Copper extraction from coarsely ground printed circuit boards using moderate thermophilic bacteria in a rotating-drum reactor

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ABSTRACT

The current work reports on a new approach for copper bioleaching from Printed Circuit Board (PCB) by moderate thermophiles in a rotating-drum reactor. Initially leaching of PCB was carried out in shake flasks to assess the effects of particle size ($-208\ \mu\text{m} + 147\ \mu\text{m}$), ferrous iron concentration (1.25–10.0 g/L) and pH (1.5–2.5) on copper leaching using mesophile and moderate thermophile microorganisms. Only at a relatively low solid content (10.0 g/L) complete copper extraction was achieved from the particle size investigated. Conversely, high copper extractions were possible from coarse-ground PCB (20 mm-long) working with increased solids concentration (up to 25.0 g/L). Because there was as the faster leaching kinetics at 50 °C *Sulfobacillus thermosulfidooxidans* was selected for experiments in a rotating-drum reactor with the coarser-sized PCB sheets. Under optimal conditions, copper extraction reached 85%, in 8 days and microscopic observations by SEM-EDS of the on non-leached and leached material suggested that metal dissolution from the internal layers was restricted by the fact that metal surface was not entirely available and accessible for the solution in the case of the 20 mm-size sheets.

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1. Introduction

Technological innovations have stimulated widespread utilization of electronic equipment, which has also resulted in a considerable increase in the generation of electronic waste (e-waste). Incineration and landfilling are often the ways to deal with electronic waste (Xiang et al., 2010), however such methods are increasingly being considered inappropriate because of their negative environmental impacts as shown by the recent studies (Brandt et al., 2001; Yang et al., 2009). Conversely, electronic wastes can also be viewed as alternative source of non-ferrous metals such as copper, nickel, and zinc as well as gold and silver (Lee and Pandey, 2012) and both pyrometallurgical and hydrometallurgical techniques can be applied for their recycling from e-wastes (Zhu et al., 2011).

Pyrometallurgy is particularly appropriate to recover copper and precious metals from some type of electronic waste such as

mobile phones, but the technique requires high grade feed and thus is not suitable for low grade e-wastes, including PCB. Moreover, pyrometallurgy is related to some environmental impacts such as greenhouse gases, formation of furans and dioxins and dust (Cui and Zhang, 2008; Ilyas et al., 2010; Zhu et al., 2013) and thus requires an off-gas treatment. In addition, rare earth metals, tantalum and gallium among other elements report to the slag phase because they are easily oxidized in the furnace atmosphere. Therefore, hydrometallurgy is considered an alternative because it is less complex and energy intensive and there is no generation of toxic gases (Tuncuk et al., 2012). Nevertheless, it is fair to admit that both approaches have their inconveniences and advantages making their combined use often the preferred scenario.

Bio-hydrometallurgy is a specialized branch of hydrometallurgy that utilizes microorganisms to solubilize metals and therefore is often viewed as eco-friendly process for the treatment of low-grade ores and wastes (Poulin and Lawrence, 1996; Watling, 2006). Although, this is one of the most promising biotechnologies in the metallurgical sector, limited research has been reported regarding the bioleaching of PCB and a few examples are

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Table 1
Bioleaching of copper from PCB.

Specific type and source of waste	Microorganisms	Leaching efficiency (%) and conditions	Type of reactor	References
PCB –208 µm + 147 µm	<i>Acidithiobacillus ferrooxidans</i> and <i>Sulfobacillus thermosulfidooxidans</i>	94% Cu extraction at 30 °C (<i>T. ferrooxidans</i>) and 99% at 50 °C (<i>S. thermosulfidooxidans</i>) in 6 days with 10 g/L Fe ²⁺ , 10 g/L of PCB and pH 1.75; 150 min ^{−1}	Shaking flask	Current work
PCB 20 mm-long	<i>S. thermosulfidooxidans</i>	85% Cu extraction in 8 days at 5 g/L Fe ²⁺ , 25 g/L PCB and pH 1.75. Rotating-drum reactor at 50 °C and 80 min ^{−1}	Rotating-drum reactor	Current work
PCB < 500 µm	<i>At. thiooxidans</i> and <i>At. ferrooxidans</i>	>90% Cu extraction in two-stages during 7 and 10 days at 5–10 g/L of PCB; 35 °C and 180 min ^{−1}	Shaking flask	Brandl et al. (2001)
PCB < 80 mesh	<i>Genera Acidithiobacillus</i> and <i>Gallionella</i>	95% of Cu in 5 days at 9 g/L of initial Fe ²⁺ , 20 g/L of PCB and pH 1.5; shaker at 30 °C and 120 min ^{−1}	Shaking flask	Xiang et al. (2010)
PCB 100–120 µm	<i>S. thermosulfidooxidans</i> and <i>Thermo- plasma acidophilum</i>	86% Cu extraction. Acid pre-leaching of 27 days and bioleaching of 280 days. Column reactor at 45 °C	Column reactor	Ilyas et al. (2010)
PCB 60–80 mesh	Enriched acidophilic bacteria	96.8% Cu extraction in 45 h; 12 g/L Fe ²⁺ , 12 g/L PCB and pH 2; shaker at 30 °C and 160 min ^{−1}	Shaking flask	Zhu et al. (2011)
TV circuit boards (STVB) < 250 µm	<i>At. ferrooxidans</i> , <i>L. ferrooxidans</i> and <i>At. thiooxidans</i>	35% Cu extraction in 90 h without external Fe ²⁺ and 89% Cu extraction at 8 g/L Fe ²⁺ at 10 g/L of PCB and pH 1.7; shaker at 35 °C and 170 min ^{−1}	Shaking flask	Bas et al. (2013)
PCB 50–150 µm	<i>S. thermosulfidooxidans</i> and <i>T. acidophilum</i>	85% Cu extraction in 18 days at 10 g/L of PCB; shaker at 45 °C and 180 min ^{−1}	Shaking flask	Ilyas et al. (2013)

