

Olive-tree polyphenols and urban mining. A greener alternative for the recovery of valuable metals from scrap printed circuit boards

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Abstract

~~The recycling of~~ Recycling printed circuit boards (PCBs) is becoming a source of precious metals ~~as well as and~~ an alternative to conventional mining. ~~a. This~~ phenomenon ~~that~~ is now known as "urban mining." In this work, a polyphenols-rich plant extract has been obtained from olive-tree leaves, and its ability to contribute to reducing four metals, namely, Ag, Cu, Cr, and Sn, that are present in scrap PCBs has been studied. ~~To recover these valuable metals, three~~ Three reductants ~~have been used (i.e.,~~ (NaBH₄, Fe⁰, and the olive-tree leaves extract) ~~and an~~ have been used to recover these valuable metals. An attempt has been made to minimize the concentration of the first two, replacing them with a natural, cheaper, and less toxic reductant. To achieve this goal, a computer-assisted factorial, composed, centered, orthogonal, and rotatable statistical design of experiments (FCCORD) has been used ~~firstly,~~ to build the experimental matrix to be carried out in the laboratory and, next, for the statistical treatment of the results. The results ~~obtained~~ show that it is possible to achieve only a partial recovery of the four metals (silver, copper, chromium, and tin) from PCBs leachates by using sodium borohydride, iron, and the extract separately. In other words, none of these three reductants alone ~~is capable of can~~ completely ~~removing~~ ing any of the four metals ~~present~~ in the leachate. Nevertheless, using the statistical design of experiments, ~~at~~ the total recovery of the four metals has been achieved ~~through the combined use of by combining~~ the three reductants in the appropriate concentrations. Hence, polyphenols-rich plant extracts in general, and olive-tree leaves extract in particular, can be regarded as promising coadjuvants in the rising field of urban mining.

Keywords: Urban mining; metal recovery; polyphenols; *Olea europaea*

1.-Introduction

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32 Circularity is ~~set to be~~ one of the cornerstones of the modern and future economy.
33 ~~What Wastes that~~ were hitherto considered ~~waste of no use~~ become new and valuable raw
34 materials; that can be given a second life. In this context, the constant ~~and almost compulsive~~
35 increase in the acquisition of commonly used ~~equipmentspieces of equipment~~, mobile phones,
36 computers, and other devices, ~~as well astogether with~~ the global growth of industrialization ~~that~~
37 ~~the world is witnessing nowadays~~, has led to the generation of ~~hugevast~~ amounts of electrical and
38 electronic waste (EEW or e-waste) ~~that~~. ~~This fact~~ may constitute a severe ~~risk for~~
39 ~~environmentenvironmental~~ or human health ~~risk~~ (Ohajinwa et al., 2018; Zeng et al., 2019; Zhang
40 et al., 2022) ~~–~~. Planned obsolescence also ~~has a deep impact on~~~~profoundly impacts~~ the
41 environment, human health, and the economy (Barros and Dimla, 2021).

42 Under the prism of the circular economy, all these risks can be turned into an opportunity.
43 Thus, the sustainability of the electronics industry, which is compromised by the scarcity of
44 natural resources, can benefit from the high value-added materials that can be recovered from the
45 ~~very~~ waste it generates. To this end, it is necessary to develop more efficient recycling processes.
46 (Silva et al., 2018).

47 Printed circuit boards (PCBs) are the most important component of electronic circuits.
48 They constitute approximately 4-7% of the weight of e-waste. PCBs are often not recycled at all
49 or, at best, only a part is recycled to recover the precious metals due to their economic value (Mir
50 and Dhawan, 2022). PCBs are mainly composed of (a) 30% polymers (styrene-acrylonitrile,
51 styrene, polystyrene, polyamide, polypropylene, high impact polystyrene, acrylonitrile-
52 butadiene-styrene, or acrylonitrile-butadiene-styrene polycarbonate, ~~ete.~~); among others); (b) 30%
53 of ceramic materials (mainly silica, alumina and calcium oxide); and (c) 40% of metals whose
54 concentration varies depending on the electrical device. On average, their content is 8-38% Fe,
55 10-27% Cu, 2-10% Al, 1-3% Pb, 0.3- 2% Ni, 200-3000 ppm Ag, 20-5000 ppm Au and 10-200
56 ppm Pd (Arshadi et al., 2018). These values are 20-250 times larger than the natural occurrence
57 of the metals in the ~~Earth's~~Earth's crust in the form of natural ores (Zhou et al., 2021). Considering
58 the current technological demand and the depletion of resources, ~~the recycling of~~ these metals
59 instead of their extraction is extremely beneficial to such an extent that it has given rise to the
60 phenomenon known as "urban mining" (Dutta et al., 2016). Apart from these valuable metals,
61 PCBs also contain elements such as Pb, Hg, As, Sb, and Cd, which are highly toxic.

62 For this reason, the recycling of PCBs has become an immediate necessity. However,
63 ~~despite the fact that even though~~ it is considered a hazardous waste, ~~very it is~~ frequently ~~it is not~~
64 ~~properly~~inadequately managed. Many developing countries in Asia and, ~~particularly,~~ mainly in
65 Africa are the ~~m~~leading destinations for a plethora of second-hand or end-of-life electronic
66 devices from the rest of the ~~w~~World, thus giving rise to an enormous pollution hazard (Ádám et
67 al., 2021; Konaté et al., 2022). Due to the heterogeneous nature of this waste, the recycling process

68 of PCBs is particularly complex. In addition, while in developed countries efforts are being
69 made to provide standards for the management and regulation of e-waste, unfortunately, in
70 developing countries, such a regulation, if it exists, is scarce and lax.

71 Moreover, many of the receiving countries in Asia and Africa lack the necessary facilities
72 and expertise for their treatment. Hence, e-waste is frequently incinerated, which ultimately
73 results in their incineration, with the subsequent release of releases highly toxic gases derived from
74 the combustion of the polymeric materials that integrate the PCBs (Rajarao et al., 2014; Wu et
75 al., 2020) and the release of highly toxic metals into the environment (Dórea, 2021; Rajarao et
76 al., 2014; Wu et al., 2020).- Alternatively, e-wastes in general and PCBs in particular end up
77 being re-sent to developed countries, where more advanced technologies -namely,
78 pyrometallurgical or hydrometallurgical processes- and facilities are available for recycling.
79 However, these recycling processes have several drawbacks that exclude them from the so-called
80 "sustainable" chemistry" or "green" chemistry.

81 Some of these These drawbacks are include excessive energy use, cost, and pollutant
82 emissions. Alternative processes, such as bio-leaching, have been proposed (Yaashikaa et al.,
83 2022)).- Another innovative and recently used method for the recovery of recovering precious
84 metals due to its lower reagent consumption is electrolysis, a process that which combines
85 leaching, electrolytic extraction, and electrowinning. Nevertheless, it is considered immature
86 (Choubey et al., 2021; Li et al., 2019; Qiu et al., 2020).

87 Different traditional methods for the recovery of recovering noble metals are described in
88 the literature (Wu et al., 2017). Particularly, in hydrometallurgical processes, conventional
89 reduction processes are carried out by displacement precipitation or cementation, in which Fe
90 powder is used as a reductant (Sethurajan et al., 2019). The main advantage of Fe versus Zn is
91 that iron is less polluting than zinc, and the excess, if any, can be easily quickly recovered due to
92 its magnetic properties. It should be noted that since the The standard reduction potentials
93 (-0.76 V) and Fe (-are -0.76 and -0.44 V) is, respectively. These values are lower than that those
94 of Ni (-0.26 V), Pb (-0.13 V), Cu (+0.34 V), Ag (+0.80 V), and Au (+i.e., -0.26, -0.13, +0.34,
95 +0.80, and +1.50 V), the use of, respectively). Thus, if Zn or Fe -and even more so Zn- implies
96 that these other metals are is used as a reductant, Ni or Pb will be reduced and precipitated along
97 with gold, silver, and copper (Gurung et al., 2013).-Also, due to the negative effects of

98 Moreover, the simultaneous presence of Sn and Ag in the leachate reduction product (is
99 undesired due to the formation of an intermetallic compound, Ag₃Sn). Hence, it seems
100 particularly useful to keep as much Sn in the solution as possible or, in other words, to minimize
101 its precipitation from the leachate.

102 Another conventional reductant is sodium borohydride which, despite its widespread use,
103 is a known pollutant that may have repercussions on health and the environment (Norouzi et al.,
104 2020). Reduction with reagents of natural origin such as polyphenols from plant extracts (e.g.,
105 olive-tree, alperujo, coffee, tea, etc.) is more benign, and its use can also contribute to solving the
106 problem of waste generation in massive quantities (Balaji et al., 2021). This latter constitutes an
107 ~~interesting~~~~exciting~~ field of study as it minimizes the use of other more expensive reducing agents
108 with ~~extremely~~~~highly~~ harmful effects on the environment.

109 However, to make ~~the~~ hydrometallurgical reduction of valuable metals from PCBs waste
110 a more sustainable process, ~~the use of~~~~using~~ more benign, naturally-occurring reductants
111 constitutes an excellent alternative. In this connection, polyphenols are among the most versatile
112 and best-known natural reductants. In terms of chemical structure, polyphenols contain more than
113 one phenol group. Polyphenols reduce cardiovascular diseases and improve health (Quiñones et
114 al., 2012). ~~This is~~ due to their ability to moderate enzymatic activities. The phenolic groups they
115 possess can act directly by capturing unpaired electrons from reactive oxygen species (ROS), thus
116 generating less reactive species. Hence, they are known primarily as antioxidant compounds, that
117 inhibit or delay oxidative damage caused by cellular respiration leading to free radicals.
118 ~~Chemically~~~~Thus, chemically~~ speaking, ~~hence,~~ polyphenols are excellent candidates to be used as
119 reducing agents in ~~a wide variety of~~~~various~~ processes.

120 On the other hand, different industrial wastes such as seeds, peels of various fruits, or
121 cereals contain large amounts of polyphenols and can be regarded as renewable raw materials
122 (Fahmy et al., 2018). Particularly, ~~the use of~~~~using~~ olive-tree leaf extracts as a source of
123 polyphenols is feasible ~~thanks due to~~ ~~theirs~~ abundance ~~of this waste in many parts of the World,~~
124 ~~and, singularly,~~ in Extremadura (SW Spain)), and its availability throughout the year.
125 Furthermore, the presence ~~in olive-tree leaves extract~~ of different kinds of polyphenols such as
126 phenylpropanoids, secoiridoids, and flavonoids ~~in olive-tree leaves extract~~ has been reported in
127 the literature (le Tutour and Guedon, 1992; Michel et al., 2015).

128 To the best of the authors' knowledge, although some preliminary results dealing with
129 the use of polyphenols in urban mining and metal recovery processes have been published in the
130 last few years (Arif et al., 2017; Inoue et al., 2015), the use of this natural extract as a coadjuvant
131 in the recovery of valuable metals from PCB leachates has not been reported in the literature to
132 date. Hence, the purpose -and the main novelty- of this work is the development of experimental
133 procedures for the extraction, precipitation, and possible recovery of the maximum amount of
134 metals such as silver, copper, chromium, and tin by reduction of leachates from the treatment of
135 PCBs, using reductants from the natural extract of olive-tree leaves to minimize the use of
136 conventional reductants (Fe^0 and NaBH_4). In this way, the process will be much more
137 environmentally friendly and affordable as the use of agro-industrial waste is optimized. The

138 statistical design of experiments is used to determine the influence of different operational
139 variables on the metal recovery efficiency.

140

141 **2.-Materials and methods**

142 *2.1- Leaching of the scrap printed circuit boards*

143 PCBs were supplied by a local e-waste recycling industry, MOVILEX, already crushed
144 and with a thermal pre-treatment to eliminate part of the Sn that is commonly found in the solder
145 joints. Initially, 12.5 g of crushed PCBs ~~were~~ weighed, and HNO₃ (69%, PanReac-
146 AppliChem, Spain) and Type-II analytical grade water (Wasserlab Ecomatic, Spain) ~~were~~
147 added in a 1:3 ratio and then refluxed for ~~2h~~two hours at 60°C, thus obtaining the leachate fraction
148 simply by decantation. Nitric acid was used as the lixiviant agent to ensure that, due to its strong
149 oxidizing character, even the ~~most~~-noble -least reactive- metals initially present in PCBs are
150 leached in cationic (oxidized) form.

151 *2.2.- Characterization of the PCBs leachate*

152 The content of different metals in the PCBs leachate was analyzed by Inductively Coupled
153 Plasma-Mass Spectrometry (ICP-MS) with the aid of an Agilent Tech 7900 equipment ~~provided~~
154 ~~with~~coupled to a dynamic range orthogonal detector system (ODS), a high-frequency hyperbolic
155 quadrupole, and a 4th generation reaction octopole system. ~~Both the~~The collision gas and the argon
156 for the plasma are 99.999% pure and have been supplied by Praxair (Madrid, Spain).

157 As internal standards, 400 µg·L⁻¹ rhodium, palladium, and indium solutions were ~~used,~~
158 ~~being~~ continuously fed into the apparatus ~~by means of employing~~ a three-channel peristaltic pump.
159 The samples were diluted at 1:10000 with ultrapure water, due to the expected high Cu
160 concentrations ~~which are~~ in the % (P/P) range. The apparatus was calibrated with several
161 ~~calibration~~ standards prepared from certified commercial multi-elemental dilutions.

162 *2.3.- Extraction of polyphenols from olive-tree leaves and determination of the polyphenols* 163 *content.*

164 The olive-tree leaves were collected in the town of Arroyo de la Luz, and subsequently
165 pre-treated. Firstly, the leaves were washed with water to eliminate possible impurities and dried
166 as much as possible with filter paper. Next, they were placed inside an oven (Selecta-P, Spain) at
167 60°C until constant weight to ensure dryness.

168 ~~To prepare the natural extract, approximately~~Approximately 12.5 g of dry olive-tree
169 leaves were weighed, ~~to prepare the natural extract~~ and ~~next~~ refluxed for 30 minutes in 250 mL
170 of Type-II analytical grade water, keeping the temperature below 80°C throughout the extraction

171 process. Once this time ~~was~~-elapsed, the system was allowed to cool down to room temperature
172 and ~~next~~ filtered.

173 A qualitative analysis of the composition of the natural extract was performed following
174 a method previously described in the literature (Dobrinčić et al., 2020). Samples were firstly
175 filtered using 0.45 µm nylon membrane filters. Next, an HPLC system (Agilent Technologies
176 HPLC 1260 Series, Santa Clara, CA, USA) equipped with ~~ana~~ UV/Vis-Photo Diode Array
177 Detector (DAD) and a Luna C18 column (5 µm, 250 mm x 4.6 mm, 100 Å; Phenomenex,
178 Torrance, CA, USA) was used to separate and identify the polyphenols present in the sample.
179 Two different mobile phases were used. The first one (A) consisted of 0.1% formic acid in water
180 (v/v), whereas the second one (B) was constituted ~~by~~of 0.1% formic acid in methanol. Also,
181 different gradients were used throughout the experiment, namely: 0–3 min, 10% B; 3–30 min,
182 50% B; 30–40 min, 60% B; 40–45 min, 60% B; 45–50 min, 100% B; 50–60 min, 10% B. ~~In all~~
183 ~~cases, a~~ constant flow rate of 1 ~~mL~~·min⁻¹ was used. in all cases. The column temperature was
184 kept constant at 30°C; the injection volume was 20 µL, and DAD operated at λ=280 nm.

185 For clarity purposes, as the extract consisted of a mixture of different polyphenolic
186 compounds, it was considered more convenient to determine the total polyphenols content in the
187 leaf extract. Quantification was carried out by UV-VIS spectrophotometry using the Folin-
188 Ciocalteu assay (Tomás-Barberán et al., 2001). ~~Briefly, the~~The method is based on the reaction
189 between phenolic compounds and Folin's reagent at basic pH, achieved by ~~the addition of~~adding
190 the necessary amount of Na₂CO₃. Folin's reagent in this assay consists of a solution of sodium
191 tungstate and sodium molybdate in phosphoric acid. ~~The~~When reduced by the phenolic groups,
192 ~~the~~ yellow phosphomolybdotungstic acid (formed by both salts in an acidic medium), ~~when~~
193 ~~reduced by the phenolic groups,~~) gives rise to an intense blue complex, whose absorbance was
194 determined spectrophotometrically with the aid of a Shimadzu UV-1800 Ultraviolet/Visible
195 scanning spectrophotometer (Cole-Parmer, United States).

196 It is worth noting that quantification was made on the base of a gallic acid standard line.
197 Hence, the concentration of polyphenols was obtained as gallic acid equivalents. The
198 experimental procedure to obtain the standard line was as follows: solutions of different
199 concentrations (ranging from 2.3 to 11.7 mg/L) of gallic acid standards were prepared in 25 mL
200 flasks from a 196 mg/L stock solution. Next, 0.5 mL of Folin's reagent and 10 mL of 7.5% Na₂CO₃
201 were added to these solutions, and the ~~volume was completed by the~~ addition of ultrapure water.
202 completed the volume. Flasks were kept in the dark for 1 hour ~~and~~. Next, the absorbance was
203 measured, at a fixed wavelength of 740 nm, against a blank prepared in the same way but without
204 gallic acid.

205 Once this calibration line was obtained, the quantification of polyphenols in the olive-tree
 206 leaves extract was performed. ~~For this purpose, 0.1 mL of the~~ extract was taken, ~~to which~~ and 0.5
 207 mL of Folin's reagent and 10 mL of Na₂CO₃ were added, and after keeping the solution for one
 208 hour in the absence of light, the absorbance was measured at 740 nm.

209 2.4- Experimental design

210 To analyze the influence of the three operational variables, namely, the concentrations of
 211 NaBH₄, Fe⁰, and natural reductant (olive-tree leaves extract, OTLE), on the recovery of the four
 212 metals, a factorial, composite, central, orthogonal, and rotatable experimental design (FCCOR)
 213 was used. The experimental design consists of 8 factorial experiments, ~~6~~six axial experiments,
 214 and ~~9~~nine replicates of the central experiment, resulting in an experimental matrix of 23 runs.

215 For the use of the statistical design of experiments to be effective, it is of the utmost
 216 importance to adequately delimit the intervals between which the operating variables will be
 217 located. For this, it is necessary to draw on the previous experience of the research team or ~~on~~
 218 results already described in the literature. As indicated in the *Introduction* section, the authors are
 219 not aware of any other similar studies published in the literature to date, so when establishing the
 220 working intervals, a series of previous experiments had to be carried out, which will be described
 221 in the *Results and discussion* section. ~~Taking into account the~~The information obtained from these
 222 previous experiments, ~~was used to determine~~ the working intervals ~~have been determined~~, which
 223 ~~have given~~gave rise to the experimental matrix shown in Table 1. ~~In this~~This table, ~~both lists~~ the
 224 coded and natural values of the operational variables for each experiment ~~are listed~~.

225 Table 1.- Coded and natural values of the operational variables for each of the 23 runs
 226 of the experimental matrix.

Run	Coded values			Natural values		
	[NaBH ₄]	[Fe ⁰]	[OTLE]	[NaBH ₄] (M)	[Fe ⁰] (M)	[OTLE] Eq. ppm
1	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
2	0	-1.68179	0	1.9·10 ⁻²	0	88
3	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
4	1	1	-1	3.1·10 ⁻²	3.4·10 ⁻²	35
5	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
6	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
7	1	-1	1	3.1·10 ⁻²	8.5·10 ⁻³	140
8	1.68179	0	0	3.8·10 ⁻²	2.1·10 ⁻²	88
9	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
10	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88

Run	Coded values			Natural values		
	[NaBH ₄]	[Fe ⁰]	[OTLE]	[NaBH ₄] (M)	[Fe ⁰] (M)	[OTLE] Eq. ppm
11	-1	-1	1	7.8·10 ⁻³	8.5·10 ⁻³	140
12	-1	-1	-1	7.8·10 ⁻³	8.5·10 ⁻³	35
13	0	1.68179	0	1.9·10 ⁻²	4.2·10 ⁻²	88
14	-1	1	1	7.8·10 ⁻³	3.4·10 ⁻²	140
15	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
16	0	0	-1.68179	1.9·10 ⁻²	2.1·10 ⁻²	0
17	1	-1	-1	3.1·10 ⁻²	8.5·10 ⁻³	35
18	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
19	0	0	1.68179	1.9·10 ⁻²	2.1·10 ⁻²	175
20	1	1	1	3.1·10 ⁻²	3.4·10 ⁻²	140
21	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
22	-1.68179	0	0	0	2.1·10 ⁻²	88
23	-1	1	-1	7.8·10 ⁻³	3.4·10 ⁻²	35

227

228

229 *2.5.- Experimental procedure for the recovery of metals.*

230 In all experiments, 25 mL of the leachate and different volumes of the natural extract are
231 added in 50 mL flasks, making up the final volume with Type-II analytical grade water.
232 ~~Following the order established in the experimental matrix, this~~ This solution was placed in a
233 beaker ~~that acts as the reactor~~, and the solid reagents ~~previously~~ weighed ~~in advance~~ were added,
234 ~~following the order established in the experimental matrix~~. The final solution was magnetically
235 stirred for 1 hour and left to stand. The experiments with the conventional reductants gave rise to
236 ~~very fast~~ speedy reactions, whereas when the natural reductant was used, the reaction took about
237 8 hours. Hence, the experiments were allowed to stand for 12 hours, and ICP-MS was used to
238 analyze the final solutions ~~were next analyzed by ICP-MS~~ following the same procedure
239 described ~~underin~~ section 2.2. Taking into account the concentration of each metal in the PCBs
240 leachate before and after the reduction treatment, the removal efficiency (*R.E.*, in percent) can be
241 calculated as:

$$242 \quad R.E = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

243 where C_0 and C_t are the concentrations of metal in the initial leachate and the treated solution,
244 respectively.

245

246 3.- Results and Discussion

247 3.1.- Characterization of the PCBs leachate

248 In the first instance, the ~~largest~~most significant possible number of elements of the
249 Periodic Table was scanned through a semi-quantitative analysis; to determine which of them
250 were found in the ~~greatest~~most significant proportion in the leachate sample. The results obtained
251 in the ICP-MS analysis are presented in Figure S1 (Supplementary material) and listed in Table
252 1. It should be noted that, for technical reasons, it was ~~not possible~~impossible to analyze the
253 silicon and gold present in the leachate samples.

254 Table 1.- Semi-quantitative ICP-MS analysis of the PCBs leachate

Atomic weight	Element	Concentration (ppm)
27	Al	117
47	Ti	32
52	Cr	137
55	Mn	78
56	Fe	2072
59	Co	60
60	Ni	2002
63	Cu	44903
66	Zn	499
69	Ga	25
88	Sr	47
90	Zr	1700
93	Nb	29
107	Ag	231
118	Sn	3273
121	Sb	162
139	La	94
140	Ce	69
141	Pr	85
146	Nd	92
157	Gd	46

Atomic weight	Element	Concentration (ppm)
165	Ho	20
208	Pb	2206
209	Bi	37
232	Th	18

255

256 From the results collected in Table 1, it can be stated that the contents of the different
 257 metals present in the PCBs leachate are comparable with others previously found in the literature
 258 (Li et al., 2018). The PCB leachate used in this work contains, in addition to the vast majority of
 259 the metals found by the referred authors, several high value-added elements such as lanthanides
 260 (Pr, Nd, Gd, Ho) as well as Nb. Due to their unique properties, rare earth elements (REE)
 261 ~~contribute to~~ improve the performance of many technological devices in terms of energy
 262 consumption, efficiency, etc. Hence, REE find ~~important~~essential applications in ~~the field of~~
 263 optical devices, magnetic materials, and, ~~above all,~~ electronics (Balaram, 2019). Hence, these
 264 elements have become strategic materials in recent years, and ~~itstheir~~ presence in scrap PCBs has
 265 been reported and analyzed ~~withfor~~ valorization purposes. The REE content of the scrap PCBs
 266 used in this work is similar to those previously reported in the literature (Anshu Priya and Hait,
 267 2018; Gonzalez Baez et al., 2022; Tantawi and Hua, 2021).

