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Enhanced Phytoextraction of Lead by Indian Mustard Using Electric Field

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A phytoextraction treatment enhanced by electric field to decontaminate a heavily Pb polluted soil has been tested in a greenhouse-scale experiment. Brassica juncea was selected as Pb-hyperaccumulator plant. The influence of the application of two Electric Potential Difference values (0.6 and 1.1 V cm^{-1}) and the addition of EDTA (2.5 mmol kg^{-1}) on biomass production, plant uptake, contaminant leaching and migration was investigated, monitoring pH, temperature and electric current through the soil. The investigated treatments were applied for 8 weeks. For the treatment with EPD application and EDTA addition, a slight decrease in biomass production, a 4-fold increase of the plant uptake and a significant Pb leached reduction compared to control were observed. The combined use of electrokinetic and phytoextraction treatments can therefore contribute to reduce significantly the remediation time and the risk of groundwater pollution, possibly representing a very promising approach to decontaminating metal-polluted soil.

1. Introduction

Soil contamination caused by heavy metals is a serious problem worldwide. Thermal treatments were shown to be inapplicable (Falciglia et al., 2011) for heavy metal polluted soils, whereas chemical-physical techniques treatments such as electrokinetic decontamination, soil washing or stabilisation/solidification (Falciglia et al., 2012) have been recently successfully applied. However, these treatments may be prohibitively costly, time consuming or environmentally unsustainable such as disposal in landfills.

Phytoremediation is an in situ technique based on an environmentally friendly approach to remediate (Saifullah et al., 2010) or stabilise (Scanferla et al., 2012) heavy metal contaminated soils.

A number of lab-, pilot- and field-scale studies have been carried out to demonstrate the capacity of several hyperaccumulator plants for extracting metals from soils. Several chelating agents, such as EDTA, EDDS and nitrilotriacetic acid, have been proposed to enhance plant uptake of heavy metals in phytoextraction. In particular, Indian Mustard (*Brassica juncea*) has been shown to be useful for Pb soil extraction when used jointly with chelates (Quartacci et al., 2006).

Overall, results show that phytoextraction is only suitable for low contaminant concentration areas and it strongly depends on the availability of the contaminants to the plant root system. As a matter of fact, despite the marked increase in metal concentrations in plant biomass after addition of amendments, the estimated time required to obtain an acceptable reduction in soil contaminant concentrations is impractically long (Dunquene et al., 2009).

Moreover, in spite of reported successes in increasing the bioavailable fraction of metals using EDTA, researchers have expressed concern about EDTA-assisted phytoextraction due to excessive levels of heavy metals in soil solution and dissolution of soil-bound metals including Pb. Plants exposed to high levels of both free Pb and free EDTA produce low biomass due to low seed germination, chlorosis, shoot desiccation and reduced transpiration (Saifullah et al., 2010). But crops should have a sufficient yield such that metals can be extracted from soil in a reasonable time scale. Further concern has been expressed regarding the increased risk of groundwater pollution associated with EDTA-assisted phytoextraction (Dunquene et al., 2009).

In order to overcome phytoextraction limitations and to enhance the process of metal plant uptake from soil, novel enhanced phytoextraction treatments were recently proposed (Pedron et al., 2009; Singh et al., 2007). Among them, the electro-phytoremediation treatment was shown to be applicable for metal polluted soil remediation (Bi et al., 2011; Zhou et al., 2007). It combines a typical phytoextraction treatment with the action of an electric field generated by coupled electrodes inserted in a soil contaminated region and connected by a Electrical Potential Difference (EPD).

The electric field applied to a conventional phytoextraction treatment generates an acid front (H^+), increases metal mobility enhancing plant metal uptake. In addition, the application of an electric field in roots zone of plants used causes a horizontal electromigration phenomenon. This could avoid or minimize, a downward metal migration due to the use of chelant agents such as EDTA. This aspect could represent a key factor in enhancing the amount of bioavailable metal for plant uptake and controlling the groundwater contamination processes.

