

Elemental copper recovery from e-wastes mediated with a two-step bioleaching process

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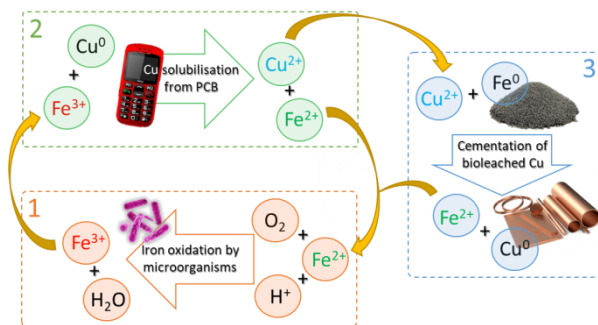
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Abstract

Copper recovery from printed circuit boards (PCB) from waste mobile phones was investigated using a two-step bioleaching process. The method consists of a first step where Fe(II) ions are biologically oxidised to Fe(III) by *Acidithiobacillus ferrooxidans*. Later, Fe (III) ions are put in contact with the PCBs for copper solubilisation. At the conditions tested in the present work, the Fe(II) bio-oxidation (first step) was almost completed in 48 h. Two different methods (filtration and sedimentation) for biomass separation before the second step were tested. No significance differences between both separation methods were observed in terms of the overall process efficiency. In both cases, using 7.5 g/L of e-waste concentration, copper recovery of 95-100% were obtained in only 48 hours. In order to test an inexpensive and environmental friendly method to recovery the copper from the leachate solution, cementation of Cu (II) with metallic iron was performed. The copper powder obtained had purity of 64.8%.

Graphical abstract



Acknowledgments

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Statement of Novelty

Bioleaching has been evaluated to recover copper from e-waste by means of a novel discontinuous process, which significantly reduced the time reported from several days to only 48 hours. Optimizing

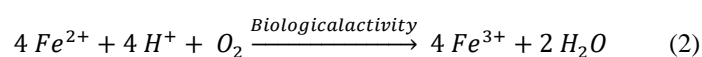
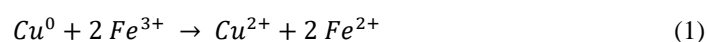
1 separately the biooxidation of Fe (II) and the subsequent copper solubilisation, it was possible to recover
2 100% of the copper in its metallic state. The reuse of streams between the different steps in a circular loop
3 enables the total metal recovery by means of a more sustainable and economic alternative with high
4 industrial potential.

6 1. INTRODUCTION

7 The increasing generation of electronic wastes is a worldwide problem. In particular, 44.7 million tons of
8 e-waste were produced in the world in 2016 and it is estimated to be more than 50 million tons by 2021
9 [1]. One of the main concerns with this type of e-waste is that they contain toxic chemicals (arsenic, lead,
10 mercury and poly-brominated flame retardants among others). On the other hand, e-waste also have a
11 significant amount of valuable metals such as copper, silver or gold, which could be recovered to be
12 reused [2]. Within the e-waste, mobile phones are one of the most important target [3]. It has been
13 reported that more than 781 million mobile phones were generated in 2015, increasing it to 877 million
14 units by 2020 [4]. In addition, it is possible to obtain 130 kg of Cu, 3.5 kg of Ag and 340 g of Au from
15 one tone of mobile phones [5]. Taking these into account, mobile phones can be considered as an
16 important source for metals extraction.

17 Currently, chemical methods such as hydrometallurgical [6] and pyrometallurgical processes, in particular
18 Rönnskar, Noranda and Umicore processes [7] are employed to recover metals from waste. Recently,
19 bioleaching has been proposed as an alternative to conventional physical-chemical processes, showing
20 important advantages such as low cost, high efficiency and environmental friendliness [8]. Bioleaching
21 process has been studied for many years in the mining field [9–11], especially when low-grade ores have
22 to be treated, due to the low cost of bioleaching process [12]. This technique, which has proven to be
23 effective in this field, has been extended for the metal extraction from other possible metals sources [13,
24 14].