summarized in Table 1. Iron-oxidizing bacteria produces ferric from ferrous iron (Eq. (1)), which can subsequently oxidize metals such as copper according to Eq. (2). In general, mesophilic bacteria belonging to the genus *Acidithiobacillus* and *Leptospirillum* are most commonly used in bioleaching.

In addition to these two bacterial genera thermophilic microorganisms may also be employed in bioleaching operations (Brandl et al., 2001; Pant et al., 2012). As a rule, leaching at elevated temperatures has the potential to result in more efficient and faster metal dissolution. In the bioleaching of copper sulfides for instance higher extractions with moderate thermophilies as compared to mesophiles were reported elsewhere (Pina, 2006; Schippers, 2007). Copper bioleaching from e-wastes with moderate thermophilies in shake flasks (Ilyas et al., 2007, 2013; Pina, 2006), stirred tanks (Ilyas et al., 2014) and lab scale columns (Ilyas et al., 2010) were also investigated. However, few studies have studied bioleaching of e-waste and printed circuit boards in particular using moderate thermophilies.

The reactors used in the bioleaching of sulfides are generally designed as stirred tank or air-lift type but concerning e-waste bioleaching there is a limited data about the type of reactor on process performance. A rotating-drum reactor could be suggested as alternative to the stirred-tank reactors with the potential advantage to treat material at increased pulp densities and reduce global energy consumption. It could be assumed that such a reactor will ensure reduced impact on the microbial cells due to the lower degree of collisions between the particles (Liu et al., 2007). Such configuration offers the possibility of using high solid loadings without negatively influencing the bio-oxidation of Fe²⁺ which tends to be the case when impeller-driven reactors are used (Jin et al., 2013).

The feasibility of copper bioleaching from fine milled PCB at low solids concentrations (up to 10.0 g/L) has been demonstrated and extractions as high as 90% were reported with mesophilic strains (Bas et al., 2013; Brandl et al., 2001; Xiang et al., 2010; Zhu et al., 2011). Nevertheless, quite few studies dealing with increased solid concentrations have been published so far likely because bacterial growth is inhibited in the presence of fine PCB particles. Although the exact nature of such deleterious effects is still unclear there are indications that are more important in the very beginning of

leaching experiments. This is because the quick release of harmful-to-bacteria species from the ground PCB is stimulated.

With the above mentioned concerns in the background, the current work proposes a different approach to PCB bioleaching, in which relatively coarse PCB sheets are leached without reducing their size down to the micrometer scale. The objective is to avoid useless overgrinding and hence reduce the overall cost associated with the fragmentation step. Another aim is to discuss the bacterial adaptation to increased PCB content and to find out the optimal pH and ferrous iron concentration for bioleaching using moderate thermophiles in a rotating-drum reactor.

2. Experimental procedure

2.1. PCB fragmentation and pre-treatment

The experiments were carried out with PCB collected from obsolete desktop computers, from which all electronic components such as capacitors and resistors were manually removed in advance. At the beginning, the dismantled boards were shredded using a metal guillotine to obtain nearly rectangular PCB fragments with 20 mm-long size. For the experiments with ground PCB, a fraction from the above-mentioned sheets was further fragmented using a laboratory hammer mill and after dry sieving the –208 µm + 147 µm particle size was selected. A second sample was subjected to a “pre-weakening” process in a laboratory jaw crusher (discharge gap 10 mm) aiming to generate cracks and to expose metals inside the PCB sheets to the leaching solutions. After jaw crusher “pre-weakening”, the samples were screened at 20 mm and the oversize fraction used for further studies. One part of this oversize material (fraction +20 mm) was subsequently submitted to a chemical pre-treatment step to remove the lacquer coating, which covered the printed circuit boards. PCB sheets (50 g) were mixed with 500 mL of aqueous solution of diethylene glycol (20% v/v) and potassium hydroxide (20% w/v) for accomplishing this task. The lacquer coating removal step was carried out under stirring at 90 °C during in 60 min. Thereafter the solid phase was filtered, washed with distilled water and then dried at 50 °C to a constant weight.

