Copper recovery from unground printed circuit board by biogenic ferric at high solid/liquid ratio

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ABSTRACT

In this work, the recovery of Cu from large waste printed circuit board (PCB) pieces by biogenic ferric sulphate at high solid to liquid ratio was studied. PCB parts were packed in a column and biogenic ferric was constantly recirculated. A high oxidation reduction potential (ORP) decrease was observed in ferric leaching due to ferric ion consumption; this drop caused a slower copper dissolution kinetics. After 25 days, 62.2% of copper was leached from PCBs column. PCBs column was connected to a flooded packed-bed (FPB) bioreactor to study the biological regeneration of ferric ion consumed in chemical reaction. The bioreactor connection enabled working at a constant ORP (700 mV vs. Ag/AgCl) during the whole test time. The improvement of oxidising conditions hugely increased copper dissolution rate, reaching 90% of copper recovery after 25 days. The FPB bioreactor operated continuously without showing inhibition problems and generating a leaching liquor with a high and constant ORP. The novel proposed configuration consists of a chemical reactor, where large PCBs pieces are piled at a high solid load, connected to a FPB bioreactor that regenerates the spent ferric ion enabling the leaching without reagents consumption, is a simple, inexpensive, low energy consumption, eco-friendly and effective system to recover copper from PCBs.

1. Introduction

Printed circuit boards (PCBs) are thin and flat pieces ubiquitous in all electronic products providing electrical interconnections, and represent approximately between 3 and to 6% of the total weight of e-waste components (Arya and Kumar, 2020). PCB composition is heterogeneous and varies depending on the equipment from which they come, as well as the year and place of manufacture (Hubau et al., 2019). PCBs essentially consist of a non-conductive thermoplastic substrate (epoxy or phenolic resin reinforced with glass fibres, alumina, silica or other inorganic materials), conductive layers of copper, and electronic components that give the circuit the unique qualities that make it fit for its intended purpose (Pietrelli et al., 2019). The electronic components contain different metals and are attached to the conductive substrate through solders typically made of lead/tin, or occasionally of gold or palladium. At the end of the useful life of the electronic devices, all these components remain in the PCBs. High concentrations of copper (8–30%), and precious metals such as Au (50–1500 ppm), Ag

(120–5000 ppm) and Pd (about 200 ppm), have been observed in waste PCBs. These values are significantly higher than those of natural resources, therefore PCBs are considered potential secondary resources (Oguchi et al., 2011).

Ferric leaching is a well-known hydrometallurgical approach used in the treatment of non-ferrous metals sulphides. Furthermore, ferric leaching can also be applied in the recovery of target metals from PCBs (E. Y. Yazici and Deveci, 2014). Ferric ion can be used in sulphate or chloride media; however, the use of ferric sulphate enables the leaching agent regeneration by ferro-oxidising microorganisms.

Ferric sulphate is a strong oxidant with a standard reduction potential of 770 mV (SHE) capable of oxidising elemental Cu with a standard reduction potential of 340 mV. Ferric ion reacts with elemental copper to give ferrous iron and copper in solution (r1). Ferric iron can be regenerated by iron-oxidising bacteria, according to 2, which would mean zero ferric iron consumption.

$$Cu + 2\,Fe^{3+} \rightarrow Cu^{2+} + 2\,Fe^{2+} \tag{r1}$$

$$Fe^{2+} + ½ O_2 + 2H^+ \rightarrow 2 Fe^{3+} + H_2O \qquad (r2)$$

Yazici and Deveci, 2014 studied the ferric leaching of copper and other metals (nickel, silver, and palladium) from pulverised waste PCBs in acidic ferric sulphate solutions obtaining good extraction yields of copper at low solid/liquid ratio. These authors observed a negative effect of increasing solid ratio on the leaching of metals, associated with the rapid consumption of ferric iron at high solid loads.

Bioleaching is an interesting alternative from the environmental point of view for the treatment of waste PCBs. However, it has been observed that the substances that constitute PCBs exert inhibitory effects on bacterial growth and therefore on metal extraction (Liang et al., 2010). This means that the application of bioleaching to the treatment of PCBs is limited to the use of low solid/liquid ratios, which makes scaling unfeasible (Becci et al., 2021). Microrespirometric monitoring tests has been used to identify inhibitory effects of dissolved metals from PCBs (Benzal et al., 2020), concluding that Ni, Cu and Al impact the activity of microorganisms depending on the concentration and the time exposed. *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* were adapted to concentrations of 20 g/L of Cu(II) with a decrease in the ferrous iron bio-oxidation rate of the order of 15% (Mazuelos et al., 2019). Other authors have reported different levels of tolerance and adaptation to Cu(II) suggesting dependence on the strain used (Orell et al., 2010). Vargas-Straube et al., 2020, observed a decrease in the ability of *Acidithiobacillus ferrooxidans* to adhere to surfaces in the presence of increasing concentrations of Cu. The adaptation of *Acidithiobacillus ferrooxidans* to 22.5 g/L of Cd(II) (Ramos-Zúñiga et al., 2019), and to 20 g/L of Ni (II) previously adapted to 20 g/L of Cu (Li and Ke, 2001), has been reported.

Hubau et al., 2018 reported the production of a biogenic lixiviant solution to recover metals from spent printed circuit boards to be of great interest. These authors used a bubble column inoculated with a microbial consortium in the presence of activated charcoal achieving a stable performance over an extended period with a Fe^{2+} oxidation rate of 1400 mg L^{-1} h^{-1}. Bio-oxidation rates of 8400 mg L^{-1} h^{-1} and 4000 mg L^{-1} h^{-1} were achieved in a packed bed (Mousavi et al., 2007) and in a bubble column (Mousavi et al., 2008), respectively. A flooded packed bed designed for a high efficiency ferrous iron bio-oxidation attained 5800 mg L^{-1} h^{-1} (Mazuelos et al., 2000).

