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REVIEW

Chromite mining pollution, environmental impact, toxicity and phytoremediation: a review

Pratyush Kumar Das[1] · **Bidyut Prava Das**[2] · **Patitapaban Dash**[1]

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Abstract

Chromite mining activities are indispensable for production of goods and services. Sukinda is a major mining site of Odisha, India, polluted by chromium, which is highly toxic in its hexavalent form. The Sukinda valley is a rich source of chromites, amounting to almost 95% of Cr available in India, and is the fourth most polluted site worldwide. Immediate solutions are needed to protect the health of biotic species of this region and their surroundings. Here we review chromite mining in India, impact of chromite pollution on plants and the environment, and phytoremediation of Cr-polluted soils.

Keywords Chromium · Environment · Heavy metal · Mining · Rhizosphere · Hyperaccumulator

Introduction

The economic stability and advancement of a country are highly dependent on its rich mineral resources. The mining sector which involves the utilization of the minerals therefore can be assumed to play a crucial role in the economic growth of a nation (Groves et al. 2007). Mining comes under the primary sector of the Indian economy and is a bulky sector as far as employment and job creation is concerned. Mining activities although contribute 10–12% of GDP of the total industrial sector in India but are also quite infamous for pollution of the environment. In about 3100 mines (both public and private) operating in India, approximately 5,60,000 people are employed daily. The complete detail on the Indian mining sector synthesized from the reports from the Indian Bureau of Mines (IBM 2000, 2004) is listed in Table 1.

The vulnerability of the mine workers to various toxic pollutants present in the mining environment may lead to deleterious health impacts. Exposure of toxic heavy metals in and around the mining sites during the mining process contributes largely to pollution of the air, water, and soil. Heavy metals being persistent in the environment are not only a major concern to public health but also affect other living organisms (Abdu et al. 2017) and the food chain (Malik et al. 2019; Sevgi et al. 2009).

Chromium (Cr) is an important mineral having worldwide importance and widely used in industrial processes. However, it expresses its toxicity on the environment and human health (Peng and Guo 2020). It is unique than other metals in a way that its toxicity is dependent on the available oxidation states—Cr(III) and Cr(VI), unlike other metals whose toxicities are based on their total available concentrations in the environment (Kimbrough et al. 1999). The trivalent state or Cr(III) is considered to be benign and an essential micronutrient (Nieboer and Jusys 1988; Kahlon et al. 2018), whereas the hexavalent form, also denoted as Cr(VI), is listed as a Group-I human carcinogen (IARC 1990). The USEPA (United States Environmental Protection Agency) classifies materials as hazardous if they contain leachable Cr(VI). Chromium occurs naturally in the environment as Cr(III), whereas the Cr(VI) form arises from various industrial activities (Mudhoo et al. 2012). The first step in the industrial use of chromium begins with the chromite mining process. Chromium is generally found to

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✉ Patitapaban Dash
patitapabandash@soa.ac.in

Pratyush Kumar Das
pratyushdas@soa.ac.in

Bidyut Prava Das
bidyutpravadas@rediffmail.com

[1] Centre for Biotechnology, Siksha 'O' Anusandhan (Deemed to be University), Bhubaneswar, Odisha 751003, India

[2] Rama Devi Women's University, Bhubaneswar, Odisha 751022, India

Table 1 Division of employment in the Indian mining sector

Total number of mines	Number of mines in the public sector	Number of mines in the private sector	Average daily employment in the public sector	Average daily employment in the private sector	Total employment
3100	800	2300	4,90,000 (87%)	70, 000 (13%)	5,60,000

be associated with iron (ferrous chromite) in the mining sites (Westbrook 1983; Hartford 1983). The problem with chromium lies in its two most stable states—Cr(III) and Cr(VI), which are inter-convertible among themselves in the environment. This inter-conversion mainly depends on the types of compounds present, pH of the environment, moisture, temperature, presence or absence of oxidizing and reducing agents, and many more. Chromium though is naturally found in the rocks in the benign Cr(III) form, but mining activities could expose the same to the environment and create a chance of inter-conversion to the highly toxic Cr(VI) form (Gunkel-Grillon et al. 2014). Thus, chromite mining is considered to be a serious threat to the environment as well as public health. The paper aims to discuss the negative impact of chromite mining on the Indian environment, with special emphasis on the Sukinda chromite mines of Odisha.

The Indian chromite situation

The worldwide shipping grade chromite resources account for over 12 billion tonnes among which the majority of the resources (95%) are located in South Africa (84%), Zimbawe (6%), 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. 1). However, as per the 2009 statistics, India is the 2nd highest chromite ore producing country in the world (Das and Singh 2011).

Indian chromite deposits account for 2% of the total resources of the world. Approximately 98.6% of chromite resources of the country are located in Odisha out of which 95% are found in the Sukinda valley, situated in Cuttack and Jajpur districts of the state. The remaining percentage of the resources are found in Jharkhand, Karnataka, Goa, Maharashtra, Tamil Nadu, and Andhra Pradesh, while very few in Manipur, Nagaland, Jammu and Kashmir, and the Andaman and Nicobar islands. Deposits of chromite in various states of India (Fig. 2) are found to be scattered over certain regions also referred to 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 (Table 2).

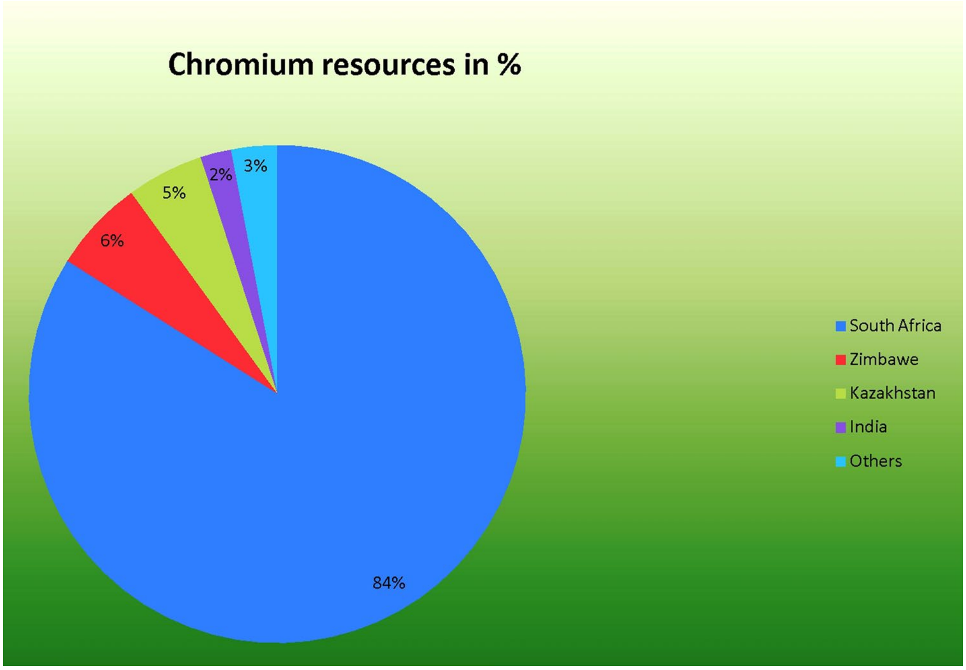

Fig. 1 Distribution of shipping grade chromite resources in the world. South Africa has the largest reserves of shipping grade chromite ores in the world followed by Zimbawe (6%), Kazakhstan (5%), and India (2%)

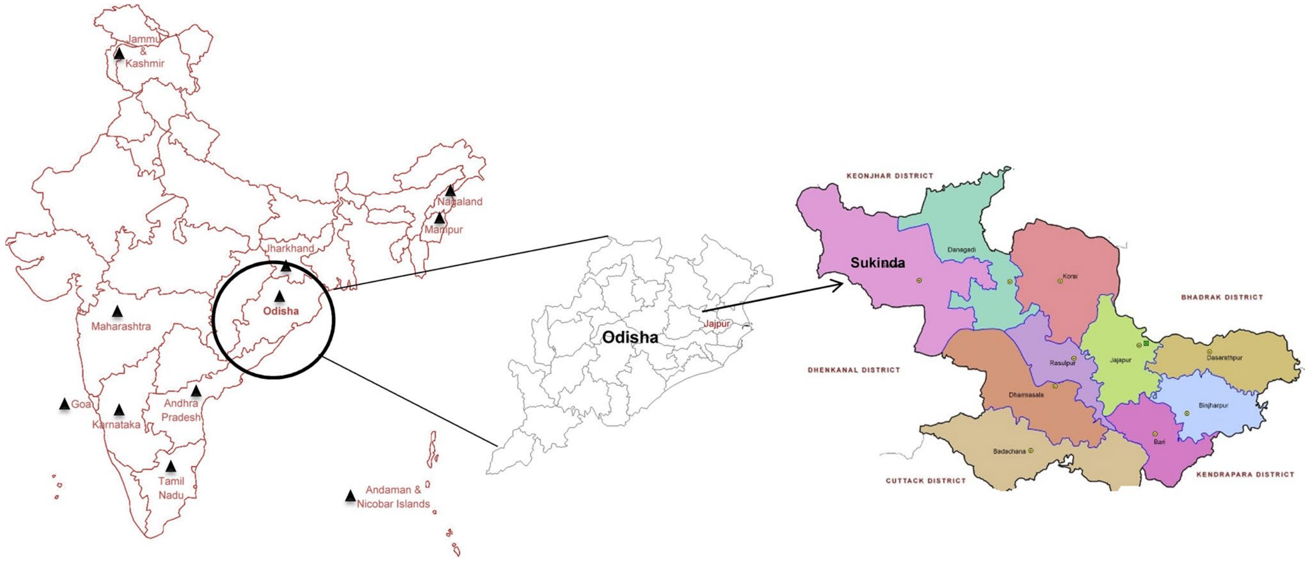

Fig. 2 Chromite deposits in various states of India. Among all states, Odisha leads the queue as the largest producer of chromite ores in the country. The Sukinda valley located in the Jajpur district of Odisha accounts for approximately 95% of India's chrome reserves

