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FATE OF CHROMIUM IN THE ENVIRONMENT

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INTRODUCTION

Chromium is an inorganic transition metal pollutant with a complex electronic and valence shell chemistry with valence states ranging from -2 to +6. From this, the most environmentally significant forms of Cr are trivalent (Cr (III)) and hexavalent (Cr(VI)). These two oxidation states differ in their mobility and toxicity. Chromium (VI) is mobile and regarded as carcinogen whereas Cr(III) is relatively immobile and less toxic. Cr (III) has a significant role in lipid and sugar metabolism and regarded as essential trace element for human and animal health and not for the plants. Though Cr (III) has its own beneficial role, its uptake in supererogatory amounts causes health effects as well as skin rashes. Since Cr (III) is less toxic and immobile, the environmental conditions and complex of physical, chemical and biological factors have the capability to convert it into Cr (VI). However, there is a statement that, in drinking water all Cr is converted to Cr (VI) by strong oxidants such as chlorine, ozone and permanganate which are utilized for attaining taste, odour removal and disinfection. Owing to Cr (VI) mobility, it

readily leaches down the soil thereby contaminating the groundwater sources.

CHEMISTRY OF CHROMIUM

Chromium occupies seventh position regarding their abundance in earth crust and sixth in case of transition metal. In serpentine and ultramafic rocks, it is present naturally as chromite or it may form complexes with other elements as in cases like bentorite ($\text{Ca}_6(\text{Cr,Al})_2(\text{SO}_4)_3$), crocoites (PbCrO_4), tarapacaitite (K_2CrO_4), and vauquelinite ($\text{CuPb}_2\text{CrO}_4\text{PO}_4\text{OH}$). This naturally occurring component has a complex electronic and valence shell chemistry with valence states varies from -2 to +6. From this, the most environmentally significant forms of Cr are trivalent (Cr (III)) and hexavalent (Cr(VI)). These two oxidation states differ in their mobility and toxicity. Chromium (VI) is mobile and regarded as a carcinogen whereas Cr(III) is relatively immobile and less toxic. Detailed information on oxidation state and environmental behavior of Cr is given in Table 1. Chromium with oxidation state 0 (metallic Cr) is found in alloys such as stainless steel and chrome plated objects. Cr(III) is regarded as an indispensable/ vital element for human beings which plays a significant role in lipid and sugar metabolism. In addition, it is used to reduce blood glucose (diabetes control) and low density proteins (LDP). Though Cr(III) has its own beneficial role, its uptake in supererogatory amounts causes health effects as well as skin rashes. Presence of Cr(III) is reported in paints, dyes, chrome plating and tanning. On other hand, Cr(VI) is regarded as a strong oxidizing agent which on inhalation leads to perforation of nasal septum, asthma, bronchitis, larynx and liver inflammation, pneumonitis and bronchogenic carcinoma. Cr(VI) compounds on skin contact induce dermatitis. Wastewater from metallurgy industry, hard plating, refractory industry and pigments production shows the dominance of

Cr(VI). Cr(III) and Cr(VI) on reaction with oxidizing or reducing agents produce unstable intermediates of Cr(IV) and Cr(V).

Table 1. Valency and environmental behaviour of Cr

Oxidation state	Environmental behaviour	Comments
0	Unstable	Does not occur naturally
+1	Unstable	-
+2	Can be oxidized to Cr ³⁺ & if the oxidizing agent is not available, it will be stable	Anaerobic condition is suitable for its Activity
+3	Highly stable	Occurs in nature in ores such as ferrochromite, forms stable compounds & high amount of energy is required for Converting it to other oxidation state
+4	Unstable	Not occur naturally, short half life & intermediate phase
+5	Unstable	Not occur naturally, long half life & intermediate phase
+6	Stable (unstable in the presence of electron donor)	Rarely occurs in nature (crocoite) but produced from anthropogenic sources & strong oxidizing

BEHAVIOUR OF CHROMIUM IN SOILS

On an average, 0.02 to 58 μmol g⁻¹ of Cr is reported in soils. The threshold levels of Cr in soils given in some developed countries are described in Table 2. Insoluble Cr(OH)₃aq or Cr(III) is the predominant Cr form that is present in the soil . The pH decides the form of Cr i.e. if pH < 4 – Cr

(H₂O)₆³⁺ dominates, pH < 5.5 - hydrolysis product like Cr(OH)₂+aq which can easily be adsorbed to clay compounds. In soils having neutral to alkaline reaction, Cr(VI) will be present in soluble form as Na₂CrO₄ to moderately soluble chromates as CaCrO₄, BaCrO₄, and PbCrO₄. HCrO₄⁻ is the dominant form of Cr(VI) in soils of pH < 6.0.