Wu et al., 2018 proposed a bio-oxidation–leaching–separation cycle to avoid the toxicity of PCBs, recovering 93.4% of copper from 100 g/L PCB (10 % s/L ratio) concentrates in 9 days, and determined the ferrous iron bio-oxidation as the rate-limited step in bioleaching. Hubau et al., 2020 reported the use of two bioleaching stages achieving high metal recovery yields (96% Cu, 73% Ni, and 85% Zn) with excess of ferric iron. However, the impact of microbial regeneration of ferric on the kinetics of metal dissolution could not be demonstrated, because its lag phase was longer than the time required for its chemical dissolution.

Few studies have been done with large pieces of PCBs. Adhapure et al., 2014 dissolved metals by bioleaching of large pieces of PCBs. After a pre-treatment with 10 M NaOH to remove the chemical coating from the boards, 940 mg/L of Cu were bioleached in 10 days. Also, Sodha et al., 2020 recovered Cu from waste PCBs plates by pre-treatment with NaOH for removal of the epoxy coating and bioleaching in a reactor equipped with aeration facility and a device to hold the multiple waste PCB plates of various dimensions in a vertical position. From 1 kg of PCB plates, the average extraction rate of copper in the first 5 days was 24.1 ± 2.15 g/per day, thereafter it decreased to 11 g/day. Rodrigues et al., 2015, described Cu bioleaching from coarse-ground PCBs by moderate thermophiles at 50 °C in a rotating-drum reactor with a solid concentration up to 2.5 % s/L ratio. In these conditions and after a pre-weakening step (via jaw crusher) followed by lacquer coating removal nearly 76% copper was extracted after 8 days, suggesting a limited release of inhibiting elements in solution.

In a previous work (Iglesias-González et al., 2021), the physical separation of the chemical ferric leaching from the regeneration of the leaching agent by bio-oxidation, was proved to be a promising configuration for the extraction of copper from large PCB pieces. Chemical leaching was performed in a 1L stirred tank reactor connected to a flooded packed bed (FPB) bioreactor that fulfilled the ferric iron demand. In the present study, the ferric leaching is conducted in a column where large pieces of PCBs are packed, forming a bed that in contact with the leaching agent exhibits a large solid–liquid ratio. First, in order to investigate the chemical process, ferric iron is constantly recirculated to the PCBs column and second, to study the biological regeneration of ferric, the column is connected to a flooded packed bed bioreactor that oxidises ferrous ion allowing the system to work without consuming leaching agent. With this configuration, most of bacteria are attached to the bioreactor and are not in contact with the waste, preventing adaptation problems and possible inhibitory effects described in the literature (Liang et al., 2013). In this study, the PCBs are not pulverised to avoid the expense of grinding and to eliminate solid–liquid separation operations. In addition, unlike other studies found in the bibliography with large pieces of PCB, in the present work no previous treatment is done to the plates.

2. Materials & methods

2.1. Sample

Waste PCBs were supplied by RECILEC, a local electronic waste management company in Seville (Spain). PCBs, as received, were cut to a suitable size to insert them into a column, on average the area was 4.4 cm^2. The Cu grade of the sample was between 25 and 40%, Ni and Zn between 1000 and 3000 ppm.

2.2. Ferric sulphate leaching

The leaching of large pieces of PCB with an acidic solution of biogenically produced ferric sulphate was studied. The biogenic ferric iron sulphate solution was produced in the bioreactor described below and was stored awaiting use. The bioreactor was fed with a solution composed of ferrous sulphate, the basic salts of the 9 K medium and adjusted to pH 1.25. Previously, to verify the possible dissolution of metals in an acid medium, tests were carried out in shaken flasks in which 3 pieces of PCB were put in contact with 100 mL of a sulphuric acid solution at pH 1.25. Fig. 1A shows a scheme of the device used for ferric leaching. A glass column (29 cm high and 3 cm in diameter) filled with 124 g of PCBs, was continuously bottom fed with an acidic ferric sulphate solution by a peristaltic pump at an average flow rate of 0.8 L/h, at room temperature. The column was fed from the bottom to ensure that was saturated. If it were irrigated from the top, there could be preferential channels. The mean residence time of the liquid in the column was 10 min. The liquid that overflows was conducted to a two-litre tank from where the pump feeds the column. This setting allows the continuous recirculation of leaching liquor. The total liquid volume in the system was 2L and the solid/liquid ratio in the column was 89%, being the concentration across the whole system 6.2%.

Leaching was conducted for 25 days by continuous recirculation of ferric to a column where PBCs were piled. During this time, the leaching liquor was replaced three times for fresh ferric sulphate solution (batches 1, 2 and 3). The initial concentration of ferric sulphate was 12.7 g/L in the first batch, 13.1 g/L in the second, and 13.8 g/L in the third one. The initial leaching pH was 1.25.

Periodically, a sample was taken from the column overflow to analyse Cu, Zn, Ni, Fe and Fe(II) in solution as well as to monitor flow rate. When pH exceeded the value of 1.4, it was adjusted to 1.25 with dilute sulphuric acid.

