***Review Article***

# The chemistry and toxicity of chromium pollution: An overview

## ABSTRACT

As a heavy metal, chromium (Cr) has significant importance in the current industrial scenario, however, it poses an environmental threat as well. Generally, there are two stable forms of Cr available in environmental matrices, the relatively less toxic trivalent Cr(III) and the highly toxic hexavalent Cr(VI). Industrial sites release hazardous Cr(VI) with effluents during the post-production stage, causing water and soil pollution worldwide. The Cr(VI) is one of the priority pollutant as per USEPA (United States Environmental Protection Agency) classification and it is one of the well known carcinogen. In most cases, it is released from anthropogenic activities like mining, steel making, welding, tanning, textile dyeing, and wood polishing etc. Whenever Cr(VI) contamination exceeds the threshold limits, it has a deleterious impact on public health and the vegetation of the site contaminated. In the present investigation, major focus is on the anthropogenic sources of Cr(VI) release into water bodies and soil, its adverse effects, as well as remediation of these emerging environmental problems. The present review focuses on the removal of Cr from environmental media by conventional biological methods. Many advanced technologies have been developed and applied recently to remove Cr from contaminated soils and water, including membrane technology, electrocoagulation, ion exchange, and electrodialysis. In addition, alternative techniques like phytoremediation processes were established which offer an environmentally sustainable, eco-friendly, and cost-effective approach to remove Cr. With an emphasis on the cleanup of soils and water systems contaminated by Cr, this review summarizes the bioavailability of Cr, the uptake pathways, the accumulation process and the current status of phytoremediation research. A recent finding about Cr localization in hyperaccumulator plant species is also described in this paper. This review describes the process of plant metabolism changes in response to Cr stress and the mechanisms that allow plants to  removing Cr through the phytoremediation process.

*Keywords:Hexavalent chromium;Chromium toxicity;Carcinogen; Phytoremediation; hyperaccmulator plant sp.*

## 1. INTRODUCTION

During the past few decades, the amount of heavy metals in the environment has grown beyond permissible limits, posing a serious threat towards the living organisms. Chromium (Cr) is a naturally occurring heavy metal and the 17th most abundant element in the earth's mantle [1]. At higher concentrations, Cr serves as a major environmental contaminant, even though it is required in trace amounts by plants and animals.From the combined results ofnatural sources and anthropogenic activities, Cr has been released into the soil, air, and water, resulting in  seriouspollution worldwide [2].When food-lands and drinking water are contaminated, Cr can easily enter the food chain and affect all life forms directly or indirectly.Cr also has toxic effects on plants, causing delays in seed germination, damaged roots, reductions in root growth, reduced biomass  and height, impairment of photosynthetic processes, membrane damage, chlorosis, necrosis, low grain yield and death of plants [3]. Cr which has oxidation states from 0 to +6, is a fairly active metal and can react easily with environmental oxygen. The most stable forms of Cr in nature are Cr(III) and Cr(VI). Depending on the solubility and mobility, Cr(VI) has higher toxicity in water systems rather than Cr(III)[1].It is possible for plants to absorb both the trivalent and hexavalent forms of Cr, however, Cr(VI) is actively taken up into the plant cells by sulfate carriers [4]. On theother hand, Cr(III) enters passively by the cation exchange sites of the plant cell walls [5].Further, carboxylic acids in the root exudates enhance Cr solubilization and thus its absorption by plants [6].To minimize the load of Cr pollution, now a day's Phytoremediation is a rapidly growing field of research to decontaminate the heavy metal from polluted sites.Phytoremediation involves various methods, including phytovolatilization, phytoextraction, phytostabilization, and hyperaccumulation [7].Research has shown that many plant species are capable of removing Cr from contaminated regions, which may be useful in phytoremediation [8].Industrial effluent sites have been using Cr hyperaccumulator and their associated microflora to remove excess toxic Cr and organic matter.Using plant-microbe interactions to detoxify Cr is also an effective strategy because it is economical, high-performing, and eco-friendly [9].Taking all aspects into account, this review discusses Cr sources, chemistry, effects, and uptake in plants.The phytoremediation approach was also discussed as a remedy for Cr detoxification in plants.

## 2. CHEMICAL PROPERTIES AND TOXICITY

Chromium is an inorganic transition metal that exists in several valence states ranging from −2 to +6 (Table 1). However, Cr(III) and Cr(VI) are of significance owing to their stability in natural environments [10].The commended permissible limit in drinking water is 50µg/L for Cr(VI) [11].

