Hydrometallurgy 180 (2018) 180–191

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Continuous production of a biogenic ferric iron lixiviant for the bioleaching of printed circuit boards (PCBs)

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ARTICLE INFO

Keywords:
Bioleaching
Bio-oxidation
Printed circuit boards
Acidophilic

ABSTRACT

Ferric iron is a low-cost oxidant frequently used in hydrometallurgy and is particularly suitable to leach various metals from printed circuit boards (PCBs). This paper presents the use of the BRGM-KCC acidophilic consortium to generate ferric iron solution in a bubble column run in continuous mode. The influence of influent ferrous iron concentration, ranging from 1 to 9 g L^{-1} on the bio-oxidation rate was studied in the presence of a solid support. The impacts of the quantity of solid support, the hydraulic residence time (HRT), the culture medium and the type of support were established. Stable performance was achieved over an extended period with a Fe^{2+} oxidation rate of 1400 mg L^{-1} h^{-1}. Cryogenic scanning electron microscopy was used to observe the attachment of cells on the solid support in different operating conditions and showed that the clogging of the solid support with jarosite precipitates influenced its colonization by the micro-organisms and the stability of the bioprocess. The operating conditions, and especially the influent ferrous iron concentration and nutritive medium composition, also influenced the structure and the abundance of the microbial community.

1. Introduction

The metal content of spent printed circuit boards (PCBs) can reach up to 35% (in weight), including precious and strategic metals even at greater concentrations than in primary resources. For instance, gold and copper are 25 to 250 times and 20 to 40 times more concentrated in spent PCBs than in ores, respectively (Tuncuk et al., 2012). Consequently, spent PCBs are becoming a valuable resource. At the same time, a lack of an appropriate treatment could be a cause of environmental pollution.

Today, high-grade PCBs are treated by pyrometallurgy to recover valuable metals but some metals, such as aluminium, iron and precious metals, are lost in the slag during this operation (Cui and Zhang, 2008) and the energy-cost of such processes is high. Moreover, the presence of plastics raises two important issues: first, the emission of toxic dioxins and furans; and second, the presence of plastics can bring about uncontrolled temperature increases leading to smelter damages (Hagelüken, 2006). Currently, the addition of PCBs to smelter feed represents at most 15% of the mass, the rest being metal concentrates. For example, PCBs make up 14% of the total throughput in the Noranda process in Canada and 10% in the Umicore process in Belgium (Cui and Zhang, 2008; Ghosh et al., 2015). Due to this limitation, the quantity of PCBs that are treated annually remains low. Therefore, the design of energy-efficient and cost-effective new processes for efficient metal recovery from PCBs is particularly important. Techniques based on mechanical processes and hydrometallurgy are emerging as alternative solutions.

Within this framework, biohydrometallurgy is very promising. In the literature, some studies deal with the use of bioleaching for the treatment of spent PCBs by means of acidophilic micro-organisms (Brandl et al., 2001; Ilyas et al., 2010). The use of such micro-organisms, which are mainly iron and sulfur-oxidizing, allows the extraction of various metals such as Cu, Ni and Zn. Although the mechanisms are not completely known, the following main reactions may occur:

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

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

The main issue raised by research studies dedicated to the development of bioleaching processes for PCBs treatment is linked to the reproducibility of the results, mainly because of the large heterogeneity of PCBs that leads to large variation of sample composition. Most

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https://doi.org/10.1016/j.hydromet.2018.07.001
Received 23 February 2018; Received in revised form 25 June 2018; Accepted 12 July 2018

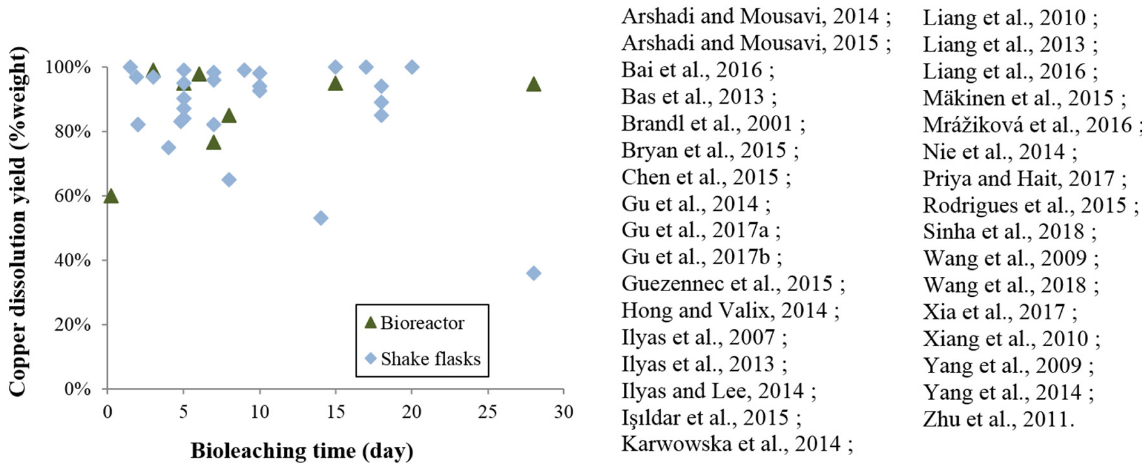

Fig. 1. Copper leaching yields versus bioleaching time in bioreactors and shake flasks in printed circuit boards bioleaching studies reported in the literature (Arshadi and Mousavi, 2014; Arshadi and Mousavi, 2015; Bai et al., 2016; Bas et al., 2013; Bryan et al., 2015; Chen et al., 2015; Gu et al., 2014; Gu et al., 2017a; Gu et al., 2017b; Hong and Valix, 2014; Ilyas and Lee, 2014; Ilyas et al., 2007; Ilyas et al., 2013; Işıldar et al., 2015; Karwowska et al., 2014; Liang et al., 2010; Liang et al., 2016; Mäkinen et al., 2015; Mrážiková et al., 2016; Nie et al., 2014; Priya and Hait, 2018; Rodrigues et al., 2015; Sinha et al., 2018; Wang et al., 2009; Wang et al, 2018; Xia et al., 2017; Xiang et al., 2010; Yang et al., 2014; Zhu et al., 2011).

