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CHEMICAL LEACHING OF CONTAMINATED SOIL – CASE STUDY

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ABSTRACT

This study presents results of chemical leaching of contaminated soil from several metallurgically loaded locality of Richnava in Slovakia, applying two chelants – Na₂EDTA and Na₃EDDS of different molar concentration, done at different leaching conditions. The lower molar concentration (2 mM) of chelants showed comparable effect on Mn, Ni, As, Sb and Co leaching. Higher extraction was revealed at application of 10 mM chelants, especially for Cu and Cd release.

Repeated washing of soil by 10 mM chelant without the media regeneration was more effective at the toxic elements removal than washing by smaller volumes of media or leaching of soil in static conditions. Final experiments focused on obtained leachates treatment showed that electrolysis and precipitation should represent a perspective way of the washing media regeneration.

Keywords: *soil, toxic elements, chemical leaching, chelant, electrolysis*

INTRODUCTION

Contamination of soils by toxic elements represents one of principal environmental problems in the world. Several clean-up methods have been investigated, which can be divided into two groups: those that remove contaminants and those that transform pollutants into harmless forms (immobilization). These clean-up technologies can be applied on- or off-site, utilizing three kinds of remediation treatments: electrical, biological, and chemical techniques [1].

The soil washing offers a permanent remediation alternative for metal-polluted sites. Soil washing is essentially a volume reduction / waste minimization treatment process. It is done on excavated (physically removed) soil (*ex situ*) or on-site (*in situ*). Several classes of chemicals used for soil washing include surfactants, cosolvents, cyclodextrins, chelating agents, and organic acids [2]. Ethylenediaminetetraacetic acid (EDTA) is the most popular chelating agent and is used in various industrial fields, as well as for soil remediation. The EDTA has a strong chelating ability for cationic heavy metals. The EDTA forms water-soluble complexes with heavy metals in soil. The EDTA

leaching can be used to treat a broad range of soil types [3,4,5,6]. However, EDTA is of low biodegradability in soil and persists under natural conditions [6]. The management of spent washing solutions makes up a significant cost of the whole remediation process. Moreover, major environmental concerns can be associated with the use of toxic or non-biodegradable agents.

Due to this, in recent years, the use of biodegradable chelating agents, mainly ethylenediamine-*N, N'*-disuccinic acid (EDDS), is becoming prominent in soil washing applications [7]. The *S, S'*-stereoisomer of EDDS is a strong transition metal chelant which was originally developed for application in laundry detergents and displayed complete degradation in natural environmental conditions, in less than 10 days [7].

The biodegradability of EDDS was studied by Meers et. al. The chelant biodegradability was compared between the different soil types. The selected soils included a moderately contaminated calcareous clayey soil, a dredged sediment derived surface soil with similar soil characteristics heavily polluted with Cd, Cr and Zn, and a sandy soil moderately contaminated by historical smelter activity (atmospheric deposition). The biodegradability of EDDS in three soils varied distinctly.

However, EDDS was fully degraded within a period of 54 days in all soils regardless of initial delay [8]. The EDDS extraction of Cu, Zn and Pb was studied by Hauser et al. [9]. While the Cu extractability was higher in batch experiments, the Zn and Pb extraction was higher in column experiments. Between 18 and 42 % of the applied EDDS was lost through biodegradation after 7 weeks.

Although, the soil washing by chelants could effectively remove heavy metals away from the soil, it may also produce secondary pollution due to effluents containing heavy metals. The disposal of secondary pollution will become then a problem to face [10]. Washed out metals can also be recovered from leachate, and then reintroduced into the social material cycle instead of being landfilled [4].

This research article concerns the study of soil chemical leaching. The aim of the study is to compare the effect of two chelants of different concentrations on toxic elements removal from the contaminated soil and the effect of leaching conditions on the removal of toxic elements. Finally, the possibility of washing media regeneration by electrolysis and precipitation on the waste material is studied and discussed.

EXPERIMENTAL

Soil sample

The soil sample of 20 kg weight was sampled from the Richnava locality (Slovakia). The sampling site was a garden often flooded by the Hornád river, flowing through this locality strongly loaded by the anthropogenic activities, especially after mining and metallurgical industry. For the experimental purposes, the soil was sieved to grain size < 4 mm. Its mineralogical composition is described more detailed in [11].

Chemical leaching

For the chemical leaching two chelants, often used for the soil remediation, were tested: Ethylenediaminetetraacetic acid disodium salt dihydrate (Na_2EDTA , denoted as M1), Ethylenediamine-*N, N'*-disuccinic acid trisodium salt (Na_3EDDS , denoted as M2).

First the influence of molar concentration of chelant on the toxic elements removal was studied. The solution of 10 mM and 2 mM of Na_2EDTA ("10 M1", "2 M1") and Na_3EDDS ("10 M2", "2 M2") were prepared. Then 300 ml of solution percolated through the 200 g of contaminated sample for 5 days. Next, the chemical leaching of soil by chelant "10 M1" in the static and dynamic conditions were tested in three case studies. In the first test 20 ml of washing solution percolated through the 200 g of soil sample for 15 days (20 ml per day, each day new medium of 20 ml, experiment was denoted

as D1). In the second test 600 ml of washing solution was overflowed through 200 g of soil sample repeatedly without the medium regeneration for more times during the 15 days (D2). The third test was static, 200 g of soil sample was put into the flask contained 600 ml of medium containing “10 M1” chelant without agitation for 15 days (S). All experiments were performed in duplicate. Finally, the “concentrations of toxic elements in the effluents were measured by atomic absorption spectrometry.

The recovery of effluents was studied, too. For the recovery experiments the washing solutions of total volume of 6 l were percolated through the soil of 3 kg (in amount approximately of 1 l per 1 day). The soil was first washed by solution containing “10 M1” chelant. Following the soil was leached by medium with “10 M2” chelant (according to the experiment described in [11]). The obtained effluents were processed by electrolysis and precipitation.

Electrolysis

The electrolysis of the effluents was performed in the laboratory conditions by simple device consisted of 12 V source and two stainless steel plates (anode and cathode). The plates were put into the beaker containing 300 ml of leachate for 48 hours. The same was repeated with the rest volume of each leachate. After that the solutions were filtered and analysed by atomic absorption spectrometry.

Precipitation

The solutions obtained from electrolysis of effluents were next processed by waste material from the lime production – portlandite $\text{Ca}(\text{OH})_2$, with the aim to precipitate residual toxic elements from the solutions. The influence of amount of portlandite onto precipitation was studied. The experiments were performed in laboratory conditions at ambient temperature. The dose of 10, 5 and 2.5 g of portlandite was added into the flasks contained 100 ml of solutions (obtained from the electrolysis) and the mixtures were shaken in laboratory shaker for 30 minutes. The pH of the solutions before and after the precipitation was measured. The solutions were filtrated and analysed by atomic absorption spectrometry.

Electron probe micro analyzer

The products obtained from the electrolysis (products from the cathode and filtrates from the solutions after the electrolysis) were observed by electron microanalyser CAMECA SX-100.

RESULTS AND DISCUSSIONS

Chemical analysis of soil sample showed contamination by toxic elements, from whose Cu, As, Sb and Ba exceeded the values of limit concentrations according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7 (for Development of risk analysis of the environment), Table 1.

Table 1 Concentrations of contaminants in studied soil sample

	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	As (mg/kg)	Sb (mg/kg)	Ba (mg/kg)
ID	500	1500	250	180	10	65	25	900
IT	600	2500	300	250	20	70	40	1000
Soil	692	541	143	86	1	364	61	3303

ID – Permissible limit of contaminant concentration in soils according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7

IT – Critical limit of contaminant concentration in soils according to the Methodical Instruction of Ministry of Environment of the Slovak Republic, No. 1/2012-7

The effect of toxic elements removal was dependent on used chelant and their concentration, Fig. 1. For both chelants higher extraction was observed in the case of their higher concentration. Using of chelants of lower concentration showed comparable effect on Mn, Ni, As, Sb and Co leaching, Table 2. The “10 M1” chelant was more effective in Pb, Zn and Cd leaching in comparison with “10 M2”. For the Cu leaching, the highest extraction was obtained by using “10 M2” chelant.

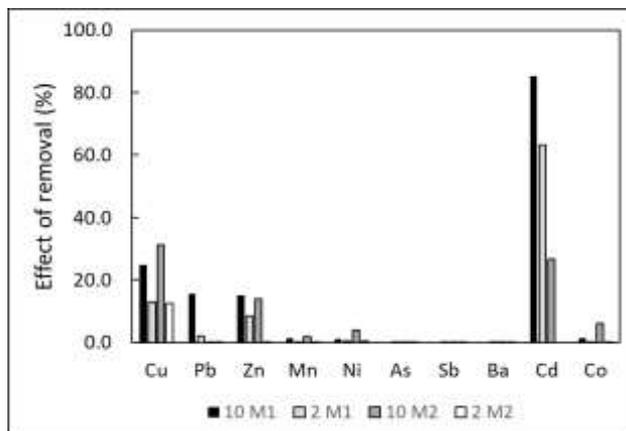


Figure 1 Comparison of effect of toxic elements removal from the soil by two studied chelants and in dependence on chelants concentrations

Table 2 Effect of toxic elements removal from the soil by chelants

chelant	Input (mg/kg)	Cu	Pb	Zn	Mn	Ni	As	Sb	Ba	Cd	Co
		692	143	541	2100	86	364	61	3303	1	25
10 M1	Removed (mg/kg)	171	22.2	82.3	29.3	0.929	0.856	0.142	0.348	0.852	0.359
	Efficiency (%)	24.8	15.5	15.2	1.4	1.1	0.2	0.2	0.0	85.2	1.4
2 M1	Removed (mg/kg)	90.6	3.1	46.1	1.11	0.334	0.686	0.129	0.214	0.633	0.062
	Efficiency (%)	13.1	2.2	8.5	0.1	0.4	0.2	0.2	0.0	63.3	0.2
10 M2	Removed (mg/kg)	216	0.368	75.5	40	3.34	0.768	0.154	0.320	0.268	1.52
	Efficiency (%)	31.2	0.3	13.9	1.9	3.9	0.2	0.3	0.0	26.7	6.1
2 M2	Removed (mg/kg)	86.7	0.003	0.301	0.061	0.369	0.711	0.125	0.199	0	0.048
	Efficiency (%)	12.5	0.0	0.1	0.0	0.4	0.2	0.2	0.0	0.0	0.2

The effect of dynamic and static conditions on toxic elements leaching by “10 M1” chelant is illustrated in Fig. 2. The repeated overflowing of soil by washing solution (condition D2) was more effective than leaching by percolation with smaller volume of washing solution during some days (D1). In addition, the advance of the D2 method has applied the same volume of washing solution without its regeneration. The most significant differences were obtained for Mn, As and Co leaching, Table 3. The leaching in static conditions in flask (S) was not so much effective as D2 method. But for Pb, As, Sb and Ba the higher removal effect was observed than for D1 method.