268 Because of the above, it can be concluded that the PCB waste used in this work can be
 269 regarded as an extremely attractive and promising source of a wide variety of metals. In the
 270 following sections, the ability of a natural reducing agent such as the polyphenols present in olive
 271 leaves to precipitate several high value-added metals (namely, Ag, Cu, Cr, and Sn) will be
 272 analyzed; in an attempt to minimize the use of other more expensive and environmentally
 273 damaging reductants.

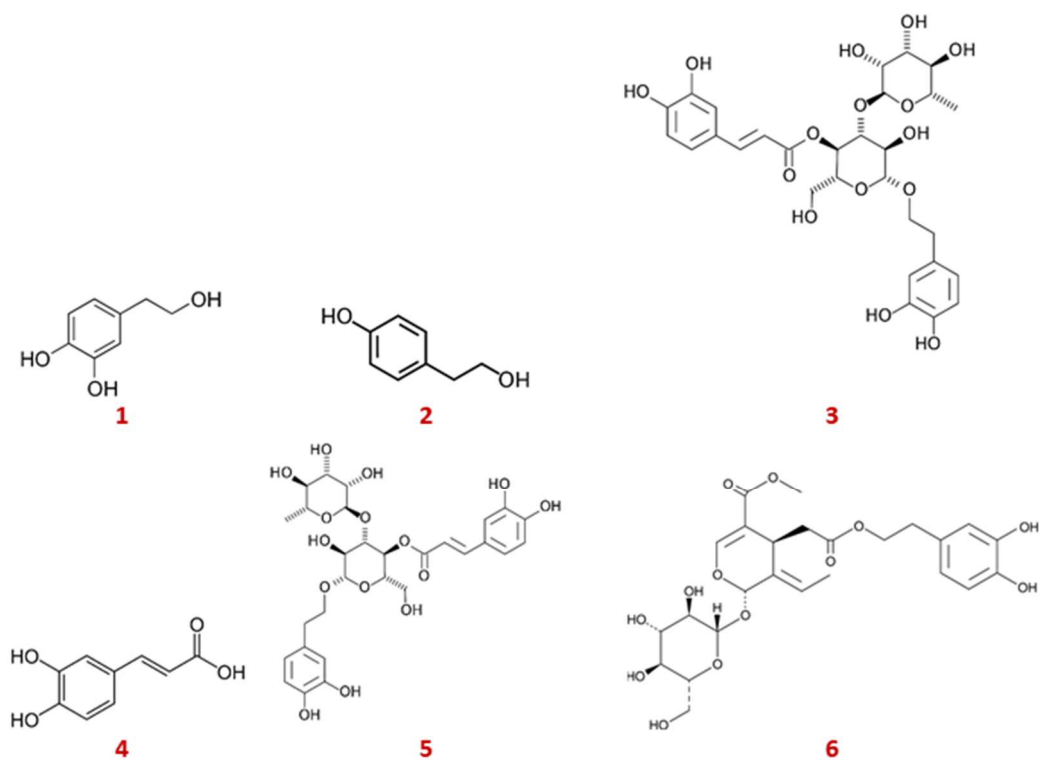
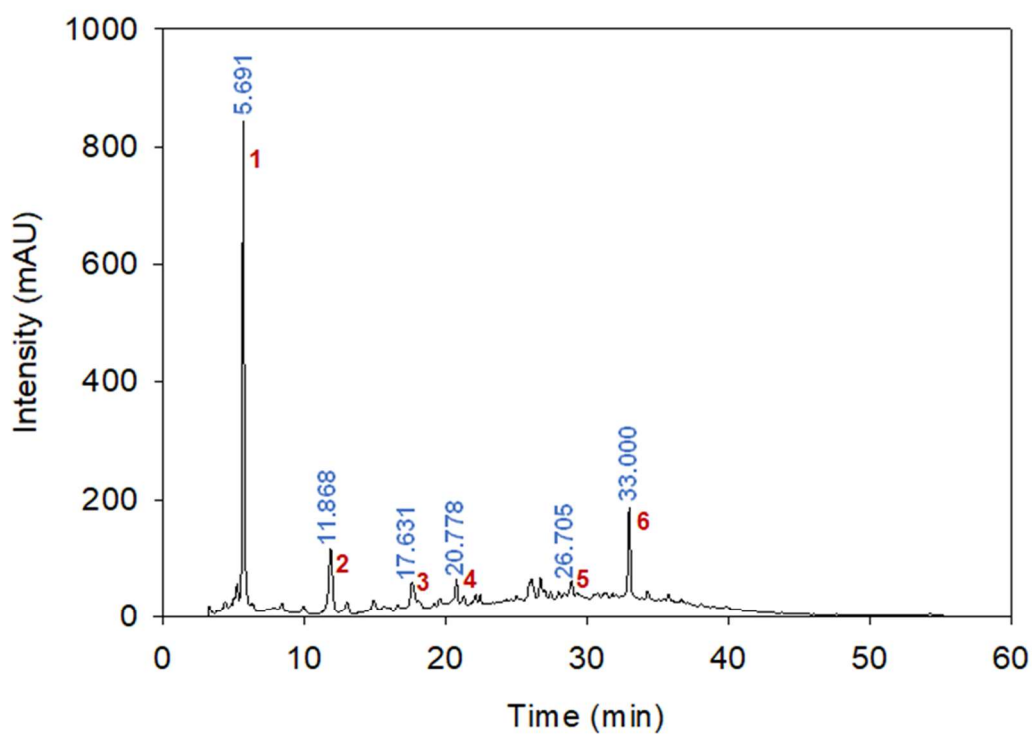
274 3.2.- Determination of the polyphenols content in the olive-tree leaves extract.

275 The ~~determination of the~~ polyphenols content in the olive-tree extract was
 276 ~~performed~~determined as described in section 2.3. Figure 1 (top) shows the HPLC chromatogram
 277 of the extract. The ~~main~~prominent peaks ~~found~~ in the HPLC-DAD have been assigned according
 278 to the literature (Balli et al., 2021; Dobrinčić et al., 2020; Richard et al., 2011). The
 279 ~~majoritary~~predominant polyphenols found in the extract are hydroxytyrosol, tyrosol, β -hydroxy-
 280 acteoside, caffeic acid, verbascoside, and oleuropein. The ~~peaks corresponding to these~~
 281 ~~compounds~~peaks have been labeled in the chromatogram, and ~~the structure of these~~
 282 ~~polyphenolstheir structures~~ are ~~also~~ shown in Figure 1 (bottom). This phenolic composition is
 283 coherent with previous results reported in the literature (Agatonovic-Kustrin et al., 2021;
 284 González et al., 2019; Oliveira et al., 2021; Quirantes-Piné et al., 2013; Topuz and Bayram, 2022).

285 As indicated under section 2.3, for simplicity and comparison purposes, the total
286 polyphenols content in the OTLE sample was quantified as gallic acid equivalents. The
287 experimental results showed that the value of A_{740} reached 2.101. This value falls outside the
288 standard line determined as described above, ~~and;~~ hence, it was necessary to perform a previous
289 dilution of 1:10.

290 Different volumes of this diluted olive extract were then taken (between 200 and 400
291 mL), and the procedure referred to above was repeated. The values of A_{740} so obtained are listed
292 in Table S2 (Supplementary material). From these values, and according to the standard line
293 obtained as described in section 2.3, the values of polyphenol concentration expressed as
294 equivalent mg of gallic acid per liter of ~~olive tree leaves extract~~ OTLE were calculated. These
295 values are also included in Table S2.

296 According to these values, and ~~taking into account~~ considering the dilutions performed,
297 the average polyphenol content (expressed as equivalent mg of gallic acid) in the olive-tree leaves
298 extract ~~resulted to be~~ was 731 ± 12 mg/L.



299

300 Figure 1.- HPLC-DAD profile of OTLE (top) and structure of the **mainprimary** polyphenols
 301 identified (bottom). 1. Hydroxytyrosol; 2. Tyrosol; 3. β-Hydroxy-acteoside; 4. Caffeic acid; 5.
 302 Verbascoside; 6. Oleuropein. Retention times are shown in blue.

303 ~~Assuming~~If we assume that all the polyphenols contained in the olive-tree leaves were
304 extracted ~~and,~~ taking into account that, ~~as indicated in the previous chapter section,~~ the extract
305 was obtained from 12.5 g of dry leaves that were kept at reflux in 250 mL of milli-Q water, the
306 polyphenol content (also expressed in equivalent mg of gallic acid) per kg of olive-tree leaves has
307 also been calculated, obtaining a value of 58496 ± 993 mg/kg. These results are of the same order,
308 or somewhat higher, than others previously reported in the literature (Bilgin and Şahin, 2013;
309 Canabarro et al., 2019; Goulas et al., 2010; Yancheva et al., 2016).

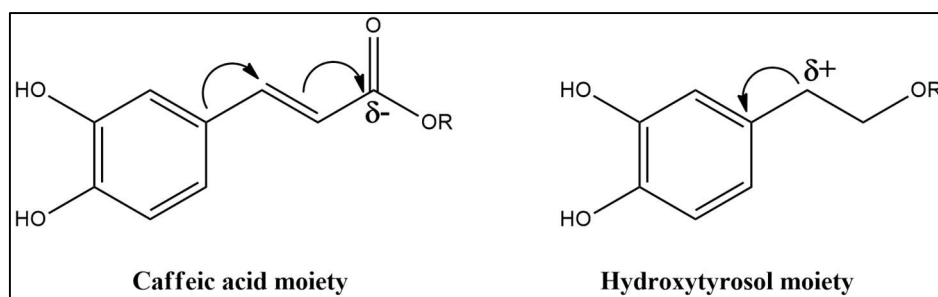
310 3.3.- Some insights into the reduction process of metals with olive-tree leaf extract polyphenols

311 Due to the structural complexity of ~~many of the naturally occurring polyphenolic~~
312 ~~compounds that are present in the OTLE, as well as a consequence of the simultaneous presence~~
313 ~~of a number of~~ polyphenols in the ~~extract~~OTLE and the occurrence of many polyphenols, the task
314 of proposing a ~~tempn~~tative mechanism for the reduction of metals initially present in the PCB
315 waste leachate is far from being easy. However, as revealed by a review of the literature
316 previously published on the redox behavior of polyphenolic compounds, the occurrence of the
317 catechol moiety is a keycrucial aspect ~~in this connection~~ (de Souza Gil et al., 2013; Li et al., 2021;
318 Moghaddam et al., 2007; Nenadis et al., 2007; Oliveira-Neto et al., 2016; Salas-Reyes et al., 2011;
319 Trabelsi et al., 2004).

320 From the structures of the ~~mainprimary~~ polyphenols found in the OTLE ~~here used~~ (Figure
321 2, bottom)), it can be seen that all of them ~~with the only exception of except~~ tyrosol (**2**) – contain
322 the catechol moiety. Furthermore, it is to be noticed that both, β -hydroxy-acteoside (**3**) and
323 verbascoside (**5**) show two catechol moieties in ~~its structure.~~their structures. In both cases, one of
324 the catechol moieties is analogous to caffeic acid (**4**), and the other ~~one~~ to hydroxytyrosol (**1**).
325 These two moieties may exhibit a slightly contrasting redox behavior because of the occurrence
326 of disparities in electron densities ~~as a consequence of~~due to the different groups attached to the
327 catechol.

328 On the one hand, as the carboxylic group of the caffeic acid substructure is not directly
329 bound to the aromatic ring, a negative charge withdrawing effect can be assigned to the stretching
330 of the -C=C- bond.

331 On the other hand, contrarily, the presence of an alkyl chain in the hydroxytyrosol
332 substructure of (**3**) and (**5**) gives rise to a positive inductive effect that results in an increase of
333 electron density on the aromatic ring. Hence, there are some slight differences in the redox
334 behavior of the catechol moiety in caffeic acid (**4**), hydroxytyrosol (**1**), and, consequently, in the
335 two polyphenols that contain boths structures, namely β -hydroxy-acteoside (**3**) and verbascoside
336 (**5**). Such differences are shown in Scheme 1 (de Souza Gil et al., 2013).

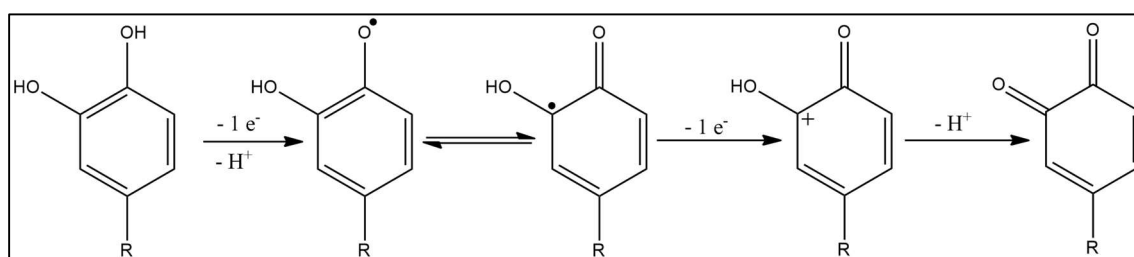


337

338

Scheme 1

339 ~~Anyhow, asAs~~ indicated above, the catechol moiety is the main responsible ~~effor~~ for the
 340 reductive character of most of the polyphenols detected in the leaf extract. It is commonly
 341 accepted that the oxidation of the catechol moiety follows a two-step mechanism, as depicted in
 342 Scheme 2.

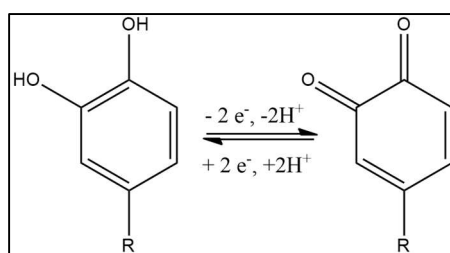


343

344

Scheme 2

345 The overall catechol oxidation mechanism, commonly known as the two-electron and
 346 two-proton mechanism, is a reversible process that can be summarized as shown in Scheme 3.



347

348

Scheme 3

349 The reduction potentials of the polyphenols ~~foundpresent~~ in the OTLE ~~fall within the~~
 350 range ~~comprised~~ between -0.1 and -0.5 V (Li et al., 2021; Nenadis et al., 2007; Oliveira-Neto et
 351 al., 2016; Trabelsi et al., 2004). ~~-~~Thus, taking into account that the reduction potentials of the
 352 metals under study are +0.8 V, +0.34 V, + 0,32 V, -0.14 V, and +0.014 V for the Ag⁺/Ag⁰,
 353 Cu²⁺/Cu⁰, Cr⁶⁺/Cr⁰, Sn²⁺/Sn⁰, and Sn⁴⁺/Sn⁰ pairs, respectively, it may be concluded that
 354 polyphenols alone would be able to reduce virtually all these metal from their positive oxidation
 355 states to oxidation state zero. Only Sn²⁺ could be more difficult to reduce by the weakest reductant
 356 polyphenols, ~~but~~. However, the concomitant occurrence of stronger more potent oxidizing

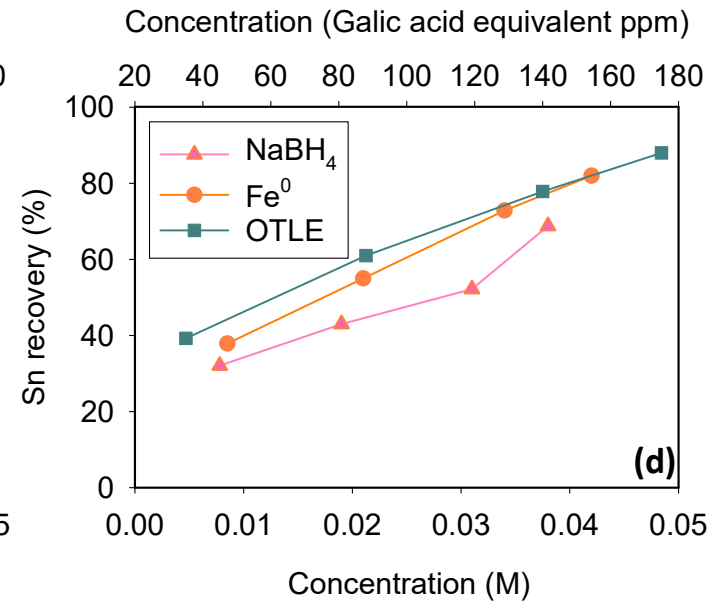
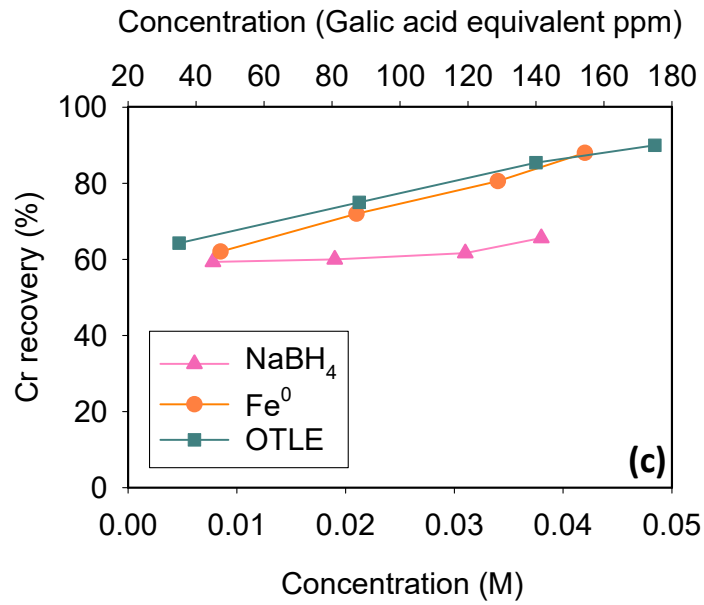
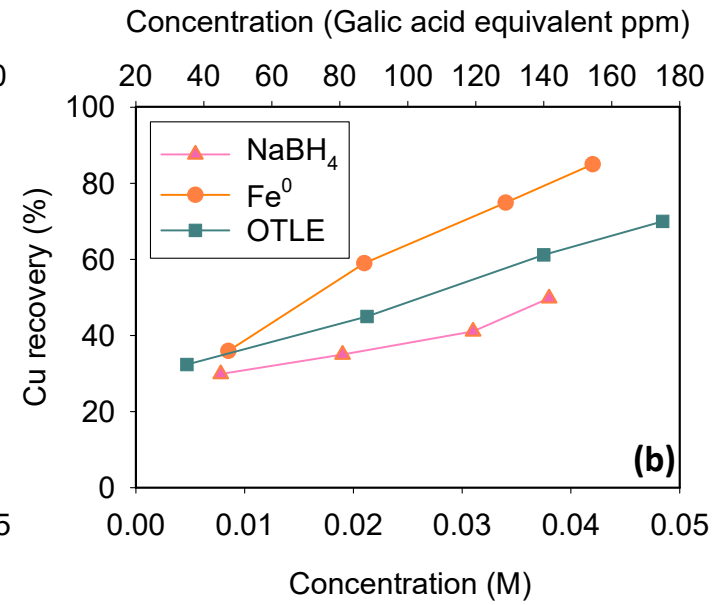
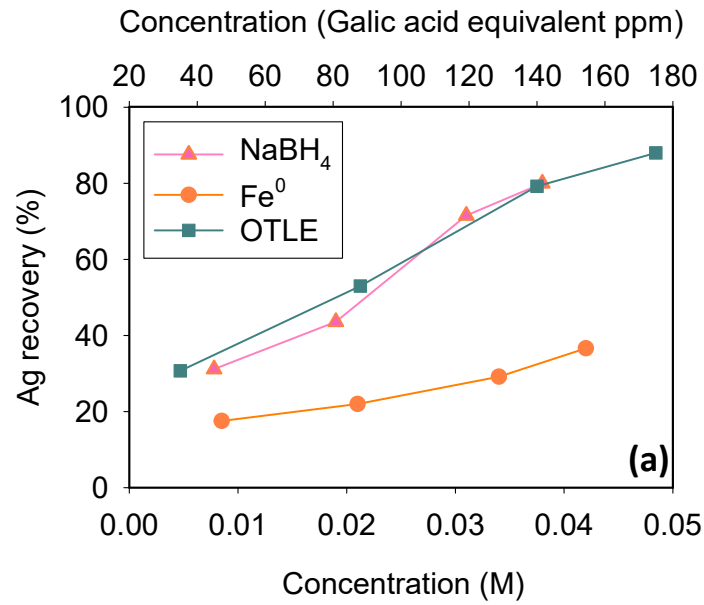
357 polyphenols makes it possible to reduce all the cations under study that were initially present in
358 the PCBs leachate, as corroborated by the preliminary experiments that will be described in the
359 next section.

360 *3.4.- Preliminary recovery experiments. Determination of the intervals of the operational*
361 *variables*

362 -Before performing the 23 runs that constitute the experimental matrix, a set of 12
363 previous trials were carried out, in which the effect of each reductant on the response variable
364 (metal recovery, in this case) was analyzed separately.

365 ~~Thus, for~~For each ~~of the metals under study~~metal, an experiment was carried out in which
366 a single reductant was introduced, and its concentration was varied within a relatively wide
367 working range. The results obtained are shown in Figure 2. ~~First of all,~~ it should be borne in mind
368 that the concentrations of NaBH₄ and Fe⁰ are expressed in molarity, whereas that of the
369 polyphenols-rich extract is indicated in equivalent ppm of gallic acid. Therefore, two abscissa
370 axes have been used in the figure, the lower one corresponding to the first two reductants and the
371 upper one to OTLE.

372



373

374

375

Figure 2.- Influence of operating variables on metal recovery. -Ag (a), Cu (b), Cr (c), and Sn (d).

376 Figure 2 shows a higher metal recovery with increasing reductant concentration ~~on an~~
377 ~~individual basis individually~~. However, for silver, an increase in Fe⁰ concentration does not result
378 in a significant increase in metal recovery, whereas iron is ~~this~~ reductant that results in the highest
379 copper recovery. This ~~fact~~ is consistent with the importance ~~that of~~ the cementation process ~~has~~ in
380 the extractive metallurgy of copper, regardless ~~of whether~~ the reductant is elemental iron or scrap
381 (Roba et al., 2018). On the other hand, ~~in the case of the use of NaBH₄ as a reductant, it NaBH₄~~ is
382 effective for the recovery of silver (almost to the same extent as the polyphenols-rich extract),
383 while for copper, the use of NaBH₄ does not represent ~~an important a~~ significant advantage.

384 For Cr and Sn, the influence of the reductants in the recovery process follows the order
385 polyphenol-rich extract > Fe⁰ > NaBH₄. ~~The use of~~ Using a strong reductant such as NaBH₄, in
386 the case of chromium, leads to a metal recovery efficiency of 60-65%. This latter is in line with
387 other results previously reported in the literature (Kuan et al., 2010; Xiu and Zhang, 2009). These
388 authors highlight the difficulties in recovering chromium from PCB leachates. However, better
389 results are achieved using Fe⁰ or polyphenols-rich extract, with the polyphenolic extract being the
390 only reducing agent whose increase in both cases results in remarkably more efficient metal
391 recovery. ~~This fact suggests that the "unconventional" reductant proposed for use in this work is~~
392 very promising for application as an alternative to the other two reductants, Fe⁰ and NaBH₄.

