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PHYSICAL-CHEMICAL PROPERTIES ANALYSIS OF THE SOIL CONTAMINATED WITH HEAVY METALS FROM COPSA MICA AREA

Ioana Monica SUR[1], Alexandra CIMPEAN[1], Valer MICLE[1], Claudiu TANASELIA[2]

[1]Technical University of Cluj–Napoca, 103–105 Muncii Blvd., 400641, Cluj–Napoca, Romania
[2]INCDO-INOE 2000 ICIA, Cluj–Napoca, 67 Donath St., Cluj–Napoca, Romania

Corresponding author email: ioanamonica_berar@yahoo.com

Abstract

The non-ferrous metallurgical activities led to the pollution of large areas of soil and affected the environment in a negative way. The problems generated by soil contamination with different pollutant substances have been, in the latest period in the center of attention for researchers from all around the world. The objective of this paper is to perform experimental researches in order to establish the physical-chemical properties of the soil from Copsa Mica area. The texture, structure, humidity and pH are the main analysis performed in order to proper establish the optimal soil cleaning technologies. In order to establish the actual pollution degree in the moment of soil sampling, was determined also the concentration of metals in the soil. For this purpose, were taken soil samples from two areas on three depth interval (0–40 cm). Determining the concentration of heavy metals on three depth levels offers the researcher a relevant view of the historical pollution of the area under study. As a result of these researches was established that the soil is polluted with Pb, Zn and Cd. The quantity on metals in the soil is way beyond the alert threshold. As a conclusion these soil need cleaning, which can be made through various methods, one of the being bioleaching, which is a biological cleaning method which implies using microorganisms in order to favor leaching and heavy metals extraction from the polluted soils.

Key words: *Copsa Mica, heavy metals, polluted soil, physical-chemical properties*

INTRODUCTION

Environment pollution is considered to be the most dangerous and constant global threat. The pollutant agents from the environment have a significant impact on the ecosystems and induce an unbalance between the environment, human component and non-human. This unbalance leads to negative effects on all life forms (Morarescu, 2014).

In Romania, intensified industrial metallurgical activity in the last 150 years has led to pollution, with aggressive and very powerful effects on the soil, especially due to the presence of heavy metals in the soil but also in the sub terrain water system, the most frequent metals being copper, lead, zinc and cadmium. The most contaminated areas in the country are Baia Mare, Copsa Mica and Zlatna (Botnariuc and Vadineanu, 1982).

The concentrations of metals from this area were studied in order to evaluate the pollution degree. The findings from 2010 highlighted high concentrations of metals near the deposits: Zn: 416 mg/kg; Pb: 284 mg/kg; Cd: 0.9 mg/kg; (Sucuturdean and Micle, 2011).

In 2012 was made a study regarding the concentration of metals from the soil surrounding the company (300 m) from different depths: Cu: 466-123.8 mg/kg; Cd: 15.8-31.4 mg/kg; Zn: 447-543 mg/kg; Pb: 148-739 mg/kg (Maria Szanto Prodan et. al., 2012).

Bioleaching, or bacterial leaching, consists in the extraction by solubilization of the metallic elements from contaminated soil using bacteria. This method does not destroy (eliminate) the pollutants, but it favors their segregation from the contaminated environment, due to the fact that the microorganisms have the property to oxidize, transforming the pollutants into sulfates with a more soluble form or ferric compounds (*Gadd, 2004; Liu* et. al., 2008 *).*

Microorganisms or bacteria used in bioleaching process oxidize directly or indirectly inorganic compounds (Jayesh et. al., 2007).

In direct process, bacteria can directly oxidize sulphur ion in sulphate from metal sulphide (Chen et. al., 2004; Liu et. al., 2008; Jayesh et. al., 2007).

Using the indirect process, oxidation of metal sulphides is generated in microbial way by ferric ions (Jayesh et. al., 2007).

General indirect leaching process is an important reaction achieved through Acidothiobacillus ferrooxidans bacteria, and involves the ferricferrous cycle (Jayesh et. al., 2007):

$4FeSO_4+O_2+2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3+2H_2O$ (1)

Groudev et al. (2001) have highlighted that the microbial activity is the most important factor in the bioleaching of metals like Cu, Zn, Cd, Pb and As. In less than 18 months, the residue concentration of metals in soil (except lead) dropped under the allowable level for the respective analyzed soil type (Groudev et al., 2001).

