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STATIC BIOLEACHING OF PC BOARDS BY *ACIDITHIOBACILLUS FERROOXIDANS*

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Abstract

Printed circuit boards (PC board) incorporated in most electrical and electronic equipment comprise metals, polymers, ceramics and toxic substances, and herein we used stationary bioleaching by *Acidithiobacillus ferrooxidans* to mobilise economically valuable metals and toxic elements from PC boards. The bioleaching experiments were performed in 250 mL Erlenmeyer flasks with 95 mL 9K medium, 5 mL inoculum and 1 g of non-sterile PC board fine powder. All flasks were cultivated stationary at 25°C for 10 or 20 days. The highest leaching efficiencies of 29 % Al, 36 % Cu, 25 % Ni, 3 % As, 45 % Cd, 17 %, Pb and 6 % Sb were recovered after 20 days bioleaching. However, these percentages obtained after 20 days bioleaching were only 4–5 % higher than the recoveries after 10 days, and precipitation of jarosite caused immobilisation of soluble metals in the medium. Our results ultimately established that static PC board bioleaching by *A. ferrooxidans* at laboratory temperature is relatively ineffective in extracting these elements.

Keywords: *Printed circuit boards, Bioleaching, Acidithiobacillus ferrooxidans, Metals, Toxic elements.*

1. Introduction

Electronic waste (e-waste) proceeds from discarded devices that use electricity; and these devices include computers, televisions, washing machines, refrigerators and cell phones [1]. Moreover, the rapid technological development in recent decades has led to a significant increase in the diversity and public consumption of these electronic and electrical devices, [2] and their reduced lifetime and high assembly costs have produced increased e-waste. This has, therefore, made e-waste the fastest growing waste stream with an estimated worldwide annual production of 50 million tonnes [3].

The basic component of most electronic and electrical devices is a printed circuit board (PC board) which forms a platform for assembling components and provides connections between the internal components [4]. Although over 68 % of the PC board weight consists of non-metallic components such as plastics, glass and ceramics, they also contain approximately 28–32 % of economically valuable metals including Al, Cu, Fe and Ni. Their main environmental hazard, however, comprises the content of toxic substances such as chlorinated and brominated flame retardants, epoxy resins and heavy metals [5]. PC board recycling is therefore imperative from both economic and environmental aspects.

The PC boards are currently recycled by pyrometallurgical, mechanical or hydrometallurgical processes. While hydrometallurgical processes mainly obtain metals from PC boards by leaching with concentrated inorganic acids, pyrometallurgical processes use PC board heat treatment and the resultant roasting, smelting and mechanical processes involve grinding and subsequent separation of metals from the non-metallic materials [6-8]. All these processes are energy intensive with high cost and the pyrometallurgical PC board processing releases dust and toxic gases such as dioxins and furans into the atmosphere [8-9].

In addition, the use of bioleaching to obtain metals from ores and wastes has attracted great interest in recent decades. These are essentially hydrometallurgical processes using microorganisms such as bacteria, archaea and fungi, which can increase the solubility of metals in substrates. The natural ability of microorganisms to oxidise or utilise organic and inorganic substrates in these processes produces a metal dissolving agent [10], and this metal recovery method is very promising because of the low operating costs, the creation of smaller volumes of less toxic wastewater and zero air contamination [11-13].

The acidophilic *Acidithiobacillus ferrooxidans* has proven one of the most important agents in industrial bioleaching of copper from low-concentrated sulphide ores [14]. This chemoautotrophic species acquire energy by oxidising Fe^{2+} ions, elemental sulphur and reduced sulphur forms to produce Fe^{3+} and sulfuric ions [15.16]. The strong acidification present in bioleaching by these bacteria combines with the strong Fe^{3+} oxidising agent to dissolve most metals from the substrates [17].

Moreover, several studies investigating PC board bioleaching by *A. ferrooxidans* have demonstrated high metal recovery efficiency. However, the bioleaching experiments were performed by continuous agitation on shakers at high temperatures [18-25], and both the high energy and operating costs involved have restricted PC board used in industrial metal extraction.

This study aims to provide an energy saving method which can be used in industrial metal recovery, and we, therefore, performed stationary bioleaching of non-sterile PC boards at laboratory temperature for 10 and 20 days. The recovery efficiency of economically valuable metals (Al, Cu and Ni) and toxic elements (As, Cd, Pb, and Sb) was then compared with the studies bioleaching PC boards on shakers at high temperatures.

2. Experimental

2.1. Materials and methods

2.1.1. Printed circuit board

The PC boards used in this study were demounted from personal computers. Initially, the capacitors, resistors, chips, fans and heatsinks were removed, and the PC boards were then ground in a laboratory vibrating mill WM4 (Czech Republic). The obtained PC board powder was sieved through a <200 μm mesh, and the resultant fine powder was used in all bioleaching experiments. Table 1 lists the content of the selected elements in this powder.

Table 1. Chemical composition of PC board fine powder used in this study

Element	Content (%)	Element	Content (%)
Al	0.821 ± 0.057	Ni	0.567 ± 0.039
As	0.215 ± 0.015	Pb	2.108 ± 0.169
Cd	0.015 ± 0.001	Sb	0.084 ± 0.051
Cu	7.368 ± 0.663		

All values are in mean (n = 3) ± S.D.

2.1.2. Microorganism and culture condition

The pure culture of *A. ferrooxidans* was obtained from the Institute of Environmental Engineering at the VŠB - Technical University of Ostrava. The standard used to grow *A. ferrooxidans* was 9K medium containing: 3 g L^{-1} $(NH_4)_2SO_4$, 0.5 g L^{-1} K_2HPO_4, 0.5 g L^{-1} $MgSO_4{\cdot}7H_2O$, 0.1 g L^{-1} KCl, Ca $(NO_3)_2$ 0.01 g L^{-1} and 44.22 g L^{-1} $FeSO_4{\cdot}7H_2O$, and the medium pH of was adjusted to 2 with H_2SO_4.

2.1.3. Bioleaching experiments

The bioleaching experiments were conducted in 250 mL Erlenmeyer flasks containing 95 mL of 9K medium and 1 g of non-sterile PC boards fine powder. The flasks were inoculated with 5 mL of pure *A. ferrooxidans* inoculum and cultivated stationary at 25°C for 10 and 20 days. The pH was measured periodically, and each bioleaching experiment was performed in triplicate.

2.1.4. Analytic methods

PC board fine powder was dissolved in aqua regia for element analysis: 1 g PC board sample and 40 mL of aqua regia were combined in 250 mL Erlenmeyer flasks, and the mixture was left to stand for 24 hours before centrifugation at 500 rpm for 15 minutes. The supernatant was stored at 4°C for element concentration analysis, and after bioleaching, the PC board, the samples were passed through 0.22 μm nitrocellulose membrane filters to remove cells and precipitates. The filtrate was then stored at 4°C until elements concentration analysis. The concentrations in the supernatant and filtrate were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, ThermoFisher iCap 7600, USA) at the following wavelengths (nm): A1 (396.153), As (193.696), Cd (228.802), Cu (327.393), Ni (231.604), Pb (220.353) Sb (206.836). The pH was measured by digital pH metre (WTW pH 3210 Germany), and element recovery was calculated by the following equation; C_F/C_E*100; where C_F is the concentration of leached elements in the solution after bioleaching experiments (mg L^{-1}), and C_E is the concentration of elements in the PC board before the bioleaching experiments (mg kg^{-1}).

3. Results and discussion

3.1. Variation in pH during PC board bioleaching

Figure 1 shows variations in solution pH during PC board bioleaching by *A. ferrooxidans*. Here, the pH increased throughout the experiment from initial pH 2 to pH 3 on the 10th day and pH 4 on the 20th day. The factors causing pH increase were proton consumption by both the alkaline substances present in the PC board [6,21] and during bacterial oxidation of Fe^{2+} ions to Fe^{3+} (1) [2,13].

$$2Fe^{2+} + 0,5O_2 + 2H^+ \xrightarrow{A.\ ferrooxidans} 2Fe^{3+} + H_2O \quad (1)$$

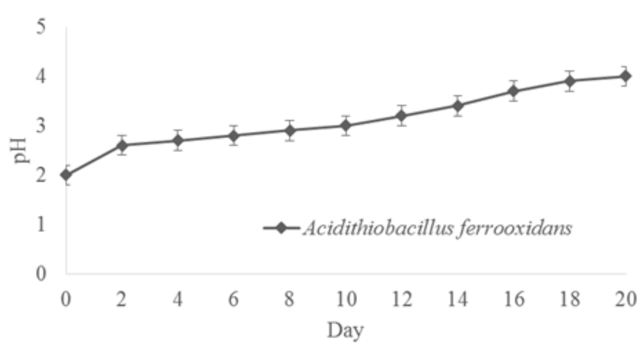

Fig. 1. Variation in pH during PC boards bioleaching by *Acidithiobacillus ferrooxidans*. All values are in mean (n = 3) ± S.D.

3.2. Recovery of economically valuable metals

The Al, Cu and Ni metals accounted for approximately 9 % of the PC boards used in the bioleaching experiments (Tab. 1). Most of these are present in elemental form, and oxidative leaching is therefore effective for their extraction. The Fe^{3+} ions produced by bacterial oxidation are strong oxidizing agents. These generate a redox potential of 0.77 V in aqueous solution [12,16,19] and can oxidise the elemental metals present in PC boards to their soluble cations while concurrently being reduced to Fe^{2+} ions (2) [6,18,26].

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

Although the produced Fe^{2+} ions are re-oxidised by the bacteria and continuously dissolve the metals from PC boards [18,19], the increasing Fe^{3+} ion concentration, higher pH values and progressive bioleaching time led to hydrolysis of the accumulated Fe^{3+} ions and formation of the red-brown $KFe_3(SO_4)(OH)_6$ jarosite precipitate (3, 4). This jarosite then reduced the concentration of iron in the medium which is required for the oxidation of metals from PC boards and acts as a source of bacterial energy [12,18].

$$Fe^{3+} + H_2O \rightarrow Fe(OH)_3 + H^+ \quad (3)$$

$$Fe(OH)_3 + SO_4^{2-} + Fe^{3+} + H_2O + K^+ \rightarrow KFe_3(SO_4)(OH)_6 + H^+ \quad (4)$$

The metal dissolution during PC boards bioleaching occurs by direct oxidation with atmospheric oxygen in an acidic environment, and this mechanism was confirmed by leaching PC boards with sulfuric acid and pure 9K medium. However, the amount of leached metals was minimal at less than 2 % (5) [12,19].

$$M^0 + 4H^+ + O_2 \rightarrow Me^{2+} + 2H_2O \quad (5)$$

The experiment results reveal higher metal leaching efficiency after longer bioleaching by *A. ferrooxidans*. While 25 % Al, 27 % Cu and 20 % Ni were leached into solution after 10 days bioleaching, the recovery increased to 29 % Al, 36 % Cu and 25 % Ni after 20 days (Fig. 2).

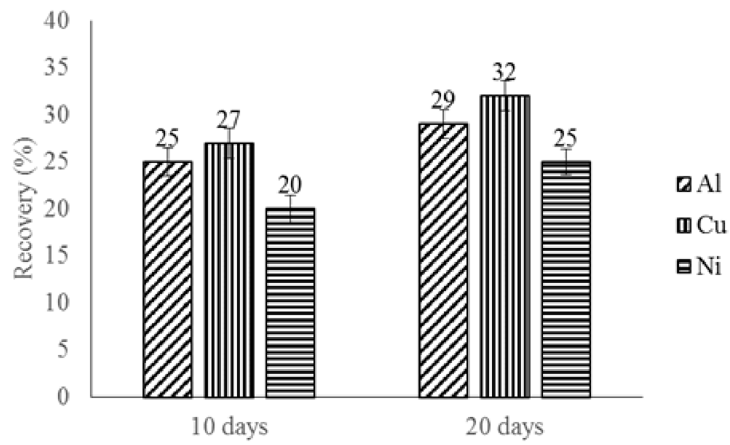

Fig. 2. Recovery of Al, Cu and Fe from printed circuit boards (PC boards) after 10 and 20 days bioleaching by *Acidithiobacillus ferrooxidans*. All values are in mean (n = 3) ± S.D.

However, this was only a slight increase in metal recovery after prolonged bioleaching, and most likely due to the precipitation of jarosite, which immobilises metals dissolved in solution [12,18,21]. In support, Choi *et al.* reported higher copper concentration in jarosite precipitates than in solutions after bioleaching of PC boards by *A. ferrooxidans* [27] and Zhu *et al.* observed jarosite coating on PC board particles which prevented leaching agent penetration to the PC board metals [12].

In addition, stationary PC board bioleaching at 25°C temperature by *A. ferrooxidans* has been shown to be inefficient in metal extraction compared to shaker experiments at high temperatures; where PC boards bioleaching experiments by *A. ferrooxidans* on shakers at 130–200 rpm and higher 28–30°C temperatures provided recovery of 75.4–90 % Al, 80–100 % Cu and 73–100 % Ni (Tab. 2).

A. ferrooxidans species optimal temperature ranges from 25–40°C, and the higher temperatures accelerate bacterial metabolic activity and chemical reaction rates [28]. Moreover, shaker bioleaching results in continuous media mixing which increases gas exchange and medium oxygenation [29], and *A. ferrooxidans* uses dissolved oxygen as an electron acceptor to obtain energy by oxidising Fe^{2+} ions, elemental sulphur and reduced sulphur compounds [15-16]. The bacterial concentration and oxidation rate then increase with increasing dissolved oxygen in the medium [30].