2.2. Microorganisms

The mesophile microorganisms utilized in the current study were isolated from a Brazilian sulfide mine, for which microbial

diversity studies revealed the predominance of *Acidithiobacillus ferrooxidans* (Azevedo, 2008). This strain was sub-cultured in a Norris medium (0.2 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.4 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.1 g/L K_2HPO_4) with 2.5 g/L Fe^{2+} ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The procedure was accomplished in an orbital shaker (New Brunswick, Innova 44) at 35 °C and 150 min^{-1} . Experiments were also carried out with the thermophilic bacterium *Sulfobacillus thermosulfidooxidans*, purchased from DSMZ – Braunschweig (ID 9293). This strain was maintained in the same Norris growth medium, which was supplemented with yeast extract (0.1 g/L). A second orbital shaker (New Brunswick, Innova 44) working at 50 °C provided mixing (150 min^{-1}). In both cases pH solution was set at 1.75 ± 0.05 .

Prior to the bioleaching experiments, the two bacterial strains were inoculated to both crushed ($-208 \mu\text{m} + 147 \mu\text{m}$) and to non-crushed (20 mm) PCB. Adaptation was performed by selecting a bacterial inoculum during its *log* phase (as indicated by redox potential values around 550 mV) and its transfer to the growth medium, while progressively increasing the PCB content (starting at 5.0 g/L solids (w/v) up to 10.0 g/L for the crushed PCB and to 25.0 g/L in the case of non-crushed PCB). Culture replications were performed on a weekly basis to maintain a bacterial population well adapted to PCB.

2.3. Bioleaching experiments

Bioleaching of ground PCB was carried out in 250-mL Erlenmeyer flasks placed in a thermostated shaker (New Brunswick Innova 44) at the Bio and hydrometallurgy laboratory of the Federal University of Ouro Preto (Brazil). Both mesophile and moderate thermophile cultures were tested under the procedure described in Section 2.2, unless otherwise stated. A suspension containing 10.0 g/L of ground PCB ($-208 \mu\text{m} + 147 \mu\text{m}$) was prepared using 100 mL of growth medium, 10% of inoculum and ferrous sulfate in predetermined concentration. Initial ferrous iron concentration was varied between 1.25 g/L and 10.0 g/L and the pH was maintained at 1.75 ± 0.05 using 1 mol/L sulfuric acid or 6 mol/L sodium hydroxide. Evaporation losses during leaching were corrected by adding distilled water to the initial recorded weight. Pulp redox potential was registered using a WTW 315 multi-meter (vs. an Ag/AgCl electrode). Sterile controls were also run in the presence of bactericide: thymol (for the mesophiles) or a mixture of 0.015% (v/v) methylparaben and 0.01% (v/v) propylparaben solution for the tests with moderate thermophile performed in the presence and absence of ferrous iron.

Another series of bioleaching experiments were performed batchwise with the 20 mm-long PCB fragments at a solid loading of 25.0 g/L in shake flasks, following the above cited procedure, but only with *S. thermosulfidooxidans* at 50 °C. After defining the optimal pH and ferrous iron initial concentration larger scale experiments were carried out at the Mineral Processing and Recycling Unit, University of Liege (Belgium) using a rotating-drum reactor pictured in Fig. 1. The reactor consisted of a perforated drum (with 10 mm openings) driven by a motor and fitted with a gas sparger (not shown in the sketch) to provide aeration with air. The perforated drum was immersed inside a fixed cylindrical compartment containing the liquid medium/pregnant leach solution. An air (fan) heater was placed as close as possible to the drum reactor in order to maintain the temperature inside the reactor at 50 ± 1 °C.

The experiments were performed at rotation speed of 80 min^{-1} using 300 g of 20 mm-long PCB sheets immersed in 12 L of medium containing 10% (v/v) of inoculum so that a 25.0 g/L pulp density was achieved. The effect from the initial Fe^{2+} concentration (2.5 g/L, 5.0 g/L, 7.5 g/L and 10.0 g/L) on copper extraction was also assessed during these experiments. At predetermined intervals, 5 mL aliquot was sampled from the leach solution and delivered

Fig. 1. Schema of the rotating-drum reactor (all dimensions in mm).

to elemental analysis. Redox potential and pH were recorded and maintained, similarly to the shaking flask tests.