The experiments carried of Berar led to the conclusion: bioleaching method, uses microorganisms to increase the solubility of metals extraction from the polluted soils (Fe: 100%; Cr: 11-25%; Cu: 40-100%; Zn: 55-94%; Cd: 17-60% şi Mn: 32-66%. (Berar et. al., 2012).

The results indicated that the bioleaching of metals is achieved by the growth of *Thiobacillus* bacteria type. After 16 weeks of treatment of bioleaching+aeration, heavy metals were extracted from soil metals, as follows: Cu: 34-70%; Zn: 36-76%; Cd: 17-38%; Pb: 44-78% (Sur et. al., 2016).

The scope of this paper is to analyse the physical-chemical properties of the soil in order to investigate the optimum cleaning method of the soil polluted with heavy metals.

MATERIALS AND METHODS

From Copsa Mica area were taken soil samples (figure 1) from different depths according with table 1. Soil sampling was done accordingly with the methodological norms from STAS 7184/1-84 and analyzed according with SR ISO 10381-6: 1997, SR ISO 11464:1998 (STAS 7184/1-84; SR ISO 10381; SR ISO 11464 standards).

Point 2 Point 1

Figure 1. Soil sampling points

Table 1. Labeling of soil samples

Sampling point	Depth	Code
Point1	0 – 5 cm	P1
	5 – 20 cm	P1'
	20 – 40 cm	P1"
Point 2	0 – 5 cm	P2
	5 – 20 cm	P2'
	20 – 40 cm	P2"

Soil samples were analyzed from physical-chemical point of view in order to establish the main characteristics which influence the decision to apply the most adequate cleaning method to the studied area. The analyzed characteristics are: humidity; pH; structure; texture and concentration of heavy metals.

The analysis of the samples was made in the Department Environmental Engineering and

Sustainable Development Entrepreneurship of the Faculty of Material and Environment Engineering, Technical University of Cluj-Napoca.

Humidity determination was made using gravimetric method accordingly with the methodological norms from STAS 7184/9-79 and processed accordingly with SR ISO 11465 norms (STAS 7184/9-79; SR ISO 11465).

pH determination was done accordingly with the methodological norms from STAS 7184/13-88 and processed accordingly with SR ISO 10390 norms.

Soil structure determination was made using Sekera method. The method consists in dispersing in water soil aggregates and comparing the results with the models presented in an auxiliary board (Micle and Berar (Sur), 2012).

Texture determination was expressed through the ratio of mass content of the main components using RETSCH AS 200 bolter equipment which has 11 bolters with the diameter of: 0.8;0.6; 0.44; 0.32; 0.20; 0.16; 0.15; 0.071; 0.63; 0.056; 0.040 mm.

In order to determine the texture of the soil, 500 g of soil/sample were weighted. Based on the soil mass remained on each bolter were determined the structural mass fractions found in the studied soil (Micle and Berar (Sur), 2012).

Determining the heavy metals concentration was analyzed in the laboratories of the Research Institute for Analytical Instruments, ICIA – Cluj-Napoca, by extracting from the soil the microelements soluble in aqua regia. The method used was inductively coupled plasma mass spectrometry (ICP-MS) with Elan DRC II spectrometer

RESULTS AND DISCUSSIONS

Soil humidity

Analyzing figure 2, it can be observed that the humidity of the samples from sampling point 2 is much bigger that the humidity of sampling point 1.

Soil pH

In figure 3 it can be observed the pH variation after its determination from each soil sample. It can be pointed out that from the results of the analyses the soil reaction is moderate alkaline no matter the place or depth of sampling.

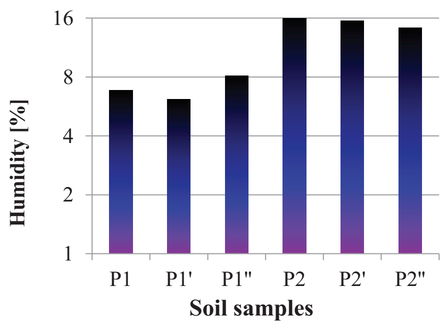

Figure 2. Soil humidity

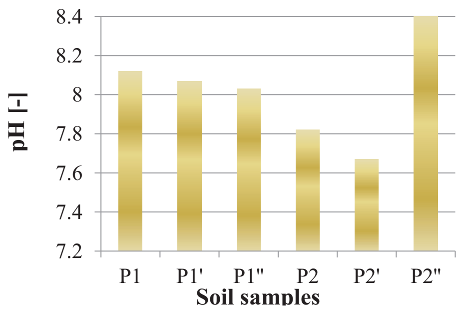

Figure 3. Soil pH

Soil structure

In the case of point 1, no matter the soil sampling depth, the soil is partially structured (Figure 4 a), the aggregates came apart in equal matter both in big parts and small parts. In the case of the second soil sampling point, the sample from 0-5 cm depth is weak structured because most of the aggregates came apart in small parts and in fewer big parts (Figure 4 b). The same weak structured soil is also in the case of samples taken from 5-20 cm depth and 20-40 cm from sampling point 2 (Figure 4 c, d).