393 ~~While in~~ In recent years there has been a growing interest in developing methods for the
394 precipitation or flotation of metals from e-waste leachates. ~~However~~, progress in this direction is
395 ~~so far scarce to date~~ (de Souza et al., 2018; Jadhao et al., 2016; Lu and Xu, 2017; Rigoldi et al.,
396 2019; Suja et al., 2018; Yang et al., 2017). In addition, as far as the literature review conducted
397 for this report was able to determine, there is no evidence of the use of polyphenols obtained from
398 plant extracts as a reductant for the precipitation of metals present in PCBs, which is the major
399 novelty of this work.

400 However, although recovery efficiencies close to 85-90% are achieved using some of the
401 reductants separately, it is worth noting that none ~~of them~~ can achieve a total recovery of the metal
402 ~~present~~ in the leachate. Therefore, it seems reasonable to analyze the effect of the three reductants
403 together to ~~try to~~ achieve a full -or nearly full- recovery of the four metallic elements individually.
404 This ~~latter~~ shows that the selective precipitation of these elements is ~~far from being easy a~~
405 challenging topic.

406 3.5.- Analysis of the statistical design of experiments

407 The use of FCCOR experimental design makes it possible (i) to analyze the relationship
408 between the selected operational variables; (ii) to predict the experimental conditions that give
409 rise to an optimum value of each of the target variables, both individually and jointly; and (iii) to
410 determine and examine the response surface and contour plots.

411 The analysis of the results in a statistical design of experiments consists of two parts:
 412 numerical analysis and graphical analysis. Both analyses are presented in the following sections,
 413 the target variables being the recovery percentages of each of the metals.

414 *3.5.1- Numerical analysis*

415 The numerical analysis can be, in turn, divided into three sections: analysis of variance
 416 (ANOVA), deduction of a regression equation, with the corresponding analysis of its correlation
 417 coefficients, and determination of the experimental conditions that give rise to an optimum for
 418 the target variable. The results of the ANOVA test are shown in Table 2.

419

420 Table 2.- Results of the analysis of variance (ANOVA). Factors with a statistically significant
 421 influence are marked in bold characters

Factor	Ag	Cu	Cr	Sn
	p-Value	p-Value	p-Value	p-Value
A: NaBH ₄	0.0008	0.0010	0.0855	0.0106
B: Fe ⁰	0.1967	0.0000	0.0049	0.0007
C: OTLE	0.0001	0.0000	0.0003	0.0012
AA	0.8116	0.0011	0.0464	0.0002
AB	0.6885	0.0764	0.9329	0.4472
AC	0.0000	0.6159	0.8603	0.1445
BB	0.0278	0.0000	0.0013	0.0004
BC	0.0986	0.0001	0.0128	0.0035
CC	0.0588	0.0000	0.0069	0.0004

422

423 From the results ~~listed~~ in Table 2, it can be stated that in the case of Ag recovery, four of
 424 the nine factors have a statistically significant effect on the response variable (i.e., they show a
 425 p-value of less than 0.05). In the case of Cu and Sn recovery, seven factors have a statistically
 426 significant effect on the response variable, and in the case of Cr, six do. -On the other hand, R²
 427 shows values of 92.02% (Ag), 96.56% (Cu), 88.70% (Cr), and 92.69% (Sn), which indicate that
 428 the proposed model can explain the variability of the experimental data in a more than acceptable
 429 way. This assertion is corroborated by the observed vs. residuals plots ~~that are~~ depicted in Figure

430 S2 (Supplementary material). These plots ~~show~~illustrate the relationship between the
 431 experimental values ~~of metal recovery~~ and ~~the ones~~those predicted by the model ~~for each of the~~
 432 ~~23 experiments of the matrix~~. Therefore, these plots provide information about the dispersion of
 433 the experimental data of the target variable with respect to the calculated values. Thus, the closer
 434 the experimental data (squares) are to the bisector of the first quadrant, the better the fit ~~of the~~
 435 ~~data by the model~~.

436 On the other hand, the mean absolute error (MAE) is defined as the average ~~of the~~
 437 difference between the experimental value and the one predicted by the model. MAE values are
 438 2.31%, 2.21%, 2.14%, and 2.61% for the percentage recovery of Ag, Cu, Cr, and Sn, respectively.
 439 These values, again, corroborate the ~~good~~excellent fitting of the experimental data to the proposed
 440 model.

441 Finally, the Durbin-Watson (DW) statistic makes it possible to detect whether the order
 442 in which the experiments composing the matrix have been carried out influences ~~in any way~~ the
 443 results obtained. In other words, the DW statistic analyzes whether the randomization of the
 444 experimental sequence is working properly. Since the p-value of this statistic is greater than 0.05
 445 for all the experimental matrices (p Ag = 0.5440; p Cu = 0.2250; p Cr = 0.4848; p Sn = 0.9442)
 446 it can be stated that there is no autocorrelation in the residuals and the randomization has been
 447 effective.

448 The second ~~and very important~~essential functionality of the statistical design of
 449 experiments is that it allows ~~to obtain~~obtaining the regression equations and correlation
 450 coefficients (the polynomial coefficients ~~of the polynomial~~ that adjusts the experimental values).
 451 For the case of the recovery of Ag, Cu, Cr, and Sn, the equations are as follows:

$$452 \text{ Ag recovery (\%)} = 78.9356 + 5.37455 [\text{NaBH}_4] + 1.64187 [\text{Fe}^0] + 6.97847 [\text{OTLE}] - \\ 453 0.249439 [\text{NaBH}_4]^2 - 0.684678 [\text{NaBH}_4] \cdot [\text{Fe}^0] - 12.2653 [\text{NaBH}_4] \cdot [\text{OTLE}] + 2.56132 [\text{Fe}^0]^2 - \\ 454 2.98468 [\text{Fe}^0] \cdot [\text{OTLE}] + 2.13705 [\text{OTLE}]^2 \quad (2)$$

$$455 \text{ Cu recovery (\%)} = 65.0431 + 4.77628 [\text{NaBH}_4] + 9.40635 [\text{Fe}^0] + 8.10258 [\text{OTLE}] + \\ 456 4.00689 [\text{NaBH}_4]^2 - 2.9617 [\text{NaBH}_4] \cdot [\text{Fe}^0] + 0.7867 [\text{NaBH}_4] \cdot [\text{OTLE}] + 6.79997 [\text{Fe}^0]^2 - 8.8617 \\ 457 [\text{Fe}^0] \cdot [\text{OTLE}] + 6.90603 [\text{OTLE}]^2 \quad (3)$$

$$458 \text{ Cr recovery (\%)} = 77.7098 + 2.03118 [\text{NaBH}_4] + 3.72446 [\text{Fe}^0] + 5.50394 [\text{OTLE}] + \\ 459 2.05116 [\text{NaBH}_4]^2 + 0.129402 [\text{NaBH}_4] \cdot [\text{Fe}^0] + 0.270598 [\text{NaBH}_4] \cdot [\text{OTLE}] + 3.87197 [\text{Fe}^0]^2 - \\ 460 4.3956 [\text{Fe}^0] \cdot [\text{OTLE}] + 3.00576 [\text{OTLE}]^2 \quad (4)$$

$$461 \text{ Sn recovery (\%)} = 58.1805 + 4.80375 [\text{NaBH}_4] + 7.15226 [\text{Fe}^0] + 6.70089 [\text{OTLE}] + \\ 462 7.14284 [\text{NaBH}_4]^2 - 1.73298 [\text{NaBH}_4] \cdot [\text{Fe}^0] - 3.44202 [\text{NaBH}_4] \cdot [\text{OTLE}] + 6.61251 [\text{Fe}^0]^2 - \\ 463 7.98298 [\text{Fe}^0] \cdot [\text{OTLE}] + 6.50644 [\text{OTLE}]^2 \quad (5)$$

464 The positive or negative sign that precedes each of the different coefficients indicates the
 465 favorable or unfavorable influence, ~~respectively~~, of the change of one or two of the operational
 466 variables on the target variable (metal recovery).

467 In general, it can be stated that the higher the absolute value of the coefficient, the greater
 468 the influence of the operational variable (or combination of variables) on the response variable.
 469 This assertion is numerically corroborated if ~~the each factor's~~ percent effect (P_n) ~~of each factor~~ on
 470 the recovery efficiency of the different metals from PCB leachate is obtained (Abdessalem et al.,
 471 2008). According to these authors, P_n can be calculated as

$$472 \quad P_n (\%) = \frac{\beta_n^2}{\sum \beta_n^2} \times 100 \quad (6)$$

473 where β_n^2 represents the squared value of each of the coefficients in equations (2) to (5) and $\sum \beta_n^2$
 474 is the sum of all the squared values of these coefficients.

475 Table 3 summarizes the P_n (%) values ~~of P_n (%)~~ obtained for the four studied metals
 476 under study. From the data contained in Table 3, it can be concluded that Ag recovery from PCB
 477 leachates is mainly governed by the concentrations of sodium borohydride (A, 11.5%) and OTLE
 478 (C, 19.38%), and, particularly, by its concomitant effect (A·C, 59.87%). On the contrary, the
 479 concentration of NaBH₄ plays a much less remarkable role in the recovery of the remaining
 480 metals, which are mainly conditioned by the concentrations of iron and the dose of polyphenol-
 481 rich olive-tree leaves extract. This latter deserves to be highlighted since these two reductants are
 482 much more benign from an environmental standpoint than NaBH₄.

483

484 Table 3.- Percent effect of each factor on the recovery efficiency of the different metals
 485 from PCB leachate.

Factor	P_n (%)			
	Ag	Cu	Cr	Sn
A: [NaBH ₄]	11.50	6.09	4.30	6.89
B: [Fe ⁰]	1.07	23.60	14.46	15.28
C: [OTLE]	19.38	17.51	31.58	13.41
A ²	0.02	4.28	4.39	15.24
A·B	0.19	2.34	0.02	0.90
A·C	59.87	0.17	0.08	3.54
B ²	2.61	12.34	15.63	13.06
B·C	3.55	20.95	20.14	19.04
C ²	1.82	12.72	9.42	12.64

486

487 The third -and perhaps most important- functionality of the statistical design of
 488 experiments resides in the fact that it is capable of predicting, at least theoretically, the
 489 experimental conditions that would lead to an optimization of the target variable (in this case, a
 490 maximization of the recovery efficiency of each of the four metals here studied). The optimal
 491 coded and natural values of the operating variables leading to such a theoretical optimum for the
 492 four experimental designs are shown in Table 4.

493

494 Table 4.- Coded and real optimum values for the recovery of Ag, Cu, Cr, and Sn from
 495 PCB leachate.

Variable	<u>Ag optimum</u>		<u>Cu optimum</u>		<u>Cr optimum</u>		<u>Sn optimum</u>	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real
[NaBH ₄]	-0.380	0.015 M	0.494	0.025 M	1.106	0.031 M	1.051	0.031 M
[Fe ⁰]	-0.128	0.019 M	1.649	0.042 M	0.607	0.029 M	1.111	0.035 M
[OTLE]	1.527	168 ppm	0.891	134 ppm	1.681	175 ppm	-1.128	58 ppm

496

497 ~~Operating under~~Under the conditions shown in Table 4, the model predicts 100%
 498 recovery for each ~~of the metals under study~~studied metal. These theoretical optima were
 499 experimentally corroborated, and the recovery of the four metals was above 95% in all cases,
 500 which is indicative of the predictive value of the proposed model.

501 It is interesting to note that the conditions under which the maximum recovery of each of
 502 the metals is achieved are very different from each other, so the simultaneous optimization of the
 503 recovery of all four metals is, *a priori*, difficult to achieve. However, as indicated above, it is
 504 interesting to try to maximize silver recovery while minimizing tin precipitation, to avoid the
 505 formation of the intermediate phase ~~and~~or the intermetallic compound, Ag₃Sn. The theoretical
 506 values of the three variables leading to these results are ~~as~~ shown in Table 5.

507

508 Table 5.- Coded and real optimum values for ~~simultaneously~~maximizing Ag recovery
 509 and minimizing Sn recovery from PCB leachates ~~simultaneously~~.

Variable	<u>Optimum values</u>	
	Coded	Real
[NaBH ₄]	0.116	0.020 M
[Fe ⁰]	-1.187	0.006 M
[OTLE]	-0.958	38 ppm

510

511 Operating under these experimental conditions, the model predicts a 75% recovery of
512 Ag, while 51% of Sn would precipitate together. Again, these results were corroborated
513 experimentally. In this case, the value of Ag recovery was slightly higher (79%) than the one
514 predicted by the model, whereas tin precipitation (52%) was of the same order as the theoretical
515 one.

516 Therefore, it can be stated that the concomitant use of the polyphenols-rich olive-tree
517 leaves extract with other traditional reductants (sodium borohydride and iron) appears ~~as a~~
518 promising ~~procedure~~ to achieve a more benign separation of valuable metals from PCB leachates.
519 Nevertheless, it also seems necessary to persevere in trying to find a Sn-selective reductant that
520 can remove Sn from the leachate (ideally in a complete manner) and then proceed to the
521 precipitation of silver under the conditions foreseen in Table 4.

522 3.5.2- Graphical analysis

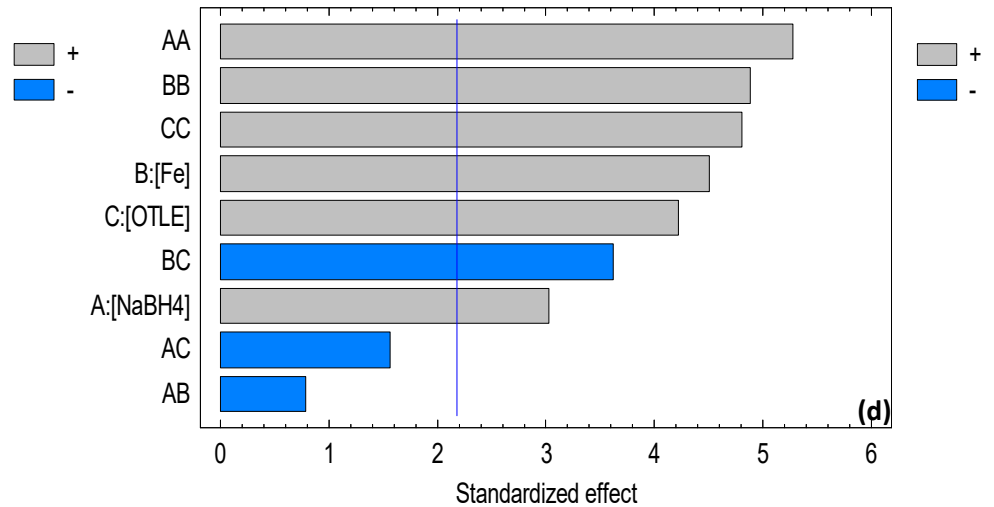
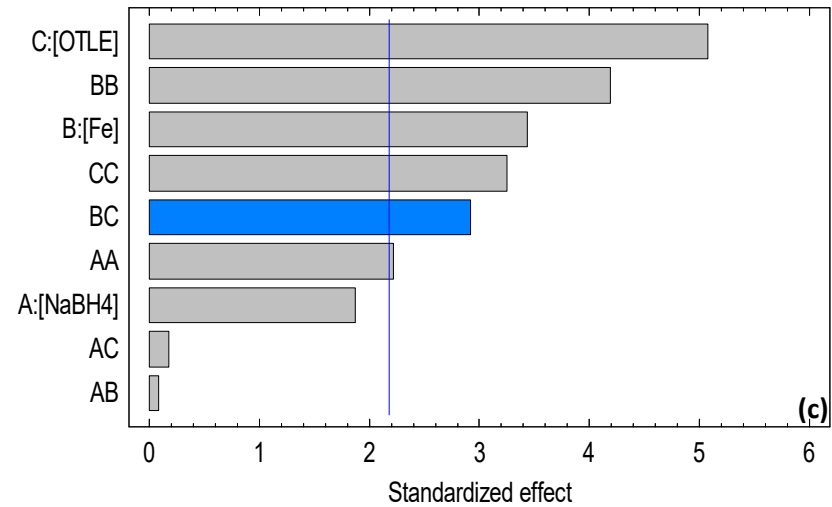
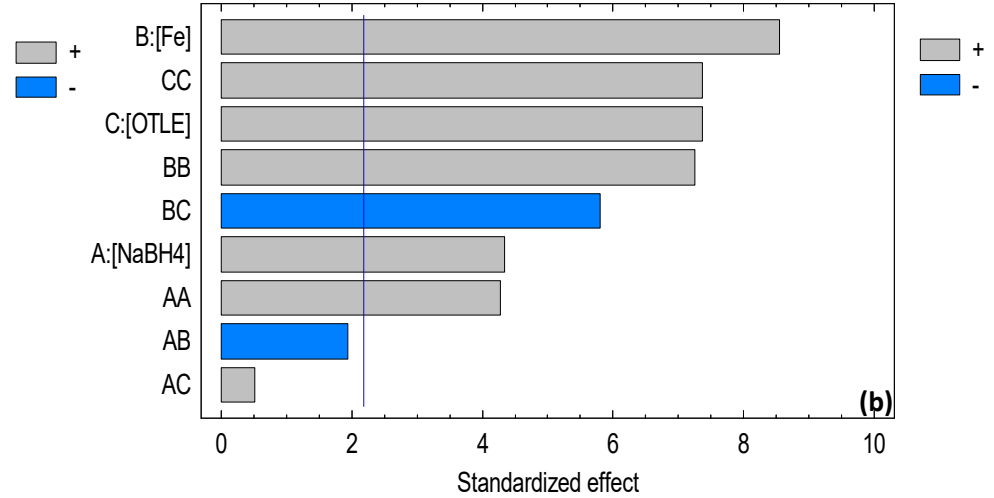
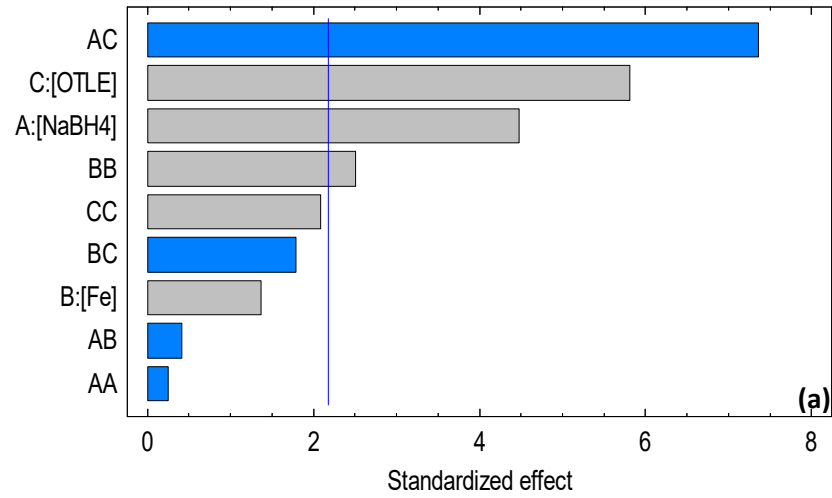
523 The graphical analysis of the results obtained in the statistical design of experiments has
524 been carried out by studying the Pareto, main effect, interactions, and response surface plots

525 Pareto factor plots can be considered ~~to some extent~~ a graphical representation of the
526 ANOVA test. ~~It consists of a series of horizontal~~ Horizontal bars representing the effect of each
527 variable, ~~these being (i.e., the concentration of NaBH₄, Fe⁰, or OTLE, as well as and~~ all their
528 combinations. The vertical line shown corresponds to a p-value of 0.05. Those factors whose
529 bar exceeds this line are considered to exert a statistically significant effect on the response
530 variable with a probability of 95%. Such variables appear in the ANOVA test (Table 2) with a p-
531 value below 0.05.

532 In addition, the ~~type of positive or negative~~ influence exerted by each variable ~~considered,~~
533 ~~i.e., whether its effect on metal recovery is positive or negative,~~ is shown in the graph. Thus, the
534 working variables represented by a gray bar have a positive effect on the target variable, while
535 those with blue bars exert a negative effect on the target variable. As expected, the factors that
536 have a positive influence on the metal recovery efficiency appear in equations (2) to (5) preceded
537 by a "+" sign, while those factors that have a negative influence on the response variable are
538 preceded by a "-" sign in these equations.

539 Pareto factor plots for the recovery of the four metals present in the PCB leachate are
540 shown in Figure 3.

541



542

543

Figure 3.- Pareto factor plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

544 As ~~can be~~ seen in the Pareto plot for Ag, the effects involving the concentrations of OTLE
545 and NaBH₄, the square of the Fe⁰ concentration, and the product of the concentration of
546 polyphenols and NaBH₄, are statistically significant with a probability of 95%.

547 Similarly, ~~in the Pareto diagram~~ for Cu ~~it can be seen that~~, the effects involving the
548 concentration of Fe⁰, NaBH₄, and OTLE and the squares of each of them, as well as the product
549 of the concentration of polyphenols and Fe⁰, are statistically significant.

550 ~~It can also be observed that, for~~ For Cr ~~recovery, the effects of the concentration of~~,
551 [OTLE], [Fe⁰], and [NaBH₄ ~~as well as~~], all their quadratic terms and the product of the
552 concentration of OTLE and Fe⁰, ~~are considered to be~~ exert a statistically significant effect.

553 Finally, for Sn ~~recovery, the effects of the~~ OTLE concentration, Fe⁰ ~~and~~, the square of
554 the OTLE concentration, ~~as well as~~ the square of [NaBH₄], and the product of [OTLE] and [Fe⁰],
555 exert a statistically significant effect on the metal recovery.

556 The main effects plot shows the influence of the different operational variables
557 individually, i.e., OTLE, Fe⁰, and NaBH₄ concentration, on the target variable. The graph
558 represents the theoretical value of the recovery efficiency calculated by equations (2) to (5) if only
559 the values of one of these variables were modified, keeping the other two ~~as constant~~ at their
560 central coded value (i.e., 0). Hence, ~~arbitrary~~ coded values -comprised between -1 and +1- are
561 given to the variable whose influence is being analyzed, and the theoretical recovery efficiencies
562 provided by the model are calculated as indicated. In this way, it can be ~~seen~~ graphically seen
563 how each of the variables involved in the process individually influences the metal recovery
564 efficiency. The main effects plots corresponding to the ~~the~~ four metals are shown in Figure 4.

565 For Ag, it can be seen that the most influential variables on recovery are [NaBH₄] and,
566 particularly, [OTLE]. Concerning [Fe⁰], this has a lesser influence, presenting a minimum
567 recovery of 79% in the central part of the operating range.

568 In the case of Cu, the three variables show similar behavior. Although a minimum
569 recovery is observed, it should be noted that as concentrations increase, Cu recovery becomes
570 higher. ~~In~~ this particular case, iron is the most influential reductant.

571 For Cr and Sn, it is inferred that an increase in concentration from a ~~certain~~ specific coded
572 value produces an increase in recovery efficiency, with Cr being higher. In general, the variables
573 that have the ~~greatest~~ most significant influence on recovery are OTLE and iron concentrations.

