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Enhanced phytoextraction of Pb and other metals from contaminated soils and associated risks

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Phytoextraction is an emerging technology for non-destructive remediation of heavy metal-polluted soils. However several issues of this technology have not been extensively investigated yet, such as in the case of the drawbacks, on soil and groundwater, of chelates application to increase metals uptake of the plants.
This study was conducted to i) verify the potential of heavy metals uptake by three different plants (Helianthus annuus, Brassica Juncea, Zea Mays) grown on pots containing two different Pb contaminated soils and ii) to test chelates effects on metals leachability on columns containing a moderately polluted industrial soil using EDTA and EDDS (3 and 5 mmol/kg both to chelates). The uptake of Pb by the plants showed a significant dependence on plant species, elapsed time and soil charachteristics. The higher Pb uptake achieved (2571 mg/kg) was obtained after 180 days in the case of silt mixture using the Helianthus Annuus. Results from leaching columns presented in this work were obtained utilizing five plexiglass columns (8 cm of diameter, 50 cm of height). The results highlight the effect of the nature and of concentration chelate solution on the hydraulic behavior of the soil. Metal concentrations in the leachate increased considerably upon the application of chelates, thus indicating the need of an appropriate control of the contaminated plume migration. Based on the obtained results, attention should be paid for long term application of chelate-assisted phytoextraction.

Introduction

The clean up of heavy metal contaminated soils is one of the worldwide issues for environmental engineering, because of the potential toxicity and high persistence of these contaminants in the soil. Phytoextraction is a remediation technology that removes metals from contaminated soil by plant absorption and translocation to harvestable plant parts and it has attracted attention for its low cost of implementation.
Metal uptake by plants involves a series of processes such as metal desorption from soil particles, transport of soluble metals to root surfaces via diffusion or mass flow, metal uptake by roots and metal translocation from roots to shoot. Chelates enhance desorption of heavy metals from the soil matrix to the soil solution, facilitate metal transport into the xylem and increase metal translocation from roots to shoots.
Various chelates, including EDTA, have been used to increase the solubility of soil metals and have been reported to have significant effects on the phytoextraction of

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several heavy metals, especially Pb (Chen et al., 2004; Wu et al., 2004; Meers et al., 2005). Although EDTA is generally recognized as the most efficient chelate to increase metal uptake by plants, it is toxic (particularly in its free form) and is poorly photo-, chemo- and biodegradable in the environment. Its prolonged presence in the soil, and its non selective nature, dramatically increase the leaching risk of heavy and alkaline earth metals such as Ca and Mg. In recent years, the focus of research in phytoextraction has shifted to some more biodegradable chelants, such as EDDS (Meers et al., 2005). Its metal chelating ability, accompanied with the short activity timespan in the soil due to rapid biodegradation seems to indicate this substance as a promising soil amendment for enhanced phytoextraction purposes. However enhancing the uptake of metals by plants, chelates also enhance the risk of heavy metals leaching in soils and the consequent risk for groundwater, as it has been extensively documented through batch and column-leaching experiments (Kos and Lestan, 2003a; Madrid et al., 2003).

In this study the metals uptake ability by some plant species grown in different soils was evaluated trough a 180 days experiment. Besides, the metal mobilization effects due to the chelating agents EDTA ed EDDS were evaluated on Pb contaminated soils through lab-scale experiments. The objectives of the study were: (1) to compare the metals uptakes by three different species (Heliathus Annuus, Brassica Juncea, Zea Mays); (2) to evaluate the mobilization effect produced by the use of EDTA and EDDS in different dosages; (3) to evaluate the changes in metal distribution in soil due to chelate addition; (4) to evaluate the hydraulic behavior of soil after the chelate treatment.

Materials and methods

Pot experiments

In this study three plant species (Helianthus Annuus, Brassica Juncea, Zea Mays) was chosen for their ability to uptake metals from soils (Chen et al., 2004; Jiang et al., 2004; Lim et al., 2004). To evaluate the different uptake two artificially contaminated soils were prepared by mixing a silt soil (S) and a high organic content (OM) respectively with a highly Pb contaminated soil (up to 30000 mg/kg_{dry}). The mixtures were crushed to pass a 2mm-sieve. The main mixtures characteristics were: 6.5 g/kg of TOC and 14981 mg/kg of Pb for the silt mixture (Pb(S)) and 89.7 g/kg of TOC and 25115 mg/kg Pb for the vegetable mixture (Pb(OM)) respectively.

Plants' biomass (shoots and stalks together) were analyzed after 120 (only OM pots) and 180 days.

(a) (b) (c)

Figure 1 Zea Mais (a), Helianthus Annuus (b), Brassica Juncea (c)

Column experiments

The soil used for the experiments was obtained by mixing three different soils, including a highly Pb-contaminated soil from an abandoned industrial site, a sandy soil from a sandpit and a silty clay collected from the 100-150 cm top layer in an agricultural area. Prior to mixing, each sample was oven-dried at 105 ± 5°C to constant weight and crushed to pass to a 2-mm sieve.

The soil leaching experiments were carried out on five lab-scale (8.0-cm inner diameter, 50-cm height) polyethylene columns using either deionized water or a chelating agent solutions (EDTA or EDDS). Column flushed with deionized water only was used as a control for comparison purposes. Each of the other columns was operated to simulate the leaching due to the application of the chelating agent in a pulse mode to the soil for one bed volume, while deionized water was continuously introduced for the rest of the experiment. Two different concentrations (3 and 5 mmol/kg of soil, respectively) of the chelating agents were tested in separate columns.

pH, total organic carbon and the concentrations of Pb, Zn, Fe, Cd, Cu, and Ni were measured on the leachates at the outlet of each column.

Sequential extraction

For the five experimental columns, Pb partitioning in the soil first and after the chelate treatment was estimated through the sequential extraction procedure proposed by Zeien and Brümmer (1989), which is based upon seven extraction steps. For each column, the procedure was applied on samples taken at two different column depths, corresponding to the top and bottom layers; for the control column the sequential extraction procedure was applied to one single sample, since the low overall extraction efficiency obtained was assumed to imply only slight changes in Pb distribution with column depth.

Results and discussions

Pot experiments

Results from pot experiments are reported in Table 1. All the three species showed remarkable uptake capacities for Pb. Brassica juncea confirmed its capacity of accumulate high levels of heavy metals (including Cd, Cr, Cu, Ni, Pb, and Zn) under some conditions that particularly enhance the solubility of the metal cations (Liphadzi and Kirkham, 2005).

Table 1 Results of pot experiments

Pot	Mixture	Plant	Pb (120 days) (mg/kg)	Pb (180 days) (mg/kg)
Pb(S)-BJ	Silt soil	Brassica J.	-	478 ± 18.5
Pb(S)-ZM	Silt soil	Zea Mays	-	891 ± 198.77
Pb(S)-HA	Silt soil	Helianthus A.	-	2571
Pb(OM)-BJ	Organic soil	Brassica J.	69 ± 23	357 ± 20
Pb(OM)-ZM	Organic soil	Zea Mays	41 ± 9.09	69 ± 17.20
Pb(OM)-HA	Organic soil	Helianthus A.	103 ± 15	340

The uptake considerably increased from 120 days to 180 days for all species and above all for Brassica Juncea (up to 500%) and Helianthus Annuus (up to 300%). Furthermore, the uptakes by these two last were higher in the case of the silt mixture than in the contaminated organic soil. Result confirms as phytoavailability of heavy metals in the soil substrate is suppressed by elevated organic matter content (Kalbitz et al., 2000; Rosselli et al., 2003). Lower differences in the uptake from the two soils were found for the case of Brassica Juncea. The highest uptake was obtained for Helianthus Annuus (2571 mg/kg Pb). Similiar results were obtained by Chen et al. (2004), with a highest amount of Pb extracted by Helianthus annuus, due to the high concentration of Pb in the shoots and the large biomass. The concentrations of Pb in the shoots of Brassica Juncea and Helianthus Annuus were 2900 and 1800 mgkg^{-1}, respectively, which were a 96-fold and 32-fold higher then the controls.

Column experiments

A first result obtained in the column experiments after the treatment with chelating agents was the sharp decrease in hydraulic conductivity which confirms other leaching column research results (Wu et al., 2004; Di Palma and Ferrantelli, 2005). The decrease was more pronounced for EDDS than EDTA, and it was higher with the increase in chelating agents dosage. This decrease can be attributed to soil dispersion, to the reverse of coagulation (Kedziorek and Bourg, 2000) or to a combination of the two. Also, the loss of soil macronutrients (Ca^{+2}, Fe^{+2}, Mg^{+2}), that compete with toxic metals for the binding sites of chelating agents, can explain the rapid decrease of the soil hydraulic conductivity as reported by Heil et. al (1999).

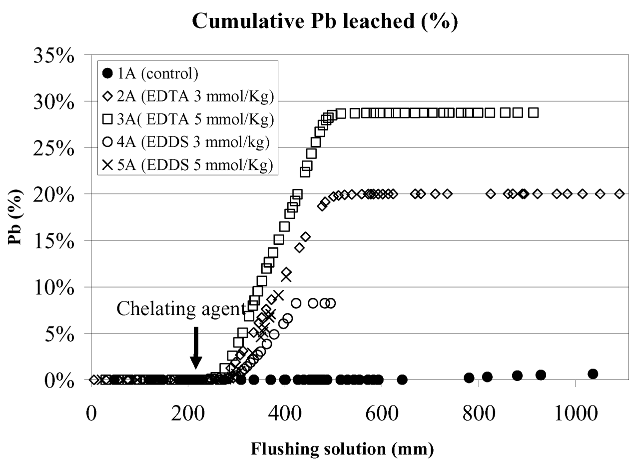

Figure 2. Cumulative Pb extracted

The cumulative Pb leached as a % of the original content in the soil is shown in Figure 2 for the different columns including the control. Metal leaching was strongly dependent on the chelate solution concentration but not on the type. Although the Pb concentrations in the column effluent were comparable for EDDS and EDTA at the same chelate dosage, the cumulative Pb removal was significantly lower for EDDS due to the clogging occurred in the columns where EDDS was used.

There was a strong relationship (a linear correlation, R^2 = 0.9579) between leachate TOC (i.e. chelate) and Pb concentration as confirmed by other studies (Chen et al., 2004; Wu et al., 2004). With regard to the other metals, it was found that EDTA is more efficient than [S,S]-EDDS in the extraction of Pb and Cd, but [S,S]-EDDS is more effective in the extraction of Cu, Zn, Fe and Ni as also reported in Meers et al. (2005).

Sequential extraction

The sequential extraction results are reported in Figure 3 in terms of Pb amounts associated to each soil fraction. In the control column soil the major portion of total Pb was associated to the easily mobilizable (60% total Pb) and occluded in Mn oxides (28% of total Pb) fractions, while the other soil fractions contained less than 13% of total Pb overall. Also after the chelant treatment, the major portion of Pb was associated to the easily mobilizable and Mn oxides fractions. A significant variation was observed in column Pb content between upper and lower layers, in particular the bottom soil layer always had higher Pb contents than the top layer. This behavior was more evident with the increase in chelant dosage.

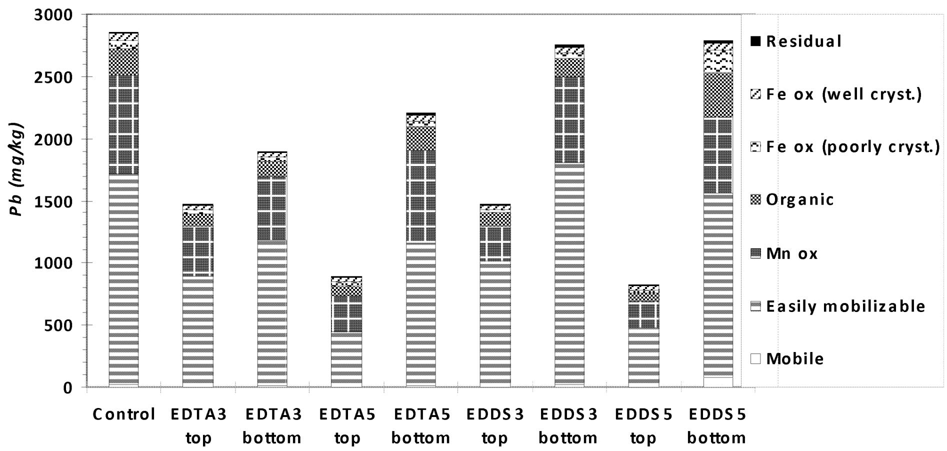

Figure 3 Results of sequential extraction.

Conclusions

Some of the issues related to Phytoremediation application to metals contaminated soils were discussed. The uptake of Pb by three different plants (Helianthus Annuus, Brassica Juncea, Zea Mays) was evaluated showing a significant dependence on plant species, elapsed time, soil charachteristics. The higher Pb uptake achieved (2571 mg/kg) was obtained after 180 days in the case of silty soil using the Helianthus Annuus.

The potential increase in metal mobilization through the use of the chelating agents EDTA ed EDDS in the phytoremediation treatment was evaluated as well through columns lab-scale experiments. A strong cumulative mobilization of heavy metals (up to 28% of total Pb in the EDTA treatment) was observed for both chelating agents, increasing with the chelant dosage, that suggests a high risk of pollution of groundwater. Despite the continuous plant growth could decrease the water content of soil, retarding the movement of Pb through the soil column and increases the adsorption of metal from soils (Chen et al., 2004), the risk of groundwater pollution in chelate application appears to be very high.

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