**Table 1. General properties of chromium**

| Name | Element group | Atomic number | Molecular weight | Electron configuration | Common oxidation states | Other oxidation states | Common ions |
|---|---|---|---|---|---|---|---|
| Chromium (Cr) | Group 6 of the transition metals | 24 | 51.9961 g $mol^{-1}$ | [Ar] $3d^5$ $4s^1$ | +2, +3,+6 | +1, +4, +5 | Cr(II), Cr(III), Cr(VI) |

Due to its strong oxidizing nature, Cr(VI) can cause many diseases like allergies, eczema, irritations, and respiratory tract disorders, as well as mutagenic and carcinogenic effects on biological systems. The toxic action of Cr(VI) complexes is due to their ability to penetrate biological membranes and undergo immediate reduction reactions resulting in the formation of oxidative stress in the organisms [12]. Different species of chromium have different colour (Table 2).

**Table 2. Colour of different species of chromium**

| Species | Oxidation state of metal | Colour |
|---|---|---|
| $K_2CrO_4$ | +6 Chromate (VI) ion | Yellow |
| $Cr_2O_7^{2-}$ | +6 Dichromate (VI) ion | Orange |
| $Cr^{3+}$ $[CrCl_2(H_2O)_4]^+$ | +3 | Green |
| $Cr^{2+}$ $[Cr(H_2O)_6]^{2+}$ | +2 | Blue |

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It is oxidized to form a thin protective coating to prevent further corrosion. Chromium does not react with water but it reacts with most acids. The reduction of Cr(VI) into Cr(III) in the presence of oxygen forms a thin layer on the metal's surface that protects it from corrosion. Trivalent chromium is less toxic and an essential element for humans and plants [13].

It is most commonly found in oxidation states 0, +2, +3 and +6 even though Cr can exist in all oxidation states from -2 to +6 (Table 1). Elemental chromium (0) is not naturally present in the earth’s crust and is biologically inert. Almost all naturally occurring Cr is trivalent, and most hexavalent Cr comes from industrial processes. In the presence of air, Cr(II) undergoes rapid oxidation, producing Cr(III).This explains why Cr(II) is not available in biological systems. The most stable oxidation state of Cr that can be found in living things is Cr(III). The most significant biological feature that distinguishes it from Cr(VI) is its low reactivity and inability to cross cell membranes easily [14]. There is an possible existence of the intermediate Cr species in different systems of environment such as reduction of Cr(VI) by Fe (II), sulfide group, molecules of natural organic matter (fulvic acids and carboxylic acid) and oxidation of Cr(III) by hydrogen peroxide ($H_2O_2$), hypochlorite (HOCl) and manganese oxides (MnOx) (Fig. 1)[15].

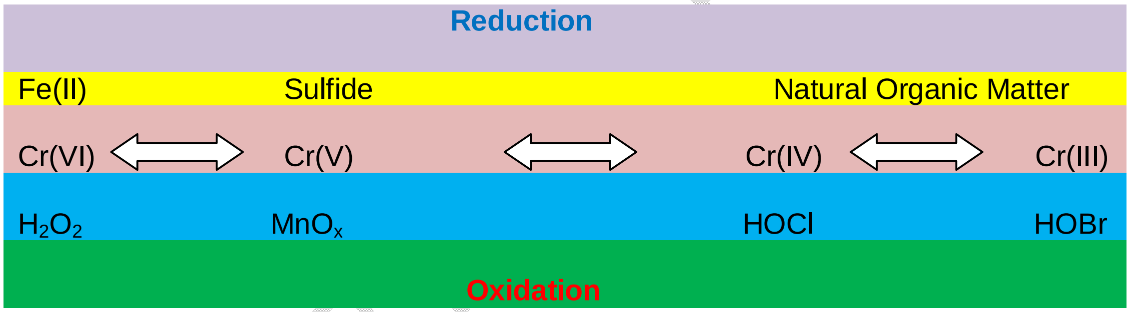

**Fig 1. Oxidation and reduction reaction of chromium**

It has been suggested that Cr(III) (e.g. $Cr_2O_3$) can be used as markers for digestion processes due to their low reactivity and absorption from the gastrointestinal tract [16-17]. As strong oxidizing agent, particularly in acidic environments, Cr(VI) is the second most stable form of Cr (Table 3).Having a strong oxidation potential,Cr(VI) binds to oxygen as chromate ($CrO_4^{2-}$) or dichromate ($Cr_2O_7^{2-}$). After being deoxygenated to Cr(III), this form of Cr crosses biological membranes easily, reacting with proteins and nucleic acids inside the cell. When it react with genetic matter, provides the carcinogenic properties in biological system.

