

Heavy metals removal from contaminated soil by EDTA

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Abstract:

The paper presents the results for washing and extraction process for different soils, for example sediment from river and sewage sludge from two different wastewater treatment plants. The extraction of heavy metals, such as Pb, Cr, Zn and Mn from contaminated materials was done with an ethylene diamine tetra acetic acid (EDTA) aqueous solution, which greatly increases the dissolution. The experimental part was divided in four parts: sample preparation, washing process, aqua regia digestion, and determination of heavy metals. The experiments were performed at different washing times, namely: 1, 3, 6, and 9 h. The determination of heavy metal concentrations was performed using atomic adsorption spectroscopy. It was found out that the process with EDTA is an efficient method for heavy metals removal, and also it was determined that around six hours is optimal reaction time.

Key words: soil pollution, heavy metals, washing process, EDTA, aqua regia

1. Introduction

Heavy metal polluted soils are a major ecological burden on the environment. Soil pollution directly refers to the condition of the soil to which a chemical substance or waste has been added and would be a direct or indirect result of human activity with a harmful effect on the environment [1]. According to the Regulation on Determination of Pollution of Agricultural Land and Forests (Ur. L. RS 6/90) [2], soils are polluted when they contain so many pollutants that their self-purification capacity is reduced, their physical, chemical and biotic properties are degraded, inhibited or prevented. Plant growth, groundwater, crops are polluted, or permanent soil fertility is otherwise impaired by pollutants [3]. Soil degradation can be divided into those caused by natural causes and those caused by humans [4].

Heavy metals are a group of metals with a specific gravity greater than 5 g / cm^3 . This group of common pollutants includes copper, lead, nickel, zinc, tin, mercury, arsenic, and cadmium, which are very dangerous to the environment and organisms. Various methods are used to remove heavy metals from contaminated soils, which are divided into physicochemical and biological methods [5,6]. Physicochemical include soil washing, solidification and stabilization, reduction, oxidation, dehalogenation, thermally accelerated extraction, contaminant evaporation vapor extraction of pollutants, incineration, pyrolysis [7,8]. Among the biological methods, phytoremediation predominates. When decontaminating soil with chemicals, the chemicals used must be removed from the soil because in some cases they may pose the same or greater potential hazard to the environment than the contaminants present in the soil. Heavy metal remediation can be accomplished by leaching a specific metal or by removing the entire concentration of contaminants, or by a combination of these methods. There are various technologies for remediation of contaminated metals [9]. Depending on the site of soil remediation, two ways are distinguished, namely:

- in situ, means that the contaminated soil is cultivated in its original place of contamination.
- ex situ, means that the contaminated soil is moved, excavated, or removed from the site.

It is well known that in situ technologies are cheaper and take longer to achieve the desired remediation goals or the prescribed level. On the other hand, ex situ remediation methods can achieve greater and more reliable disposal efficiency in a much shorter time [10].

Soil washing can be done in two ways: serial washing and column washing. EDTA is the most common variant for cleaning contaminated soil [11]. The process of washing the soil can also be divided according to the location of soil washing. The first method is the remediation of contaminated soils by in situ washing, where the washing solution is applied to the unexcavated contaminated zone by flooding or spraying. The transfer of contaminants to groundwater must be prevented by appropriate site-specific control measures. In situ washing is a promising technology and one of the alternative methods to reduce the amount and impact of soil contamination. The in situ washing effect is limited by the permeability of the soil. The solvent first reacts with the contaminants and is then pumped to the surface. Whenever possible, attempts should be made to remove the contaminants and regenerate and reuse the solvent [12].

The second method of washing does not take place at the site of contamination, but the contaminated soil is excavated and homogenized by seeding in the first stage. Stones and other larger particles are removed. This is followed by a process of leaching the soil, during which water and various chemicals, usually mixtures of acids and chelating agents, flow into the reactors. The most commonly studied chelating agent for soil washing is ethylenediaminetetraacetic acid (EDTA) and its salts, since it achieves a significant increase in the mobilization

of cationic heavy metals and has low toxicity to the aquatic environment and bioaccumulation in living organisms [13]. EDTA can accelerate the mobilization of metals by two mechanisms: rapid, thermodynamically favourable complex formation between certain cationic metals and EDTA, and slow dissolution of EDTA. The former can directly break some of the weak bonds between metals and soil. In old, contaminated areas, most metal species are bound to oxides or organic material, and dissolution promoted by EDTA may play an important role in the overall removal of metal. EDTA-induced degradation also involves two steps: rapid adsorption of free or complex EDTA to specific surface areas with surface complexation that can destabilize metal-oxygen bonds in the mineral structure, followed by dissociation of the metal structure from the oxide structure, resulting in kinetic separation of the metals and possibly increasing the mobility of EDTA-destabilized metals in the washed soil. In some studies, metals have been found to adsorb more poorly in washed soils. Some studies have also shown that the mobility of some heavy metal residues (e.g., Pb) increased after seven days of abiotic aging, which may result in the magnitude of metal mobility causing new problems for aquatic resources, as metal contaminants could migrate from soil to groundwater [13].

High concentrations of EDTA solution can cause dissolution of oxides, carbonates, and organic matter and significantly alter both the physical structure and chemical properties of the soil. Dilute EDTA solution, on the other hand, has a positive effect on the release of labile metal fractions and causes minimal damage to soil structure. However, an EDTA solution with low concentration may not always release the majority of the labile metal fractions that are the source of metal mobility in the washed soil. The time that the soil is exposed to the rinsing process is also very important, which is studied in detail in this article.

The aim of the present work is to study the process of heavy metal removal with EDTA and to determine the efficiency of the process as a function of operating time.

2. Experiment

In order to determine the washing time of the sample with EDTA, the experiment was divided into four parts: sample preparation, washing procedure, aqua regia digestion and determination of heavy metal content in the sample by atomic adsorption spectroscopy.

2.1 Sample preparation

The samples were selected in different areas. River sediment (1), sludge from industrial wastewater treatment plant (2) and municipal sludge from municipal wastewater treatment plant (3) were analysed. The samples were dried at 105 °C until constant weight, a mixing process was performed to ensure homogeneity.



Figure 1: Three different samples

2.2 Washing procedure

Soil washing was carried out by the ex-situ method using EDTA ligand in an acidic medium. The experiments were carried out in two replicates. 2.5 g of the dry sample was weighed, 32 ml of 0.1 M EDTA was added and stirring was started. The washings were carried out for different lengths of 1, 3, 6 and 9 hours. After the washing time, filtration was started, the cake was dried at room temperature and the contents of the filtrate were determined: Cu, Cr, Mn, Fe and Ni (Table 1).

Table 1: Filtrate analyses

	Washing time [h]	Cu [mg/L]	Cr (VI) [mg/L]	Mn [mg/L]	Fe [mg/L]	Ni [mg/L]
Sample 1	1	>1,5	0	0,2	>1	>1,5
	3	>1,5	0	0,3	0,5	>1,5
	6	>1,5	0	1,5	>1	>1,5
	9	>1,5	0	>1,5	>1	>1,5
Sample 2	1	>1,5	0	0,2	>1	>1,5
	3	>1,5	0	0,3	0,5	>1,5
	6	>1,5	0	1,5	>1	>1,5
	9	>1,5	0	>1,5	>1	>1,5
Sample 3	1	>1,5	0	0,2	>1	>1,5
	3	>1,5	0	0,3	0,5	>1,5
	6	>1,5	0	1,5	>1	>1,5
	9	>1,5	0	>1,5	>1	>1,5

2.3 Aqua regia digestion

Aqua regia is a corrosive acid obtained by combining hydrochloric acid and nitric acid (V) in the ratio 3 : 1. The acid mixture is unstable, so it must be used immediately after preparation [14].

1.5 g of the sample (filter cake or untreated sample) was weighed. The samples were then transferred to a 100 ml flask and slightly moistened with distilled water, 21 ml of 30 % HCl and 7 ml of 65 % HNO₃ were added. The solution was heated to 110 °C until the solutions boiled slightly. The temperature was maintained for the next two hours. The cooled mixtures were transferred over filter paper into a 100 ml flask. The insoluble residue on the filter paper was washed with distilled water. The samples in the flasks were made up to the mark with deionized water and mixed well.

2.3 Heavy metal determination

The contents of copper, chromium, manganese, iron, nickel, lead and zinc were determined in the samples prepared as described in point 2.3. Tables 2, 3 and 4 show the results of the measurements, Cu, Mn and Ni were not detected.

Table 1: Heavy metals in sample 1

Washing time [h]	Cu [mg/L]	Cr [mg/L]	Mn [mg/L]	Fe [mg/L]	Ni [mg/L]	Pb [mg/L]	Zn [mg/L]
0	0	0,15	0	0,30	0	<0,10	3,40
1	0	0,10	0	0,30	0	<0,10	2,38
3	0	0,15	0	0,30	0	<0,10	2,22
6	0	0,05	0	0,20	0	<0,10	1,54
9	0	0,05	0	0,15	0	<0,10	1,62

Table 3: Heavy metals in sample 2

Washing time [h]	Cu [mg/L]	Cr [mg/L]	Mn [mg/L]	Fe [mg/L]	Ni [mg/L]	Pb [mg/L]	Zn [mg/L]
0	0	0,02	0	0	0	<0,10	0,93
1	0	0,02	0	0	0	<0,10	0,46
3	0	0,02	0	0	0	<0,10	0,55
6	0	0	0	0	0	<0,10	0,44
9	0	0	0	0	0	<0,10	0,52

Table 4: Heavy metals in sample 3

Washing time [h]	Cu [mg/L]	Cr [mg/L]	Mn [mg/L]	Fe [mg/L]	Ni [mg/L]	Pb [mg/L]	Zn [mg/L]
0	0	0,20	0	0,07	0	<0,10	2,97
1	0	0,05	0	0,04	0	<0,10	1,5
3	0	0,05	0	0,04	0	<0,10	1,37
6	0	0,02	0	0,04	0	<0,10	1,55
9	0	0,02	0	0	0	<0,10	1,22

The highest concentration (3.4 mg/L) was measured in sample 1 for zinc. In addition to zinc, chromium and iron were also detected in the first sample. Lower levels of chromium and zinc were detected in the second sample, which was industrial sludge. The third sample also contained chromium, iron and zinc, but their content was slightly lower than in sample 1.

3. Results

Figures 2, 3 in 4 show the results of the variation of the concentration of each metal in the samples as a function of time.

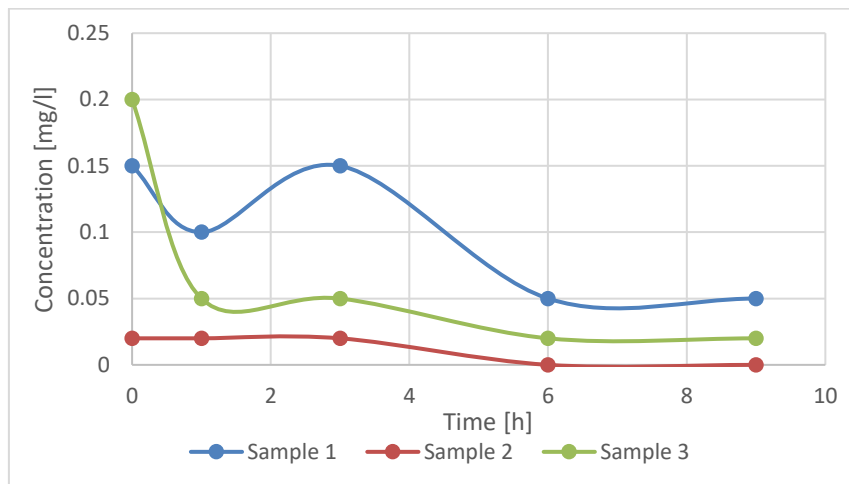


Figure 2: Concentration of chromium in individual samples as a function of processing time

The chromium content in the first sample decreased from 0.15 mg/L to 0.05 mg/L, a 66.67% reduction in heavy metal content. The second sample initially contained 0.02 mg/L of chromium ions. After six hours of washing, this heavy metal was no longer detectable. In the third sample, the chromium concentration drops were from 0.2 mg/L to 0.02 mg/L. It was also found out that the situation does not improve between six and nine hours of washing.

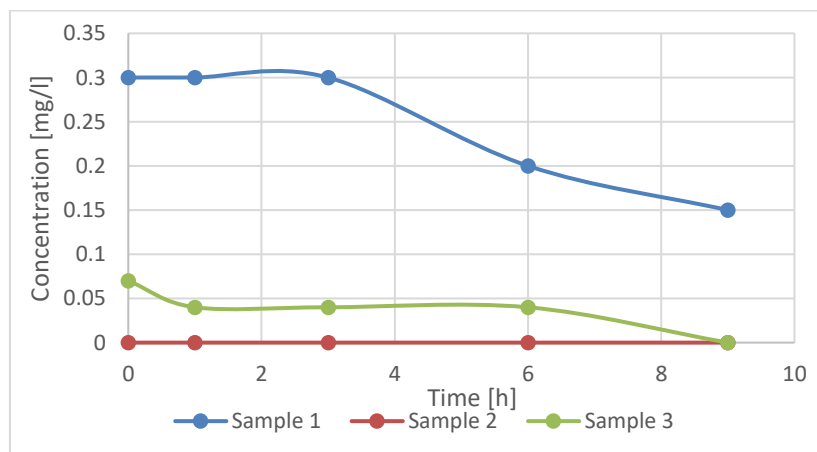


Figure 3: Concentration of iron in individual samples as a function of processing time

Sample 1 contained 0.3 mg/L of iron before purification. At the end of the nine-hour experiment, a value of 0.15 mg/L was reached, which means that 50 % of the iron was eliminated with the help of EDTA. Between six and nine hours, the concentration did not change significantly. No iron was detected in sample 2. Sample 3 contained 0.07 mg/L of iron and was not measured in the sample after nine hours.

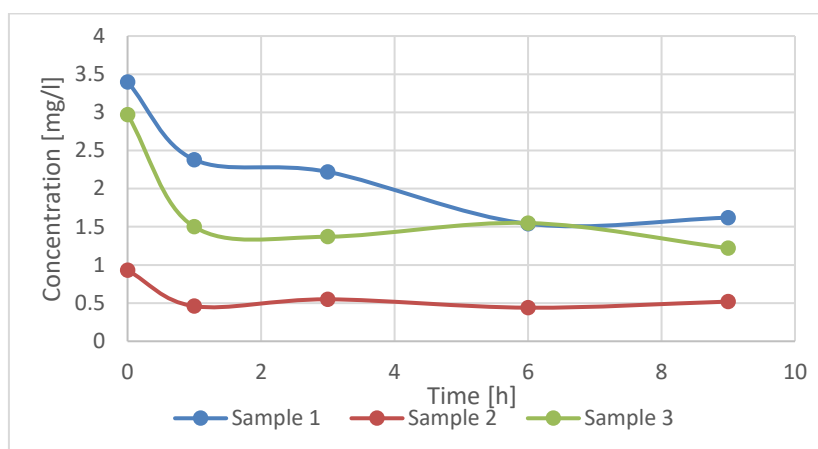


Figure 4: Concentration of zinc in individual samples as a function of processing time

The zinc concentrations in the samples were the highest among all the elements observed. In all the three samples, it was observed that zinc was not excreted significantly after four hours of washing. Sample 1 had a value of 3.4 mg/L. After nine hours, 1.62 mg/L was measured, corresponding to an efficiency of 52.35 %. Sample 2 contained 0.93 mg/L of zinc. After washing, the zinc content was 0.52 mg/L, which is 44.09 % less zinc in our sample. Sample 3 recorded a value of 2.97 mg/L. The final value stopped at 1.22 mg/L, which is 58.92 % less zinc in the sample.

Extending the reaction time from 6 hours to 9 hours has no significant effect on the efficiency of metal removal from contaminated soils. It is also necessary to take into account the economic aspect, which obviously implies additional costs due to the extension of the washing time. From these findings, it can be concluded that the most suitable washing time is six hours, which was also confirmed in the literature [15]. With different reaction times, the results of the experiments showed that increasing the reaction time could not increase the extraction rate. On the contrary, a long reaction time would improve the possibility of redissolving the heavy metals in the soil. In our case, especially zinc, whose concentration even increases in the first two samples, which is confirmed by [16], where the authors state that the rate of metal removal with EDTA depends more on the chelate concentration than on the washing time.

The analysis of the samples was carried out by digestion. Previously, after washing the soil, the filtrate was also analysed. The concentration values in the filtrate after 9 hours were high, namely copper, manganese and nickel showed values of more than 1.5 mg/L. This is in contrast to our results after digestion, where exactly these three heavy metals as well as Pb were not detected. This raises the question of why aqua regia digestion did not eliminate these metals. In an article by the authors Park and Son [10], it is described that the heavy metals were excluded from the samples using a metal separator system (Gerhardt SMA20A). The concentrations of Cu, Pb and Mn in the extracted and filtered liquid were then analysed by inductively coupled plasma emission spectrometry (ICP-OES) (Varian 720- ES). The reason they gave for a deviant analysis of these heavy metals was that mechanical mixing can be too rapid or uncontrolled, releasing impurities that are marginally bound to the surface of the particles and removing them from the impurities.

4. Conclusion

Contamination of soils, river sediments and sludges from wastewater treatment plants with heavy metals is a major environmental burden and requires special analyses. In this study, three different samples of contaminated soils were tested for decontamination using EDTA leaching method. The experiments were conducted with different washing times, namely: 1, 3, 6 and 9 h. It was found that in sample 1, the content of chromium, iron and zinc decreased from 50 % to 66.7 %. Sample 2 contained only a small amount of chromium and zinc, and again the positive effects of EDTA leaching are evident. Sample 3 initially contained 0.07 mg/L of iron, but after EDTA treatment, iron was no longer detected. It was also found that the extension of the reaction time from 6 hours to 9 hours had no significant effect on the efficiency of the extract, especially on the excretion of chromium and zinc. Soil pH plays an important role in the absorption of heavy metals because it directly controls the solubility and hydrolysis of metal hydroxides, carbonates, and phosphates. It also affects the formation of ion pairs, solubility of

organic material, surface charges of Fe, Mn and Al oxides, therefore pH analyses are carried out with HNO₃, HCl, H₂SO₄ to enhance the extraction of heavy metals from contaminated samples.

5. References

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