

Original Article

Biosolubilization of Heavy Metals Present in Polluted Soils from Romplumb Area, Baia-Mare

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Abstract

Soil pollution with heavy metals from metallurgical activities constitutes serious problems for both environment and humans. Iron and sulfur oxidizing microorganisms, from category *Acidithiobacillus ferrooxidans* and *thiooxidans*, can solubilise heavy metals from soils by well known bioleaching techniques. This study shows the ability and capability of mentioned microorganisms to treat soils contaminated with heavy metals in laboratory conditions, using 100 ml Erlenmeyer flasks, at 35 °C and an agitation speed of 200 rpm with thermostatic Microbiological Incubator with mixing pan Heidolph model Titramax 1000. Experimental researches were conducted on soil samples taken from inside of the precinct Romplumb, Baia Mare. These studies were conducted to determine at the same time and behavior of heavy metals from soils taken in terms of their extraction of these soils, by methods which involve the use of microorganisms. Another purpose of this research is related to determination of the heavy metals solubilization efficiency under conditions designed to optimize the action of microorganisms. The end of the paper is reserved for conclusions and observations resulting from processing and interpretation of results for all tests.

Keywords: *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, solubilization soils, heavy metals

1. Introduction

The mining activity practices in Baia-Mare for over 100 years, led to pollution and economic sealing of large areas of land, and adversely affected the environment, which now represents a significant risk to human health. The actual sources of pollution, current or historical, in Baia Mare Depression are: *SC Romplumb SA*, *SC Cuprom SA* and *CNMPN Remin SA*.

The mining activities left over wide areas ponds; mine waste dumps and the underground waters that come across the existing mine galleries spring out contaminated, sometimes in an uncontrolled manner.

Heavy metals are present in the environmental factors from this area and significantly affect local ecosystems and human health (Coman M. et colab, 2010). One of the methods most often used in bioremediation operations of contaminated soils is *bioleaching*. This technology is specific of soils from vicinity or within of Baia-Mare, from area steel company S.C. Romplumb S.A. (Cociorhan Camelia et al., in press). *Bacterial leaching/biosolubilization* is a process in which the microorganisms are used in reduce of heavy metals such as lead, copper, zinc and cadmium, by transforming compounds toxic into nontoxic, environmentally safe and/or human health.

2. Material and Method

For conducting of the experiments soil samples taken from the precinct of the Romplumb, Baia-Mare, on the surface (0 – 10 cm) and deep (10 – 20 cm) were used. Treating this type of soil was

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conducted over a period of 72 hours, where have been tested nine samples of work, from which:

- variants 1 and 2 were achieved by *bioleaching*, with soil taken from the surface (0 – 10 cm), at a ratio solid/liquid 1 : 5,
- variants 3 and 4 were tested with soil taken from deep (10 – 20 cm), by *bioleaching*, at a ratio solid/liquid 1 : 5,
- working variant no. 5, considered blank, is subject to a treatment by *natural leaching with water* was conducted with soil collected from the surface, i.e. 0 – 10 cm and at a ratio solid/liquid 1 : 5,
- working variant no. 6 formed with soil taken from deep 10 – 20 cm, at a ratio solid/liquid 1 : 5, was treated by *natural leaching with water*,
- working variants no. 7 and 8 were treated by *bioleaching*, with soil taken from the surface 0 -10 cm and at a ratio solid / liquid 1 : 10, and
- working variant no. 9 of the test, was performed with soil taken from deep 10 -20 cm, at a ratio solid/liquid 1 : 10 and was treated by *bioleaching*.

All the samples were tested in 100 ml Erlenmeyer flasks and were subjected to a continuous shaking at 200 rpm and maintained at a temperature of 35 °C during the entire duration of the test. These conditions were ensured by *Microbiological incubator thermostated* with stirring pan *Heidolph*, model *Titramax 1000*.

The soil used was weighed in *Petri dishes* with *analytical balance Partener WPS 210/C/2* precisely 0,01g. Samples were placed in 100 ml Erlenmeyer flask which was added over the liquid (nutrient solution 9K or water) depending on desired treatment option. After sample preparation work they were weighed, the masses being retained as information of each study. The liquid samples was measured with different size of cylinders, liquid samples were taken with manual pipettes of 10 ml. For pH measurement was used portable pH-meter *Consort P 901*. Samples were filtered through black band filter paper *Filtrax*

Microrganisms were taken from a pyrite concentrate heap near the former *Central Flotation Baia Mare*, and the culture of microorganisms has been developed in *medium 9K Silverman & Lundgren, adapted to the specific tests the area: (FeSO₄ · 7H₂O) - 22 g ; (NH₄)₂SO₄ - 3 g ; Mg SO₄ - 1 g ; KHH₂PO₄ - 1 g ; KCl - 0.5 g ; Distilled water; pH is corrected to 2.5 with H₂SO₄ or NaOH, (Cociorhan Camelia et colab, 2010).*

Analyses of concentrations of dissolved elements were made by *mineralization with aqua regia*, and then by *atomic emission spectrometry in inductively coupled plasma (ICP – OES)* in

specialized laboratories of Research Institute for Analytical Instrumentation - ICIA Cluj – Napoca.

In the following is presented in a sequence established according to the sampling depths in the area of Baia Mare, the results obtained from tests achieved in contaminated soil analysis, taking into account the following parameters: sampling depth, ratio solid/liquid, variants of work, type of sample with indication of corresponding code, the content of samples work which were tested, utilized treatment variant, dislodged volume which subsequently filled with new solution with the same concentration, treatment duration, temperature.

3. Results and Discussions

Parameters whose variation was followed in the performance of the tests are: pH, conductivity, dissolved of heavy metals concentrations in the fluid, the ratio solid/liquid, type of soil used.

At 24 h, 48 h and 72 h of aqueous suspension preparation of the samples this were reweighed and was achieved and was achieved by trying to bring the amount evaporated every day with acidulated water. This monitoring was done for evaporate of liquid contents, because the content of samples showed a high evaporation, due to the high temperature. After the completion of homogenization of aqueous suspension by pipetting, liquid samples were collected after 24 h, 48 h and 72 h. The volume of liquid dislodged was completed at each sampling, with new solution of the same concentration.

In fig. 1, is shown pH variation according on time, for each variant of work. For test samples were made four measurements of pH. The first measurement was done after the preparation of aqueous suspension, and the next measurement was done after the 24 h, followed by a measurement at 48 h and another at the end of test, after the 72 h of treatment.

Samples 1 - 4 of this test were samples treated by *bioleaching*, at ratio solid/liquid 1 : 5. For this samples, **initial value** of pH was within the range 2.05 – 2.16. After **24 hours**, pH value showed an increase against to initial value being in the range 2.21 – 2.39, this means an optimal microbial growth and activity within the 24 hours to prepare the aqueous suspension.

To achieve measurements at **48 h** and **72 h**, values had decreased such as initial values and those to 24 h, ranging between 1,80 – 1,93.

Samples 5 – 6, were treated by leaching with natural water, at ratio solid/liquid 1 : 5. For this samples, pH value achieved at **24 h** had an increase

against to **initial value**. However, at **48** and **72 h**, pH value had a decrease against to initial value and

those made at 24 h. During testing, pH value for this samples, 5 and 6, ranged between 3,56 – 4,59.

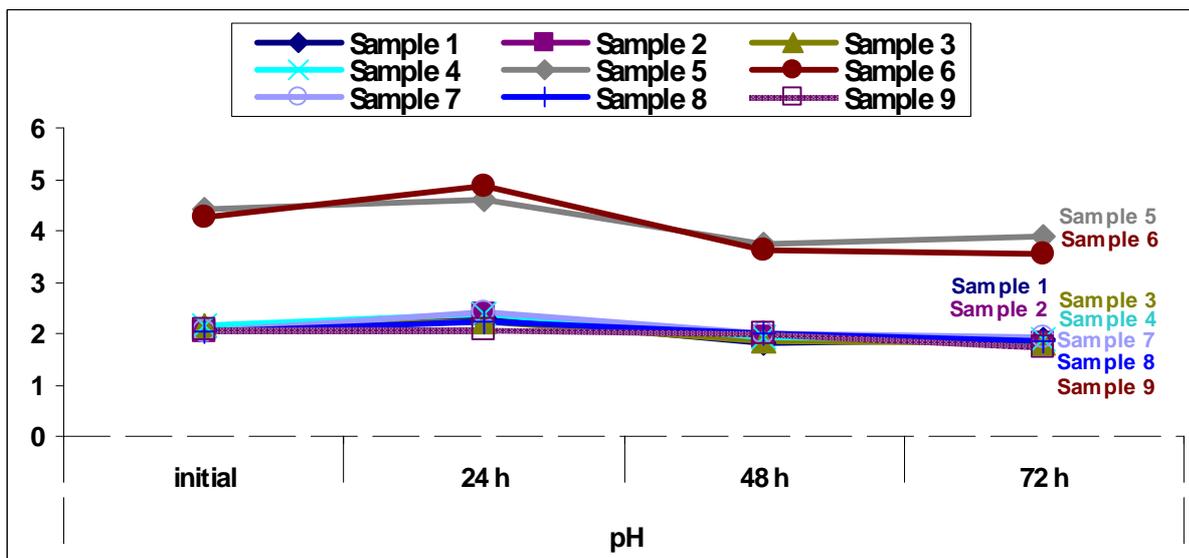


Figure 1. pH variation function of time

Samples 7 - 9 of this test were samples treated by bioleaching, at ratio solid/liquid 1 : 10. **Initial value** of pH was within the range 2,02 – 2,08. To achievement measurements at **24 h**, pH value showed an increase against to initial value was included in the optimum microbial activity. The pH achieved at **48 h** and **72 h**, both showed a decrease against to initial values those at 24 h.

The duration of the test the optimum pH was at 24 hours after the preparation of aqueous suspension. After 48 and 72 hours the pH of the

samples tested had a higher acid character than the initial and 24 hours.

In fig. 2, is presented the extraction of *Pb*, *Cu*, *Zn*, *Cd* percentage obtained for **samples number 1**. On this sample, the most significant results are obtained by **cadmium**, with an average over 40% during the treatment.

It is followed by **zinc**, with an average approx. 35%, and **lead** obtained an extraction average approx. 28%. Unlike to Cd, Zn and Cu, Pb has obtained an insignificant extraction.

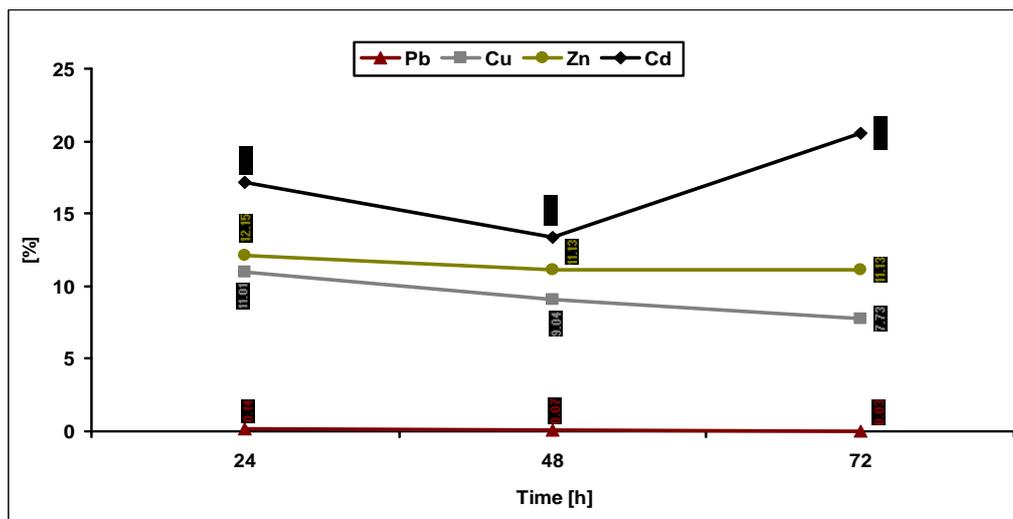


Figure 2. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 1

For **sample no. 2** (fig. 3), have achieved the following average percentage extraction: **cadmium** over 50%, **copper** approx. 20%, **zinc** over

36% and **lead** and to this sample showed significant extraction (an average of 0,2%).

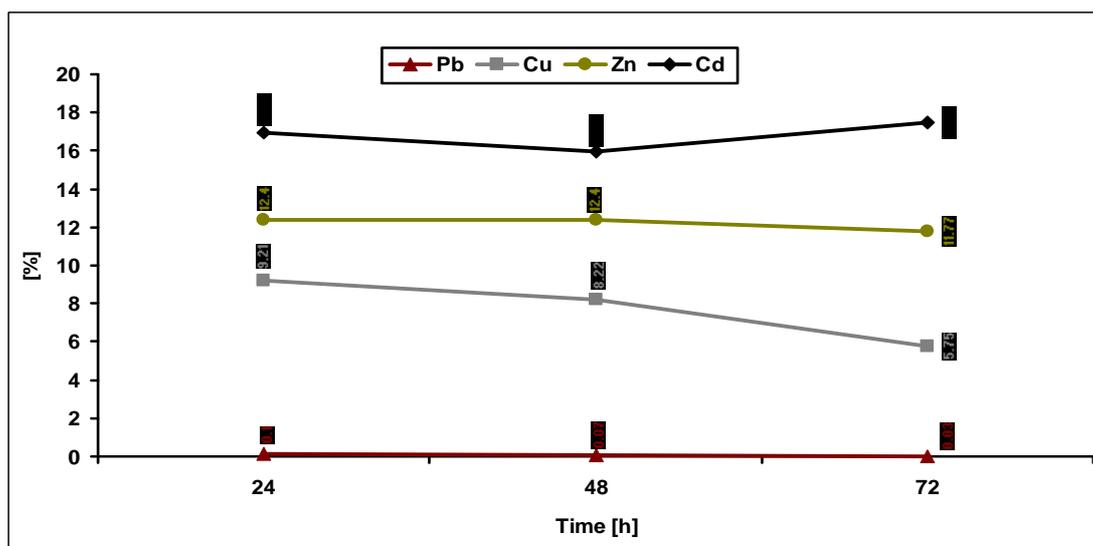


Figure 3. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 2

All chemical elements analyzed the *samples no. 3 and 4*, showed a decrease of solubilization yield percentage into the liquid after the 48 hours of treatment, compared with that analyzed after the

first 24 hours of treatment and after which it can be seen from figs. 4 and 5 an increase or maintain, the case, at the end of test, i.e. after 72 hours.

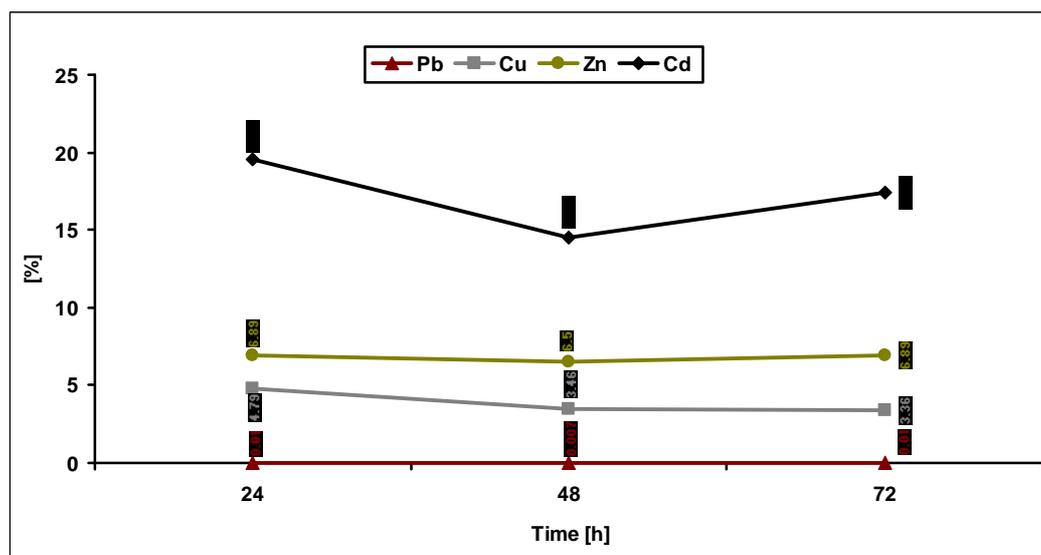


Figure 4. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 3

The most significant yield extraction presented at both samples is by the *cadmium, zinc and copper*.

Lead does not show extraction yields. For *sample no. 5* (fig. 6), the most significant yield is obtained by *Zn* (12,86 %) after 24 hours of treatment, and then following a decrease of efficiency (0,16 % at 48 h and 0,36% at 72 h of treatment). The rest of the elements analyzed, doesn't showed significant extraction yields. In *sample no. 6*, analyzed chemical elements doesn't

show significant extraction yields (fig. 7). In *sample no. 7 and 8*, all chemical elements analyzed showed a decrease of percentage yield solubilization in liquid after 48 hours of treatment, compared to those analyzed after 24 hours of treatment after which it can be seen in figs. 8 and 9, an increase or maintenance, depending on situation at the end of the test period, i.e. after 72 hours.

The most significant yield extraction is shown by *Cd, Zn and Cu*. *Pb*, doesn't show significant extraction yields.

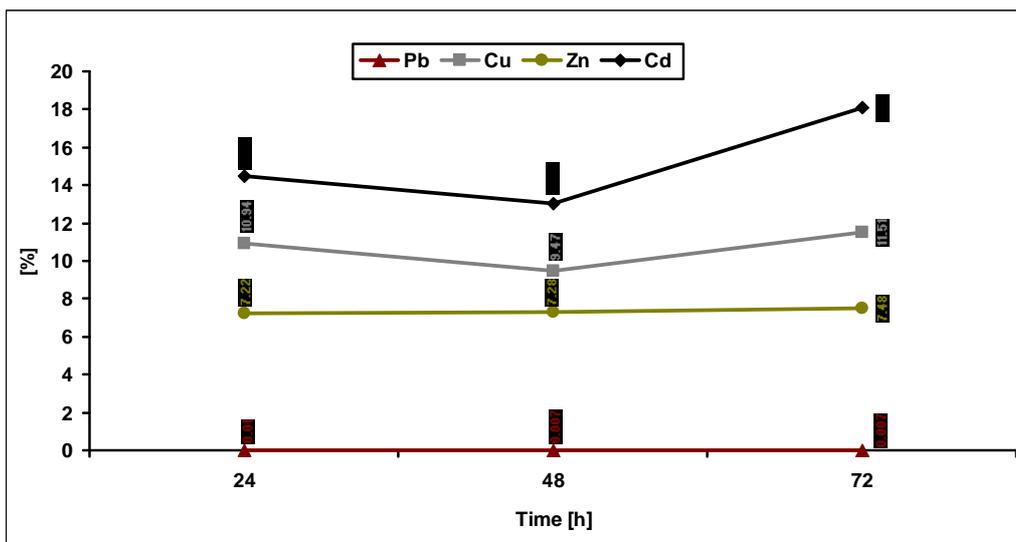


Figure 5. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 4

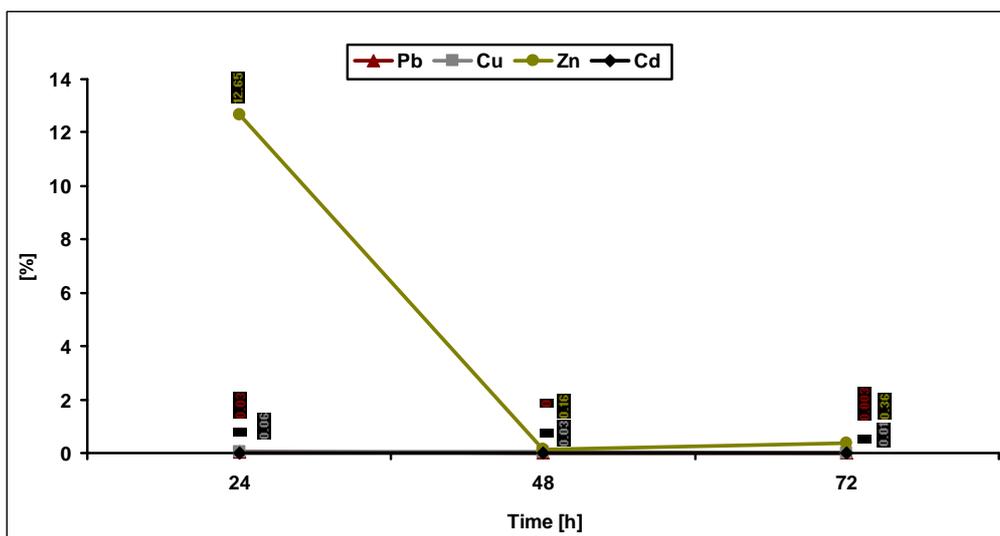


Figure 6. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 5

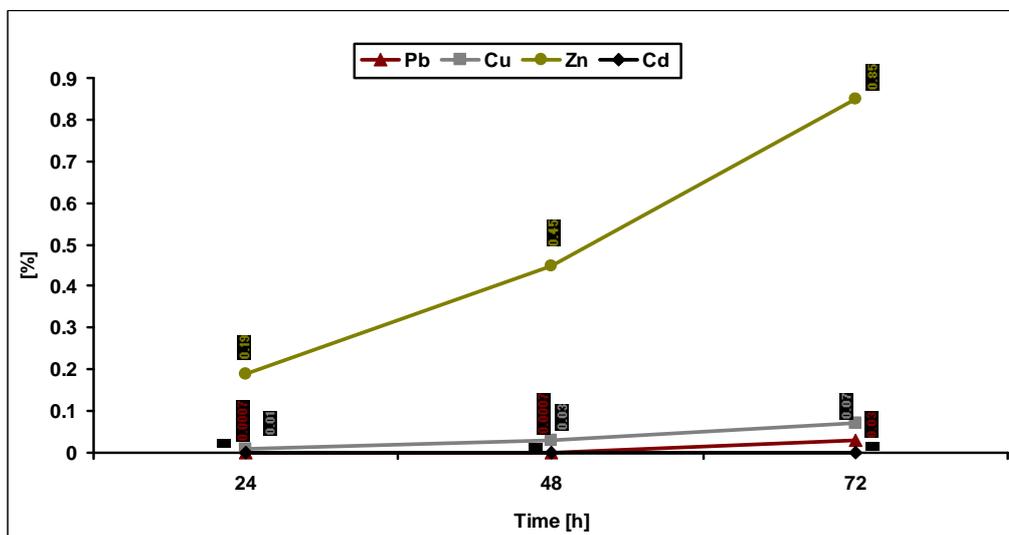


Figure 7. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 6

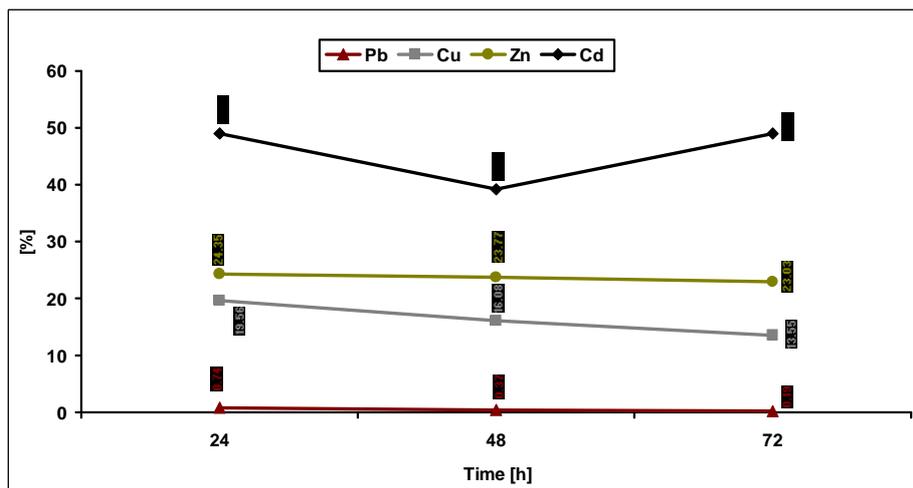


Figure 8. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 7

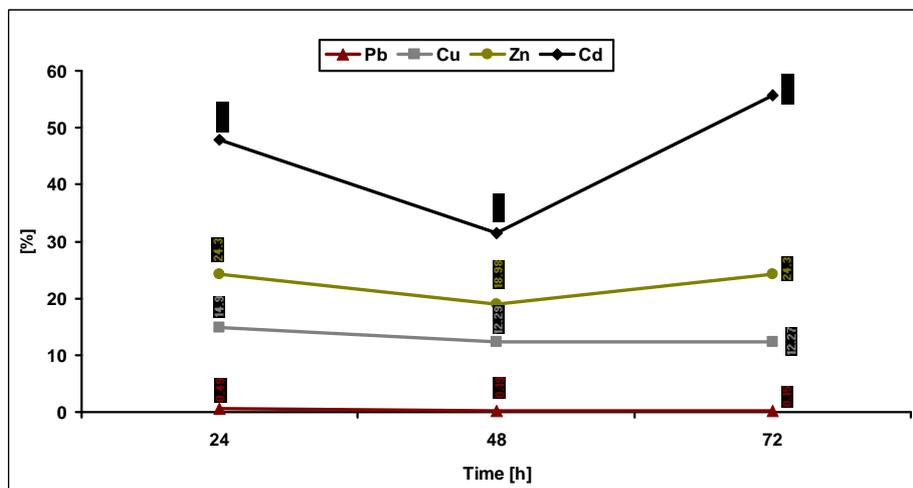


Figure 9. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 8

In figure 10, are presented the concentrations of *Pb*, *Cu*, *Zn* and *Cd* percentage yield solubilization in liquid after 72 hours of treatment of samples by *bioleaching*. Thus, *Cd*

presented the highest levels of solubilization, followed by *Zn* and *Cu*, but, with the visible differences of solubility. For this sample also, the *lead*, showed insignificant results of solubilization.

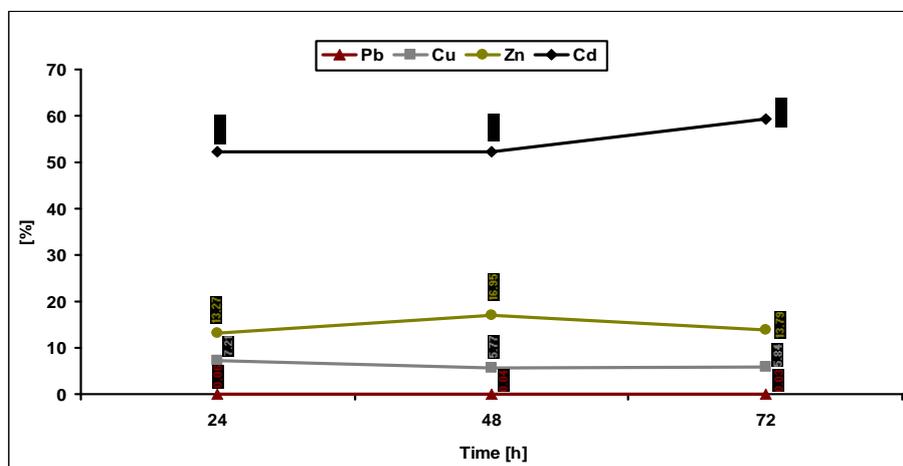


Figure 10. Percentage of Pb, Cu, Zn, Cd biosolubilization in liquid for sample no. 9

4. Conclusions

From that 4 chemical elements analysis, Cd shows the most significant yield extraction. It is followed by Zn and Cu, but with obvious differences of solubilization. For all samples analyzed, lead presents insignificant results of solubilization.

Comparison between the two soil types used, sample soil from surface shows the highest levels of solubilization.

The highest levels of solubilization are obtained on the treated samples by *bioleaching*. While, the samples treated by *leaching with natural water* (samples 5 and 6, blank work samples of the test), presents insignificant results of solubilization.

On duration of the test, the optimum pH was at 24 hours after the preparation of aqueous suspension. After 48 and 72 hours, the pH of the samples tested had a higher acid character than the initial and 24 hours.

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