Programme

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Use of leonardite humic acids for metals extraction in mine soils

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Mine soils usually exhibit high levels of metal contamination. Phytoextraction is an environmental friendly and cost-effective technique for soil remediation, which consists of removal of metals from soil by plant roots and their translocation to aerial parts. Humic substances used as soil amendments could enhance metal mobility and uptake by plants due to formation of soluble complexes. This study aimed to evaluate the effects of a commercial humic acid derived from leonardite added at different rates and pH to a contaminated soil from an abandoned copper mine in Colmenarejo (Madrid, Spain) on metal mobility. The objective was to assess its potential as soil amendment for phytoextraction. Soil samples (10 g) were sequentially extracted 6 times with 20 mL of solution containing humic acid at: 0 (control), 0.25, 1, and 5 g L^{-1}. Solutions were previously adjusted to pH: 4, 6.1 (natural soil pH) and 8. Extracts were analyzed for pH, electrical conductivity, metal concentrations (Cu and Zn) and ratio of absorption at 465 to 665 nm (E4/E6) as an indirect measure of soluble organic matter content. Results showed that addition of higher doses of humic acid increased soluble organic matter content, and therefore extracted a higher concentration of Zn and particularly Cu, due to formation of soluble humic complexes. At higher pH humic acid became more soluble and managed to extract increasing amounts of metals, except in the highest humic acid treatment due to its precipitation or flocculation. The use of this humic acid as soil amendment could promote metal phytoextraction by tolerant plants in contaminated mine soils, but it should be applied at proper pH and other soil conditions to avoid risk of metal leaching to groundwater.

Keywords: humic acid, mine soil, phytoremediation, heavy metal

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USE OF LEONARDITE HUMIC ACIDS FOR METALS EXTRACTION IN MINE SOILS

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INTRODUCTION

Mine soils usually exhibit high levels of heavy metal contamination, which severely affect vegetation cover and it poses risk for human and animal health, as well as for metal leaching to groundwater. Phytoextraction is an environmental friendly and cost-effective technique for soil remediation, which consists of removal of metals from soil by plant roots and their translocation to aerial parts. However, in mine sites abandoned long time ago, metals could be strongly retained in soil, which limits the application of phytoextraction. Humic substances used as soil amendments could enhance metal mobility and uptake by plants due to formation of soluble complexes.

This study aimed to evaluate the **effects on metal mobility and potential for phytoextraction of a commercial humic acid derived from leonardite**, through a sequential extraction procedure using humic acid added at different doses and pH to a contaminated soil from an abandoned mine.

MATERIALS AND METHODS

Soil samples

Abandoned copper mine "Antigua Pilar" in Colmenarejo (Madrid, Spain), exploited from 1886 to 1915. Soil samples collected within the top 25 cm from several points around mine dumps. Samples air-dried and sieved to < 2mm.

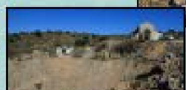
Humic acid

Solid humic acid product (HA) **Humitec Extra Dry** (TRADECORP, Spain), derived from American leonardite.

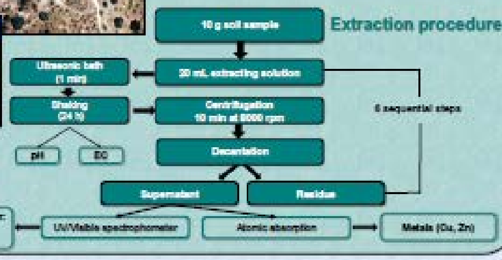
Extracting solutions (treatments)				
Adjusted pH	Doses of humic acid (dissolved in distilled water)			
	0 g L^{-1}	0.25 g L^{-1}	1 g L^{-1}	5 g L^{-1}
4.5	T0-4.5	T1-4.5	T2-4.5	T3-4.5
6.0 (soil)	T0-6.0	T1-6.0	T2-6.0	T3-6.0
8.0	T0-8.0	T1-8.0	T2-8.0	T3-8.0

Colmenarejo mine soil	
Clay (%)	7
Sand (%)	79
pH 1:2.5 (w/v)	5.9
EC (dS m^{-1})	0.05
Organic carbon (%)	0.32
Total Cu (mg kg^{-1})	2808
Total Zn (mg kg^{-1})	240
Total Cd (mg kg^{-1})	3.2
Total As (mg kg^{-1})	2796

HA Humitec Extra Dry	
pH (1%)	11.2
Density (g cm^{-3})	0.6
Solubility (g L^{-1})	100
Organic carbon (%)	39
Total extractable humic (%)	65
Humic acids (%)	53
Fulvic acids (%)	12
Total Cu (mg kg^{-1})	8.5
Total Zn (mg kg^{-1})	119

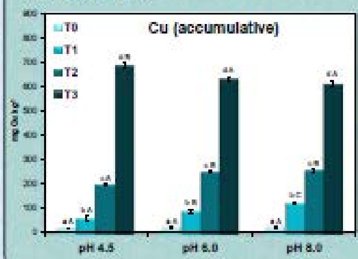


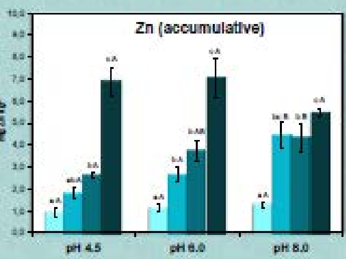
Extraction procedure

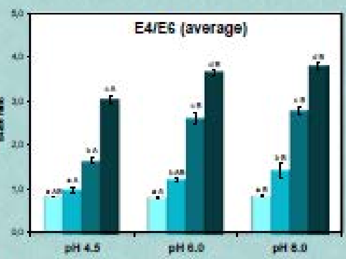


RESULTS

- Higher doses of HA increased Cu mobility due to the formation of stable complexes with soluble humic substances, given the great affinity of Cu for organic compounds.
- Increasing pH values managed to extract higher Cu due to the greater solubility of HA (T1 and T2). However, there was an opposite trend with the greatest dose of HA (T3), which reduced Cu extraction at higher pH; excessive pH could have led to precipitation processes or flocculation of metal-humic complexes by cation bridging.
- The most effective treatment was T3 (5 g L^{-1}) at pH 4.5, which extracted 24% of total Cu.
- Extracted Zn was considerably lower than Cu, given the low Zn concentration of this soil and its lesser affinity for humic substances.
- Zn exhibited a similar trend as Cu; higher doses of HA increased Zn extraction. Humic and fulvic acids from this commercial product also managed to mobilize Zn due to formation of soluble complexes.
- Intermediate doses of HA (T1 and T2) increased extracted Zn with higher pH due to the greater solubility of HA.
- Treatment T3 managed to extract the greatest amount of Zn, although it was only 3% of total Zn.
- E4/E6 indirectly determines of soluble organic matter content.
- Higher doses of HA increased E4/E6.
- Higher pH values increased E4/E6 and, therefore, soluble organic matter content due to the solubilization of humic acids.
- There was a significant and positive correlation between E4/E6 and Cu (r = 0.77; P < 0.01) and Zn (r = 0.68; P < 0.01), what could indicate the mobilization of metals by the soluble organic matter provided by HA. E4/E6 was also correlated with pH (r = 0.63; P < 0.01). Metal concentrations were not correlated with pH.







Means with the same lowercase letter are not significantly different among treatments for the same pH; means with the same capital letter are not significantly different among pH for the same treatment (P < 0.05).

CONCLUSIONS

The application of this commercial humic acid enhanced metal mobility in soil.

The addition of greater doses of humic acid increased soluble organic matter content, and therefore extracted a higher concentration of Zn and particularly Cu, due to formation of soluble humic complexes. At higher pH, humic acid became more soluble and managed to extract increasing amounts of metals.

The use of humic substances as soil amendment could promote metal phytoextraction by tolerant plants in contaminated mine soils, but it should be applied at proper pH and other soil conditions to avoid risk of metal leaching to groundwater.

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