HEXAVALENT CHROMIUM (VI): ENVIRONMENT POLLUTANT AND HEALTH HAZARD

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ABSTRACT

Cr (VI) is a notorious environmental pollutant because it is a strong oxidant and much more toxic than Cr (III). It has wide applications in various industries such as stainless steel, electroplating of chrome, dyes, leather tanning and wood preservatives. High doses of Cr (VI) have been associated with birth defects and cancer. Plants and animals do not bio accumulate chromium; therefore, the potential impact of high chromium levels in the environment is highly toxic to plants and animals. In human beings this toxicity may be expressed as skin lesions or rashes and kidney and liver damage. Chronic exposure to Cr (VI) in the form of lead chromate effects on carcinogenicity and is found to induce persistent or increasing chromosome damage. Cr (VI) is mobile in soil, more toxic, and penetrates more readily into the cell membranes than the trivalent form. Many factors like the biotic and abiotic factors in the environment, and characteristics of the pollutant influence the toxicity of chromium on microorganisms. The adverse effects of chromium can be seen in many microbe-mediated processes including carbon mineralization, nitrogen transformation and mineralization of phosphorous and sulfur. The presence of chromium decreases microbial populations and also affects microbial respiration. Chromium is found to be both toxic and mutagenic to various microorganisms. A case study reflects the chromium contamination in the water bodies in and around Sukinda mines of Orissa state in India and its effect on the potential users of the contaminated water. The paper provides a social awareness among the public and suggests some remediation techniques to reduce the contamination.

Key Words: Hexavalent chromium, Carcinogenicity, Microbe-mediated processes, Oxidizing agent, Genotoxicity

INTRODUCTION

Chromium (Cr) is one of the world’s most strategic, critical and highly soluble metal pollutant having wide range of uses in the metals and chemical industries. Cr is used principally in stainless steel and non-iron alloy production for platting metals, development of pigments, leather processing and production of catalysts, surface treatments and in refractories. Chromium exists in the environment in several diverse forms such as trivalent [Cr (III)] and hexavalent, of which hexavalent chromium [Cr (VI)] is a so-called carcinogen and a potential soil, surface water and ground water contaminant. Whereas it’s reduced trivalent form (Cr³⁺) is much less toxic, insoluble and a vital nutrient for humans. Cr (III) occurs naturally in the environment and is an essential nutrient required by the human body.

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Chromium metal is a steel-gray solid with a high melting point. Chromium compounds, mostly in chromium (III) or chromium (VI) forms produced by the chemical industry are used for chrome plating, in the manufacture of dyes and pigments, leather tanning and wood preserving. Smaller amounts are used in drilling muds, rust and corrosion inhibitors, textiles and toner for copying machines. Chromium enters the environment mostly in the chromium (III) and chromium (VI) forms as a result of natural processes and human activities. Chromium toxicity is further confirmed from a case study on Sukinda mines.

**METHODOLOGY**

The trivalent form occurs naturally in many fresh vegetables and fruits, meat, grains, and yeast. Relatively insoluble, it is the most prevalent form in surface soils where oxidation processes (which convert chromium from the hexavalent to trivalent form) are most common. Hexavalent chromium also occurs naturally, notably in water-saturated (reducing) conditions, and it is an indicator of human pollution. Inside cells, Cr (III) formed from Cr (VI) can complex with organic compounds, interfering with metallo–enzyme systems at high concentrations\(^9\). Chromium (VI) has been shown to have carcinogenic and allergenic effects in humans and animals.

**Source of Occupational Exposure**

An about 13 million metric tone of Cr was produced annually in 2002. Historically about 60-70\% of Cr ores are used in alloys\(^12\). These alloys comprise stainless steel, which contains Fe, Cr, and Ni in varying proportions to accomplish the requirement. Cr alloys have a moderate electrical resistivity and are used for heating elements. Cr can be highly polished and is resistant to attack by continuous oxidation, leading to its use in alloy that are resistant to corrosion. Cr (III), referred as chrome alum, is used for tanning leather, pigments and wood preservatives (Na\(_2\)Cr\(_2\)O\(_7\)). About 4\% is used as chromic acid and used for electroplating or as an oxidant. Chromium is used as corrosion –resistant decorative plating agent. K\(_2\)Cr\(_2\)O\(_7\), a form of chromium has been used in the leather production industry as a tanning agent. Chromates are compounds used in the textile industry as a mordant. Products that contain Cr (VI) include paints, pigments, inks, fungicides, and wood preservatives, chrome plating and leather tanning.\(^{10-11}\)

