

# **Influence of Bacterial Culture to Copper Bioleaching from Printed Circuit Boards**

Anna MRAŽÍKOVÁ<sup>1)</sup>, Renáta MARCINČÁKOVÁ<sup>2)</sup>, Jana KADUKOVÁ<sup>3)</sup>, Oksana VELGOSOVÁ<sup>4)</sup>

<sup>1)</sup> RNDr.; Department of Material Science, Faculty of Metallurgy, TUKE – Technical University in Košice; Letná 9, 042 00 Košice, Slovak Republic; e-mail: anna.mrazikova@tuke.sk, tel.: (+421) 55 602 25 44

<sup>2)</sup> RNDr.; Department of Material Science, Faculty of Metallurgy, TUKE – Technical University in Košice; Letná 9, 042 00 Košice, Slovak Republic; e-mail: renata.marcincakova@tuke.sk, tel.: (+ (+421) 55 602 25 33

<sup>3)</sup> prof. RNDr., PhD.; Department of Material Science, Faculty of Metallurgy, TUKE – Technical University in Košice; Letná 9, 042 00 Košice, Slovak Republic; e-mail: jana.kadukova@tuke.sk, tel.: (+421) 55 602 25 44

<sup>4)</sup> doc. Ing., PhD.; Department of Material Science, Faculty of Metallurgy, TUKE – Technical University in Košice; Letná 9, 042 00 Košice, Slovak Republic; -mail: oksana.velgosova@tuke.sk, tel.: (+421) 55 602 25 33

#### Summary

Copper bioleaching from printed circuit boards (PCBs) by acidophilic bacteria of Acidithiobacillus ferrooxidans and mixed bacterial culture of Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans was investigated. The bacteria were isolated from the acid mine drainage in Smolnik in Slovakia, grown and acclimated in the presence of PCB waste and consequently were used as bioleaching bacteria to solubilize copper from PCBs. The higher copper solubilization was mainly achieved by mixed bacterial culture. The higher copper bioleaching rate was observed in the first 14 days using mixed culture, when 60% of Cu bioleaching efficiency was achieved. In the case of the pure bacterial culture only 22% Cu was solubilized up to this day.

Keywords: bioleaching, electronic scrap, metals, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans

## Introduction

Recycling of electronic waste has become an important subject of many studies not only from the waste treatment point of view but also from valuable metal recovery. Among electronic wastes, printed circuit boards (PCBs) have quite diverse composition, containing polymers, ceramics and metals. The metals content is around 28–30% (copper: 10–20%, lead: 1–5%, nickel: 1–3% and precious metals like silver, platinum and gold are also present in the electronic scrap to a total of 0.3–0.4%) (Ilyas, 2010).

The quantity of metals, especially copper, turns the electronic scrap into an interesting raw material from the economic point of view. If PCBs are not recycled or treated appropriately, the heavy metals such as copper, lead and nickel and halogenated burn – resisting materials being a part of them, can consequently, be dispersed to the environment what can lead to serious environmental problems (Wang et al.,2009, Saidan et al.,2012).

The use of microorganisms for metal recovery from waste electronic equipment could be an economical alternative to such processes as pyrometallurgy, hydrometallurgy or mechanical processes, since using biological techniques for recycling PCBs, could increase metal recovery efficiencies. Thermal or physico-chemical methods alone are less successful as shown in copper and gold mining, where low-grade ores are biologically treated to obtain metal values (Wang, 2009). *Acidithiobacillus ferrooxidans* is a major participant in consortia of microorganisms used for industrial recovery of copper (bioleaching or biomining) (Valdés, 2008, Bálintová, Luptáková, 2012). *A. ferrooxidans* and *A. thiooxidans* can grow and utilize ferrous iron or elemental sulfur and thus produce ferric ions (Eq. 1) or sulfuric acid (Eq. 2) that are important as leaching agents in metal recovery from primary and secondary sources (Eq. 3, 4, 5) (Lee and Pandey, 2011).

In the present study the copper leaching from PCBs by acidophilic sulfur and iron oxidizing cultures was investigated. High amounts of different metals present in PCBs have a toxic effect on bacteria, however, as it was reported by Brandl et al. (2001), the bacterial strain of *A. ferrooxidans* can to a certain extent tolerate high metal concentrations.

