CHROMIUM : AS A POLLUANT

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Key words: Chromium, Toxicity, Bioremediation, Chelation.

ABSTRACT

Contamination of chromium is considered a serious environmental pollutant due to wide industrialization. The chromium concentration in plants 0.006 to 18 ppm and soil ranging from 10 to 50 ppm depending on parent material. According to Environmental Protection Agency (EPA) < 0.1 ppm concentration of chromium in drinking water is permissible on the basis of health considerations. Toxicity of Cr to plants depends on its valence state Cr (VI) is highly toxic & mobile, where as Cr (III) is less toxic. Cr (VI) is present as either dichromate \((\text{Cr}_2\text{O}_7^{2-})\) in acidic environments or as chromate \((\text{CrO}_4^{2-})\) in alkaline environments. Chromium toxicity affects the plant dry matter yield as well as some physiological processes such as photosynthesis, mineral nutrition etc. Remediation of soils contaminated with Cr using bioremediation, chelation and remediation by reduction techniques appears to have great potential for clean up of Cr - Contaminated soils and water.

INTRODUCTION

Chromium was first discovered in the Siberian red lead ore (crocoite) in 1798 by the French chemist Louis - Nicholas Vauquelin. Chromium is a greek word (Chroma = colour), which means coloured compounds. Due to wide industrial use, chromium is considered a serious environmental pollutant. Contamination of soil and water by chromium is of recent concern chromium occurs nature in bound forms that constitute 0.1 - 0.3 mg kg\(^{-1}\) of the Earth’s Crust. A maximum acceptable concentration of 0.05 mg L\(^{-1}\) (50 mg L\(^{-3}\)) for
Chromium in drinking water has been established on the basis of health considerations. Toxicity of chromium to plants depends on its valence state, Cr (VI) is highly toxic and mobile (which are usually occurs associated with oxygen as chromate (CrO$_4^{2-}$) or dicromate (Cr$_2$O$_7^{2-}$)). Whereas, Cr (III) is less mobile, less toxic and is mainly found bound to organic matter in soil and aquatic environments (Becquer et al. 2003). Chromium is a major source of aquatic pollution in India but the main areas for their concentration are TamilNadu, Uttar Pradesh and West Bengal.

**Position in the periodic table**

Chromium (atomic number 24, atomic mass 51.99) has an outer electronic configuration of 3d$^5$ 4s$^1$ and belongs to VI B group or chromium group on the periodic table. In soil the ionic form of chromium that is observed by plants are Cr$^{+3}$ and Cr$^{+6}$. Cr (III) was absorbed more rapidly than Cr (VI). The different oxidation state of chromium and its compounds is given in below (Table 1).

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Oxidation state</th>
<th>Electronic configuration</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>O</td>
<td>(Ar) 4s$^2$ 3d$^5$</td>
<td>Cr (Co)$_6$</td>
</tr>
<tr>
<td>2.</td>
<td>+1 (Unstable)</td>
<td>(Ar) 3d$^5$</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>+2 (Chromium)</td>
<td>(Ar) 3d$^4$</td>
<td>Cr, Cr$_2$O$_7$, Cr$_2$O$_6$, Cr$_2$O$_4$ Crystalloid, CrO$_2$, Cr$_2$O$_3$, Cr$_2$O$_4$, Cr$^{+6}$</td>
</tr>
<tr>
<td>5.</td>
<td>+4 (Unstable)</td>
<td>(Ar) 3d$^2$</td>
<td>CrF$^+$, Cr$_2$O$_7$, Cr$_2$O$_4$, Cr$_2$O$_3$, Cr$_2$O$_4$, Cr$^{+6}$</td>
</tr>
<tr>
<td>6.</td>
<td>+5 (Unstable)</td>
<td>(Ar) 3d$^1$</td>
<td>CrF$_5$</td>
</tr>
<tr>
<td>7.</td>
<td>+6 (Stable)</td>
<td>(Ar)</td>
<td>K$_2$Cr$_2$O$_7$, K$_2$Cr$_2$O$_4$, Cr$^{+6}$</td>
</tr>
</tbody>
</table>

Note: Cr$^{+6}$ are maximum stable, because it is not both oxidising and reducing agent.

**Chromium in the environment**

Chromium is found in all phases of the environment including air, water and soil (Table 2).

The chromium concentration in soil ranges from 10 to 50 mg kg$^{-1}$ (Adriano, 1986). Cr concentration varies widely in the atmosphere from background concentration of 5.0 x 10$^{-6}$ to 1.2 x 10$^{-3}$ µg m$^{-3}$ in air samples from remote areas such as Antarctica and Greenland to 0.015 to 0.03 µg m$^{-3}$ in air samples collected over urban areas (Nriagu, 1988).

**Anthropogenic source of chromium**

Cr and its compounds have multifarious industrial uses. They are extensively employed in leather processing and finishing (Nriagu, 1988) in the production of refractory steel, drilling muds, electroplating cleaning agents, and catalytic manufacture and in the production of chromic acid. Hexavalent chromium (VI) compunds are used in industry for metal planting, cooling
tower water treatment, hide tanning and until recently, wood preservation. These anthropogenic activities have led to the wide spread contamination that Cr shows in the environment and have increased its bioavailability and bioaccumulation. (Kotas and Stasicka, 2000).

The leather industry is the major cause for the high influx of Cr to the biosphere, accounting for 40% of the total industrial use (Barnhart, 1997). In India, about 2000 to 32000 tons of elemental Cr annually escape into the environment from tanning industries. Even if the recommended limit for Cr concentration in water are set differently for Cr (III) (8 µg L⁻¹) and Cr (VI) (1 mg L⁻¹), it ranges from 2 to 5µ g L⁻¹ in the effluents of these industries (Chandra et al. 1997).

