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RECOVERY OF COPPER FROM ORE DUMP USING BIOLEACHING APPROACH

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ABSTRACT
Bioleaching is an environmentally-friendly approach for the extraction of useful metals from low-grade ores and secondary mineral materials.
The object of this paper was to examine the possibility of microbiological solubilisation of copper from ore dump by *Acidithiobacillus* sp. B2.

Leaching experiments were performed by the shake flask testing technique at 28 ^{o}C, during two-week period. The percentage of the copper leached at the end of this experiment was 31%.

INTRODUCTION
Bioleaching is a process in mining and biohydrometallurgy (natural processes of interactions between microbes and minerals) that extracts valuable metals from a low-grade ore with the help of microorganisms such as bacteria or archaea.

Microbial methods for recovering metals are important for following reasons:
1) Waste materials is being used as a raw material giving the metal as that final product, that would be irretrievably lost; 2) Microbial leaching methods are several times cheaper compared to the conventional one that are inapplicable for the low grade ores; 3) Minimum threats to the environment [1].

In order to extract copper from the ore dump, microbial leaching has been conducted in laboratory using the culture of *Acidithiobacillus* sp. B2. Parameters, like chemical characteristics of tailings, solid-liquid ratio, number of bacteria, leaching time, pH decreasing, percentage of pyrite sulphur consumption as well as the percentage of the leached copper, were determined.

METHODS
Chemical analysis of the ore dumps
Silicate analysis of the ore dumps was conducted using the conventional method, by alkaline fusion with $NaKCO_3$ and dissolution in HCl [2]. From the filtrate Fe, Al, Ti, Ca and Mg, were determined while the residue was further treated with HF in order to obtain volatile SiF_4, from which the SiO_2 content was determined. The remaining precipitate was treated again as silicate material.

For the determination of alkaline metals and copper, the sample was decomposed with a mixture of $HClO_4$ and HF, while for the determination of phosphorus, the sample was decomposed with a mixture of aqua regia and $HClO_4$.

The alkaline metals and copper were determined by atomic emission flame spectrophotometry; Fe, Al, Ti, Ca, Mg by atomic absorption flame spectrophotometry. Sulphide sulphur from the ore dumps was determined gravimetrically after oxidation with $KClO_3$ and HNO_3 followed by precipitation as $BaSO_4$. Correction on sulphate sulphur from the ore dumps was determined in the "soda-extract" (boiling solution of Na_2CO_3), as $BaSO_4$ [2].

Analysis of 16S rRNA gene sequences

Isolation of microorganisms Iron-oxidizing *Acidithiobacillus* sp. B2 was performed from water samples taken from Lake Robule, in the copper mine in Bor, Serbia. Analysis of 16S rRNA gene sequences The genomic DNA of iron-oxidizing *Acidithiobacillus* sp. B2 was extracted using DNeasy Blood & Tissue Kit (Qiagen, USA). The 16S rRNA genes were amplified by PCR using 27F(50-AGAGTTTGATCMTGGCTCAG-30;and 1492R (50-TACGGYTACCTTGTTACGACTT-30. Amplified fragments were purified with the QIAquick PCR Purification Kit (Qiagen, USA) and sequenced using the commercial MACROGEN (Netherland) service. The isolated strain was identified using the EzTaxon-e server on the basis of 16S rRNA sequence data. The iron-oxidizing *Acidithiobacillus* sp. B2 strain isolated exhibited the following characteristics: motility, cell size 1.5 0.5 lm, growth using sulphur, thiosulfate, ferrous iron, and pyrite as electron donors. The identification was performed by sequence analysis of the 16S rRNA gene, and the gene sequence of analyzed strain was deposited in NCBI GenBank under accession number KC691309. Molecular characterization indicated that the isolated strain belongs to the genus *Acidithiobacillus* with 99.28 % pairwise similarity with *Acidithiobacillus ferrivorans* NO-37(T) (AF376020), 98.54% with *Acidithiobacillus ferridurans* ATCC 33020(T) (AJ278719) and 98.21% similarity with *Acidithiobacillus ferrooxidans* ATCC 23270(T) (CP001219) [3].