Table 2. PC board bioleaching experiments by *Acidithiobacillus ferroxidans* with their experimental conditions and highest recoveries

Bioleaching (days)	Temperature (°C)	Shaker (rpm)	Recovery (%)	Literature
18	30	170	94 Cu, 81 Ni, 64 Pb	[18]
9	28	150	99 Cu, 74 Pb	[19]
20	30	170	100 Cu, 100 Ni	[20]
10	30	150	90 Al, 90 Cu, 90 Ni, 0 Pb	[21]
7.25	30	160	85.24 Al, 96,75 Cu	[22]
3	30	170	75.4 Al, 96,8 Cu	[23]
10	32	200	80 Cu, 73 Ni, 72 Pb	[24]
20	30	170	100 Cu, 100 Ni	[25]

Although abiotic oxidation of Fe^{2+} to Fe^{3+} ions can occur during bioleaching due to high dissolved oxygen concentrations (6), this is almost negligible at pH below 4 [31].

$$M^0 + 4H^+ + O_2 \rightarrow Me^{2+} + 2H_2O \quad (6)$$

3.3. Recovery of toxic elements

The toxic elements As, Cd, Pb and Sb which account for more than 2 % of PC board are most commonly present as alloys (Tab. I). The *A. ferrooxidans* bioleaching recovery results revealed 2 % As, 32 % Cd, 13 % Pb and 4 % Sb recovery after 10 days bioleaching and this increased to.3 % As, 45 % Cd, 17 % Pb and 6 % Sb after 20 days bioleaching (Fig. 3). Cd was, therefore, most efficiently recovered from PC boards by *A. ferrooxidans* bioleaching.

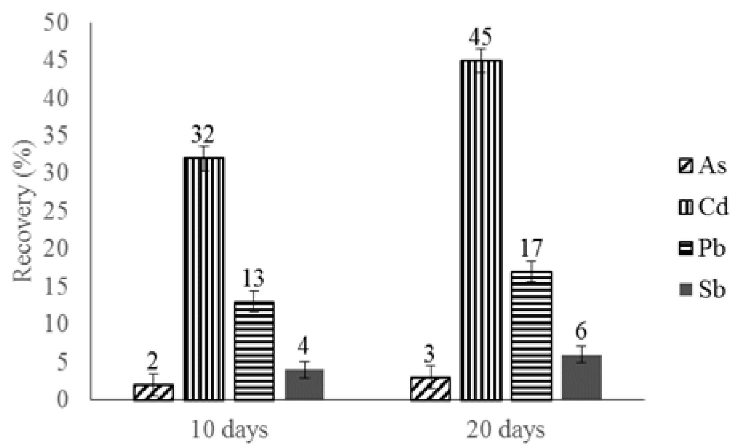

Fig. 3. Recovery of As, Cd, Pb and Sb from printed circuit boards (PC boards) after 10 and 20 days bioleaching by *Acidithiobacillus ferrooxidans*. All values are in mean (n = 3) ± S.D

Similar results were recorded by Karwowska *et al.* who reported over 93% Cd extracted by a mixed acidophilic sulphur-oxidizing bacterial culture after 2 days PC board bioleaching on a 100 rpm shaker at laboratory temperature [32]. Liang *et al.* found 72 % Pb recovery from PC board bioleaching by *A. ferrooxidans* at 32°C and 200 rpm shaking [24]. In contrast, Brandl *et al.* experienced different results with no PC board Pb bioleaching by *A. ferrooxidans* using 150 rpm shaking at 30°C, and the Pb dissolved in the solution precipitated as $PbSO_4$ [21].

The latest literature reviews reveal no research has concentrated on the mobilisation of As and Sb toxic semimetals by microbial leaching of PC boards. Previously, only low concentrations of these metals were recovered even after 20 days bioleaching, thus indicating their poor solubility from PC boards alloys. Moreover, Savvilotide *et al.* obtained similar results from leaching PC boards with a mixture of concentrated inorganic acids at different temperatures. These authors found that 0.16 % was their highest As recovery following one-hour leaching of PC boards at 80°C with a mixture of concentrated acids and water in the 5:1:4 ratio of HCl: HNO_3:

H_2O. In addition, the highest Sb recovery they observed was 0.5 % after one-hour leaching PC boards with a mixture of hydrochloric acids and water HCl: H_2O (3:2) at 80°C [33].

4. Conclusions

The stationary PC boards bioleaching by *A. ferrooxidans* at laboratory temperature proved inefficient for element extraction. The lower than expected element recovery was most likely due to the low dissolved oxygen concentration in the medium, which is so important for bacterial metabolism, and also the lower bioleaching temperature, which slowed bacterial metabolic activity.

In conclusion, the highest recovery of economically valuable metals of 29 % Al, 36 % Cu, 25 % Ni and toxic elements 3 % As, 45 % Cd, 17 % Pb and 6 % Sb occurred after 20 days bioleaching, and although this was an improvement on the recovery rate after the shorter 10 day bioleaching, the increased recovery percentages measured only 4-5 %. Finally and most importantly, the jarosite precipitation emanating from higher pH values and longer bioleaching period retarded recovery rates by immobilising the metals dissolved in solution.

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