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Analyse, Méthodologies de Traitement et Réhabilitation des Sols et Eaux Souterraines Pollués
Analysis, Treatment Methodologies and Remediation for Polluted Soils and Groundwater

Phytoremediation of Cr(VI) polluted soil

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Chromium natural occurence

	Abundance
Universe	15,000 ppb
Sun	20,000 ppb
Meteorites	3,000 ppm
Air	0.01-0.03 µg/m^3
Sea water	0.3 ppb
Rivers	1 ppb
Continental crust	80-200 ppm
Ultramafic igneous rocks	1,000-3,400 ppm
Basaltic igneous rocks	40-600 ppm
Granitic igneous rocks	2-90 ppm
Shales and clays	30-590 ppm
Coals	10-1,000 ppm

Chromium natural occurence in food

Food	Mean concentration (µg/kg)
Fresh vegetables	30-140
Fresh fruits	90-190
Dairy products	100
Chicken eggs	160-520
Whole fish	50-80
Meat	110-230
Seafoods	120-470
Grains and cereals	40-220
Refined sugar	20
Cigarette tobacco	240-14,600

Chromium natural occurence in human body

Tissue / fluid	Mean content
Human body	30 µg/kg (dry weight)
Serum	0.006 µg/L
Urine	0.4 µg/L
Breast milk	0.3 µg/L
Lung	203 µg/kg (wet weight)
Hair	0.234 mg/kg
Nail	0.52 mg/kg

Sources of chromium soil contamination

- Chrome electroplating;
- Wood preserving;
- Leather tanning;
- Manufacturing of dyes and pigments;
- Textile industries (dyes);
- Disposal of commercial products containing chromium;
- Disposal of chromium waste from industry;
- Disposal of coal ash from electric utilities;
- Combustion processes (burning of coal and oil);
- Sewage sludge and municipal refuse incineration;
- Steel production;
- Chemical manufacturing and use of compounds containing chromium;
- Refractory production;
- Cement production.

Chromium in the environment

Although chromium can exists in oxidation states ranging from (-IV) to (+VI), in natural environments Cr exists in two main oxidation states: Cr(+VI) and Cr(+III), characterized by different chemical behaviour and toxicity.

