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Co-processing of sulfidic mining wastes and metal-rich post-consumer wastes by biohydrometallurgy

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ABSTRACT

The consequence of a strong economic growth in emerging countries combined with the rise of the world population is an increase in the demand for raw materials, leading to growing concern regarding their availability and the global efficiency of the supply chain. These tensions reinforce the need to associate the development of the recycling industry to the identification of new resources which could be used for the recovery of valuable materials. The purpose of this study is to develop a novel biological co-processing approach for the recovery of strategic metals in both sulfidic mining wastes and post-consumer wastes (WEEE). The principle of this treatment is based on two steps: mine wastes are biologically oxidized, resulting in the production of a ferric iron-sulfuric acid lixiviant solution which is used to leach base and other soluble metals contained in e-scraps. Batch tests were carried out using flotation tailings wastes containing 60% of pyrite and grinded Printed Circuit Boards (PCB < 750 μm) with a solid load of 2.5%. Two series of tests were conducted in order to study the influence of the ferric iron concentration and of the bacterial activity on metals dissolution. Results showed that a higher ferric iron concentration led to an increase in the dissolution rate of copper which is the main metal contained in the PCBs. Moreover, a dissolution yield of 98.3% was reached for copper after 2 days when bacterial activity was observed, corresponding to an increase of about 20% compared to the tests without bacterial activity. Finally, this study highlights the importance of the availability of ferric iron and of the bacterial oxidation of ferrous iron for the feasibility of this bioleaching process dealing with the recycling of PCBs.

1. Introduction

Among the different types of secondary post-consumption wastes, e-wastes represent the fastest growing and most problematic waste stream in the world. In the EU, 9.7 million tons were produced in 2009 and this is estimated to grow to a projected 12.3 million tons per year by 2020 (Huisman et al., 2008). Recovering metals from e-waste is potentially more energy efficient than mining raw material. However, they are highly complex in terms of structure and composition as very little consideration is given to end-of-life reprocessing during the design and construction of electronic goods. As a result it is not always possible to feed such waste into conventional recycling streams. Many of the metals on the "criticality" list are found in significant quantities in e-wastes (EU, 2014). The majority of the value in e-waste is in the printed circuit boards (PCBs). On average 90% of the intrinsic economic value of PCBs is in the precious metals that they contain (Cui and Zhang, 2008). They also contain some critical metals such as gallium. 65% of the world's gallium production ends up in PCBs and no current process for its recovery exists. Copper is also very important: it is much more abundant in e-wastes and PCBs than the higher value metals, that is why its recovery and recycling are crucial given the increasing scarcity and complexity of copper ore.

Pyrometallurgy is the traditional choice for metal refining from processed (usually upgraded) e-waste, resulting in the production of precious metal-bearing copper bullion (Tuncuk et al., 2012). It can be done within existing smelters treating mineral concentrates, where e-waste may be combined (10–15%) with a copper concentrate (Cui and Zhang, 2008). However, it is energy intensive and requires a relatively high grade feed material, and the ceramics from e-waste contribute to increase the final slag volume. Compared to pyrometallurgy, hydrometallurgical processes offer relatively low capital cost and are particularly suitable for small-scale installations (Tuncuk et al., 2012). An added advantage is their flexibility, offering a possibility for selective extraction of base and precious metals of interest in e-waste and PCBs. Since major metals exist in their elemental or alloy form in PCBs, their hydrometallurgical extraction has been tested using various

