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Harzadous Impact of Chromium on Environment and its Appropriate Remediations

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Properties

Chromium, one of the toxic metals is detectable in earth's crust in small quantities associated with other metals, particularly iron. The atomic weight of chromium is 51.996. It melts at 1,875 °C and boils at 2,680 °C. The specific gravity of chromium is 7.19 g cm⁻³. It forms a number of salts, which are characterized by a variety of colors, solubilities and other properties. The name "chromium" is from the Greek word for color. Most important chromium salts are sodium and potassium chromates and dichromates and the potassium and ammonium chrome alums.

Oxidation States

Chromium can occur under several oxidation states from Cr (0) to Cr (VI). Trivalent chromium Cr (III) occurs naturally in rocks, soil, plants, animals and volcanic emissions (Duffs, 2005). This form is believed by many to play a nutritional or pharmaceutical role in the body, but its exact mechanism of action is unknown. Cr (III) is used industrially as a brick lining for high-temperature industrial furnaces and to make metals, metal alloys and chemical compounds (Barantsevs *et al.*, 2004). Hexavalent chromium, Cr(VI), is produced industrially when Cr(III) is heated in the presence of mineral bases and atmospheric oxygen (for instance, during metal finishing processes). It is the form of chromium that has proven to be of the greatest occupational and environmental health concern. Cr(VI) compounds are emitted into the air, water and soil by a number of different industries. In the air, chromium compounds are present mainly as fine dust particles that eventually settle over the land and water.

Entrance into the Environment

Chromium enters environmental waters from anthropogenic sources such as electroplating factories, leather tanneries, wood preserving, metal processing, chromium plating, alloy preparation, leather tanning, petroleum refining and manufacturing of automobile parts and textile manufacturing facilities (Panov *et al.*, 2003; Huang *et al.*, 2004). Chromium also enters groundwater by leaching from soil. In aqueous environments, however, Cr mainly exists in two oxidation states: Cr(VI) and Cr(III). Aqueous Cr(VI) is present in anionic forms whose compounds are generally soluble over a wide pH range. Hydrolysis of Cr(VI) yields a number of pH-dependent species, that is, H₂CrO₄, HCrO₄⁻, CrO₄⁻² and Cr₂ O₄⁻². On the other hand, the main aqueous Cr(III) species are Cr⁺³, Cr (OH)⁺², Cr(OH)⁺², Cr(OH)₃⁰ and Cr(OH)₄⁻, while polymeric species such as Cr₂ (OH)₂⁺⁴, Cr₃ (OH)₄⁺⁵ and Cr₄ (OH)₆⁺⁶ are insignificant in natural systems. In the pH range encountered in natural waters, most Cr(III) exists in the least insoluble form of Cr (OH)₃ (Smith and Ghiassi, 2006).

Industrial Application

It has been estimated that workers in some 80 different professional categories may be exposed to Cr(VI). Various Cr(VI) compounds are used in leather tanning, the production of textiles, dyes, pigments and chrome plating (Cristian *et al.*, 2005). Other sources of chromium emissions include oil

and coal combustion, stainless steel welding, steel production, cement plants, industrial paint and coating manufacture and cooling towers, which use Cr(VI) as a rust inhibitor for their submerged moving parts (Potgieter *et al.*, 2003). Occupational exposures to Cr(VI) compounds can be quite acute (Proctor *et al.*, 2004).

Manufacturing of Chromium Salts

Chromium (II) and (III) chemicals are also manufactured but in small amounts as compared to chromium (VI). Chromium dichloride (CrCl₂) and chromium sulfate (CrSO₄) are examples of the former and chromium trifluoride (CrF₃), chromium trichloride (CrCl₃) and chromium nitrate (Cr(NO₃)₃) are examples of the latter. Chromium platers use heated baths of H₂Cr₂O₇ to plate chromium onto pieces of other metals. Under an electric current, the hydrated dichromate ions move toward the positive electrode, which is the metal to be plated. The hydrogen and oxygen gases formed escape the bath forming aqueous acidic chromate laden mists.