Leaching experiments design

The leaching experiments were carried out with bacterium *Acidithiobacillus* sp. B2. Experimental conditions were: leaching period of 14 d, leaching solution (g/dm^3): $FeSO_4 x 7H_2O$ (5), $(NH_4)_2SO_4$ (3), K_2HPO_4 (0.5), $MgSO_4$ (0.5), KCl (0.1), $Ca(NO_3)_2$ (0.01), (1K) at a pH of 2.5 in 500 mL Erlenmeyer flasks at a pulp454 density of 10% (m/V) (10 g leaching substrate in 100 ml solution). The control suspension had the same chemical content and pH value as the suspension with *Acidithiobacillus* sp. B2, but the *Acidithiobacillus* sp. B2 culture had been inactivated by sterilization. Experiment was performed on a horizontal shaker New Brunswick Scientific. The incubation temperature was 28 °C and the rotation speed 180 rpm. Number of microorganisms, concentration of copper and pH were analysed every seventh day during the period of 14 day.

The bacteria oxidized pyrite to sulfuric acid and $FeSO_4$, which was then microbiologically oxidized to iron(III) sulphate ($Fe_2(SO_4)_3$). Iron(III) sulphate is very important in the bioleaching process, because this compound is a strong oxidizing agent, so pyrite oxidation continued.

Bioleaching occurs according to the following chemical reactions:

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2H_2SO_4 + 2FeSO_4$

$2FeSO_4 + H_2SO_4 + 0.5O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$

$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S\downarrow$

$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$

Key role of *Acidithiobacillus* sp. B2 is to regenerate sulphur acid and Fe^{3+}, which is strong oxidizing agent. All these things lead to lower pH and leaching of copper from solid phase.

RESULTS AND DISCUSSION

Samples were taken from eight different locations on Bor ore dumps. Chemical analyses of ore dumps are presented in Table 1.

Table 1. Chemical analyses of ore dump

Component	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	S	P_2O_5
%	59.29	14.56	2.65	1.03	0.98	1.30	2.80	0.070
Component	Fe_{total}	Fe^{2+}	Cu	Cu_{ox}	$S_{sulphide}$	$S_{sulphate}$	MnO	LOI
%	8.38	4.20	0.22	0.02	1.3	1.5	0.01	8.07

The X-ray powder diffraction analyses show that ore dump contents quartz, feldspars, amphibole, pyrite,talc.

The initial number of microgranisms was $3x10^7$ per ml. This number increased during experiment, and after seven days itwas $4x10^8$/ml, and on the end of the experiment it was $2x10^8$/ml.

During the leaching process, pyrite sulphur (sulphide sulphur) content in suspension with *Acidithiobacillus sp.* B2 decreased from 1.3% to 0.7%, while in the control suspension its content decreased from 1.3% to 1.2%. Obtained results confirm the role of microorganism in pyrite oxidation, as well as in process of copper leaching from ore dump.

Change of pH and percentage of copper leached in suspension with bacteria, aswell as in control suspension, were determined on start and on the 7^{th} and 14^{th} day of experiment. The results obtained are presented on Figure 1. and Figure 2.