The chromium content as well as other heavy metals in any soil depends initially on the nature of parent materials. Flanagan (1969) reported that the concentration of heavy metals was higher in basaltic rocks and comparatively low in granite rocks and Vine and Tourlets (1970) reported that the heavy metal composition in coal ash (Table 3). Some fertilizers and soil amendments also contain chromium in soil (Table 4).

Uptake of chromium

Chromium is a toxic, non-essential element to plants, hence they do not posses specific mechanisms for its uptake. Therefore, the uptake of this heavy metal in through carriers used for the uptake of essential metals for plant metabolism. The pathway of Cr (VI) transport is an active mechanism involving carriers of essential anions such as sulphate (Cervantes et al. 2001). Fe, S and P are known also to complete with Cr for carrier binding (Wallace et al. 1976).

Independent uptake mechanisms for Cr (VI) and Cr (III) have been reported in barley. The use of metabolic inhibitors diminished Cr (VI) uptake whereas it did not affect Cr (III) uptake, indicating that Cr (VI) uptake depends on metabolic energy (Skeffington et al. 1976). An active uptake of both Cr species, slightly higher for Cr (III) than for Cr (VI), was found in the same crop (Ramachandran et al. 1980).

Chromium toxicity in plants

Toxicity of Cr to plants depends on its valence state, Cr (VI) is highly toxic and mobile whereas Cr (III) is less toxic. Toxic effects of Cr on plant growth and development include alterations in the germination process as well as in the growth of roots, stems and leaves, which may affect total dry matter production and yield. Cr also causes deleterious effects of plant physiological processes such as photosynthesis, water relation and minerals nutrition.

In plans, high levels of Cr supply can inhibit seed germination and subsequent seedling growth. Peralta et al., (2001) found that 40 ppm of Cr (VI) reduced by 23% the ability of seeds of lucerne (Medicago sativa) to germinate and grow in the contaminated medium. Reductions of 32-57% in sugarcane bud germination were observed with 20 & 80 ppm Cr, respectively (Jain et al. 2000).

Remediation of chromium contaminated soils and water

Chromium remediation through microorganism or plants may be the best technology in present to clean up Cr contaminated sites. Yadav et al. (2005) gives some remediation process for Cr contaminated soil and water which are given below:

1. Bioremediation - The decontamination of polluted or degraded soils by means of enhancing the chemical degradation or other activity of soil organisms. Losi et al. (1994), they found that organic matter content, bioactivity and oxygen status were among the important factors. Under aerobic field moist conditons, organic matter rich soil reduced 96% of added Cr (VI). Organic matter enhances the reduction of chromate in soil by increasing microbial activities. Bacterial populations resistant to as much as 500 mg L⁻¹ Cr (VI) were directly isolated from two uncontaminated soils.

2. Phytoremediation - Phytoremediation of Cr pollution can be achieved by using plants to remediate heavy metal contaminated sites called phytoremediation. Shahandesh and Hossner (2002) reported that the Brassica juncea and Helianthus annus plant species absorbed maximum Cr concentration about 1400 mg kg⁻¹.

3. Rhizofiltration - Another promising clean up technology appears to be rhizofiltration which involves use of plant roots to remove contaminants such as heavy metals from contaminated water (Dushenkov et al. 1995). Generally aquatic plants are growing in contaminated water. Examples- Scirpus lecusteris, Phragmites karka and Bacopa monnieri.

4. Phytostabilisation - The extraction of metal from polluted soils into harvestable plant tissues (Phytostabilisation). Very few plant species such as Sutera fodia, Dicoma niccolifera and Leptospermum Scoparium have been reported to accumulate Cr to high concentrations in their tissues.

5. Chelation - Nutrient culture studies revealed a marked enhancement in uptake and translocation of chelated ⁵¹Cr in P. verlraris. Cr chelated by DTPA was most effectively translocated followed by ⁵¹Cr-EDTA and ⁵¹Cr-EDDHA (Alhalyc et al. 1995).

6. Remediation by reduction of Cr (VI) in soils - Remediation by reduction schemes employing microbiological and chemical processes. Many new techniques and chemical reaction have been developed for the remediation of Cr (VI) - contaminated soils and ground water including those using carbon based minerals, zero and divalent Fe, reduced sulphur containing compounds and H₂ gas. The rates and extent of reduction of Cr (VI) by each of these are dependent on pH, aeration status and the concentration and reactivity of the reducing agent.

Manures have been used successfully to reduce Cr (VI) in chromite ore processing, residue - enriched soils (Higgins et al. 1997). Zero valent Fe has been especially with reactive permeable barrier walls (Puls et al. 1999) and divalent Fe has been used for reduction of Cr (VI) in soil and aqueous systems, with Fe (II) in soluble and insoluble forms and with and without light induced reduction of Fe (III), (Buerge and Hug, 1999). Reduced sulphur containing compounds (eg. Fe (II) sulfides, dithionite etc) have been used to reduce Cr...
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CONCLUSION

Chromium is a metal found in nature deposits. The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil and coal. The greatest use of Cr is in metal alloys such as stainless steel, protective coatings on metal, magnetic tapes and pigments for paints, cements, paper etc.

According to EPA found Cr to potentially cause the following health effects when people are exposed to it at levels skin irritation or ulceration, damage to liver, kidney, circulatory and nerve tissues. If the Cr (VI) compounds present in high concentration can increase the risk of lung cancer.

Chromium bioremediation through microorganism or plants may be best technology in present to clean up Cr contaminated sites and these technologies are eco friendly.

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