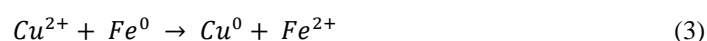
25 Bioleaching is based on the release of metals from metal concentrates, as e-waste or ores, using
26 microorganism's activity. Regarding to the microorganisms, chemoautotrophic bacteria are one of the
27 most useful to bioleach [15, 16]. They are aerobic and grow in very acidic conditions (pH, 1.5 – 3.0)
28 [17]. The microorganism has an indirect role in copper bioleaching. In fact, copper is oxidized by Fe(III)
29 ions which in turn, are reduced to Fe(II). The task of the microorganism is the oxidation of Fe(II) to
30 Fe(III), regenerating the agent responsible of copper bioleaching [8]. According to these authors, an iron
31 cycle occurs during the leaching process of copper following Eq. (1) and (2).



34 Most studies dealing with bioleaching have been performed in one step using different kind of
35 microorganisms [18–20]. In one-step bioleaching, iron oxidation and bio-mediated leaching reagent
36 recovery process itself are developed in the same reactor. However, it has been reported that the bacteria
37 could be affected by toxic compounds which could be found in the e-waste treated [21–23]. For this
38 reason, a bioleaching process carried out in two steps could be very suitable in order to avoid toxicity
39 issues and thus, improve the extraction of metals during the bioleaching [24, 25]. The goal of the first
40 step is to obtain the Fe (III) ions required in the second step to extract the copper from the PCB waste (Eq
41 1). It's important to consider that iron may be found in different speciation forms dependent on the pH
42 media [26]. So the speciation form of iron is crucial for its solubility and bioavailability by
43 microorganisms [27]. In the two steps processes, the microorganisms growth is performed in the absence
44 of electronic scrap and then, the scrap is added to the culture to carry out the leaching process [28–30]. In
45 general, the two steps method allows to leach larger amount of e-waste. However, most of the two steps
46 bioleaching experiments reported in the literature took from 3 to 15 days to obtain acceptable copper
47 recoveries [24, 28–30]. These are quite long time for an economically viable application, especially to
48 scale-up the technology as an alternative to conventional processes.

49 Once copper has been bioleached from the electronic waste, different methods can be applied in order to
50 transform copper ions in aqueous solutions into its metallic form. [31–33]. One of the simplest and lowest

1 cost method is cementation, which consists of precipitating a metal ion from a liquid solution by a more
2 reducing metal [34]. This method has been extensively used in the hydrometallurgy field. However this
3 technique has seldom been used in the bioleaching area [35, 36]. According to Dib and Makhloufi [37],
4 cementation of copper is usually performed by iron which reacts with copper ions followigEq. (3).



6 The aim of the present work was to optimize the copper bioleaching from e-waste through a two-step
7 process in order to shorten process execution times. The optimal conditions for the biological oxidation of
8 iron by the activity of *Acidithiobacillus ferrooxidans*, in the first step were established. Two different
9 methods to separate the biomass after the first-step were studied in order to reuse the biomass. In the
10 second step, copper dissolution kinetic was monitored. Finally, the cementation process was tested as the
11 simplest way to obtain copper in its metallic state from the bioleaching solution and the overall process
12 efficiency was analyzed in terms of metal recovery and time.

14 2. MATERIALS AND METHODS

16 2.1. Electronic scrap

17 The printed circuit boards (PCB) used in this study came from end-of-life mobile phones model NOKIA
18 3510. All the mobile phones used corresponded to the same model in order to homogenize the initial
19 sample. The main electronic components such as battery, resistors, capacitors and chips, among others,
20 were separated manually. Then, the PCBs were crushed and sieved and the particles between 0.2 and
21 1.00mm of diameter were collected for experimental purposes.

22 2.2. Microorganisms and mineral medium

23 The bacterial strain *Acidithiobacillus ferrooxidans* (ATCC23270) was used in the biological step. It was
24 kindly provided by the Department of Chemical Engineering from the University of País Vasco (Spain).
25 The mineral medium used in the experiments contained (in g.L⁻¹): (NH₄)₂SO₄ 3.00; K₂HPO₄ 0.50; MgSO₄
26 · 7 H₂O 0.50; KCl 0.10; Ca(NO₃)₂ · 4 H₂O 0.014 and FeSO₄·7 H₂O 30. The medium was prepared
27 dissolving all the components (except FeSO₄·7 H₂O) in 900 mL of distillate water. The pH was adjusted
28 with H₂SO₄ 10 N to pH 1.7. Then, 30 g of FeSO₄·7 H₂O were dissolved in 100 mL of distillate water and
29 the pH was also adjusted with H₂SO₄ 10 N to 1.7. After that, both solutions were mixed and the pH was
30 readjusted again to 1.7 if it was necessary.

