STUDIA UBB CHEMIA, LXIV, 1, 2019 (p. 41-52)
(RECOMMENDED CITATION)
DOI:10.24193/subbchem.2019.1.03

LEAD AND COPPER REMOVAL FROM MULTI-METAL CONTAMINATED SOILS THROUGH SOIL WASHING TECHNIQUE USING HUMIC SUBSTANCES AS WASHING AGENTS: THE INFLUENCE OF THE WASHING SOLUTION pH

GIANINA ELENA DAMIAN[a*], VALER MICLE[a], IOANA MONICA SUR[a]

ABSTRACT. The effect of three humic washing solution pH values (3.0, 7.0 and 9.6-its natural pH) on the removal efficiency of Pb and Cu from multi-metal contaminated soil collected nearby "Larga de Sus" mine from Zlatna (Alba County, Romania) was investigated, at laboratory scale, by an ex-situ soil washing technique. In this study, a commercial soluble humic sample extracted from German Leonardite was used as washing agent to remove Pb and Cu from polluted soil. Soil washing experiments were conducted in a stirrer with orbital-rotation oscillation at a liquid/solid ratio (L/S ratio; mL:g) of 8:1, concentration of humic washing solution of 2% and various stirring times (4, 6, 12, 24 and 40 hours). The removal efficiency of Cu and Pb increased with increasing pH from 3.0 to 9.6. In investigated experimental conditions, the best removal efficiencies (60.3% in case of Cu and 48.08% in case of Pb) were obtained at alkaline pH values of humic washing solution.

Keywords: *humic substances, soil washing, heavy metals, washing solution pH*

INTRODUCTION

Soil contamination with lead and copper is a worldwide concern associated with anthropogenic activity, especially with mining and metallurgical activity [1]. Up to now, there are a variety of decontamination methodologies for soil remediation. Soil washing, that generally uses chemical solutions to

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[a] *Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering, Department of Environmental Engineering and Sustainable Development Entrepreneurship, 103-105 Muncii Ave, Cluj Napoca, Romania*
* *Corresponding author: gianina_ln@yahoo.com*

extract heavy metals from soil, represents a valid, efficient, rapid, relatively inexpensive and very promising method for removing heavy metals from multi-metal contaminated soils, as reported by many researchers [2-6]. However, soil washing is a promising strategy if the applied extracting agent minimally changes the original solid matrix, original characteristics and does not leave toxic residues in the treated soil [7]. For these reasons, humic substances that are natural organic compounds ubiquitous in the environment [8] may have the potential of becoming extracting agents in soil washing technology because are environmentally benign, can support soil structure and improve soil physical, chemical and biological properties [9]. They have a strong propensity to form stable complexes with heavy metals cations in the pH range encountered in the soil environment [10]. Humic carboxylic -COOH and phenolic -OH groups from their structure besides alcoholic and amin functional groups are mainly involved in the formation of metal-humic complexes [11].

However, the ability of humic substances to complex with cations is strongly pH dependent. Humic substances change their structure depending on pH and the type of metals present. Humic substances are made up of hundreds of different molecules of many different sizes with many ways to orient themselves by twisting, bending, compressing, and expanding. They are held together loosely by weak forces in a colloidal state. Slight changes in pH will actually cause the humic polymers to fracture, breaking up the original molecules. The fractured molecules are then free to associate with numerous other free radicals, metals or impurities. High pH makes humic substances open up their long-chain polymers, whereas low pH makes them close (aggregation of the humic molecules) [12]. Increasing the H^+ concentration (decreasing pH) causes the protonation of the humic carboxylic -COOH groups, which eventually leads to precipitation - this usually begins at pH ~ 3-2 and reaches completion at pH ~ 2-1 [13]. The aggregation reduces the exposure of functional groups [12]. Deprotonating of these functional groups occurs at increasing pH and these behave as negatively charged moieties, attracting the positively charged heavy metal ions and protons (binding heavy metals) [14]. It is known that humic substances have a higher affinity for Pb^{2+} and Cu^{2+} that react with carboxylic and phenolic groups. The higher pH of the solution, the higher is the adsorption ability of the ions [15].

