

## Toxicity Concerns of Hexavalent Chromium from Tannery Waste

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### ABSTRACT

Environmental pollution by toxic heavy metals results largely from industrial activities, although sources such as agriculture and sewage disposal also contribute to some extent. Industrial wastewater discharged from tanneries contains hexavalent chromium and other toxic compounds. Chromium (VI) is soluble, toxic, mutagenic, teratogenic, and known to cause several adverse effects on human health. It can alter the genetic materials and cause cancer. The toxicity occurs in humans because of environmental pollution through soil or water contamination or due to occupational and non-occupational exposure of heavy metals. Chromium (VI) is transported into the cells through sulfate transport mechanism. To meet the challenge of toxic chromium (VI) pollution in environment, several treatment technologies such as physical, chemical and biological have been employed. However, the unregulated treatment process for disposal of polluted effluent has led to contamination of biotic and abiotic components of the environment. Whereas, bioremediation primarily using microorganisms offers a clean and cost effective technique for transforming toxic chromium (VI) into its non-toxic or less-toxic forms.

**Keywords:** Bioremediation; Chromium (VI); Environment; Pollution; Toxicity

### INTRODUCTION

Industrial wastewater is heavily polluted with hazardous heavy metals that cause hazardous effects to plants, animals and humans life. It is due to the bioaccumulation of such toxic heavy metal in the aquatic life which is ultimately transferred to human bodies through ecosystem (Garg et al. 2012).

Tanneries are one of the most polluting industries mainly causing chromium pollution. In India, there are more than 2500 tanneries, and 80% of them are engaged in chrome tanning process (Shukla et al. 2009). The tannery waste containing large quantity of organics and tannins is released into the environment which causes soil and water pollution along with serious threat to aquatic life and human health. The high-exhaust chrome tanning method leads to wastewater levels of 500-1000 mg Cr<sup>6+</sup> l<sup>-1</sup> (Aravindhan et al. 2004). The discharge of toxic chromium containing waste from leather industry has become a matter of prime concern and is listed as priority pollutants by Environmental Protection Agency (EPA) and World Health Organization (WHO). Metal pollutants affect ecosystem

function, and impose an economic and public health burden.

Chromium is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases. It exists in various oxidation states ranging from +2 to +6. The most stable forms are Cr<sup>6+</sup> and Cr<sup>3+</sup>, although they significantly differ in biological, geochemical and toxicological properties (Garg et al. 2012). In India, the standard limit for Cr<sup>6+</sup> discharge in inland surface waters is 0.1 mg l<sup>-1</sup> (Bhide et al. 1996). The permissible value established by the U.S. EPA is 0.05 mg l<sup>-1</sup>. However, in trace quantities, chromium is an essential nutrient for humans, setting such permissible limits is essential, because at elevated levels Cr is toxic (Lee et al. 2008).

Any industrial activity using metals has an inherent problem of disposing metal-laden waste. It is essential to realize that physical removal of metal from solution occurs only when it is appropriately immobilized. The procedure of metal removal from solutions often leads to effective metal concentration. The ultimate removal is attained only when the metal

becomes concentrated to the point where it can be either returned to the process or resold. This aspect of operation deals with the potential recovery of metal, which ideally should go hand-in-hand with the removal aspect. This makes the overall method an ultimately effective means for controlling the use of metals by humans in technological procedure (Tripathi M, Ph.D. thesis 2013).

To meet the challenge of chromium pollution resulting from tannery waste, a concerted effort has been undertaken that involves both better surveillance of chromium use, and improvements in in-plant and end-of-pipe treatment technologies. Presently, 60% of tannery effluent generated in India is treated by 250 individual and 60 common-effluent treatment plants (Buljan and Sahasranaman 1999). However, complete removal of chromium has not been achieved, and has evolved a new problem relating to safe disposal of metal-laden sludge. Regions where treated effluent and sludge from treatment plants were disposed of onto arable land have resulted in a significant buildup of chromium content in the soil. Chromium waste, when disposed of via land application is also known to leach to ground water (Sakhivel et al. 1999). The sludge generated in these treatment plants is not safe for land disposal due to the presence of high levels of metals and the associated toxicity of their leachates (Srinath and Ramteke 1999), and concern for metal species accumulation in plants (Barman et al. 2000).