Chromium (VI) chemical behaviour

pH < 6.5: $HCrO_4^{-}$ / $Cr_2O_7^{2-}$

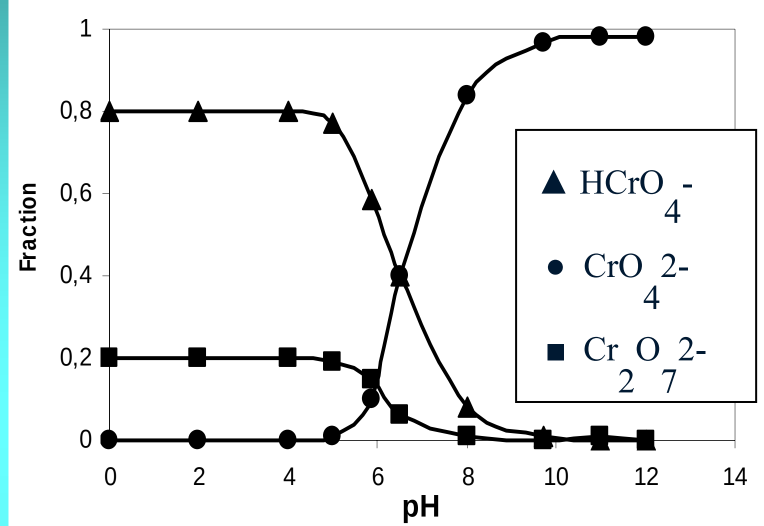
pH > 6.5: CrO_4^{2-}

pH < 0: H_2CrO_4, $Cr_3O_{10}^{2-}$

$Cr_4O_{13}^{2-}$

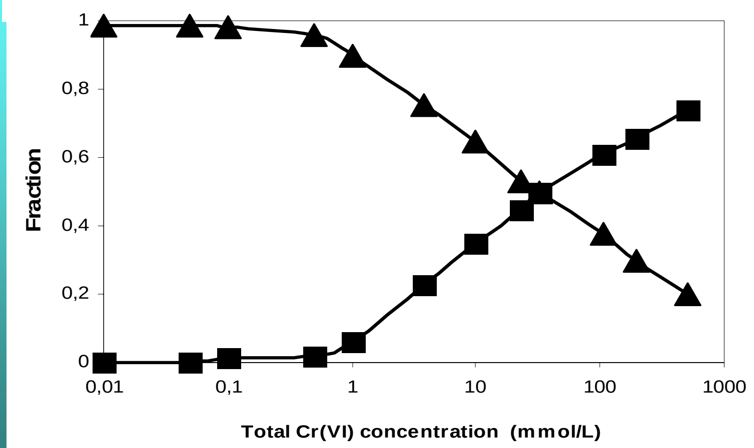
Significant solubility

Significant mobility



Distribution of Cr(VI) species as function of pH

$C_{Cr(VI)}$ = 5 mmol/L



Distribution of Cr(VI) species as function of total Cr(VI) concentration, pH 4

Chromium (III) chemical behaviour

pH < 3.0: Cr^{3+}

pH = 3.0 - 5.5: $Cr(OH)^{2+}$

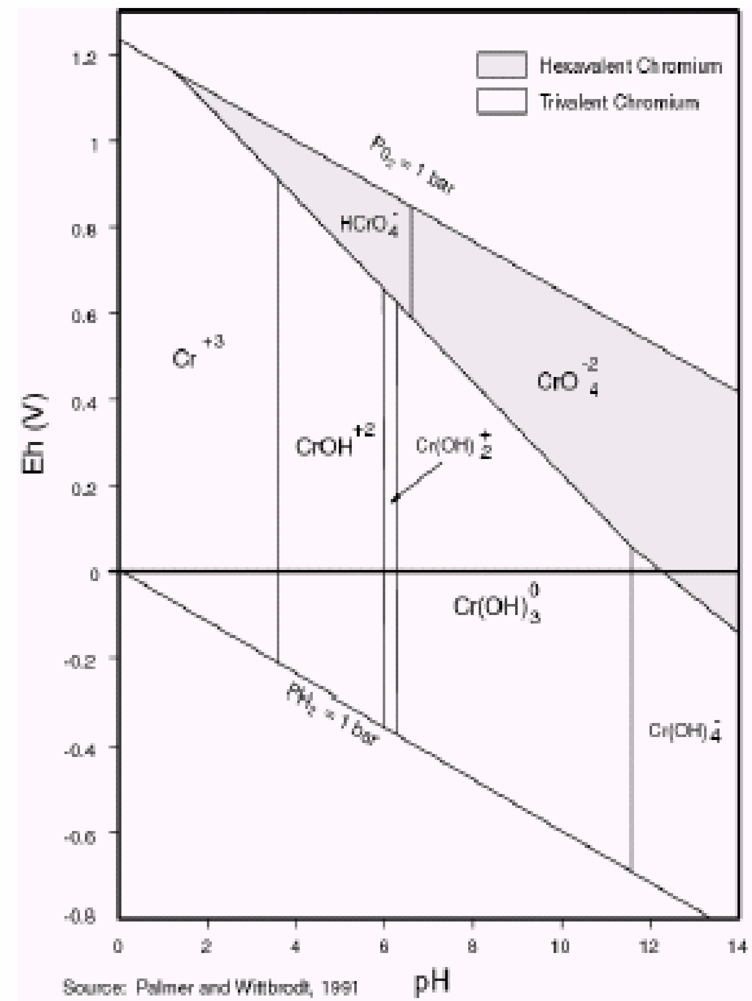
pH = 5.5 - 6.0: $Cr(OH)_2^{+}$

pH = 6.0 - 11.5: $Cr(OH)_3$, Cr_2O_3

pH > 11.5: $Cr(OH)_4^{-}$

Low solubility

Low mobility



Chromium (VI) toxicological behaviour

- Highly toxic to humans, animals, plants and microorganisms;
- Known human carcinogen by the inhalation route of exposure;
- Animal carcinogen by the oral route of exposure.

