaching was performed as a pre-treatment before the EW process itself. In the second

471 case, EW was carried out after hydrometallurgical processes. In another study, EW was

472 used after a high-pressure oxidative leaching and solvent extraction for copper recovery

473 from AMD [25]. In that work, a solution with a high concentration of copper was

474 introduced into the EW system (25-45 g/L), achieving a current efficiency of 95%.

475 On the other hand, Janin et al. [32] explored different ways to recover As, Cr, and Cu

476 from acid leachates. In that case, sulphuric acid leachate from chromated copper arsenate-

477 treated wood was used. In fact, although the initial solution was different from the one

478 used in this work, the procedure carried out was similar: copper recovery by

479 electrodeposition under similar experimental conditions and using H_2SO_4 as acidic

480 medium. Indeed, the same type of electrodes were used: titanium coated with iridium

481 oxide (Ti/IrO_2) anodes and stainless-steel cathodes (AISI 316 L). Thus, our results are in

482 agreement with theirs, since it was possible to recover 99% Cu from 1.8 L of leachate at

483 pH 1.3 after 90 min. In other words, less time was required for the copper extraction,

484 although a higher active surface area was employed ($220\ cm^2$ vs $56\ cm^2$), by using 4

485 anodes and 4 cathodes placed alternatively.

486 Yan et al. [33] also used a leaching process followed by electrodeposition for copper and

487 lead recovery. In that case, the leaching process was carried out using nitric acid with a

488   liquid-solid ratio of 20:1 (v/w). In that study, worse results were obtained in comparison

489   with the ones obtained in our work: a copper removal rate of 79.9% and a copper recovery

490   rate of 59.8% were achieved by applying 10 A current (i.e., 154 A/m^2 current density). In

491   comparison with that study, in the present work it was possible to extract more than 98%

492   of copper and recover more than 89%, applying a slightly higher current density (200

493   A/m^2) and with a higher initial copper concentration (1000 vs 43.5 mg/L).

494   Garrido et al. [34] studied electro-ED for copper recovery from alkaline leaching with

495   highly selective ammoniacal complexing agents. Although less time was required for the

496   copper extraction (3 h in comparison with 5 h, in our work), it was also possible to extract

497   less copper (around 89% vs 98%). Cifuentes et al. [35] performed ED to separate iron

498   and copper from a simulated copper EW electrolyte, obtained in mine extraction in Chile.

499   Thus, synthetic solutions with copper and iron were treated and mixed with sulphuric

500   acid. In that previous study, the initial Fe concentration was similar to that of the current

501   study (500 mg/L and 620 mg/L, respectively). In that work, 96.6% extraction was

502   possible after 24 h of ED operation. In contrast, in our work, it was possible to extract

503   more copper (98.3%) in shorter time (5 h). Ottosen et al. [36] also studied ED for metal

504   removal. In that case, Cu, Pb and Cl removal from fly ashes, suspended in water was

505   reported, obtaining 90% removal of copper working at 8 A/m^2.

506   Alorro et al. [37] proposed other copper extraction techniques, such as the carrier-in-pulp

507   method to recover metals from fly ashes. In that case, the carrier material was set in direct

508   contact with the pulp (leachate) for 3 h, at pH 5-6, under constant stirring. Subsequently,

509   the leached metal and the carrier were extracted by magnetic separation. Thus, that

510   method did not allow selective elements recovery, such as copper since all metals from

511   the leachate were absorbed and the extraction purity was diminished. Thus, EW could be

512   a better solution for copper recovery. Besides, Tang et al. [38] used a solvent leaching

513 and an extraction process for Cu and Zn extraction from MSW incineration fly ashes. In

514 that case, leachate was obtained by mixing HCl 3 M for 20 h. Then, copper was separated

515 from the leachate with a commercial extraction reagent, named LIX860N-I. Copper

516 recovery achieved was higher than 90% after 5 min. However, in that study, the initial

517 Cu^{2+} concentration was much smaller than that used in the present work (24.3 vs 1000

518 ppm). Last, Nobahar et al. [39] proposed a treatment train integrating solvent extraction

519 and electrochemical recovery for copper recovery from AMD. Results showed that the

520 proposal could be an efficient option to recover around 96% of the copper in only 15 min.

521 **4. CONCLUSIONS**

522 BA is one of the main by-products generated from MSW incineration, which can

523 represent environmental and economic problems. For that reason, its reuse and

524 valorisation have become an important issue in the last decades, following circular

525 economy approaches. In this work, the integration of SL extraction and EW processes

526 were proposed for the revalorization of BA by means of copper recovery. SL extraction

527 was carried out with sulphuric acid to obtain a leachate containing heavy metals; while in

528 the EW process, several operation parameters such as current density, electrodeposition

529 time, initial Cu^{2+} concentration and pH, were studied. The optimal operation conditions

530 for the maximum Cu recovery (90% deposited on the cathodes) and extraction (98%),

531 were the following: treatment of a leachate with an initial Cu^{2+} concentration of 1 g/L at

532 pH 1.5, operating 200 A/m^2 for 5 h. From the results, the integration of SL extraction and

533 EW processes seems to be a promising methodology for the recovery of copper from WtE

534 plants, which treat MSW and produce large amounts of BA via incineration. In future

535 work, a flow electrochemical cell with porous electrodes is planned to be used for EW to

536 enhance the current efficiency from values obtained here (i.e., lower than 30%).

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