31 2.3. Bioleaching experiments

32 Bioleaching experiments were performed in two steps. The first one consists of the biological oxidation of
33 Fe(II). Two series of experiments were carried out at initial pH 1.7 in which the pH was controlled at this
34 value during the experiment whereas in the other one, the pH was not controlled. Each flask was initially
35 inoculated with 30% of fresh culture using the medium described in the above section, using a total
36 volume of 350 mL in 500 mL baffled Erlenmeyer flask. Furthermore, an abiotic control was also
37 performed under the same conditions. The flasks were maintained at 30 °C in an orbital shaker incubator
38 at 130 rpm and the pH and the oxidation-reduction potential periodically. When all the Fe(II) had been
39 oxidized to Fe(III) by the microorganisms, it was considered that the first step was finished. Afterwards,
40 solution containing this biogenerated Fe(III) was put in contact with the e-waste. This second step was
41 performed with 350 mL of Fe(III) biogenerated solution and 2,625 g of waste in 500 mL baffled
42 Erlenmeyer flasks in an incubator at 30 °C and 130 rpm during 2 days. Samples taken every 2-3 hours
43 during the two steps were filtered and diluted before being analysed to determine the iron and/or copper
44 concentration.

46 Two different methods (filtration and sedimentation) were tested to separate the biomass from Fe(III)
47 solution before step 2 in order to reuse the biomass in step 1 and also to avoid its inhibition by the
48 possible toxic metals bioleached during the step 2. For the filtration, a 0.22 µm membrane filter of

1 cellulose acetate was used whereas for the sedimentation, the solution was transferred to a beaker and
2 after 2 hours of settling, the solution is separated from the biomass by decanting.

4 **2.4. Cementation experiments**

5 After bioleaching, Cu(II) present in the bioleached solution was reduced to metallic copper by
6 cementation. 100 mL of the bioleachate, previously filtered by 0.45µm membrane, were placed in a 250
7 mL Erlenmeyer flask with 4 g/L of iron filings (7439-89-6, *Fischer Scientific*). The process was
8 performed in an incubator at 130 rpm and 25°C. Samples of the solution were taken every hour and they
9 were filtered and diluted before being analysed to determine their Cu(II) content. When all the copper had
10 been cemented, the solution was decanted and the solid copper obtained was dried and analysed for its
11 composition as described in section 2.5.

12 **2.5. Analytical methods**

13 In order to determine the metal content in the PCB and in the copper powder obtained by cementation,
14 0.15 g of each sample were digested with 10 mL of HNO₃:HCl (3:1) at 150 °C for 15 minutes in a
15 microwave apparatus (*Microwave System, Milestone, Italy*). Cu, Pb, Ni and Fe were determined by
16 atomic absorption spectrometry (*Solar S2, Thermo Scientific, United States*) in triplicate and the
17 coefficient of variation were among 2,9 and 4,4%. The other metal (Ag, Au, Mn, Pd, In, Sn and Co) were
18 determined by ICP/MS (*7500CX, Agilent Technologies, United States*).

19 Total iron and copper ions concentration in the bioleachates were analysed by an atomic absorption
20 spectroscopy (*Solar S2, Thermo Scientific, United States*). Fe(II) determination was carried out by the
21 1,10-phenanthroline method [38] with an UV/VIS spectrophotometer (*Lambda 25, PerkinElmer, United*
22 *States*). The same spectrophotometer was used for optical density measurements, using the method
23 described by Barron et Luecking (1990) [39]. Oxidation-reduction potential and pH were measured with a
24 multimeter (*MultiLine Multi3620 IDS, WTW, Germany*). Solid copper powder obtained by cementation
25 was analysed by SEM microscopy (*TS-1000, Hitachi, United States*), and it was characterized by Energy
26 Disperse Spectroscopy (EDS), connected to SEM microscope (*XFlash Min SVE, Hitachi, United States*).

28 **3. RESULTS AND DISCUSSION**

30 **3.1. PCB metal composition**

31 The PCBs metal composition used in this study is showed in Table 1. Cu was found to be the major
32 component and the total metal content per kilogram was 452245 mg. Therefore, PCB of mobile phones
33 could be a good source of this metal to take advantage of them in comparison to the metals found in some
34 ores, which have a copper concentration between 0.5 and 3.0% generally [40–42].

