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Research on Contaminated Soils from Baia Mare Area and their Remediation by *In Situ* Bio-Leaching Technique

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Abstract

The mining activity and the activities related to non-ferrous metallurgy, which were practiced in the Baia Mare, led to the pollution of large areas of land and adversely affected the environment, while they were representing a risk to human health. In the first part of the paper, the physical and chemical properties of soil and the content of metals (copper, lead and zinc) in the soil samples are presented. The effectiveness of the in situ bio-leaching technique applied to the soil polluted with heavy metals, is presented in the second part of this study.

Keywords: bio-leaching, copper, lead, zinc, soil pollution

1. Introduction

In the Baia Mare area the soil pollution with heavy metals is recognized today as a significant problem, representing a serious risk to human health and the environment [9]. The high contents of heavy metals in soils are related to anthropogenic sources: mining and metallurgy. The content of heavy metals in soils from this area is significant because of the high values of Pb, Cu and Zn.

The excessive quantities of heavy metals in soil inhibit plant growth and adversely affect nitrogen fixation by microorganisms. The results of the experiments performed worldwide, in which the *Thiobaccilus* type bacteria were used, have showed leaching effectiveness for metals, as follows: Cu 69 – 92 %; Pb 10 – 54 %; Zn 88 – 97 [3], Zn 80 % and Cu 24 % [6]. Nationally, on the SNP Petrom – Doljchim platform, experiments were performed on a facility in order to obtain data to demonstrate the maximum depth to which the bio-leaching technology is viable.

The extraction effectiveness of copper was 95 %. The optimum temperature and the aeration have proved to be very important factors in bacterial leaching of the metal [4, 5].

2. Research methodology

Two soil samples in their natural state were taken from the Baia Mare area, as follows (fig. 1): a sample from the surface (0 – 10 cm) and a sample from depth (60 – 70 cm). The soil sampling was done according to STAS 7184/1-75.

The preparation, the chemical and physical analysis of soil samples were performed in *The National Institute of Research and Development in Soil Science, Agrochemistry and Environment– Bucharest*.

In the first stage, the soluble heavy metals from soil (Pb, Zn, Cu), extracted in aqua regia, were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using FMD SpectroFlame 07 spectrometer (Spectro, Germany).

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Figure 1. The sampling model of soil assays

In the second stage of research, investigations on the extraction of heavy metals from contaminated soils, using *Thiobacillus ferrooxidans* type microorganisms (140 x10^6), were performed.

These microorganisms were selected from the sampling area of soil assays (Baia Mare) and were grown on a 9K type nutrient medium [7] under controlled temperature (29°C) and a pH between 2.5 and 3.0.

The soil samples, taken in their natural state, were brought in the laboratory into the sample container, later being decanted into glass containers. The soil sample used in the experiment was placed on a gravel drainage layer, sort of 30 – 45 mm.

The extraction was carried out only on the sample from depth because in this case the metal content exceeded the alert threshold.

The bio-leaching solution consisting of indigenous microorganisms was added through the top of the glass container filled with soil.

To achieve the extraction of metals a diffused aeration (8 bars) was performed.

The assurance of the oxygen supply necessary to the microorganisms present both in soil and in the bio-leaching solution (9 K medium) was the aim of the aeration.

The stages through which this experiment was conducted are shown in figure 2.

In order to validate the in situ bio-leaching decontamination process, weekly soil samples were taken for 5 weeks.

These samples were analyzed in the Research Institute for Analytical Instrumentation, Cluj – Napoca, in order to determine the content of metals.

