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COMPARATIVE STUDIES OF ONE-STAGE AND TWO-STAGE PROCESSES OF RECOVERY OF COPPER FROM PCB

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PCBs are mainly treated by pyrometallurgy to recover valuable metals. However pyrometallurgy is high energy-cost process and due to presence of plastics in PCBs causes the emission of toxic compounds. Therefore, the development of environmentally friendly, cost- and energy-efficient new processes for efficient metal recovery from PCBs is of particular important. From this point of view bioleaching is considered as a novel promising approach for metal mobilization from various secondary raw materials and wastes. Bioleaching experiments were performed using *Leptospirillum ferriphilum* CC in the following modes: PCBs were added simultaneously with inoculum, after 24 and 48 hours of cultivation of in order to enhance efficiency of copper recovery. From data obtained it can be concluded that optimal condition for copper recovery is the set of experiment when PCBs were added simultaneously with inoculation of *L. ferriphillum* CC. The maximum rate of dissolution of copper (0.120 g/L h) was observed in this mode of the experiment. Besides both the higher dissolution rate and larger amount of copper is observed at 2.5 % of PD.

Printed circuit board (PCBs) – bioleaching – Leptospirillum ferriphilum – copper recovery

Տպագիր տպատախտակները (SSS-PCB) հիմնականում մշակվում են հրամետալուրգիական եղանակով՝ արժեքավոր մետաղները վերականգնելու համար: Սակայն՝ հրամետալուրգիան բարձր էներգիա- և ծախսատար գործընթաց է և PCB-ներում պլաստիկի առկայության պատճառով առաջացնում է թունավոր միացությունների արտանետում: Ուստի էկոլոգիապես մաքուր, ոչ ծախսատար և էներգաարդյունավետ նոր գործընթացների մշակումը PCB-ներից մետաղների արդյունավետ վերականգնման համար հատկապես կարևոր է: Այս տեսանկյունից կենսատարրալուծումը համարվում է որպես նոր խոստումնալից մոտեցում՝ տարբեր երկրորդական հումքերից և թափոններից մետաղների կորզման համար: Կենսատարրալուծման փորձերն իրականացվել են *Leptospirillum ferriphilum* CC-ի կիրառմամբ հետևյալ տարբերակներով. PCB-ներն ավելացվել են բակտերիալ կուլտուրայի ներմուծման հետ միաժամանակ, կուլտուրայի աճեցումից 24 և 48 ժ հետո՝ պղնձի վերականգնման արդյունավետությունը բարձրացնելու նպատակով: Ստացված տվյալներից կարելի է եզրակացնել, որ պղնձի կորզման համար լավագույն տարբերակը PCB-ների ավելացումն է *L. ferriphillum* CC-ի ներարկման հետ միաժամանակ: Փորձի այս տարբերակում նկատվել է պղնձի տարրալուծման առավելագույն արագությունը (0,120 գ/լ ժ): Ընդ որում պղնձի տարրալուծման ամենաբարձր արագությունը և կորզված պղնձի առավելագույն քանակությունը դիտվել են ապարախյուսի 2.5% խտության (PD) դեպքում:

Տպագիր տպատախտակ (SSS - PCB) – կենսատարրալուծում – Leptospirillum ferriphilum – պղնձի կորզում

Печатные платы (ПП) в основном обрабатываются пирометаллургией для извлечения ценных металлов. Однако пирометаллургия является высокоэнергоемким процессом и из-за присутствия пластмасс в ПП вызывает выделение токсичных соединений. Поэтому разработка экологически чистых, экономичных и энергоэффективных новых процессов эффективного извлечения металлов из ПП имеет особое значение. С этой точки зрения биовыщелачивание рассматривается как новый перспективный подход к мобилизации металлов из различного вторичного сырья и отходов. Эксперименты по биовыщелачиванию проводили с применением *Leptospirillum ferriphilum* CC в следующих режимах: ПП добавляли одновременно с инокулятом, через 24 и 48 часов культивирования для повышения эффективности извлечения меди. Из полученных данных можно сделать вывод, что оптимальным условием извлечения меди является постановка опыта, когда ПП вносили одновременно с инокуляцией *L. ferriphillum* CC. При этом режиме эксперимента наблюдалась максимальная скорость растворения меди (0,120 г/л ч). Причем, более высокая скорость растворения и наибольшее количество извлечения меди наблюдались при 2,5% ПД.