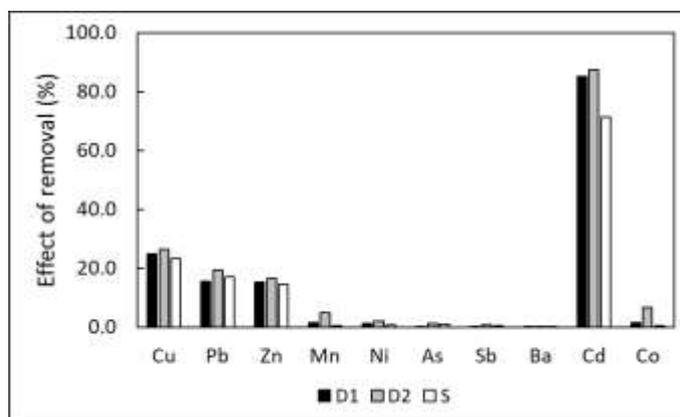


Figure 2 Comparison of effect of toxic elements removal from the soil by “10 M1” chelant in different dynamic and static conditions

Table 3 Effect of toxic elements removal from the soil by "10 M1" chelant in different dynamic and static conditions

Leaching	Input (mg/kg)	Cu	Pb	Zn	Mn	Ni	As	Sb	Ba	Cd	Co
		692	143	541	2100	86	364	61	3303	1	25
D1	Removed (mg/kg)	171	22.2	82.3	29.3	0.929	0.856	0.142	0.348	0.852	0.359
	Efficiency (%)	24.8	15.5	15.2	1.4	1.1	0.2	0.2	0.0	85.2	1.4
D2	Removed (mg/kg)	182	27.8	88.6	98.7	1.73	4.59	0.349	0.679	0.875	1.64
	Efficiency (%)	26.3	19.4	16.4	4.7	2.0	1.3	0.6	0.0	87.5	6.6
S	Removed (mg/kg)	161	24.3	77.7	10.0	0.618	3.66	0.273	0.660	0.714	0.075
	Efficiency (%)	23.2	17.0	14.4	0.5	0.7	1.0	0.4	0.0	71.4	0.3

The leaching experiments pointed at the possibility of removing toxic elements from the contaminated soils and revealed the suitable application of bio-degradable chelant Na₃EDDS for these purposes, which effect was comparable with chelant Na₂EDTA. In the case of using the non-biodegradable chelant, the conditions of soil leaching also plays a significant role. In this case the repeated overflowing of washing solution without its regenerations seems to be the most effective.

The effective and low-cost way of regeneration of washing solutions was tested, too. The effluents after the chemical leaching containing "10 M1" and "10 M2" chelants were processed by electrolysis and subsequent precipitation by portlandite with the aim to remove contaminants from the solutions.

The concentrations of toxic elements in effluents after the chemical leaching and in the solutions after the electrolysis are shown in Table 4. The value of concentration of each element in the solution was compared with the admissible limited value according to the Government Direction of Slovak Republic No. 269/2010 (concerning with requirements on quality of surface water). After the electrolysis only Fe, Sb exceeded the limited value for solution with "10 M1" chelant and Fe, Cd for the "10 M2" chelant (Fe content in the soil sample was 50400 mg/kg). The most contaminants were removed from the leachates.

The products after the electrolysis (precipitates from the cathode and from the filtrate) were observed by electron microanalyzer. The product from the cathode after the electrolysis of effluent with "10 M1" chelant consisted predominantly from the metallic Cu (almost 61 wt. %). The sequence of Cu crystallization on the cathode can be observed in Fig. 3.

The point EDX analysis confirmed the presence of Cu and also small content of Zn (1.7 wt. %) in the precipitate. The Cu was present on the edge of the product and also on the surface of Ca matrix. The filtrate contained higher ratio of Fe in the form of oxides present in the MgCa matrix, Fig. 4, what was confirmed also by EDX analysis.

Table 4 Concentration of toxic elements in the effluents after the chemical leaching of soil and in the solutions after the electrolysis

		Concentration of toxic elements in leachates before electrolysis and in solution after electrolysis (mg/l)								
Toxic elements		Cu	Pb	Zn	Fe	Mn	As	Sb	Ba	Cd
Limit (mg/l)		1	0.05	5	1	3	0.1	0.025	1	0.005
M1	Leachate	54.7	4.87	25.4	6.75	0.849	0.758	0.095	0.217	0.244
	Solution	0.874	0.000	0.086	1.42	0.058	0.000	0.030	0.055	0.000
	Efficiency (%)	98.4	100.0	99.7	79.0	93.2	100.0	68.4	74.7	100.0
M2	Leachate	69.1	8.24	24.9	30.2	3.34	2.12	0.130	0.212	0.222
	Solution	0.970	0.020	0.560	2.41	0.240	0.000	0.000	0.115	0.011
	Efficiency (%)	98.60	99.76	97.75	92.02	92.81	100	100	45.75	95.05

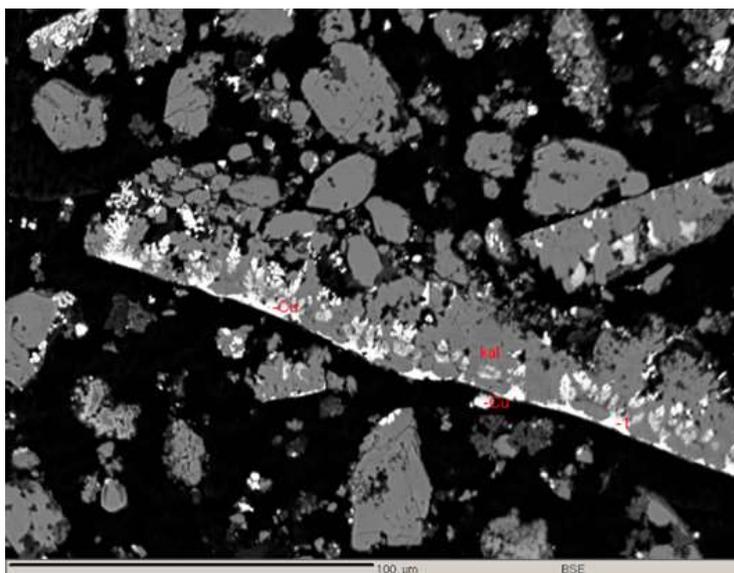


Figure 3 (left) BSE image of product obtained from the cathode after the electrolysis of effluent with “10 M1” chelant

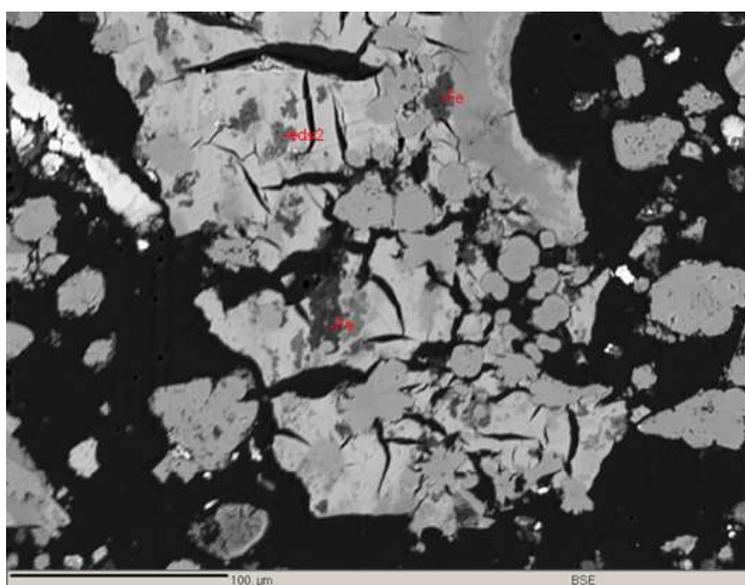


Figure 4 (right) BSE image of product obtained from the filtrate after the electrolysis of effluent with “10 M1” chelant

Next, the solutions obtained by the electrolysis were processed by the precipitation using different doses of portlandite. However, the experiments were done in longer time intervals, slight differences in concentrations of studied elements in the solutions after the electrolysis were measured, Table 5. Probably, some precipitates were dissolved back into the solution. The pH of the solutions after the electrolysis was about 8 and increased up to 13 after the portlandite addition.

In the case of “10 M1” chelant all studied doses of portlandite were effective in decreasing of the concentration of toxic elements in the solutions onto permission limits. For solutions with “10 M2 chelant” only the highest dose of portlandite was able to decrease the concentrations of toxic elements. Using 5 g of portlandite was not sufficient for Cd precipitation, weight of 2.5 g portlandite was not effective enough for Cd and Cu precipitation from the solutions.

Table 5 Concentration of toxic elements in the solutions after the electrolysis and precipitation by portlandite

Toxic elements/Limit (mg/l)			Concentration of toxic elements in solutions (mg/l)								
			Cu	Pb	Zn	Fe	Mn	As	Sb	Ba	Cd
			1	0.05	5	1	3	0.1	0.025	1	0.005
M1	10 g	Input	0.874	0.000	0.086	1.42	0.058	0.000	0.030	0.055	0.000
		Output	0.549	0.000	0.053	0.000	0.000	0.000	0.000	0.000	0.000
		Efficiency (%)	37.19	0.00	38.37	100	100	0.00	100	100	0.000
	5 g	Input	0.874	0.000	0.086	1.42	0.058	0.000	0.030	0.055	0.000
		Output	0.726	0.000	0.000	0.000	0.000	0.000	0.023	0.000	0.000
		Efficiency (%)	16.93	0.00	100.0	100.0	100.0	0.00	23.33	100.0	0.00
	2.5 g	Input	0.874	0.000	0.086	1.42	0.058	0.000	0.030	0.055	0.000
		Output	0.849	0.000	0.000	0.28	0.000	0.000	0.024	0.000	0.000
		Efficiency (%)	2.86	0.000	100	80.28	100	0.00	20.00	100	0.00
M2	10 g	Input	1.12	0.030	0.510	2.08	0.260	0.020	0.020	0.000	0.013
		Output	0.76	0.000	0.15	0.000	0.000	0.00	0.000	0.000	0.000
		Efficiency (%)	32.14	100.00	70.59	100.00	100.00	100.00	100.00	0.00	100.00
	5 g	Input	1.12	0.030	0.510	2.08	0.260	0.020	0.020	0.000	0.013
		Output	0.93	0.000	0.200	0.090	0.030	0.00	0.000	0.000	0.010
		Efficiency (%)	16.96	100.00	60.78	95.67	88.46	100.00	100.00	0.00	23.08
	2.5 g	Input	1.12	0.030	0.510	2.08	0.260	0.020	0.020	0.000	0.013
		Output	1.04	0.000	0.240	0.74	0.120	0.000	0.000	0.000	0.011
		Efficiency (%)	7.14	100.00	52.94	64.42	53.85	100.00	100.00	0.00	15.38

CONCLUSION

From the experimental study described in the paper, the following conclusions can be drawn:

1. The use of Na₂EDTA and Na₃EDDS for soil washing contaminated soil is an available option to remove most of the mobile fraction of the toxic elements bound to the soil particles;
2. use of biodegradable Na₃EDDS showed higher extraction of toxic elements, except Pb and Cd;
3. using of lower concentration of chelants in the washing solutions was not so effective in removal as using their higher concentration;
4. the best method of chemical leaching seems to be the repeated overflowing of soil by washing solution without its regeneration, what is also interesting from the economic point of view.
5. The effluents can be effectively regenerated by the electrolysis. The product from the electrolysis contained high amount of metallic Cu, which could be returned into the metallurgical industry;
6. the remaining toxic elements in the solutions can be precipitated by 10 g/l portlandite;
7. the recovery solutions should be used for the soil washing again.

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