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Contribution to Heavy Metals Extraction from Contaminated Soil Using Acid and Chelating Agents

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Abstract

The contamination of soils with heavy metals is a very important environment issue, given the rapid development of agriculture and industry. Heavy metals are harmful to humans, animals and tend to bioaccumulation in the food chain.

The paper presents the results obtained in heavy metals (lead, copper and zinc) leaching from contaminated soil due to the industrial activity, using nitric acid (HNO3) and as chelating agents ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). These reactants are capable to extract heavy metals contaminants from soil into the solution, for soil decontamination.

Laboratory tests were performed using a contaminated soil sample collected from the contaminated site, an old industrial area in Romania. The physical and chemical characteristics of soil sample were determinate in agreement with national standards.

The results from this study suggested that the strong acid and the chelating agents were both effective in heavy metals extraction, the latter compounds could be more useful in soil washing because they are less harmful to the soil environment.

Key words: *heavy metals, soil decontamination, EDTA, NTA, nitric acid.*

Introduction

Many sites in Romania have been heavily polluted with organic and inorganic contaminants resulting from various activities including mining, electroplating, metal working, battery recycling, chemical processing, use of sewage sludge as fertilizer etc. The hazardous substances contained in soil and water requires remediation to avoid further environment degradation.

Heavy metals are harmful to humans, animals and tend to bioaccumulation in the food chain. They can reduce the growth of plants when they are present in excessive quantities [1], they can affect the activity of microorganisms adversely affecting important biological processes such as nitrogen fixation [2] in soil enzyme activity [3] and microbial biomass production [4]. Copper, zinc and lead significantly increase the C/N ration temporarily [5].

The mechanisms of heavy metals toxicity include binding more strongly to functional sites that are normally occupied by essential metals, blocking the essential functional groups of biologically important molecules such as enzymes, changing the conformation of biological (i.e.

proteins and nucleic acids), disrupting the integrity of entire cells and/or their membrane, making them inactive, decomposing essential metabolites and changing the osmotic balance around the cells [6].

The order of toxicity for plants generally seems to be Cu>Zn>Pb [7]. The toxicity of heavy metals is very well known and is strongly dependent on the bioavailability – the degree to which a contaminant is available for uptake by an organism.

Metal bioavailability in soil is influenced by several factors: pH, soil type, redox potential, organic matter content, metal species etc, pH being particularly important because it controls the metal behavior and other processes in soil. Lead is the least mobile heavy metal in soil, being immobilized by organic matter or oxides (e.g. Al2O3): the bioavailable fraction is usually low even in cases where total soil lead content is high [8].

To combat such threats to human health some technologies have been developed for treating of soils contaminated with heavy metals. Soil washing is one of such technologies for the removal of heavy metals from contaminated soil.

Two categories of extracting agents include acids and chelating agents which are capable of desorbing heavy metals contaminants from soil into the solution [9]. Acid extraction acts using ion – exchange and soil matrix dissolution for metals solubilization; although acids increase efficiently metal solubility they may destroy soil structure, leaving it unsuitable for recultivation [10]. Chelating agents contain functional groups capable of complexing heavy metals bound to soil particles. A good solubilization of metal occurs when the metal has a greater affinity for chelating agent than for soil attachment [11].

Typical chelating agents include ethylenediamine tetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), citric acid, [SS] ethylenediamine dissuccinate (SS- EDDS) etc. [12 – 16]. It is important to understand that metal extraction procedures and extracting agents are quite diverse and in most instances result in substantial differences in extraction efficiency [6].

The aim of this study was to assess the effectiveness of nitric acid and of two chelating agents named ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) in extraction of Pb, Cu and Zn from a contaminated soil sample collected from an industrial metallurgical site in Romania.

Materials and Methods

Contaminated soil

Contaminated soil sample was collected from the old Romanian industrial area at a depth of 0…20 cm, air dried for 6 days and sieved to remove non – soil impurities. Previous investigation resulted that the main contaminants in this area are Pb, Cu and Zn [17]. Fraction smaller than 2 mm was analyzed for physical and chemical characteristics determination. These characteristics are presented in tables 1 and 2. In agreement with UNESCO classification, the soil from contaminated area is Chernozem. The pH was measured in the clean liquor above the soil in agreement with Romanian Standard ISO 10390 – 1999 using a pH - metter and the heavy metal content in agreement with Romanian Standard ISO 11047 – 1999, by atomic absorption spectrometry. Humus content of soil was determined in agreement with Romanian Standard 7184/21 – 82, total carbon – Romanian Standard ISO 10694/1998, total nitrogen – Kjeldahl modified method in agreement with Romanian Standard ISO 112617/2000, potassium – Romanian Standard 7184/18 – 80 and phosphorus extract in ammonium acetate lactate, in agreement with Romanian Standard 7184/19 – 82.

Table 1. Some characteristics of contaminated soil

pH	Humus %	C %	N_t %	K ppm	P ppm	CEC* cmol/kg	Pb mg/kg	Cu mg/kg	Zn mg/kg
8.22	2.03	1.21	0.183	184.2	31.5	1.43	573.97	575.41	590.36

**Cation Exchange Capacity*

Table 2. Particle size distribution (%) of the < 2mm soil sample

Clay less than 0.002 mm	Dust 0.02 – 0.002 mm	Sand 2.0 – 0.02
36.25	34.74	29.01

In table 3 are presented the limits of concentration of lead, copper and zinc in soil, predicted by Romanian Environment Law.

Table 3. Limit values for metal concentration in soil predicted by Romanian Environment Law, in mg metal/kg dried soil

Metal	Normal value	Limit of alert*		Limit of intervention**	
		Sensible area***	Less sensible area****	Sensible area***	Less sensible area****
Copper	20	100	250	200	500
Lead	20	50	250	100	1000
Zinc	100	300	700	600	1500

The definition of the marked factors in table 3 have is the following:

Limit of alert* - in these areas authorities has to be informed about the pollution to take supplementary monitoring measures.

Limit of intervention** - the evaluation of risk is obligatory and measures must to be taken to reduce the concentration of pollutants.

Sensible area *** means agricultural areas and domestic farms.

Less sensible area**** means industrial areas.

From the data presented in tables 1 and 3 is obvious that the concentration of lead and copper from polluted soil exceed the limit of intervention for sensible areas and zinc concentration is close enough from this limit. Consequently, urgent measures must be taken by authorities to reduce the concentration of these metals in soil.

Extraction agents

For heavy metal extraction from contaminated soil were used the following compounds: HNO_3 solution (reagent grade), EDTA (99% purity) and NTA (99% purity) crystals, delivered by Merck Company. Solution preparation consisted of dissolving crystals of chelating agents or concentrated acid in distilled water in the appropriate quantities to obtain the diluted solutions.

Extraction tests

10 grams of soil samples weighted using an analytical balance with ± 0.01 g accuracy were mixed with 100 ml of extracting agent (aqueous solutions of HNO_3, EDTA and NTA), in a Erlenmeyer glass of 250 ml, at ratios extracting agent: soil between 1...50 mmol: kg soil and nitric acid aqueous solutions to ensure pH value in solution between 2…7. The contact time was

30 hours to ensure that chemical equilibrium was reached [10]. After solid: liquid separation, in liquid phase the concentration of dissolved metals was measured using an absorption spectrometer instrument Analytic Jena – ZEEnit 700 BU, in agreement with Romanian Standard ISO 11047 – 1999.

The removal (extraction) efficiency (%) was calculated as follows:

$$\% \text{ removal} = \frac{\text{mg metal extracted/kg soil}}{\text{mg metal total/ kg soil}} x100$$

Results and Discussions

In the batch studies was considered the influence of the contaminant nature, pH and concentration of the extracting agent on the metal removal efficiency from contaminated soil having the characteristics presented in tables 1 and 2.

Lead extraction

Figures 1 and 2 present lead extraction from contaminated soil using as extracting agents EDTA – NTA and nitric acid, respectively. Removal efficiencies of lead from contaminated soil were considered when molar ratios of extracting agents EDTA or NTA: soil varied between 1…50 (mmol agent/kg soil) and nitric acid aqueous solution concentrations were selected to ensure the pH domain of 2…7 in solution.

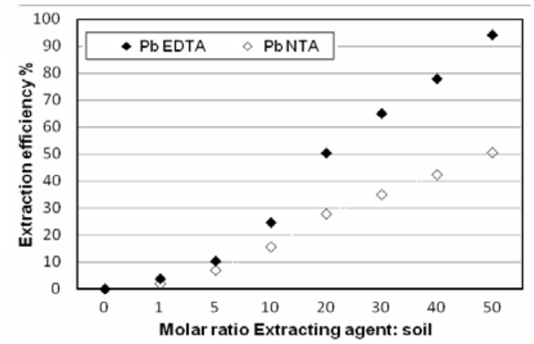

Fig. 1. The influence of molar ratio extracting agent: soil upon removal (extraction) efficiencies of lead from contaminated soil

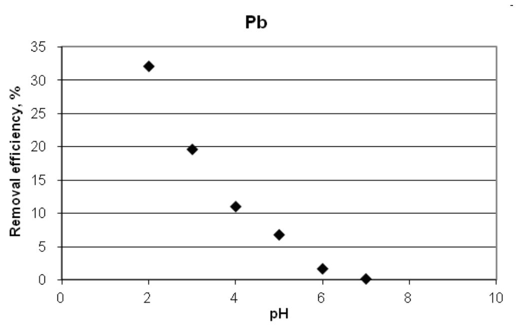

Fig. 2. The influence of pH upon removal (extraction) efficiencies of lead from contaminated soil using HNO_3

The results indicate that all the three extracting agents were effective in lead extraction. The extraction efficiency increase with increasing the ratio extraction agent: soil for both extracting agents used in this work. Concerning the capability of lead extraction of the chelating agents EDTA and NTA, EDTA was more effective than NTA for given molar ratios.

Lead removal efficiency of EDTA ranged from 3.77% at molar ratio EDTA: soil of 1 to 93.99% at molar ratio EDTA: soil of 50.

Lead efficiency of extraction with NTA ranged from 1.85% at molar ratio NTA: soil 1 and 50.5% at molar ratio NTA: soil of 50.

Concerning the extraction of lead in nitric acid solutions, the efficiency ranged between 0.1% at pH 7 and 52.1% at pH 2.

Our results are in agreement with the previous results of Elliot and Brown [18]. They found that, given equal concentration of reagents, EDTA is more effective extracting agent than NTA because the stability constant of the complex $[Pb\text{-}EDTA]^{2-}$ (18.0) is much greater than those of Pb – NTA complex (11,4).

In the case of lead contaminated soil sample, the lead extraction efficiency, in decreasing series could be written: EDTA > NTA > HNO_3.

Copper extraction

Figures 3 and 4 present copper extraction from contaminated soil using as extracting agents EDTA – NTA and nitric acid, respectively. Removal efficiencies of lead from contaminated soil were considered when molar ratios of extracting agents EDTA or NTA: soil varied between 1…50 (mmol. agent/kg soil)and nitric acid aqueous solution concentrations were selected to ensure pH solution in the domain 2…7.

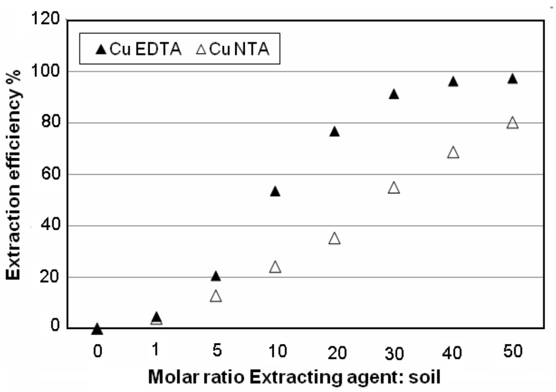

Fig.3. The influence of molar ratio extracting agent: soil upon removal (extraction) efficiencies of copper from contaminated soil

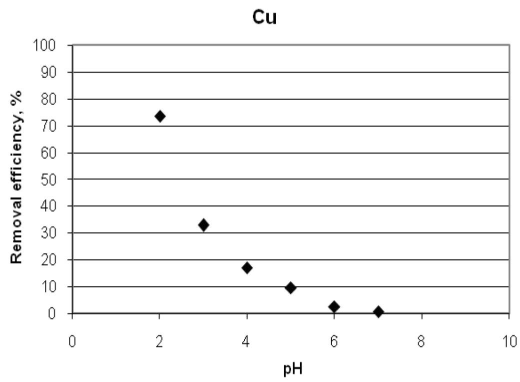

Fig. 4. The influence of pH upon removal (extraction) efficiencies of copper from contaminated soil using HNO_3

The data presented in figures 3 and 4 indicate that all extracting agents were effective in copper extraction from contaminated soil, the extraction efficiency increased with the increasing the ratio extracting agent: soil (figure 3) and with the pH decreasing in solution (figure 4).

Referring to copper extraction from contaminated soil using chelating agents EDTA and NTA is evident from figure 3 that extraction efficiency is higher when used EDTA than NTA.

The extraction efficiency with EDTA ranged between 4.75 % at molar ratio EDTA: soil of 1 and 97.42 at molar ratio EDTA: soil of 50.

Copper extraction with NTA as chelating agent ranged from 3.93% at molar ratio NTA: soil of 1 to 80.2% at molar ratio NTA: soil of 50.

The extraction efficiency of copper with HNO_3 solution ranged between 0.25% at pH 7 and 73.56% at pH 2.0

The decreasing extraction efficiency for copper extraction from contaminated soil could be written: EDTA > NTA > HNO_3, similar with the series for lead.

The results concerning the higher efficiency of EDTA in comparison with NTA are in agreement with the data presented in Encyclopedia [19] about the stability constant of the complex $[Cu\text{-}EDTA]^{2-}$ (20.5), much greater than those of Cu – NTA complex (14.2) and these values are higher than the corresponding values for lead complexes. For this reason the efficiency in lead extraction is smaller than those corresponding to copper extraction.

Zinc extraction

The efficiency of zinc extraction from contaminated soil sample using as extracting agents EDTA - NTA and nitric acid solutions, in various molar ratios extracting agent: contaminated soil, and concentrations are presented in figures 5 and 6, respectively.

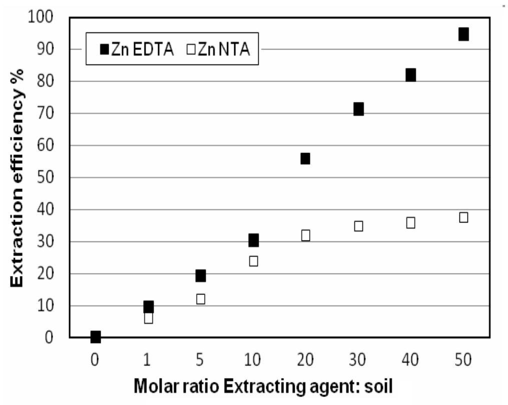

Fig.5. The influence of molar ratio extracting agent: soil upon removal (extraction) efficiencies of zinc from contaminated soil

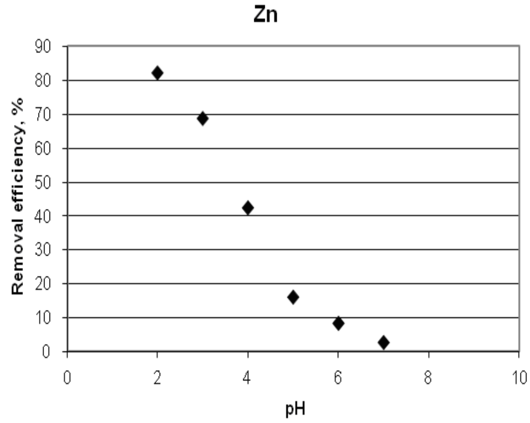

Fig. 6. The influence of pH upon removal (extraction) efficiencies of zinc from contaminated soil using HNO_3

The same remark is valid for zinc extraction from contaminated soil: all extracting agents were effective in zinc extraction. It is evident that the extraction efficiency increases with the increasing molar ratio of extracting agent: soil for EDTA and NTA agents (figure 5). The extraction of zinc is higher with solution pH decreasing (figure 6)

Referring to the use of chelating agents, EDTA was more effective than NTA; zinc efficiency removal with EDTA ranged from 4.62% at molar ratio EDTA: soil of 1 to 94.52 at molar ratio EDTA: soil of 50.

Zinc extraction with NTA as chelating agent ranged from 2.2% at molar ratio NTA: soil of 1 to 47.4% at molar ratio NTA: soil of 50.

These results confirm the higher efficiency of EDTA in comparison with NTA and they are in agreement with the data presented in Encyclopedia [19]; the stability constant of the complex $[Zn\text{-}EDTA]^{2-}$ (18.3) is much higher than that of Zn – NTA complex (12.0) and these values are higher than the corresponding values for lead complexes, but smaller than the corresponding values for copper complexes.

The efficiency extraction of zinc with HNO_3 solutions ranged between 1.65% at pH 7.0 and 82% at pH 2.0

The effect of pH on extraction efficiency of heavy metals from contaminated soil is better illustrated in figures 7,8 and 9. In order to have a common parameter in all extraction solutions when EDTA or NTA were used, pH was measured. Based on these data the graphs from figures 7,8 and 9 were plotted.

In the case of zinc extraction from contaminated soil the decreasing series of extracting agent efficiency is: EDTA > HNO_3>> NTA

Finally, the decreasing removal efficiency series for each extracting agent are:

For EDTA: Cu> Zn> Pb;
For NTA: Cu > Pb > Zn;
For HNO_3: Zn > Cu > Pb.

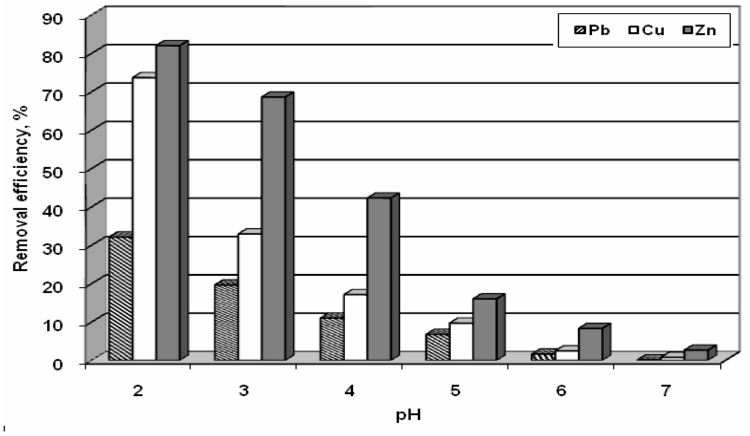

Fig. 7. The extraction of Pb,Cu and Zn using HNO_3 solution as extracting agent

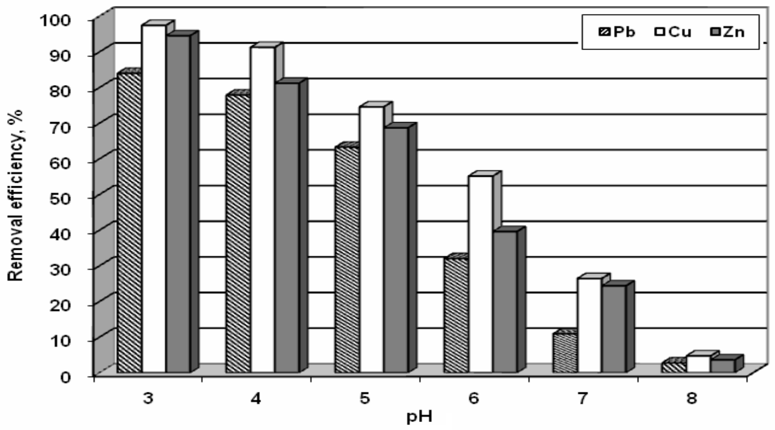

Fig.8. The extraction of Pb,Cu and Zn using EDTA as extracting agent

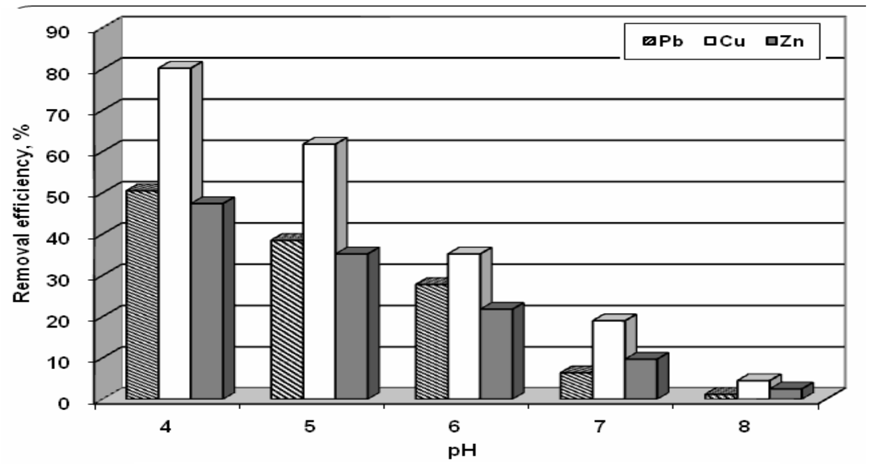

Fig. 9. The extraction of Pb, Cu and Zn using NTA as extracting agent

From figures 7, 8 and 9 is evident that pH influences the efficiency of heavy metals extraction from contaminated soil especially when HNO_3 was used as extracting agent one hand; on the other hand, the high acidity in soil could destroy the soil matrix, making the treated soil unsuitable for recultivation. In the case of chelating agents EDTA and NTA is evident that the chelatization of metals is the mechanism responsible for their solubilization from soil matrix. At equal pH values the extraction efficiency of chelating agents are higher for all metals in comparison with the solubilization efficiency of HNO_3.

Conclusions

Laboratory tests were performed using a contaminated soil sample collected from the contaminated site, an old metallurgical area in Romania. The physical and chemical characteristics of soil sample were determinate in agreement with national standards.