Therefore, investigating extractability of Cu and Pb from contaminated soil using humic substances solution as a function of washing solution pH is of great interest in terms of environmental impact of these metals and due to the ability of humic substances to change their structure for bounding Cu and Pb and others heavy metals as a function of pH.

Inspite of the fact that many researchers studied the potential of humic substances to extract heavy metals from contaminated soil through soil washing, investigating various factors affecting the process [3-5, 9, 10, 16], not much attention has been given to investigating the ability of humic substances to extract Cu and Pb from soil as a function of pH and on the effect of humic solution pH on the Cu and Pb removal efficiency [6, 17, 18].

Consequently, the aim of the present research was to investigate the influence of the humic washing solution pH on the Cu and Pb removal from soil collected nearby “Larga de Sus” mine from Zlatna (Alba County, Romania) using commercial humic substances extracted from Leonardite as washing agent for contaminated soil and to extend the knowledge regarding the ability of humic substances to extract Cu and Pb from soils at various humic solution pH values.

RESULTS AND DISCUSSION

Soil characterization. The initial values of heavy metals concentration in the soil sample collected nearby “Larga de Sus” mine are significant and were compared with normal values and threshold limits established by Romanian legislation [19]. As it can be seen in Figure 1, the concentration of Cu and Pb exceeds more than 2 and 6 times the intervention threshold limit, respectively.

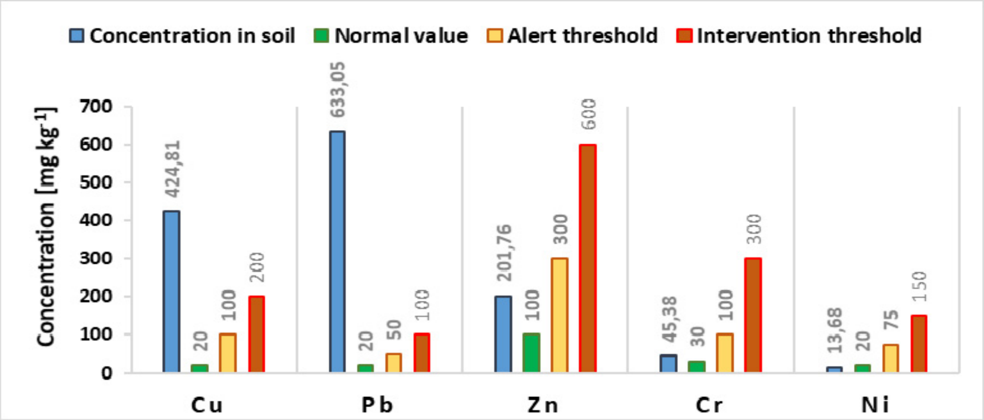

Figure 1. Heavy metals concentration of soil collected nearby “Larga de Sus” mine

On the contrary, the concentration of Zn and Cr in soil sample used in washing experiments exceeds only the normal value of Zn and Cr stipulated by the same legislation, while Ni concentration doesn't exceed any limit established by Romanian legislation in case of Ni.

According to the measured pH value, soil collected nearby "Larga de Sus" mine was classified as slightly acidic (pH: 5.86).

Washing experiment results. The influence of the humic washing solution pH on the Cu and Pb removal efficiency from soil collected nearby "Larga de Sus" mine in comparison with blank samples (samples without humic substances) at various pH values, along stirring time is illustrated in Figure 2.

Along investigated stirring time, Cu removal efficiency from soil collected nearby "Larga de Sus" mine increase as the pH of the humic washing solution increase (Figure 2a). Highest Cu removal efficiency (60.3 %) was observed in case of using humic washing solution at an alkaline pH (9.6-its natural pH), while the lowest Cu removal efficiency, ranging from 1.1% to 18.7%, was recorded in acidic conditions (pH of humic washing solution: 3.0). Instead, in the absence of humic substances in the washing solution, when pH was increased, Cu removal efficiency from soil collected nearby "Larga de Sus" mine decreased (Figure 2a). In the absence of humic substances in the washing solution, when pH was increased from acidic to alkaline values, Cu removal efficiency decreased from values range between 38.3% and 43.2% to values range between 4.1% and 9.5%, along investigated stirring time. This fact was expected as it is well known that using distilled water with strong acids as washing solution for heavy metal contaminated soil favors the extraction of heavy metals from soil. Similar percentages (40%-61%) were obtained by Moutsatsou et al. (2006) when studied the extractability of heavy metals from multi-metal contaminated soil using 1M HCl as washing agent.