**Table 3. Cr oxidation numbers, type and environmental behavior**

| Valency | Environmental behavior | Remark |
|---|---|---|
| Cr | Unstable | |
| Cr(I) | Unstable | |
| Cr(II) | Readily oxidize to $Cr^{3+}$, but stable only in the absence of any oxidant | Active under anaerobic condition |
| Cr(III) | Most stable | Considerable energy required to convert to lower or higher state |

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| | | |
|---|---|---|
| Cr(IV) | Forms unstable intermediate reactions to trivalent and oxidation state | Exhibit this phase during oxidation and reduction |
| Cr(V) | Unstable intermediate | Observed during oxidation and reduction |
| Cr(VI) | In acidic conditions demonstrates very high positive redox potential and unstable in the presence of electron donors | Strongly oxidizing |

*Ref: [10]*

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## 3. SOURCES OF CHROMIUM CONTAMINATION

Rocks, soils, and volcanic dust contains Cr, which are naturally available in the lithosphere. In the course of anthropogenic polluting activities, Cr surpasses the natural background concentration in the environment resulting in harmful and lethal effects on both on living organisms and their environment. The numerous sources of Cr include industrial processes like wood preservation, tanning, electroplating, textile dyeing, alloy manufacturing, pulp and paper processing, ferrochrome production, aerospace material production and maintenance, chemical production etc. Living organisms and plants require trace amounts of chrome, but at higher levels, it can be toxic and mutagenic [18].

### 3.1 Natural sources

The primary and most abundant natural source of Cr is the Earth's crust. It is highly concentrated (200 mg kg$^{-1}$) in igneous rocks and in the Earth's oceanic crust in serpentinite and ophiolite complexes [19-20]. During the weathering of Cr-containing rocks and diagenetic reactions, Cr releases into the soil, water and readily adsorbs on clay minerals with hydroxides [Al(III), Fe(III)][19].There is also a small amount of Cr found in fresh vegetables, as well as in many food supplements.

### 3.2 Anthropogenic sources

Many food supplements and rocks contain optimum concentrations of naturally occurring Cr, but human interference has increased Cr concentrations in the environment worldwide and poses a serious threat to the environment and humans. Major anthropogenic Cr flows through the release of various industrial applications such as refractories and foundry sands for their heat resistance, fossil fuel combustion, waste incineration, electroplating, tanning, textile dyeing, corrosion inhibition, and wood preservation [21-22]. In addition to wood preservatives, Cr can be used in the production of chrome pigments (e.g., lead chromate), which can be applied to paints, printing inks, and anticorrosive materials [23]. A total of 12.5 million tons of Cr are consumed globally every year, 85% of it by the metallurgical industry and 15% by other industries[24]. Ferrochromium is used to produce Cr-containing steel and contains 40–80% Cr with iron. The material is used in the production of full alloy steel, bearing and high-speed steels, tool steel, superalloys, and welding materials [20].

## 4. CHROMITE MININGPOLLUTION SCENARIO IN INDIA

In industrial processes, Cr plays a vital role due to its high importance worldwide. But this metal is highly toxic to the environment and human health [25]. The first step in the industrial use of Cr begins with the chromite mining process. The natural form of Cr in rocks is Cr(III), but mining activities could expose it to the environment and cause inter-conversion to the highly toxic Cr(VI) form [26]. Thus, chromite mining is considered a serious threat to the environment as well as public health.

There are over 12 billion tonnes of shipping grade chromite resources in the world, of which the majority (95%) are found in South Africa (84%), Zimbabwe (6%), and Kazakhstan (5%). India (2%) lies 4th in the list followed by other countries like Brazil, USA, Canada, Russia, Finland, and others which collectively account for the remaining 3% of the share (Fig. 2) [27]. In 2009, India was the 2nd largest producer of chromite ore in the world [28].

