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Abstract: During bioleaching, the use of bacteria allows the dissolution of metals with markedly reduced amount of reagents and mild pressure and temperature conditions, compared to usual operating conditions. In our study, acidophilic bioleaching was applied to comminuted spent printed circuit boards (PCBs). These wastes contain various metals, including precious and base metals, with concentrations that are generally higher than those found in primary resources. Some studies already demonstrated the efficiency of PCBs bioleaching but significant variations are observed between reported bioleaching rates. In the present study, a double-stage bioreactor has been designed and used in order to bioleach comminuted PCBs in continuous mode. The first stage of the continuous bioreactor was a bubble column in which the acidophilic consortium BRGM-KCC mainly composed of *Leptospirillum ferriphilum* and *Sulfobacillus benefaciens* was used to oxidize Fe(II) into Fe(III). The resulting leaching solution was employed to leach the metals contained in PCBs under mechanical stirring in the second stage of the bioreactor. Such a configuration was particularly relevant to reduce the impact of PCBs toxicity on bacterial growth and to maximize bioleaching rates. The culture was able to slowly adapt to PCBs (1% w/v). Consequently, with 48 hours residence time, main metals were dissolved with high yields : 96% Cu, 85% Zn, 73% Ni and 93% Co. When the solid concentration was increased up to 1.8%(w/v), it resulted in higher dissolution rates.

Keywords: Bioleaching, Printed circuit boards, Acidophilic, Recovery, WEEE.

1. Introduction

Spent printed circuit boards (PCBs) are raising attention because they contain almost 35% of metals including precious and strategic metals even at greater concentration than in primary resources [1]. Consequently, spent PCBs are becoming a valuable resource. Today, high-grade PCBs are treated by pyrometallurgy to recover precious metals but many strategic metals are lost in the slag during this operation and the energy-cost of such processes is more and more disadvantageous. Therefore, the design of energy-efficient and cost-effective new processes capable to perform efficient metal recovery from PCBs is particularly important. Emerging techniques based on mechanical processes and hydrometallurgy appear as alternative solutions. In particular, biohydrometallurgy could be very promising. In the literature, few studies deal with the use of bioleaching for the treatment of spent PCBs by means of acidophilic microorganisms. Following main reactions may occur:

$$2Fe^{3+} + M^0 \rightarrow 2Fe^{2+} + M^{2+} \text{ (chemical)} \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \text{ (biological)} \quad (2)$$

In the literature, most studies dedicated to acidophilic bioleaching of spent PCBs were performed at the lab scale in shake flasks and several parameters were studied. Staggering the addition of PCBs from the inoculation appeared particularly important, as PCBs may be responsible for inhibition phenomena towards the growth and activity of microorganisms [2]. In order to avoid such limitations, a double-stage continuous bioreactor was designed. In the first stage, ferrous iron is biologically oxidized while in the second stage, comminuted spent PCBs are leached, using the biogenic lixiviant solution produced in the first stage. The present paper focuses on the results obtained with this double-stage continuous bioreactor.

2. Materials and methods

2-1. Growth medium and bacterial culture

The inoculum used for continuous cultures was obtained from the BRGM-KCC microbial consortium subcultured on pyrite tailings. This consortium has already been fully described [3]. The predominant organisms in the culture are affiliated to the genera *Leptospirillum*, *Acidithiobacillus* and *Sulfobacillus*. The culture medium, adjusted to pH 1.1, consisted of 0.40 $g.L^{-1}$ $(NH_4)_2SO_4$, 0.81 $g.L^{-1}$ H_3PO_4 85%, 0.48 $g.L^{-1}$ KOH, 0.52 $g.L^{-1}$ $MgSO_4.7H_2O$ and 1 $g.L^{-1}$ Fe(II) as $FeSO_4.7H_2O$.

2-2. Printed Circuit Boards

A sample of 526 kg of medium-grade spent PCBs from the Small Waste Electrical and Electronic Equipment category was collected. PCBs were shredded to 750 µm using a shear shredder and a laboratory knife mill and were successively divided using quartering methodology [4]. To determine metal concentrations, a triplicate of 40 g-samples of shredded PCBs was leached at reflux during 2 hours with 450 mL of aqua regia (HNO_3:HCl 1:3). After filtration, leachates were analyzed to determine metal concentrations, which are given in Table 1.

Table 1: Major metal concentrations (in % weight) in 40 g-samples of PCBs.

	Cu	**Fe**	**Al**	**Zn**	**Sn**	**Pb**	**Ni**	**Co**
Concentration (%)	14.58%	12.23%	6.04%	1.67%	1.67%	1.17%	0.34%	0.036%

2-3. Description of experimental setup during continuous experiments

Continuous culture experiments were carried out in a two-stage bioreactor. The first stage was a bubble column of 200 mL filled with 150 mL of liquid and 15 g of activated charcoal as solid support. This bubble column, fully described elsewhere [5], was immersed in a water bath at 35 °C, aerated with air flow between 20 and 30 $L.h^{-1}$. Air was enriched with 1% CO_2 and hydraulic residence time set to 3.2 h. The second stage was a stirred tank reactor (STR) of 2.25 L continuously fed by the leaching solution produced in the bubble column. The hydraulic residence time reached 48 h in this reactor, maintained at 35 °C. Comminuted spent PCBs were continuously added with a dosing screw. The solid concentration was set to 1%(w/v) and then 1.8% (w/v). The bubble column was inoculated with the BRGM-KCC culture at 10%v/v and was first operated in batch mode before switching into continuous mode when the redox potential reached 900 mV vs SHE.

3. Results

3-1. Bioleaching kinetics at 1%(w/v) PCBs concentration

At the beginning of the study, the PCBs concentration was set to 1%(w/v), to evaluate the ability of bacteria to dissolve metals and to grow in the second stage (STR reactor). The microbial concentration in the liquid phase was correlated to Fe(III) concentration in the STR. Both increased over time, to reach a permanent regime after 1600 h (see Figure 1). Dissolution kinetics followed the same trend with a slow increase over time, to reach high kinetics after 1600 h (see Table 2).

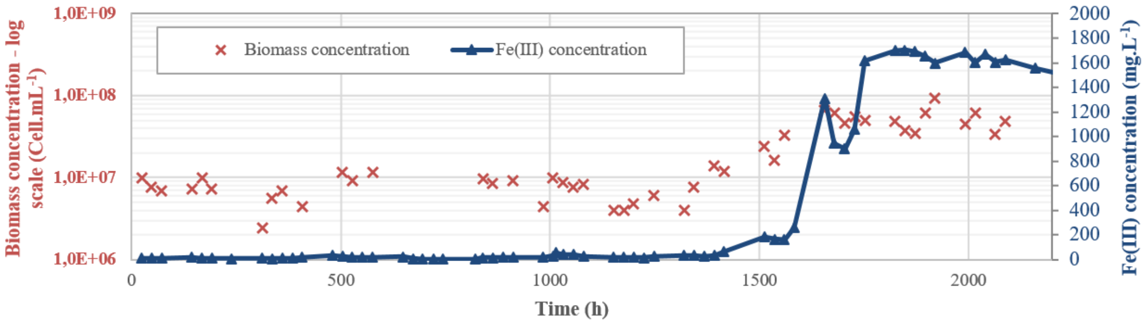

Figure 1: Biomass and Fe(III) concentration in the 2nd stage of the continuous bioreactor

Table 2: Dissolution rates and yields during continuous bioleaching at 1%(w/v) of PCBs.

	Cu	Fe	Al	Zn	Sn	Pb	Ni	Co
Dissolution rates ($mg.L^{-1}.h^{-1}$)	28.33	12.17	6.04	2.71	0.40	0.28	0.45	0.067
Dissolution yields (%)	96%	59%	49%	85%	11%	12%	73%	93%

3-2. Bioleaching kinetics at higher solid concentration (1.8%(w/v))

After the increase of solid concentration, metals dissolution rates increased gradually and stabilized after 1000 hours (see Table 3). Higher dissolution yields were reached. For Cu, dissolution yield was above 100%. This could reflect a problem during the determination of Cu concentration in the initial sample of PCBs. The redox potential was higher than 880 mV vs SHE for both solid concentrations, which showed that all Fe(II) produced by the dissolution of metals was oxidized. Concerning biomass concentration, the total cell concentration reached 2.10^8 cells/mL at 1.8%(w/v), while it reached 5.10^7 cells/mL at 1%(w/v).

Table 3: Dissolution rates and yields during continuous bioleaching at 1.8%(w/v) of PCBs.

	Cu	Fe	Al	Zn	Sn	Pb	Ni	Co
Dissolution rates ($mg.L^{-1}.h^{-1}$)	62.50	34.48	11.67	5.63	0.69	0.34	1.08	0.117
Dissolution yields (%)	115%	76%	52%	91%	11%	8%	86%	87%

4. Discussion

At the beginning of the study of PCBs bioleaching in continuous mode with 1%(w/v) PCBs, slow increase in metals dissolution yields was observed and can be attributed to cells adaptation phases. Initially, bacteria entering the second stage (STR) were not able to grow or to oxidize Fe(II) noticeably. Metals dissolution was mainly related to chemical leaching by incoming Fe(III) (1 $g.L^{-1}$) and sulfuric acid. Then, metal dissolution rates increased but no Fe(III) is detected, since its consumption for metal leaching is faster than its regeneration. Finally, the number of cells exponentially increased in the liquid phase. The microbial culture regenerated Fe(III) much faster than the consumption of Fe(III) by the metal dissolution reactions, so that only Fe(III) was detected. High dissolution kinetics were obtained. Microbial adaptation was also noticed when the solid concentration was increased to 1.8%(w/v). This concentration did not inhibit the bacterial growth and activity. The higher concentration of substrate favored the growth of micro-organisms in the second stage.

5. Conclusion

A continuous double stage bioreactor was used to carry out the bioleaching of spent PCBs. The adaptation of microbial culture to PCBs with solid concentrations up to 1.8%(w/v) led to high dissolution kinetics for most metals (Cu, Ni, Zn, Fe and Co).

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