The results of this study indicated that the extraction of heavy metals – lead, copper and zinc - from contaminated soil is strongly dependent of the nature of contaminants, the extracting agent, the concentration of extracting agent and the pH, in the case of the contaminated soil used in these experiments.

Having in view these findings, before initiating a remediation process is obligatory to develop treatability studies, to find the most effective extracting agent and the optimal concentration of the agent for a particular contaminated soil.

The results of this study showed that copper was easier to remove than lead when using chelating agents EDTA and NTA and zinc was easier to remove when using HNO_3 solution. Referring to the chelating agents, our results are in agreement with the data previous found concerning the dependence between the extraction efficiency and the stability constants of soluble complexes formed between chelating agent and metals.

The chelating agents could be more suitable for soil washing process because they are more environmentally benign than the acids and they also have regeneration potential.

Acknoledgements

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Contribuții la extragerea cu ajutorul unui acid şi a unei substanțe chelatizante a metalelor grele din solurile contaminate

Rezumat

Contaminarea solului cu metale grele este o problema de mare actualitate in lumea intreaga, prezenta metalelor grele in sol reprezentand o amenintare pentru mediul inconjurator si pentru sanatatea umana.

Lucrarea prezinta rezultatele obtinute la extragerea metalelor grele (plumb, cupru şi zinc) din sol contaminat datorita activitatii industriale, folosind ca extractanti acidul azotic si ca agenti chelatizanti acidul etilendiamino tetraacetic (EDTA) si acidul nitrilotriacetic (NTA).

Experimentarile de laborator au constat din colectarea si caracterizarea fizico – chimica aprobelor de sol din zona contaminata, in conformitate cu standardele nationale si din experimentarile de extractie propriu zisa.

Rezultatele obtinute arata cu claritate ca toti reactivii utilizati sunt capabili sa extraga metalele grele contaminante: agentii chelatizanti sunt insa de preferat acidului azotic deoarece sunt mai putin periculosi fata de mediul inconjurator.