574

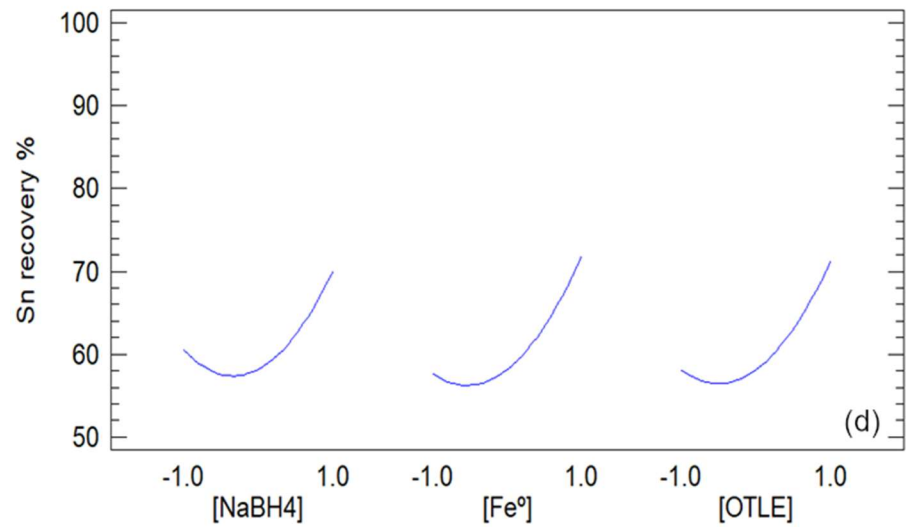
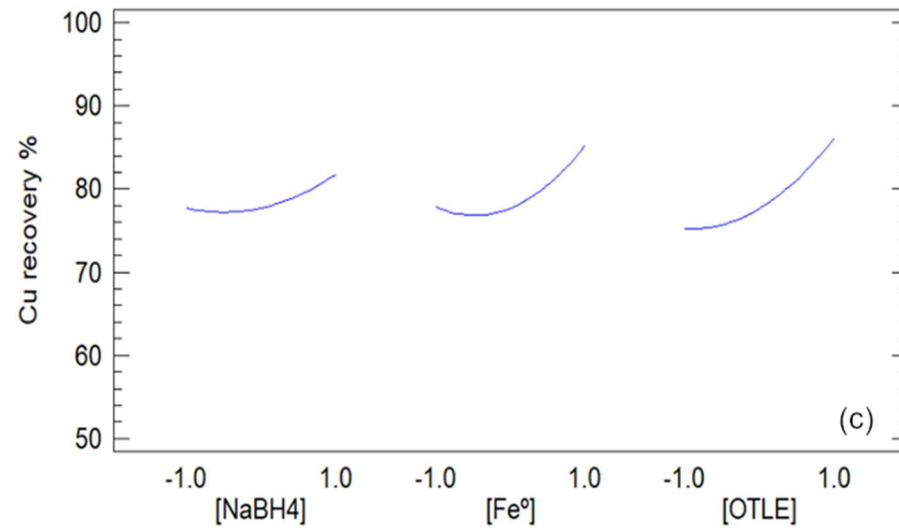
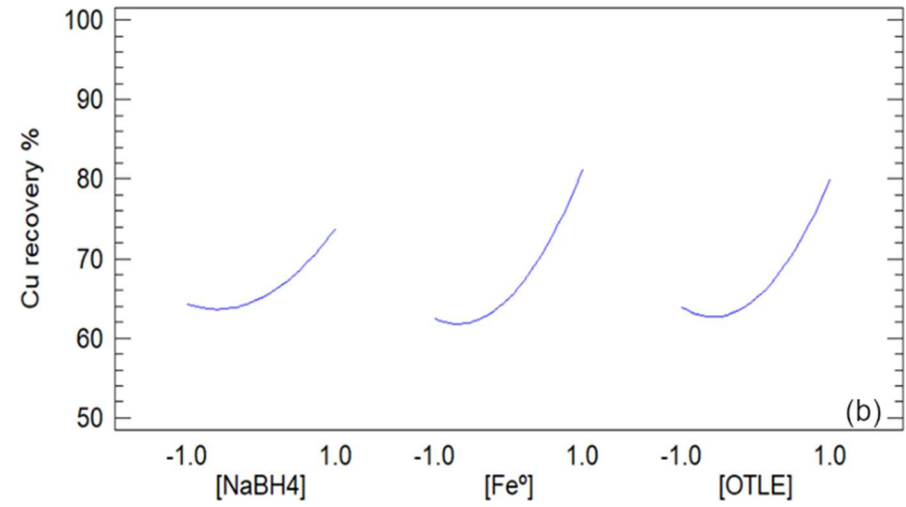
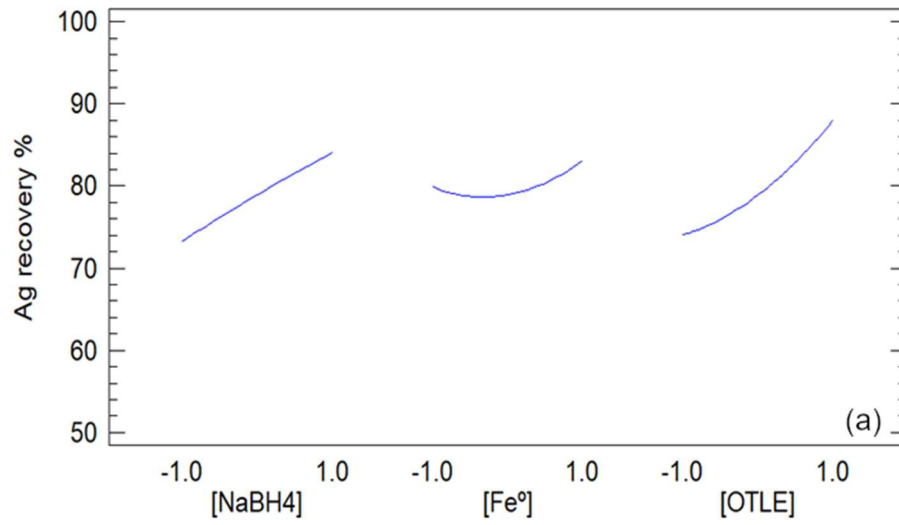


Figure 4.- Main effect plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

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579 Another plot of great interest is the interaction graph (Figure 5). This plot makes it
580 possible to study whether the change in an operational variable affects (or not) how the other
581 variables influence the target variable, i.e., whether or not there are interactions between the
582 operational variables. This latter is one of the greatestmost valuable potentialities of the statistical
583 design of experiments and justifies, from a methodological standpoint, its use as opposed to the
584 traditional method of modifying "one factor at a time" (OFAT method). The OFAT method is
585 valid if it is assumed that interactions do not exist between operational variables, i.e., that a change
586 in one of them does not affect the way how the rest influence the target variable.

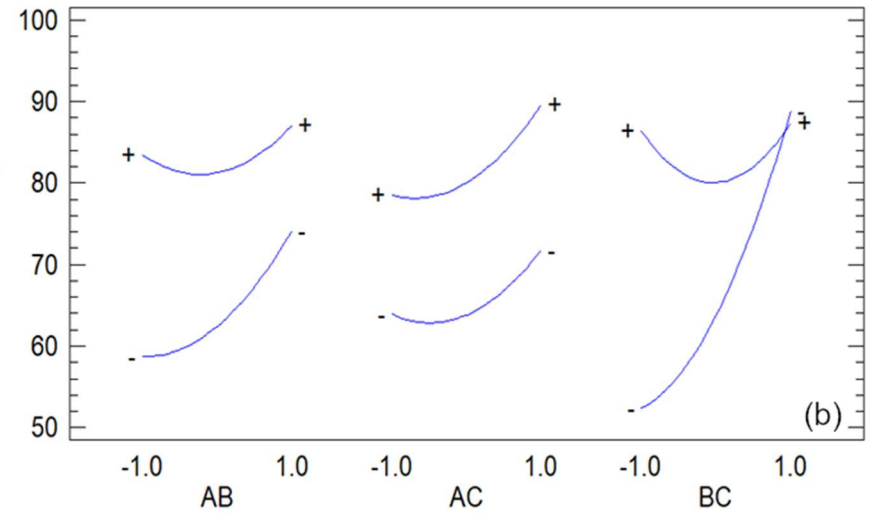
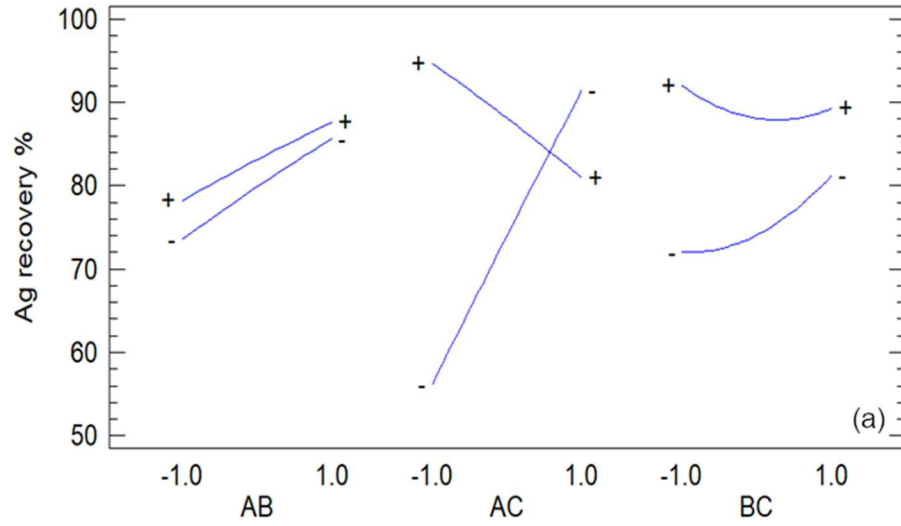
587 In the graph of interaction between variables, where A, B, and C correspond to $[\text{NaBH}_4]$,
588 $[\text{Fe}^0]$, and [OTLE], respectively, each pair of curves represents the evolution of the percentage
589 of metal recovery when (a) arbitrary coded values -comprised between -1 and +1- are given to
590 one of the variables; (b) the second variable is fixed at a coded value either equal to +1.0
591 (maximum value, line marked with the "+" sign) or equal to -1.0 (minimum value, line marked
592 with the "-" sign); and (c) the third variable remains constant at its central value (i.e., 0). ~~Operating~~
593 thisThis way, the theoretical recovery efficiencies are calculated from equations (2) to (5) ~~taking~~
594 ~~into account~~, considering what has just been exposed. If the curves of a pair of variables are
595 parallel, the modification of one of them does not affect the way how the other one influences the
596 recovery efficiency or, in other words, no interaction is found between this pair of variables. On
597 the contrary, if two lines intersect, the interaction is evident. An intermediate situation can also
598 be found, where none of the ~~above-mentioned~~abovementioned behaviors are clearly
599 ~~observed~~appreciated.

600 The data depicted in Figure 5 reveal a very different behavior for Ag and Cu. For Ag, an
601 interaction between $[\text{NaBH}_4]$ and [OTLE] is observed, giving rise to an "X-shaped" plot, or else
602 they tend to cross at one of the extremes of the ~~working~~operating range (in this case, the upper one). In
603 contrast, the curves are parallel or show no tendency to intersect for the other pairs of variables.

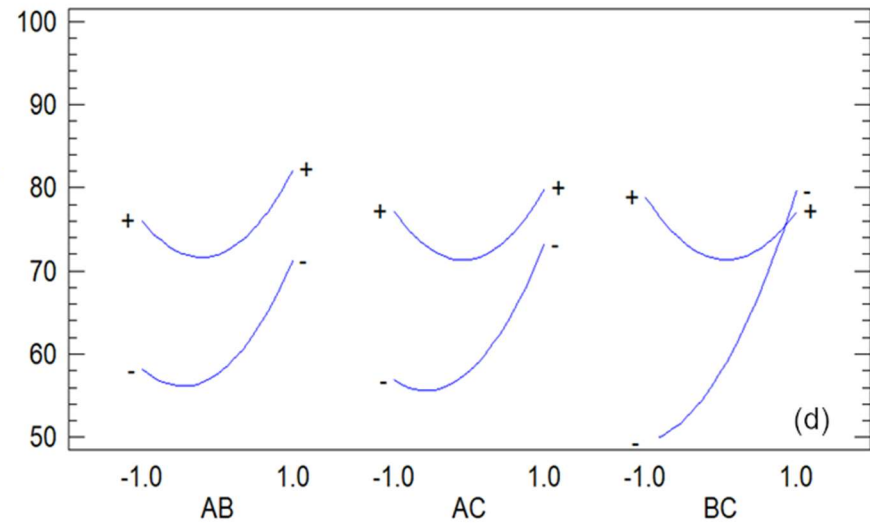
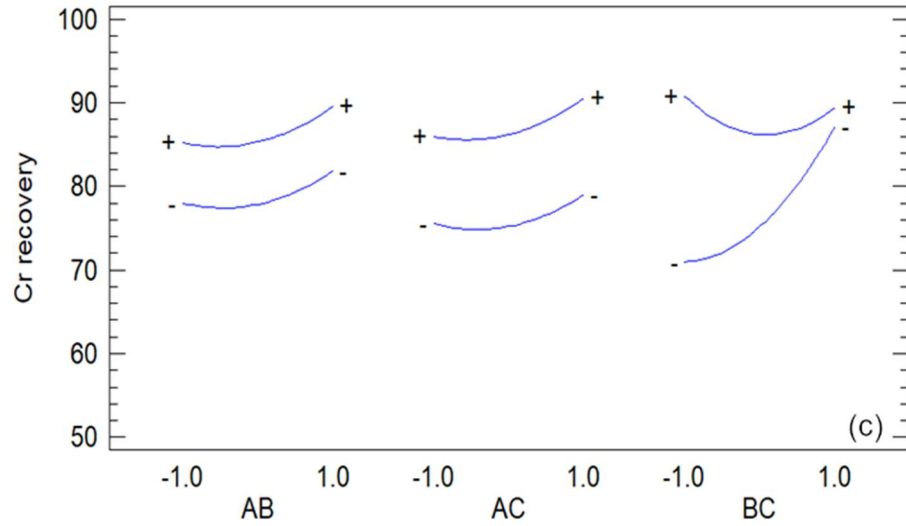
604 Unlike Ag, Cu shows a slight interaction at the end of the upper working range between
605 iron and the polyphenol-rich extract. On the other hand, for Cr, an interaction between $[\text{Fe}^0]$ and
606 [OTLE] in the upper zone of the plot is observed. For Sn, however, such an interaction is much
607 more evident.

608 ~~On the other hand, the variable interaction plots for Cr and Sn point to an interaction~~
609 ~~between $[\text{Fe}^0]$ and [OTLE] in the upper zone of the plot, where the curves tend to intersect in the~~
610 ~~case of Cr and do so clearly for Sn.~~

611



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Figure 5.- Interaction plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

615 The response surface plot is probably the most important of those that make up the
616 graphical analysis since it graphically represents the regression equation that fits the experimental
617 data. In addition, it provides ~~very valuable~~precious information ~~both in terms of estimating to~~
618 estimate the design optimum and the influence of each operational variable on the response
619 variable.

620 In designs including three working variables, as is the case, it is necessary to fix one of
621 them and give values to the other two in the regression equations (2) to (5). In this case, it was
622 decided to take the least influential variable as fixed, assigning its optimum value. Thus, for silver,
623 the iron concentration was kept constant, while for Cu, Cr, and Sn, the NaBH₄ concentration was
624 the constant term, in all cases at their corresponding optimal values.

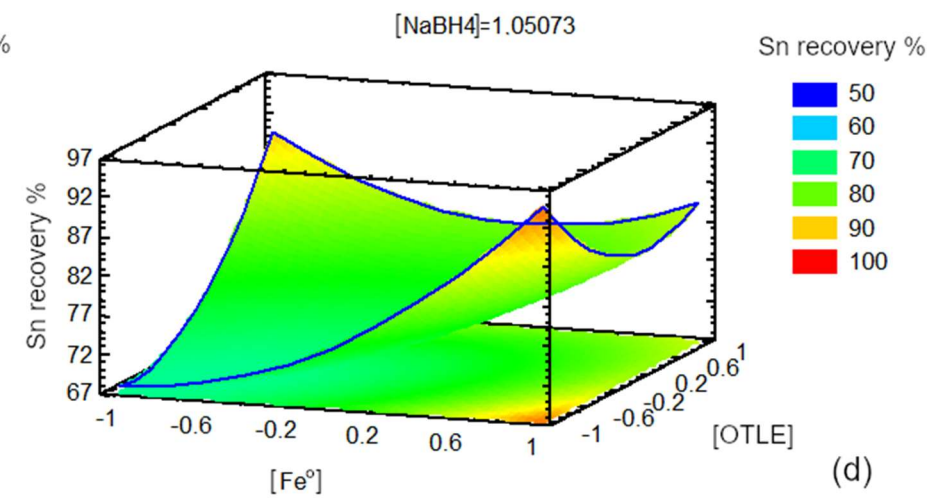
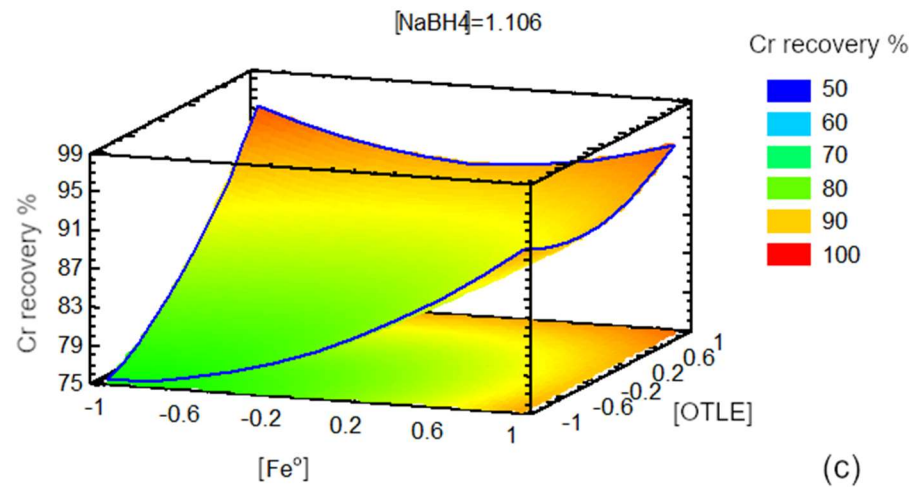
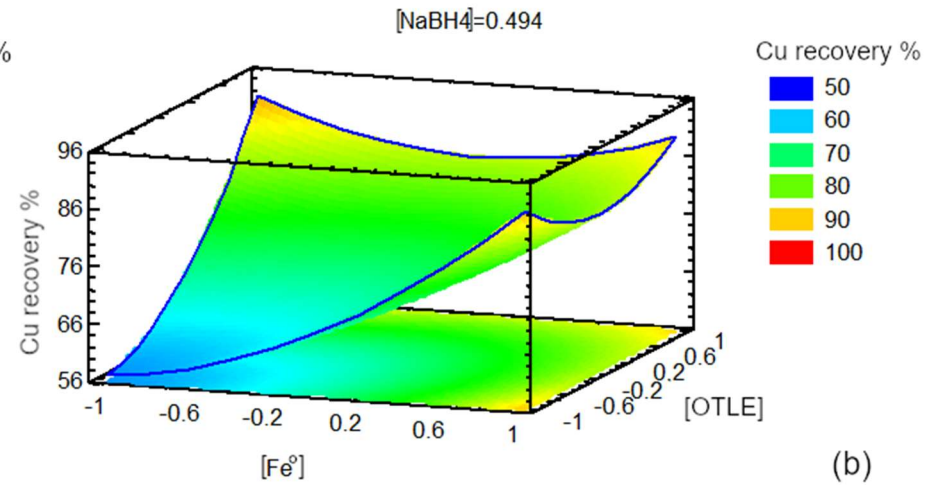
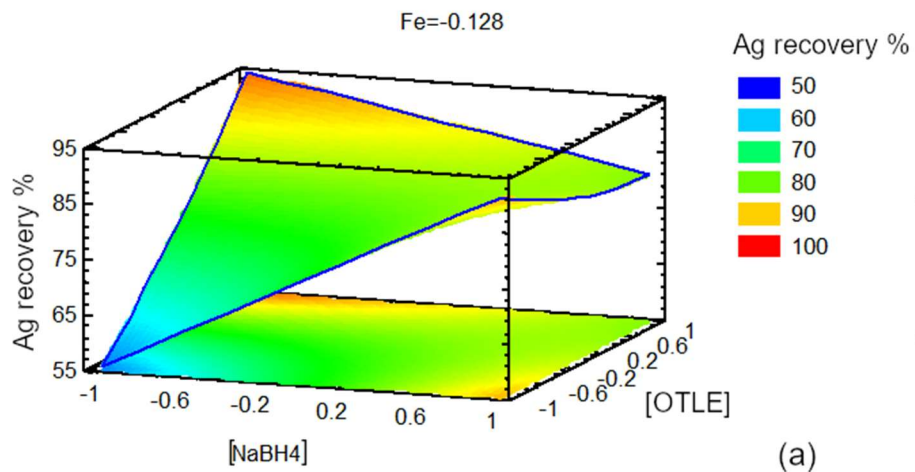
625 Figure 6 shows that the conditions to reach the optimum silver recovery correspond to
626 [NaBH₄] values close to -1 and [Fe⁰] values close to 1. However, as indicated in Table 4, the
627 optimum silver recovery is outside the study region. Despite this, conditions are found where the
628 recovery is very close to 95%. It is observed that when [NaBH₄] takes low values, [OTLE] exerts
629 a notable influence, while when it takes high values, this influence is softened. This fact
630 corroborates the ~~existence of~~ interactions between the variables, as observed in Figure 6.

631 As with silver, it can be seen in Figure 6 that ~~for copper~~ the optimum recovery value for
632 copper is outside the study region. However, it is possible to obtain a recovery of close to 91%.
633 ~~The existence of interactions is~~Interactions are also evident, in this case, between [Fe⁰] and
634 [OTLE].

635 The response surface curve for Cr shows that several zones allow recoveries greater than
636 90%. Again, the optimum falls outside the study region. However, recoveries of around 95% are
637 achieved under certain conditions, and ~~the existence of~~ interactions between [Fe⁰] and [OTLE]
638 can also be seen ~~as well~~.

639 Comparing the response surface plot for Sn with the rest of the metals, it can be observed
640 that, in general, its recovery tends to be lower. However, at values of [Fe⁰] and [OTLE] close to
641 1 and -1, respectively, 94% of tin can be recovered.

642 From all the ~~exposed above~~, it can be affirmed that the proposed method allows maximum
643 recovery of all metals above 90%, which makes the joint use of three reductants, iron, sodium
644 borohydride, and polyphenol-enriched extract, an extremely promising up-and-coming alternative
645 for the precipitation of valuable metals from PCB leachates.



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Figure 7.- Response surface plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

651 4.- Conclusions

652 From the results obtained in this work, the following conclusions may be drawn:

653 ■ An olive-tree leaf extract (OTLE) with a high polyphenols content has been prepared and
654 characterized in terms of phenolic composition. Hydroxytyrosol, tyrosol, β -hydroxy-
655 acteoside, caffeic acid, verbascoside, and oleuropein were identified as the main
656 constituents of the extract.

657

658 ■ The reductive ability of these polyphenols has been used to ~~achieve the reduction of~~reduce
659 four valuable metals present in a Printed Circuit Boards (PCB) leachate, which constitutes
660 the main novelty of this research work.

661

662 ■ The separate use of three reductants, ~~namely,~~sodium borohydride, iron, and olive-tree
663 leaves extract, makes it possible to ~~achieve a partial recovery of~~partially recover four metals
664 (namely, silver, copper, chromium, and tin) from printed circuit board acidic leachates.
665 However, none of these three reductants alone ~~is capable of~~can completely removinge any
666 of the four metals ~~present~~ in the leachate.

667

668 ■ ~~A total~~Total recovery of the four metals has been achieved by ~~the combined use~~
669 ~~of~~combining the three reductants in the appropriate concentrations.