In the presence of humic substances in the washing solution, at pH 7.0 the Cu removal efficiency range from 10.4% to 27.4% along investigated stirring time, while in the absence of humic substances in the washing solution, Cu removal efficiency range from 22.7% to 26.5% along investigated stirring time.

The results indicated in Figure 2a also show that Cu removal efficiency was improved with more than 2 to 9 times when washing solution contained humic substances besides distilled water (pH 9.6) unlike when measurements were made on samples in absence of humic substances.

But, in acidic conditions, Cu removal efficiency decreased by 2 to 38 times when washing solution contained humic substances besides distilled water and HCl than when the humic substances were missing from washing solution. The same fact was observed after 4, 12, 24 and 40 hours at pH 7. Thus, the ability of humic substances to remove Cu from soil is inhibited in acidic conditions (in the presence of HCl). Others authors [17] have also reported similar findings for removal of Cu from soil by humic substances and suggested that the decreasing of Cu removal efficiency with decreasing the humic washing solution pH may be attributed to the fact that a low pH values (pH 2-3), humic substances molecules become more compact, its functional groups (mainly humic carboxylic -COOH groups) involved in the formation of metal-humic complexes protonate and thus the ability of humic substances to attract the positively charged heavy metal ions is decreased [12-14]. Whereas, improved Cu removal efficiency at higher pH is due to the increased formation of Cu-humate complexes and because there is no strong competition from H^+ for COOH binding sites [17].

In the case of Pb (Figure 2b), at shorter stirring times (up to 6 hours), increasing humic washing solution pH to 9.6 does not led to an important increase in Pb removal efficiency. Instead, Pb removal efficiency even decreased with increasing pH of the humic washing solution. More accurate, Pb removal efficiency was 11.9%, 11.02% and 0.29% in the case of the pH of the humic washing solution of 3.0, 7.0 and 9.6, respectively. The same fact was observed in absence of humic substances along all investigated stirring time: as pH was increased, Pb removal efficiency decreased from values range between 14.6% and 37.9% to values range between 0.7% and 4.1%.

But, at 6 hours of stirring, increasing humic washing pH from 3.0 to 9.6 led to an increase in Pb removal efficiency from 23.9% to 48.08%. After 6 hours of stirring, the values of Pb removal efficiency obtained in case of humic washing solution at pH 3.0, 7.0 and 9.6 (23.9%, 27.2% and 48.08%) are higher than the value obtained on samples in absence of humic substances (17.1%, 11.7% and 1.54%). The improved Pb removal efficiency observed in the presence of humic substances at high pH values is because there is no strong competition from H^+ for COOH binding sites of the humic substances [17] and could be attributed to the fact that humic substances open up their long-chain polymers, the humic carboxylic -COOH groups deprotonate and behave as negatively charged moieties, attracting the positively charged Pb ions [12-14] increasing the formation of Pb-humate complexes.

After this stirring time, in the presence of humic substances in the washing solution, Pb removal efficiency does not follow the same trend. Thus, after 12 hours of stirring, Pb removal efficiency was highest at pH 3.0 (35.4%) and at pH 9.6 (34.1%) than at pH 7.0 (15.7%). After 12 hours of stirring, at all investigated pH values, the Pb removal efficiency is higher in the presence of humic substances than in the absence of humic substances in washing solution (Figure 2b).

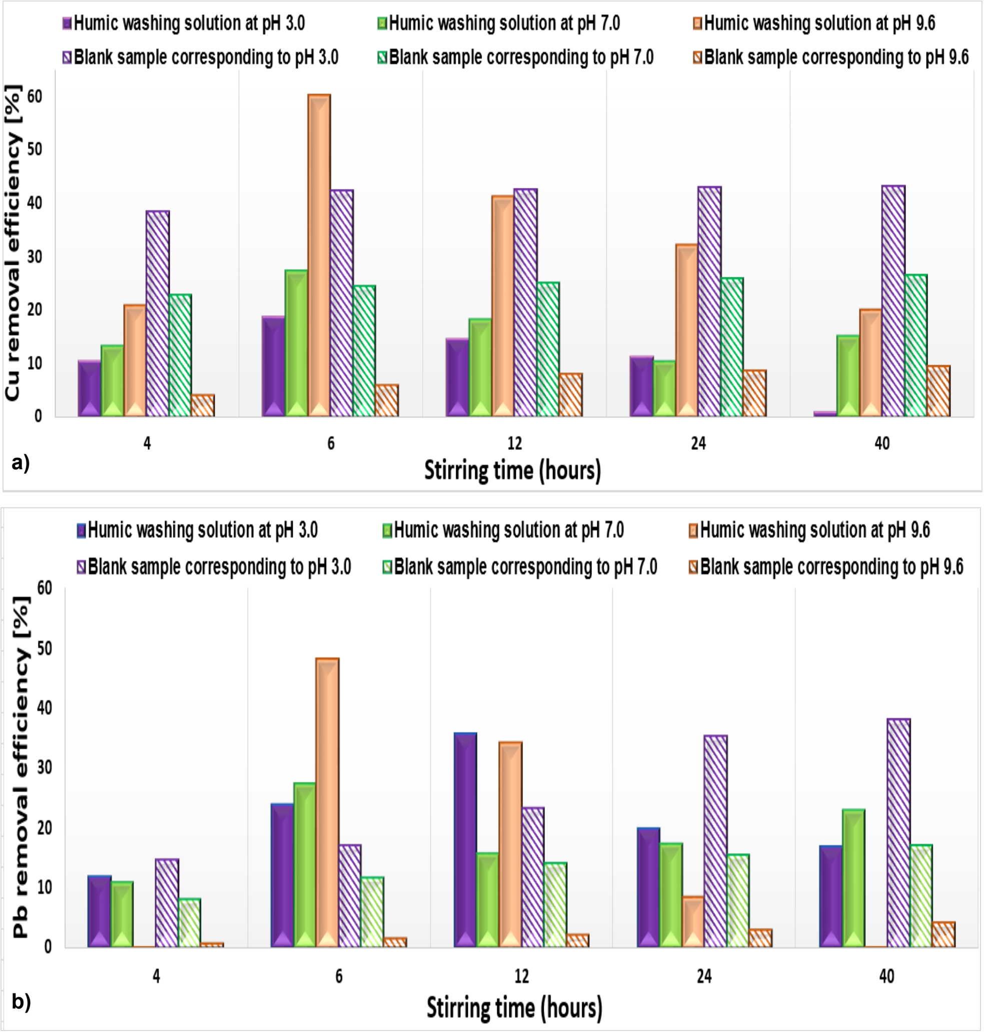

Figure 2. The effect of the washing solution pH on Cu (a) and Pb (b) removal efficiency from soil during investigated stirring time

After 24 hours of stirring, the Pb removal efficiency is higher in the presence of humic substances in washing solution than in the absence of humic substances in washing solution except for acidic conditions when the absence of humic substances in washing solution gave better results. In the presence of humic substances in the washing solution, Pb removal efficiency slightly increased with decreasing pH of the humic washing solution and after the investigated stirring time (40 hours), Pb removal efficiency was highest at pH 7.0 (22.8%) than at pH 3.0 and 9.6. Similar results were obtained by Kulikowska et al. (2015) that noted that Pb removal using humic substances from sewage sludge compost was highest at pH 7.0 than at alkaline and acidic pH or having the same value on both acidic and alkaline conditions. Others authors reported that Pb removal efficiency with citric acid decreased with increasing pH (over pH = 4.0) [20]. Also, Pb solubility reached a maximum at pH 7.1 and then decreased presenting insignificant alteration up to pH = 8.9 when Pb mobilization under 0.1M EDTA was studied [2].

The observed variation of Pb removal efficiency with pH along stirring time, in the presence of humic substances in the washing solution, indicates that the optimal pH for leaching Pb from soil collected from “Larga de Sus” mine using humic washing solution depends also on stirring time.

Thus, at shorter stirring times (up to 6 hours) and at longer stirring times (over 24 hours) acidic or neutral pH is more indicated for humic washing solution than alkaline pH in order to obtain highest Pb removal efficiencies, whereas between 6-12 hours of stirring alkaline pH would give better removal efficiencies than neutral and acidic pH. Besides stirring time available and chosen for soil remediation, choosing the optimal pH of the humic washing solution for leaching Pb from soil collected from “Larga de Sus” mine should also depend on the optimal pH of the humic washing solution for leaching Cu and others heavy metals present in the soil sample.

Thus, after 6 hours of stirring, an alkaline pH (9.6) of the investigated humic washing solution would give the highest removal efficiency for both Cu and Pb (60.3% and 48.08%), whereas if only shorter stirring time is available for soil remediation (up to 4 hours), a neutral pH of the investigated humic washing solution will be best to effectively remove both Cu and Pb than acidic or alkaline pH. But to generalize this statement, should also consider the influence of the humic washing solution pH on leaching others heavy metals or others pollutants present in the soil sample in order to achieve an effective and whole soil remediation.

The variation of Cu and Pb concentration from soil collected nearby “Larga de Sus” mine as a function of humic washing solution pH, along stirring time is illustrated in Figure 3.

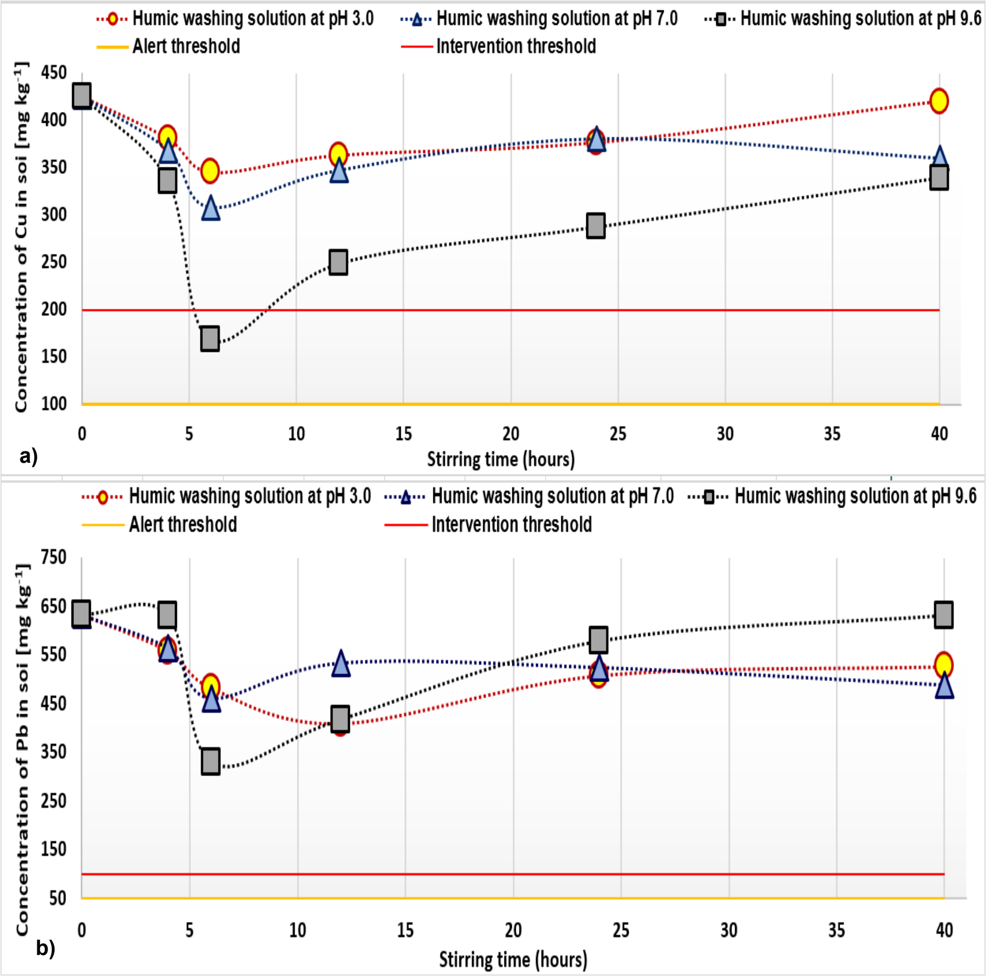

Figure 3. The variation of Cu (a) and Pb (b) concentration in soil during investigated stirring time as a function of humic washing solution pH

In investigated experimental conditions, after 6 hours of stirring, the concentration of Cu from soil decreased with more than 30 mgkg^{-1} below the intervention threshold limit (200 mgkg^{-1}) established by Romanian legislation [19] when pH of the humic washing solution was 9.6 (Figure 3a). The concentration of Pb from soil decreased to almost half of its initial value, after 6 hours of stirring, in case of humic washing solution with pH 9.6 (Figure 3b), but didn't decrease under the alert limits established by the same legislation.

Along all investigated stirring time, when pH of the humic washing solution was decreased to neutral and acidic pH values, the limits established by the Romanian Legislation were reached neither in the case of Cu nor in the case of Pb.

Thus, the removal of Cu and Pb from the soil collected from “Larga de Sus” mine in the presence of humic substances in washing solution is favored by high pH values of the washing solution. In the absence of humic substances in the washing solution, the removal of Cu and Pb from studied soil is favored by low pH values of the washing solution.

CONCLUSIONS

The present study has evidenced that Cu and Pb removal from soil collected nearby “Larga de Sus” mine from Zlatna (Alba County, Romania) using commercial humic substances extracted from Leonardite as washing agent is highly dependent on humic washing solution pH and on stirring time.

In the presence of humic substances in the washing solution, the Cu removal efficiency increase with increasing the pH of the humic washing solution. The highest Cu removal efficiency (60.3 %) was observed after 6 hours of stirring, in case of using humic washing solution at an alkaline pH (9.6-its natural pH), while only 10.4-27.4% and 1.1-18.7% of Cu was leached at pH 7.0 and 3.0, respectively. In the absence of humic substances in the washing solution, the highest Cu removal efficiency (43.2%) was obtained in acidic conditions.

In case of Pb, in the presence of humic substances in the washing solution, the results indicated that optimal pH for leaching Pb from soil collected from “Larga de Sus” mine depend more on stirring time, acidic or neutral pH being more indicated than alkaline pH up to 6 hours and over 24 hours of stirring. After 6 hours of stirring, an alkaline pH (9.6) of the investigated humic washing solution gave the highest removal efficiency for both Cu and Pb (48.08%). The values obtained after 6 hours of stirring are significantly higher in the presence of humic substances in washing solution (pH 9.6-natural pH) than in the absence of humic substances in the washing solution (pH 3.0), for both Cu and Pb.

EXPERIMENTAL SECTION

Study area and sampling. The contaminated soil sample used in soil washing experiments was collected from 10-90 cm depth from a pasture located at about 800 meters downstream the “Larga de Sus” mine (Figure 4).

The study area falls within the Zlatna mining perimeter located in South Apuseni Mountains (Alba County, Romania), where the extraction of gold-silver and polymetallic ores of Cu, Zn, and Pb date from the Dacian-Roman period [21].

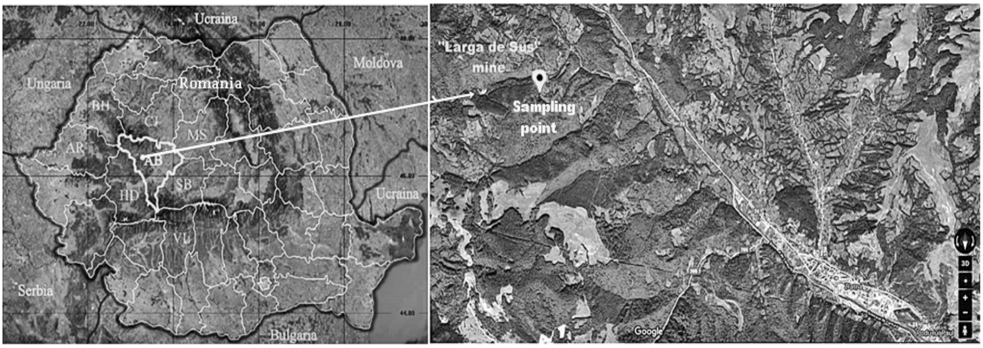

Figure 4. Location of the “Larga de Sus” mine and sampling point

Heavy metals concentration of the collected soil sample was determined through Atomic Absorption Spectrometry (AAS) using a SHIMADZU AA-6800 spectrometer.