2.4. Analysis and characterization

Metal concentration in the solid PCB was determined by inductively coupled plasma -atomic emission spectrometry (ICP-AES) – Varian Series II, following sample (1.0 g) digestion with aqua regia and dilution in 250 mL volumetric flasks. All chemical analysis for the solid phases were carried out in triplicate and the mean value used. The global assay of the PCB has indicated that the base metals accounted for approximately 30% of the sample, with copper being present in majority ($28.5 \pm 0.1\%$). Fe (0.51%), Zn (0.41%) and Ni (0.07%) have also been detected. Metal concentrations in the leach solutions were likewise determined by ICP-AES and used for calculation of copper extraction.

Ferrous iron was assayed by titration with standard potassium dichromate solution in the presence of a 1 M H_2SO_4 :1 M H_3PO_4 using barium diphenylamine sulfonate as indicator. The concentration of Fe^{3+} was calculated from the difference between total iron and Fe^{2+} concentrations. The acid consumption was determined considering the amount of sulfuric acid (98%) used for keeping pH constant during leaching in rotating-drum reactor. The surface morphology and the internal structure of the PCB were studied by SEM (Tescan Vega 3). Energy dispersive X-ray spectroscopy (EDS) (Oxford) was used to quantify the residues after leaching and to detect residual copper inside leached PCB as well. All chemicals used in this study were of analytical grade (AR) unless otherwise stated and all solutions were prepared with distilled water.

3. Results and discussion

3.1. Bioleaching in shake flasks

3.1.1. Effect of pulp density and initial ferrous iron concentration

The heterogeneous composition of PCB sheets, which contain metals, polymers and ceramics (Ilyas et al., 2010; Zhu et al., 2013) could induce inhibiting effects on bacterial growth during bioleaching, although the exact compounds accounting for such effects remain unclear (Brandl et al., 2001). In the current work, such inhibiting effects were verified through solution potential (Eh), which is an indirect assessment of bacterial growth in the reactor. Fig. 2(a) and (b) shows similar Eh profiles both in the presence and absence of PCB only for solid contents of up to 2.5 g/L at both temperatures when ground PCB ($-208 \mu\text{m} + 147 \mu\text{m}$) was bioleached in the presence of 2.5 g/L Fe^{2+} , prior to bacterial adaptation. Impaired bacterial growth was inferred at higher PCB content (5.0 g/L and 10.0 g/L) because the solution potential remained

Fig. 2. Influence of solid density (a and b) and Fe²⁺ concentration (c and d) on redox potential during shake flask leaching of ground PCB. Experimental conditions: temperature 30 °C (a and c) and 50 °C (b and d), 2.5 g/L Fe²⁺ (a and b), pH 1.75; 150 min⁻¹; pulp density of 10.0 g/L (c and d).

below that observed with lower solid content (2.5 g/L), leveling out at 550 mV between day 3 (at 30 °C) and 5 (at 50 °C). If detrimental effects were absent, Eh values between 650 and 700 mV would be expected, irrespective of the strain studied as observed in the experiment with no PCB.

After adaptation to ground PCB, an Eh increase was observed in the presence of 10.0 g/L solids at both temperatures and values around 650 mV were recorded at 30 °C within three days (Fig. 2(c)) irrespective of the initial Fe²⁺ concentration. Similar behavior was depicted in the experiments with *S. thermosulfidooxidans*, at 50 °C, but with slightly lower Eh values (around 600 mV) as depicted in Fig. 2(d). This difference was most likely because both microorganisms have different ferrous iron oxidation rates. Furthermore, the control experiments performed at the concentration of 5.0 g/L of Fe²⁺ showed Eh values around 450 mV, clearly indicating a lack of Fe²⁺ oxidation in the absence of each bacteria. Fig. 3(a) and (b) present copper extractions at different ferrous iron concentration for mesophiles and moderate thermophiles, respectively. Copper was almost completely extracted in 5 and 3 days, at 30 °C and 50 °C, respectively, when bioleaching was performed with adapted bacteria. These periods are similar to that reported by Xiang et al. (2010), who studied PCB leaching (20 g/L) with *At. ferrooxidans*. Conversely, Ilyas et al. (2013) reported a lag phase of 5 days during bioleaching with *S. thermosulfidooxidans* in the presence of 7 g/L PCB. The same authors carried out experiments with increasing PCB content and observed that at 22 g/L PCB there was no efficient leaching of metallic copper, indicating that such solid content did not enable bacterial growth.