Essentiality and Toxicity

Chromium is present in food and feed plants, but the form is not well characterized (Cary, 1982; Das *et al.*, 2005). The likely form is soluble chromium (III) organic compounds such as chromium (III) oxalate in plants (Smith *et al.*, 1989). Chromium is an important micronutrient for animals and humans (Bahijri and Mufti, 2002). Humans must consume organically bound or chelated chromium as part of the proper metabolism of Glucose Tolerance Factor (GTF). Although chromium (VI) can be rapidly absorbed through the intestinal wall, any ingested chromium (VI) is believed to be quickly reduced in the stomach where the pH is around 1 and numerous organic reducing agents can be found.

Chromium plays a key role in the biological life but above critical level it is toxic (Balamurugan *et al.*, 2004; Han *et al.*, 2004;) mutagenic (Gili *et al.*, 2002; Puzon *et al.*, 2002; Wise *et al.*, 2005), carcinogenic (Codd *et al.*, 2003; Reddy *et al.*, 2003; Sato *et al.*, 2003) and teratogenic (Asmatullah *et al.*, 1998). Trivalent form of chromium is more common and its compounds are less soluble and less toxic than hexavalent chromium (Smith and Ghiassi, 2006). Trivalent chromium forms stable complex with legends on DNA, proteins and small molecules such as glutathionein (Adach and Cielak-Golonka, 2005). Trivalent chromium binds to the DNA template cause increased DNA polymerase processivity and decreased DNA replication fidelity. These alterations in DNA function can result in greatly increased bypass of oxidative DNA lesions, which are promutagenic (Adach and Cielak-Golonka, 2005).

Toxicity Towards Plants

In chromium contaminated sites not only human, animal and microbial life damage but the effects on plants are also equally pronounced. Due to chromium accumulation reduction in plant production along with toxicity in the nutritional contents are also observed (Pandey and Sharma, 2003; Klumpp *et al.*, 2002). Some plants show tolerance against chromium, but some have acquired the ability to accumulate chromium (Tripathi and Chandra, 1991). The root and shoot growth rate and leaf chlorosis could be elicited in hyacinth (*Eichornia crassipes*) by exposure to chromium and copper for several weeks (Hafeez and Ramzan, 2002). In *Triticum aestivum*, hexavalent chromium showed adverse effect on the growth parameters and also caused accumulation of chromium in the plants (Faisal *et al.*, 2005). The hexavalent chromium salt has more adverse effect on germination and growth of *Helianthus annuus* (Faisal and Hasnain, 2005) and *Vigna radiata* (Hsu and Chou, 1992). The effect of chromium on the cortical cells of meristematic zone was observed in *Pisum sativum* L. (Gabara *et al.*, 1992). Chromium toxicity on the seed germination and growth of *Phaseolus vulgaris* was markedly increased with an increase in its concentration (Zeid, 2001). Plants growing in higher concentration of chromium

take up more chromium, which accumulate in the plant tissues and via plants enter in the food chain. At a concentration of >0.2 mM Cr(VI), Citrullus plant showed growth depression with chlorosis and loss of turgor of middle leaves (Dube *et al.*, 2003). Growth of mustard (*Sorghum bicolor* L.) plants decreased by increasing the concentration of Cr(VI) from 50 to 100 μ M (Shanker and Pathmanabhan, 2004). *Lamina minor* accumulated Cr(III) in smaller quantities as compared to Cr(VI) which poses more toxic effects on growth parameters as compared to Cr(III). In *Brassica juncea* Cr(VI) application caused growth retardation, reduces the number of palisade and spongy parenchyma cells in leaves, results in clotted depositions in the vascular bundles of stems and roots and increases the number of vacuoles and electron dense materials along the walls of xylem and phloem vessels (Han *et al.*, 2004). When *Vigna radiata* plants were treated with Cr(VI), chlorophyll and protein content decreased while activity of catalase, peroxidase, glucose-6-phosphate dehydrogenase and superoxide dismutase increased. Concentration of chlorophyll a and b, soluble protein and grain production decreased significantly in maize plants exposed to Cr(VI) (Sharma *et al.*, 2003).