**Physical Existence of Chromium**

In solution, hexavalent chromium exists as hydrochromate (HCrO\(_4^–\)), chromate (CrO\(_4^{2–}\)), and dichromate (Cr\(_2\)O\(_7^{2–}\)) ionic species. The proportion of each ion in solution is pH dependent. In basic and neutral pH, the chromate form predominates. As the pH is lowered (6.0 to 6.2), the hydrochromate concentration increases. At very low pH, the

<table>
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<tr>
<th>Industry</th>
<th>Types of Hexavalent Chromium Chemicals</th>
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<tr>
<td>Pigments in paints, inks, and plastics</td>
<td>Lead chromate (PbCrO(_4)) zinc chromate (ZnCrO(_4)) -barium chromate -calcium chromate -potassium dichromate -sodium chromate</td>
</tr>
<tr>
<td>Anti-corrosion coatings (chrome plating, spray coatings)</td>
<td>Chromic trioxide (chromic acid) -zinc chromate (ZnCrO(_4)) -barium chromate (BaCrO(_4)) -calcium chromate -sodium chromate -strontium chromate (SrCrO(_4))</td>
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<tr>
<td>Stainless steel</td>
<td>Hexavalent chromium (when cast, welded, or torch cut), Ammonium dichromate ((NH(_4))(_2)Cr(_2)O(_7)) -potassium chromate -potassium dichromate -sodium chromate</td>
</tr>
<tr>
<td>Wood preservation</td>
<td>Chromium trioxide</td>
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<tr>
<td>Leather tanning</td>
<td>Ammonium dichromate ((NH(_4))(_2)Cr(_2)O(_7))</td>
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dichromate species predominate. The primary sources of hexavalent chromium in the atmosphere are chromate chemicals used as rust inhibitors in cooling towers and emitted as mists, particulate matter emitted during manufacture and use of metal chromates, and chromic acid mist from the plating industry.

**Regulatory limits for chromium exposure**

Due to toxicity concerns, in the USA concentration of total Cr are regulated at 0.1 mg/L in drinking water, 5 mg/L leached from solids in the Toxicity Characteristic. The hexavalent form is relatively soluble and can move more readily through soil to groundwater. The typical ratio of chromium in plants to chromium in soil is estimated at 0.0045 (or 0.45%). EPA has set a limit of 100 µg chromium(III) and chromium(VI) per liter of drinking water (100 µg/L). The Occupational Safety and Health Administration (OSHA) has set limits of 500 µg water soluble chromium(III) compounds per cubic meter of workplace air (500 µg/m³), 1,000 µg/m³ for metallic chromium(0) and insoluble chromium compounds, and 52µg/m³ for chromium(VI) compounds for 8-hour work shifts and 40-hour work weeks.

**RESULTS AND DISCUSSION**

Hexavalent chromium in contact with skin acts as both sensitizer and irritant. After entering the organism, it gets reduced to trivalent chromium, which then binds to proteins and creates haptens which trigger immune system reaction. Once developed, chrome sensitivity becomes fairly persistent; in such cases, even contact with chromate-dyed textiles or wearing of chromate-tanned leather shoes can cause or exacerbate dermatitis. When air-containing chromium is inhaled, chromium particles can be deposited in the lungs. Those deposited in the upper part of the lungs are usually coughed up and swallowed. Some that deposit deep in the lungs can dissolve, which allows chromium to pass through the lining of the lungs and enter the bloodstream. The finding of deadly effects following dermal exposure suggests that chromium is absorbed through the skin, although information on the percent absorbed is limited. Once in the bloodstream, chromium moves to all parts of the body. It is not metabolized, but hexavalent chromium is reduced by enzymatic reactions to trivalent chromium in the body. Ingestion of food is the key source of chromium exposure for most people in the US. On average, adults take in an estimated 60 µg of trivalent chromium every day with their food. A small amount about 0.5% of Cr (III) and 10% of Cr (VI) will pass through the lining of the intestines and enter the bloodstream. From there, chromium is distributed to all parts of the body. It then passes through the kidneys and is eliminated in the urine in a few days. The trivalent form in food can attach to other compounds that make it easier for chromium to be absorbed and enter the bloodstream from the stomach and intestines.