After 25 days of operation, the PCBs were washed with a solution of sulphuric acid at pH 1.25. They were removed from the column, dried, weighed, and digested with aqua regia to determine copper content and copper leaching yield.
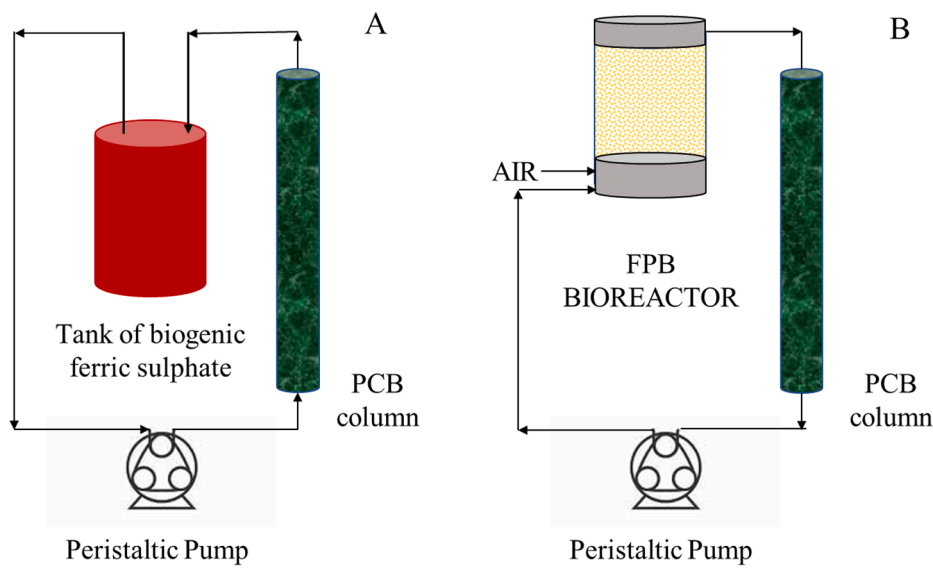
Fig. 1. Schematic of the device used for ferric sulphate leaching of PCBs packed in a column (A), and idem connected to the bioreactor for ferric iron regeneration (B).

2.3. Ferric sulphate leaching assisted by bioreactor

With the aim of bio-oxidising the ferrous iron produced in the ferric leaching of PCBs, the column, above described, was connected to a bioreactor. as shown in Fig. 1B.

The bioreactor was a flooded packed bed (FPB) developed for the oxidation of ferrous ion (Mazuelos et al., 1999), (Mazuelos et al., 2000). Biomass was immobilised in a biofilm that covers the surfaces of inert siliceous stone particles of 6–8 mm, by the procedure proposed by Mazuelos et al. (2001). Bioreactor was inoculated with a bacterial consortium originally isolated from Rio Tinto Mines drainage waters consisted mainly of *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, and some heterotrophic bacteria (mostly related with *Acidophilium* genus) (Mazuelos et al., 2012). The bacterial consortium was routinely maintained on a modified 9 K medium at pH 1.25.

Liquid was fed by a peristaltic pump and air by a compressor controlled by a rotameter (750 mL/h). Solution outlet was placed at the top of the FPB bioreactor by overflow.

The column, filled with 100 g of PCB, was continuously fed with biogenic ferric sulphate solution coming from the bioreactor and the pregnant liquor that came out of the bottom of the column, was fed to the bioreactor. The average flow rate was 0.8 L/h. The mean residence time of liquid in the column was 10 min, The initial ferric solution had a concentration of 20 g/L of iron (III). The total liquid volume in the system was 736 mL and the solid/liquid ratio in the column was 65.4% which means a solid/liquid ratio in the whole system of 13.6%. The evaporation losses, associated to aeration in the bioreactor, were replaced with an aqueous solution of sulphuric acid at pH 1.25 at the inlet of the column. Periodically, part of pregnant liquor solution was purged and replaced by copper-free biogenic ferric sulphate solution.

Once the operation was finished, the PCBs were washed with a solution of sulphuric acid at pH 1.25. They were removed from the column, dried, weighed, and digested with aqua regia to determine copper content and copper extraction.

2.4. Analysis and control

During the tests, pH, ORP and copper and iron concentrations were periodically controlled, pH was periodically adjusted with the addition of dilute sulphuric acid. Metals in solution were measured by atomic absorption spectrophotometry (2380 spectrophotometer Perkin Elmer,

United States). Ferrous iron concentration was determined by automatic titration with $K_2Cr_2O_7$.

Leaching residues were subjected to acid digestion with aqua regia (HCl/HNO$_3$ 3:1) to determine the copper extraction and the initial copper grade. Initial copper grade in PCB samples was determined as the sum of the copper dissolved by ferric leaching, that which recovered in the acid wash and that which analysed in the final residue.

3. Results

3.1. Ferric leaching

Leaching of PCBs piled in a column was conducted for 25 days by continuous recirculation of a biogenic ferric sulphate solution. During this period, the leaching solution was replaced three times (batches 1, 2 and 3).

Fig. 2A shows ORP evolution over time and Fig. 2B and Fig. 2C show the evolution of copper and ferrous iron concentrations, respectively, during the ferric leaching test. Squares represent the first batch of ferric ion used. Copper was dissolved at an average rate of 55 mg $Cu^{2+}L^{-1}h^{-1}$. It is observed that the copper output corresponds to a sudden drop in potential and an increase in ferrous iron concentration. After that, as the potential remained constant, it was decided to change the leaching solution for fresh ferric (second batch). The second batch of ferric corresponds to triangles, and again a sharp drop in potential was observed, which then varied slightly. With the drop in potential, a significant increase in copper concentration was observed, which then varied at an average rate of 17 mg $Cu^{2+}L^{-1}h^{-1}$. The third batch is represented by circles, observing a similar behaviour regarding ORP, however with a lower average rate of copper leaching, specifically 10 mg $Cu^{2+}L^{-1}h^{-1}$. The decrease in copper leaching kinetics in batches 2 and 3, despite having introduced ferric sulphate with the same characteristics as those of batch 1, could be justified by the peculiar structure of the PCBs. That is a multilayer structure consisting of fiberglass epoxy resin covered by copper foil on both sides. First, the most accessible copper (copper on PCB surface) was rapidly dissolved by ferric ion, and then the copper that was arranged inside the layers began to react. The kinetics slowed down due to the decrease in ferric iron concentration and, also, due to the resistance to mass transfer in the inner layers. The average ferrous iron generation rate was 144 mg $Fe^{2+} L^{-1}h^{-1}$ in the first batch, 25 in the second and 18 mg $Fe^{2+}L^{-1}h^{-1}$ in the third one. The rate of ferrous ion
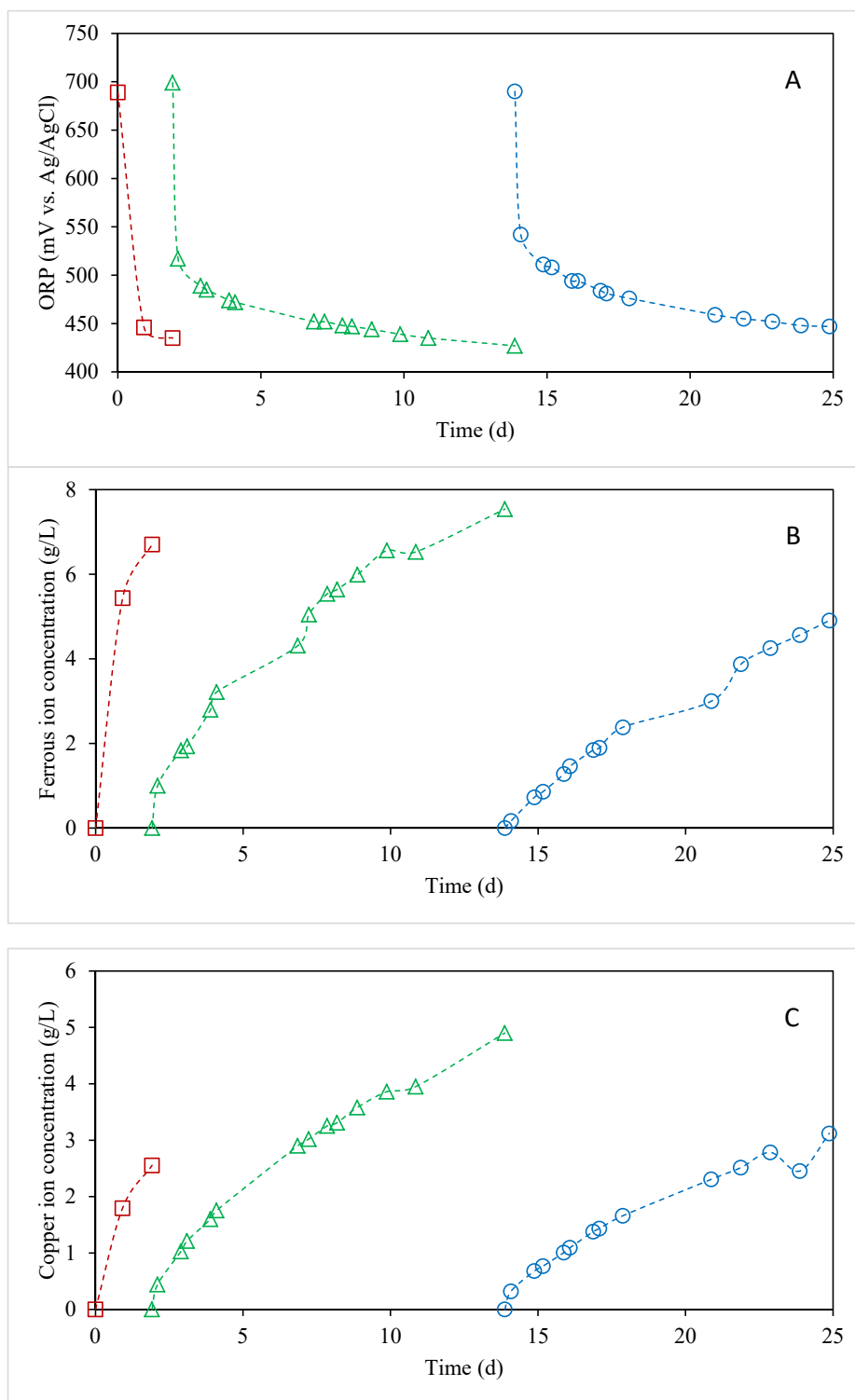
Fig. 2. Leaching of PCB piled in column with continuous ferric sulphate recirculation. Solid/liquid ratio 89%. Evolution over time of (A) ORP, (B) copper concentration, and (C) ferrous iron concentration in ferric leaching. Squares: first batch, triangles: second batch, and circles: third batch.

generation drops in each batch, because of the slower oxidation rate of copper.

Fig. 3 shows the evolution of the concentrations of minority metals such as Zn (empty symbols) and Ni (filled symbols). It is observed how the leaching speed follows a similar trend to that of copper, being faster in the first batch than in the subsequent ones. In the last batch, the concentration of both metals remains almost constant, achieving a dissolution of 94% of Ni and 99% of Zn.

Fig. 4 shows the evolution of total and ferric iron concentrations as well as pH (secondary y-axis) during ferric leaching test. The total iron concentration is kept constant in each batch with small fluctuations corresponding to the dissolved iron from PCBs and to the one that precipitates. Ferric iron concentration decreased as the reaction progressed, and the ferric iron consumption rate was lower in successive batches. These observations are in agreement with the results of a previous work in which the kinetics of leaching of large pieces of PCB in stirred tanks
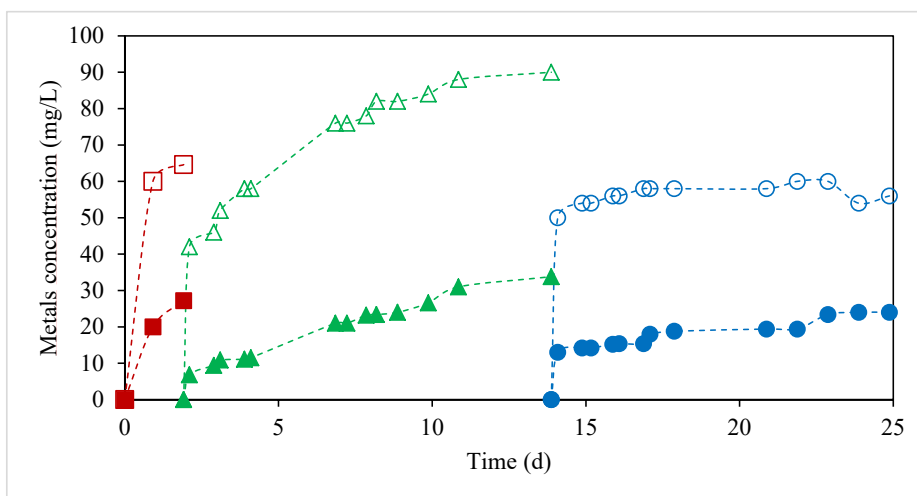
Fig. 3. Leaching of PCB piled in column with continuous ferric sulphate recirculation. Solid/liquid ratio 89%. Evolution over time of Ni (filled symbols) and Zn (empty symbols) concentrations, in ferric leaching. Squares: first batch, triangles: second batch, and circles: third batch.
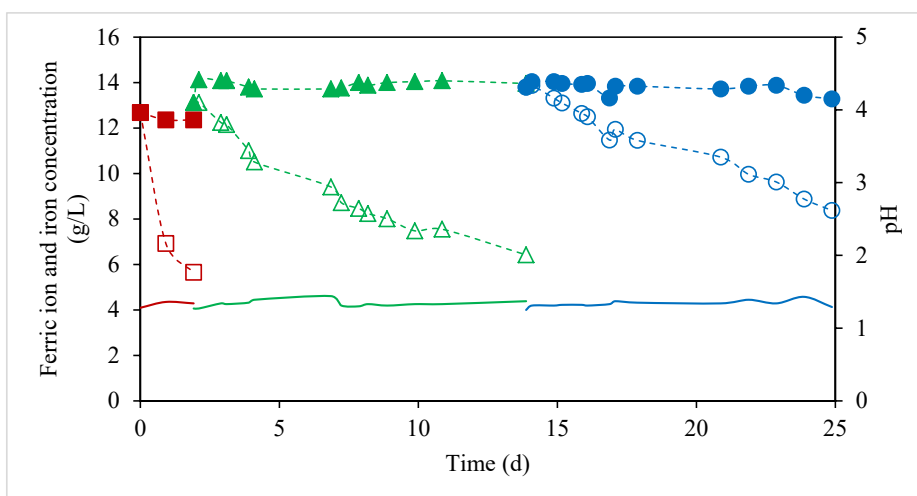

Fig. 4. Leaching of PCB piled in column with continuous ferric sulphate recirculation. Solid/liquid ratio 89%. Evolution over time of total iron concentration (filled symbols), ferric iron concentration (empty symbols) and pH (lines in secondary y-axis) in ferric leaching. Squares: first batch, triangles: second batch, and circles: third batch.

with ferric iron in excess over the stoichiometric was limited by the rate mass transfer (Iglesias-González et al., 2021).

There were no large variations in pH, it only had to be adjusted twice, in which it slightly exceeded the value 1.4, which indicates a low acid consumption. This together with the fact that in the preliminary tests at pH 1.25 no solubilization of metals was observed confirms that the contribution of the acid to the leaching is negligible.

Under the conditions tested, it took 25 days to extract just over 60% of the copper contained in large pieces of PCBs with an initial copper grade of 25%. With the first batch of biogenic ferric sulphate, 15% of the copper was leached in 2 days, with the second 42.5% in 12 more days, and with the third, 62.2% of Cu was leached in 9 more days. The solubilization of other elements such as zinc and nickel (initially 3030 g/t Zn and 1297 g/t Ni) reached 99 and 94% respectively. The gold content in the final leaching residue was 32 g/t. Gold and other precious metals retained in the leaching residue could be recovered in a later stage.

3.2. Ferric leaching assisted by bioreactor.

In this section, the results of ferric leaching of 100 g of PCBs with the column connected to a bioreactor for ferrous iron bio-oxidation are

shown. From Fig. 2 it can be deduced that copper leaching rate was higher at higher potentials. A high ORP decrease was observed in ferric leaching due to ferric ion exhaustion and this drop caused a slower copper dissolution kinetics. To promote high ORP values, in the following experiment two modifications were implemented: 1) the initial concentration of ferric was increased to 20 g/L, and 2) the column was connected to a bioreactor for the bio-oxidation of the ferrous ion generated, as shown in Fig. 1. These modifications are supported by the results obtained by Iglesias-González et al. (2021)

Fig. 5 shows the evolution of ORP and pH over time at the outlet of the bioreactor (inlet of the column) and at the outlet of the column (inlet of the bioreactor). Filled squares show the ORP at the input, and empty squares at the output of the column (chemical reactor). The trend of both lines is similar. At the beginning there was a fall in potential, which then grew and remained constant due to microbial activity. This indicated a good response from the bioreactor. The ORP of the solution entering the column (bioreactor outlet) remained practically constant throughout the operation (700 mV vs. Ag/AgCl), which means that the bioreactor was able to oxidise all the ferrous ion generated in the column and to fulfil the objective of keeping the ferric concentration constant. It should be noted that this configuration allowed to operate at very high potentials
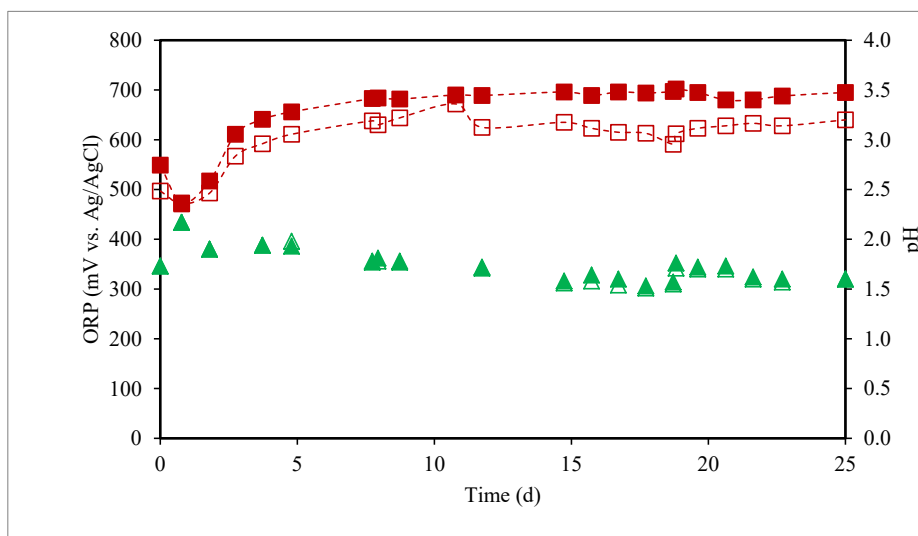
Fig. 5. Ferric leaching of PCB piled in column assisted by bioreactor for ferrous iron bio-oxidation. Solid/liquid ratio 65.4%. Evolution of ORP (squares) and pH (triangles) over time, at the input (filled symbols), and at the output (empty symbols) of the column.