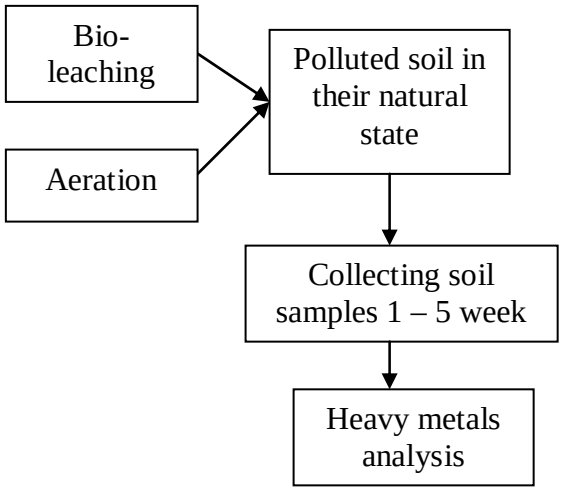

Figure 2. The scheme of soil treatment

3. Results and discussions

3.1. Physical and chemical properties

The structural differentiation is very important for the soil profiles. The surface soil sample has a silty clay texture (LP). The soil sample taken from depth is made up of 55.8% arenaceous coarse sand (UG). The pH values indicate an increase in pH with the depth. The surface soil sample has the highest humus content. The cation exchange capacity is identical for both samples. The soils studied are characterized by a nutrient content between 0.113 and 0.332, and the C/N ratio is high for the two samples.

Table 1. The physical and chemical properties of the soil samples

Characteristics \ Depth (cm)	0 – 10	60 – 70
Structure (dimensionless)	LP	UG
pH (units of pH)	5.15	6.50
Humus (%)	6.17	2.10
Humidity (%)	34.2	21.21
Cation exchange capacity (*me/100 g sol)*	23.25	25.93
C org (%)	3.58	1.22
Nt (%)	0.332	0.113
C/N (dimensionless)	10.78	10.79

3.2. The metals content

The content of heavy metals in soils indicates that the analyzed soil from the investigated area is polluted, in varying degrees, with Pb, Cu and Zn [1, 2]. The amount of heavy metals existing in the researched soil samples was correlated with the alert threshold values of the Order 756/1996.

In the soil sample taken from surface (0 – 10 cm) the content of all those three metals studied (Pb, Cu, Zn) is below the alert threshold (figure 3).

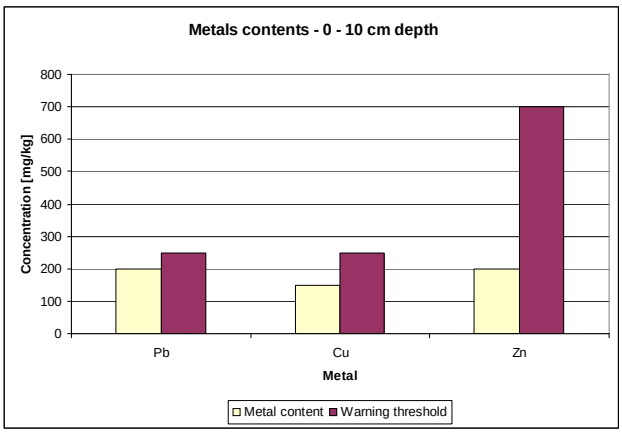

Figure 3. The metals content of the surface soil sample

The sample taken from the depth presents values of heavy metals that exceed the alert threshold. In the case of Pb the threshold is exceeded of 72 times, respectively 26 times for Cu and Zn (figure 4). This soil requires treatment to remove heavy metals. The soil sample, subjected to in situ bio-leaching treatment for 5 weeks, was taken in the natural state of the depth of 60 – 70 cm. Analyzing the graph shown in figure 5 on the quantity of heavy metals in soil sample subjected to the experiment, the extraction of metals by microorganisms during the 5 weeks of experiment was observed.