The present study aimed to evaluate the copper leaching efficiencies from PCBs by the metal-adapted pure culture of *A. ferrooxidans* and metal-adapted mixed culture of *A. ferrooxidans* and *A. thiooxidans* and determine the relationship between the pH of the

$$2F3^{2+} + 0.5O_2 + 2H^+ \to 2Fe^{3+} + H_2O \tag{1}$$

$$S^{0} + 1,5O_{2} + H_{2}O \rightarrow SO_{4}^{2-} + 2H^{+}$$
 (2)

$$MS + 2Fe^{3+} \to M^{2+} + 2Fe^{2+} + S^{0}$$
(3)

$$MS + 2O_2 \to M^{2+} + SO_4^{2-} \tag{4}$$

$$M(Cu, Ni, Zn, Co, Al) + Fe_2(SO_4)_3 \to MSO_4 + 2FeSO_4$$
(5)

leaching media and percentages of copper releases into the solution during the bioleaching processes.

#### Materials and methods

The isolates used in the experiments were recovered from the acid mine drainage in Smolník. Two kinds of cultures, A. ferrooxidans and A. thiooxidans, were grown and acclimated in the presence of PCBs for two weeks and then used as bioleaching bacteria to solubilize metals from PCBs. The chemical composition of the two bioleaching media used for the experiments is shown in Table 1. Electronic scrap, in the form of printed circuit boards, was crushed to particle size of 1-1000 mm. The pH values of bioleaching media were adjusted to pH = 1.5 with 10M H<sub>2</sub>SO<sub>4</sub> since the scrap is generally alkaline in nature. Analysis of the electronic scrap before bioleaching revealed the presence of Cu (19.21%), Zn (1.17%), Ni (0.32%), Al (1.73%). Metal concentrations of PCBs were determined by atomic absorption spectrophotometer (Perkin Elmer 3100).

Leaching experiments were carried out in 250 ml Erlenmayer flasks containing 190 ml of culture media depicted in Table 1 to which 2 g of PCBs were added. Each flask was inoculated with 10 ml metal-adapted bacterial culture of *A. ferrooxidans* or mixture of *A. ferrooxidans* and *A. thiooxidans*. Simultaneously, control leaching under the same conditions but without any bacteria was carried out.

## **Results and discussion**

Bacterial culture media (the pure culture of *A. fer-rooxidans* and mixed culture of *A. ferrooxidans* and *A. thiooxidans*) are designed as main influential factors in examination of effect of leaching time on the percentage of copper solubilization from the PCBs. The copper

leaching efficiencies by the pure culture of *A. ferrooxi*dans, mixed culture of *A. ferrooxidans* and *A. thiooxi*dans are shown in Fig. 1. In the first days of copper bioleaching the leaching rate in system with the pure bacteria was low in comparison with system containing the mixed culture. In the first 10 days of bioleaching the bioleaching rate was low and after that the increase of copper leaching was observed. As regards the bioleaching by mixed culture, the bioleaching rate was higher than using the pure culture, however, more significant increase was observed after ten days. The amount of copper solubilized into the solution was 650 mg/l (22%) and 1266 mg/l (60%) on the 14<sup>th</sup> day by the pure and mixed bacterial cultures, respectively.

The experimental results also revealed that the percentages of copper solubilized in the leaching medium in the absence of bacteria under the same experimental conditions as those in bioleaching processes were found to be less than 3.0% (Fig. 1, Fig. 2).

Fig. 3 depicts the acid consumption during bioleaching and control leaching processes. During the bioleaching the pH values in both cases increased from 1.5 to 2.26 in the first 10 days. After that it remained more or less constant, about 2, until the end of bioleaching processes. No significant pH changes were observed in control leaching. The increase was only in the range of 1.5 to 1.86.

