Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. X, 2021
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

ECOLOGICAL RESTORATION OF THE POLLUTED SOILS WITH HEAVY METALS. CASE STUDY: CUPROM SA BAIA MARE BRANCH

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Abstract

The paper aimed to present a possible solution for ecological restoration of the soils polluted with heavy metals from the premise of Cuprom SA Bucharest, Baia Mare branch. This premise is famous for a prolonged industrial activity in smelting and refining metallic ores, especially copper, lead and precious metals as gold and silver. The impact over the environment during the production phase was well documented, but after the plant ceased the activity in 2009, the land remained as heavily polluted industrial area in the way of the urban development. The paper presents a possible solution to restore these soils polluted with heavy metals from the premise using an innovative method of soil washing under specific conditions to remove the mobile fraction of the pollutants from the matrices of the soil. The solution presented is minimum invasive, with promising results in the laboratory phase, applicable on site and cost effective.

Key words: *ecological restoration, heavy metals, Cuprom SA.*

INTRODUCTION

The impact of the human activity over the environment is a subject of actuality, largely debated and with influence over all the aspects of the human society. Even if we refer to climate change, deforestation, uncontrolled development or industrialization, environment protection is and provocative and debatable subject of our daily actuality.

Romania has a history, like most of the countries from the former communist bloc, regarding industrial sites largely and uncontrollable developed in the mid XX^th^ century, disregarding any environmental laws and principles, and abandoned from various reasons after 1990.

In Romania has resulted from the former industrial activity a number of 1682 contaminated sites from which 395 represent potentially contaminated sites, whose level of contamination was not determined yet, and the rest of 1287 proved and documented contaminated sites. (National Strategy and National Plan of Action for Management of the Contaminated Sites from Romania, 2015).

In Maramures region the industrial sites were related to mining activity and mineral processing due to the fact that this region is rich in mineral ores.

The activity left behind a series of industrial sites, landfills and mining sites polluted with heavy metals, actually abandoned. These sites still affect the quality of the environmental factors even after 25 years after the activity cease.

The problem with the industrially contaminated sites from the region is that the pollutants identified here are not biodegradable, can be mobilized by the variations in the environmental factors, can accumulate in time.

Cuprom SA Bucharest, Baia Mare branch was an industrial processing plant placed in the industrial zone in the eastern side of Baia Mare which was specialized in producing copper, lead and rare metal (gold and silver) production. The activity was placed on a 58 ha surface and after its closure in 2009 the plan was abandoned, partially demolished and fragmented.

Various remedial approaches were proposed during the years for decontaminating the site and reintroducing the placement in the industrial zone. Many of them were impossible to apply due to the level of contamination and many were more expensive than the value of the land itself which leaded to uninterested from the possible investors.

Worldwide a large number of studies were conducted to reduce the risk of potentially toxic elements to human health and the ecosystem (Hasegawa et al., 2019).

These remediation technologies are categorized into three broad groups: physical, chemical, and biological, and have been analyzed and described in several reviews (Shahid et al., 2012; Saifullah et al., 2015; Begum et al., 2016; Rahman et al., 2016; Khalid et al., 2017).

The Cuprom site was analyzed in the possibility of remedial solutions, described in various articles (Boros et al., 2015; Damian et al., 2008; Coman et al., 2010)

A most recent trend in remedial solution for heavy metal polluted industrial soils represents the soil washing method using chelators. The method offered good results in laboratory analysis in specific regions, as reviewed by Hasegawa et al., 2019, for reducing lead, copper and zinc concentrations.

In this study a soil washing method was applied on the soils from Cuprom SA Baia Mare Branch to determine the capability of this method to stabilize and reduce the heavy metal load in a less expensive and non-invasive way.

MATERIALS AND METHODS

Considering the large surface of the industrial site and the legal situation and also the uneven distribution of the pollutants in the land, we decided to survey a well delimited surface of 5000 sqm from the site. The choice of the survey area was delimited so it contains the documented pollution hot-spots based on bibliographic study.

The areal includes objectives as: Oxygen factory, Smelting, Electrolysis and the Copper factory. Geographically the area of research is delimited in the square formed by the coordinates (Table 1, Figure 1).

Table 1. Research area delimitation
(coordinates in Stereo 70)

Point	Coord. X	Coord. Y
1	394972.3386	684931.0393
2	395445.3700	685046.7763
3	395480.3657	684897.5287
4	395007.5597	684790.4465

Figure 1. Research area (image source: Google Earth)

Soil samples were collected from 12 points from the research area to characterize the initial load in heavy metals. The soil samples were collected in correspondence with the national law Ord. 184/1997, Appendix A3, from 5 and 30 cm depth. The samples were marked and stored in plastic sealed bags until they arrival in the laboratory. The sample place was identified in geographical coordinated using a GPS in order to identify on the map.

The soil samples were dried to a constant weight in an oven at 65°C, and reduced to a size of 2 mm by separating foreign objects and materials and shredding.

The collected samples were divided quantitatively into two sub-samples, one to analyze the initial load of the site and one for experimenting soil washing technology using chelators.

The metal concentration from the soil samples was determined using atomic absorption spectrometry with Perkin Palmer PinAAcle 900T spectrometer according to the methodology provided by SR ISO 11466:99 and SR ISO 11047:1999.

The researched metal composition was reduced to lead, copper and zinc identified as the main pollutants according to previous documenttations (Damian et al., 2008).

The concentrations of lead copper and zinc in the sampled area at 5 cm depth are presented in the Table 2 and at 30 cm depth in Table 3 comparatively with limit values from the national law Order 756/1997.

For a visual characterization of the distribution of the pollutants in the surveyed area a spatial distribution was performed using software Surfer 16.

The values of concentration were integrated in the software according to sample location and interpolated using Kriging method. The spatial distribution was overlay on the orthophoto plan.

The second batch sample were submitted to a soil washing technology using chelators in a variation of pH conditions.

The performance of chelators in washing processes has been widely assessed, and they have been found to efficiently remove potentially toxic elements and to have less severe effect on the environment (Peters, 1999; Tandy et al., 2004; Begum et al., 2012, Hasegawa et al., 2019). Chelators also have high complex formation constants under weakly acidic to alkaline conditions, and to not require the use of heating or strong acids during extraction. Chelators are thus considered to be suitable extractants for a wide variety of potentially toxic elements and are expected to reduce the cost and the environmental burden of the metal extraction process (Hasegawa et al., 2011; Pinto et al., 2014; Begum et al., 2016, Hasegawa et al., 2019).

In our study we used EDTA (2,2’,2”,2”’ - (ethane-1,2-diyldinitrilo) tetra-acetic acid) in concentration of 0.1 mol/l and 0.01 mol/l.

Seven samples were created from the collected soil, using quarter method and were treated as follows:

Sample 1 - pH correction to neutral and periodic mixing with EDTA solution 0.1 mol/l in a ratio of 5 g soil/1 g EDTA solution;

Sample 2 - pH correction to 3 and periodic mixing with EDTA solution 0.1 mol/l in a ratio of 5 g soil/1 g EDTA solution;

Sample 3 - natural pH and periodic mixing with EDTA solution 0.1 mol/l in a ratio of 5 g soil/ 1 g EDTA solution;

Sample 4 - pH correction to neutral and periodic mixing with EDTA solution 0.01 mol/l in a ratio of 5 g soil/1 g EDTA solution;

Sample 5 - pH correction to 3 and periodic mixing with EDTA solution 0.01 mol/l in a ratio of 5 g soil/1 g EDTA solution;

Sample 6 - natural pH and periodic mixing with EDTA solution 0.01 mol/l in a ratio of 5 g soil/1 g EDTA solution;

Sample 7 - blank sample.

Analytical grade solutions were used during the study without further purification.

The EDTA solutions were created using distilled water produced by a Fistreem Cyclone water distillate. The samples were weight using a Kern laboratory scale with the precision of 0.0001 g. The solutions were prepared using an Unimax 1010 orbital agitator. The pH of the samples was determined using a Hanna HI 99121 pH-meter. For pH correction to neutral a solution of Na (OH) 1 mol/l was used and respective H_2SO_4 1% solution to correct the pH to 3.

Mixing of the samples with the EDTA solutions were performed weekly for a period of 3 moths (91 days). The samples were placed inside vessels from plastic inert materials, perforated at the bottom and with collectors for the washing solution. The chelator was dosed by spraying over the sample in a time span of 5 minutes for letting the chelator to react and absorb in the material.

This method of applying was used to simulate an onsite application without removing the soil. After the experimentation period the samples were analyzed regarding the concentration of heavy metal by atomic absorption spectrometry.

RESULTS AND DISCUSSIONS

The initial contamination of the surveyed area reflected the prepositions of the bibliographical study revealing concentrations 570x higher than normal values for copper, 354x higher than normal values for lead and 292x higher than normal values for zinc. The values reflect a high-level contamination and an uneven distribution of the contamination in the surveyed area, as presented in the tables and figures below.

Table 2. Level of contamination at 5 cm depth

Contamination at 5 cm (mg/kg soil)			
Sample point	*Cu*	*Pb*	*Zn*
Electrolysis	3400	1640	1433
Eastern extremity of Electrolysys	7033	3577	2790
Product Storage	3180	1520	1507
Smelting	2913	1537	2107
Oxygen factory	5776	4243	29166
Normal values (Ord. 756/1997)	*20*	*20*	*100*
Attention level for less sensitive use	*250*	*250*	*700*
Intervention level for less sensitive use	*500*	*1000*	*1500*

A series of hot-spots are identified regarding the spatial distribution of the pollutants, in the extremity of the Electrolysis we observe an accumulation of copper and lead at 5 and 30 cm depth and a surface accumulation of zinc in the area of the Oxygen factory.

Table 3. Level of contamination at 30 cm depth

Contamination at 30 cm (mg/kg soil)			
Sample point	*Cu*	*Pb*	*Zn*
Electrolysis	2972	1413	1445
Eastern extremity of Electrolysys	11399	7076	7033
Product Storage	3667	1807	1870
Smelting	3533	2127	2297
Oxygen factory	2666	2263	2610
Normal values (Ord. 756/1997)	*20*	*20*	*100*
Attention level for less sensitive use	*250*	*250*	*700*
Intervention level for less sensitive use	*500*	*1000*	*1500*

In all of the samples the concentration is above the normal values indicated by the national legislation and in some cases the values are 20 times higher than the intervention level of contamination for less sensitive use.

Observing the depth of the contamination we decided to sample deeper, at 2 m depth to identify the level of expansion of the heavy metal contamination in the soil. A sample was taken from the depth of 2 m in the middle of the survey area revealing a concentration 2150 mg Cu/kg soil, 1547 mg Pb/kg soil and 753 mg Zn/kg soil, values high above normal concentration according to national standards.

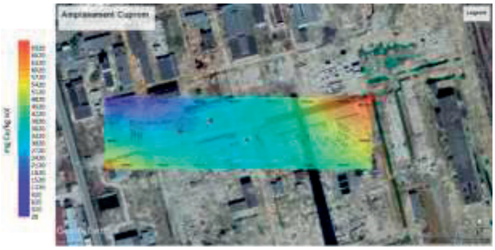

Figure 2. Copper dispersion at 5 cm depth

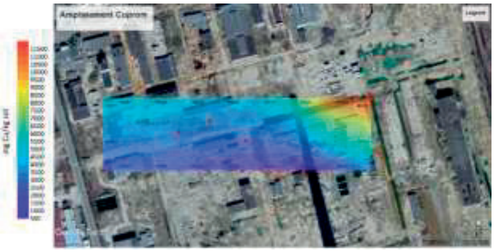

Figure 3. Copper dispersion at 30 cm depth

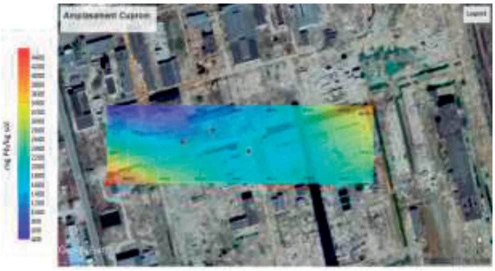

Figure 4. Lead dispersion at 5 cm depth

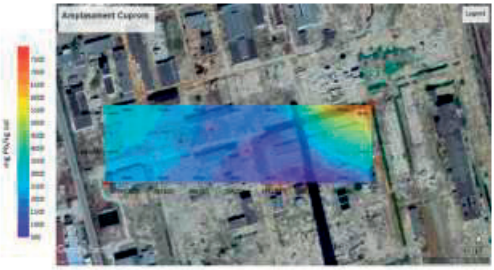

Figure 5. Lead dispersion at 30 cm depth

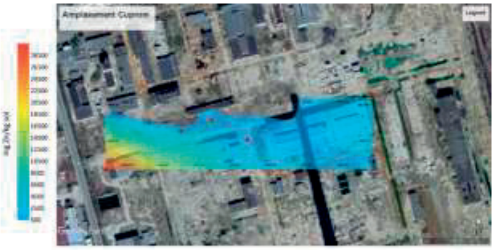

Figure 6. Zinc dispersion at 5 cm depth

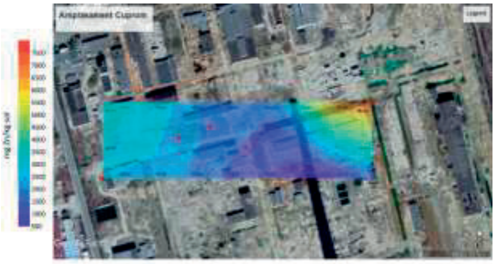

Figure 7. Zinc dispersion at 30 cm depth

The values identified at 30 cm and completed with the 2 m depth sample values proves the migration of pollutants in depth during the almost 100 years of industrial activity o site due to natural leaching or repeated in depth interventions on the site which determined a mixing of the structural composition of the soil.

