INFLUENCE OF CHROMIC IONS IN MAIZE CULTIVATION (*ZEA MAYS*) AFTER THE ADDITION OF NATURAL MINERALS AS SOIL AMENDMENTS

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ABSTRACT

The present study examines the efficiency of natural materials regarding the retention of trivalent and hexavalent chromium, from maize (*Zea Mays*). The natural materials that have been used as soil amendments were zeolite, bentonite and goethite. Specifically, 1.0 kg of soil and 1.0 g of each soil amendment were added in plant pots. Two doses of chromic ions, i.e. 50 mg Cr(III) L^{-1} in the form of $Cr(NO_3)_3$ or 1 mg Cr(VI) L^{-1} in the form of CrO_3 were added to plant pots. Then, plant seeds of maize crops were cultivated. Five treatments were realized for each dose of chromic ions (5 x 2) but only three contained soil amendment. Each treatment was repeated three times. The statistical results of the greenhouse experiments were analyzed by LSD test with significance 95% ($p<0.05$) using Stratgraphics Plus 8.1 package. According to the results, the addition of trivalent chromium in soil has shown that zeolite was the only soil amendment that increased the dry weight of biomass. Zeolite and bentonite as soil amendments reduced significantly the total chromium in plants compared to all the other treatments after the addition of 50 mg Cr(III) L^{-1} to soil. The addition of hexavalent chromium in soil has shown that bentonite was the only soil amendment that increased the dry weight of biomass and the plants' height. All soil amendments reduced to zero the total chromium concentration measured to plants after the addition of 1 mg Cr(VI) L^{-1} to soil.

Keywords: Zeolite, bentonite, goethite, maize, soil amendments

1. Introduction

Industrial wastewaters and polluted soils often contain high amounts of heavy metals that would endanger public health and the environment. Heavy metals are not biodegradable and accumulate in living organisms causing diseases (Barros *et al*., 2004). The emission of liquid effluents from industries such as Cr, Cu, Zn, Ni and Cd are consider as prior metals for potential hazard to fauna and flora. Cadmium and chromium are the most toxic metals compared to all others. Chromium oxidation states vary from -2 to +6 but only +3 and +6 are stable in common environmental conditions. Hexavalent chromium presents high mobility and toxicity leading to human cancer while trivalent chromium is less toxic and immobile (López-Luna *et al*., 2009). Cr(VI) can create complexes with chemical species in the soil. The reduction of oxidation state from Cr(VI) to Cr(III) due to the presence of organic matter has been reported in the past (Mishra *et al*., 1995).

The proposed methods for heavy metal removal from wastewaters, groundwaters and topsoil are separated on chemical and microbiological ones. Methods such as chemical extraction with inorganic and organic acids, elektrokinetic treatment, microbiological leaching have been tested in the past (Sprynskyy, 2009; Wozniak and Huang, 1982; Tyari *et al*., 1988). The application of different new additives to waters and soils for the removal or immobilization of the excessive amounts of heavy metals is a promising new research field.

The objective of this study is to evaluate the removal of chromic ions from soils cultivated with maize using soil amendments such as zeolite, bentonite, goethite and zeolite-goethite composites.

2. Materials & methods

2.1. Natural minerals as adsorbents

The examined adsorbents were zeolite (Z), bentonite (B) and goethite (G). Zeolite and bentonite were bought from S&B Company (Greece). Goethite was prepared in the laboratory according to Schwertmann and Cornell method (2000).

2.2. Soil experiments

Greenhouse experiments were conducted for the determination of chromic ions' influence on soil cultivated with maize after the use of zeolite (Z), bentonite (B) and goethite (G). Specifically, 1.0 kg of soil, 1.0 g of each soil amendment based on zeolite (Z), bentonite (B) and goethite (G) were used. Two doses of chromic ions, i.e. 50 mg Cr(III) L^{-1} in the form of $Cr(NO_3)_3$ and 1 mg Cr(VI) L^{-1} in the form of CrO_3 were added to plant pots. Then, plant seeds of maize crops were cultivated (Table 1).