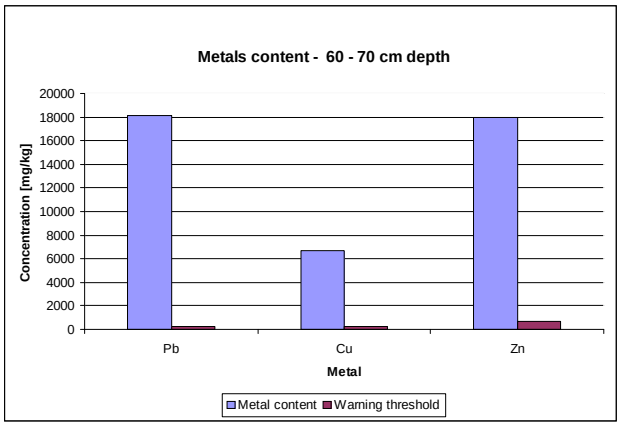

Figure 4. The metals content of the soil sample taken

Analyzing the graph in the figure 5 on the soil subjected to the experiment it can be seen that both lead and zinc were extracted very well in the first week, presenting sharp linear decreases. After the first week of the experiment, zinc continues to be extracted, but lead has stability until the fourth week when a new phase of extraction begins. The curve performed for Cu (figure 5) shows a slight decrease in the first two weeks of the contact between the two media (9K medium and polluted soil), after that a linear decrease is observed. Thus it can be seen that in just five weeks of treatment with bio-leaching solution of the polluted soil, high percents of effectiveness were obtained:

- Zn: 89 %
- Cu: 71 %
- Pb: 68 %.

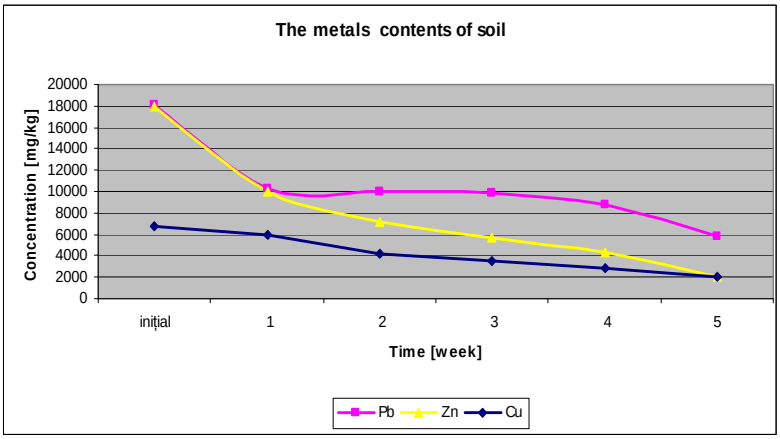

Figure 5. The metals content of soil as function of time

Following these extractions for those five weeks of treatment, the effectiveness of the in situ bio-leaching process was calculated. The experimental results obtained were processed.

The graph in figure 6 represents the variation of effectiveness, which was obtained for the biological remediation process, as a function of time.

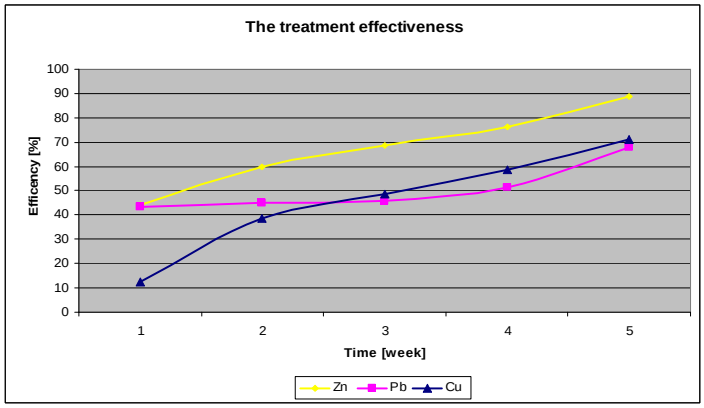

Figure 6. The treatment effectiveness of soil as a function of time

4.Conclusions

The results of the analysis of the soils sampled from Baia Mare area showed that these area is polluted with Pb, Cu, Zn, the concentrations exceeding the alert threshold. The experimental results obtained showed that the bio-leaching of metals was achieved by the utilization of the *Thiobaccilus* type bacteria. After only five weeks of experiment, the effectiveness of the extraction of heavy metals were obtained, as fallow: Zn – 89 %, Cu – 71 %, Pb – 68 %. The experiments carried out have led to the conclusion that the application of the bio-leaching technology for these metals is an effective biological method of treating polluted soils. This method involves the use of microorganisms to promote the solubilization and the extraction of heavy metals from polluted soils.

Acknowledgements

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