**Carcinogenicity**

Hexavalent chromium compounds have been confirmed to be carcinogenic on the basis of epidemiologic investigations of workers and of experimental studies with animals. Chronic inhalation of hexavalent chromium compounds presents an increased risk of lung cancer, with the degree of risk depending on the particular salts and their solubility under biological conditions, on the circumstances of exposure, and on such concomitant risk factors as cigarette smoking. Epidemiologic studies conducted in the USA 40 years ago, demonstrated a 10 to 30 fold-increased risk of lung cancer among workers of the chromate industry compared to the general population. In most studies, a positive correlation between duration of exposure and lung cancer death was found. Hexavalent chromium is extremely toxic and is considered by the World Health Organization and the United States Environmental Protection Agency to be a human carcinogen. The International Agency for Research on Cancer (IARC) in 1990...
concluded that there was sufficient evidence in humans for the carcinogenicity of chromium (VI) compounds as encountered in the chromate production, chromate pigment production, and chromium plating industries for the carcinogenicity of chromium (VI) compounds in humans based on the combined results of epidemiological studies, carcinogenicity studies in experimental animals, and evidence that chromium (VI) ions generated at critical sites in the target cells are responsible for the carcinogenic action observed.

**Genotoxicity**

Hexavalent chromium is genotoxic. It appears that the mechanism of genotoxicity relies on pentavalent or trivalent chromium, an intracellular reduction product of hexavalent chromium after its penetration into the cell. Hexavalent chromium compounds have been consistently genotoxic, inducing a wide variety of effects, counting DNA damage, gene mutation, sister chromatid exchange, chromosomal aberrations, cell transformation, and dominant lethal mutations. Hexavalent chromium compounds have caused developmental effects in rodents in the lack of maternal toxicity following oral administration. Because of structural similarity to phosphate, which is transported into all types of cells, if Cr (VI) does reach a cell, it can enter it. Once Cr (VI) enters the cell, it is chemically transformed to the more stable Cr (III). The process by which Cr (VI) is reduced to Cr (III) can cause many forms of DNA damage: oxidative DNA lesions such as strand breaks, chromium-DNA adducts, DNA-DNA interstrand cross-links, and DNA-protein cross-links. (An adduct is a modification of a biological molecule—in this case, DNA—caused by the covalent attachment of a chemical, such as chromium; cross-links are a specific class of adduct.) Those studies, published in the March 1994 issue of *Molecular Carcinogenesis* indicate that Cr (III)-induced DNA-DNA interstrand cross-links are the lesions responsible for blocking DNA replication. This observed mutagenicity complements other studies on Cr (III)-dependent DNA lesions, which demonstrate the importance of a Cr (III)-dependent pathway in Cr (VI) carcinogenicity. Further studies are investigating the relative importance of oxidative and Cr (III) pathways in genetic damage caused by exposure to Cr (VI).

**Groundwater Contamination**

Chromium (VI) in ground water has generally been assumed to be anthropogenic (manmade) contamination, since it is used in a number of industrial applications, including electroplating, tanning, Industrial water-cooling, Paper pulp production and petroleum refining. Severely infected with cancerous dyes and chemicals from defunct industries, the drinking water has been rendered extremely toxic. A basic chrome sulfate manufacturing plant for tanneries has left a legacy of chromium, lead, and pesticide (i.e. DDT and Lindane) pollution. Huge amounts of the chemical waste produced here were buried on the grounds of the old plant. This contaminated material has contaminated groundwater, and therefore wells and drinking water. A 1997 study conducted by the Central Pollution Control Board on the groundwater quality in Kanpur revealed Cr VI levels of 6.2 mg/l; the Indian government places the limit at .05 mg/l. In addition to chromium, the study revealed high concentrations of iron, fluoride, alkalinity, coliform, pesticides, dissolved solids, and hardness. The tanneries discharge their toxic waste laden with Cr VI into the sewage system. This effluent is carried through the main drainage system to the centralized treatment plant. The treated water is then used for farming irrigation or released directly into the river. The resulting sludge from the treated wastewater is left to dry on sludge beds and subsequently dumped outside of the treatment plant.
Occupational exposures

It’s been long years since it was first noticed that workers in the chrome ore manufacturing developed lung cancer more often than the rest of the population. Occupational exposures to Cr (VI) compounds can be quite acute. Although breathing in Cr (VI) at concentrations as low as 2 µg/m³ can cause sneezing and irritation of the nasal mucosa, air concentrations of Cr (VI) compounds can get much higher than that in certain workplace settings. In chrome plating workshops with local exhaust, for example, concentrations usually range from 10 to 30µg/m³; in shops without local exhaust, concentrations can climb to 120µg/m³. Arc, stainless steel, and alloy steel welding can produce even higher concentrations; according to IARC, depending on the process, welding fumes have been found to hold concentrations as high as 1,500µg/m³. Home exposures can also come from living near hazardous waste sites.