Toxicity Towards Animals

Chromium also shows toxicity towards different animals (Fatima *et al.*, 2005; Geetha *et al.*, 2005). Exposure of *Rana ridibunda* to either Cr or a mixture of Cr and Cd caused a decrease in liver GST and P450-MO and renal GST activities (Kostaropoulos *et al.*, 2005). It was observed that treatment of rats with chromium (0.8 mg/100 g body weight/day) for a period of 28 days caused significant increase in chromium content while lowering the body weight along with the organ (kidney, testis, spleen, cerebrum and cerebellum) weight, (Dey *et al.*, 2003). Beside this there was a significant decrease in the DNA and RNA content and in liver, cerebrum and cerebellum significant decreases in total protein content was also observed (Dey *et al.*, 2003). The application of higher dose of chromium in drinking water during embryonic development in mice results in reduced fetal weight, retarded fetal development and higher incidence of dead fetuses (Junaid *et al.*, 1995). Animal studies on the carcinogenicity of various chromium species have generally suggested that water-insoluble species, CaCrO_4 in particular (Levy *et al.*, 1986), are the causative agent of respiratory cancers (Gad, 1989). Studies have showed the toxicity of chromium picolinate in renal impairment, skin blisters and pustules, anemia, hemolysis, tissue edema, liver dysfunction; neuronal cell injury, impaired cognitive, perceptual and motor activity; enhanced production of hydroxyl radicals, chromosomal aberration, depletion of antioxidant enzymes and DNA damage in mice (Bagchi *et al.*, 2002). In mice, potassium dichromate treatment (20 mgCr kg^{-1}), as Cr(VI) compound, significantly elevated the level of lipid peroxidation as compared with the control group. This was accompanied by significant decreases in nonprotein sulfhydryls (NPSH) level, superoxide dismutase (SOD) and catalase (CAT) enzyme activities as well as a significant chromium accumulation (Bosgelmez and Gvendik, 2004).

Toxicity Towards Humans

Certain Cr(VI) compounds have been found to be carcinogenic in humans, but the evidence to date indicates that the carcinogenicity is site-specific-limited to the lung and sinonasal cavity and dependent on high exposures, such as might be encountered in an industrial setting (Feng *et al.*, 2003). It has been reported that trivalent chromium salts are poorly absorbed through the gastrointestinal tract. Hexavalent chromium compounds are approximately 1000-fold more cytotoxic and mutagenic than trivalent chromium compounds in cultured diploid human fibroblasts, but both hexavalent and trivalent chromium compounds induce dose-dependent anchorage independence in human diploid fibroblasts (Biedermann and Landolph, 1990). Cr(VI) can cause a wide range of other health effects. Inhaling relatively high concentrations of some forms of Cr(VI) can cause a runny nose, sneezing, itching, nosebleeds, ulcers and holes in the nasal septum (Banerjee *et al.*, 2003). Short-term high-level inhalational exposure can cause adverse effects at the contact site, including ulcers, irritation of the

nasal mucosa and holes in the nasal septum (Stohs *et al.*, 2001). Hexavalent chromium compounds induce dose-dependent cytotoxicity and anchorage independence in cultured human diploid fibroblasts (Biedermann and Landolph, 1987). Cr(VI) is one of the most highly allergenic metals, second only to nickel (Bock *et al.*, 2003).