It is acknowledged that dissolution of metallic copper requires an oxidizing agent as suggested by Eq. (2). Therefore higher initial Fe²⁺ concentrations would result in faster dissolution rates of

metallic copper (assuming that bioleaching proceeds via the indirect non-contact mechanisms), which was confirmed in Fig. 3(a) and (b). Actually, increasing Fe²⁺ concentrations up to 10.0 g/L exercised a positive effect on copper leaching in both systems (mesophiles and moderate thermophiles) because copper extractions of 94% and 99% were achieved using mesophilic and moderate thermophile cultures, respectively. Nevertheless, a concentration of 5.0 g/L ferrous iron could be considered as an optimal value in both cases. Furthermore 48% and 53% copper extractions were observed in the abiotic controls containing 5 g/L Fe²⁺ at 30 °C and 50 °C, respectively (Fig. 3(a) and (b)), highlighting the positive effect of the presence of bacteria. It is worth noting that bioleaching studies carried out with ground PCB (50–150 µm) performed by Ilyas et al. (2007) using moderate thermophilic microorganisms and 10.0 g/L of PCB showed slightly lower copper extractions than those achieved in the current study (>94%), in the 72–89% range over a period of 18 days.

Ferrous iron bio-oxidation plays a key role in copper dissolution as suggested by the low copper extraction in the control experiments (control tests) performed in the presence and absence of ferrous ions (Fig. 3(a) and (b)). In the tests without ferrous iron addition, copper extractions reached 21.7% and 28% at 30 °C and 50 °C, respectively, i.e., figures lower than those achieved in the control test. The fact that the experiments with 5.0 g/L always outperform those with no external ferrous iron indicates that the chemical oxidation of ferrous iron by oxygen was much faster than the oxidation of metallic copper by the same oxidant (Eq. (3)). Copper leaching in the latter case was governed by the oxygen introduced in the system by stirring (Bas et al., 2013; Brandl et al., 2001).

Fig. 3. Effect from initial Fe^{2+} concentration and temperature (30 °C (a) and 50 °C (b)) on copper extraction from ground PCB. Effect of pre-weakening fragmentation and lacquer coating removal (c) and initial Fe^{2+} concentration on copper extraction (d) from non-ground PCB during bio-leaching at 50 °C. Experimental conditions: ground PCB ($-208 \mu\text{m} + 147 \mu\text{m}$) in shake flasks ((a) and (b)): pulp density 10.0 g/L, pH 1.75, 150 min^{-1} ; non-ground PCB (20 mm) in shake flasks (c) and (d): 50 °C, pulp density 25.0 g/L, 5.0 g/L Fe^{2+} , pH 1.75, 150 min^{-1} .

Although bioleaching could be performed in the presence of 10.0 g/L ground PCB, adaptation of both strains to higher PCB content was not possible during the course of the current study. Therefore, the investigation shifted to the bioleaching of non-grounded PCB (20 mm-long sheets), expecting that the release of harmful-to-microorganisms compounds could be limited. Under such conditions, bacterial adaptation could be facilitated however copper extraction might be reduced due to the non-complete liberation of metallic copper. Another advantage of this approach would be the possible cost reduction due to the elimination of fine grinding. Therefore, the subsequent series of experiments were envisaged using explicitly coarser non-ground PCB and *S. thermosulfidooxidans* was selected due to the faster leaching kinetics fostered by higher temperatures.

3.1.2. Experiments with 20 mm-long PCB sheets

With PCB sheets *S. thermosulfidooxidans* could tolerate pulp densities of up to 25 g/L. In addition, two pretreatments were performed to expose copper inside the 20 mm-long sheets: (i) pre-weakening" i.e. fragmentation in a jaw crusher and (ii) removal of the lacquer coating the sheets.

Fig. 3(c) report on the results of the tests with such PCB fragments at 25.0 g/L solids, in which the effect of PCB "pre-weakening" and lacquer removal on copper extraction were assessed. As shown in Fig. 3(c) the effect of lacquer removal was evident, with nearly 60% copper recovery as compared to merely 20% extraction from the "as received" PCB. Combining pre-weakening and lacquer removal brought further positive effects on copper extraction which attained 70%, against 60% with lacquer removal only (Fig. 3(c)).

To explain the phenomena observed during PCB bioleaching, microscopic observations of PCB samples before and during bioleaching were carried out. Fig. 4(a) shows a SEM image of a cross-sectional area of an "as-received" 20 mm-long PCB fragment. It could be concluded that copper is present as four layers (two internal and two external) sandwiched between fiberglass and polymer structures, possibly an epoxy resin (Zhu et al., 2013). Furthermore, Fig. 4(b) and (c) depict details of a cross-sectional area of a PCB sheet before and after lacquer removal, whereas Fig. 4(d) and (e) shows a frontal view of PCB surface with and without lacquer coating, respectively. The purpose of the lacquer coating seen in Fig. 4(b) and (d) was to prevent the copper surface from oxidation. However, it also hindered copper bioleaching by restricting the access of the oxidizing agent (Fe^{3+}) toward the metal surface. Removal of the lacquer coating as seen in Fig. 4(c) and (e) exposed the copper layers, facilitating metal leaching.