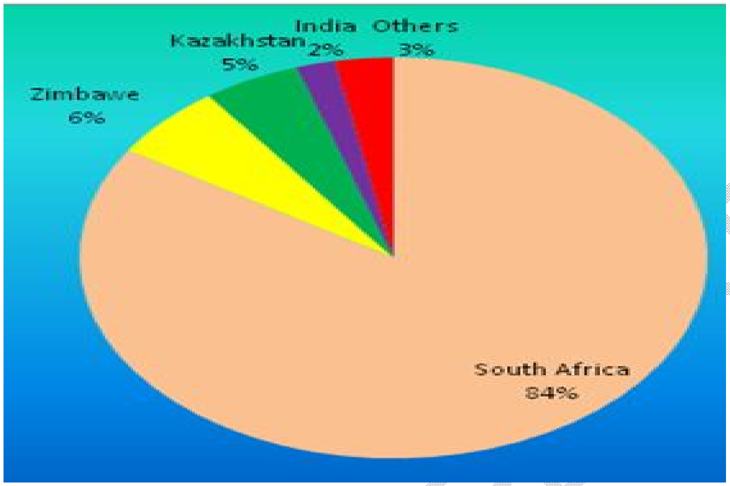

**Fig 2. Distribution of shipping grade chromite resources in the world. South Africa has the largest reserves of shipping grade chromite ores in the world followed by Zimbawe (6%), Kazakhstan (5%), and India (2%)**

Globally, Indian chromite deposits account for 2% of all resources. There are approximately 98.6% of chromite resources in Odisha, with 95% located in the Sukinda valley, located in Cuttack and Jajpur districts. The remaining percentage of the resources are found in Jharkhand, Karnataka, Goa, Maharashtra, Tamil Nadu, and Andhra Pradesh, while very few are found in Manipur, Nagaland, Jammu and Kashmir, and the Andaman and Nicobar islands. The chromite deposits of different Indian states are scattered over certain areas also known as 'belts'. The major chromite belts are the Sukinda, Bhalukasuni—Nilgiri and Ramagiri in Odisha, Jojohatu—Roroburu in Jharkhand, Bhandara—Nagpur, Chandrapur and Sindhudurg in Maharashtra, Janaram block, Konayyapalem block, Linganapetta block, Sriramgiri block and Kondapalli block in Andhra Pradesh, Nuggihali and Sindhuvalli—Talur in Karnataka, Karunglapatti, Sitampundi, and Solavanur-Mallanayakkanpalaiyam–Karapaddi in Tamil Nadu [27].

While India's extensive use of Cr resources has brought economic benefits to the nation, it has also caused significant damage to the environment and the people. In India, most of the Cr pollution is caused by mining sites and certain industries (mainly tanneries, dye manufacturing, and steel manufacturing). Tata Environmental Research Institute reported that out of the 7.2 million tons of hazardous waste generated by Indian industries each year, approximately 72% are disposed of in an improper fashion [29]. Chromite mining

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is largely responsible for maximum environmental contamination, due to improper disposal of wastes that contain Cr(VI).

### 4.1 Chromite mining at Sukinda valley, Odisha

Approximately 98.6% of chromite resources of the country are located in Odisha. The major mining belts of Odisha are Sukinda, Nilgiri and Ramagiri and their Cr concentration is shown below (figure. 3) [30].