As a side effect, the heating of the soil, due to resistance to the passage of electric current, enhances soil microbial activity. Indeed it has been shown that temperature and electric fields influence plants behaviour and metal uptake (Baghour et al., 2002) by modifying plant tissue structure. Furthermore, the possibility of increasing the metal extraction efficiency of EDTA in extraction (Martinez et al., 2003) and phytoextraction (Chen et al., 2007) treatment by using heat stress was shown, and this may be fundamental for the minimization of chelates used.

This study aims to explore the response of *B. juncea* to the electric field application in order to evaluate feasibility of enhanced phytoextraction for full scale polluted soil remediation.

The specific objectives of the work were (i) to assess the influence of electric treatments on plant biomass production, plant Pb uptake, and Pb leaching and migration in a greenhouse-scale experiment, and (ii) to assess the applicability of enhanced phytoextraction by means of management and technical considerations.

2. Materials and methods

2.1 soil contamination, experimental apparatus and plant grown

Laboratory experiments were carried out using a sandy-silt soil collected from a farming area near Riesi (Caltanissetta, Italy). The soil was collected from the 40 cm top soil layer. After grass debris removal and air drying, the soil samples were sieved < 2 mm and analyzed (Table 1). The soil was artificially contaminated with a $Pb(NO_3)_2$ solution to obtain a homogeneous Pb concentration of 3,300 mg kg^{-1} soil. After contamination procedure, the soil was kept for 1 week and then fertilized. Therefore, it was moisturized, covered and allowed to equilibrate in a cellar at 20 °C for a total period of 3 months. Before planting 10 soil samples were collected and analyzed for Pb content.

Table 1: Physicochemical properties of the soil

Parameter	Value*
pH	8.3
Sand (%) >0.05 mm	49.2
Silt (%) 0.05-0.001 mm	38.4
Clay (%) <0.001 mm	12.4
Bulk density (g cm^{-3})	1.43
Field capacity (%)	28.8
Organic Matter (g kg^{-1})	5.5
C.S.C. (cmol kg^{-1})	16.2

* Results are the mean of four replicates.

For experiment a plexiglas apparatus of size 350 x 250 x 150 mm was used for each tested treatment. Each apparatus was filled with 10 kg_{DW} and a reservoir was connected to the bottom for the leachate collection. Two stainless steel electrodes were inserted into the soil and connected to a EPD generator and an amperometer for constant voltage application and electric current monitoring, respectively. Pots containing 10 kg_{DW} of soil were used as controls (without EPD application).

Indian mustard [*B. juncea* (L.) Czern.] was planted at a density of 40 seeds per reactor or pot. After 25 d of growth, the seedlings were thinned to eighteen plants for each reactor or pot. During the experiments the plants were irrigated every 2 or 3 d and soil water content was maintained at 70 % of field water capacity. After the growing period EDTA as Na_2-EDTA [pH 4.68, Electric Conductivity (EC) $0.30 \cdot 10^4$ µS cm^{-1}] at 2.5

mmol kg^{-1} was added to the soil surface dissolved in the irrigation solution and EPD was applied for a period of 30 d, at fixed intervals, totaling 106 h.
Two values of EDP (15 and 30 V) generating an electric field of 0.6 and 1.1 V cm^{-1}, respectively, were applied to uncontaminated and Pb contaminated soil, with or without EDTA addition. Carried out runs were 15-Pb, 30-Pb, 15-Pb-EDTA, 30-Pb-EDTA, 15-EDTA and 30-EDTA and controls (C-Pb-EDTA, C-EDTA, C-Pb and C). Treatments were carried out in triplicate and mean and standard deviation values for shoot Pb concentration and shoot biomass production were reported. Significant differences of shoot Pb concentration for different groups were analyzed using Tukey's multiple range test. Statistical significance was $p < 0.05$.

2.2 Monitoring, sampling and analytical methods

When an electrical potential is applied in a saturated soil, its temperature increases and different chemical reactions take place (Amrate et al., 2005). They change soil temperature and pH profiles which could hinder contaminant migration in soil or plant grown. This investigation monitored daily the current intensity, temperature variation in soil, and pH in 3 different soil regions (anode, middle and cathode).
Four weeks after the application of the treatments, all plants were harvested, cutting 1 cm above the soil surface to minimize contamination by soil. The harvested plants were rinsed with deionized water, oven dried at 105 °C for 72 h, ground into a fine powder, then weighed. For each reactor where the contaminated soil was treated by electric field, three soil samples were collected in anode, middle and cathode region. For the controls, 3 soil samples were randomly collected. Soil samples were oven dried and weighed. For all reactors, the total amount of leachate was weighed and three samples were collected for analysis. All the samples were kept in a closed vessel at 4 °C before analysis for Pb content using an ICP-OES (Perkin Elmer Optima 4300 with Dual View).

3. Results and discussion

3.1 Current intensity, pH and temperature profiles

Figure 1-a shows the current intensity versus time during EPD application.

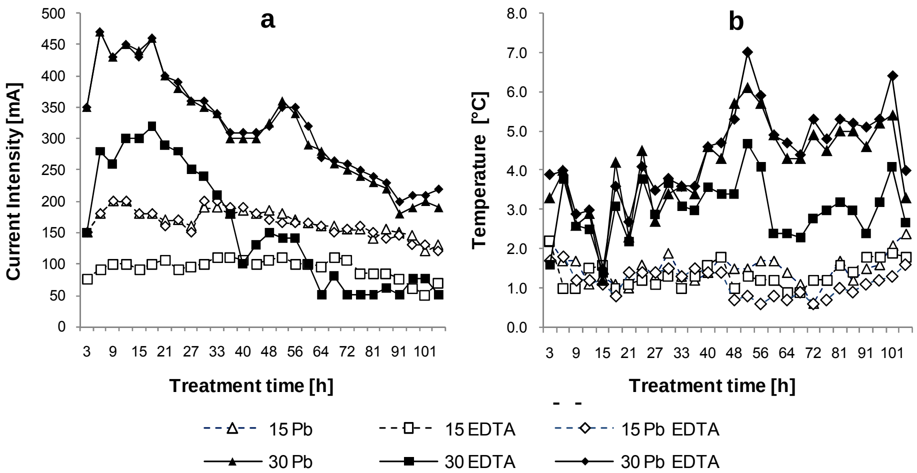

Figure 1: Variation of a) current intensity and b) temperature in soil during the treatment

Higher values were obtained when 30 V was applied with no significant difference between treatment with or without EDTA addition. A maximum current value of 460 mA was recorded for 30-Pb-EDTA. As expected, lowest intensity current occurred in uncontaminated soil due to the lower soil electric conductibility. For all treatments with EDP application, the electric current tended to decrease with time, more quickly for the soil where 30 V was applied, due to the reduction of soil electric conductance caused by hydroxide precipitation near cathode region.
Significant soil temperature increase was observed at the end of every daily electric treatment (Figure 1-b). A maximum difference between pre- and post-treatment up to 7 °C was recorded when an EPD of 30 V was used. Therefore EPD application can remarkably increase soil temperature and this aspect could be a key factor in promoting microbial activity in the root soil region and, consequently, plant metal accumulation.

Soil pH (Figure 2) varied in the 5.4 and 12.8 range during electric treatment for the setup where EPD was applied. In control setup pH values remained constant and close to the initial value. As expected, a decrease and an increase of pH values were observed for anode and cathode regions, respectively, due to proton generation at the positive electrode and hydroxide precipitation at the negative electrode. The change was rapid and wide for setup where EPD of 30 V was applied, on the other hand pH values diverge slowly from the neutral in uncontaminated soil (15-EDTA and 30-EDTA). This phenomenon is possibly due to lower intensity current crossing the soil.

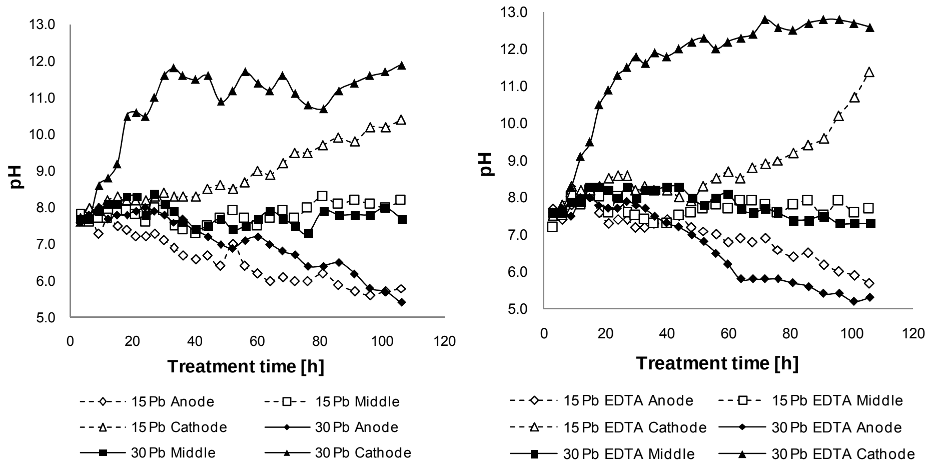

Figure 2: Change of pH profile in anode, middle e cathode soil regions during the treatment

3.2 Plant growth and lead uptake

For the uncontaminated soil the highest biomass production was observed in the case where the electric field was applied (Figure 3-a). For the treatments of Pb contaminated soil, the presence of contaminant jointly with electric field results in the lowest biomass production.

Uptake results (Figure 3-b) show no significant difference between 15 and 30 V potentials and a very low lead concentration in biomass plant in the cases where EDTA was not added. Specifically the accumulation of lead in the biomass was enhanced significantly by DC voltage application jointly with EDTA dosage with average values up to 4-fold compared to EDTA only (4,000 vs 1,000 mg kg^{-1}). Similarly, in the biomass production results, no significant difference in Pb uptake was observed changing EPD application.

Dry matter production and phytoextraction results obtained for C-Pb-EDTA (about 200 g_{dw} m^{-2} and 1,000 mg kg^{-1} respectively) are comparable to data reported by Blaylock et al. (1997). Results obtained with the electric field with respect to the chelant agent alone are in agreement with the study of Lim et al. (2004) where a Pb-contaminated soil was used and a short treatment period (1 h daily for 9 d) was investigated. However, the excellent uptake data in plant stems seen in our experiments are not comparable to those generated in Lim's experiments.

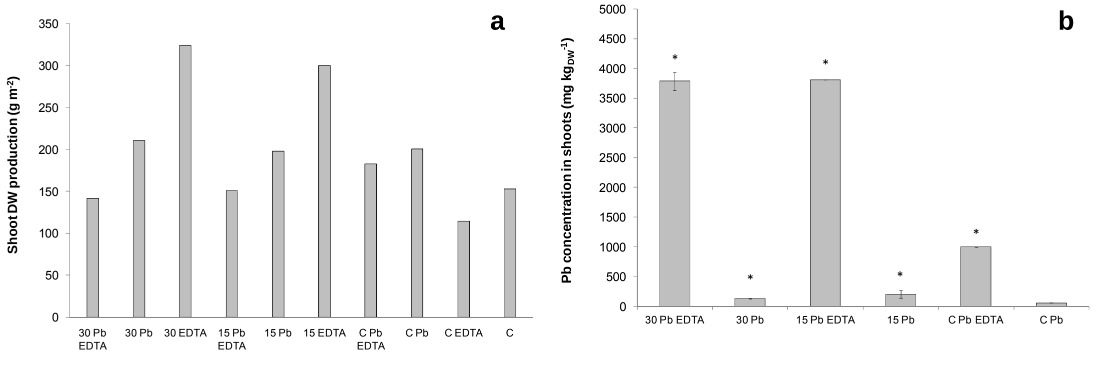

Figure 3: Figure 3: a) Biomass production (dry weight) and b) Pb concentration of shoot plants grown on contaminated soil (Pb 3,289 mg kg^{-1}) and clean soil for different test conditions

In terms of total leached Pb, results (Table 2) show a very high difference between treatments with and without EDTA addition (5.15 vs 0.017 g m^{-2}).

Table 2: Pb uptake of Brassica J. and specific amount of Pb in leachate

Treatment	Uptake ($g\ m^{-2}$)	Leachate ($g\ m^{-2}$)	R (L/U)
30-Pb-EDTA	537.54	2.54	4.725
30-Pb	28.69	0.015	0.523
15-Pb-EDTA	575.31	2.145	3.728
15-Pb	39. 80	0.013	0.327
C-Pb-EDTA	183.10	5.15	28.126
C-Pb	12.19	0.017	1.395

This highlights the possibility of reaching a significant metal migration only by an EDTA addition and remarks the risks related to potential groundwater pollution. Results also show that when an electric field (up to 1.1 V m^{-1}) was applied, a very significant reduction of Pb amount in leachate is achievable. In fact, observations indicate indeed a maximum reduction of the downward Pb migration of 57% for the 30-Pb-EDTA treatment compared to control.

4. Applicability of enhanced phytoextraction

Phytoextraction efficacy depends essentially both on the concentration of contaminants in the harvested biomass (uptake) and on the biomass production. Efficacy of the treatment can be expressed as percentage of metal annual reduction in soil [R(%)] (Duquène et al., 2009):

$$R(\%)=\frac{C_{plant}\cdot B_{plant}}{C_{soil}\cdot m_{soil}}\cdot 100 \qquad (1)$$

where C_{plant} is the metal concentration in shoot (g kg^{-1}), B_{plant} is the dry biomass production per year (kg m^{-2}), C_{soil} is the initial metal concentration in soil (g kg^{-1}) and m_{soil} is the mass of the contaminated soil layer (kg m^{-2}).

Residual metal concentration in soil after a selected phytoextraction time or the time required to reach a specific remediation target can be calculated according to the following equation:

$$C_{soil,t}=C_{soil,\ t=0}\cdot e^{\left(-\frac{C_{plant}\cdot B_{plant}}{C_{soil}\cdot m_{soil}}\cdot t\right)} \qquad (2)$$

where $C_{soil,t}$ is the heavy metal concentration in the soil (kg m^{-2}) at treatment time t (t) and $C_{soil,t=0}$ is the initial heavy metal concentration in the soil (t = 0) (kg m^{-2}).

Based on obtained uptake experimental data, the annual removal percentage (R) and the time (t_{10}) required to reach a 10% reduction in metal concentration in soil were calculated by Eq(1) and Eq(2) respectively for both enhanced (30-Pb-EDTA) and a conventional (C-Pb-EDTA) treatment.

Calculation was performed assuming a rooting depth of 20 cm, a soil density of 1,400 kg m^{-3} and an initial metal concentration in soil ($C_{soil,t=0}$) of 3,000 mg kg^{-1}. Based on data reported by Duquène et al. (2009) and the results obtained in the present experiment, a biomass production (B_{plant}) of 0.9 and 1.2 kg m^{-2} were assumed for (30-Pb-EDTA) and a conventional (C-Pb-EDTA) treatment, respectively. In the present experiment, calculated B_{plant} values were lower because the cultivation period was shorter (eight weeks instead of a full growing season).

An annual removal percentage (R) and time (t_{10}) of 0.429 % and 0.143 %, and of 23 and 70 y were obtained for the enhanced and the conventional phytoextraction treatment, respectively. Consequently, for the elctro-phytoextraction treatment the time was 3-fold lower than the conventional one. R values obtained for enhanced treatment are very high if compared to other literature findings (Blaylock et al., 1997; Quartacci et al., 2006) where phytoextraction treatments with amendment addition were investigated resulting in reduced treatment times, even if overall higher than those required for the application of other treatments such as chemical or physical ones.

5. Conclusions

Several conclusions can be drawn according to the experimental data presented above:

1. A 4-fold increase in plant uptake is achievable applying an EPD value up to 30 V jointly with EDTA addition.
2. The addition of EDTA or other chelants in soil is always needed to mobilize Pb in phytoextraction treatment (enhanced by electric field or not) but their concentration is minimized by electric field application.
3. The amount of Pb leached can be highly reduced by the presence of a horizontal electric field in soil.
4. A conditioning treatment of the soil is needed in order to maintain its pH values below neutral condition and therefore ensure a constant electric current flow in soil and a good plant biomass production.
5. The enhanced uptake values observed results in a reduction of the remediation time and this makes the phytoextraction treatment more efficient and cost-effective.
6. Obtained experimental data may represent the basis for a feasibility study of full-scale remediation treatment of a Pb polluted soil.

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