

Soluble potassium salts of humic acids as washing agent for lead and copper polluted soils

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Abstract. Numerous washing agents were investigated for remediation of heavy metal polluted soils (e.g. HCl, HNO₃, organic acids, salts, EDTA, surfactants). However, in spite of their proved capacity to extract heavy metals from polluted soils, they are environmentally problematic. Therefore, a soluble commercial sample of a naturally occurring organic compound (i.e. potassium salt of humic acids extracted from Leonardite coal) was tested as a possible substitute. Preliminary extraction experiments were conducted, at laboratory scale, on 5 g real polluted soil samples in a 100 mL capacity beaker. The polluted soil was stirred for 8 and 10 hours with a washing solution containing 2% and 5% soluble potassium salts of humic acids at a solid/liquid (S/L) ratio of 1:8 (g:mL) in an orbital oscillating-rotating stirrer. In investigated experimental conditions, soluble potassium salts of humic acids extracted up to 74% copper (Cu) and 75% lead (Pb) indicating the potential of soluble potassium salts of humic acids to become a possible alternative washing agent for soil remediation and to circumvent the disadvantages of synthetic chemicals generally used in soil washing technology.

Key Words: humic acids, soil washing, heavy metal pollution, soil remediation.

Introduction. Soil washing is commonly used worldwide as it provides high heavy metal removal efficiencies in a short time and is considered one of the most valid, efficient and relatively inexpensive alternative in polluted heavy metal soil remediation (Conte et al 2005; Soleimani et al 2010; Yang & Hodson 2019).

However, soil washing is a promising soil decontamination method if the applied extracting agent is inexpensive, easily available and minimally changes the original solid matrix, original characteristics and does not leave toxic residues in the treated soil (Race et al 2016). These previously mentioned properties of washing agents cannot be applied to the conventional washing agents generally used in soil washing technology due to their efficiency since many research studies identified adverse effects related by their use. For example, acids are toxic to soil microorganisms, can change the soil pH and structure and cause massive nutrient loss decreasing soil productivity (Gusiatin 2018). Surfactants use may be limited by their intrinsic biological toxicity (Conte et al 2005). Conventional chelators (EDTA) are detrimental to soil microbial health due to their toxicity and persistence in the environment (Meng et al 2017; Gusiatin 2018). Moreover, the price of generally used washing agents raises additional problems (Kulikowska et al 2015).

Thus, the key to this technology is the use of an inexpensive, natural, easily available and environmentally benign washing agent that must be, in the same time, appropriate for satisfactory soil decontamination (Gusiatin 2018).

Regarding this matter, humic acids contained in humic substances that are a class of natural organic compounds ubiquitous in the environment (Perminova & Hatfield 2005) seem to possess substantial capacity to extract heavy metals from soils due to their structure (Soleimani et al 2010). In aqueous solutions functional groups of the humic acids containing carbon, oxygen, nitrogen, hydrogen, sulfur, and phosphorus become predominantly negatively charged due to proton dissociation and the dissociated groups can interact with heavy metal cations present in soil (Shaker & Albishri 2014). Moreover, it was reported that humic acids can improve soil physical, chemical, and biological properties (Meng et al 2017) since it is well known that humic acids are also soil constituents.

Therefore, the aim of the present research was to investigate, at laboratory scale, the possibility and efficiency of using soluble potassium salts of humic acids extracted from Leonardite coal (commercially available as Powhumus WSG-85) as washing agent

for the removal of copper (Cu) and lead (Pb) from heavy metal polluted soil collected from Zlatna mining perimeter (Alba County, Romania).

Material and Method

Soil sample. Heavy metal polluted soil was collected from Zlatna mining perimeter located in Alba County (Romania). Heavy metals concentration of the sample collected and used in extraction experiments was measured by Atomic Absorption Spectrometry (AAS) using a SHIMADZU AA-6800 spectrometer. A complete analysis could be found in our previously published study (Damian et al 2019).

Soluble humic acid substance used for extraction experiments. A solid sample of soluble potassium salts of humic acids obtained through alkaline extraction from Leonardite coal (commercially available as Powhumus WSG-85) was used in extraction experiments. The experiments were performed in March 2018. For extraction experiments, 3 g and 5 g of soluble potassium salts of humic acids were mixed with 100 mL distilled water. The humic acid substance used in this study is recommended as a high-quality plant growth stimulant and soil conditioner (www.humintech.com). Elemental analysis of the soluble potassium salts of humic acids sample was provided by the supplier (Humintech GmbH). The results indicated a high content of calcium (10300 mg kg^{-1}), potassium (99300 mg kg^{-1}) and magnesium (1230 mg kg^{-1}). The heavy metals concentration of the humic sample was determined by Atomic Absorption Spectrometry (AAS). The heavy metal content and other characteristics of the humic substance sample used in this research could be found in our previously published study (Damian et al 2019).

Extraction experiments. Extraction experiments were conducted, at laboratory scale, on 5 g polluted soil samples in a 100 mL capacity beaker by single step extraction. The polluted soil was stirred for 8 and 10 hours with a washing solution containing, respectively, 2% and 5% soluble potassium salts of humic acids at a solid/liquid (S/L) ratio of 1:8 (g:mL) in an orbital oscillating-rotating stirrer (Figure 1).

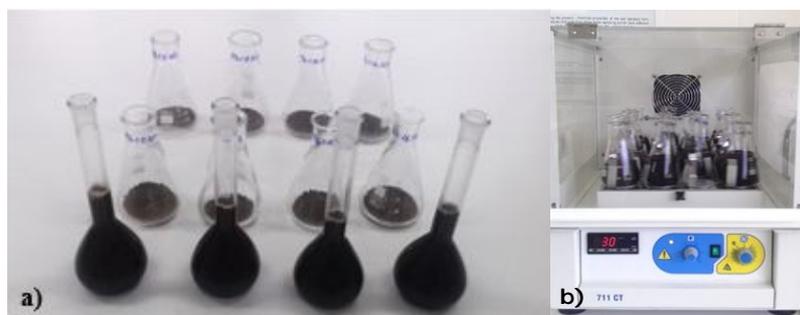


Figure 1. a) Washing solution containing soluble potassium salts of humic acids prepared to be placed in contact with the polluted soil samples; b) The orbital oscillating-rotating stirrer used in extraction experiments.

After stirring of polluted soil with the washing solution containing soluble potassium salts of humic acids for investigated time intervals, samples were collected and filtered. Decontaminated soil samples were dried at 95°C for about 1 hour. The Cu and Pb concentration from soil after the extraction process was determined by AAS. Prior the AAS analysis 3 g of decontaminated soil was crumbled, sieved and combined with 1 mL distilled water, 21 mL of concentrated HCl (hydrochloric acid) and 7 mL of concentrated HNO_3 (nitric acid). The mixture was then heated on a sand bath for about 2 hours. After cooling, the supernatants were filtered into a 100 mL capacity volumetric beaker, distilled water was added to the mark and heavy metal concentration was determined through AAS.

The extraction experiments and AAS analysis was performed in duplicate at $25 \pm 0.5^{\circ}\text{C}$ and the average values were reported.

The extraction efficiency of Cu and Pb (η) from soil after the washing process was determined using the following equation (Sur et al 2018):

$$\eta (\%) = \frac{m_e}{m_i} * 100$$

where: m_e is the concentration of extracted pollutant (mg kg^{-1}); m_i is the initial pollutant concentration present in the soil (mg kg^{-1}).

Results and Discussion. The extraction efficiency of Cu and Pb from soil during the investigated stirring time for both investigated concentrations of washing solution in soluble potassium salts of humic acids is indicated in Figure 2. Accordingly, the variation of Cu and Pb concentration in soil during investigated stirring time is illustrated in Figure 3a and Figure 3b, respectively.

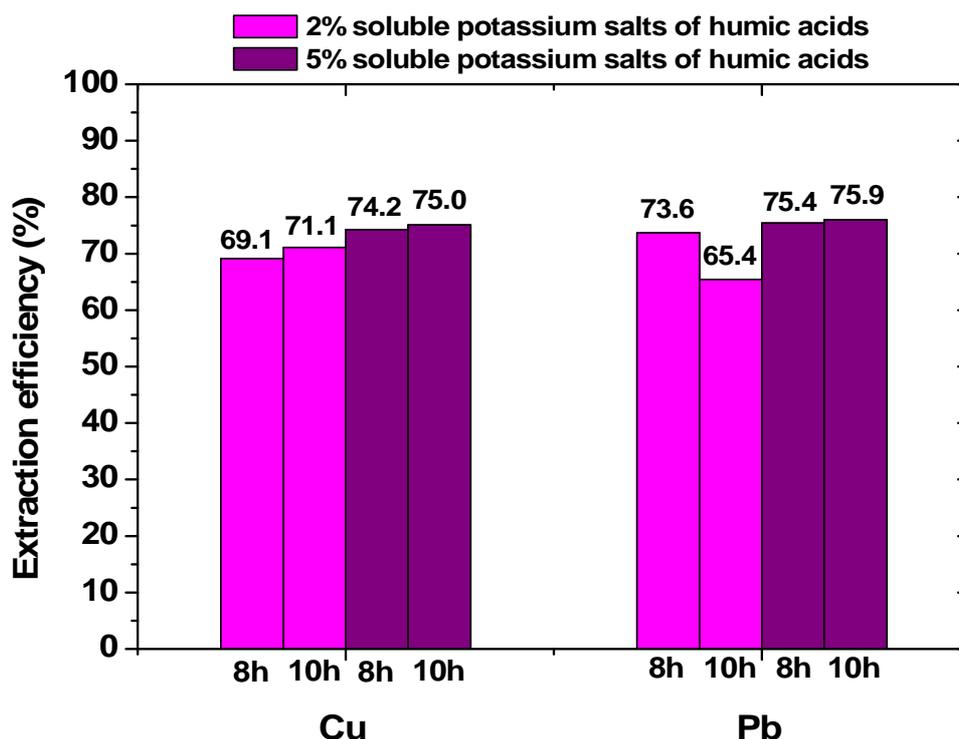


Figure 2. The extraction efficiency of Cu (a) and Pb (b) from soil.

As seen in Figure 2, the Cu extraction efficiency slightly increases with the increasing of stirring time and concentration of washing solution in soluble potassium salts of humic acids. Therefore, at the same S/L ratio, extraction efficiency increase with more than 3.9 to 5.1% when the concentration of washing solution in soluble potassium salts of humic acids increase from 2 to 5%.

Instead, in the case of Pb, after 10 hours of stirring, extraction efficiency sharply increases with more than 10% as the concentration of washing solution in soluble potassium salts of humic acids increases from 2 to 5% (Figure 2). But after 8 hours of stirring the extraction efficiency growth was lower (1.76%).

Increasing Cu and Pb extraction efficiency with increasing of concentration of washing solution in soluble potassium salts of humic acids could be due to the fact that at high concentrations of washing solution, more metal binding sites of humic acids are available for heavy metal extraction. Similar results were obtained by Yang & Hodson (2019) that reported that high concentrations of synthetic humic-like acid provided more metal binding sites for metals, resulting in the increasing of percent of metals removal.

Regarding the variation of investigated heavy metals in the soil during the extraction process, from Figure 3 it is obvious that the concentration of Pb and Cu decrease along investigated stirring time. The lowest Cu concentration in soil (105.9 mg kg^{-1}) was noted after 10 hours of stirring of polluted soil with the washing solution

containing 5% soluble potassium salts of humic acids. On the other side, increasing the concentration of washing solution in soluble potassium salts of humic acids lead to a higher extraction of Cu from soil. Therefore, after 8 hours of stirring, the concentration of Cu from soil decreased with more than 20 mg kg⁻¹ when concentration of washing solution was increased from 2 to 5%.

Moreover, in the investigated experimental conditions, the concentration of Cu from soil decreased under the intervention threshold established by Romanian legislation (Order no. 756/1997): 200 mg kg⁻¹. The concentration of Cu in soil, almost reaches the warning threshold established by the same legislation (100 mg kg⁻¹).