Table 2. Permissible level of Cr (mg kg⁻¹) in soils

Metals	Country	Permissible limit (mg kg ⁻¹)
Total Cr	Australia	50
Cr(III)	New Zealand	600
	UK	600
	Canada	250
	US	1500
	Germany	200
Cr(VI)	New Zealand	10
	UK	25
	Canada	8

The transportable forms (CrO₄²⁻ and HCrO₄⁻) of Cr present in the soils are capable of washing to deeper soil layers causing water pollution. The aforesaid mobile forms can be reduced by reducing compounds like Fe²⁺ or S²⁻ through dechromification. Dechromification is a vital process and in its absence all atmospheric oxygen threats all life on earth. The donor groups present in the humic acids forms stable complexes with Cr³⁺ . Cr³⁺ can be converted to Cr⁶⁺ and vice versa under the conditions of oxidation and reduction which depends on factors like pH, concentration of oxygen, the presence of catalyst and ligands (Parameswari, 2009)..

Since Cr(III) salts are utilized in tanning process, the sludge generated from the above process evidenced their presence, which marks a threat to the environment and can't be used safely and efficiently. The next big hurdle is the cost involved in their disposal. Illegal dumping of waste water and

sludge from tanneries has led to serious environmental pollution. Among the Indian tanneries, over 60 percent were located in Dindigul, Erode and Vellore districts of Tamil Nadu, where Cr contamination is reported. The analytical results of soil and water samples collected around tanning industries of Vellore district revealed that they are contaminated to the core by Cr, which exceeds the permissible limits given by different countries. Indiscriminate disposal methods contaminate our environment and can easily enter into our food chain.

EFFECT OF EFFLUENT DISCHARGE INTO THE SOIL

The addition of tannery effluent is reported to have an undesirable effect on soil properties. The total porosity and hydraulic conductivity of the soil decreased as a result of addition of tannery effluent, while the bulk density of soil was increased. This may be attributed to the twin effect of direct

accumulation of large quantities of organic and inorganic materials as well as the interaction of Na with exchangeable complex resulting in deflocculation. It is estimated that tanning industry wastes have already degraded over 50,000 ha of Productive agricultural lands in Vellore, Erode and Dindigul districts of Tamil Nadu. As a result, there was a reduction in total cropped area to the extent of 10.5 and 41% in Vellore and Dindigul districts respectively in 20 years. A six-fold increase in the sodium content and EC increase from 0.64 to 2.29 dS m⁻¹ in the soils that are contaminated with tannery effluent was noticed (Sebastian et al., 2009).

REMEDICATION OF CR CONTAMINATED SOIL

Various conventional methods for remediating chromium, its advantages and disadvantages are given in Table 3.

Table 3. Management techniques for remediation Cr contaminated soil

S.No	Technology	Advantage	Disadvantage
Cr(VI) removal			
1	Excavation & Off-site disposal	Applicable for compact soil volumes, timely implementation & complete removal is possible	Through this technique, some Cr(VI) become airborne which causes health hazard, may invoke land disposal restrictions, expensive
2	Soil washing	Reduction in contaminated soil volumes that needs treatment	Cr from soil can be leached to H ₂ O & pollute water sources, this method is not suitable when Cr is strongly bound.
3	Soil Flushing	Insitu method, doesnot require excavation	
Cr(VI) immobilization			
4	Solidification/ Stabilization exsitu	Inexpensive	Cr(VI) need to be reduced to Cr(III), may become air borne when excavated and causes health hazard, Generates huge volume of solidified mass that requires disposal.

5	Solidification/ Stabilization insitu	Excavation is not required, applicable for sites with high water table	Needs reduction of Cr(VI) to Cr(III), inappropriate where there is a need of reducing total Cr levels.
6	Vitrification	In situ reduction and immobilization of Cr(VI)	High energy requirements and additives, may require soil dewatering
Cr(VI) reduction to Cr(III)			
7	Chemical method	Insitu method	Needs reducing agents, inappropriate where there is a need of reducing total Cr levels.
8	Biological method	In situ method, applicable to the areas with high water table where leaching of Cr(VI) from soil is possible	Slow technique, inappropriate where there is a need of reducing total Cr levels, needs controlled pH, O ₂ and nutrient levels.

(Avudainayagam et al.,2003)

CONCLUSION

Considering the Cr toxicity, it is necessary for regulating it and protecting the health of human and environment. Hence, application of organic amendments viz., Farm Yard Manure, compost, vermicompost, biochar etc may reduce the detrimental effect of chromium in soil and improve crop productivity.

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