Печатные платы (ПП) – биовыщелачивание – Leptospirillum ferriphilum *–*
извлечение меди

The Waste Electronic and electrical equipments (WEEE) constitutes the 8% of the total municipal waste, and it continues to increase by 4-5 % every year [9]. There are four main sources of WEEE: small/large home appliances, hospital medical equipment, office machines, and industrial equipment/machines.

The PCBs are the main part of WEEE, and constitute the 3-5% of the WEEE amount [5, 13]. PCBs are composed by 20 % Cu, 5 % Al, 1% Ni, 1.5 % Pb, 2 % Zn, 3 % Sn (w/w) with 250 ppm Au, 1000 ppm Ag and 110 Pd [1, 5, 9, 10, 13]. Recycling of PCBs is of both environmental and economic importance. The disposal of PCBs can result in release of potentially toxic elements into water and soil, causing food chain toxicity risks [14]. On the other hand PCBs could be secondary source for valuable metals: Cu, Zn, Al, Ni, Au etc.

PCBs are mainly treated by pyrometallurgy to recover valuable metals but some of them such as aluminum, iron and precious metals, are lost in the slag during this operation [4]. Besides, pyrometallurgy is high energy-cost process. Moreover, the presence of plastics in PCBs causes the emission of toxic dioxins and other compounds. Therefore, the development of cost- and energy-efficient new processes for efficient metal recovery from PCBs is of particular important.

From this point of view biohydrometallurgy is very promising technology. Well-known commercial application of biohydrometallurgy to process mineral ores is bioleaching [3]. In comparison with conventional pyrometallurgy, this biological approach is more cost efficient, simpler and environmentally friendly. Bioleaching is based on the ability of microorganisms, bacteria or fungi, to produce leaching agents. In particular, acidophilic autotrophic microorganisms can oxidize metal sulfides (direct mechanism) [6] and ferrous iron to ferric iron, a strong oxidative agent or elemental sulfur to sulfuric acid thus producing leaching agents (indirect mechanism) [11]. So, compared to chemical treatment, in case of bioleaching the necessary reagents for metal recovery are biologically produced that implies obvious advantages both for the process economics and environmental impact in terms of carbon emissions.

In fact, bioleaching today is considered as a novel approach for metal mobilization from various secondary raw materials and wastes. In the literature, some studies deal with the use of bioleaching for the treatment of spent PCBs by acidophilic microorganisms [2, 7, 8]. The use of such microorganisms, which are mainly iron and sulfur-oxidizing bacteria, 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:

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

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

The published literature data have revealed that leaching of PCBs is inhibited by metal ions released. Therefore, the toxicity of metal ions is considered as a key factor which limits pulp density and leaching efficiency [2]. To overcome such issues, staggering the production of the lixiviant and addition of the materials in a two-step process has been suggested.

The aim of this work is to carry out comparative studies of one-stage and two-stage processes of treatment of PCB, representing direct and indirect bioleaching mechanisms, in terms of effectiveness of recovery of copper.

Materials and methods. Preparation of PCBs. In this work the multi-layer printed circuit boards originating mainly from discarded laptops were used. The PCB samples were cut by scissors into pieces (1.5 × 1 cm) which were further used in the experiments. Before bioleaching, the existing passive layer (green solder mask) of the PCBs was removed by boiling the fragmented PCBs in 10 % NaOH for 15 minutes. Afterwards, the samples were thoroughly washed with distilled water, dried and preserved for bioleaching. Pretreatment of PCBs before bioleaching can be described by the following scheme (fig.1).