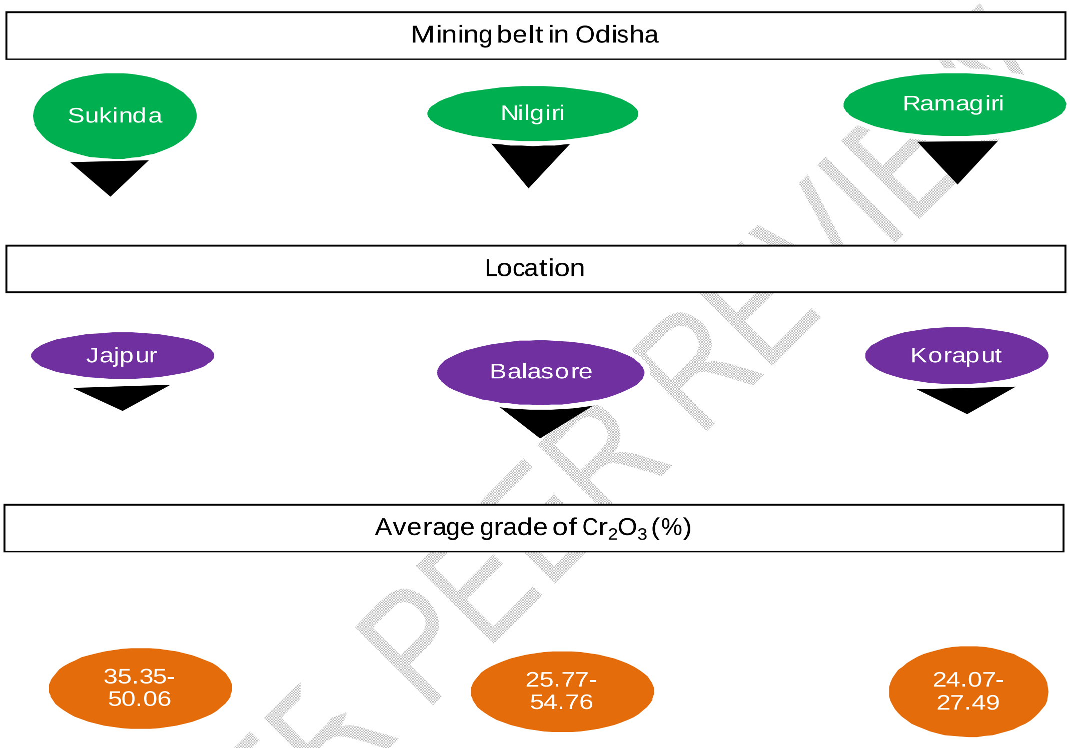

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**Fig 3. Deposits and the average grade of chromite available in Odisha.**

Sukinda valley, located in the Jajpur district of Odisha, is one of the most alarming examples of Cr(VI) pollution in India. It accounts for approximately 95% of the total chromite reserves of the country. Approximately 97% of the state's chromite reserves are located in the south Kaliapani mining area in the Sukinda valley [31]. The valley contains around 183 million tons of deposits [32] and produces around 3.8 million tons of chromite ore per year [33-34]. Due to excessive mining of chromite ores, the valley has become the fourth most polluted place in the world [35]. India's largest open cast mine is the chromite mine of TISCO in the Sukinda valley. A few of the other open cast mines in the region are operated by companies like Orissa Mining Corporation Ltd (OMC), Indian Metals & Ferro Alloys Ltd (IMFAL), Ferro Alloys Corporation Limited (FACOR), and Balasore Alloys [30]. Thousands of tons of waste are generated by the mines in the valley and thus spread to nearby water bodies and leach into the groundwater, contaminating local drinking water supplies. The contamination mainly occurs due to Cr(VI), which is considered a major environmental carcinogen and is highly toxic [36]. In addition to the lack of sufficient space for disposing of waste, another major problem exists. Due to the same problem of inadequate space, the Bhimtanagar chromite mine operated by Tata Iron and Steel Company(TISCO) has dumps

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reaching an abnormal height of 80 m. High concentrations of Cr(VI) and Cr(III) have been detected in the waters of the Damsalanallah that drains the Sukinda valley and also in the downstream of the river Brahmani and the Dhamra estuary, though in lesser quantities [27]. It was also found that water samples collected from wells located within the chromite belt region of Sukinda were contaminated. Samples of surface water used for drinking in the area contained much higher concentrations of Cr(VI) than the maximum permissible limit. It was found that the Cr(VI) concentration in the effluent channel of the TISCO chromite beneficiation plant reached 52 mg/l [37]. BRGM, France, completed a project titled 'Development of Application Techniques for Environmental Management of Mines and Waste Recoveries' and prepared a Regional Environmental Impact Assessment (REA) report in collaboration with the Indian Bureau of Mines. According to the monitoring report generated by REA, surface water quality in DamsalaNallah exceeded drinking water standards. The majority of the groundwater samples investigated exceeded the quality standards for drinking water. Furthermore, the region's fauna and flora were found to be highly contaminated. In all the sampling points, Cr(VI) was found to be present at a higher concentration [30]. Due to intensive mining activities in the region, the release of high loads of Cr(VI) leads to environmental deformation.