studies dedicated to acidophilic bioleaching of spent PCBs to date have been performed in simple shake flasks and the quantity of PCBs added for each batch test is often too low to be representative of the whole composition of the PCB sample. Moreover, the results are highly variable as important parameters, such as dissolved oxygen concentration, pH or micro-organisms are diverse. Fig. 1 illustrates the discrepancy in copper bioleaching yields reported in the literature for spent PCBs in shake flask and reactor studies.

Finally, the addition point of raw material after inoculation influences greatly PCB bioleaching efficiency. This parameter appears particularly important as PCBs may be responsible for the inhibition of microbial growth and activity (Liang et al., 2013). Staggering the production of the lixiviant and the addition of the e-waste in a two-step process can greatly increase leaching rates (Yang et al., 2009; Guezennec et al., 2015). However, this requires the establishment of a stable steady-state operation in the first stage where biomass production and ferrous iron bio-oxidation occur (Reaction 2). The literature shows that a vast number of iron bio-oxidation studies in continuous mode have been done to develop a large range of applications. Some studies are summarised in Table 1. In this table, the study duration is the time before authors change any parameters once steady state is reached. Most of these works investigated multiple parameters to avoid kinetic limitations and to achieve the highest bio-oxidation rate. The first parameter is the characteristics of the influent, i.e. pH (Kaksonen et al., 2014a; Kinnunen and Puhakka, 2005) and ferrous iron concentration (Gómez and Cantero, 2003) since these parameters influence significantly the kinetics of bio-oxidation. The second parameter is the composition of the gas flow to avoid any limitation in carbon dioxide (required for bacterial growth, as it is the sole carbon source available) and/or oxygen (required for microbial oxidation of ferrous iron, see Reaction 1). Bastías and Gentina (2010) improved their chemostat performance by enriching air with 4% CO_2. Kinnunen and Puhakka (2004) detected an oxygen limitation when using air and used a 99.5% O_2/0.5%CO_2 gas mixture to obtain a maximal oxidation rate of 26.4 $g\,L^{-1}\,h^{-1}$. This parameter is closely linked to the presence and the type of solid support, which will impact the gas-liquid mass transfer. First studies were performed without using solid support but performance was limited due to limited biomass and cell wash out at low hydraulic residence times (HRT; Halfmeier et al., 1993a). Consequently, many solid supports were developed and investigated (Grishin and Tuovinen, 1988), e.g. polystyrene (Karamanev and Nikolov, 1988), quartz sand (Halfmeier et al., 1993b), Ni-alloy fibers (Gómez and Cantero, 2003) and activated charcoal (Kinnunen and Puhakka, 2004). The goal was to obtain large surface areas and high numbers of attached cells without slowing down mass transfer. Activated charcoal was reported as one of the best solid supports in terms of bio-oxidation performance due to its porosity which enables the retention quantities of large biomass (Jensen and Webb, 1995). Grishin and Tuovinen (1988) reported a maximal oxidation rate of 52.6 $g\,L^{-1}\,h^{-1}$ in a bioreactor with 50 mL of activated charcoal.

However, due to the high concentrations of ferric iron, Ebrahimi et al. (2005) suggested that the presence of jarosite precipitates in the bioreactor modifies the bio-oxidation rates and yields over long periods of time and affects mass transfer near the solid support. The formation of jarosite precipitates was extensively described (Kaksonen et al., 2014c); the following reaction occurs:

$$A^{+} + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow AFe_3(SO_4)_2(OH)_6 + 6H^{+} \quad (3)$$

Where A^{+} is a cation (potassium K^{+}, sodium Na^{+}, ammonium NH_4^{+}, hydronium H_3O^{+}).

During 6 months, Halfmeier et al. (1993b) operated a fixed-bed reactor in continuous mode and revealed transport limitation and long-term stability issues. Kinnunen and Puhakka (2004) highlighted the influence of jarosite accumulation on oxidation performance in a fluidized-bed reactor, with a majority of cells attached on jarosite, creating instabilities when removing these precipitates. They revealed some difficulties to maintain constant jarosite formation rate, and thus, to maintain stable performance (Kinnunen and Puhakka, 2005). Recently, Kaksonen et al. (2014a, 2014c) investigated the use of these precipitates as solid support. Ebrahimi et al. (2005) used this method to develop an airlift reactor that presented stable performance over long periods of time to establish a process of H_2S removal. The use of a settler (Kaksonen et al., 2014a, 2014c) to remove excess sludge maintained stable performance.

This paper reports the performance and the limitations obtained for the bio-oxidation of ferrous iron in a bubble column run in continuous mode, which will be used as the first stage of a biolixiviant reactor for leaching spent PCBs. The influence of influent ferrous iron concentration on the bio-oxidation rate was studied over an extended period of time. The influence of the type and quantity of solid support and of the medium composition on bio-oxidation yield were investigated. The colonization of solid support was observed by cryogenic scanning electron microscopy to understand the phenomena that affect the stability of bio-oxidation performance. The main objective of the study was to determine the operating parameters which enabled stable and maximal performance over a period of several weeks.