670

671 ■ The factors that influence the recovery of silver from the leachate at most are the
672 concentrations of polyphenol-rich olive-tree leaves extract and sodium borohydride. For
673 the other three metals (Cu, Cr, and Sn), the factors that most influence the recovery
674 efficiency are the iron concentration and the polyphenol-rich olive-tree leaves extract
675 concentration. Therefore, it can be stated that the latter represents a ~~very~~promising
676 alternative to ~~the use of~~fusing conventional reductants (and, particularly, NaBH₄). This ~~latter~~
677 may result in ~~the implementation of~~implementing a greener alternative in the emerging
678 field of urban mining.

679

680 ■ ~~An optimization~~Optimization of the four metals' recovery process ~~of the four metals~~
681 ~~individually~~ has been achieved. ~~Operating under~~Under the appropriate conditions, it is
682 possible to recover 100% of all of them. However, the optimum values are outside the
683 interval (-1, +1). Hence, new experiments that better delimit the working interval are being
684 carried out with promising results.

685

686 ▪ Due to the problems implied by the presence of tin in the precipitate obtained (especially
687 concerning the formation of intermetallic compounds ~~and~~/or intermediate phases), it is
688 considered very convenient to continue the investigation by trying to maximize the
689 recovery of Ag, Cu, and Cr while keeping Sn in solution, so that it does not interfere in the
690 separation of the rest of metals.

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694 **CRedit author statement**

695 **María F. Alexandre-Franco:** Conceptualization, Methodology, Validation; **Carmen**
696 **Fernández-González:** Conceptualization, Methodology, Validation; **Gemma Reguero-Padilla:**
697 Investigation, Visualization; **Eduardo M. Cuerda-Correa:** Conceptualization; Formal analysis;
698 Writing - Original Draft, Supervision.

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960

Olive-tree polyphenols and urban mining. A greener alternative for the recovery of valuable metals from scrap printed circuit boards

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Abstract

Recycling printed circuit boards (PCBs) is becoming a source of precious metals and an alternative to conventional mining. This phenomenon is now known as "urban mining." In this work, a polyphenols-rich plant extract has been obtained from olive-tree leaves, and its ability to contribute to reducing four metals, namely, Ag, Cu, Cr, and Sn, that are present in scrap PCBs has been studied. Three reductants (NaBH_4 , Fe^0 , and the olive-tree leaves extract) have been used to recover these valuable metals. An attempt has been made to minimize the concentration of the first two, replacing them with a natural, cheaper, and less toxic reductant. To achieve this goal, a computer-assisted factorial, composed, centered, orthogonal, and rotatable statistical design of experiments (FCCORD) has been used to build the experimental matrix to be carried out in the laboratory and, next, for the statistical treatment of the results. The results show that it is possible to achieve only a partial recovery of the four metals (silver, copper, chromium, and tin) from PCBs leachates by using sodium borohydride, iron, and the extract separately. In other words, none of these three reductants alone can completely remove any of the four metals in the leachate. Nevertheless, using the statistical design of experiments, the total recovery of the four metals has been achieved by combining the three reductants in the appropriate concentrations. Hence, polyphenols-rich plant extracts in general and olive-tree leaves extract in particular can be regarded as promising coadjuvants in the rising field of urban mining.

Keywords: Urban mining; metal recovery; polyphenols; *Olea europaea*

1.-Introduction

Circularity is one of the cornerstones of the modern and future economy. Wastes that were hitherto considered of no use become new and valuable raw materials that can be given a second life. In this context, the constant increase in the acquisition of commonly used pieces of

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33 equipment, mobile phones, computers, and other devices, together with the global growth of
34 industrialization, has led to the generation of vast amounts of electrical and electronic waste (EEW
35 or e-waste). This fact may constitute a severe environmental or human health risk (Ohajinwa et
36 al., 2018; Zeng et al., 2019; Zhang et al., 2022). Planned obsolescence also profoundly impacts
37 the environment, human health, and the economy (Barros and Dimla, 2021).

38 Under the prism of the circular economy, all these risks can be turned into an opportunity.
39 Thus, the sustainability of the electronics industry, which is compromised by the scarcity of
40 natural resources, can benefit from the high value-added materials that can be recovered from the
41 waste it generates. To this end, it is necessary to develop more efficient recycling processes. (Silva
42 et al., 2018).

43 Printed circuit boards (PCBs) are the most important component of electronic circuits.
44 They constitute approximately 4-7% of the weight of e-waste. PCBs are often not recycled at all
45 or, at best, only a part is recycled to recover the precious metals due to their economic value (Mir
46 and Dhawan, 2022). PCBs are mainly composed of (a) 30% polymers (styrene-acrylonitrile,
47 styrene, polystyrene, polyamide, polypropylene, high impact polystyrene, acrylonitrile-
48 butadiene-styrene, or acrylonitrile-butadiene-styrene polycarbonate, among others); (b) 30% of
49 ceramic materials (mainly silica, alumina and calcium oxide); and (c) 40% of metals whose
50 concentration varies depending on the electrical device. On average, their content is 8-38% Fe,
51 10-27% Cu, 2-10% Al, 1-3% Pb, 0.3- 2% Ni, 200-3000 ppm Ag, 20-5000 ppm Au and 10-200
52 ppm Pd (Arshadi et al., 2018). These values are 20-250 times larger than the natural occurrence
53 of the metals in the Earth's crust in the form of natural ores (Zhou et al., 2021). Considering the
54 current technological demand and the depletion of resources, recycling these metals instead of
55 their extraction is extremely beneficial to such an extent that it has given rise to the phenomenon
56 known as "urban mining" (Dutta et al., 2016). Apart from these valuable metals, PCBs also
57 contain elements such as Pb, Hg, As, Sb, and Cd, which are highly toxic.

58 For this reason, the recycling of PCBs has become an immediate necessity. However,
59 even though it is considered a hazardous waste, it is frequently inadequately managed. Many
60 developing countries in Asia and mainly in Africa are the leading destinations for a plethora of
61 second-hand or end-of-life electronic devices from the rest of the World, thus giving rise to an
62 enormous pollution hazard (Ádám et al., 2021; Konaté et al., 2022). Due to the heterogeneous
63 nature of this waste, the recycling process of PCBs is particularly complex. In addition, while in
64 developed countries efforts are being made to provide standards for the management and
65 regulation of e-waste, unfortunately, in developing countries, such a regulation, if it exists, is
66 scarce and lax.

67 Moreover, many receiving countries in Asia and Africa lack the necessary facilities and
68 expertise for their treatment. Hence, e-waste is frequently incinerated, which releases highly toxic
69 gases and metals into the environment (Dórea, 2021; Rajarao et al., 2014; Wu et al., 2020).
70 Alternatively, e-wastes in general and PCBs in particular end up being re-sent to developed
71 countries, where more advanced technologies -namely, pyrometallurgical or hydrometallurgical
72 processes- and facilities are available for recycling. However, these recycling processes have
73 several drawbacks that exclude them from the so-called "sustainable" or "green" chemistry.

74 These drawbacks include excessive energy use, cost, and pollutant emissions. Alternative
75 processes, such as bio-leaching, have been proposed (Yaashikaa et al., 2022). Another innovative
76 method for recovering precious metals due to lower reagent consumption is electrolysis, which
77 combines leaching, electrolytic extraction, and electrowinning. Nevertheless, it is considered
78 immature (Choubey et al., 2021; Li et al., 2019; Qiu et al., 2020).

79 Different traditional methods for recovering noble metals are described in the literature
80 (Wu et al., 2017). Particularly, in hydrometallurgical processes, conventional reduction processes
81 are carried out by displacement precipitation or cementation, in which Fe powder is used as a
82 reductant (Sethurajan et al., 2019). The main advantage of Fe versus Zn is that iron is less
83 polluting than zinc, and the excess can be quickly recovered due to its magnetic properties. The
84 standard reduction potentials of Zn and Fe are -0.76 and -0.44 V, respectively. These values are
85 lower than those of Ni, Pb, Cu, Ag, and Au (i.e., -0.26, -0.13, +0.34, +0.80, and +1.50 V,
86 respectively). Thus, if Zn or Fe is used as a reductant, Ni or Pb will be reduced and precipitated
87 along with gold, silver, and copper (Gurung et al., 2013).

88 Moreover, the simultaneous presence of Sn and Ag in the leachate reduction product is
89 undesired due to the formation of an intermetallic compound, Ag_3Sn . Hence, it seems particularly
90 useful to keep as much Sn in the solution as possible or, in other words, to minimize its
91 precipitation from the leachate.

92 Another conventional reductant is sodium borohydride which, despite its widespread use,
93 is a known pollutant that may have repercussions on health and the environment (Norouzi et al.,
94 2020). Reduction with reagents of natural origin such as polyphenols from plant extracts (e.g.,
95 olive-tree, alperujo, coffee, tea, etc.) is more benign, and its use can also contribute to solving the
96 problem of waste generation in massive quantities (Balaji et al., 2021). This latter constitutes an
97 exciting field of study as it minimizes the use of other more expensive reducing agents with highly
98 harmful effects on the environment.

99 However, to make the hydrometallurgical reduction of valuable metals from PCBs waste
100 a more sustainable process, using more benign, naturally-occurring reductants constitutes an
101 excellent alternative. In this connection, polyphenols are among the most versatile and best-

102 known natural reductants. In terms of chemical structure, polyphenols contain more than one
103 phenol group. Polyphenols reduce cardiovascular diseases and improve health (Quiñones et al.,
104 2012) due to their ability to moderate enzymatic activities. The phenolic groups they possess can
105 act directly by capturing unpaired electrons from reactive oxygen species (ROS), thus generating
106 less reactive species. Hence, they are known primarily as antioxidant compounds that inhibit or
107 delay oxidative damage caused by cellular respiration leading to free radicals. Thus, chemically
108 speaking, polyphenols are excellent candidates to be used as reducing agents in various processes.

109 On the other hand, different industrial wastes such as seeds, peels of various fruits, or
110 cereals contain large amounts of polyphenols and can be regarded as renewable raw materials
111 (Fahmy et al., 2018). Particularly, using olive-tree leaf extracts as a source of polyphenols is
112 feasible due to its abundance, singularly in Extremadura (SW Spain), and its availability
113 throughout the year. Furthermore, the presence of different kinds of polyphenols such as
114 phenylpropanoids, secoiridoids, and flavonoids in olive-tree leaves extract has been reported in
115 the literature (le Tutour and Guedon, 1992; Michel et al., 2015).

116 To the best of the authors' knowledge, although some preliminary results dealing with the
117 use of polyphenols in urban mining and metal recovery processes have been published in the last
118 few years (Arif et al., 2017; Inoue et al., 2015), the use of this natural extract as a coadjuvant in
119 the recovery of valuable metals from PCB leachates has not been reported in the literature to date.
120 Hence, the purpose -and the main novelty- of this work is the development of experimental
121 procedures for the extraction, precipitation, and possible recovery of the maximum amount of
122 metals such as silver, copper, chromium, and tin by reduction of leachates from the treatment of
123 PCBs, using reductants from the natural extract of olive-tree leaves to minimize the use of
124 conventional reductants (Fe^0 and NaBH_4). In this way, the process will be much more
125 environmentally friendly and affordable as the use of agro-industrial waste is optimized. The
126 statistical design of experiments is used to determine the influence of different operational
127 variables on the metal recovery efficiency.

128

129 **2.-Materials and methods**

130 *2.1- Leaching of the scrap printed circuit boards*

131 PCBs were supplied by a local e-waste recycling industry, MOVILEX, already crushed
132 and with a thermal pre-treatment to eliminate part of the Sn that is commonly found in the solder
133 joints. Initially, 12.5 g of crushed PCBs was weighed, and HNO_3 (69%, PanReac-AppliChem,
134 Spain) and Type-II analytical grade water (Wasserlab Ecomatic, Spain) was added in a 1:3 ratio
135 and then refluxed for two hours at 60°C , thus obtaining the leachate fraction simply by
136 decantation. Nitric acid was used as the lixiviant agent to ensure that, due to its strong oxidizing

137 character, even the noble -least reactive- metals initially present in PCBs are leached in cationic
138 (oxidized) form.

139 2.2.- *Characterization of the PCBs leachate*

140 The content of different metals in the PCBs leachate was analyzed by Inductively Coupled
141 Plasma-Mass Spectrometry (ICP-MS) with the aid of an Agilent Tech 7900 equipment coupled
142 to a dynamic range orthogonal detector system (ODS), a high-frequency hyperbolic quadrupole,
143 and a 4th generation reaction octopole system. The collision gas and the argon for the plasma are
144 99.999% pure and have been supplied by Praxair (Madrid, Spain).

145 As internal standards, 400 $\mu\text{g}\cdot\text{L}^{-1}$ rhodium, palladium, and indium solutions were
146 continuously fed into the apparatus employing a three-channel peristaltic pump. The samples were
147 diluted at 1:10000 with ultrapure water due to the expected high Cu concentrations in the % (P/P)
148 range. The apparatus was calibrated with several standards prepared from certified commercial
149 multi-elemental dilutions.

150 2.3.- *Extraction of polyphenols from olive-tree leaves and determination of the polyphenols* 151 *content.*

152 The olive-tree leaves were collected in the town of Arroyo de la Luz and subsequently
153 pre-treated. Firstly, the leaves were washed with water to eliminate possible impurities and dried
154 as much as possible with filter paper. Next, they were placed inside an oven (Selecta-P, Spain) at
155 60°C until constant weight to ensure dryness.

156 Approximately 12.5 g of dry olive-tree leaves were weighed to prepare the natural extract
157 and refluxed for 30 minutes in 250 mL of Type-II analytical grade water, keeping the temperature
158 below 80°C throughout the extraction process. Once this time elapsed, the system was allowed to
159 cool down to room temperature and filtered.

160 A qualitative analysis of the composition of the natural extract was performed following
161 a method previously described in the literature (Dobrinčić et al., 2020). Samples were firstly
162 filtered using 0.45 μm nylon membrane filters. Next, an HPLC system (Agilent Technologies
163 HPLC 1260 Series, Santa Clara, CA, USA) equipped with a UV/Vis-Photo Diode Array Detector
164 (DAD) and a Luna C18 column (5 μm , 250 mm x 4.6 mm, 100 Å, Phenomenex, Torrance, CA,
165 USA) was used to separate and identify the polyphenols present in the sample. Two different
166 mobile phases were used. The first one (A) consisted of 0.1% formic acid in water (v/v), whereas
167 the second one (B) was constituted of 0.1% formic acid in methanol. Also, different gradients
168 were used throughout the experiment, namely: 0–3 min, 10% B; 3–30 min, 50% B; 30–40 min,
169 60% B; 40–45 min, 60% B; 45–50 min, 100% B; 50–60 min, 10% B. A constant flow rate of 1

170 mL·min⁻¹ was used in all cases. The column temperature was kept constant at 30°C; the injection
171 volume was 20 µL and DAD operated at λ=280 nm.

172 For clarity purposes, as the extract consisted of a mixture of different polyphenolic
173 compounds, it was considered more convenient to determine the total polyphenols content in the
174 leaf extract. Quantification was carried out by UV-VIS spectrophotometry using the Folin-
175 Ciocalteu assay (Tomás-Barberán et al., 2001). The method is based on the reaction between
176 phenolic compounds and Folin's reagent at basic pH, achieved by adding the necessary amount
177 of Na₂CO₃. Folin's reagent in this assay consists of a solution of sodium tungstate and sodium
178 molybdate in phosphoric acid. When reduced by the phenolic groups, the yellow
179 phosphomolybdotungstic acid (formed by both salts in an acidic medium) gives rise to an intense
180 blue complex, whose absorbance was determined spectrophotometrically with the aid of a
181 Shimadzu UV-1800 Ultraviolet/Visible scanning spectrophotometer (Cole-Parmer, United
182 States).

183 It is worth noting that quantification was made on the base of a gallic acid standard line.
184 Hence, the concentration of polyphenols was obtained as gallic acid equivalents. The
185 experimental procedure to obtain the standard line was as follows: solutions of different
186 concentrations (ranging from 2.3 to 11.7 mg/L) of gallic acid standards were prepared in 25 mL
187 flasks from a 196 mg/L stock solution. Next, 0.5 mL of Folin's reagent and 10 mL of 7.5% Na₂CO₃
188 were added to these solutions, and the addition of ultrapure water completed the volume. Flasks
189 were kept in the dark for 1 hour. Next, the absorbance was measured, at a fixed wavelength of
190 740 nm, against a blank prepared in the same way but without gallic acid.

191 Once this calibration line was obtained, the quantification of polyphenols in the olive-tree
192 leaves extract was performed. 0.1 mL extract was taken, and 0.5 mL of Folin's reagent and 10 mL
193 of Na₂CO₃ were added, and after keeping the solution for one hour in the absence of light, the
194 absorbance was measured at 740 nm.

195 *2.4- Experimental design*

196 To analyze the influence of the three operational variables, namely, the concentrations of
197 NaBH₄, Fe⁰, and natural reductant (olive-tree leaves extract, OTLE), on the recovery of the four
198 metals, a factorial, composite, central, orthogonal, and rotatable experimental design (FCCOR)
199 was used. The experimental design consists of 8 factorial experiments, six axial experiments, and
200 nine replicates of the central experiment, resulting in an experimental matrix of 23 runs.

201 For the use of the statistical design of experiments to be effective, it is of the utmost
202 importance to adequately delimit the intervals between which the operating variables will be
203 located. For this, it is necessary to draw on the previous experience of the research team or results
204 already described in the literature. As indicated in the *Introduction* section, the authors are not

205 aware of any other similar studies published in the literature to date, so when establishing the
 206 working intervals, a series of previous experiments had to be carried out, which will be described
 207 in the *Results and discussion* section. The information obtained from these previous experiments
 208 was used to determine the working intervals, which gave rise to the experimental matrix shown
 209 in Table 1. This table lists the coded and natural values of the operational variables for each
 210 experiment.

211 Table 1.- Coded and natural values of the operational variables for each of the 23 runs
 212 of the experimental matrix.

Run	Coded values			Natural values		
	[NaBH ₄]	[Fe ⁰]	[OTLE]	[NaBH ₄] (M)	[Fe ⁰] (M)	[OTLE] Eq. ppm
1	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
2	0	-1.68179	0	1.9·10 ⁻²	0	88
3	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
4	1	1	-1	3.1·10 ⁻²	3.4·10 ⁻²	35
5	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
6	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
7	1	-1	1	3.1·10 ⁻²	8.5·10 ⁻³	140
8	1.68179	0	0	3.8·10 ⁻²	2.1·10 ⁻²	88
9	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
10	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
11	-1	-1	1	7.8·10 ⁻³	8.5·10 ⁻³	140
12	-1	-1	-1	7.8·10 ⁻³	8.5·10 ⁻³	35
13	0	1.68179	0	1.9·10 ⁻²	4.2·10 ⁻²	88
14	-1	1	1	7.8·10 ⁻³	3.4·10 ⁻²	140
15	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
16	0	0	-1.68179	1.9·10 ⁻²	2.1·10 ⁻²	0
17	1	-1	-1	3.1·10 ⁻²	8.5·10 ⁻³	35
18	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
19	0	0	1.68179	1.9·10 ⁻²	2.1·10 ⁻²	175
20	1	1	1	3.1·10 ⁻²	3.4·10 ⁻²	140
21	0	0	0	1.9·10 ⁻²	2.1·10 ⁻²	88
22	-1.68179	0	0	0	2.1·10 ⁻²	88
23	-1	1	-1	7.8·10 ⁻³	3.4·10 ⁻²	35

213

214

215 2.5.- *Experimental procedure for the recovery of metals.*

216 In all experiments, 25 mL of the leachate and different volumes of the natural extract are
217 added in 50 mL flasks, making up the final volume with Type-II analytical grade water. This
218 solution was placed in a beaker, and the solid reagents previously weighed were added, following
219 the order established in the experimental matrix. The final solution was magnetically stirred for 1
220 hour and left to stand. The experiments with the conventional reductants gave rise to speedy
221 reactions, whereas when the natural reductant was used, the reaction took about 8 hours. Hence,
222 the experiments were allowed to stand for 12 hours, and ICP-MS was used to analyze the final
223 solutions following the same procedure described in section 2.2. Taking into account the
224 concentration of each metal in the PCBs leachate before and after the reduction treatment, the
225 removal efficiency (*R.E.*, in percent) can be calculated as:

$$226 \quad R.E = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

227 where C_0 and C_t are the concentrations of metal in the initial leachate and the treated solution,
228 respectively.

229

230 3.- Results and Discussion

231 3.1.- *Characterization of the PCBs leachate*

232 In the first instance, the most significant possible number of elements of the Periodic
233 Table was scanned through a semi-quantitative analysis to determine which of them were found
234 in the most significant proportion in the leachate sample. The results obtained in the ICP-MS
235 analysis are presented in Figure S1 (Supplementary material) and listed in Table 1. It should be
236 noted that, for technical reasons, it was impossible to analyze the silicon and gold present in the
237 leachate samples.

238 Table 1.- Semi-quantitative ICP-MS analysis of the PCBs leachate

Atomic weight	Element	Concentration (ppm)
27	Al	117
47	Ti	32
52	Cr	137
55	Mn	78
56	Fe	2072
59	Co	60
60	Ni	2002

Atomic weight	Element	Concentration (ppm)
63	Cu	44903
66	Zn	499
69	Ga	25
88	Sr	47
90	Zr	1700
93	Nb	29
107	Ag	231
118	Sn	3273
121	Sb	162
139	La	94
140	Ce	69
141	Pr	85
146	Nd	92
157	Gd	46
165	Ho	20
208	Pb	2206
209	Bi	37
232	Th	18

239

240 From the results collected in Table 1, it can be stated that the contents of the different
241 metals present in the PCBs leachate are comparable with others previously found in the literature
242 (Li et al., 2018). The PCB leachate used in this work contains, in addition to the vast majority of
243 the metals found by the referred authors, several high value-added elements such as lanthanides
244 (Pr, Nd, Gd, Ho) as well as Nb. Due to their unique properties, rare earth elements (REE) improve
245 the performance of many technological devices in terms of energy consumption, efficiency, etc.
246 Hence, REE find essential applications in optical devices, magnetic materials, and electronics
247 (Balaram, 2019). Hence, these elements have become strategic materials in recent years, and their
248 presence in scrap PCBs has been reported and analyzed for valorization purposes. The REE
249 content of the scrap PCBs used in this work is similar to those previously reported in the literature
250 (Anshu Priya and Hait, 2018; Gonzalez Baez et al., 2022; Tantawi and Hua, 2021).

251 Because of the above, it can be concluded that the PCB waste used in this work can be
252 regarded as an extremely attractive and promising source of a wide variety of metals. In the
253 following sections, the ability of a natural reducing agent such as the polyphenols present in olive

254 leaves to precipitate several high value-added metals (namely, Ag, Cu, Cr, and Sn) will be
255 analyzed in an attempt to minimize the use of other more expensive and environmentally
256 damaging reductants.