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oxidants (lixiviants; hydrogen peroxide, oxygen, ferric iron, etc.) under acidic (HCl, H_2SO_4, HNO_3 etc.) or ammoniacal and chloride leaching environments (Quinet et al., 2005; Deveci et al., 2010; Huang et al., 2009; Kasper et al., 2011; Tuncuk et al., 2012). These studies have shown a different degree of base and precious metals recovery efficiency. However, these processes require the consumption of a high amount of chemicals. The use of microorganisms for the recovery of metals could then be an economic and environmental alternative. Biohydrometallurgy is an established technology for concentrates and mineral processing wastes. It has been recognized as a potential technology for the treatment of metallic wastes (Bryan et al., 2012). It has been used to recover copper and zinc from slags, galvanic sludge, fly ash and filter dust with recoveries close to 100% (Krebs et al., 2006). Studies into the bioleaching of e-waste have mainly involved the treatment of printed circuit boards (PCBs). The use of organic acids produced by various fungi or biogenic cyanide has been examined, particularly for the recovery of gold and other noble metals (Brandl et al., 2001; Faramarzi et al., 2004; Brandl et al., 2008; Chi et al., 2011). However, such approaches require the selective cultivation of specific microorganisms in circum-neutral media rich in organic substrates. This often requires aseptic growth conditions and is unlikely to be practical when treating large volumes of non-sterile e-wastes. Further, the majority of the cyanide produced is consumed by the copper which is in much higher concentrations relative to target metals such as gold. Therefore, the use of ferric iron and/or proton lixiviants produced by extreme acidophiles would be preferable and more practical. Indeed, there is no need for sterile conditions and culture media are relatively simple comprising key nutrients such as sources of nitrogen, potassium and phosphorus. In mineral bioleaching the source of iron and sulfur which are oxidized by the microbial community to produce the oxidizing acidic lixiviant solution is contained in pyrite or other sulfide minerals. In the current e-waste bioleaching practices, this source of iron and sulfur must be provided in addition to the nutritive medium. This is usually realized in the form of ferrous sulfate with acidity provided via pH control with sulfuric acid or through addition of elemental sulfur. The studies published so far (Zhu et al., 2011; Yang et al., 2009; Xiang et al., 2010; Liang et al., 2010; Karwowskaa et al., 2014; Hong and Valix, 2013; Ilyas et al., 2010; Cerruti et al., 1998) were carried out in shake flasks in liquid media containing ferrous iron, sometime amended with elemental sulfur and inoculated with pure or mixed cultures of iron- and sulfur-oxidizing microorganisms. Ground e-waste (usually PCBs) was either added immediately, in a one-step process, or following initial substrate oxidation (and thus lixiviant production) in an indirect two-step or multi-step process. The toxicity of the e-waste on the microorganisms has been shown to be the major problem preventing efficient leaching. Staggering the production of the lixiviant and the addition of the e-waste in a two-step process could then greatly increase leaching rates. Furthermore, PCBs are highly acid-consuming and require a high degree of pH modification to maintain an acidic environment necessary for the microbial action and metal solubility. The necessary addition of chemical products will increase the operating cost of such processes.

In addition to deposits of secondary post-consumer wastes (the classical target of the urban mining concept), old waste deposits related to past mining and metallurgical activities can also be significant reserves of valuable base or strategic metals as well as mineral substances. Before the 20th century, only a single or, at best, a couple of metals were extracted from any given mine. The other elements were either not detected by contemporary analytical methodology or considered as mineralogical "exotica". As demonstrated by European FP7 research project ProMine (http://ptrarc.gtk.fi/ProMine/default.aspx) these types of mining and metallurgical residues contain not only rare and precious metals but also appreciable amounts of "residual" base metals (Cu, Ni, Zn, Co...) which must not be neglected in today's context of resource scarcity and the environmental management of post mining activities.

While current laboratory-scale studies provide evidence that biohydrometallurgical reprocessing of e-wastes and mining wastes are technically possible, the wider economics of such type of processes are unlikely to be favorable with the current state-of-the-art and the competition with "classical" pyro and hydro options. Using an industrial ecology approach and including the potential costs associated with the "no action scenario" in terms of waste management, a co-processing concept was envisaged.

The purpose of this study is therefore to develop a novel biological co-processing approach for the recovery of strategic metals in both sulfidic mining wastes and post-consumer wastes (e-scraps). The principle of this treatment is based on two steps: mine wastes are biologically oxidized, resulting in the production of a ferric iron-sulfuric acid lixiviant solution which is used to leach base and other soluble metals contained in e-scraps. By decoupling lixiviant production from PCB leaching in a two-step process, it is assumed that issues of toxicity will be avoided.

Bioleaching batch tests were performed using flotation tailings wastes containing 60% of pyrite in a first step, and, in a second step, grinded Printed Circuit Boards (PCB < 750 μm) with the lixiviant produced by the bioleaching of the sulfidic wastes. The results were compared to those obtained in abiotic conditions using a synthetic leaching solution instead of a solution produced biologically.

2. Materials and methods

2.1. Wastes

The mining wastes used in this study are flotation tailings mainly composed of pyrite (60%). They contain also cobalt (0.06%), copper (0.19%) and gold (1 g/t). These wastes have been chosen for their high content of pyrite, which makes them particularly suitable for bioleaching. The electronic wastes are computer PCBs grinded first under 3 mm using a shear shredder and then under 750 μm using a laboratory knife mill (Retsch, model SM2000).

2.2. Bacterial culture and nutrients

The tests were run using BRGM-KCC acidophilic and moderate thermophilic (40 °C) microbial consortium which has already been fully described (Battaglia et al., 1994; d'Hugues et al., 2003). The predominant organisms in the culture are affiliated to the genera *Leptospirillum*, *Acidithiobacillus* and *Sulfobacillus*. These bacteria are autotrophic and known as iron-oxidizer. They are also known for their tolerance to high concentrations of various metals especially copper (Guezennec et al., 2014). The culture used as

Table 1
Average metal content in PCBs used for this study.

Cu	Fe	Ni	Pb	Zn	Sn	Ag	Au	Pd	Ga	Co	Mo
g/kg						ppm					
215.1	24.3	2.4	17.5	14.6	34.6	393.6	143.9	42.4	7.9	29.2	11.2