compared to those observed in the bibliography in bioleaching tests, between 150 and 300 mV (Arshadi et al., 2019) or 321–575 mV (Sodha et al., 2020).

The pH was kept below 2 by adding sulphuric acid to the bioreactor outlet, when necessary, pH values at the inlet and at the outlet of the column were similar (filled and empty triangles Fig. 5), indicating no acid consumption by chemical reaction. The pH tended to rise due to the regeneration of ferrous iron in the bioreactor (r2). The sum of the copper dissolved by ferric leaching, and the analysed in the final residue supposed a grade of copper in the initial PCBs of 30%, and a 90% of copper extraction after 25 days of leaching.

4. .

Fig. 6 shows the evolution of Cu concentration and the percentage of Cu dissolution over time. Fluctuations in copper concentrations correspond to pregnant solution purges and Cu-free liquor replacements. First purge was carried out almost at the beginning, 18 h after starting the test, when the copper concentration reached 8 g/L, later the copper concentration continued to increase to 18 g/L, at which point Cu was again purged. Two other purges were performed on days 17 and 19. The

percentage of Cu dissolution curve (squares) has 4 zones: 1) between 0 and 5 days where the initial Cu dissolution rate was very fast and then slows down; 2) a linear zone between 5 and 12 days with an abnormally low leaching rate; 3) another linear zone between 12 and 19 days where the leaching rate was faster, from 50 to 82% of Cu dissolution; and 4) a final linear depletion zone. At first, the copper leaching rate was faster because the more accessible copper, the exposed copper on the outer surfaces of the plates, was dissolving. Then limitations by mass transfer began because Fe(III) ions had to reach the internal metallic copper layers. It is interesting to note that the kinetics slowdown observed in the interval 5–12 days coincides with the highest recorded copper concentration values (10–18 g/L). As can be seen in the third zone, the dissolution rate increased when the copper loaded liquor was changed to a copper-free ferric solution (second and third purges). This seems to indicate that high concentrations of Cu in bulk solution are responsible for the decrease in the leaching rate, which would not be an inconvenience in an industrial application in which the copper is constantly purged from the system for its recovery.

In relation to the high concentrations of copper in the liquor, it should be noted that the operation of the bioreactor was not affected, since, as it can be seen Fig. 5, the potential at the outlet remained
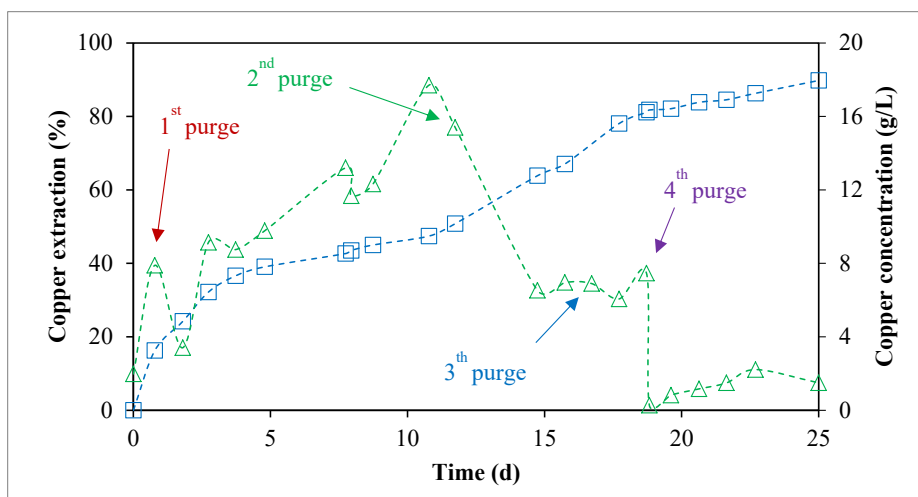

Fig. 6. Ferric leaching of PCB piled in column assisted by bioreactor for ferrous iron bio-oxidation. Solid/liquid ratio 65.4%. Squares: Cu dissolution percentage and triangles (secondary y-axis): Cu concentration. The points at which Cu is purged from the leaching solution are indicated.

constant (700 mV) which means that all the ferrous iron that entered the bioreactor as a result of the leaching reaction is bio-oxidised inside. These results are in accordance with Mazuelos et al. (2019) that examined the effect of Cu(II) on continuous Fe(II) bio-oxidation using a packed bed bioreactor with supported cells, and concluded that bio-oxidation was possible in the presence of 20 g L^{-1} of Cu(II).

Since ferrous iron concentrations in the system were low, the bioreactor was oversized. This means that if the PCB column had been larger, the bioreactor probably would have worked satisfactorily too.