Chromium (III) toxicological behaviour

- Less toxic than Cr(VI);
- No evidence of Cr(III) carcinogenity;
- In small amounts, Cr(III) is an essential micronutrient for lipid, protein and fat metabolism in animals and humans.

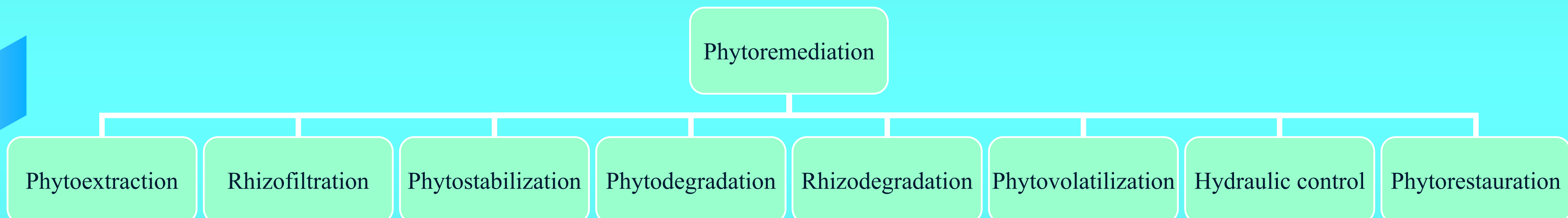
Traditional soil remediation techniques

- Soil flushing
- Soil washing
- Solidification/Stabilization
- Excavation and landfilling
- Vitrification
- Incineration
- Electrokinetic treatment

In most cases, these techniques are expensive and technically limited to highly polluted and relatively small areas. Therefore, when vast areas of land have been contaminated, alternative remediation strategies are necessary.

Soil phytoremediation

The use of plants for the in situ remediation of soil contaminated with organic or inorganic pollutants



Phytoextraction

1. Extraction and accumulation of metals in plant tissues;
2. Harvesting of the above ground plant material;
3. Recovery of high-price metals from the harvested plants (phytomining), or

   Burning of the harvested plants and disposal under controlled conditions (usual metals).

Basic conditions of plants used for metal phytoextraction

- Tolerate, uptake and accumulate high metal concentrations (hyperaccumulator plants);
- High soil-to-shoot transfer factors;
- High biomass production;
- Fast grow.

Hyperaccumulator plants

Disadvantages:

- High percentage of hyperaccumulators are found exclusively in tropical regions; therefore, they don't grow, or grow slowly, under temperate climate;
- Low biomass;
- From over 400 hyperaccumulator species identified, more than 80% accumulate Ni rather than other metals.

Most hyperaccumulator plants cannot remove large quantities of heavy metals in a given period of time per unit of land area.

Species that accumulate lower metal concentrations but are high biomass producers may also be used for phytoextraction.

Cr(VI) hyperaccumulator plants

- Leptospermum scoparium (New Zealand tea tree) (Lyon et al., 1971);
- Commelina communis L (Asiatic dayflower) (Tang et al., 2002);
- Pteris vittata (Chinese brake fern) (Su et al., 2005);
- Salsola kali (Tumbleweed) (Gardea-Torresdey et al., 2005);
- Leersia hexandra Swartz (Southern cutgrass) (Zhang et al., 2007);
- Brassica juncea (Indian mustard) (Hema et al., 2008).

Objective of the study

To investigate the capacity of *Zea mays* (corn), a crop plant with large yields and fast growth, to remediate hexavalent chromium polluted soils.