Fig. 1. View of shredded PCBs after: dismantling and components removal (a), being cut (b) and chemical pretreatment (c)

Culture growth and lixiviant preparation. *Leptosprillum ferriphilum* CC (OM272948) was grown at 40ºC in a MAC medium containing 44.2 g/L $FeSO_4$ x $7H_2O$. For bioleaching of PCBs culture liquid obtained after cultivation of *L. ferriphilum* CC in MAC medium for 4-5 days was used as lixiviant. Cells number was determined by direct counting under a microscope (Optica B-810, Italy) using a Thoma Chamber. The initial cell number for *L. ferriphilum* CC was 2.5 x 10^7 cells/mL.

Bioleaching. Bioleaching of PCBs was performed using iron oxidizing bacteria *L. ferriphilum* CC in the following modes:

PCBs were added:

a) simultaneously with inoculation (direct mechanism),
b) after 24 hours of cultivation of *L. ferriphilum* CC,
c) after 48 hours of cultivation of *L. ferriphilum* CC.

Bioleaching experiments were performed in 250 mL Erlenmeyer flasks placed on an orbital shaker-incubator (Biosan, Latvia) run at 170 rpm and temperature of 40ºC. Tests were performed at pulp densities (PD) of 5, 10, 15% PCBs with pH of the lixiviant adjusted to 1.5 using a 10 N H_2SO_4.

Chemical analysis. Copper concentration in leaching solution after bioleaching was determined by atomic absorption spectrometry (AAS). Concentrations of Fe^{3+} and Fe^{2+} were determined by the complexometric method with EDTA. The calculation of metal recovery has followed equation 1.

$$MR(\%) = \frac{CM1x100}{m\,x\,CMs} \qquad (1)$$

where MR is metal recovery, %
CM*l* – concentration of leached metal in the pregnant leaching solution (PLS), %
CM*s* – metal concentration in the input solid, %
m – mass of used PCBs, g
100 – volume of the leachate inside the flasks, mL.

The redox potential was measured with an oxidation/reduction potentials (ORP) electrode met BNC-connector (Pt/Ag/AgCl) of Hi2211-01 Benchtop pH/mV Meter (SevenExcellece, Mettler Toledo). pH was determined with a Hi2211-01 Benchtop pH/mV Meter equipped with an Ag/AgCl electrode.

All experiments were performed in triplicate. The data presented here are the average values from the repeated experiments with ±2% variation.

Results and Discussion. Bioleaching of PCBs was performed using iron oxidizing bacteria *L. ferriphilum* CC, isolated in Armenia from bioleaching pulp of copper concentrate [12].

Addition of PCB to flasks, containing 7.1g/L Fe^{2+} simultaneously with inoculum of *L. ferriphilum* CC (version 1) resulted in 86,7, 38.0 and 0.1 % copper bioleaching for 48 hours at 2.5, 5.0, and 7.5 % pulp density (PD), respectively. For 72 h copper recovery from PCBs increased up to 100, 56 and 1.15 % at PD of 2.5, 5.0, and 7.5 %, respectively. During 96 hours copper recovery from PCBs reached to 86.4% and 5.0 % at PD of 5.0, and 7.5 %, respectively (fig 2).

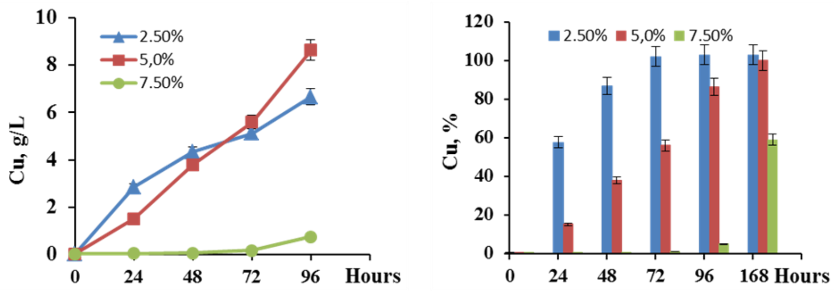

Fig. 2. Bioleaching of copper from PCBs by iron oxidizing bacteria. PCBs were added simultaneously with inoculation of *L. ferriphilum* (Fe^{2+} - 7.1g/L, initial pH 1.5, Eh- 420mV, t - 37^0C, 170 rpm)

During bioleaching of PCBs pH of the solution increased from 1.5 to pH 2.4, 2.5 and 3.1 at 2.5, 5.0 and 7.5% of PD. Respectively. Oxidation reduction potential (ORP) of leaching solution decreased from 420 mV to 357, 350 and 341 mV at 2.5, 5.0 and 7.5 % PD, respectively. At 7.5% PD, ORP decreases to 290 mV for 120 hours of PCBs treating process.

Addition of PCB in flasks after 24 hours cultivation of *L. ferriphilum* CC (version 2) resulted in 36.2, 8.6 and 2.68 % of copper dissolution for 48 h at 2.5, 5.0 and 7.5 % PD, respectively. For 72 hours copper bioleaching increased up to 54.5, 20.7 and 5.0 % at 2.5, 5.0, and 7.5 % of solid concentrations, respectively and only within 144 h, copper bioextraction reached significant values of 100, 93 and 64 % respectively (fig.3).

Maximum rates of copper extraction were 0.12, 0.096 and 0.007g/l h at 2.5, 5.0 and 7.5 PD, respectively.

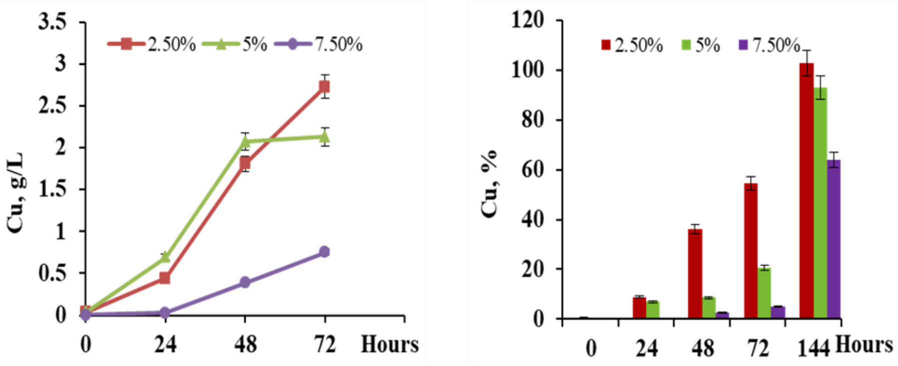

Fig. 3. PCBs were added after 24 hours of cultivation of *L. ferriphilum* CC (Fe^{2+} - 7.1g/L, pH 1.5, Eh- 420mV, t - 37^{0}C, 170 rpm)

During bioleaching of copper pH of the leaching medium increased from 1.5 to pH 2.0-2.2 and changes in medium properties occur as the result of oxidation of ferrous iron to ferric iron by bacteria according to reaction:

$$2FeSO_4 + 1/2O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

Thus, oxidation of ferrous iron is an acid consumption process and resulted in increase of pH of the medium.