#### Conclusion

In this study the influence of metal-adapted bacterial strains and their consortium on copper leaching from PCBs was investigated. The use of the acidophilic bacteria plays very important role in the copper extraction from the eletronic waste used for the experiments. The metal-adapted mixed bacterial culture

Composition	9K medium (A. ferrooxidans)	Mixed medium (A. ferrooxidans and A. thiooxidans)
KCl	0.1	0.1
$(NH_4)_2SO_4$	3.0	2.0
K <sub>2</sub> HPO <sub>4</sub>	0.5	0.25
MgSO <sub>4</sub> .7H <sub>2</sub> O	0.5	0.25
Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O	0.014	_
FeSO <sub>4</sub> .7H <sub>2</sub> O	44.2	44.2
$H_2SO_4$	1–5ml	1–5ml
Sulfur powder		5

Table 1. Chemical composition of two kinds of the bacterial cultures (g.l<sup>-1</sup>) Tabela. 1 Skład chemiczny dwóch rodzajów kultur bakterii (g.l<sup>-1</sup>)



Fig. 1. Copper concentrations in solution during bioleaching of PCBs Rys. 1. Stężenia miedzi w roztworze podczas bioługowania obwodów drukowanych



Fig. 2. Percentage of copper solubilized by *A. ferrooxidans* and mixed culture of *A. ferrooxidans* and *A. thiooxidans* on the 14<sup>th</sup> and 21<sup>st</sup> day

Rys. 2. Procent miedzi roztworzonej przez A. *ferrooxidans* oraz mieszane kultury bakterii A. *ferrooxidans* i A. *thiooxidans* w dniu 14 i 21



Fig. 3. Changes in pH during bioleaching and control leaching processes Rys. 3. Zmiany pH podczas bioługowania i kontrolowanego procesu ługowania

was found to be more effective, able to leach more than 60% of Cu. Time-course of the copper bioleaching was also much faster during the first 21 days compared to the pure bacterial culture. The least copper leaching efficiency (only 3%) was reached in the leaching medium with absence of bacteria.

#### Acknowledgements

The work was fully supported by a grant from the Slovak National Grant Agency under the VEGA Project 1/0235/12.

## Literatura – References

- 1. Ilias Sadia et al.: Column bioleaching of metals from electronic scrap. Hydrometallurgy. 101, 2010, p.135 140.
- 2. Wang Jingwei et al.: Bioleaching of metals from printed wire boards by Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans and their mixture. Journal of Hazardous Material, 172, 2009, p.1100-1105.
- 3. Saidan et al.: Leaching of Electronic Waste Using Biometabolished Acids. Chinese Journal of Chemical Engineering, 20(3), 2012, p. 530- 534.
- 4. Valdés Jorge et al.: Acidithiobacillus ferrooxidans metabolism: from genome semence to industrial applications. BMC Genomics, 2008, 9:597.
- 5. Bálintová M., Luptáková A.: Úprava kyslých banských vôd. Košice, Stavebná fakulta, Technická univerzita, 2012, s 131. ISBN 978-80-553–0868–5.
- 6. Lee Jae-chun, Pandey Banshi Dhar.: Bio-processing of solid wastes and secondary resources for metal extraction A review. Waste Management, 22, 2012, p.3-18.
- 7.Brandl H. et al.: Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi, Hydrometallurgy, 59, 2001, p.319-326.

## Wpływ kultur bakteryjnych na ługowanie miedzi z płytek drukowanych

Zbadano bioługowanie miedzi z obwodów drukowanych (PCB – printed circuit board) za pomocą kwasolubnych bakterii Acidithiobacillus ferrooxidans oraz mieszanych kultur bakterii Acidithiobacillus ferrooxidans i Acidithiobacillus thiooxidans. Bakterie wyodrębniono z kwaśnego drenażu kopalń w Smolniku na Słowacji, wyhodowano oraz zaklimatyzowano w obecności odpadów PCB i w konsekwencji użyto jako czynnika bioługującego w celu roztworzenia miedzi z PCBs. Wyższy stopień bioługowania miedzi został zaobserwowany w pierwszych 14 dniach używając kultur mieszanych, gdy to osiągnięto wydajność równą 60%. W przypadku czystych kultur bakterii wynik ten wyniósł jedynie 22%.

Słowa kluczowe: bioługowanie, elektroodpady, metale, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans