Green technologies for remediation of contamined soils with heavy metals in the former gold mining areas

Adriana Mihaela Chirilă Băbău, Valer Micle, Ioana Monica Sur

Department of Environmental Engineering and Sustainable Development Entrepreneurship, Faculty of Materials and Environmental Engineering, Technical University of Cluj-Napoca, Cluj-Napoca, Romania. Corresponding author: A. M. Chirilă Băbău, adriana.babau@yahoo.com

Abstract. Soil pollution with heavy metals is one of the most discussed global environmental problems. Due to the performed activities in the past, in gold mining area, resulted in the environment several sources of pollution such as: mine galleries, tailing ponds, dumps of steril and leakages of mine, which are very dangerous for environment because these are loaded with large amounts of heavy metals. Soil pollution with heavy metals represents a negative impact on the environment and human health. For this reason it is necessary to develop friendly technologies, efficient and with a low cost. At present, in order to remedy the polluted soils with heavy metals, the technologies of interest are biotechnologies. The experiment aimed to determine the effect of the variation in concentration of copper on the germination and growth of seeds of *Zea mays*. After 7 days the seed germination rate was high for the low concentration or control sollution and decreased dramatically with the increase in concentration. Applying the phytoremediation technology with *Agrostis capillaris* on the tailings pond had a positive effect which has been quantified by the slight decrease in the concentration of metals in the soil into plants. The experimental results obtained on application of the bioleaching treatment on a contaminated soil with heavy metals by using two extraction solutions (water and 9K medium) have shown that in optimal treatment conditions, zinc can be extracted with a yield of 34-86% and copper with a yield of 52-92%. These studies presents some of the green technologies which can be applied in the former gold mining area

Key Words: environment, green technologies, heavy metals, soil pollution, mining area.

Introduction. Pollution from mining industry raises big issues alongside pollution from the tailing ponds and sterile dumps. The improper management in the past has resulted in accumulation of heavy metals in the environment which contributed to soil contamination, destroying the texture, green landscapes, groundwater pollution and decreased biodiversity (Liu 2008; Băbuț et al 2011).

Heavy metal pollution of soils is one of the most important environmental problems of pollution out of worldwide (Wang et al 2002; Panagos 2013; Liedekerke et al 2014).

Due to the acute toxicity of heavy metals, there is an immediate need to develop efficient methods with low cost for minimizing, eliminating, stabilization and degradation of these pollutants (McGrath et al 2002).

Currently, the bioremediation is one of the most important directions for the development of remediation internationally techniques (Jing et al 2007; Coman et al 2009; Boroș et al 2016a).

Soil pollution sources in the former gold mines areas. Unfortunately, pollution problems do not disappear with the cessation of mining activities. Abandoned mine sites are believed to be large amounts of waste with a high content of heavy metals and particulate matter, which by their drainage by rivers or storm waters affecting large areas. Therefore, abandoned mining sites are sources of environmental pollution.

After the mining activities deployment was created following sources of soil pollution: mine galleries, tailings pond, dumps of steril and leakages of mine, which are submitted in Figure 1.

The main heavy metals that exist on the surface and subsoil of these polluting sources are: copper, zinc, lead, and cadmium, which are very dangerous for the environment and human health.

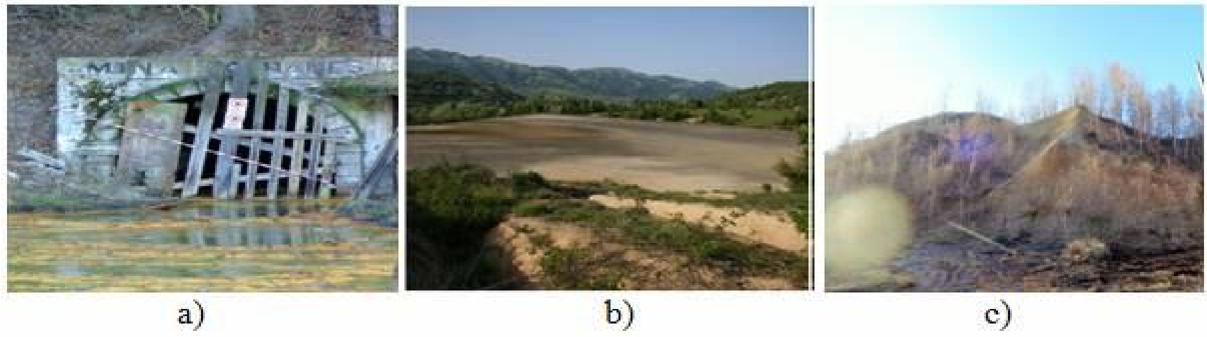

Figure 1. The main sources of soil pollution in the former gold mines area: a) – Haneș mine and leakages of mine; b) the tailings pond from Zlatna (Stancu 2013); c) – Radeș dump from Almaşu Mare.

Effects of heavy metals on soil. The heavy metals are dangerous only when they reach the soil solution where it can be absorbed by plants (Saxena et al 1990; McGrath et al 2002). Their effects depend on their solubility in the soil (Karaca et al 2010). Soil pollution with heavy metals can cause an imbalance of physical, chemical and biological soil, decreasing biological activity, inhibition may occur, affect nitrification and it has a toxic action for plants (Neag 1997; Kumar & Nagendran 2007). Copper appears in the soil in a concentration of 1 to 20 ppm. At a concentration of more than 0.1 ppm in the soil is toxic to most plants. In soils rich in organic matter and clay, mobility of copper can be reduced. Lead accumulated in large quantities in the soil can cause disorders of metabolism of microorganisms particularly affecting the breathing process and multiplication of cells (Du et al 2009). The zinc is present in soil in concentration between 30 and 50 ppm (Karaca et al 2010). The excess of zinc in the soil, reduce biological activity and this leads to degradation of the structure and stability of structural aggregates of water which favors erosion and compaction. The cadmium is one of the most dangerous heavy metals. Naturally, it appears in the soil at a concentration below 1 ppm (Bosecker 1997; Karaca et al 2010).

Therefore, contaminated soils with heavy metals present a major threat both on long-term agriculture and human life (Raspa & Gussepe 2005). These metals affect the particularly the breathing process and multiplication of cells (Wani et al 2008).

Green technologies for remediation of contaminated soils with heavy metals. Soil remediation is performed by processes with very long-time or expensive or very difficult to apply (Karaca et al 2010). Regardless of the application site, soil remediation technology is based on four main groups of methods, such as: physical, chemical, thermal and biological (Bosecker 1997). These methods of remediation intended to destroy, remove or immobilize the pollutants from soil.

Phytoremediation. Phytoremediation is both an in situ and ex situ technique (Raskin et al 1997; Oh et al 2014; Boroș et al 2016b). The technologies that have been identified to reduce pollutants in the environment are phytoextraction, phytostabilization, phytodegradation, rhizodegradation, rhizofiltration and phytovolatilization (US EPA 2000; McGrath & Zhao 2003; Alkorta at al 2004; Arthur at al 2005; Marques at al 2009; Ali at al 2013; Arbaoui et al 2013; Meuser 2013; Boroş & Micle 2014).

In order to develop an effective remedial solutions on the surface of tailings from Zlatna, Stancu realized an experiment of phytoremediation (Figure 2).

In all of these experiments was investigated the possibility of using a combination of amendments applied to the dump material, a dominant species of herb namely *Agrostis capillaris* variety of metal, with inoculation of microorganisms (bacteria or fungi mycorrhizae consortium). In the figure below (Figure 3) are presents elements of interest such as: copper and zinc which are present in the spectrum. The map of these elements (SEM image) showing their association with root surface (Stancu 2013).

Figure 2. The application and homogenization amendments on each experimental plot (Stancu 2013).

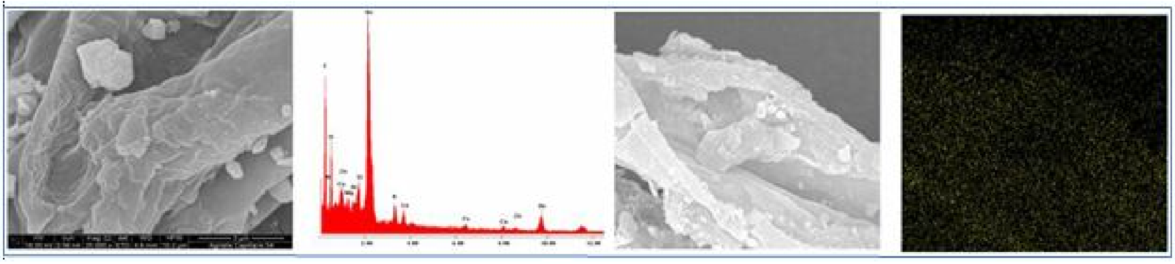

Figure 3. Images microscopy (SEM) and energy dispersion spectrum of X-ray (EDX) of the species *Agrostis capillaris* has been increased on a medium inoculated with a consortium of bacteria (Stancu 2013).

Applying species *Agrostis capillaris* on the tailings pond had a positive effect which has been quantified by the slight decrease in the concentration of metals in the soil into plants (Boroș 2016). Following realized investigations on tailings pond resulted that phytoremediation is an environmental friendly solution, efficient and with a low cost.

Near of Miami-Erie canal near Miamisburg were taken soil samples to be analyzed in the laboratory. The soil was polluted with heavy metals. In order to test the phytoremediation technology in a glasshouse were planted willow plant (*Tripsacum dactyloides*) taken from the soil in the pots on Miami Erie channel, in order to remove heavy metals from soil in the plant (Figure 4).

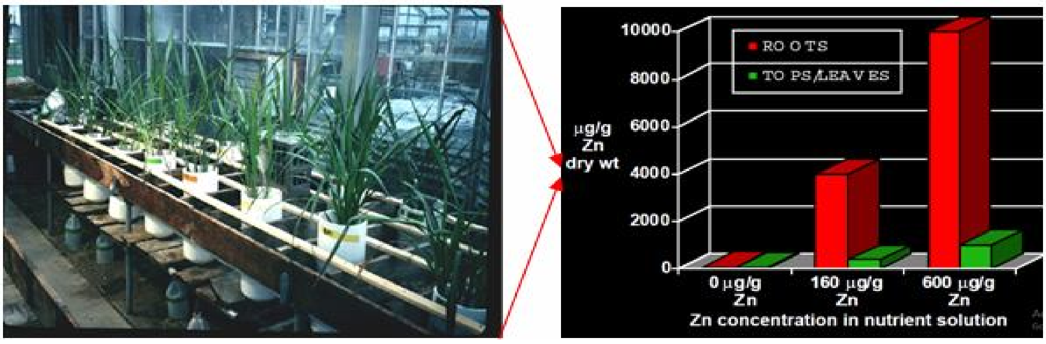

Figure 4. The average concentration values of zinc in the tissues of *Tripsacum dactyloides* using chelating agents (Hinchman et al 1998).

After the experiments performed it is found the use of chelating agents that diluted in Aqueous solution on the plant *Tripsacum dactyloides* increase the accumulation of zinc from soil into the plant (Hinchman et al 1998).

Caraiman (2011) conducted a study which consisted in the development, implementation, testing and demonstrating the effectiveness of an experimental model of phytoremediation for decontamination of a site in Iași polluted by Cd and Zn. The concentration of Cd and Zn present in the soil after harvesting the plants analyzed within the context of the Order 756/1997 on "Approval of the regulation of environmental pollution assessment" shows that the soil was decontaminated analyzed using all the plants studied, but maximum metal removal rate it was obtained from rapeseed as cadmium and zinc.

One of the plants with great potential in phytoremediation its *Zea mays*, a very common plant crops.

Boroş & Micle (2015) conducted an experiment that followed to determine the effects of copper on seed germination (Figures 5 and 6) of corn (*Zea mays*) and sunflower (*Helianthus annuus*). Figures 6 and 7 show the results obtained after performed experiment of phytoremediation.

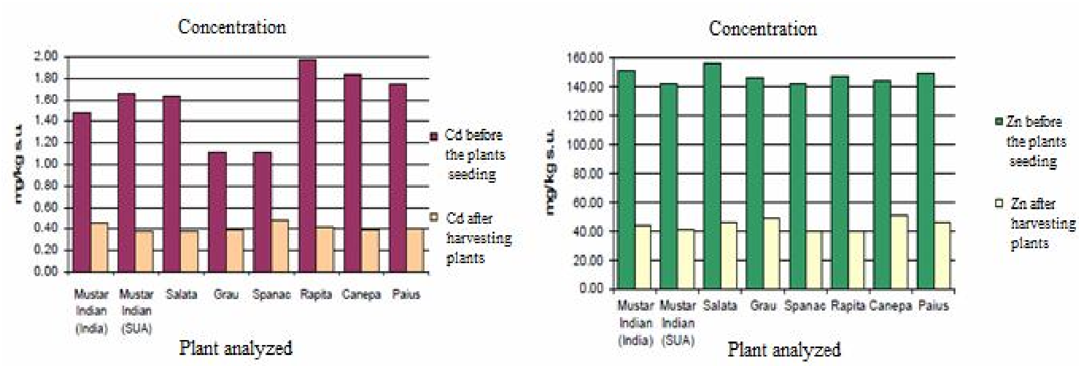

Figure 5. The concentration of Zn (II) and Cu (II) into the soil before sowing and harvesting of plants (Caraiman 2011).

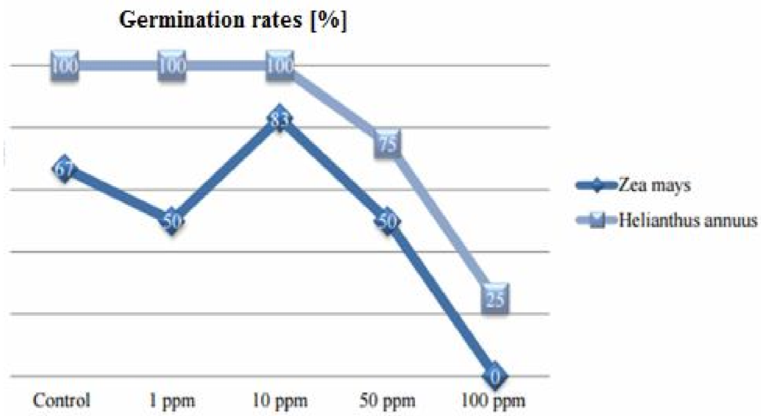

Figure 6. Tolerance at copper of test seed (Boroș & Micle 2015).

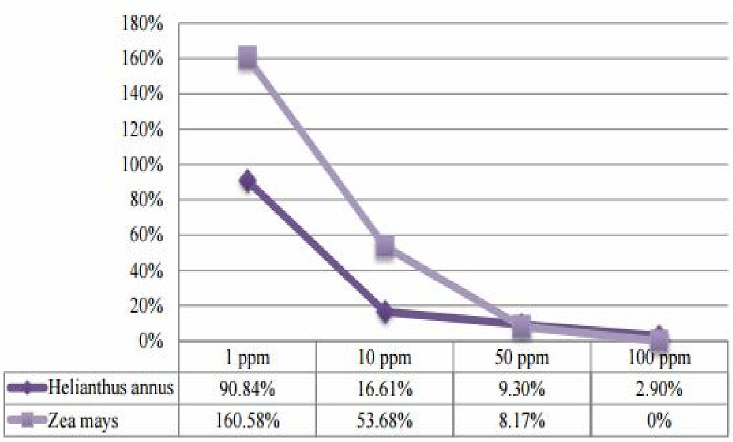

Figure 7. Germination rates of seeds (Boroș & Micle 2015).

From the results of the tests performed on plants studied and it is found that at low concentrations of copper, plants grow better as the control solution because it is a trace element. As the concentration increases, toxicity effects are increasingly visible. Copper is an enzyme inhibitor and the result is a reduction in the rate of seed germination.

Bioleaching. Bioleaching is the process of using bacteria to dissolve metals, such as: nickel, copper, zinc, cobalt, lead, arsenic and others. Bioleaching works by using specific bacteria that can essentially "eat" the metal content out of ore. The bacteria most active in bioleaching belongs to the *Thiobacillus* family (Cociorhan et al 2011; Sur & Micle 2012).

Bacteria could be pumped underground, allowed time to dissolve the metal content, and then flushed back to surface.

Bioleaching is a treatment which allows the biological extraction of inorganic pollutants. If it is applied in controllable conditions may the innovative solution for the treatment of polluted soils with heavy metals (Mulligan et al 2004).

Bioleaching is achieved when bacteria feed on the minerals of the soil. This separates the metals and allows them to be flushed out in a solution. When compared with chemical methods of separation bioleaching is slow, but clean and effective (http://www.pythongroup.ca/mining-news/article/id/56).

Kumar & Nagendran (2007) tested the bioleaching technology on soil polluted with heavy metals from Ranipet, an industrial town from State Tamil Nadu, India. Experiments were performed in order to assess the influence of initial pH of the system on bioleaching of chromium, zinc, copper, lead and cadmium from metal contaminated soil (Figure 8). pH at the end of four weeks of bioleaching at different initial pH (3-7) was between 0.9 - 1.3.

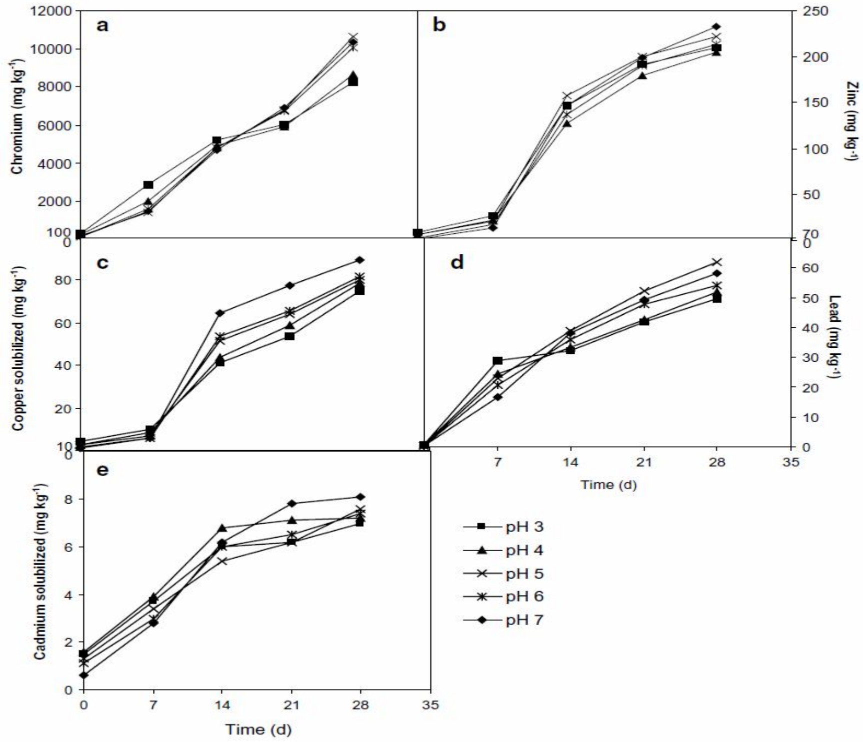

Figure 8. Influence of initial pH on solubilization of: (a) Cr; (b) Zn; (c) Cu; (d) Pb (e) Cd as a function of time during bioleaching (Kumar & Nagendran 2007).

The results of the present study are encouraging in order to develop the bioleaching process for decontamination of heavy metal contaminated soil. Chromium, zinc, copper, lead and cadmium solubilization ranged from 59 % to 98 % at different values of initial pH (Kumar & Nagendran 2007). Also, the bioleaching was tested in Chile on a contaminated soil with copper (Figure 9).

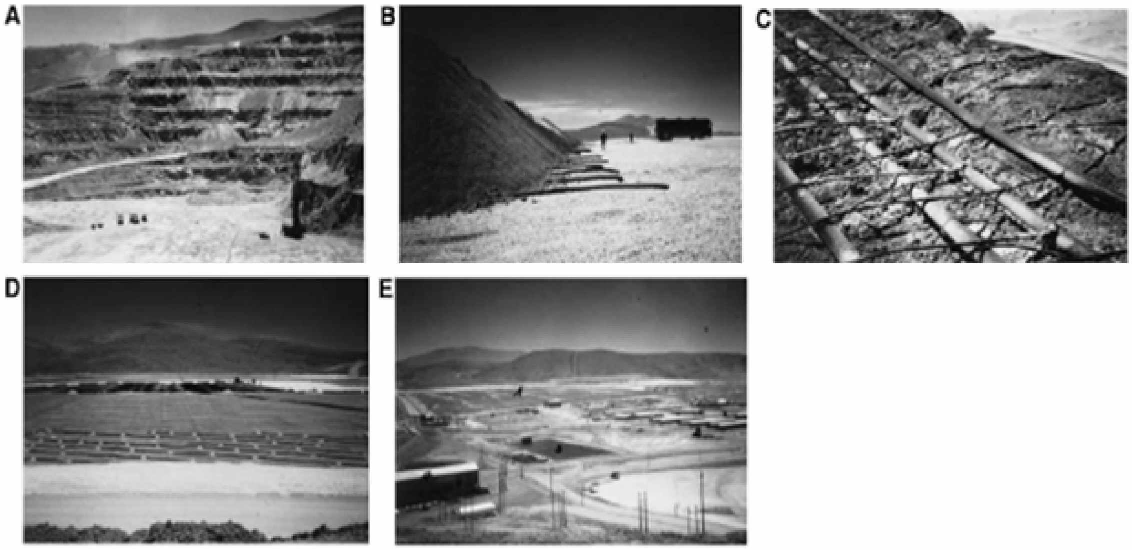

Figure 9. Bioleaching of cooper ore in Chile. A: open-cast mining of cooper ore, B: preparation of dumps for leaching, C: Irrigation by perforated tubes, D: Dump leachig area, covered for insulation, E:overall view of the leaching operation plant desulfurare (Bosecker 1997).

Another example comes from Kerman province of Iran. Also was tested here the bioleaching technology in order to extract copper from contaminated soil (Figure 10). After applying the bioleaching technology was found that it was a success.

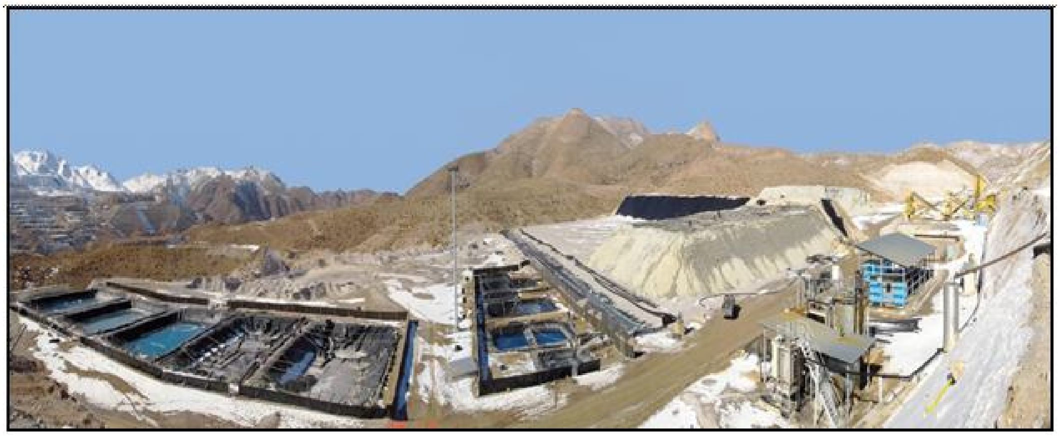

Figure 10. Demonstration plant at the Sarcheshmeh Copper Complex, located in the province of Kerman, Iran (Gericke et al 2009).

In 2009, John William Neale mentioned that for to overcome the slow and incomplete extraction of copper from chalcopyrite is necessary to optimize the process of bioleaching at high temperatures using thermophiles. The experiment was performed in Tasmania, through which was demonstrated that from chalcopyrite-containing concentrates was extracted 95% copper through many stages of the plant operated continuously where and the key parameters were delivery of sufficient oxygen and carbon dioxide for microbial growth and its oxidation (Gericke et al 2009).

Sur & Micle (2012) conducted a study in which they are appreciate achieve high efficiency of extraction of zinc, lead, cadmium, manganese and copper by in situ bioleaching. The experiment consisted mainly in pouring soil samples taken in the natural state in a glass container. These were placed on a drainage layer of gravel 30-45 mm. Over this soil was added solution composed of indigenous microorganisms (*Thiobacillus ferrooxidans*) taken from the soil studied and developed in the laboratory environment 9K (Berar (Sur) et al 2011; Sur & Micle 2012).

Acceleration of the metal extraction was achieved by an aeration system to a pressure of 8 bar with the aid of a compressor. During 16 weeks, these soils samples were under bio-leaching treatment. After this time interval had passed, soil samples taken were analyzed for the concentration of metals (Berar (Sur) et al 2011). Figures 11 and 12 shows the results obtained after performed experiment.

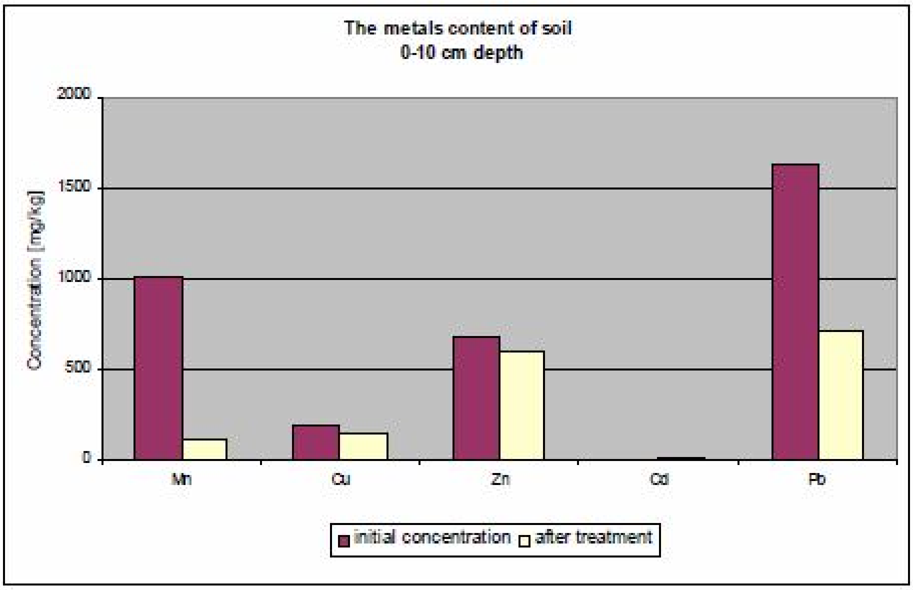

Figure 11. Content of metals - sample A1 (Sur & Micle 2012).

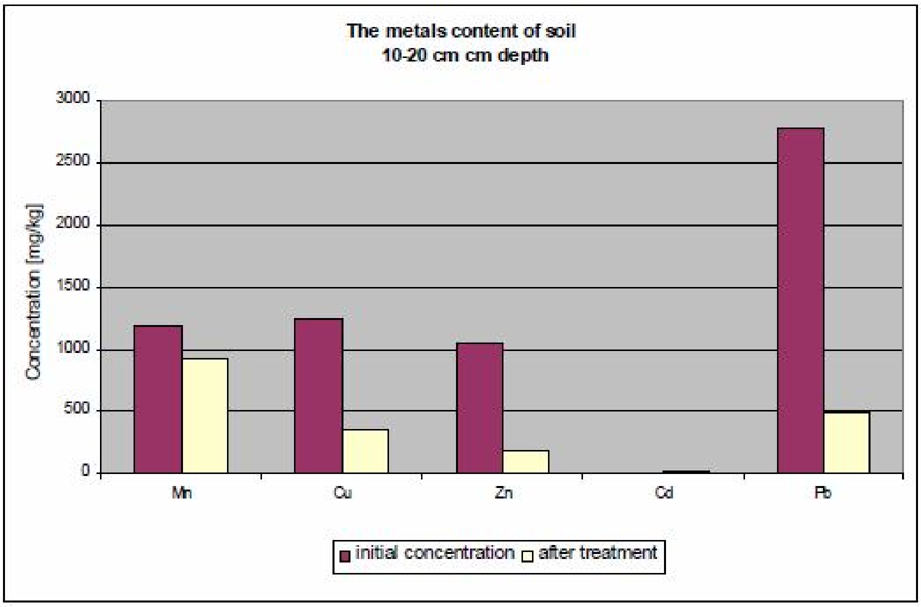

Figure 12. Content of metals - sample A2 (Sur & Micle 2012).

The results obtained highlighted that the bio-leaching of metals depends on the growth of *Thiobaccilus* type bacteria, the extraction efficiencies are obtained, as follows: Mn 89 %, Pb 56 – 82 %, Zn 82 % and Cu 72 % (Sur & Micle 2012).

Conclusions. Application of green technologies on polluted soils with heavy metals can lead to remedy them and also it is possible to intervene on the mechanisms and processes that occur in the relationship between plants and microorganisms, for the improve soil remediation process. This is possible only through a scientific research.

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Authors:
Adriana-Mihaela Chirilă Băbău, Technical University of Cluj Napoca, 103–105 Muncii Avenue, 400641, Cluj Napoca, Romania, e-mail: adriana.babau@yahoo.com
Ioana-Monica Sur, Technical University of Cluj Napoca, 103–105 Muncii Avenue, 400641, Cluj Napoca, Romania, e-mail: ioanamonica_berar@yahoo.com
Valer Micle, Technical University of Cluj Napoca, 103–105 Muncii Avenue, 400641, Cluj Napoca, Romania, e-mail: valer.micle@sim.utcluj.ro

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