Title. Bioleaching of metals from e-waste using immobilized biomass of mesophilic *Acidithiobacillus ferrooxidans*.

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Abstract: Among the secondary post-consumption wastes, **e-wastes** represent the fastest growing waste stream in the world being heterogeneous and diverse in terms of structure and composition. Consequently, it is difficult to feed such waste into conventional recycling streams. Biometallurgy could prove a competitive and applicable technique for recovering valuable metals from these materials. The objective of the study is to test the feasibility of biometallurgy for recycling secondary raw materials, rendering the presently uneconomic raw materials economically viable, thus contributing directly to the circular economy. Long-term objective is to study the peculiarities of bioleaching of secondary raw materials, reveal the role of bacteria in these processes and develop the concept on the mechanism of bioleaching of secondary raw materials. Comparative chemical leaching of printed circuit boards (PCBs) by ferric sulfate $Fe_2O_{12}S_3xH_2O$ solution and biogenic Fe^{3+} obtained by immobilized biomass of *Acidithiobacillus ferrooxidans* 61 (Armenia) and *Acidithiobacillus* GR1 (Bulgaria) has been performed. The intensity of zero valent copper oxidation was correlated to the ratio of Fe^{3+}/Fe^{2+} ions in the solution. It was revealed that recovery of metals from PCBs by biogenic Fe^{3+} occurred 2-3 times more intensively than that by $Fe_2O_{12}S_3xH_2O$ solution. The use of $Fe_2O_{12}S_3xH_2O$ solution for leaching of PCBs resulted in intensive precipitation of Fe^{3+} and generation of jarosite, while in case of biogenic Fe^{3+} the amount of jarosite was significantly lower. It is supposed that Fe^{3+} in biogenic solution is mainly in the form of complexes with organic compounds produced by bacteria, which prevent its precipitation as jarosite. It is assumed that chemical leaching by biogenic Fe^{3+} integrated into the processes of leaching of PCB's may contribute to intensification of extraction of copper and other valuable metals from different secondary resources.

Keywords: Printed circuit boards (PCBs), *Acidithiobacillus ferrooxidans*, Biogenic ferric iron solution, Leaching

1. Introduction

Recovering metals from e-waste is potentially more energy efficient than recovering them from mineral raw materials. However, e-wastes are highly complex in terms of structure and composition and comprise many individual sub-components but the majority of the value is in the PCBs. For example many of the 'critical" metals are found in non-negligible amount in e-wastes and recent estimates showed that on average 90% of the intrinsic economic value of PCBs is in the precious metals that they contain [1]. PCB's are among the most complex sub-components of e-waste and most difficult to reprocess, hence it is difficult to feed such waste into conventional recycling streams. Usually after disassembling and upgrading, the recovered materials are re-treated or purified using pyrometallurgical or hydrometallurgical processes or combination between both. The bio-hydrometallurgy which has its nature-doing roots using microorganisms to enhance the dissolution of metals from mineral ores could offer viable alternative to the classical hydrometallurgy by avoiding the use of corrosive chemicals (acids, bases). Its generic principles have recently stimulated a research in metals recovery from high value secondary sources (e-wastes, catalysts), but systematic work on zero-valent metals bio-leaching from materials with complex composition has been done rather sporadically. This work aims to fill some of these gaps by studying key biological characteristics of the leaching system with the final aim to understand the role which the MO play in boosting the bio-leaching efficiency through increased IOR (iron oxidation rate) and improved resistivity. In bioleaching metals, the regeneration of the leaching solutions is considered to be an important phase for the development of an efficient technology [2-4]. The regeneration of leaching liquors actually results in reduction of Fe (III), as the key component of leaching liquors is ferric ion (Fe (III)) which represents a strong oxidizer for sulfide minerals. At present regeneration of ferric ion in operating leaching technologies is realized by chemical methods mainly by chlorine, ozone, hydrogen peroxide which renders the process more complicated and cost inefficient. The use of microorganisms allows simplifying the process of regeneration of leaching solutions and significantly decreases cost as microorganisms are considered to be unexhausted catalysts. On the other hand, immobilization of microorganisms on natural carriers will contribute to the intensification of regeneration of ferric ion. By increasing microbial biomass density it will significantly allow to enhance conversion rate of Fe^{2+}/Fe^{3+}.

2. Materials and methods

2-1. Culture condition and immobilization

At. ferrooxidans 61 (KM819692) used in this study were previously isolated from AMD in Armenia (Vardanyan et al., 2016) and *Acidithiobacillus* sp. GR1 - from Bulgaria. Both cultures were grown at a temperature of 30-35ºC in 9K medium [5] using 18g/L $FeSO_4x7H_2O$ as energy source.

For immobilization processes as a carrier FISH biomass (biopur) were used.

2-2. Determination of metals

Aliquot samples were taken during leaching experiments and analyzed by ICP-OES and atomic absorption for determination of Al, Zn, Fe and Cu. Ferrous iron (Fe^{2+}) was determined by a redox reaction using potassium chromate ($K_2Cr_2O_7$).

2-3. Bioleaching of PCB's

The leaching experiments were performed in glass tank at 110 ºC at 500 rpm stirring. pH was controlled with 10N H_2SO_4, Eh - by the ferric iron and ferrous iron ratio. The leaching experiments were performed by biogenic and chemical solutions of $FeSO_4x7H_2O$. For obtaining chemical ferric iron $Fe_2O_{12}S_3xH_2O$ (84g/L) salt solution was used. Biogenic ferric iron was obtained by the oxidation of ferrous iron (Fe (II)) by immobilized on biopur of *At. ferrooxidans* 61 and *Acidithiobacillus* sp. GR1.