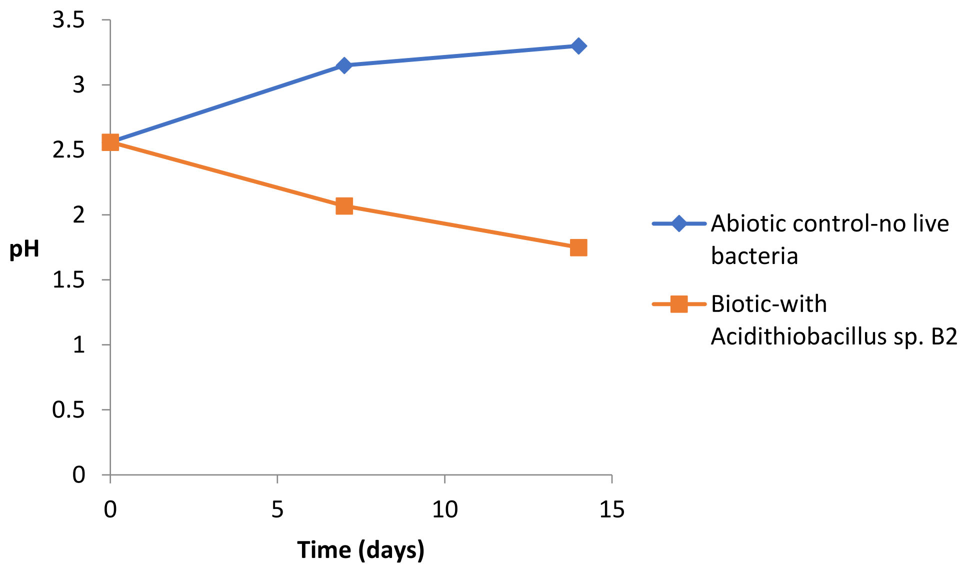

Figure 1. pH profiles during bioleaching of ore dumps in suspension with *Acidithiobacillus* sp. B2 and control suspension

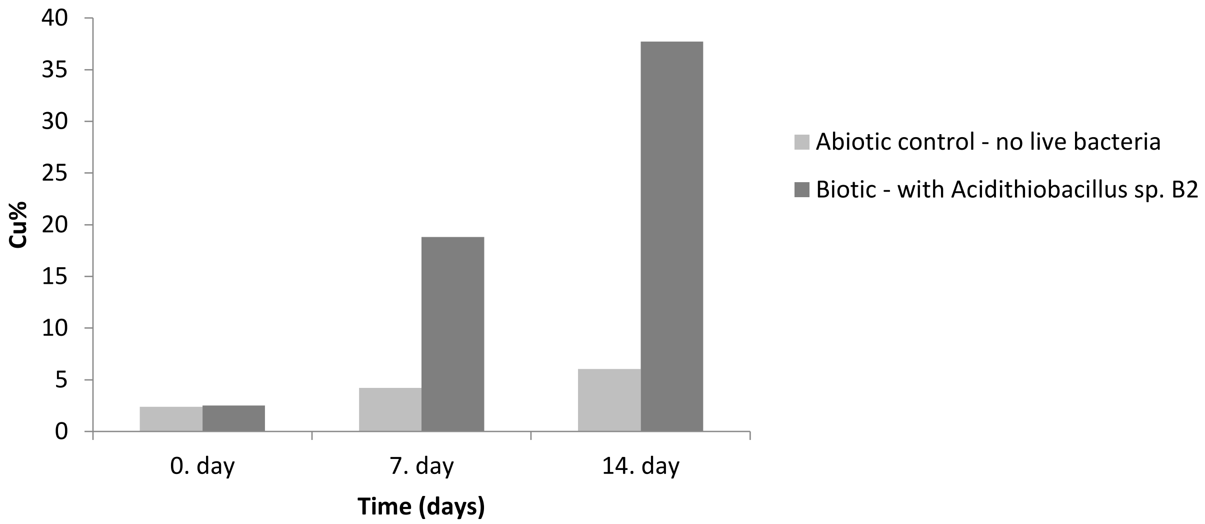

Figure 2. Amount of Cu leached during the process on shaker

Obtained results indicate that there is relationship between copper leaching and decrease of pH value, which is directly correlated with concentration of bacterially produced sulfuric acid in leaching medium.

The percentage of leached copper, resulting from the activity of *Acidithiobacillus* sp. B2, *(i.e.* the effective metal leaching), was calculated by subtraction of percentage metal leaching in the control suspension from that in the *Acidithiobacillus* sp. B2 suspension, and it equals 31%.

CONCLUSION

These results showed that microbiological treatment of ore dump had been efficient, and the future task is tooptimize this process in order to get larger amount of copper leached. It could be probably achieved by increasing the number of microorganisms in suspension, or increasing the time of leaching.

Microbial methods of leaching ore dump plays very important role for obtaining the additional amounts of metals and in the concept of environmental protection, because it allows use of relatively simple technology to control and redirect uncontrolled loss of metals into the soil and watestreams.

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