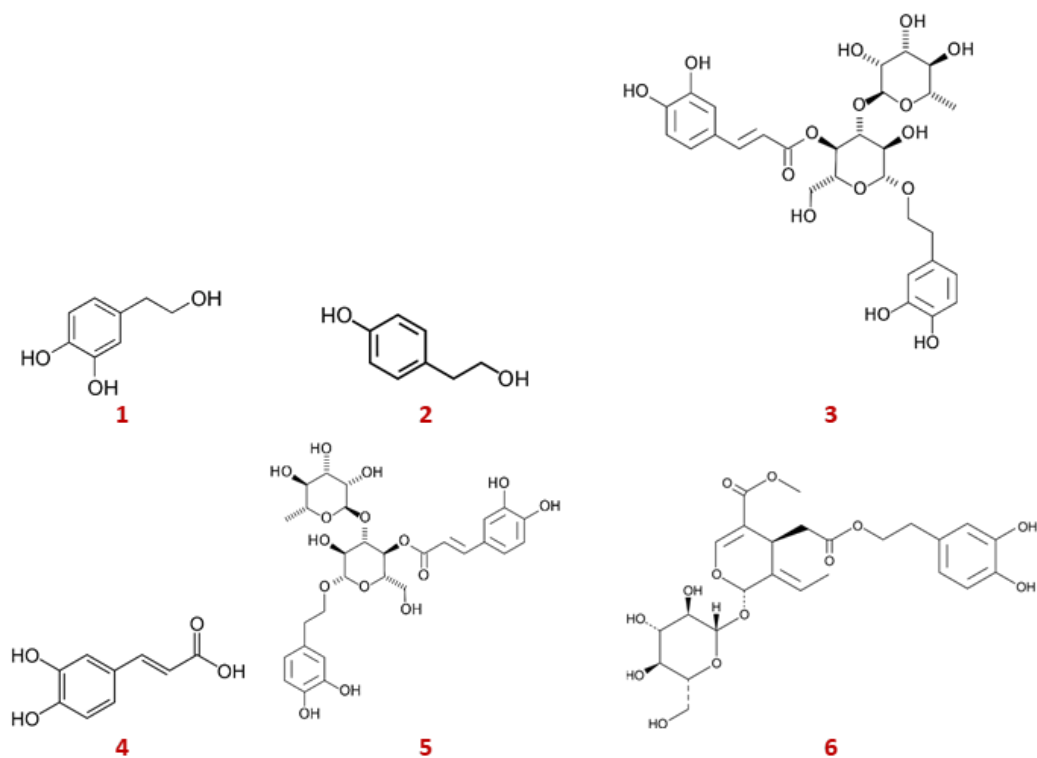
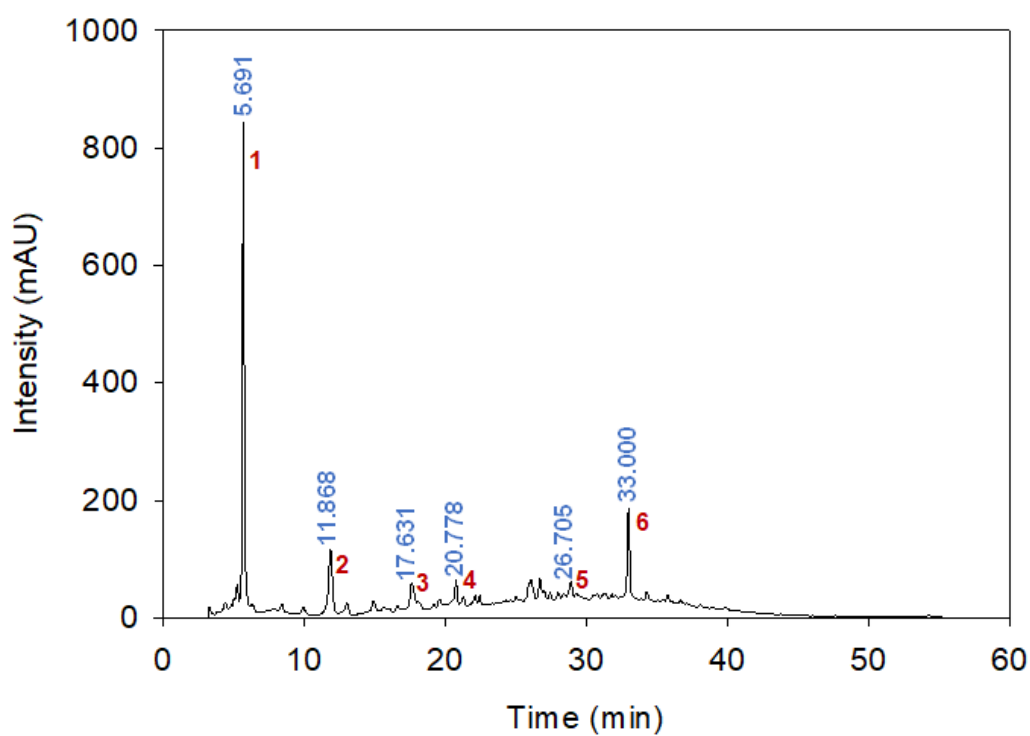
257 3.2.- *Determination of the polyphenols content in the olive-tree leaves extract.*

258 The polyphenols content in the olive-tree extract was determined as described in section
259 2.3. Figure 1 (top) shows the HPLC chromatogram of the extract. The prominent peaks in the
260 HPLC-DAD have been assigned according to the literature (Balli et al., 2021; Dobrinčić et al.,
261 2020; Richard et al., 2011). The predominant polyphenols found in the extract are hydroxytyrosol,
262 tyrosol, β -hydroxy-acteoside, caffeic acid, verbascoside, and oleuropein. The corresponding
263 peaks have been labeled in the chromatogram, and their structures are shown in Figure 1 (bottom).
264 This phenolic composition is coherent with previous results reported in the literature (Agatonovic-
265 Kustrin et al., 2021; González et al., 2019; Oliveira et al., 2021; Quirantes-Piné et al., 2013; Topuz
266 and Bayram, 2022).

267 As indicated under section 2.3, for simplicity and comparison purposes, the total
268 polyphenols content in the OTLE sample was quantified as gallic acid equivalents. The
269 experimental results showed that the value of A_{740} reached 2.101. This value falls outside the
270 standard line determined as described above; hence, it was necessary to perform a previous
271 dilution of 1:10.

272 Different volumes of this diluted olive extract were then taken (between 200 and 400
273 mL), and the procedure referred to above was repeated. The values of A_{740} so obtained are listed
274 in Table S2 (Supplementary material). From these values, and according to the standard line
275 obtained as described in section 2.3, the values of polyphenol concentration expressed as
276 equivalent mg of gallic acid per liter of OTLE were calculated. These values are also included in
277 Table S2.

278 According to these values, and considering the dilutions performed, the average
279 polyphenol content (expressed as equivalent mg of gallic acid) in the olive-tree leaves extract was
280 731 ± 12 mg/L.



281

282 Figure 1.- HPLC-DAD profile of OTLE (top) and structure of the primary polyphenols

283 identified (bottom). 1. Hydroxytyrosol; 2. Tyrosol; 3. β-Hydroxy-acteoside; 4. Caffeic acid; 5.

284 Verbascoside; 6. Oleuropein. Retention times are shown in blue.

285 If we assume that all the polyphenols contained in the olive-tree leaves were extracted,
286 taking into account that the extract was obtained from 12.5 g of dry leaves that were kept at reflux
287 in 250 mL of milli-Q water, the polyphenol content (also expressed in equivalent mg of gallic
288 acid) per kg of olive-tree leaves has also been calculated, obtaining a value of 58496 ± 993 mg/kg.
289 These results are of the same order, or somewhat higher, than others previously reported in the
290 literature (Bilgin and Şahin, 2013; Canabarro et al., 2019; Goulas et al., 2010; Yancheva et al.,
291 2016).

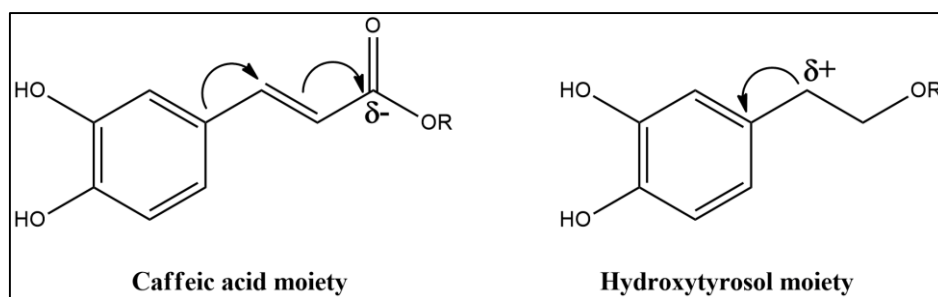
292 *3.3.- Some insights into the reduction process of metals with olive-tree leaf extract polyphenols*

293 Due to the structural complexity of the polyphenols in the OTLE and the occurrence of
294 many polyphenols, the task of proposing a tentative mechanism for the reduction of metals
295 initially present in the PCB waste leachate is far from being easy. However, as revealed by a
296 review of the literature previously published on the redox behavior of polyphenolic compounds,
297 the occurrence of the catechol moiety is a crucial aspect (de Souza Gil et al., 2013; Li et al., 2021;
298 Moghaddam et al., 2007; Nenadis et al., 2007; Oliveira-Neto et al., 2016; Salas-Reyes et al., 2011;
299 Trabelsi et al., 2004).

300 From the structures of the primary polyphenols found in the OTLE (Figure 2, bottom), it
301 can be seen that all of them -except tyrosol (**2**) – contain the catechol moiety. Furthermore, it is
302 to be noticed that both β -hydroxy-acteoside (**3**) and verbascoside (**5**) show two catechol moieties
303 in their structures. In both cases, one of the catechol moieties is analogous to caffeic acid (**4**) and
304 the other to hydroxytyrosol (**1**). These two moieties may exhibit a slightly contrasting redox
305 behavior because of the occurrence of disparities in electron densities due to the different groups
306 attached to the catechol.

307 On the one hand, as the carboxylic group of the caffeic acid substructure is not directly
308 bound to the aromatic ring, a negative charge withdrawing effect can be assigned to the stretching
309 of the -C=C- bond.

310 On the other hand, contrarily, the presence of an alkyl chain in the hydroxytyrosol
311 substructure of (**3**) and (**5**) gives rise to a positive inductive effect that results in an increase of
312 electron density on the aromatic ring. Hence, there are some slight differences in the redox
313 behavior of the catechol moiety in caffeic acid (**4**), hydroxytyrosol (**1**), and, consequently, in the
314 two polyphenols that contain both structures, namely β -hydroxy-acteoside (**3**) and verbascoside
315 (**5**). Such differences are shown in Scheme 1 (de Souza Gil et al., 2013).



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317

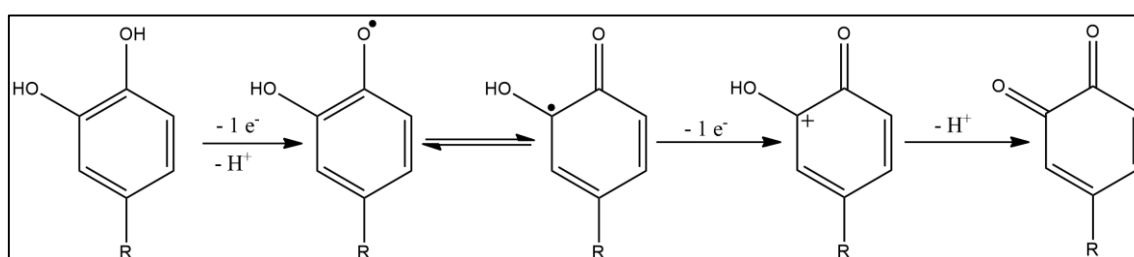
Scheme 1

318

319

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As indicated above, the catechol moiety is the main responsible for the reductive character of most of the polyphenols detected in the leaf extract. It is commonly accepted that the oxidation of the catechol moiety follows a two-step mechanism, as depicted in Scheme 2.



321

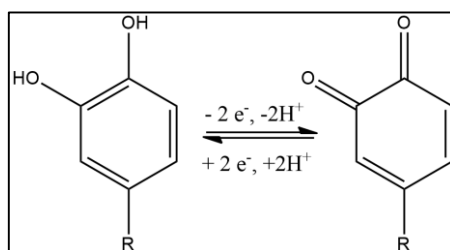
322

Scheme 2

323

324

The overall catechol oxidation mechanism, commonly known as the two-electron and two-proton mechanism, is a reversible process that can be summarized as shown in Scheme 3.



325

326

Scheme 3

327

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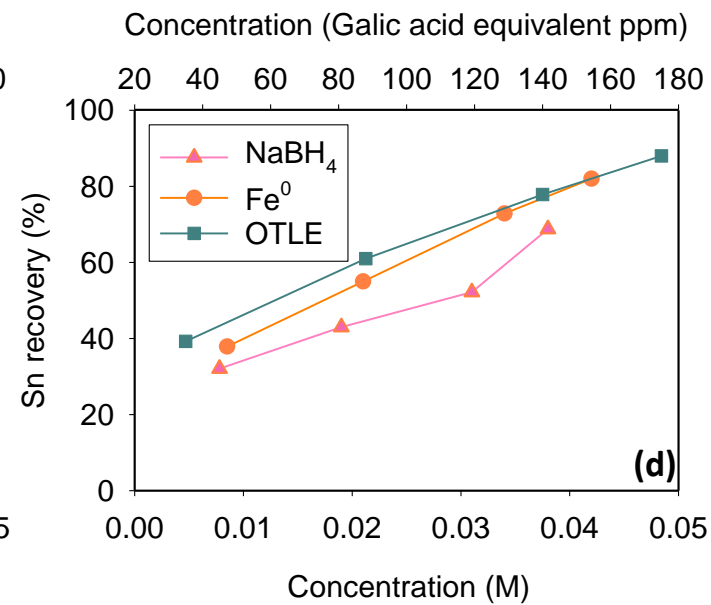
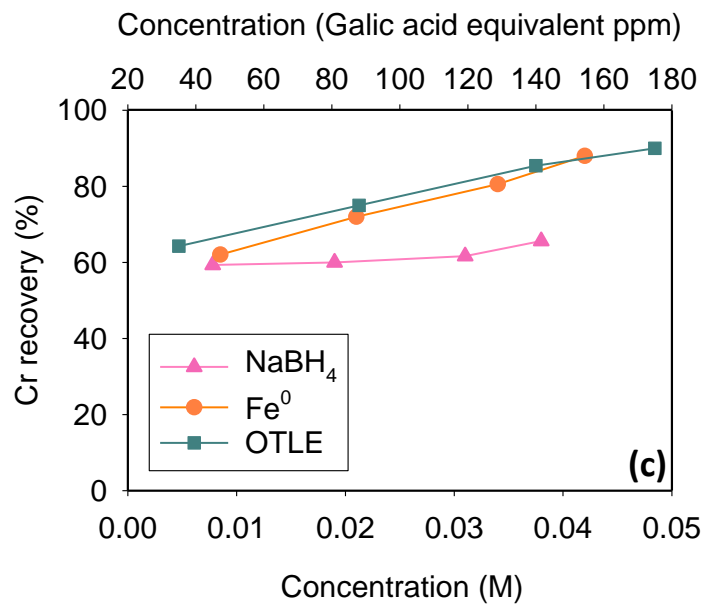
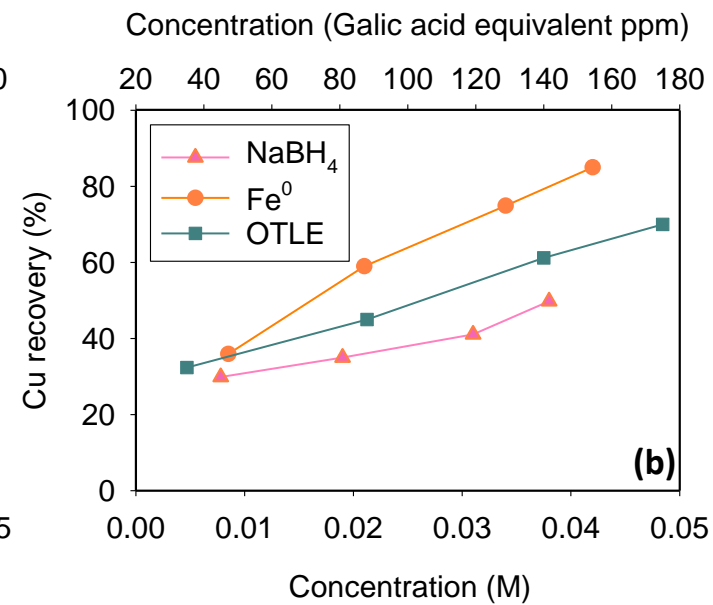
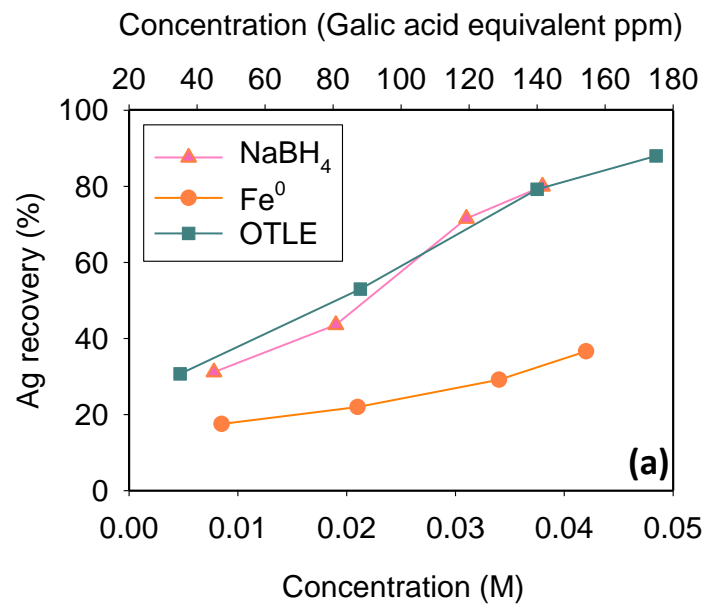
The reduction potentials of the polyphenols present in the OTLE range between -0.1 and -0.5 V (Li et al., 2021; Nenadis et al., 2007; Oliveira-Neto et al., 2016; Trabelsi et al., 2004). Thus, taking into account that the reduction potentials of the metals under study are +0.8 V, +0.34 V, +0.32 V, -0.14 V, and +0.014 V for the Ag^+/Ag^0 , $\text{Cu}^{2+}/\text{Cu}^0$, $\text{Cr}^{6+}/\text{Cr}^0$, $\text{Sn}^{2+}/\text{Sn}^0$, and $\text{Sn}^{4+}/\text{Sn}^0$ pairs, respectively, it may be concluded that polyphenols alone would be able to reduce virtually all these metal from their positive oxidation states to oxidation state zero. Only Sn^{2+} could be more difficult to reduce by the weakest reductant polyphenols. However, the concomitant occurrence of more potent oxidizing polyphenols makes it possible to reduce all the cations under

335 study that were initially present in the PCBs leachate, as corroborated by the preliminary
336 experiments that will be described in the next section.

337 *3.4.- Preliminary recovery experiments. Determination of the intervals of the operational*
338 *variables*

339 Before performing the 23 runs that constitute the experimental matrix, a set of 12 previous
340 trials were carried out, in which the effect of each reductant on the response variable (metal
341 recovery, in this case) was analyzed separately. For each metal, an experiment was carried out in
342 which a single reductant was introduced, and its concentration was varied within a relatively wide
343 working range. The results obtained are shown in Figure 2. First, it should be borne in mind that
344 the concentrations of NaBH₄ and Fe⁰ are expressed in molarity, whereas that of the polyphenols-
345 rich extract is indicated in equivalent ppm of gallic acid. Therefore, two abscissa axes have been
346 used in the figure, the lower one corresponding to the first two reductants and the upper one to
347 OTLE.

348



349

350

351

Figure 2.- Influence of operating variables on metal recovery. Ag (a), Cu (b), Cr (c), and Sn (d).

352 Figure 2 shows a higher metal recovery with increasing reductant concentration
353 individually. However, for silver, an increase in Fe^0 concentration does not result in a significant
354 increase in metal recovery, whereas iron is the reductant that results in the highest copper
355 recovery. This fact is consistent with the importance of the cementation process in the extractive
356 metallurgy of copper, regardless of whether the reductant is elemental iron or scrap (Roba et al.,
357 2018). On the other hand, NaBH_4 is effective for the recovery of silver (almost to the same extent
358 as the polyphenols-rich extract), while for copper, the use of NaBH_4 does not represent a
359 significant advantage.

360 For Cr and Sn, the influence of the reductants in the recovery process follows the order
361 polyphenol-rich extract > Fe^0 > NaBH_4 . Using a strong reductant such as NaBH_4 , in the case of
362 chromium, leads to a metal recovery efficiency of 60-65%. This latter is in line with other results
363 previously reported in the literature (Kuan et al., 2010; Xiu and Zhang, 2009). These authors
364 highlight the difficulties in recovering chromium from PCB leachates. However, better results are
365 achieved using Fe^0 or polyphenols-rich extract, with the polyphenolic extract being the only
366 reducing agent whose increase in both cases results in remarkably more efficient metal recovery.
367 This fact suggests that the "unconventional" reductant proposed for use in this work is very
368 promising for application as an alternative to the other two reductants, Fe^0 and NaBH_4 .

369 In recent years there has been a growing interest in developing methods for the
370 precipitation or flotation of metals from e-waste leachates. However, progress in this direction is
371 scarce to date (de Souza et al., 2018; Jadhao et al., 2016; Lu and Xu, 2017; Rigoldi et al., 2019;
372 Suja et al., 2018; Yang et al., 2017). In addition, as far as the literature review conducted for this
373 report was able to determine, there is no evidence of the use of polyphenols obtained from plant
374 extracts as a reductant for the precipitation of metals present in PCBs, which is the major novelty
375 of this work.

376 However, although recovery efficiencies close to 85-90% are achieved using some of the
377 reductants separately, it is worth noting that none can achieve a total recovery of the metal in the
378 leachate. Therefore, it seems reasonable to analyze the effect of the three reductants together to
379 achieve a full -or nearly full- recovery of the four metallic elements individually. This latter shows
380 that the selective precipitation of these elements is a challenging topic.

381 *3.5.- Analysis of the statistical design of experiments*

382 The use of FCCOR experimental design makes it possible (i) to analyze the relationship
383 between the selected operational variables; (ii) to predict the experimental conditions that give
384 rise to an optimum value of each of the target variables, both individually and jointly; and (iii) to
385 determine and examine the response surface and contour plots.

386 The analysis of the results in a statistical design of experiments consists of two parts:
 387 numerical analysis and graphical analysis. Both analyses are presented in the following sections,
 388 the target variables being the recovery percentages of each of the metals.

389 *3.5.1- Numerical analysis*

390 The numerical analysis can be, in turn, divided into three sections: analysis of variance
 391 (ANOVA), deduction of a regression equation, with the corresponding analysis of its correlation
 392 coefficients, and determination of the experimental conditions that give rise to an optimum for
 393 the target variable. The results of the ANOVA test are shown in Table 2.

394

395 Table 2.- Results of the analysis of variance (ANOVA). Factors with a statistically significant
 396 influence are marked in bold characters

Factor	Ag	Cu	Cr	Sn
	p-Value	p-Value	p-Value	p-Value
A: NaBH ₄	0.0008	0.0010	0.0855	0.0106
B: Fe ⁰	0.1967	0.0000	0.0049	0.0007
C: OTLE	0.0001	0.0000	0.0003	0.0012
AA	0.8116	0.0011	0.0464	0.0002
AB	0.6885	0.0764	0.9329	0.4472
AC	0.0000	0.6159	0.8603	0.1445
BB	0.0278	0.0000	0.0013	0.0004
BC	0.0986	0.0001	0.0128	0.0035
CC	0.0588	0.0000	0.0069	0.0004

397

398 From the results in Table 2, it can be stated that in the case of Ag recovery, four of the
 399 nine factors have a statistically significant effect on the response variable (i.e., they show a p-
 400 value of less than 0.05). In the case of Cu and Sn recovery, seven factors have a statistically
 401 significant effect on the response variable, and in the case of Cr, six do. On the other hand, R²
 402 shows values of 92.02% (Ag), 96.56% (Cu), 88.70% (Cr), and 92.69% (Sn), which indicate that
 403 the proposed model can explain the variability of the experimental data in a more than acceptable
 404 way. This assertion is corroborated by the observed vs. residuals plots depicted in Figure S2

405 (Supplementary material). These plots illustrate the relationship between the experimental values
 406 and those predicted by the model. Therefore, these plots provide information about the dispersion
 407 of the experimental data of the target variable with respect to the calculated values. Thus, the
 408 closer the experimental data (squares) are to the bisector of the first quadrant, the better the fit.

409 On the other hand, the mean absolute error (MAE) is defined as the average difference
 410 between the experimental value and the one predicted by the model. MAE values are 2.31%,
 411 2.21%, 2.14%, and 2.61% for the percentage recovery of Ag, Cu, Cr, and Sn, respectively. These
 412 values, again, corroborate the excellent fitting of the experimental data to the proposed model.

413 Finally, the Durbin-Watson (DW) statistic makes it possible to detect whether the order
 414 in which the experiments composing the matrix have been carried out influences the results
 415 obtained. In other words, the DW statistic analyzes whether the randomization of the experimental
 416 sequence is working properly. Since the p-value of this statistic is greater than 0.05 for all the
 417 experimental matrices (p Ag = 0.5440; p Cu = 0.2250; p Cr = 0.4848; p Sn = 0.9442) it can be
 418 stated that there is no autocorrelation in the residuals and the randomization has been effective.

419 The second -and essential- functionality of the statistical design of experiments is that it
 420 allows obtaining the regression equations and correlation coefficients (the polynomial coefficients
 421 that adjust the experimental values). For the case of the recovery of Ag, Cu, Cr, and Sn, the
 422 equations are as follows:

$$423 \quad \text{Ag recovery (\%)} = 78.9356 + 5.37455 [\text{NaBH}_4] + 1.64187 [\text{Fe}^0] + 6.97847 [\text{OTLE}] - \\ 424 \quad 0.249439 [\text{NaBH}_4]^2 - 0.684678 [\text{NaBH}_4] \cdot [\text{Fe}^0] - 12.2653 [\text{NaBH}_4] \cdot [\text{OTLE}] + 2.56132 [\text{Fe}^0]^2 - \\ 425 \quad 2.98468 [\text{Fe}^0] \cdot [\text{OTLE}] + 2.13705 [\text{OTLE}]^2 \quad (2)$$

$$426 \quad \text{Cu recovery (\%)} = 65.0431 + 4.77628 [\text{NaBH}_4] + 9.40635 [\text{Fe}^0] + 8.10258 [\text{OTLE}] + \\ 427 \quad 4.00689 [\text{NaBH}_4]^2 - 2.9617 [\text{NaBH}_4] \cdot [\text{Fe}^0] + 0.7867 [\text{NaBH}_4] \cdot [\text{OTLE}] + 6.79997 [\text{Fe}^0]^2 - \\ 428 \quad [\text{Fe}^0] \cdot [\text{OTLE}] + 6.90603 [\text{OTLE}]^2 \quad (3)$$

$$429 \quad \text{Cr recovery (\%)} = 77.7098 + 2.03118 [\text{NaBH}_4] + 3.72446 [\text{Fe}^0] + 5.50394 [\text{OTLE}] + \\ 430 \quad 2.05116 [\text{NaBH}_4]^2 + 0.129402 [\text{NaBH}_4] \cdot [\text{Fe}^0] + 0.270598 [\text{NaBH}_4] \cdot [\text{OTLE}] + 3.87197 [\text{Fe}^0]^2 - \\ 431 \quad 4.3956 [\text{Fe}^0] \cdot [\text{OTLE}] + 3.00576 [\text{OTLE}]^2 \quad (4)$$

$$432 \quad \text{Sn recovery (\%)} = 58.1805 + 4.80375 [\text{NaBH}_4] + 7.15226 [\text{Fe}^0] + 6.70089 [\text{OTLE}] + \\ 433 \quad 7.14284 [\text{NaBH}_4]^2 - 1.73298 [\text{NaBH}_4] \cdot [\text{Fe}^0] - 3.44202 [\text{NaBH}_4] \cdot [\text{OTLE}] + 6.61251 [\text{Fe}^0]^2 - \\ 434 \quad 7.98298 [\text{Fe}^0] \cdot [\text{OTLE}] + 6.50644 [\text{OTLE}]^2 \quad (5)$$

435 The positive or negative sign that precedes each of the different coefficients indicates the
 436 favorable or unfavorable influence of the change of one or two of the operational variables on the
 437 target variable (metal recovery).

438 In general, it can be stated that the higher the absolute value of the coefficient, the greater
 439 the influence of the operational variable (or combination of variables) on the response variable.
 440 This assertion is numerically corroborated if each factor's percent effect (P_n) on the recovery
 441 efficiency of the different metals from PCB leachate is obtained (Abdessalem et al., 2008).
 442 According to these authors, P_n can be calculated as

$$443 \quad P_n (\%) = \frac{\beta_n^2}{\sum \beta_n^2} \times 100 \quad (6)$$

444 where β_n^2 represents the squared value of each of the coefficients in equations (2) to (5) and $\sum \beta_n^2$
 445 is the sum of all the squared values of these coefficients.

446 Table 3 summarizes the P_n (%) values obtained for the four studied metals. From the data
 447 contained in Table 3, it can be concluded that Ag recovery from PCB leachates is mainly governed
 448 by the concentrations of sodium borohydride (A, 11.5%) and OTLE (C, 19.38%) and, particularly,
 449 by its concomitant effect (A·C, 59.87%). On the contrary, the concentration of NaBH₄ plays a
 450 much less remarkable role in the recovery of the remaining metals, which are mainly conditioned
 451 by the concentrations of iron and the dose of polyphenol-rich olive-tree leaves extract. This latter
 452 deserves to be highlighted since these two reductants are much more benign from an
 453 environmental standpoint than NaBH₄.

454

455 Table 3.- Percent effect of each factor on the recovery efficiency of the different metals
 456 from PCB leachate.

Factor	P _n (%)			
	Ag	Cu	Cr	Sn
A: [NaBH ₄]	11.50	6.09	4.30	6.89
B: [Fe ⁰]	1.07	23.60	14.46	15.28
C: [OTLE]	19.38	17.51	31.58	13.41
A ²	0.02	4.28	4.39	15.24
A·B	0.19	2.34	0.02	0.90
A·C	59.87	0.17	0.08	3.54
B ²	2.61	12.34	15.63	13.06
B·C	3.55	20.95	20.14	19.04
C ²	1.82	12.72	9.42	12.64

457

458 The third -and perhaps most important- functionality of the statistical design of
 459 experiments resides in the fact that it is capable of predicting, at least theoretically, the
 460 experimental conditions that would lead to an optimization of the target variable (in this case, a
 461 maximization of the recovery efficiency of each of the four metals here studied). The optimal

462 coded and natural values of the operating variables leading to such a theoretical optimum for the
 463 four experimental designs are shown in Table 4.

464

465 Table 4.- Coded and real optimum values for the recovery of Ag, Cu, Cr, and Sn from
 466 PCB leachate.

Variable	<u>Ag optimum</u>		<u>Cu optimum</u>		<u>Cr optimum</u>		<u>Sn optimum</u>	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real
[NaBH ₄]	-0.380	0.015 M	0.494	0.025 M	1.106	0.031 M	1.051	0.031 M
[Fe ⁰]	-0.128	0.019 M	1.649	0.042 M	0.607	0.029 M	1.111	0.035 M
[OTLE]	1.527	168 ppm	0.891	134 ppm	1.681	175 ppm	-1.128	58 ppm

467

468 Under the conditions shown in Table 4, the model predicts 100% recovery for each
 469 studied metal. These theoretical optima were experimentally corroborated, and the recovery of
 470 the four metals was above 95% in all cases, which is indicative of the predictive value of the
 471 proposed model.

472 It is interesting to note that the conditions under which the maximum recovery of each of
 473 the metals is achieved are very different from each other, so the simultaneous optimization of the
 474 recovery of all four metals is, *a priori*, difficult to achieve. However, as indicated above, it is
 475 interesting to try to maximize silver recovery while minimizing tin precipitation to avoid the
 476 formation of the intermediate phase or the intermetallic compound, Ag₃Sn. The theoretical values
 477 of the three variables leading to these results are shown in Table 5.

478

479 Table 5.- Coded and real optimum values for maximizing Ag recovery and minimizing
 480 Sn recovery from PCB leachates simultaneously.

Variable	<u>Optimum values</u>	
	Coded	Real
[NaBH ₄]	0.116	0.020 M
[Fe ⁰]	-1.187	0.006 M
[OTLE]	-0.958	38 ppm

481

482 Operating under these experimental conditions, the model predicts a 75% recovery of
 483 Ag, while 51% of Sn would precipitate together. Again, these results were corroborated
 484 experimentally. In this case, the value of Ag recovery was slightly higher (79%) than the one

485 predicted by the model, whereas tin precipitation (52%) was of the same order as the theoretical
486 one.

487 Therefore, it can be stated that the concomitant use of the polyphenols-rich olive-tree
488 leaves extract with other traditional reductants (sodium borohydride and iron) appears promising
489 to achieve a more benign separation of valuable metals from PCB leachates. Nevertheless, it also
490 seems necessary to persevere in trying to find a Sn-selective reductant that can remove Sn from
491 the leachate (ideally in a complete manner) and then proceed to the precipitation of silver under
492 the conditions foreseen in Table 4.

493 3.5.2- Graphical analysis

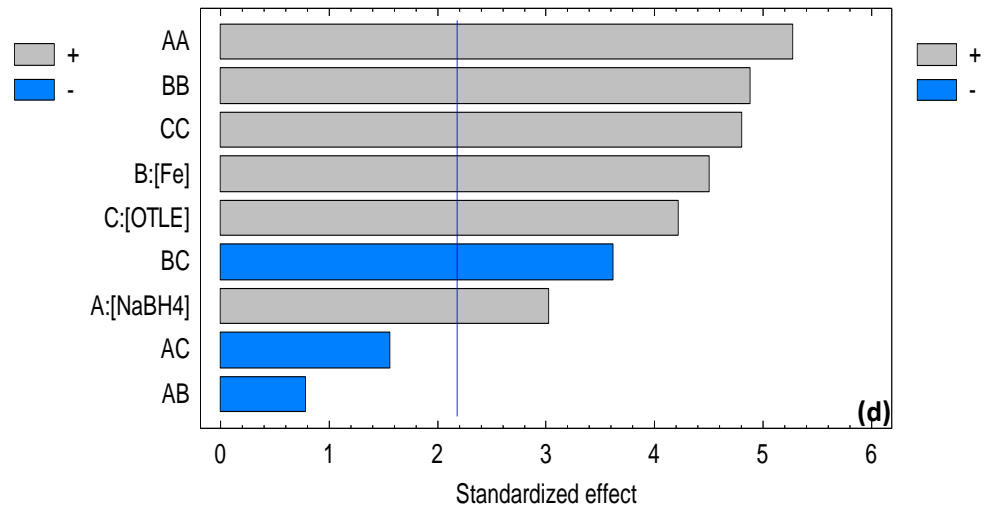
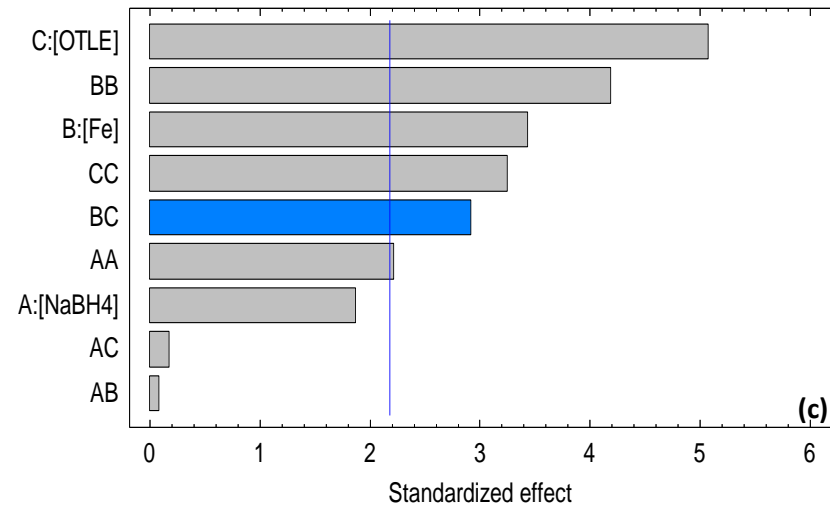
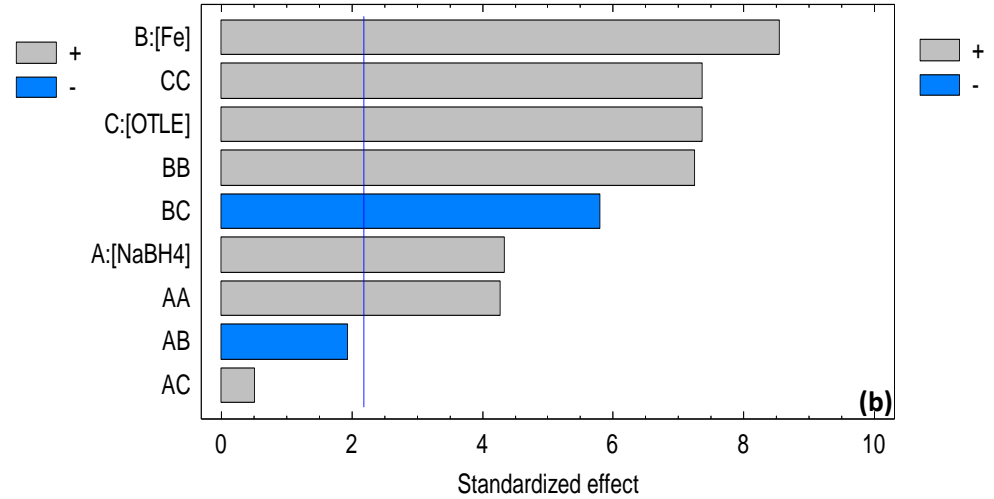
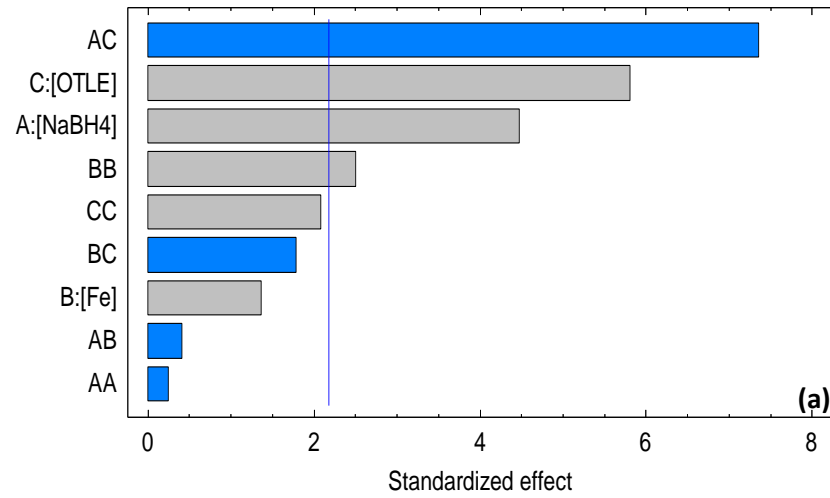
494 The graphical analysis of the results obtained in the statistical design of experiments has
495 been carried out by studying the Pareto, main effect, interactions, and response surface plots

496 Pareto factor plots can be considered a graphical representation of the ANOVA test.
497 Horizontal bars represent the effect of each variable (i.e., the concentration of NaBH₄, Fe⁰, or
498 OTLE, and all their combinations). The vertical line shown corresponds to a p-value of 0.05.
499 Those factors whose bar exceeds this line are considered to exert a statistically significant effect
500 on the response variable with a probability of 95%. Such variables appear in the ANOVA test
501 (Table 2) with a p-value below 0.05.

502 In addition, the positive or negative influence exerted by each variable is shown in the
503 graph. Thus, the working variables represented by a gray bar have a positive effect on the target
504 variable, while those with blue bars exert a negative effect on the target variable. As expected,
505 the factors that have a positive influence on the metal recovery efficiency appear in equations (2)
506 to (5) preceded by a "+" sign, while those factors that have a negative influence on the response
507 variable are preceded by a "-" sign in these equations.

508 Pareto factor plots for the recovery of the four metals present in the PCB leachate are
509 shown in Figure 3.

510



511

512

Figure 3.- Pareto factor plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

513 As seen in the Pareto plot for Ag, the effects involving the concentrations of OTLE and
514 NaBH_4 , the square of the Fe^0 concentration, and the product of the concentration of polyphenols
515 and NaBH_4 are statistically significant with a probability of 95%.

516 Similarly, for Cu, the effects involving the concentration of Fe^0 , NaBH_4 , and OTLE and
517 the squares of each of them, as well as the product of the concentration of polyphenols and Fe^0 ,
518 are statistically significant.

519 For Cr, [OTLE], [Fe^0], and [NaBH_4], all their quadratic terms and the product of the
520 concentration of OTLE and Fe^0 exert a statistically significant effect.

521 Finally, for Sn, OTLE concentration, Fe^0 , the square of the OTLE concentration, the
522 square of [NaBH_4], and the product of [OTLE] and [Fe^0] exert a statistically significant effect on
523 the metal recovery.

524 The main effects plot shows the influence of the different operational variables
525 individually, i.e., OTLE, Fe^0 , and NaBH_4 concentration, on the target variable. The graph
526 represents the theoretical value of the recovery efficiency calculated by equations (2) to (5) if only
527 the values of one of these variables were modified, keeping the other two at their central coded
528 value (i.e., 0). Hence, arbitrary coded values -comprised between -1 and +1- are given to the
529 variable whose influence is being analyzed, and the theoretical recovery efficiencies provided by
530 the model are calculated as indicated. In this way, it can be graphically seen how each of the
531 variables involved in the process individually influences the metal recovery efficiency. The main
532 effects plots corresponding to the four metals are shown in Figure 4.

533 For Ag, it can be seen that the most influential variables on recovery are [NaBH_4] and,
534 particularly, [OTLE]. Concerning [Fe^0], this has a lesser influence, presenting a minimum
535 recovery of 79% in the central part of the operating range.

536 In the case of Cu, the three variables show similar behavior. Although a minimum
537 recovery is observed, it should be noted that as concentrations increase, Cu recovery becomes
538 higher. In this particular case, iron is the most influential reductant.

539 For Cr and Sn, it is inferred that an increase in concentration from a specific coded value
540 produces an increase in recovery efficiency, with Cr being higher. In general, the variables that
541 have the most significant influence on recovery are OTLE and iron concentrations.

542

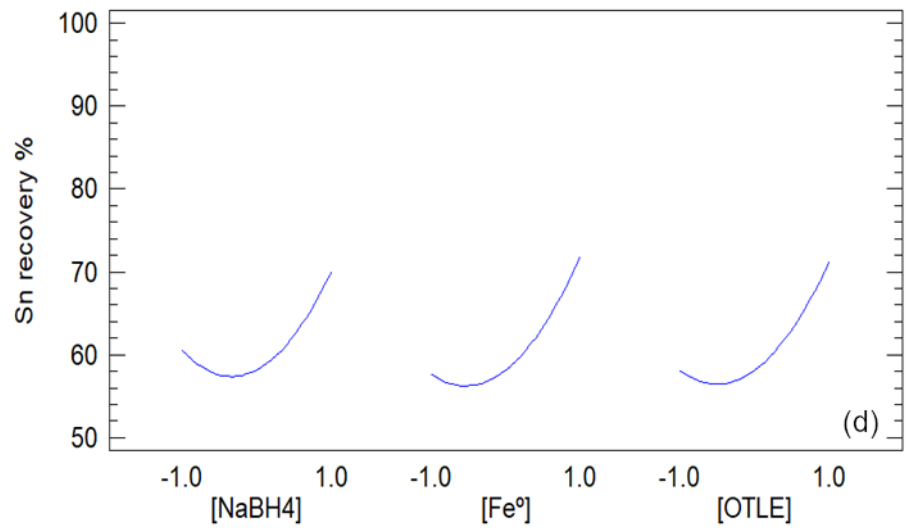
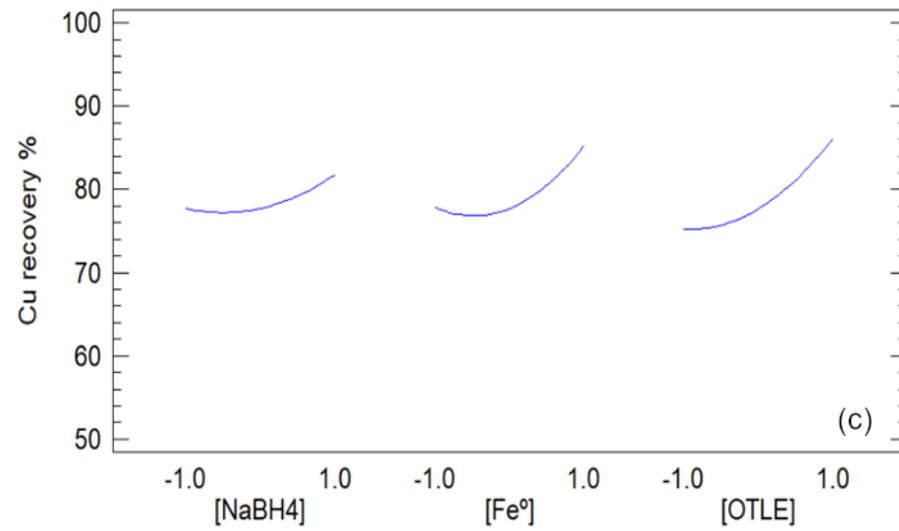
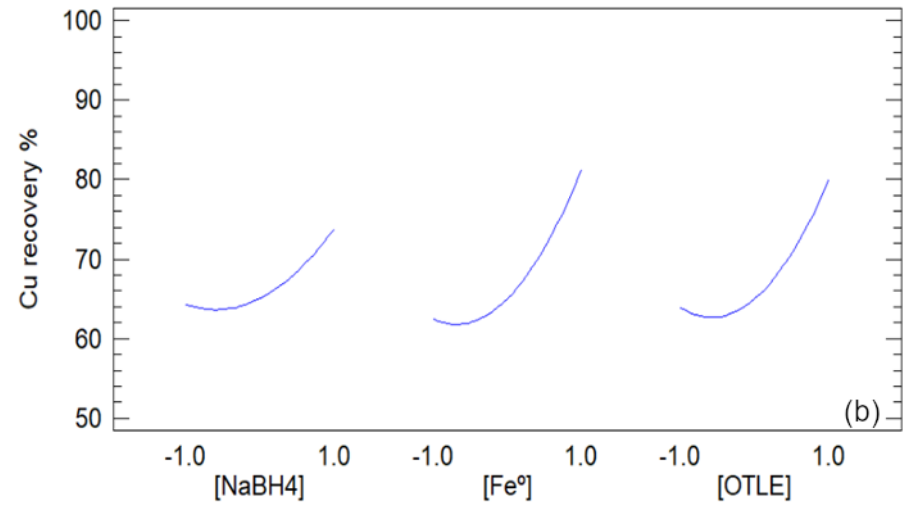
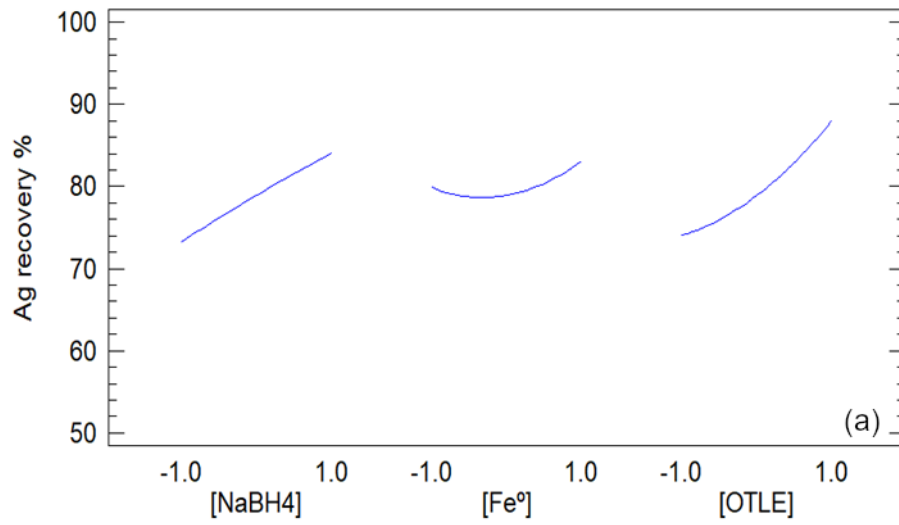


Figure 4.- Main effect plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

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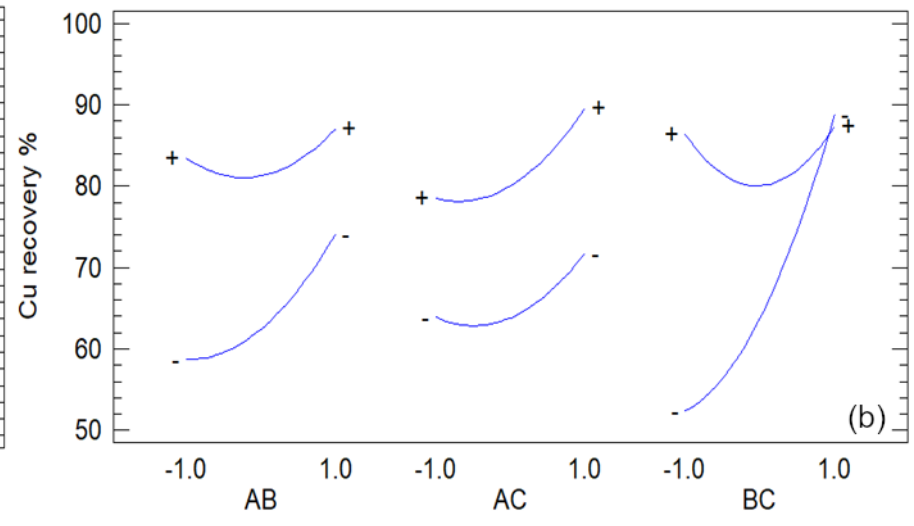
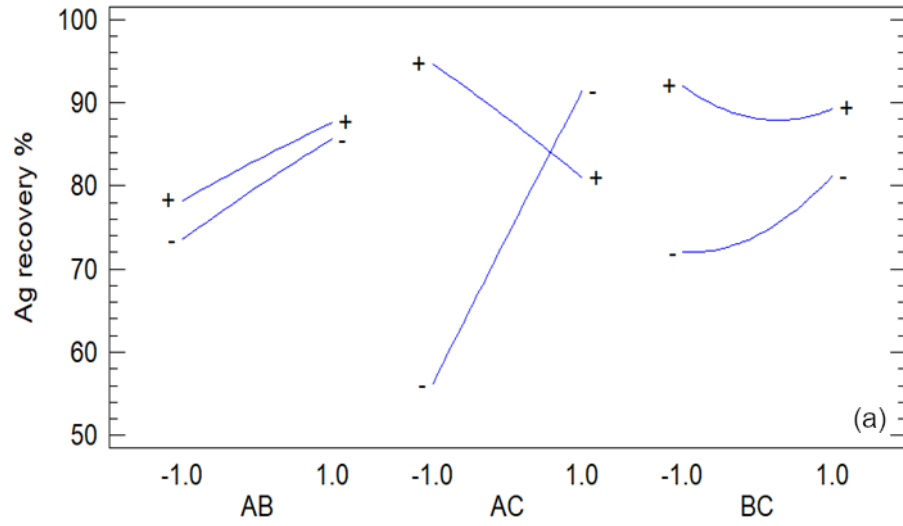
547 Another plot of great interest is the interaction graph (Figure 5). This plot makes it
548 possible to study whether the change in an operational variable affects (or not) how the other
549 variables influence the target variable, i.e., whether or not there are interactions between the
550 operational variables. This latter is one of the most valuable potentialities of the statistical design
551 of experiments and justifies, from a methodological standpoint, its use as opposed to the
552 traditional method of modifying "one factor at a time" (OFAT method). The OFAT method is
553 valid if it is assumed that interactions do not exist between operational variables, i.e., that a change
554 in one of them does not affect the way how the rest influence the target variable.

555 In the graph of interaction between variables, where A, B, and C correspond to $[\text{NaBH}_4]$,
556 $[\text{Fe}^0]$, and [OTLE], respectively, each pair of curves represents the evolution of the percentage of
557 metal recovery when (a) arbitrary coded values -comprised between -1 and +1- are given to one
558 of the variables; (b) the second variable is fixed at a coded value either equal to +1.0 (maximum
559 value, line marked with the "+" sign) or equal to -1.0 (minimum value, line marked with the "-"
560 sign); and (c) the third variable remains constant at its central value (i.e., 0). This way, the
561 theoretical recovery efficiencies are calculated from equations (2) to (5), considering what has
562 just been exposed. If the curves of a pair of variables are parallel, the modification of one of them
563 does not affect the way how the other one influences the recovery efficiency or, in other words,
564 no interaction is found between this pair of variables. On the contrary, if two lines intersect, the
565 interaction is evident. An intermediate situation can also be found where none of the
566 abovementioned behaviors are clearly appreciated.

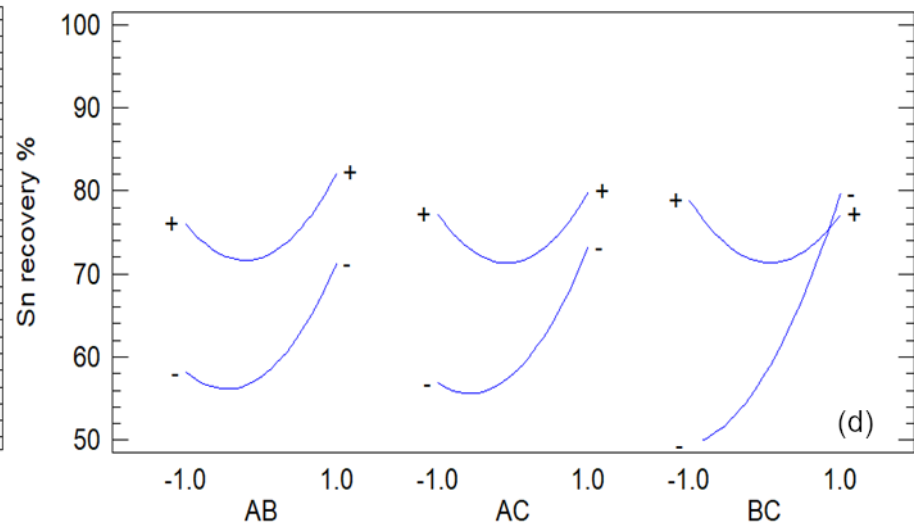
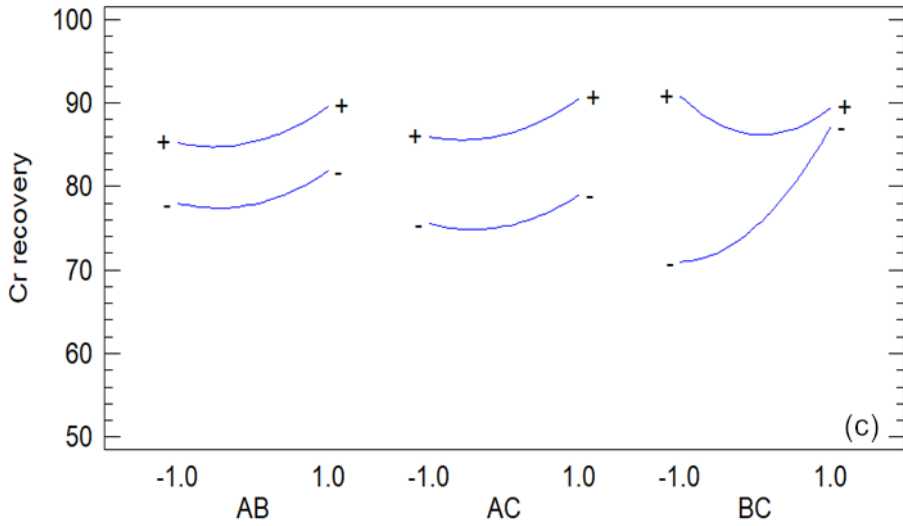
567 The data depicted in Figure 5 reveal a very different behavior for Ag and Cu. For Ag, an
568 interaction between $[\text{NaBH}_4]$ and [OTLE] is observed, giving rise to an "X-shaped" plot, or else
569 they tend to cross at one of the extremes of the operating range (in this case, the upper one). In
570 contrast, the curves are parallel or show no tendency to intersect for the other pairs of variables.

571 Unlike Ag, Cu shows a slight interaction at the end of the upper working range between
572 iron and the polyphenol-rich extract. On the other hand, for Cr, an interaction between $[\text{Fe}^0]$ and
573 [OTLE] in the upper zone of the plot is observed. For Sn, however, such an interaction is much
574 more evident.

575



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Figure 5.- Interaction plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

579 The response surface plot is probably the most important of those that make up the
580 graphical analysis since it graphically represents the regression equation that fits the experimental
581 data. In addition, it provides precious information to estimate the design optimum and the
582 influence of each operational variable on the response variable.

583 In designs including three working variables, as is the case, it is necessary to fix one of
584 them and give values to the other two in the regression equations (2) to (5). In this case, it was
585 decided to take the least influential variable as fixed, assigning its optimum value. Thus, for silver,
586 the iron concentration was kept constant, while for Cu, Cr, and Sn, the NaBH₄ concentration was
587 the constant term, in all cases at their corresponding optimal values.

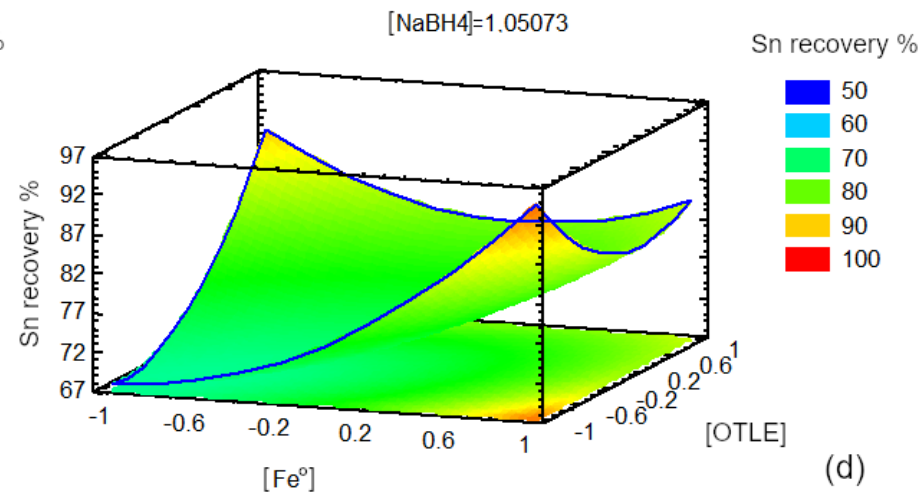
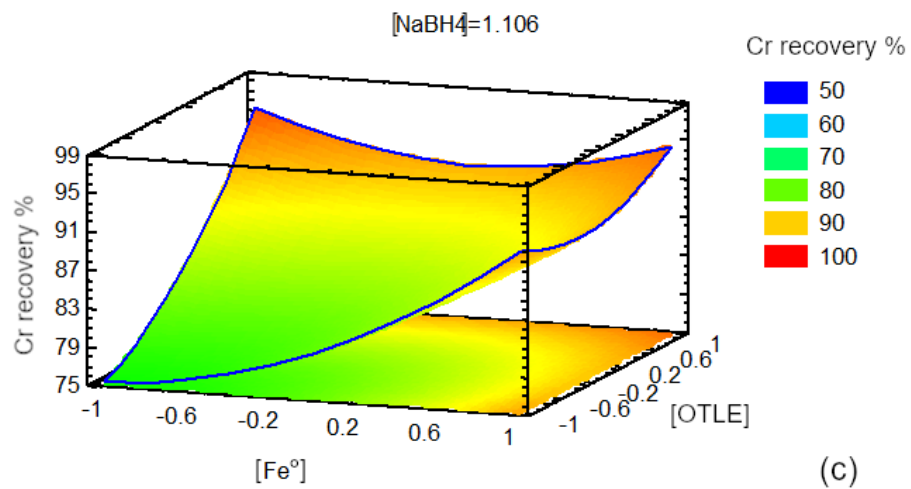
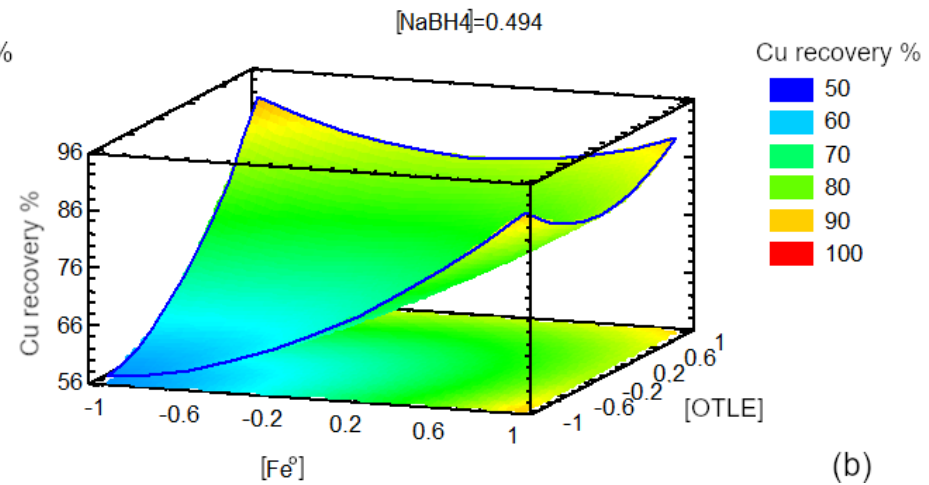
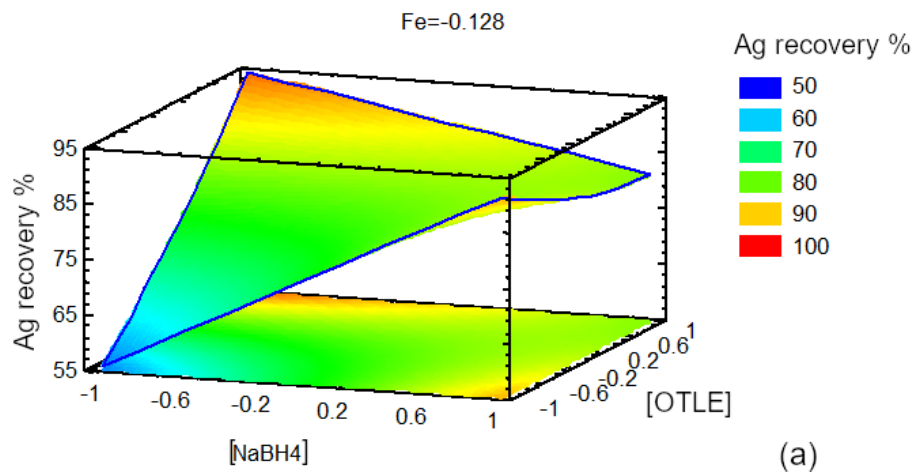
588 Figure 6 shows that the conditions to reach the optimum silver recovery correspond to
589 [NaBH₄] values close to -1 and [Fe⁰] values close to 1. However, as indicated in Table 4, the
590 optimum silver recovery is outside the study region. Despite this, conditions are found where the
591 recovery is very close to 95%. It is observed that when [NaBH₄] takes low values, [OTLE] exerts
592 a notable influence, while when it takes high values, this influence is softened. This fact
593 corroborates the interactions between the variables, as observed in Figure 6.

594 As with silver, it can be seen in Figure 6 that the optimum recovery value for copper is
595 outside the study region. However, it is possible to obtain a recovery of close to 91%. Interactions
596 are also evident, in this case, between [Fe⁰] and [OTLE].

597 The response surface curve for Cr shows that several zones allow recoveries greater than
598 90%. Again, the optimum falls outside the study region. However, recoveries of around 95% are
599 achieved under certain conditions, and interactions between [Fe⁰] and [OTLE] can also be seen.

600 Comparing the response surface plot for Sn with the rest of the metals, it can be observed
601 that, in general, its recovery tends to be lower. However, at values of [Fe⁰] and [OTLE] close to
602 1 and -1, respectively, 94% of tin can be recovered.

603 From all the above, it can be affirmed that the proposed method allows maximum
604 recovery of all metals above 90%, which makes the joint use of three reductants, iron, sodium
605 borohydride, and polyphenol-enriched extract, an up-and-coming alternative for the precipitation
606 of valuable metals from PCB leachates.



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Figure 7.- Response surface plots for the recovery of the four metals: Ag (a), Cu (b), Cr (c), and Sn (d).

612 4.- Conclusions

613 From the results obtained in this work, the following conclusions may be drawn:

614 ■ An olive-tree leaf extract (OTLE) with a high polyphenols content has been prepared and
615 characterized in terms of phenolic composition. Hydroxytyrosol, tyrosol, β -hydroxy-
616 acteoside, caffeic acid, verbascoside, and oleuropein were identified as the main
617 constituents of the extract.

618

619 ■ The reductive ability of these polyphenols has been used to reduce four valuable metals
620 present in a Printed Circuit Boards (PCB) leachate, which constitutes the main novelty of
621 this research work.

622

623 ■ The separate use of three reductants, sodium borohydride, iron, and olive-tree leaves
624 extract, makes it possible to partially recover four metals (namely, silver, copper,
625 chromium, and tin) from printed circuit board acidic leachates. However, none of these
626 three reductants alone can completely remove any of the four metals in the leachate.

627

628 ■ Total recovery of the four metals has been achieved by combining the three reductants in
629 the appropriate concentrations.

630

631 ■ The factors that influence the recovery of silver from the leachate at most are the
632 concentrations of polyphenol-rich olive-tree leaves extract and sodium borohydride. For
633 the other three metals (Cu, Cr, and Sn), the factors that most influence the recovery
634 efficiency are the iron concentration and the polyphenol-rich olive-tree leaves extract
635 concentration. Therefore, it can be stated that the latter represents a promising alternative
636 to using conventional reductants (and, particularly, NaBH_4). This latter may result in
637 implementing a greener alternative in the emerging field of urban mining.

638

639 ■ Optimization of the four metals' recovery process has been achieved. Under the appropriate
640 conditions, it is possible to recover 100% of all of them. However, the optimum values are
641 outside the interval (-1, +1). Hence, new experiments that better delimit the working
642 interval are being carried out with promising results.

643

644 ■ Due to the problems implied by the presence of tin in the precipitate obtained (especially
645 concerning the formation of intermetallic compounds or intermediate phases), it is
646 considered very convenient to continue the investigation by trying to maximize the

647 recovery of Ag, Cu, and Cr while keeping Sn in solution, so that it does not interfere in the
648 separation of the rest of metals.

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652 **CRedit author statement**

653 **María F. Alexandre- Franco:** Conceptualization, Methodology, Validation; **Carmen**
654 **Fernández- González:** Conceptualization, Methodology, Validation; **Gemma Reguero-**
655 **Padilla:** Investigation, Visualization; **Eduardo M. Cuerda-Correa:** Conceptualization; Formal
656 analysis; Writing - Original Draft, Supervision.

657

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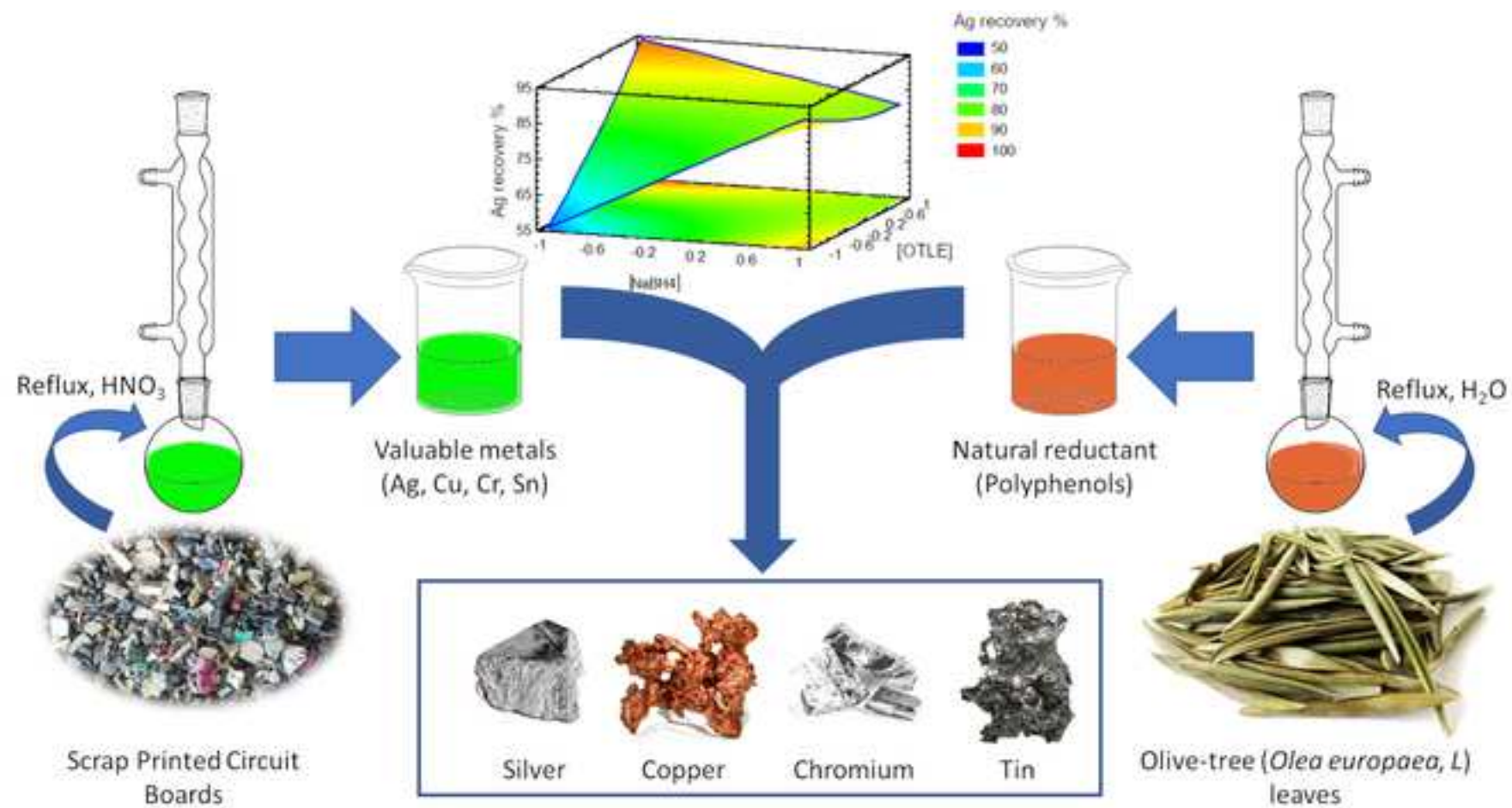
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CRedit author statement

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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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: