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Research article

Assisted green remediation of chromium pollution

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ABSTRACT

The effects of application of two anions commonly found in subsurface environments, phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}), on hexavalent chromium (Cr(VI)) uptake and translocation by *Zea mays*, were investigated using pot-culture experiments. The two anions were tested as potential agents to mobilize Cr(VI) from polluted soil (50, 75 and 100 mg kg^{-1} dw) at a dose of 16.7 mmol kg^{-1}. Metal uptake from soil to roots and subsequent transfer to shoots was discussed in terms of bioconcentration factor (BCF) and translocation factor (TF). The overall order of BCFs and TFs which resulted from this study was: $PO_4^{3-} > H_2O > SO_4^{2-}$; in the same time, metal concentration in plants tissues decreased in the order: root > stem > leaf. The present study suggests that PO_4^{3-} may be used as an environmentally compatible alternative to non-biodegradable synthetic chelants, to enhance the efficiency of Cr(VI) phytoextraction with *Z. mays*.

1. Introduction

Contamination of soils with metal ions has become a major environmental problem because, unlike most organic contaminants, they are non-biodegradable and can accumulate in living tissues (Ali et al., 2013). Hexavalent chromium (Cr(VI)) compounds, with high toxicity and mobility in the environment, have numerous industrial applications that may contribute to soil pollution (Gheju, 2011). Conventional soil remediation technologies (excavation, incineration, soil washing, soil flushing etc.) are not feasible for large-scale sites because they are expensive and cause disturbance to the soil microflora (Ali et al., 2013). Phytoremediation is a biological ”green” technology which consists in the use of living plants for the in situ treatment of contaminated soils, sediments, sludge and waters (Rezania et al., 2016). Because it has several important advantages (cost effective, non-disruptive to the soil, environmental friendly), this technology is considered a promising alternative to conventional remediation methods (Vigliotta et al., 2016). Phytoextraction, one of the phytoremediation techniques, is based on the extraction of pollutants from soil or water, followed by their concentration in the harvestable parts of plants (Bhargava et al., 2012). Unfortunately, biological limitations of the involved plants (slow growing rate, small biomass yield) lead to long times needed for the remediation of a contaminated site by phytoextraction (Rezania et al., 2016). In addition, a high percentage of all identified metal hyperaccumulators are suited only to tropical climate conditions (Gupta, 2013). Therefore, in last years, several approaches have been employed to overcome these disadvantages. On the one hand, the use of agronomic crops, with large biomass production and rapid growth, has been proposed as a viable substitute to hyperaccumulator plants (Ciura et al., 2005). On the other hand, different strategies have been used to enhance the efficiency of phytoextraction, including (1) addition of organic or inorganic complexing reagents (Wang et al., 2017), (2) inoculation of plants with rhizospheric microorganisms resistant to metals (Silva et al., 2014), (3) rotation of summer metal-accumulating crops with winter crops (Fumagalli et al., 2014), (4) co-planting of a metal hyperaccumulator plant with a low metal accumulating crop (Wu et al., 2007), (5), co-application of nano-particles (Liang et al., 2017), and (6) development of transgenic plants with improved phytoremediation capabilities (Cherian and Oliveira, 2005). *Zea mays* is a crop plant with rapid grow, large biomass yields (Wuana and Okieimen, 2010) and a root system that extends approximately 1.5 m laterally and 2.0 m downwards (Plessis, 2003). To the best of our knowledge, reports about Cr(VI) phytoextraction using *Z. mays* are few. Experiments carried out by Mishra et al. (1995) indicated that while in roots the uptake of chromium was greater when irrigating water contained Cr(III), a higher uptake in aerial parts of

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the plants was observed when the initial supply was Cr(VI). Shams et al. (2010) found that even though *Z. mays* showed high tolerance towards chromium, only negligible metal concentrations were detected in leaves. The synergic activity of Streptomyces sp. MC1 actinobacteria and *Z. mays* was successfully evaluated by Polti et al. (2011), as a strategy to reduce the bioavailable Cr(VI) fraction in soil. Chigbo and Batty (2014) have shown that joint contamination of chromium and benzo[a]pyrene had an enhancing effect on the accumulation and translocation of chromium in *Z. mays*. Analysis of *Z. mays* grown on anthropogenically polluted soil indicated that, since the accumulation rate in the seeds was low, it seems to be no health risk for animal breeding and population due to the consumption of maize grown in the polluted area (Wahsha et al., 2014). Almaroai et al. (2012) studied the effect of co-presence of organic synthetic chelants and low-molecular-weight organic acids on chromium solubilization, uptake, and translocation in maize, showing that EDTA and citric acid were the most efficient. To the authors knowledge, the use of two inorganic anions commonly found in subsurface environments, phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}), as amendments for enhanced phytoextraction of Cr(VI) with *Z. mays* has not been researched. Previous studies have revealed that anions present in the subsurface environment, such as PO_4^{3-}, may compete with Cr(VI) for sorption sites on redox-active minerals (Brown et al., 2001). Therefore, such anions could lead to a change in the mobility and bioavailability of Cr(VI) in soil, with possible positive effects on the phytoremediation process. Starting from this presumption, the aim of our study was to examine the influence of PO_4^{3-} and SO_4^{2-} application on the uptake and translocation of Cr(VI) by *Z. mays*.

2. Materials and methods

2.1. Soil sampling and preparation

Soil for this study was collected from the top 15 cm at a public garden in Timisoara. The characteristics of the soil are given in Table S1, supplementary material. The soil was air-dried at room temperature and ground to pass through a 2 mm mesh. Then, 0.5 L plastic pots were filled with 300 g soil, which was rehydrated with 100 mL solution of appropriate Cr(VI) concentration, in order to yield Cr(VI) concentrations of 50, 75 and 100 mg kg^{-1} dry weight (dw) soil (Table 1). Control pots were similarly prepared, by mixing soil with distilled water instead of Cr(VI) solution. The soil was then allowed to equilibrate for a period of 15 days, and 10 seeds of *Z. mays* were sown in each pot, at constant temperature environment (22 ± 2 °C). Three irrigation solutions were used: (1) tap water, (2) 0.05 M sodium phosphate (Na_3PO_4) prepared with tap water, and (3) 0.05 M sodium sulfate (Na_2SO_4) prepared with tap water. Twenty five milliliters irrigation solutions were applied to pots weekly after plants have emerged from soil, as shown in Table 1.

Table 1
Experimental operating parameters.

Irrigation solution	Cr(VI) soil concentration (mg kg^{-1} dw)	Dose of anion applied to soil (mmol kg^{-1} dw)
Na_3PO_4 0.05 M	ND	16.7
	50	16.7
	75	16.7
	100	16.7
Na_2SO_4 0.05 M	ND	16.7
	50	16.7
	75	16.7
	100	16.7
Tap water	ND	0
	50	0
	75	0
	100	0

ND = not detectable.

2.2. Analysis of Cr(VI) in soil and plants

Plants were harvested 5 weeks after emergence, divided into roots, stems and leaves, thoroughly washed with deionized water, and air-dried at room temperature four weeks. Alkaline digestion method 3060A of EPA was followed for the extraction of Cr(VI) from soil and plants (USEPA, 1996). Then, Cr(VI) concentration was measured in aqueous extracts by optical emission spectrometry (Agilent 4100 MP-AES). The mean values of two replicates are reported for each analysis. Two-way ANOVA (Microsoft Excel 2010 statistical tool) was performed to test the significance of each of the two independent variables (irrigation treatment, Cr(VI) soil concentration) for the dependent variable (Cr(VI) concentration in plant tissues), at a 95% confidence level. Selective extractions from soil were performed in order to assess how chromium was bound (supplementary material). The bioconcentration factor (BCF) and translocation factor (TF) were used to assess the ability of plants in accumulating Cr(VI) and the allocation of Cr(VI) in plant tissues, respectively (supplementary material).

3. Results and discussion

The results of selective extraction analysis (Fig. 1) revealed a high bioavailable Cr(VI) fraction; this result is consistent with previous reports suggesting that in neutral-to-alkaline soils (our soil: pH 6.8) Cr(VI) exists mostly in soluble, but also in moderately-to-sparingly soluble chromates (Polti et al., 2011). *Z. mays* seeds showed germination of 100%, irrespective of the Cr(VI) soil concentration and nature of irrigation solution. Plants grew relatively normally in the Cr(VI) contaminated soil; none of the treatments significantly affected plant height (Fig. 2); differences were, however, noticed with regard to plant biomass (Fig. 3). Additionally, pale appearance of some leaves was observed only for the highest concentration of Cr(VI) in soil. Control plants (grown on original, non-spiked soil) contained no Cr, regardless of the irrigating solution used (data not shown). This is in accord with the analysis of

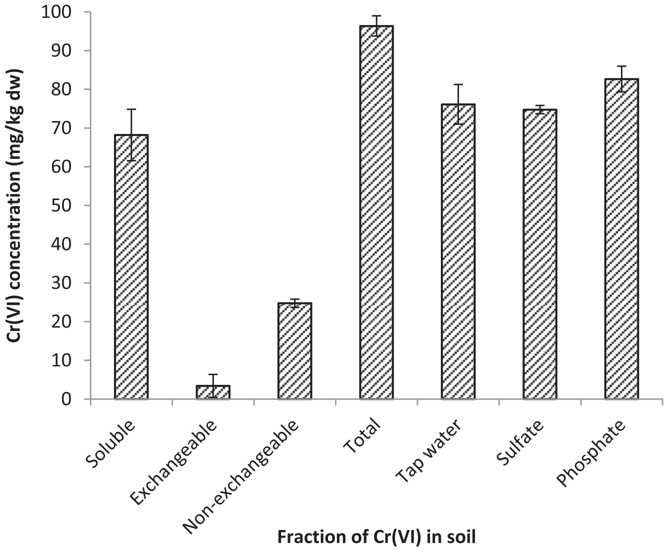

Fig. 1. Forms of Cr(VI) in soil contaminated at level of 100 mg/kg.

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