Soil Microbial community response to Cr (VI)

The activities, ecologies and population of many microorganisms in many habitats are adversely influenced by increased deposition of harmful pollutants into the environment. These pollutants may be derived from industrial or domestic sources. Microbes are the key components in the biogeochemical cycling of various chemical elements, in the incorporation of energy, in the processes necessary for the maintenance of the fertility of aquatic and terrestrial habitats, and for waste reduction. Pollutants affect complex microbial interactions and can cause elimination, diminution, or enhancement of specific microbial populations and hence affect the ecology of the biosphere. Chromium is one of the heavy metals that have adverse effects on microbes and treatment process. The toxicity and potential carcinogenicity has led to the concern about its effects in the environment. The adverse effects of chromium can be seen in many microbe-mediated process including carbon mineralization, nitrogen transformation and mineralization of phosphorus and sulfur. The presence of chromium decreases microbial populations and also affects microbial respiration. Chromium is found toxic and mutagenic to various microorganisms. Chromium also affects the growth rate, Monod constant and microbial population in the treatment process. Various factors like acclimation, injection and temperature influence the effects of chromium on treatment plant. Chromium-contaminated industrial effluents are mainly responsible for environmental pollution by toxic and highly mobile, hexavalent chromium. The aqueous Cr (VI) concentrations of 100 to 200 mg/L are in the range where Cr (VI) toxicity to bacteria has been reported. The dilution plate-count method, using media amended with Cr (VI) at concentrations ranging from 50 to 1000 mg/ml, was used to compare the sizes of Cr (VI)-resistant bacterial populations from a soil contaminated with [Cr (VI)] and without any history of Cr contamination. The results suggest that Cr-resistant microorganisms may be present in soils, even those with no history of Cr contamination.

A Case study on Sukinda mines

Sukinda chromite valley is one of the major chromite deposits of the country and produces nearly 8% of chromite ore. In the Sukinda mining area, around 7.6 million tons of solid waste have been generated in the form of rejected minerals, overburden material/waste rock and sub-grade ore that may be resulting in environmental degradation, mainly causing lowering in the water table vis-a-vis decline in surface and ground water quality. The Sukinda valley, spread over Orissa’s Dhenkanal and Jajpur districts, and the site of India’s largest chrome ore deposits, ranks fourth in the ‘Blacksmith Institute Pollution Report for 2007, released on September 12. About 97% of India’s chrome reserves, Sukinda’s opencast mines, the largest chromite ore mines in the world, are an environmental
hazard, as addressed by Blacksmith Institute. The report says: “Twelve mines continue to operate without any environmental management plans, and over 30 million tonnes of waste rock are spread over the surrounding areas and the Brahmani riverbanks. Approximately 70% of the surface water and 60% of the drinking water contains hexavalent chromium at more than double national and international standards. It is further reported that chromite mine workers in Sukinda are constantly exposed to contaminated dust and water. Gastrointestinal bleeding, tuberculosis and asthma are common ailments observed among the workers. Infertility, birth defects, and stillbirths have also been recorded.

Sukinda is a classic example of pollution where the wastes are spread over a large area and residents are affected by the chromium through multiple pathways. The pollution problem from the chromite mines is well known phenomena and the mining industry has taken limited steps to reduce the levels of contamination by installing treatment plants. However, according to state audits from Orissa, these fail to meet agency regulations. Various organisations have carried out studies proving the debilitating health impacts of the toxic pollution. However, remedial action remains piecemeal with no decisive plans to provide for effective health monitoring and abatement programmes.

**CONCLUSION**

Thus chromium bioremediation through Bioremediation may be the best-suited technology in present context to clean up Cr contaminated sites and these technologies are eco-friendly and cost effective. Cr(VI) is readily immobilized in soils by adsorption, reduction, and precipitation processes. In regions, where Cr(VI) contamination of the environment represent a major area of concern,
the use of Cr-hyper-accumulator plant species or Cr-reducing microorganisms may represent a cost efficient and highly effective technology for the removal and detoxification of the toxic forms of Cr.

REFERENCES