## 5. TOXICITY OF HEXAVALENT CHROMIUM

Mining of chromite ores has also increased in response to the excessive demand for the metal. The earth's surface contains the non-toxic trivalent form of Cr; however, open pit mining activities expose the Cr(III) to atmospheric air and water, where it can oxidize to the toxic hexavalent form (Cr(VI)). It is estimated that a large amount of fine ore particles and dust generated are blown into the air where they can cause Cr(VI) contamination through atmospheric deposition [38]. Mines also use water to control dust during drilling and other mining operations. Water from these mine washes can seep into the groundwater and contaminate nearby water bodies [39]. As Cr(VI) levels increase in soils and water bodies, it accumulates in plants and crops, allowing it to easily be transferred from one food source to another. The presence of Cr(VI) may affect some beneficial microflora in the soil, resulting in loss of soil fertility. Humans are also equally or even to a longer extent victimized upon exposure to the Cr(VI) via various media. Humans are exposed to Cr(VI) via inhalation, oral intake as well as dermal contact [28]. Air dispersed with Cr(VI) particulates, which may arise from mining activities, poses a serious threat to human health and may cause several lung and respiratory ailments. There is also the possibility of stomach and alimentary canal diseases occurring from the consumption of contaminated water or food crops by Cr(VI). Human activities such as bathing, cleaning, and washing in rivers and ponds near mining localities may also cause various skin diseases caused by Cr(VI) contamination. Several studies have examined the toxicological effects of this heavy metal on humans, animals, and microbes. In the following section, we discuss briefly the toxicological implications of Cr(VI) for living biota associated with mining sites and nearby areas. Various parameters related to plant growth, development, and physiological processes have been reported to be adversely affected by Cr(VI) (Table 4).

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**Table 4. Impacts of Cr (VI) on growth and physiology of plant**

| Impact of Cr(VI) | Possible reasons | References |
|---|---|---|
| Reduction in germination percentage | Decrease in amylase activities leading to decreased availability of sugar to the developing embryos<br>During germination, Cr (VI) may have caused a decrease in the activity of key enzymes involved in carbohydrate, amino acid, and peptide metabolism | [40-41] |

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|---|---|---|
| Inhibition of growth of radicals | May be due to the toxic effect of Cr(VI) | [42] |
| Inhibition of root growth, reduction in lateral roots | Inhibition of root cell division and elongation, collapsing of root tissues leading to the inability of absorbing water and essential nutrients from the soil<br>Extension of the cell cycle | [43-44] |
| Reduction in shoot length | Reduced root growth and subsequently reduced transport of water and nutrients to shoots<br>Cr also affects the cellular metabolism of shoots | [45-47] |
| Reduction in leaf numbers and leaf area | Reduction in the number of leaf cells and the cell size of the leaves.<br>Loss of turgidity<br>Necrosis, permanent wilting, drying, etc. | [48-49] |
| Decreased plant yield | Decreased leaf numbers, surface area, and functions may be responsible | [44] |
| Inhibits photosynthesis | Ultrastructural changes in the chloroplast<br>Affects pigment synthesis by competing with Mg and Fe for assimilation and transport to leaves<br>Increases production of reactive oxygen species (ROS) leading to pheophitinization and deformation of thylakoid membranes | [50-52] |
| Decreases uptake and translocation of essential micronutrients | Displacement of the nutrients from the physiological binding sites | [53] |
| Increased activity of antioxidant enzymes | Protection of plants from oxidative injury by controlling the superoxide radicals generated by Cr(VI)- induced inhibition of the mitochondrial electron transport chain | [54] |
| Degradation of proteins | Binds to the protein or displaces metals from the protein's active center | [55-56] |
| Blocks electron transport chain | Binds to the cytochrome $a_3$ inhibiting cytochrome oxidase activity<br>Generates toxic oxygen free radicals in the mitochondria | [57-58] |

The toxicity of Cr(VI) affects the overall health of the plants, thereby leading to plant death. A large portion of biodiversity loss at industrial and mining sites is associated with Cr(VI) toxicity, which may cause a perturbation in environmental homeostasis. High levels of Cr(VI) concentration in the soil also lead to poor crop growth and reduced crop yield which may affect overall crop production of a place. The loss of crops may further hinder the financial and economic growth of farmers of the region. Cr(VI) is a proven sensitizer of the skin as well as the respiratory tract. Upon continuous exposure, it leads to nasal irritation and may cause perforations [59-60]. During the reduction of Cr(VI) into Cr(III) in a living body, a number of intermediates are formed, including Cr(V), Cr(IV), and reactive oxygen species (ROS). Specifically, Cr(V) forms bulky DNA adducts in the p53 gene of human lung cells. The ROS formed also induce oxidative damage to the DNA of the p53 gene [61]. P53 functions as a tumor suppressor gene that regulates the expression of multiple target genes under various cellular stress conditions and helps in DNA repair. Damage to this particular gene causes a failure of the DNA repair mechanism, which leads to mutations and uncontrolled cell divisions, causing lung cancer. Inhalation of Cr(VI) concentration exceeding 0.001 mg/m3 through the mouth may also cause stomach ulcers [62]. Cr(VI) negatively affects myocardial activity. It can either be caused by direct effects on blood vessels or