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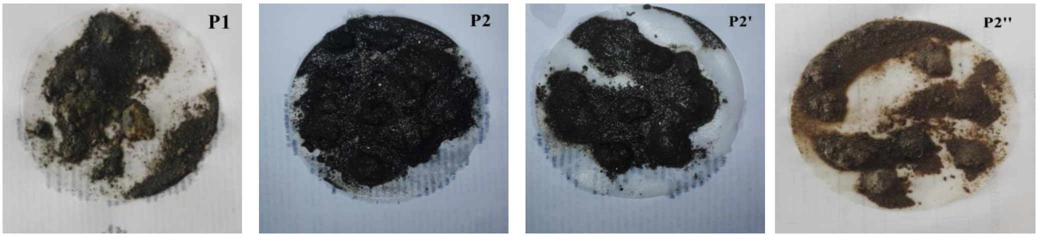

a) b) c) d)

Figura 4. Soil structure: a) sample P1; b) sample P2; c) sample P2'; d) sample P2"

Soil texture

Analyzing figure 5 in which is presented the soil texture from the 2 sampling points, it can be concluded that both samples have a coarse texture.

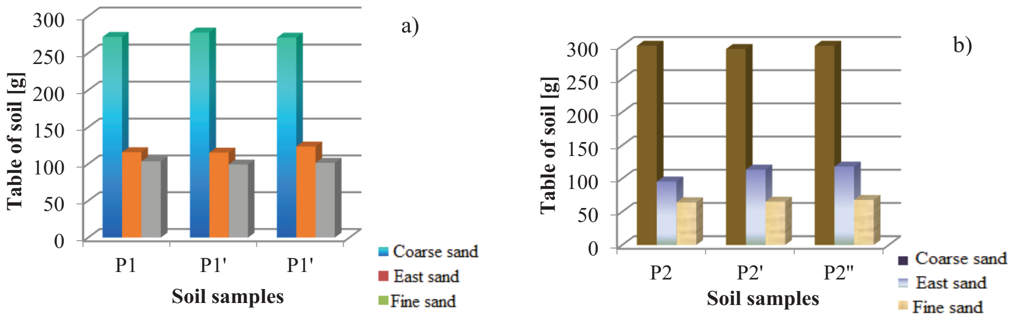

Figure 5. Texture fractions of the analyzed soil: a) Point 1; b) Point 2

Heavy metals concentration

The concentration of heavy metals determined at the assays from Copsa Mica area were compared with the average value of the normal contents with the maximum allowable values and with the values of the warning threshold and intervention one, for soil less sensible according to Order 756/1997.

Lead is the metallic element with the fastest deposition and with the highest excess level of the maximum allowable concentration in almost every environment component (Ludusan, 2007).

The accumulation of lead in soil has toxic effects, producing the inhibition of the enzymatic processes, reducing the elimination intensity of the carbon dioxide and reducing the number of microorganisms, all this with heavy consequences concerning the absorption of the nutrient elements by plants (Ludusan, 2007). In addition, it induces derangements in the metabolism of the microorganisms, affecting especially, the breathing and cell multiplication processes (Ludusan, 2007).

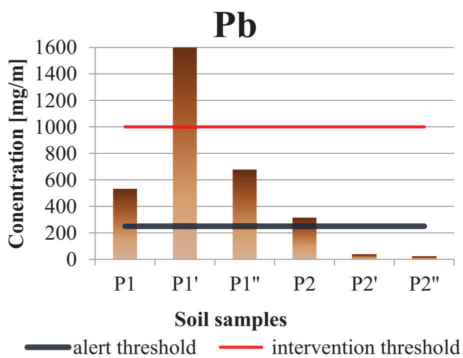

Figure 6. Pb concentration in sampling points

In the case of lead, the indicated values in sampling point 1 are above the alert threshold and intervention threshold. Exceeding the alert

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threshold (250 mg/kg) for Pb was 6.5 times at sample P1'. In sampling point 2, pollution is present only at the surface sample (P2), slightly exceeding the alert threshold (Figure 6).