The soil washing method applied had the goal to reduce the concentration of contaminants under the limit of intervention which will allow to use the site for further industrial development. The results, after applying the method for 3 months, are presented in the Table 4.

Table 4. Contamination after soil washing

	Variation	Cu (mg/kg soil)	Pb (mg/kg soil)	Zn (mg/kg soil)
Sample 1	pH 7, EDTA 0.1 mol/l 5:1	2080	1320	1920
Sample 2	pH 3, EDTA 0.1 mol/l 5:1	2920	1646	1723
Sample 3	pH natural, EDTA 0.1 mol/l 5:1	2290	1376	2056
Sample 4	pH 7, EDTA 0.01 mol/l 5:1	2820	2423	1727
Sample 5	pH 3, EDTA 0.01 mol/l 5:1	2626	2460	1800
Sample 6	pH natural, EDTA 0.01 mol/l 5:1	2743	1706	2256
Sample 7	blank	3256	2680	2306

For comparation a blank sample was made to reflect the initial level of contamination of the sample. All the seven samples were formed from the same type of material, contaminated soil from the site, and equal regarding the quantity and physical characteristics.

The natural pH of the samples, determined at the beginning of the procedure was 8.46. The alkalinity of the sample is due to the fact that the soil is a mixture of imported materials during the functioning of the plant. The pH value varies in the sampled region from 2.5 - strong acidic to 9.2 - alkaline. By mixing the samples to obtain the blank the pH stabilized at the pH of 8.46.

The variation of pH in the determination of chelator efficiency from 3 to the natural pH of 8.46 is due to the variation of the pH of the soil in the sampled region. It is observable from the table above, the most significant results for copper and lead reduction are met at neutral pH with the higher concentration of chelator dosed in the sample.

Regarding the zinc reduction the most satisfying result is in acidic conditions with high concentration of chelator, but almost the same result is obtained at neutral pH with low concentration of the chelator.

The results prove that EDTA chelators work for reducing the concentration of heavy metals in the polluted soils from Cuprom SA Baia Mare and the best results are in neutral pH conditions.

A further research is in progress to determine if a prolonged administration of the chelator can reduce the concentration below the intervention level and an installation is during development for administrating the solution in site and recover the leachate for reusing in the process.

As observed by other researchers (Polettini et al., 2007; Zou et al., 2009; Qi et al., 2011; Hasegawa et al., 2019) the chelator assisted soil decontamination process is highly influenced by the pH value. The solution pH influences several factors e.g., the aqueous species concentration of the potentially toxic elements, the solubilization of the chelators, the sorption and desorption of the pollutants, the ionic exchange and the re-adsorption mechanism of the metal-chelator complexes, among others (Hasegawa et al., 2019). The same influence is clearly observed in the polluted soils from Cuprom SA Baia Mare which determined a variation in the pollutant concentration reduction.

CONCLUSIONS

Chelator assisted decontamination is an experimental method of reducing heavy metal pollutants from the industrially contaminated sites. It is a method which has to be proved for each type of soil due to the fact that it can be very easily influenced by the composition of the soil, the natural conditions, in special the natural pH of the material on which it will be applied.

This technology of decontamination showed significant results for the soils contaminated with heavy metals from the premise of Cuprom SA Baia Mare, by reducing the concentration of copper with 36%, the concentration of lead with 50% and the concentration of zinc with 25%.

The level of contamination of the site is very high and various and the goal is to reduce the amount of pollution in the limits in which the site can be used as industrial site for further development. In this direction a further research is necessary to determine the limits of the technology and a direct application in the field regarding also the recovery of the chelators and the possibility of recovery also of the metals extracted.

The advantage of the technology is that it is a reduced invasive method and uses available and cheap materials as the chelators. The technology does not involve massive excavations and displacement of the soil. The most important advantage of the technology is that it can be adapted on the level of contamination of the soil.

Heavy metal polluted industrial sites are a national ecological issue in Romania. These sites, even if the activity is ceased, continue to create severe ecological disasters especially in the mining regions. Heavy metal polluted soils, water and the mobilization of dust containing heavy metals from these sites affect the quality of life and the health of population located in the nearby of these premises.

The urban development from the recent years determined the expansion of the cities incorporating the former industrial sites which continue to create a significant impact over the economy and environment.

ACKNOWLEDGEMENTS

This research work was carried out in the documentation phase of the PhD thesis "Research regarding recovery by ecological restoration of the sites polluted with heavy metals from Baia Mare Urban system" with the support of University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca.

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