Five treatments were realized for each dose of chromic ions (5 x 2) but only three contained soil amendment. Each treatment was repeated three times. As a consequence thirty treatments were realized (eighteen with soil amendments called as Z or G or B according to the amendment used each time, three with no soil amendment but with Cr(III) called as M-Cr(III), three with no soil amendment but with Cr(VI) called as M-Cr(VI) and six with no soil amendment and no chromic ions called as M). Forty five days after germination the plants were collected, washed with dilute 1 M HCL and then with deionized water. The plants were dried in an oven at 70°C for 48 h, their above ground biomass weight and height were measured and the samples were milled into fine pounder and stored in plastic bags for further analysis. Total chromium in crops were determined with Perkin Elmer 3300 atomic absorption spectrophotometer after the dry ashing procedure of 1 g of each plant sample at 520°C for 24 h and the ash washing with 20 mL of 20% HCL (Jones *et al*., 1990). Chromium availability was determined with the soil to plant transfer coefficient (T_c) which was calculated according to the equation, $T_c = (PQ_t - PQ_c) / AD$, where PQ is the plant quantity of Cr (mg per pot), t and c denote treatment and control, AD is the added Cr (mg per pot). PQ values were calculated as the result of the Cr concentration in plant (mg Cr per kg in plant) multiplied by the above ground plant dry matter weight (g per pot).

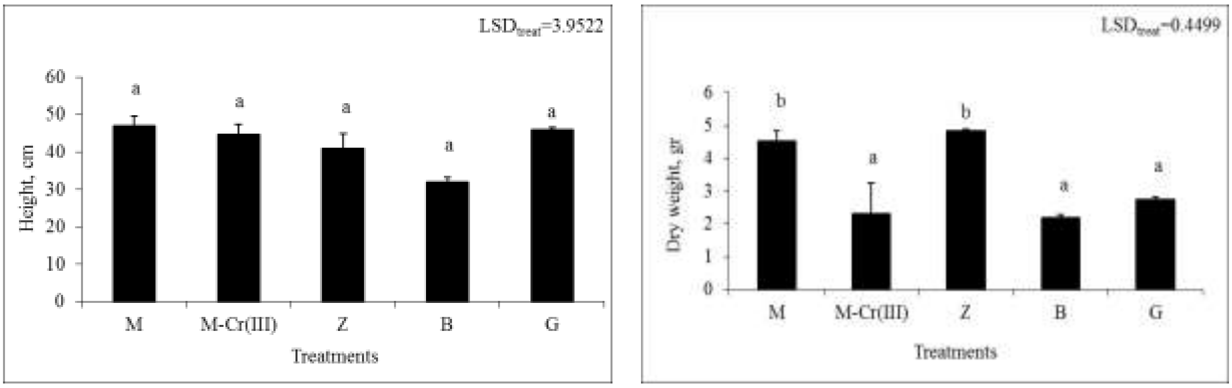
Table 1: Schematic representation of greenhouse experiments

Treatment	Amendments			Chromic ions	
	Z	B	G	Cr(III)	Cr(VI)
1	x	-	-	x	-
2	-	x	-	x	-
3	-	-	x	x	-
4	-	-	-	x	-
5	-	-	-	-	-
6	x	-	-	-	x
7	-	x	-	-	x
8	-	-	x	-	x
9	-	-	-	-	x
10	-	-	-	-	-

The experiments took place from May to June 2010 at the greenhouse of the School of Agriculture Sciences of the University of Thessaly. The physicochemical characteristics of soil, which was selected from Velestino area in Volos (Central Greece), show soil pH equal to 8.82, low concentrations of organic matter (<2.3%) and nitrogen (<0.22%). The water storage capacity of soil remained stable at 65% and the temperature ranged from 25-35°C. The statistical results of the greenhouse experiments were analyzed by LSD test with significance 95% ($p<0.05$) using Stratgraphics Plus 8.1 package.

3. Results & discussion

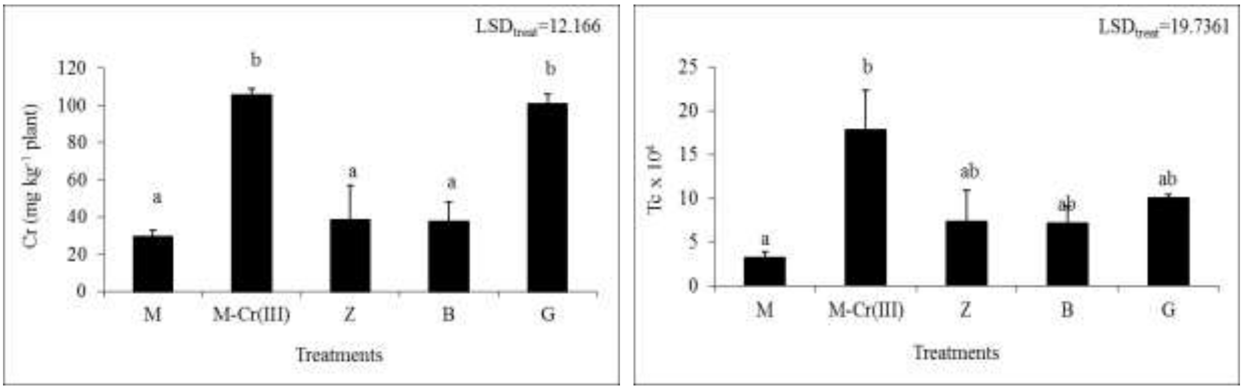
3.1. Plant Characteristics and Cr(III) transfer



(a) (b)

Figure 1: (a) Height and (b) dry weight of the plants for the five different treatments, where treatments with different letters have significant differences at $p<0.05$. Bars represent standard errors of the mean of the replicates of each treatment.

According to the statistical analysis of the height of plants for different soil amendment, there were no significant differences between the M control and the Cr treatments (M-Cr(III), Z, B, G) in plants' height (Fig. 1a). Comparing the dry weight of plants in the different treatments, it seems that the dry weight of plants decreased significantly at M-Cr(III) compared to the M control indicating the high levels of Cr(III) on maize causing toxic results to plant (Fig.1b). From the three soil amendments, only zeolite increased the dry weight of maize plants compared to the M-Cr(III) treatment. According to Gollovatyj *et al*. (1999) the effect of chromium during the early plant growth and development has as a result the reduction of yield and biomass of corn plants due to poor production and storage of nutrients in the storage parts of the plant. The Shankera *et al*. (2005) reported that the production of maize and barley decreased due to the presence of chromium.

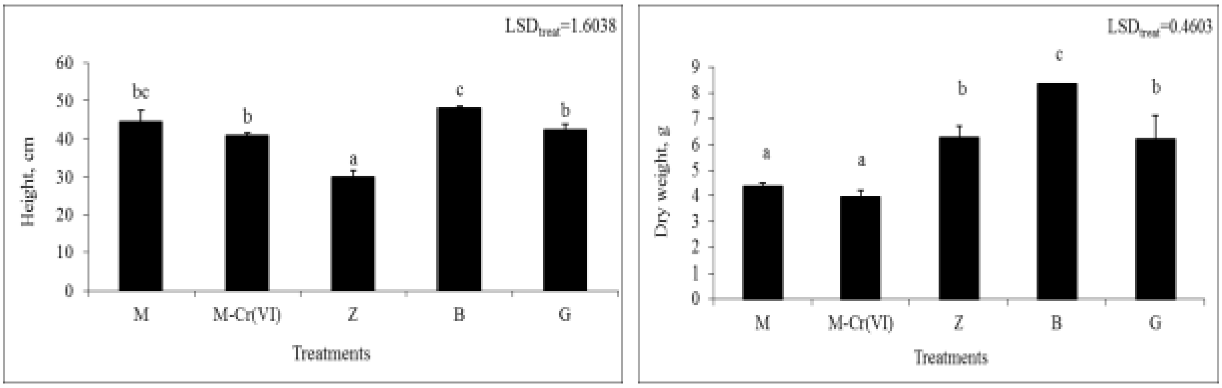


(a) (b)

Figure 2: (a) Total chromium in the plants grown and (b) soil-to-plant transfer coefficients (mg of Cr(III) in plant per kg of added Cr(III) in soil) for the five different treatments, where treatments with different letters have significant differences at $p<0.05$. Bars represent standard errors of the mean of the replicates of each treatment.

Total Cr in plant biomass increased in the M-Cr(III) treatment compared to the M control (Fig.2a). Zeolite and bentonite additions in soil as amendments reduced total Cr levels in plant compared to M-Cr(III). On the contrary the use of goethite as soil amendment increased the concentration of total chromium in plants. Mishra *et al*. (1995) studied the uptake of chromium from maize which has grown in soil with pH 8.8. Chromium was added with water irrigation in four proportions (0.5, 1.0, 5.0 and 25.0 μg/mL) in all pots. The concentration of trivalent chromium in the plants of the four doses were 47, 115, 307 and 1586 μg Cr(III)/g dry weight, respectively. As a conclusion, the increased concentration of chromium in soil has as a result the increased concentration of trivalent chromium in plants, which was confirmed in the study with the M- Cr(III) treatment. Chromium quantity transfer coefficients (T_c) was higher at M-Cr(III) treatment than all the others (Fig. 2b). The addition of soil amendments reduced the soil-to-plant transfer coefficients compared to M-Cr(III).