In fact, irritation of the skin a most frequently reported human health effect from exposure to Cr(VI), taking the form of skin ulceration (dermatosis) and allergic sensitization (dermatitis) (Hansen *et al.*, 2003). Indeed, dermatosis was the first observed health effect associated with chromium exposure, although improved industrial hygiene practices have greatly reduced its incidence (Refiye *et al.*, 2005). Once absorbed into the blood system there are various antioxidants that act as reducing agents, such as glutathione and ascorbate, which rapidly reduce chromium (VI) to chromium (III). Respiratory cancer is the health effect of most concern and is the basis for the regulation of chromium (VI) (O'Brien *et al.*, 2003). There is also some indication that chromium (VI) may cause cancer of the upper airways and upper gastrointestinal tract, such as the esophagus, larynx, trachea and stomach (Xie *et al.*, 2005). Chromium concentration in the lungs was found to increase with age for both occupationally and environmentally exposed individuals (Xie *et al.*, 2005). The upper lobes tended to have higher concentrations than lower lobes and cancerous portions of lungs showed the highest chromium concentrations. However, large doses of chromium into the blood can result in acute kidney and liver damage (Dey *et al.*, 2003). Research on the carcinogenicity of chromium (VI) has focused on the fact that chromate ions quickly pass through cellular and nuclear membranes, while the trivalent species are many orders of magnitude slower (Pas *et al.*, 2004). Once in the cytoplasm, chromate ions can either pass the nuclear membrane and be reduced to chromium (III) or be reduced in the cytoplasm. Because neither Cr(VI) nor Cr(III) reacts strongly with DNA, it is thought that the reduction of Cr(VI) to Cr(III), either in the cytoplasm, nucleus, or the blood, produces free radicals, which in turn can bind to DNA (Medeiros *et al.*, 2003). Indeed, the DNA-protein crosslinks induced by chromate have been used as a biomarker for chromium exposure (Taioli *et al.*, 1995).

Toxicity Towards Microorganisms

Most microorganisms (protozoa, fungi, algae, bacteria and cyanobacteria) are able to accumulate chromium (Dursun *et al.*, 2003; Pas *et al.*, 2004; Faisal and Hasnain, 2005). In general, toxicity for most microorganisms occurs in the range of 0.05-5 mg Cr L⁻¹ of medium. In *Saccharomyces cerevisiae* chromium caused oxidative damage to cellular proteins (Sumner *et al.*, 2005). Reduced growth of mycelium in many fungi is due to the toxic effect of hexavalent chromium (Lozovaia *et al.*, 2004). Studies of *Shewanella oneidensis* showed that the growth was much inhibited even at a low concentration (0.015 mM) of Cr(VI) (Viamajala *et al.*, 2004). Incubation of *E. coli* cells with 10 mM of hexavalent chromium and 3 mM hydrogen peroxide caused the degradation of double-strand DNA *in vivo*, which was suppressed by the addition of mannitol (Itoh *et al.*, 1994). Cr(VI) caused decrease in cell size, the structure of cell wall, as well as the redox reaction caused by the exudate or enzyme when the cultures of *Chlorella pyrenoidosa*, *Synechococcus*, *Spirulina maxima*, *Spirulina platensis*, *Selenastrum capriornutum* and *Scenedesmus quadricauda* were grown in chromium solutions (Chen *et al.*, 2003).

Remediation Strategies

To minimize the environmental contamination, much effort has been made to treat hexavalent chromium in wastewater. Developing health-based clean up standard and remediation strategies for chromium-contaminated soils based on the hexavalent forms of this heavy metal is a complex and controversial task.

Conventional Methods

Conventional methods for treatment of contaminated hexavalent chromium include chemical reduction followed by precipitation, ion exchange and adsorption on coal, activated carbon, alum, kaolinite and flyash. However, most of these methods require either high energy or large quantities of chemicals and therefore more practical, cost effective methods are being explored (Ohtake and Silver, 1994).

Abiotic Reduction

In some natural system conditions exist where oxidation and reduction of chromium can both occur (Bartlett, 1991). For example, as mentioned above, in aquatic systems chromate ions may be reduced to Cr^{3+} . Manganese dioxide can then oxidize Cr^{3+} back to chromate. If the water is well aerated and sunlight can penetrate to a sufficient depth, the manganese will be reoxidized, allowing more reduced chromium to be oxidized. Just as manganese can be reoxidized by sunlight and oxygen, iron (III) can also be reduced by sunlight to iron (II), which can then reduce chromium (VI) to (III). Indeed, Kaczynski and Kieber (1993) reported a diurnal variation in the ratio chromium (III)/(VI) in pH neutral lakes caused by indirect action of sunlight on chromium via iron and manganese. The ratio chromium (III)/(VI) may also be affected by the photo disassociation of chromium from organic materials (Kaczynski and Kieber, 1993).