Materials and methods

- Soil sample was collected from the arable horizon (0-30 cm depth) of a public garden located in Timisoara;
- The experiment was conducted in 500 mL plastic pots filled with 300 g of homogenized air-dried soil;
- Potassium dichromate solution was applied to soil, yielding the concentrations of 20, 40 and 60 mg Cr(VI) /kg dw soil;
- The soil was then allowed to equilibrate for a period of 15 days; Afterwards, 10 seeds of *Zea mays* were sown on the surface of each pot;
- Pots were irrigated with water once a week with deionised water;
- After 40 days of Cr(VI) exposure, plants were harvested, separated in different parts (roots, stems and leaves) and cleaned;
- The plant parts were dried in an oven at 80^{o} C for two days and then ashed in a muffle furnace at 600°C for 6 h;
- The ash was dissolved in a mixture of 2 M HCl and 1 M HNO_3 and analyzed for Cr(VI) by the 1,5-diphenylcarbazide colorimetric method.

Results

Cr(VI) concentration in plant tissues, as a function of Cr(VI) concentration in soil

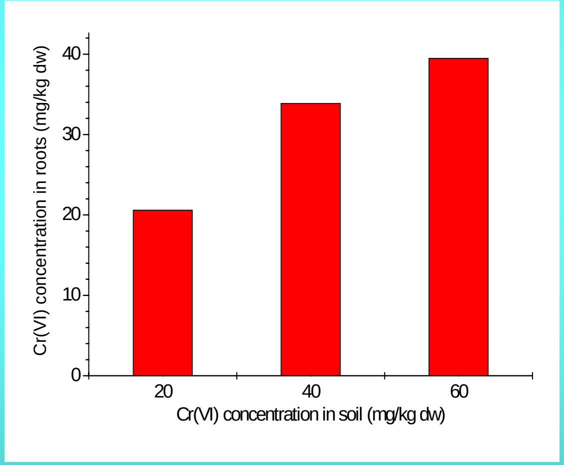


Figure 1. Cr(VI) concentration in root tissues, as a function of Cr(VI) concentration in soil

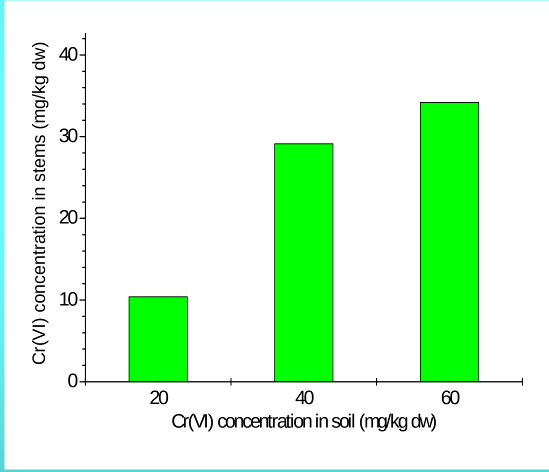


Figure 2. Cr(VI) concentration in stem tissues, as a function of Cr(VI) concentration in soil

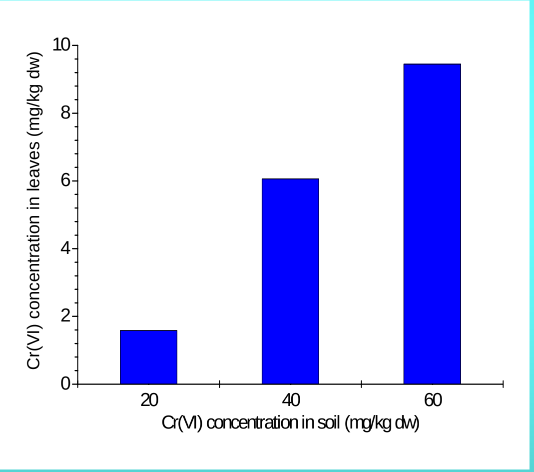


Figure 3. Cr(VI) concentration in leaf tissues, as a function of Cr(VI) concentration in soil