High concentration of Zinc in soil, forming small solid particles, is due to metallurgical industry. It appears in soil, generally in concentration between 30-50 ppm (Ludusan, 2007). Zinc excess can provoke most frequently modification of the physical and physical-chemical properties, thus reducing the biological activity in the soil (Ludusan, 2007).

In plants, zinc is toxic at concentrations higher that 400 ppm (dry substance), being accumulated in high proportion in the green organs of the plants and has a low toxicity for animals (Ludusan, 2007). Concerning humans, the allowable limit in food is 50 ppm (Ludusan, 2007). The toxic effects of zinc produce derange in the enzymatic activity of microorganisms from the soil and damage to the vegetative cells that come in contact with it (Ludusan, 2007).

Cadmium is more stable in soil than in air and water (Ludusan, 2007). Cadmium attachment, absorption and distribution in soil depend on: pH, soluble organic matter content, metal oxide content, clay type and content (Ludusan, 2007).

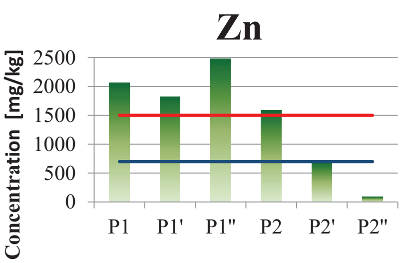

Figure 7. Zn concentration in sampling points

Regarding Zn and Cd, it can be seen that their concentration value is exceeding both the alert and intervention thresholds in both sampling points and on all sampling depths.

Zinc concentration (Figure 7) is presenting high values on five of the investigated samples, exceeding the alert threshold (700 mg/kg), with only one exception, soil sample P2'' from sampling depth 20-40 cm, its concentration being slightly under the normal value of 100 mg/kg. In the soil samples taken from the studied area, the Cd concentration has high values on all sampling depths, exceeding the alert threshold (5 mg/kg), with the exception of sample P2" from sampling depth 20-40 cm, which has the value below the normal (1 mg/kg).

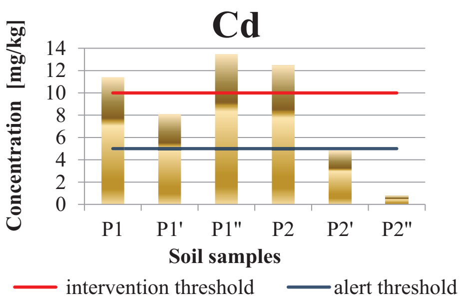

Figure 8. Cd concentration in sampling points

The Zn and Cd concentration decreases with depth in the case of sample P2, while sample P1 has a variation of the concentration function the depth. One proposed method for cleaning the soil contaminated with heavy metals from Copsa Mica area is bioleaching. This consists in extraction of the heavy metals by leaching using bacteria (Micle, 2009). The most used bacteria for bioleaching are: *Thiobacillus ferrooxidans, Thiobacillus thiooxidans, Ferroobacillus ferrooxidans*. This method has numerous advantages like: being innovative, easy to implement, financially convenient and applicable on large areas.

CONCLUSIONS

Heavy metals pollution from Copsa Mica is admitted to be a significant problem, representing a major risk for the health of the population and for the environment. As a result of the long term activity of the company, all environment factors have suffered emissions.

In order to point out the concentration of heavy metals from the studied area, soil samples were taken and subjected to different analyses in order to establish the quantity of heavy metals and also some physical characteristics of the soil like: texture, structure, soil humidity and its pH. Most of the samples point out that the soil from the investigated area is weakly structured, having a coarse texture and with high values of pH (>7). The Pb concentration in sampling point 1 exceeds the alert threshold and intervention threshold, and in sampling point 2, the pollution is present only at surface sample. The Zn and Cd concentration exceeds the alert and intervention threshold in both points in all three sampling depths. Zn and Cd concentration is decreasing with depth for sample P2, while sample P1 has a variation of the concentration function the depth.

A proposed method for cleaning the soil from Copsa Mica area contaminated with heavy metals is bioleaching. This consists in extraction of the metals from the polluted soil by leaching, using bacteria (Micle, 2009). The most used bacteria for bioleaching are: *Thiobacillus ferrooxidans, Thiobacillus thiooxidans, Ferroobacillus ferrooxidans*.

This method has numerous advantages like: being innovative, easy to implement, financially convenient and applicable on large areas.

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