Prior to the AAS analysis, the soil sample was dried at 95°C, crumbled and milled to pass through a 250 μm sieve. Then, 3g of the processed sample was placed with 1ml distilled water, 21 ml of concentrated HCl (Hydrochloric Acid) and 7 ml of concentrated HNO_3 (Nitric Acid) in a 100 ml glass flask and left for mineralization for 2 hours (glass flask was heated on a sand bath).

The mineralised sample was then filtered into a 100 ml volumetric flask, filled to the mark with distilled water and analysed for heavy metal concentration.

Reference solutions for spectrometer calibration were also prepared using analytical grade chemicals and distilled water.

Soil pH was measured in a suspension of soil and distilled water at a L/S ratio (mL:g) of 2.5:1 using a Hanna HI 3512 pH-meter.

Humic substance. The heavy metals concentration of the humic sample was determined by AAS. For the AAS analysis, humic sample, dissolved in distilled water in which was added hydrogen peroxide (H_2O_2) at a humic substances solution:H_2O_2 ratio of 5:1, was mineralized for 1 hour on a sand bath. After cooling, mineralized sample was filtered through 0.45 μm pore size filter into a 50 ml glass flask and analysed for heavy metals concentration using a SHIMADZU AA-6800 spectrometer.

pH of the humic sample was measured using a Hanna HI 3512 pH-meter in a suspension of humic substance and distilled water at a L/S ratio of 20:1 (mLg^{-1}). The results obtained are summarised in Table 1.

Table 1. Characteristics of humic sample used for soil washing experiment

Parameter	Unit	Value	Parameter	Unit	Value
Water content	%	17.7[a]	pH	-	9.60[b]
Loss of ignition of dry substance as humic acids	%	70.7[a]	Cu	mg L^{-1}	0,6785[b]
			Pb	mg L^{-1}	< IDL*[b]
Calcium (Ca)	mgkg^{-1}	10300[a]	Ni	mg L^{-1}	0,1433[b]
Potassium (K)	mgkg^{-1}	99300[a]	Cr	mg L^{-1}	< IDL*[b]
Magnesium (Mg)	mgkg^{-1}	1230[a]	Zn	mg L^{-1}	< IDL*[b]

[a] provided and determined by Humintech GmbH (supplier) through accredited laboratories
[b] determined
*IDL: Instrument detection limit

Soil washing experiment. The soil washing experiment using washing solution with humic substances and washing solution without humic substances (blank washing solution) was conducted at a L/S ratio of 8:1 (mLg^{-1}) in a 100 ml batch reactor with continuous orbital rotation-oscillation stirring at 100 oscillations/minute. Polluted soil was stirred with blank washing solution and 2% humic washing solution having different pH values (3.0, 7.0 and 9.6) for different time intervals (4, 6, 12, 24 and 40 hours) then samples were collected and filtered through 0.45 µm pore size filter. The natural pH of the humic washing solution (9.6) was decreased to neutral and acidic values using concentrated HCl (35-38%), pH being measured using a Hanna HI 3512 pH-meter. The pH of the blank washing solution was decreased with the same volume of concentrated HCl used to decrease the pH of the humic washing solution.

The concentration of Cu and Pb from treated soil samples was determined by AAS. For the AAS analysis, treated soil samples were subjected to the same processing steps as explained above.

Removal efficiency of metal ions by soil washing was calculated using the following equation [14]:

$$\text{Removal efficiency (\%)} = [(C_0 - C_F) / C_0] * 100$$

where, C_0 is initial metals concentration (mgkg^{-1}) of soil, and C_F is the final concentration of metals (mgkg^{-1}) in soil, after soil washing treatment.

All the experiments and analyses were performed in duplicate at 25°C and the average values were reported. All chemicals were of analytical grade or ultra-pure.

ACKNOWLEDGMENTS

The authors thank sales team from S.C. SEMPLANT ROMHOL S.R.L Company (Bucharest, Romania) and HUMINTECH GmbH Company (Grevenbroich, Germany), for supplying the soluble humic sample extracted from German Leonardite (commercially found as Powhumus WSG-85).

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