The ORP of the medium is determined by the ratio of Fe^{3+}/ Fe^{2+}. As copper dissolves, the potential of the medium decreases from 420 mV to 336-360 mV depending on PD, which can be explained by the reaction:

$$Fe_2(SO_4)_3 + Cu^0 \longrightarrow 2FeSO_4 + CuSO_4$$

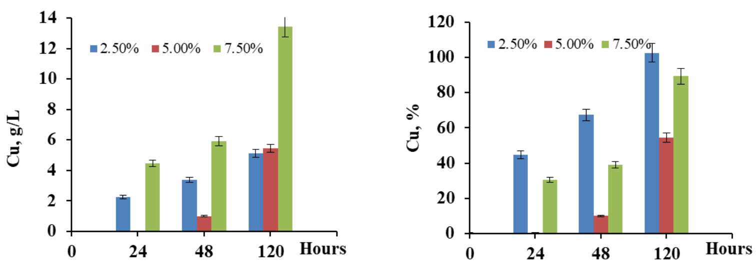

Fig. 4. PCBs were added after 48 hours of cultivation of *L. ferriphilum* CC (Fe^{2+} - 7.1g/L, pH 1.5, Eh- 420mV, t - 37^{0}C, 170 rpm)

The addition of PCBs after 48 h of cultivation of *L. ferriphilum* CC (version 3) for the next 48 hours led to dissolution of 67.4, 10 and 39% copper at 2.5, 5.0 and 7.5% PD, respectively. Copper bioleaching reached 100, 54.5 and 89.5% within 120 h at 2.5, 5.0, and 7.5% PD, respectively (fig.4).

It is obvious that compared to the first version, in this version significantly increase in the extraction of copper observed at 5.0 and 7.5% of PD (fig.4).

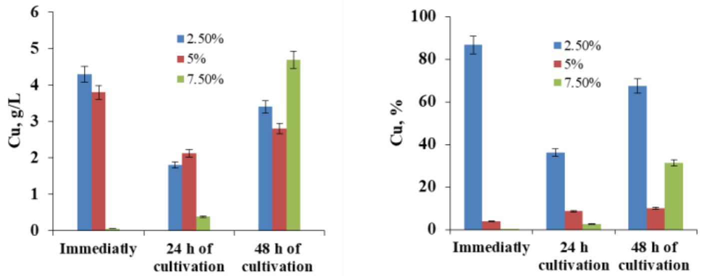

Fig.5. Comparative bioleaching of copper during 48 hours at different modes of setting up the experiment: a) Immediately, b) after 24 h c) after 48 h of cultivation of *L. ferriphilum* (Fe^{2+} - 7.1g/L, pH 1.5, Eh- 420mV, t - 37°C, 170 rpm)

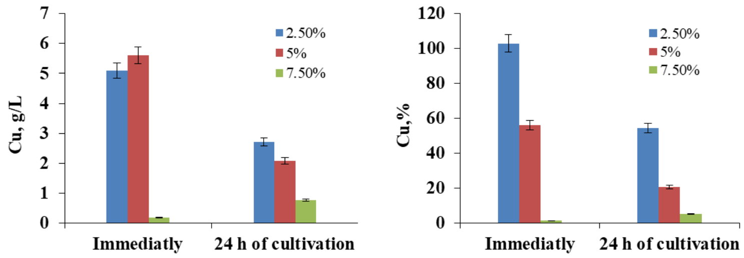

Fig. 6. Bioleaching of copper during 72 h with different modes of setting up the experiment: a) Immediately, b) after 24 h of cultivation of *L. ferriphilum*, (Fe^{2+} - 7.1g/L, pH 1.5, Eh- 420mV, t - 37°C, 170 rpm)

Thus summarizing data obtained for 48 (fig.5) and 72 (Fig.6) hours of bioleaching of copper from PCBs at different mode of setting experiment it can be concluded that optimal condition for copper extraction is observed at the set of experiment when PCBs are added simultaneously with inoculation of *L. ferriphillum* CC. The maximum rate of dissolution of copper (0.120 g/L h) in this mode was higher compared with version 2 (0.096g/l h) and version 3 (0.007 g/L h). At this set of experiment both the higher dissolution rate and larger amount of copper is observed at 2.5% of PD.

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