To remediate toxic hexavalent chromium from the contaminated environment, it is necessary first to take up this toxic Cr(VI) and then reduced it in to Cr(III).

Cr Phytoremediation

There are conflicting views concerning the uptake and translocation of chromium (VI) in plants (Citterio *et al.*, 2003; Han *et al.*, 2004). Ramachandran *et al.* (1980) suggest that CrO_4^{-2} is reduced to chromium (III) at the surface of root cells. Other studies found chromium (VI) in plants, which suggest that dissolved chromium (VI), may be taken up by plants without immediate reduction. For instance, chromate was found in the xylem sap of *L. scoparium* but not in the soluble plant fraction (Cary *et al.*, 1977). Also, it has been shown that chromium (VI) enters the plant through the root by active transport in barley (*Hordeum vulgare* L.) (Cary, 1982). Uptake of CrO_4^{-2} by intact barley seedlings was stimulated by Ca^{+2} but inhibited by SO_4^{-2} and other Group VI anions. Chromate appears to be reduced during passage from culture solutions to plant leaves (Cary *et al.*, 1977). Higher concentrations of chromium have been reported in plants growing in high chromium-containing soils (e.g., soil near ore deposits or chromium-emitting industries and soil fertilized by sewage sludge) compared with plants growing in normal soils. However, most of the increased uptake of chromium results in accumulation in the roots and only a small fraction of the total chromium is translocated to the above-ground part of edible plants (Gardea-Torresdey *et al.*, 2004; Faisal and Hasnain, 2005). Leaves usually contain higher chromium concentrations than grains (Smith *et al.*, 1989). In an attempt to design crop practices that might increase the chromium in food and feed crops, Faisal *et al.* (2005) also found that plants accumulated chromium from nutrient solutions but retained most of this chromium in the roots. It was found that plant tissues that tend to accumulate iron also accumulate chromium (Burd *et al.*, 1998). Chromium uptake was found to increase with increasing chromate concentration, and most of the chromium accumulated by the roots was present in a soluble, non-particulate form in the plant vacuoles. Although chromium is largely retained in the roots of plants, the oxidation state of chromium, the pH and the presence of humic substances and plant species affect plant uptake and transport (Smith *et al.*, 1989).

Microbial Reduction

Microorganisms have the potential to accumulate chromium (Ozdemir *et al.*, 2003) and reduce chromium (VI) to chromium (III) (Desjardin *et al.*, 2003; Camargo *et al.*, 2004; Ramirez-

Ramirez *et al.*, 2004). Although high levels of chromium (VI) are toxic to microorganisms (Bartlett, 1991). Chromium is important to yeast metabolism (Coleman, 1988) and sorption of Cr(VI) by several species of yeast has been reported (Rapoport and Muter, 1995; Babyak *et al.*, 2005). Chromium accumulation has been shown to occur in bacteria periphytic to a crab (*Helice crassa*) carapace and in sewage fungus (Coleman, 1988) and may contribute to the presence of chromium in the food chain.

Bacterial Reduction

Many types of chromium resistant bacteria, which have developed different strategies to overcome heavy metal stress in the environment are now known (Faisal *et al.*, 2005). Bacterial resistance to chromate can be due to chromosomal borne (Peitzsch *et al.*, 1998; Juhnke *et al.*, 2002) or plasmid mediated (Peitzsch *et al.*, 1998) or both (Peitzsch *et al.*, 1998; Juhnke *et al.*, 2002). Some bacterial strains are able to reduce toxic hexavalent chromium to less toxic trivalent chromium (Konovalova *et al.*, 2003; Faisal and Hasnain, 2004; Thacker and Madamwar, 2005). Reduction of hexavalent chromium by microorganisms has been reported under a number of conditions and by a variety of bacterial species (Faisal and Hasnain, 2004; Faisal *et al.*, 2005; Thacker and Madamwar, 2005). Although different genera of bacteria are involved in the reduction of hexavalent chromium to trivalent chromium but *E. coli*, *Bacillus* sp, *Pseudomonas fluorescens* LB300, *Desulfovibrio vulgaris*, *Pseudomonas ambigua* G-1 and *Alcaligenes eutrophus* are most pronounced (Peitzsch *et al.*, 1998).