The results obtained by connecting the column to the bioreactor for the regeneration of the ferric iron were much better than those obtained in the column without connecting to the bioreactor. To achieve more than 60% extraction in the first case required 14 days while in the second, 25 days. Under the conditions tested, 90% of the copper contained in 100 g of PCB pieces was leached in 25 days when FPB bioreactor continuously regenerated the leaching agent. These differences are greater if it is considered that the initial Cu grade in PCBs treated only by ferric leaching was 25% and that of those treated by bioreactor-assisted ferric leaching was 30%.

5. Conclusions and outlooks

Ferric leaching of large waste PCB parts at high solid to liquid ratio is strongly dependent on the concentration of ferric iron. A high ORP decrease was observed in ferric leaching due to ferric ion exhaustion, this drop caused a slower copper dissolution kinetics. The connection of the reactor to a FPB bioreactor for the oxidation of the generated ferrous iron, enabled a constant ORP (about 700 mV vs. Ag/AgCl) during the whole test time. The improvement of oxidising conditions hugely increased copper dissolution rate, reaching 90% of copper recovery after 25 days. The performance of FPB bioreactor has been excellent. It has operated continuously during the 25 days without showing inhibition problems and generating a leaching liquor with a high and constant ORP.

The proposed configuration for the copper recovery from waste PCBs consists of a chemical reactor, where large PCBs pieces are piled in a column (heap or vat) at a high solid load, connected to a FPB bioreactor that regenerates the spent ferric ion enabling the leaching without reagents consumption. Copper could be recovered by a conventional hydrometallurgical process as solvent extraction and electrowinning.

This configuration has the following advantages: The process runs under mild temperature and atmospheric pressure conditions. PCBs are not ground, and the liquid circulates through the system and the solids remain in the column avoiding solid–liquid separation stages. It works in a closed circuit, with the consequent saving of water and reagents. The high solid to liquid ratio enables the use of smaller installations. There is no contact between bacteria and waste which avoids inhibitory effects. The use of a bioreactor allows to keep the ferric concentration constant which improves the kinetics of copper dissolution. The separation of the chemical and biological reactors gives robustness to the system and allows to enhance the operation of each reactor independently, for example, it could be possible to carry out the chemical reaction at high temperature without detriment to the bacterial population. In short, this is a simple, efficient, low-cost, and environmentally friendly process.

CRediT authorship contribution statement

Nieves Iglesias-Gonzalez: Investigation, Methodology, Formal analysis, Conceptualization, Data curation, Writing – original draft, Writing – review & editing. **Pablo Ramirez:** Investigation, Formal analysis, Writing – review & editing. **Juan Lorenzo-Tallafigo:** Investigation, Formal analysis, Writing – review & editing. **Aurora Romero-García:** Investigation, Methodology. **Alfonso Mazuelos:** Investigation, Conceptualization, Methodology, Writing – review & editing. **Rafael Romero:** Supervision, Validation. **Francisco Carranza:** Resources, Supervision, Methodology.

Declaration of Competing Interest

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.

References

Adhapure, N.N., Dhakephalkar, P.K., Dhakephalkar, A.P., Tembhurkar, V.R., Rajgure, A. V., Deshmukh, A.M., 2014. Use of large pieces of printed circuit boards for bioleaching to avoid "precipitate contamination problem" and to simplify overall metal recovery. MethodsX 1, e181–e186. https://doi.org/10.1016/j.mex.2014.08.011.

Arshadi, M., Yaghmaei, S., Mousavi, S.M., 2019. Optimal electronic waste combination for maximal recovery of Cu-Ni-Fe by Acidithiobacillus ferrooxidans. J. Clean. Prod. 240, 118077. https://doi.org/10.1016/j.jclepro.2019.118077.

Arya, S., Kumar, S., 2020. Bioleaching: urban mining option to curb the menace of E-waste challenge. Bioengineered 11 (1), 640–660. https://doi.org/10.1080/21655979.2020.1775988.

Becci, A., Amato, A., Rodríguez-Maroto, J.M., Beolchini, F., 2021. Bioleaching of End-of-Life Printed Circuit Boards: Mathematical Modeling and Kinetic Analysis. Ind. Eng. Chem. Res. 60 (11), 4261–4268. https://doi.org/10.1021/acs.iecr.0c05566.

Benzal, E., Cano, A., Solé, M., Lao-Luque, C., Gamisans, X., Dorado, A.D., 2020. Copper Recovery from PCBs by Acidithiobacillus ferrooxidans: Toxicity of Bioleached Metals on Biological Activity. Waste Biomass Valorizat. 11 (10), 5483–5492. https://doi.org/10.1007/s12649-020-01036-y.

Hubau, A., Chagnes, A., Minier, M., Touzé, S., Chapron, S., Guezennec, A.G., 2019. Recycling-oriented methodology to sample and characterize the metal composition of waste Printed Circuit Boards. Waste Manag. 91, 62–71. https://doi.org/10.1016/j.wasman.2019.04.041.

Hubau, A., Minier, M., Chagnes, A., Joulian, C., Perez, C., Guezennec, A.G., 2018. Continuous production of a biogenic ferric iron lixiviant for the bioleaching of printed circuit boards (PCBs). Hydrometallurgy 180, 180–191. https://doi.org/10.1016/J.HYDROMET.2018.07.001.

Hubau, A., Minier, M., Chagnes, A., Joulian, C., Silvente, C., Guezennec, A.-G., 2020. Recovery of metals in a double-stage continuous bioreactor for acidic bioleaching of printed circuit boards (PCBs). Sep. Purif. Technol. 238, 116481. https://doi.org/10.1016/j.seppur.2019.116481.

Iglesias-González, N., Carranza, F., Mazuelos, A., Romero, R., Lorenzo-Tallafigo, J., Romero-García, A., Ramírez, P., 2021. The BRISA process as a path for efficient copper recovery from waste PCBs. Hydrometallurgy 205, 105750. https://doi.org/10.1016/j.hydromet.2021.105750.

Li, H., Ke, J., 2001. Influence of Ni^{2+} and Mg^{2+}on the growth and activity of Cu^{2+}-adapted Thiobacillus ferrooxidans. Hydrometallurgy 61, 151–156. https://doi.org/10.1016/S0304-386X(01)00167-0.

Liang, G., Mo, Y., Zhou, Q., 2010. Novel strategies of bioleaching metals from printed circuit boards (PCBs) in mixed cultivation of two acidophiles. Enzyme Microb. Technol. 47 (7), 322–326. https://doi.org/10.1016/j.enzmictec.2010.08.002.

Liang, G., Tang, J., Liu, W., Zhou, Q., 2013. Optimizing mixed culture of two acidophiles to improve copper recovery from printed circuit boards (PCBs). J. Hazard. Mater. 250–251, 238–245. https://doi.org/10.1016/J.JHAZMAT.2013.01.077.

Mazuelos, A., Carranza, F., Palencia, I., Romero, R., 2000. High efficiency reactor for the biooxidation of ferrous iron. Hydrometallurgy 58 (3), 269–275. https://doi.org/10.1016/S0304-386X(00)00141-9.

Mazuelos, A., García-Tinajero, C.J., Romero, R., Iglesias-González, N., Carranza, F., 2019. Causes of inhibition of bioleaching by Cu are also thermodynamic. J. Chem. Technol. Biotechnol. 94 (1), 185–194. https://doi.org/10.1002/jctb.5761.

Mazuelos, A., Moreno, J.M., Carranza, F., Palomino, C., Torres, A., Villalobo, E., 2012. Biotic factor does not limit operational pH in packed-bed bioreactor for ferrous iron biooxidation. J. Ind. Microbiol. Biotechnol. 39, 1851–1858. https://doi.org/10.1007/s10295-012-1187-9.

Mazuelos, A., Palencia, I., Romero, R., Rodríguez, G., Carranza, F., 2001. Ferric iron production in packed bed bioreactors: influence of pH, temperature, particle size, bacterial support material and type of air distributor. Miner. Eng. 14 (5), 507–514. https://doi.org/10.1016/S0892-6875(01)00038-3.

Mazuelos, A., Romero, R., Palencia, I., Iglesias, N., Carranza, F., 1999. Continuous ferrous iron biooxidation in flooded packed bed reactors. Miner. Eng. 12 (5), 559–564. https://doi.org/10.1016/S0892-6875(99)00037-0.

Mousavi, S.M., Jafari, A., Yaghmaei, S., Vossoughi, M., Turunen, I., 2008. Experiments and CFD simulation of ferrous biooxidation in a bubble column bioreactor. Comput. Chem. Eng. 32 (8), 1681–1688. https://doi.org/10.1016/j.compchemeng.2007.08.010.

Mousavi, S.M., Yaghmaei, S., Jafari, A., Vossoughi, M., Ghobadi, Z., 2007. Optimization of ferrous biooxidation rate in a packed bed bioreactor using Taguchi approach. Chem. Eng. Process. Process Intensif. 46 (10), 935–940. https://doi.org/10.1016/j.cep.2007.06.010.

Oguchi, M., Murakami, S., Sakanakura, H., Kida, A., Kameya, T., 2011. A preliminary categorization of end-of-life electrical and electronic equipment as secondary metal resources. Waste Manag. 31 (9-10), 2150–2160. https://doi.org/10.1016/j.wasman.2011.05.009.

Orell, A., Navarro, C.A., Arancibia, R., Mobarec, J.C., Jerez, C.A., 2010. Life in blue: Copper resistance mechanisms of bacteria and Archaea used in industrial biomining of minerals. Biotechnol. Adv. 28 (6), 839–848. https://doi.org/10.1016/j.biotechadv.2010.07.003.

Pietrelli, L., Ferro, S., Vocciante, M., 2019. Eco-friendly and cost-effective strategies for metals recovery from printed circuit boards. Renew. Sustain. Energy Rev. 112, 317–323. https://doi.org/10.1016/j.rser.2019.05.055.

Ramos-Zúñiga, J., Gallardo, S., Martínez-Bussenius, C., Norambuena, R., Navarro, C.A., Paradela, A., Jerez, C.A., 2019. Response of the biomining Acidithiobacillus ferrooxidans to high cadmium concentrations. J. Proteomics 198, 132–144. https://doi.org/10.1016/j.jprot.2018.12.013.

Rodrigues, M.L.M., Leão, V.A., Gomes, O., Lambert, F., Bastin, D., Gaydardzhiev, S., 2015. Copper extraction from coarsely ground printed circuit boards using moderate thermophilic bacteria in a rotating-drum reactor. Waste Manag. 41, 148–158. https://doi.org/10.1016/J.WASMAN.2015.04.001.

Sodha, A.B., Tipre, D.R., Dave, S.R., 2020. Optimisation of biohydrometallurgical batch reactor process for copper extraction and recovery from non-pulverized waste printed circuit boards. Hydrometallurgy 191, 105170. https://doi.org/10.1016/j.hydromet.2019.105170.

Vargas-Straube, M.J., Beard, S., Norambuena, R., Paradela, A., Vera, M., Jerez, C.A., 2020. High copper concentration reduces biofilm formation in Acidithiobacillus ferrooxidans by decreasing production of extracellular polymeric substances and its adherence to elemental sulfur. J. Proteomics 225, 103874. https://doi.org/10.1016/j.jprot.2020.103874.

Wu, W., Liu, X., Zhang, X.u., Zhu, M., Tan, W., 2018. Bioleaching of copper from waste printed circuit boards by bacteria-free cultural supernatant of iron–sulfur-oxidizing bacteria. Bioresour. Bioprocess. 5 (1) https://doi.org/10.1186/s40643-018-0196-6.

Yazici, E.Y., Deveci, H., 2014. Ferric sulphate leaching of metals from waste printed circuit boards. Int. J. Miner. Process. 133, 39–45. https://doi.org/10.1016/j.minpro.2014.09.015.