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indirectly by a reduction in pulmonary function [63]. A pregnant woman who is occupationally exposed to Cr(VI) may transfer the toxic heavy metal to the fetus from the placenta [64]. As a nutrient, Cr is also needed by microorganisms in small quantities. It has been found that excessive amounts of Cr in the environment can negatively affect these microorganisms [65]. As well as inhibiting cell division, Cr(VI) causes elongation and enlargement of bacterial cells, thus inhibiting their growth. It has also been found that bacteria exposed to Cr(VI) show changes in morphology [66] and a reduction in pathogenicity [67] Green algae have been found to be affected by Cr(VI), which inhibits the photosynthesis process [42]. With its high solubility and mobility, Cr(VI) can easily penetrate bacterial cell membranes and enter cytoplasm, contributing to toxic effects [68].

## 6. PHYTOREMEDIATION OF HEXAVALENT CHROMIUM

Hexavalent chromiumis more toxic to the plants than trivalent chromium. Plants can be used to decontaminate soil from organic nutrients and heavy metals like Cr through phytoremediation, a growing eco-friendly process. This method is cheap or cost-effective and has almost completely removed metals from the contaminated site. Phytoremediation involves five processes like phytotransformation, rhizoremediation, phytostabilization, phytoextraction, and rhizofiltration [20]. The higher plant can accumulate a high concentration of Cr from the soil through the root of the plant. The mechanisms of wilting and plasmolysis of root cells are mainly playing a key role in removing heavy metals from contaminated biota [69]. It was found that the common water hyacinth *Eichhornia crassipes* can readily remove Cr from its environment as a result of a hydroponic experiment carried out for one month at different metal concentrations [70]. *Ipomoea aquatica* is a fast-growing aquatic macrophyte that could effectively remove Cr from contaminated water within a short period of time [71]. Recent research aimed to improve phytoremediation by using chelators including EDTA, Ca, and Zn$^{2+}$ to increase metal or Cr bioavailability and uptake by plants treated with high Cr concentration levels. Chromium is found at a high level after phytoremediation in roots and less at aerial parts [72]. A phytoremediation process also involves phytostabilization and phytoextraction, with the help of plant growth-promoting bacteria (PGPB). In this way, the bacteria help accumulate toxic metals in plant cells and enhance plant growth [73].

## 7. CONCLUSION

Chromium (Cr) as a heavy metal is very detrimental to human health, animals, and the environment when its concentration level goes beyond the standard permissible limit. Industrial activities particularly open pit mining contribute a substantial amount of Cr to the environment through atmospheric deposition. Mines also use water to control dust during drilling and other mining operations. If this Cr-rich water is not properly treated, then it finally mixes with the neighbouring water bodies and pollutes the water. But this pollution does not remain in water alone but spreads to other abiotic components of the environment such as soil, groundwater, and even to biotic components like plants and animals. As a result, the ecological balance of the environment is affected seriously. There are a number of methods of treating Cr from tannery wastewater. Some of these methods result in more than 90% Cr removal from the tannery wastewaters. Typically, these sorts of technologies are expensive, sophisticated, and energy-intensive and need skilled personnel as well to operate. The suitability of phytoremediation is useful in this context. Its cost-effectiveness and zero maintenance make this technique preferable over other techniques. Further study is highly required to improve the efficiency of this process of remediation of Cr(VI) from contaminated water bodies near mining area. Phytoremediation of Cr contaminated sites is a rapidly growing area of research. Knowledge of suitable indigenous plants, that can bioremediate Cr is particularly limited, and needs to be further explored. One of the key aspects is to develop

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transgenics to enhance their tolerance and accumulation rate at environmentally relevant concentrations. More research is needed to understand the mechanism ofinterconversion of the Cr species within the plant system and its localization following uptake which would help in developing the transgenics for effective Cr phytoremediation.

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