### Toxicity of Chromium

Hexavalent chromium is toxic to most of the plants at concentrations that vary from 5 to 100 mg kg<sup>-1</sup> of available chromium in soil. Because of its high oxidizing potential, Cr<sup>6+</sup> exhibits mutagenic and carcinogenic effects on biological systems (Garg et al. 2012). The toxic effects of Cr<sup>6+</sup> are discussed here.

### Genotoxic Effect

The toxic and mutagenic effects of chromium have been reported to occur at concentrations between 10-12 mg l<sup>-1</sup>, which are inhibitory to most soil bacteria in liquid media. These effects are attributed to alteration of genetic material and altered metabolic and physiological reactions (Losi et al. 1994). Cr<sup>6+</sup> does not interact directly with DNA and thus its genotoxicity is attributed to its intracellular reduction to Cr(III) via reactive intermediates. The resulting types of DNA damage are oxidative DNA damage, and Cr<sup>3+</sup>-DNA

interactions. Due of its structural similarity to sulfate (SO<sub>4</sub><sup>2-</sup>), CrO<sub>4</sub><sup>2-</sup>, in some species crosses the cell membrane via the sulfate transport system (Tripathi M, Ph.D. thesis 2013).

Under normal physiological conditions, after crossing the membrane Cr<sup>6+</sup> reacts spontaneously with intracellular reductants (e.g., ascorbate and glutathione) to generate the short-lived intermediates Cr<sup>5+</sup> and/or Cr<sup>4+</sup>, free radicals and the end-product Cr<sup>3+</sup>. Cr<sup>5+</sup> undergoes a one-electron redox cycle to regenerate Cr<sup>6+</sup> by transferring the electron oxygen. The process produces reactive oxygen species (ROS) that includes singlet oxygen (O) and superoxide (O<sup>2-</sup>) (Cheng et al. 2010), hydroxyl (OH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) radicals that easily combine with DNA-protein complexes. Hence, Cr<sup>4+</sup> binds to cellular materials and deters their normal physiological functions (Cervantes et al. 2001). The genotoxic effect of Cr ion however cannot be fully explained by the sole action of ROS. Intracellular cationic Cr<sup>3+</sup> complexes can interact electro statically with negatively charged phosphate groups of DNA, which could affect replication, transcription and cause mutagenesis (Cervantes et al. 2001). Cr<sup>3+</sup> interferes with DNA replication to produce an increased rate of transcription errors in the cell's DNA. Additionally, Cr<sup>3+</sup> may alter the structure and activity of enzymes by reacting with their carboxyl and thiol groups (Cervantes et al. 2001).

### Effect of Occupational and non Occupational Exposure to Chromium

Cr<sup>6+</sup> is highly mobile and water soluble, whereas Cr<sup>3+</sup> is relatively inert, chemically more stable and less bioavailable due to its negligible permeability to biomembranes (Pal et al 2005). Cr<sup>6+</sup> is nearly 100 times toxic (Garg et al. 2012) and 1000 times more mutagenic than Cr<sup>3+</sup> (Barrera et al 2008). The toxicity occurs in humans due to environmental pollution via soil or water contamination or due to occupational exposure. The metal toxicity causes serious morbidity and mortality. Even a slight elevation in the level of Cr<sup>6+</sup> elicits environmental and health problems because of its high toxicity, mutagenicity and carcinogenicity (Garg et al. 2012). Soluble Cr<sup>6+</sup> poses a significant carcinogenic risk if ingested. This is attributed to low pH of the stomach as particulate chromate dissolves at low pH (Holmes et al. 2008). The toxic and mutagenic effects of chromium on microorganisms have been reported to occur at concentrations between 10-

12 mg l<sup>-1</sup>, which are inhibitory to most soil bacteria in liquid media. These effects are attributed to alteration of genetic material and altered metabolic and physiological reactions (Losi et al. 1994).

Occupational exposure to chromium has been identified as an important risk factor for human lung cancer. This metal also irritates airways, causes nasal and skin ulcerations and lesions, causes perforation of the nasal septum, asthma, dermatitis and other allergic reactions (Tripathi M, Ph.D. thesis 2013). Ingesting Cr<sup>6+</sup> causes stomach and intestinal damage and can lead to cancer. In lab animals, Cr<sup>6+</sup> damages sperm and male reproductive systems, and in some cases, has damaged the developing fetus (Tripathi M, Ph.D. thesis 2013).