3.2. Plant Characteristics and Cr(VI) transfer

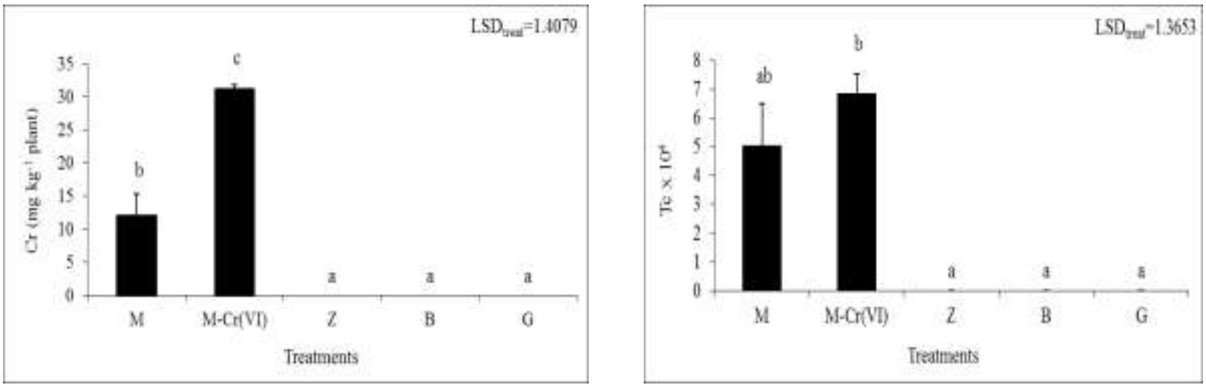


(a) (b)

Figure 3: (a) Height and (b) dry weight of the plants for the five different treatments, where treatments with different letters have significant differences at $p<0.05$. Bars represent standard errors of the mean of the replicates of each treatment.

According to the statistical analysis of the height of plants for different soil amendment (Fig.3a), the plant height decreased at M-Cr(VI) treatment by 9% compared to the M control. Bentonite was the only amendment, which increased significantly the plants' height. Mallick *et al.* (2010) found that the addition of hexavalent chromium in soil where maize was cultivated led to short and dark plant roots with few root hair. Also Cr(VI) addition reduced the shoot length due to Cr(VI) toxicity. The dry weight of each plant decreased at M-Cr(VI) treatment by 10.6% compared to the M control (Fig. 3b). Dry weight increased significantly after the addition of zeolite (Z), bentonite (B) and goethite (G) as soil amendments compared to the M and M-Cr(VI) treatments. Especially, the addition of bentonite increased the dry weight by 52.5% compared to the M-Cr(VI) treatment. Wyszkowski and Radziemska (2010) studied the effect of hexavalent chromium in maize and the impact of zeolite addition. Using various doses of chromium, from 0 to 150 mg kg^{-1} found that the increase of chromium concentration, increased the biomass of the plants, while zeolite addition has no positive effect on the biomass in contrast to our results in which zeolite addition increased the plant dry weight by 38.1% compared to the M-Cr(VI) treatment.

Total chromium in plant biomass increased significantly at M-Cr(VI) treatment compared to the M treatment (Fig. 4a). The use of zeolite (Z), bentonite (B) and goethite (G) adsorbed the whole quantity of chromium in soil leading to zero total chromium concentration in the plant. Gheju *et al*. (2009) added 40 mg Cr(VI) kg^{-1} of soil where maize cultivated. They found that the plant had a concentration of 15.1 mg Cr(VI) kg^{-1} of plant. Chromium quantity transfer coefficients (T_c) was higher at M-Cr(VI) treatment compared to all the others (Fig. 4b). All soil amendments reduced to zero the soil-to-plant transfer coefficients compared to the M and M-Cr(VI) treatments indicating that total chromium concentration in plants was zero.



(a) (b)

Figure 4: (a) Total chromium in the plants grown and (b) soil-to-plant transfer coefficients (mg of Cr(VI) in plant per kg of added Cr(VI) in soil) for the five different treatments, where treatments with different letters have significant differences at $p<0.05$. Bars represent standard errors of the mean of the replicates of each treatment.

4. Conclusions

The following conclusions should be mentioned:

- The addition of trivalent chromium in soil has shown that zeolite was the only soil amendment that increased the dry weight of biomass.
- Zeolite and bentonite as soil amendments reduced significantly the total chromium in plants compared to all the other treatments after the addition of 50 mg Cr(III) L^{-1} to soil.
- The addition of hexavalent chromium in soil has shown that bentonite was the only soil amendment that increased the dry weight of biomass and the plants' height.
- All soil amendments reduced to zero the total chromium concentration measured to plants after the addition of 1 mg Cr(VI) L^{-1} to soil.

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