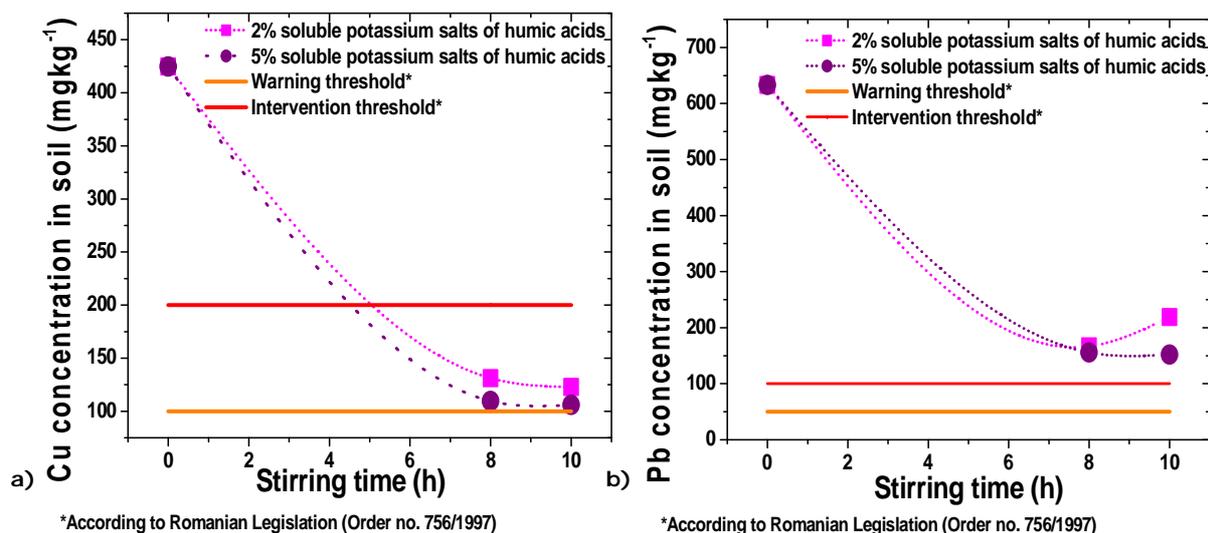


Figure 3. The variation of Cu (a) and Pb (b) concentration in soil during investigated stirring time.

In the case of Pb, the lowest concentration in soil (151.9 mg kg⁻¹) was observed after 10 hours of stirring of polluted soil with the washing solution of 5% concentration in soluble potassium salts of humic acids. Same as in the case of Cu, increasing the concentration of washing solution in soluble potassium salts of humic acids from 2 to 5% lead to a better increase of Cu extraction from soil, the concentration of Pb from soil decreasing from 218.9 to 151.9 mg kg⁻¹ after 10 hours of stirring. But, even if the concentration of Pb from soil was decreased by more than 4 times towards its initial value, the warning or intervention thresholds established by Romanian legislation in the case of Pb were not reached.

Also, in the case of Pb, between 8 and 10 hours of stirring of polluted soil with the washing solution of 2% concentration in soluble potassium salts of humic acids was noted an increase in Pb concentration in soil from 166.7 mg kg⁻¹ to 218.9 mg kg⁻¹ indicating a reabsorption of Pb from washing solution onto soil. This could be due to the various strength and stability of the active centers of humic acids (Klucakova 2012) and due to the competition of others heavy metals or mineral elements (Ca, Mg, Fe, Al, etc.).

Conclusions. The preliminary results revealed that the Cu and Pb extraction efficiency increases with the increasing of stirring time and concentration of washing solution in soluble potassium salts of humic acids. In investigated experimental conditions, after 10 hours of stirring, up to 74% Cu and 75% Pb was extracted from soil when the concentration of washing solution in soluble potassium salts of humic acids was increased from 2 to 5%. In the same experimental conditions, the concentration of Cu from soil was decreased with more than 94.1 mg kg⁻¹ below the intervention threshold established by Romanian legislation.

Therefore, the present study indicates that soluble potassium salts of humic acids may become a possible effective alternative washing agent for soil remediation and may be used as a substitute for generally used washing agents.

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