3. Results and Discussions

For abiotic test 800 mL biogenic Fe^{3+} obtained by GR1 (18 g/L Fe^{2+}) were used for leaching of 4% PCB (32g). The initial pH of experiment was 1.95, Eh was 677.5. The experiment was performed under pressure at 110°C temperature and 500 rpm conditions.

As shown in the Fig. 1b, the leaching reactions mainly occurred at the first 1.5 h. Almost 50% Cu was dissolved (Fig. 1).

In case of using of chemical solution of Fe^{3+} in leaching experiments at the same conditions, copper recovery was 35% after 150 min (Fig. 2).

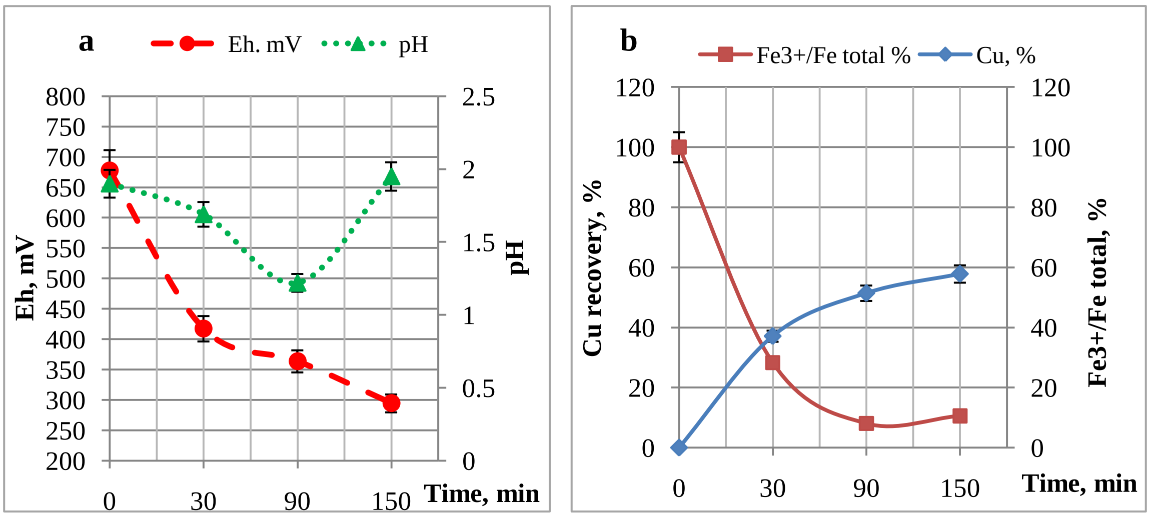

Fig. 1. Evaluation of pH, Eh parameters (a), copper recovery and ferric iron proportion (b) in the abiotic leaching of PCBs

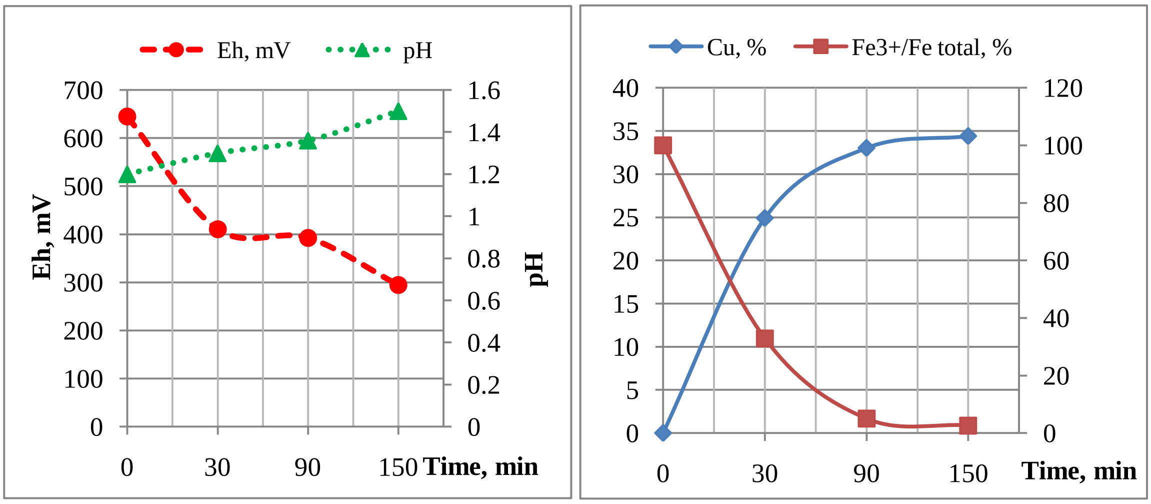

Fig. 2. Evaluation of pH, Eh parameters (a), copper recovery and ferric iron proportion (b) in the abiotic leaching of PCBs by chemical solution of Fe^{3+}.

4. Conclusion

Thus, *Acidithiobacillus* ferrooxidans 61 and *Acidithiobacillus* sp. GR1 immobilized on biopur can be prospective to be applied in the technological processes for rapid regeneration of oxidizer – Fe (III). It can be concluded that leaching of PCB's with Fe (III) solution obtained by the immobilized cells of *Aacidithiobacillus* sp. GR1 allows to increase on average 2-3 times the extraction of iron and copper, 1.5 times Zn, 4 times Al from PCB's. Chemical oxidation of PCB's by biogenic ferric iron Fe(III) obtained by the immobilized biomass of CM integrated into biohydrometallurgical technology allows significantly increasing the efficiency of subsequent bioleaching process and the extent of recovery of copper, zinc etc. from ores and refractory concentrates.

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