35 **3.2. Optimization of biological Fe(II) oxidation**

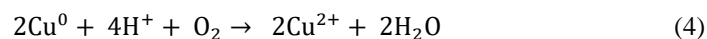
36 Figure 1 shows the concentration of Fe(II) and Fe(III) ions over time. As can be seen, practically all the
37 Fe(II) ions was oxidised to Fe(III) in 45 hours in presence of microorganisms whereas in the abiotic test
38 the Fe(II) remained almost unchanged. Some authors have observed that the oxidation of Fe(II) into
39 Fe(III) is not only consequence of microorganisms' activity but also chemical oxidation has an important
40 contribution to the oxidation of this metal [43, 44]. However, in the present work, under the conditions
41 applied, in 45 hours no chemical oxidation was produced. It means that the chemical oxidation of iron is
42 too slow to be significant in this period of time. In the case of the flasks with the adjusted pH, H₂SO₄ 10N
43 was added by dropwise at different times to maintain the pH between 1.7 and 1.8, following the
44 methodology described in the section 2.3. As it can be observed, in both biotic experiments, with and
45 without controlled pH a 100% oxidation of Fe(II) was achieved. In the biotic flask subjected to pH
46 control, after 3 hours, Fe(II) concentration constantly decreased becoming zero after 45h whereas Fe(III)
47 concentration increased achieving a concentration near 6000 mg/L in 45 hours. This indicates that under
48 the activity of the microorganisms the whole Fe(II) was transformed into Fe(III). It is noticed that the

1 microorganisms oxidized 0.125 g/L of Fe(II) per hour, which is a similar oxidation rate that are reported
2 by Choi et al (0,15-0,13g/L per hour) [17] and Xiang et al. (0,125 g/L per hour) [45] , despite 9 g/L of
3 Fe(II) was used in their mineral media instead of the 6 g/L was used herein. Initial Fe (II) concentration,
4 culture medium and hydraulic residential time influences notably the oxidation rate in continuous
5 production of Fe (III) [46]. Nonetheless, it is important to highlight that in the experiment carried out with
6 controlled pH the total iron concentration remains constant (6000mg/L). However, when there is no acid
7 addition during the biological oxidation, after 30 hours the total iron concentration decreased from 6000
8 mg/L to under 4000 mg/L. This loss of iron may be attributed to the precipitation of the iron ions as
9 Fe(OH)₃ due to the alkalisation of the media (pH>4) and the formation of jarosite [47].

10 **3.3. Cu extraction from PCBs with bio-generated Fe(III) after biomass separation**

11 To avoid the presence of the biomass during the second step, two methods, sedimentation and filtration,
12 were tested in the present work. Filtration was set through a 0.22 µm membrane filter and clarification of
13 the media by decantation which was monitoring by determining the optical density (OD) at 500 nm [36]
14 along time (Fig. 2). Results for decantation showed a sharp drop of OD in two hours. After this time, the
15 optical density had been reduced from 1.00 to 0.17 and remained practically unchanged until 24 hours.
16 Therefore, for practical considerations, the supernatant after two sedimentation hours was taken for
17 leaching tests, although the biomass has not been completely removed from the solution. Figure 3 shows
18 the Fe(II) and Fe(III) concentrations and copper recovery along time after filtration. Figure 4 shows the
19 copper recovery and the concentrations of Fe(II) and Fe(III) ions during the leaching stage with the
20 solution obtained after decanting.

21 Regarding filtration, greatly fast extraction of copper was observed at first and then a much slower phase.
22 After 6 hours, 60% of the copper present in the PCB was removed and put into solution. This
23 phenomenon could be attributed during the first hours, when Fe(III) is not limiting, to a quickly extraction
24 from the most readily available sites on the waste particles instead of those internal parts with difficult
25 accessibility. During the first 6 hours, Fe(III) decreased from 4000 to 400 mg/L. Then, it decreased
26 slowly until 24 hours when practically all the Fe(III) was reduced to Fe(II). From this moment, both
27 Fe(II) and Fe(III) concentrations remained constant during the rest of the experiment which would mean
28 that copper concentration should be also constant (see Eq. 1). Nevertheless, from 24 hours to the end of
29 the experiment, copper still increased despite of the fact that the Fe (III) has run out after 24 hours in the
30 leaching solution. This can be attributed to copper oxidation by the dissolved oxygen in the acidic
31 medium [48]. These authors affirmed that the continuous stirring of the leaching solution causes the
32 oxygen gas incorporation and its dissolution in the liquid, which is able to oxidize metallic copper (Eq. 4).
33 This is probably why the removal in 6 hours was quite superior (53%) to those obtained the next 42 hours
34 of contact (41%). Bas et al. [19] also described the copper solubilisation by the action of the oxygen,
35 working at pH 1.7 and 35°C during 90 h, although the effect was observed since the beginning of the
36 experiment. Taking into account the conditions of the experiments in the present study (pH 1.75 and
37 30°C), it is assumed that dissolved oxygen is also the responsible of the copper solubilization. Both
38 reactions occur simultaneously but at different kinetics. Only when Fe(III) is completely depleted the
39 unique effect of copper oxidation by the dissolved oxygen in the acidic medium is clearly appreciable for
40 long time exposure.”



42 Figure 4 shows the copper recovery after decanting. As can be seen, the velocity of copper extraction was
43 very similar to the velocity obtained after the total separation of biomass by filtration (see Fig. 3).
44 However, regarding Fe(III) concentration, in this case decreased near 60% during the first 6 hours but,
45 after this period, the Fe(III) concentration increased whereas the Fe(II) concentration decreased. This
46 behaviour can be attributed to the presence of microorganisms, since, although almost all the
47 microorganisms have been removed by settling and decantation, the separation was not about 100% so
48 the remaining microorganisms could oxidize the Fe(II) from the solution.

49 After the biological production of Fe(III), this ion has to be kept in contact with the PCB in order to
50 extract the copper from the electronic scrap. Generally, this contact is done by the direct addition of the e-
51 waste in the solution where the microorganisms have been grown when the color of the medium turned

1 red which indicate that all the Fe(II) has been oxidized [29] or at different times during the growth stage
2 [30, 45].

3 Some of these studies present experiments using bio-generated Fe(III) filtered solutions to remove the
4 biomass and it is compared to the copper extraction from the waste using the filtered and the non-filtered
5 solutions. However, the results are contradictory. Yang et al. [29] affirmed that the copper extraction after
6 72 h is nearly 100% in the presence of biomass whereas if it is removed from the solution, the copper
7 extraction in 72 h is only 10%. On the other hand, Shah et al. [30] affirmed that after 6 days of contact
8 between the bio-generated Fe(III) solution and the waste, the presence or the absence of the biomass in
9 the solution involves just a difference of 10% of leached copper (89% extraction in the filtered solution
10 and 99% in the non-filtered solution). The main difference between these studies is the contact time since
11 the first one took 72 h whereas the second one took 6 days. Even so, the influence of biomass in the
12 copper extraction when Fe(III) has been obtained by biological oxidation is not clear in the literature. In
13 the light of results obtained herein, there is no significant differences in copper recovery independently on
14 the method used to separate the biomass. Moreover, the extraction is nearly 100% of the copper contained
15 in the e-waste in 48 h in both cases. Therefore, the experimental time described in other works [28, 30,
16 45] has been clearly reduced due to an accurate control of process conditions. Moreover, taking into
17 account the results obtained in the present work, although sedimentation does not lead to a complete
18 remove of biomass, it is simpler and cheaper than filtration, especially when the bioleaching process has
19 to be adapted to an industrial scale.

20 **3.4. Cementation of bioleached copper**

21 The suitability of the cementation process to recover metallic copper by addition of metallic iron, (Eq. 3),
22 was investigated. This reaction is spontaneous because copper is higher on the galvanic series than iron.
23 In this study the leaching solution obtained in the previous section using the sedimentation method was
24 put in contact with metallic iron to obtain a metallic copper.

25 Considering that the Cu(II) concentration obtained after bioleaching was 3000 mg/L, 4 g/L of metallic
26 iron filings were used since this is 150% the concentration needed to react with the copper according to
27 the stoichiometry of the cementation reaction (Eq. 3). A greater amount of iron than what is
28 stoichiometrically needed was added due to it improves the efficiency of the process [37]. The experiment
29 was done under orbital agitation at 130 rpm and at 25 °C.

30 Figure 5 shows the concentration of Cu(II), Fe(II) and Fe(III) in the solution along time over the
31 cementation process. As it can be seen, the concentration of copper decreased from 3000 mg/L to 0 mg/L
32 in only 2 hours. Anastassakis et al.(2015) spend more than 8 hours to remove all the solubilized copper
33 from the solution by cementation [49]. As a consequence of the redox reaction, the scrap iron used (Fe⁰)
34 was oxidized into Fe(II) ions. For this reason, the Fe(II) concentration was found to be 7000 mg/L after
35 the cementation process, since 4000 mg/L were initially in solution and came from the bioleaching
36 process whereas the other 3000mg/L were obtained by oxidation of the metallic iron filings. It is noticed
37 that Fe(II) was not virtually oxidized at the conditions tested, so the concentration of Fe(III) remained
38 constant at concentrations below 1000mg/L during the whole experiment.

39 The solid copper was recovered as powder on the surface of iron filings. Because of the stirring,
40 mechanical friction between the copper powder and the metallic iron copper breaks off from the layer
41 deposited on the iron metal. This fact made easier the separation of the copper by filtration or decanting.
42 During the cementation, copper was obtained as a fine brown powder (Fig. 6). This powder was analysed
43 following the procedures described in section 2.5. and the results showed the following content (in
44 mg/kg):Cu (648000), Ni(57), Fe(208879), Ag(11), Au(57), Al (33), Pd(5), In(5), Sn(59), Pb(150), Co
45 (11) and Mn (1414). This cemented powder had a content of copper close to 70%. The most important
46 impurities in the powder were iron (21%) and manganese (0.14%). The concentration of the other metals
47 was negligible.

48 Figure 7 shows the morphology of the powder obtained by SEM microscope. The images demonstrate
49 that copper was crystallized as small spherical structures. In order to determine the impurities, the

1 composition of the powder obtained was determined by its analysis conducted with an energy-dispersive
2 X-ray spectroscopy (EDS) (Fig. 8). Basically, EDS spectrum showed the presence of copper and iron. It
3 is possible that iron was not separated from the copper completely, as stated previously, so some metallic
4 iron fillings that have not react with soluble copper during the cementation remained mixed with the
5 powder. In spite of this, no more metals were found during the analysis which means that the purity
6 obtained could be improved conducting a refining step of the copper powder after the cementation
7 process.

8 After cementation, 2.96 g of metallic copper were obtained from a litre of bioleaching solution. This
9 metallic copper had a purity close to 70%, which means that other metals or impurities have been also
10 cemented during the process as it is explained above. This can affect the final use of the copper obtained
11 [50]. Nevertheless, cementation is a very economical and simple process to obtain metallic copper. Even
12 though, if more purity is needed, there are methods to do after the cementation such as solvent-extraction
13 or electrowinning in order to obtain high purity copper [31, 51]. Despite of that, the cementation has also
14 the advantage that the solution obtained after the process contains an important amount of Fe(II) in
15 solution which could be reused as electron donor in the leaching agent production step [45]. However,
16 this solution might also contain other metals that could be toxic for the microorganisms [52, 53], so that,
17 the toxicity on the biological activity should be analysed.

18 19 **4. CONCLUSIONS**

20 Under the conditions applied in this study, initial concentration of Fe(II) 6 g/L and pH control between
21 1,7-1,8, Fe(II) is completely oxidized by microorganisms into Fe(III) in 45 h. The extraction of copper
22 from the PCBs, after removing the biomass, is not influenced by the method applied to separate the
23 biomass. Sedimentation and filtration gave very similar percentages of copper extraction (close to 100%
24 in 48h). Filtration allowed to remove the whole biomass, present whereas after sedimentation some
25 biomass remained in suspension. This is possibly why the Fe(III) concentration slightly increased along
26 the extraction process after sedimentation. To the best of our knowledge, this is the first time that
27 sedimentation and filtration techniques (between the oxidation step and the leaching step in two steps
28 bioleaching) have been compared for copper recovery from PCBs. Since both techniques gave good
29 results, the use of filtration or sedimentation depends on the final aim. In this sense, filtration removes all
30 the biomass but its maintenance is more complicated and expensive than the maintenance of a settler,
31 especially when the process is carried out at industrial scale.

32 Finally, it was possible to conclude that the cementation procedure allowed to obtain elemental copper
33 from the extract in a simply, low cost and environmental friendly way with a relative interesting purity.

34 In conclusion, the overall process of copper extraction has been optimized in this work by significantly
35 reducing the experimental time without losing efficiency and allowing the recirculation of the biomass
36 before being affected by the possible toxic effect of the leached metals from PCBs.

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