Cr(VI) is known to be reduced both aerobically and anaerobically in different bacterial systems (Guha *et al.*, 2001; Megharaj *et al.*, 2003; Viera *et al.*, 2003; Faisal and Hasnain, 2004). In anaerobic systems, membrane preparations reduce Cr(VI) and Cr(VI) has been shown to serve as a terminal electron acceptor (Lovley and Phillips, 1994). Aerobic reduction of Cr(VI) has been found to be associated with soluble proteins (Ishibashi *et al.*, 1990). Lovley and Phillips (1994) reported that the sulfate-reducing bacterium *Desulfovibrio vulgaris*, which was capable of enzymatically reducing Fe (III) and U (VI), could also act as Cr(VI) reducers in the presence of H₂ as the electron donor. Although Fude *et al.*, (1994) also found Cr(VI) reduction by a consortium of sulfate-reducing bacteria in a medium containing reducing agents such as ascorbic acid and thioglycolate, the interpretation of the results must be cautioned because those reducing agents might chemically react with Cr(VI), resulting in conversion of Cr(VI) to Cr(III) (Hamilton and Wetterhahn, 1988). Environmental factors, including pH, temperature and other electron acceptor as well as waste characteristics (metal ions, initial Cr(VI) and biomass concentrations) affecting Cr(VI) removal capability were quantified. With the addition of biological inhibitors such as penicillin, cycloserine, or chloramphenicol, the loss of Cr(VI) reduction activity in microbial cells under reducing conditions clearly indicates that Cr(VI) reduction is an enzymatically catalyzed reaction. Such evidence was found with both growing cultures (Wang *et al.*, 1989) and resting cells (Llovera *et al.*, 1993). Other evidence for enzymatic roles in microbial Cr(VI) reduction includes: Cr(VI) was reduced faster with higher cell densities (Chen and Hao, 1996); Cr(VI) reduction occurred only in the presence of cells or cell extracts and electron donors (Lovley and Phillips, 1994); the Cr(VI) activity was lost when the Cr(VI)-reducing cell extracts were heated at 100 °C (Ohtake and Hardoyo, 1992); Cr(VI) reduction was incomplete with inadequate acetate concentration (Chen and Hao, 1996); and the highest rates of Cr(VI) reduction all occurred during the exponential growth phase of three different strain cells (Apel and Turick, 1991). All these observations strongly suggest that Cr (VI) reduction in biological systems is directly related to microbial activities. The reduced Cr existed mainly in the medium, forming insoluble Cr as Cr (OH)₃ (Shen and Wang, 1994; Faisal and Hasnain, 2004).

Factors Affecting Chromate Reduction

Factors affecting chromate reduction are temperature, pH, gases and organic substance and poisons chemicals. Bacteria can reduce hexavalent chromium under mild conditions. This process may

be the best mechanism to assure hexavalent chromium treatment. Commonly used chemical reduction generally occurs only over narrow range of pH. These methods are not only costly but the productions of toxic byproducts are also a problem. Bacterial reduction of hexavalent chromium as a means of bioremediation has several potential advantages.

- Reduction occurs under neutral pH.
- It requires neither chemical additives nor aeration.
- No toxic byproduct is formed.
- Anaerobic reduction minimizes excess sludge production in aqueous systems.
- The activity is reproducible and reusable.

Conclusions

Reduced chromium forms insoluble chromium hydroxide at a neutral pH. These chromium compounds are very stable and they are unavailable to living organisms. No microbial activity has been found so far that is able to oxidize reduced chromium. The feasibility of the bioremediation process has been examined in the laboratories and is now proceeding to the developmental stage. So it is postulated that the use of microbes creates the right methods for environmental pollution control.

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