Results

Cr(VI) concentration in plant tissues, as a function of plant part

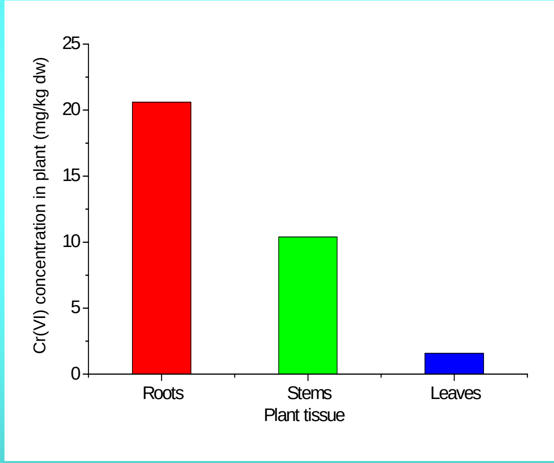


Figure 4. Cr(VI) concentration in plant tissues, at 20 mg Cr(VI) /kg dw soil

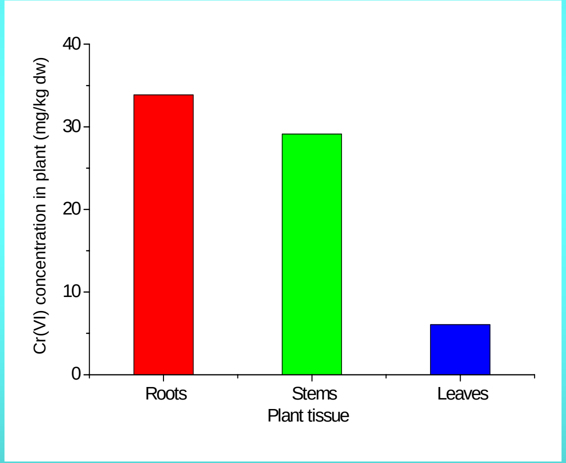


Figure 5. Cr(VI) concentration in plant tissues, at 40 mg Cr(VI) /kg dw soil

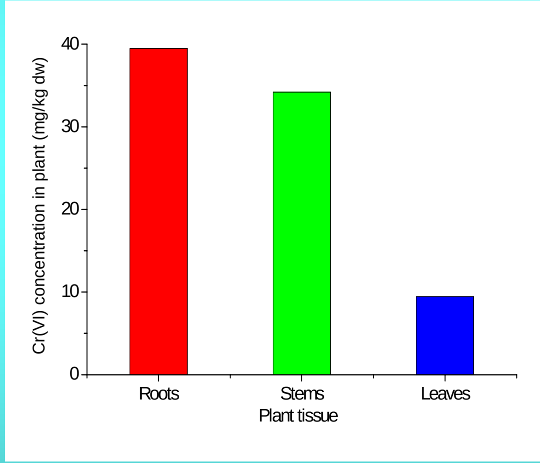


Figure 6. Cr(VI) concentration in plant tissues, at 60 mg Cr(VI) /kg dw soil

Conclusions

- Hexavalent chromium is a toxic metal and needs to be removed from polluted soils;
- Most currently available soil remediation technologies are uneconomical; therefore, they are limited to small areas;
- Phytoextraction can represent a cheaper alternative soil remediation method;
- There are no well established Cr(VI) hyperaccumulator plants;
- This study investigated the capacity of *Zea mays* (corn), a crop plant with large yields and fast growth, to remediate hexavalent chromium polluted soils;
- Cr(VI) concentration in plant organs increased with the increase of Cr(VI) soil concentration;
- Cr(VI) was immobilized mainly in roots, and its concentration in plant organs decreased in the following order: roots > stems > leaves;
- Cr(VI) was poor translocated from the roots to the shoot; however, the increase in Cr(VI) soil concentration improved the translocation of Cr(VI) to the above ground plant parts;
- Although *Zea mays* seem to be a low hexavalent chromium-accumulating plant, it could be a potential phytoremediator of contaminated soils because it's a plant specie with large biomass and fast growth.

Future work

- Since no visible phytotoxic symptoms were observed on *Zea mays* over the Cr(VI) concentration range 20 - 60 mg/kg d.w. soil, separate laboratory studies will be conducted on this plant with the aim to investigate the phytoremediation of soils affected by higher amounts of hexavalent chromium.

- Long term field studies will be conducted, which will allow plants to reach their maturity, in order to determine the capacity of mature plants to extract and accumulate hexavalent chromium from polluted soils.

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