The dissolution of copper before and after PCB "pre-weakening" by means of a jaw crusher can be seen in the SEM images 5(a) and 5(b), respectively. Cracks introduced in the PCB resulted in an improvement in copper extraction by facilitating solution diffusion toward the inner PCB layers (Fig. 5(b)). In particular the jaw crusher impact has provoked cracks to emerge inside PCB structure as could be seen from the SEM images in Fig. 5(b). Thus the "pre-weakened" polymer and fiberglass structure has favored the leaching solutions to access the copper surface.

For the PCB sample submitted to both jaw crushing and lacquer removal, further tests assessed the effect of the initial ferrous iron concentration on copper leaching as shown in Fig. 3(d). The results indicate copper extraction of nearly 76% in the presence of 5.0 g/L ferrous iron (the best result) within eight days of leaching with *S.*

Fig. 4. SEM micrographs of a cross sectional area of PCB fragments showing 4 copper layers (a), lacquer covering the entire section (b), view after lacquer coating removal (c); SEM frontal view of PCB surface with lacquer coating (d) and after removal of the lacquer coating (e).

thermosulfidooxidans. However, such outcome is lower than the one observed with the ground PCB (97%) and might be ascribed to the smaller degree of copper exposure at coarser particle sizes. Jarosite precipitation on the PCB surface was detected in the tests with 7.5 g/L and 10.0 g/L Fe^{2+} as inferred from Fig. 6, in which a precipitate (most likely jarosite) was observed after eight days of leaching. Other elements were also observed, which come from the elements forming the PCB sheet (Dang et al., 2008; Ilyas et al., 2013). In these two initial Fe^{2+} concentrations the copper extraction was reduced (Fig. 3(d)).

3.1.3. Effect of pulp pH the on degree of copper extraction

It is known that bacterial growth and substrate utilization are influenced by pH solution (Bhatti et al., 2012; Dopson et al., 2008, 2009). More precisely values below pH 1.2 have been shown to hamper *S. thermosulfidooxidans* growth whereas jarosite precipitation depletes solution from ferric iron when pH is increased to values above 2. Moreover according to Petersen and Dixon

(2007a) microbial activity is also affected when the pH is maintained above this value. The effects of pH on both leaching kinetics and copper extraction is witnessed by tests at the optimal ferrous iron concentration of 5.0 g/L. Fig. 7 shows the effect of pH on copper dissolution during bioleaching with *S. thermosulfidooxidans* already adapted to PCB. The perusal of the results indicates that copper extraction reached 76% within one week when pH was maintained at 1.5 and 1.75. The pH value of 1.75 was selected for the subsequent series of experiments in the rotating-drum reactor because it would have favorable effects on acid consumption, an issue with direct practical implications.

3.2. Bioleaching in the rotating-drum reactor

The effect of ferrous iron concentration on copper bioleaching inside the rotating-drum reactor was investigated in the presence of *S. thermosulfidooxidans* at 50 °C, pH 1.75. From the results reported thus far (Fig. 3(c)) it was conceivable that moderate

Fig. 5. SEM micrographs/BSE of bioleached 20 mm PCB: without pre-weakening but with lacquer removal only (a); jaw-crusher pre-weakening followed by lacquer removal (b). Experimental conditions in rotating drum reactor: 50 °C, pulp density 25.0 g/L, pH 1.75, 80 min⁻¹.

Fig. 6. EDS analysis of precipitated compound developed during bioleaching at 10.0 g/L initial ferrous iron. Experimental conditions in rotating drum reactor: 50 °C, pulp density 25.0 g/L, pH 1.75, 80 min⁻¹.

thermophiles would be able to withstand elevated solid loadings of the coarse PCB sheets in the drum reactor. Therefore the experimental program in this reactor was performed at 25.0 g/L solids using jaw-crushed and lacquer-free PCB.

Fig. 8(a) shows the evolution of Eh in the rotating-drum reactor. Under all conditions tested the Eh trend suggested good bacterial growth. In the test aiming at ferrous iron oxidation in the absence of PCB, Eh values above 550 mV were observed after the fourth day; an observation confirming the relatively fast bacterial growth in the reactor. When PCB was present, a slower increase in Eh was observed regardless of the amount of ferrous iron initially present. Nevertheless, the highest Eh values were achieved for 2.5 g/L and 5.0 g/L ferrous iron concentrations. Moreover, Fig. 9(a) suggests that when Fe²⁺ was supplied at initial concentration of 7.5 g/L and 10.0 g/L (implying in theoretically higher Fe³⁺ concentrations), lower final copper extractions were observed in comparison to the

tests at 5.0 g/L. It could be inferred that increasing the initial ferrous iron concentration to 7.5 g/L and 10.0 g/L coupled with the elevated temperature might have contributed to iron precipitation and hence to lowering redox potential. This hypothesis is supported by the results seen in Fig. 8(b) which presents the highest reduction in the Fe_{tot} concentration in the leaching system with time for experiments with 7.5 g/L and 10.0 g/L. Fig. 8(b) also suggests that the jarosite formation might have hampered copper dissolution by blocking the lixiviant access to the metallic copper.