Nonoccupational exposure to the metal occurs via ingestion of chromium-containing food and water, whereas occupational exposure occurs via inhalation. Chromium<sup>3+</sup> is poorly absorbed, regardless of the route of exposure, whereas Cr<sup>6+</sup> is more readily absorbed (Ray and Ray 2009). Humans as well as animals accumulate chromium in various locations such as lung, liver, kidney, spleen, adrenals, plasma, bone marrow, red blood cells, etc. The respiratory and dermal toxicity is well documented (Holmes et al. 2008).

Physiologically, Cr<sup>6+</sup> is toxic due to its membrane permeability that results in the functional change of the lung, respiratory tract, liver, pancreas and kidney (Tripathi M., Ph.D. thesis 2013). Gibb et al. (2000 a,b) reported several ailments associated with Cr<sup>6+</sup> exposure that include nasal irritation and ulceration, skin irritation, eardrum perforation and lung carcinoma. Hexavalent chromium can accumulate in the placenta thereby impairing fetal development in mammals (Saxena et al. 1990). In their study, Maria et al. (1999) found that workers exposed to tanning process had several ailments pertaining to general health diminishing. They were hypoglycaemia with respiratory cancer and nephrotic ailments. Epidemiological studies on industrial workers exposed to Cr<sup>6+</sup> had a higher incidence of respiratory cancers than the normal population (Norseth 1986; Langard 1990). Katz and Salem (1994) reported nasal mucous membrane perforation in exposed workers at tannery, galvanoplastic and chromate production units. Additionally, renal and hepatic toxicity have been reported in workers exposed to Cr<sup>6+</sup> (Verschoor 1988), nephrotoxicity and

hepatotoxicity (Ueno 1992) in experimental animals causing DNA damage such as single strand breaks and DNA-protein cross-links in cultured and *in vivo* cells (de Flora et al. 1990). Overexposure to Cr<sup>6+</sup> reportedly produced allergic dermatitis, ulceration in the skin, mucous membranes and nasal septum, renal tubular necrosis and increased risk of respiratory tract cancer (Flavio et al. 2004). Doses of Cr<sup>6+</sup> greater than 10 mg kg<sup>-1</sup> diet of humans affect mainly the gastrointestinal tract, kidneys and probably the hematopoietic system. Heavy metals are predominantly present in many industrial effluents along with other toxic organic and inorganic compounds. In such environments they can exert toxicity in a complex manner. Binary mixtures of free cyanide plus Cr<sup>6+</sup> resulted in more fish lethality than predicted by either response addition or concentration addition models (Leduc et al. 1982).

### Mechanism of Cr<sup>6+</sup> toxicity

Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Under normal physiological conditions, Cr<sup>6+</sup> is believed to be reduced inside the cell through reactive short-lived intermediates such as Cr<sup>5+</sup> and/or Cr<sup>4+</sup> free-radicals to the more stable Cr<sup>3+</sup> (Xu et al. 2004; Pal et al. 2005; Cheung et al. 2006) by cellular reductants such as glutathione, cysteine, ascorbic acid, riboflavin, and NADH-dependent flavoenzymes such as microsomal cytochrome P<sub>450</sub> reductase (de Flora et al. 1990; Sugiyama 1992). Therefore, the formation of paramagnetic species such as Cr<sup>5+</sup> might play an important role in the induction of the toxic properties of Cr<sup>6+</sup>. In fact, Cr<sup>6+</sup>/Cr<sup>5+</sup>, Cr<sup>5+</sup>/Cr<sup>4+</sup> and Cr<sup>3+</sup>/Cr<sup>2+</sup> oxidation/reduction couples have been shown to serve as cyclical electron donors in a Fenton-like reactions, which generate active oxygen species such as hydroxyl radicals, that are known to produce a number of toxic effects (Luo et al. 1996; Shi et al. 1999). Ueno et al. (2001) reported that hydroxyl radicals formed during Cr<sup>6+</sup> reduction may play an important role in the DNA strand breaks caused by the metals, and implied that the levels of Cr<sup>6+</sup> inside the cells may not always be related to the induction of DNA strand breaks.

### CONCLUSIONS

Chromium (VI) is one of the major environmental toxicants. The pollution of such

toxic heavy metals pose adverse effects to human health and ecosystem. Thus, detoxification of Cr (VI) is necessary before discharge in to the environment. There must be proper cost effective ecofriendly treatment technology to remove toxicity caused by Cr (VI) containing waste.

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