As mentioned above, the highest degree of copper extraction corresponding to 85% was reached after seven days for the test performed with 5.0 g/L of Fe²⁺ - Fig. 9(a). This level of extraction when compared to 44% for the control experiment supports the indirect mechanism hypothesis in which the bacteria oxidizes Fe²⁺ to Fe³⁺ in solution and the latter diffuses to the metal-solution interface to dissolve metallic copper from PCB (Crundwell, 2003; Watling

Fig. 7. Influence of pH on the extraction of copper during bioleaching of non-ground PCB in shake flasks. Experimental conditions: 50 °C, pulp density 25.0 g/L, 5.0 g/L Fe^{2+} , 150 min^{-1} .

Fig. 8. Influence of initial ferrous iron concentration on redox potential (a) and on Fe_{tot} concentration (b) in rotating drum reactor. Experimental conditions: 50 °C, pulp density 25.0 g/L, pH 1.75, 80 min^{-1} .

et al., 2008). It should also be added that jarosite precipitation (Fig. 6) could act as either a diffusion barrier for the oxidant toward the metal surfaces (Zhu et al., 2011) or reduce the total available

Fig. 9. Effect of initial ferrous iron concentration on copper extraction (a) and evolution of concentration of total and ferric iron and copper extraction degree with 5.0 g/L Fe^{2+} (b) in rotating drum reactor. Experimental conditions: 50 °C, pulp density 25.0 g/L, pH 1.75, 80 min^{-1} .

oxidant concentration. It is known that jarosite precipitation is spontaneous at pH values above 2.2, but the precipitation kinetics is chemically controlled, which means that when temperature increases, precipitation takes place even at pH below 2.0 which is the case in the current work (Daoud and Karamanev, 2006; Ozkaya et al., 2007; van Hille et al., 2010). In addition although every measure has been taken to maintain pH at constant value of 1.75, the fact that pH control was done manually could not exclude that at certain leaching periods slight pH increase occurred.

Experiments with 5.0 g/L ferrous iron lead to a marked increase in copper leaching kinetics after 48 h, reaching 75% extraction in the following three days (day 2–5), accompanied by a concomitant raise in ferric iron concentration inside the rotating-drum reactor – Fig. 9(b). In such a way the results pictured in Fig. 9(b) are confirming the hypothesis of fast bacterial growth already suggested by the Eh trend seen in Fig. 8(a). Nevertheless, it should be mentioned that the relatively low Eh values shown in Fig. 8(a) (<550 mV) could be explained by the fast consumption of ferric iron due to its reaction with metallic copper (Eq. (2)). Consequently, Eh values were low and similar to those recorded at non-inoculated systems (Petersen and Dixon, 2007b). Moreover Fig. 9(a) and (b) suggest that copper leaching was low at the beginning of the experiment (until day 2). During this period the process was limited by the Fe^{3+} concentration (lag phase) and when ferric iron started to emerge it was directly consumed by the metallic copper. Between days 2 and 4 ferric iron accumulated in solution and as a consequence the copper dissolution kinetics was accelerated. Metal dissolved during this period came mostly from the external copper layers in the PCB sheets as implied from Fig. 10.

Furthermore, such increase in ferric iron concentration (Fig. 9(b)) could be explained by the reduction of copper available from the external layers as suggested by Fig. 10 (please compare the y scale in both figures). The EDS analysis revealed that metal dissolution did not occur uniformly on the entire external copper surface, as expected for an electrochemical mechanism (Fig. 10). Fig. 10 also suggested that the outer copper layer began to disappear and metal dissolution slowed down after four days as also inferred from Fig. 9(a). The presence of polymer and fiberglass shown in Fig. 5(a) and (b)) might have contributed to slow lixiviant diffusion toward the internal metallic copper and restricted the total recovery to 85% after seven days – Fig. 9(b).

As expected, the redox potential was lower in the control experiment – Fig. 8(a) due to the low Fe^{2+} oxidation rate, the latter being a pure chemical process. It is worth mentioning that the re-oxidation of ferrous iron is catalyzed between 10^5 and 10^6 times by microorganisms (Ozkaya et al., 2007). It could also be inferred that the observed Eh and copper extraction trends could be related to the lag phase taking place in the batch experiments. Ilyas et al. (2013) showed that after a lag phase period of six days adapted *Sulfobacillus* strain was able to sustain up to 20.0 g/L (optimum concentration 10.0 g/L) of ground PCB (50–150 μm). As seen in Fig. 9(a), a satisfactory extraction within a short lag phase was achieved in our case using 20 mm-long PCB fragments at solid concentration of 25.0 g/L. This approach enables to work with coarse particles while achieving copper extractions similar to the values reported in the literature for pulverized PCB (Table 1).

The evolution of both pH and acid consumption was also monitored. The results depicted in Fig. 11(a) suggest that the bio-leaching of PCB was accompanied by an increase in pH during the first two days of experiment, after which the pH stabilized below 2 in all inoculated tests. Similar findings were reported during column bioleaching of ground PCB (–8 mm + 3 mm) (Ilyas et al., 2013). According to Brandl et al. (2001), pH increases mainly because of the presence of alkaline components in the PCB particularly in the non-metallic fractions. Notwithstanding, a pH decrease was

Fig. 11. Evolution of pH (a) and acid consumption (b) in rotating drum reactor. Experimental conditions: 50 °C, pulp density 25.0 g/L, pH 1.75, 80 min⁻¹.

Fig. 10. EDS analysis of copper on the surface of PCB after 4 (a) and 8 (b) days of leaching. Experimental conditions in rotating drum reactor: 50 °C, pulp density 25.0 g/L, pH 1.75, 80 min⁻¹.

noticed from the third day onwards which further stabilized around 1.75 – Fig. 11(a). Jarosite precipitation was observed for all Fe^{2+} concentrations tested, particularly at 10.0 g/L and accounted for the low pH recorded under this condition (Fig. 6).

The experimental conditions in the rotating-drum reactor enabled an accurate determination of acid consumption during bioleaching. Addition of sulfuric acid was required to keep pH within the targeted value of 1.75 ± 0.05 and resulted in an acid consumption ranging from 155 g $\text{H}_2\text{SO}_4/\text{kg}$ (for 10.0 g/L ferrous iron) to 451 g $\text{H}_2\text{SO}_4/\text{kg}$ PCB (for the non-inoculated experiment) – Fig. 11(b). The lowest acid consumption was observed for the inoculated experiment carried out with 10.0 g/L ferrous iron concomitantly to important jarosite and acid production. An acid consumption of 188 g $\text{H}_2\text{SO}_4/\text{kg}$ PCB was calculated for the tests performed in the 2.5–7.5 g/L Fe^{2+} range. It should be recalled that results in Fig. 9(a) indicated that the fastest copper leaching rate was observed during the first four days – and that over that period a larger amount of sulfuric acid was added to maintain pH at its optimal value – Fig. 11(b). Studies done elsewhere (Bas et al., 2013), indicate that during experiments carried out at pH 1.7 using ground ($\sim 250 \mu\text{m}$) PCB and mixed mesophile strains an acid consumption of 550 g $\text{H}_2\text{SO}_4/\text{kg}$ PCB was observed.

The technology proposed herein would be best suited for either small scale operations or residues with low copper content. As bioleaching has been industrially applied to the processing of refractory gold ores (gold locked inside pyrite grains) and copper sulfides the scale-up of such a biotechnology is feasible and a cost effective industrial application is forecasted. Nevertheless, future work is required to address such issues. Another interesting aspect would be to investigate the potential of using bioelectrochemistry to recovery copper from the solution purification.

4. Conclusions

When finely ground PCB ($\sim 208 \mu\text{m} + 147 \mu\text{m}$) were bioleached in shake-flask mode in the presence of 10.0 g/L initial ferrous iron it was possible to leach within six days 94% and 99% of copper at 30 °C and 50 °C using mesophilic and moderate thermophile cultures respectively, however at low solids density (10.0 g/L). Substantial jarosite precipitation was observed under these conditions but without negatively affecting copper dissolution. Copper extraction increased concomitantly with the initial ferrous iron concentration only during the first two days. For the entire leaching duration however 5.0 g/L has been established as an optimal concentration. When coarser PCB (20 mm) were bioleached in shake flasks at 50 °C and initial ferrous iron concentration kept at 5.0 g/L it was possible to increase pulp solids density up to 25.0 g/L. Under these conditions and when PCB were subjected to a pre-weakening step (via jaw crusher) followed by lacquer coating removal nearly 76% copper was extracted of eight days also suggesting a limited release of inhibiting elements in solution. Bioleaching with moderate thermophiles at 50 °C and 5.0 g/L ferrous iron concentration has enabled faster copper extraction than the one at 30 °C, but care should be exercised if the solution potential is chosen to monitor bacterial growth since the available metallic copper rapidly reduces ferric iron to its divalent state. Leaching of coarse PCB (being pre-weakened and having lacquer coating removed before leaching) inside an aerated rotating-drum reactor has been found more efficient than leaching in shake-flasks. The maximum degree of copper extraction (85%) was reached after eight days for the bio-assisted test compared to 44% for the abiotic one. Also, acid consumption was more than two times lower for the biotic leaching than the abiotic one at the same initial concentration of ferrous iron – 5.0 g/L. The results are suggesting that bioleaching appears as a promising approach for processing PCB derived from electronic waste and could be

integrated into a global copper recycling process from such sources. Further studies however are needed to confirm the approach feasibility and to enable higher than the tested degree of solids loading.

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