The large exploitation and utilization of chromium resources in India, although have benefitted the nation economically, in the process have also dealt with heavy damage to the environment and the people. Most of the chromium-related pollution occurring in India mainly arises from mining sites and certain specific industries (especially tanneries, dye, and other chemical manufacturing industries and steel manufacturing plants). Tata Environmental Research Institute reported that out of the 7.2 million tons of hazardous wastes generated from Indian industries each year, approximately around 72% are disposed of in an improper fashion (TERI 2003). We infer that the chromite mining industry is largely responsible for maximum contamination of the environment, due to improper disposal of wastes containing Cr(VI) as the major contaminant.

Chromite mining at Sukinda Valley

The most dreaded example of hexavalent chromium (Cr(VI)) pollution in India lies in the Sukinda valley located in the Jajpur district of Odisha. It accounts for approximately 95% of the total chromite reserves of the country. The south Kaliapani mining area situated in the Sukinda valley accounts for approximately 97% of the chromite reserves of the state (IBM 2010). The valley contains around 183 million tons of deposits (Tiwary et al. 2005) and produces around 3.8 million tons of chromite ore per year (Das and Mishra 2010; Dhal et al. 2011). Widespread contamination of the valley due to excessive mining of chromite ores has made it to be considered as the fourth most polluted place in the world (Blacksmith Institute report 2007). The chromite mine of TISCO in the Sukinda valley is the largest open cast mine in India. Some of the other open cast mines in the region are operated by companies like Orissa Mining Corporation Ltd (OMC), M/s Indian Metals & Ferro Alloys Ltd (IMFAL), FACOR, and Balasore alloys (IBM 2013). A huge amount of wastes (in million tons) are generated by the mines operating in the valley and thus spread to nearby water bodies and leach into the groundwater, contaminating the water used for drinking purposes in the locality. The contamination mainly occurs due to Cr(VI), which is considered a major environmental carcinogen and is highly toxic (Mishra and Sahu 2013). Lack of adequate space for disposal of generated wastes is also a major problem and needs to be looked upon seriously. The Bhimtanagar chromite mine operated by M/S TISCO consists of dumps reaching to an abnormal height of 80 m due to the same problem of space adequacy. High concentrations of Cr(VI) and Cr(III) have been detected in the waters of the Damsala nallah that drains the Sukinda valley and also in the downstream of the river Brahmani and the Dhamra estuary, though in lesser quantity. Water samples collected from the wells falling within the chromite belt region of Sukinda have also been found to be contaminated (OPCB 2000). Analysis of surface water samples used for drinking purposes in the area revealed a much higher concentration of Cr(VI) than the maximum permissible limit of 0.1 mg/l. At one of the sampling points in the effluent channel of the chromite beneficiation plant of TISCO, the Cr(VI) concentration was found to be as high as 52 mg/l (Dubey et al. 2001).

Indian Bureau of Mines in collaboration with BRGM, France, carried out a project titled 'Development of Application Techniques in relation to Environmental Management

Table 2 Deposits and the average grade of chromite available in India. *Source*: IBM (2013)

State	Mining belt	Location	Topography	Average grade of Cr_2O_3 (%)
Odisha	Sukinda	Jajpur district	20° 53′ 00″ N–85° 53′ 00″ E	35.35–50.06
	Bhalukasuni—Nilgiri	Balasore district	21° 29′ 30″ N–86° 42′ 00″ E	25.77–54.76
	Ramagiri	Koraput district	18° 46′ 00″ N–82° 15′ 00″ E	24.07–27.49
Jharkhand	Jojohatu—Roroburu	Anjadbera and Sahadeva reserve forest area, Chaibasa	21° 31′ 00″ N–85° 38′ 00″ E	46.0–51.6
Maharashtra	Bhandara—Nagpur	Pauni, Bhandara district	20° 47′ 00″ N–79° 39′ 00″ E	52.0
	Chandrapur	Taka, Nagpur district	20° 40′ 00″ N–79° 24′ 55″ E	23.50–35.28
		Ballarpur, Chandrapur district	20° 40′ 15″ N–79° 23′ 15″ E	Data unavailable
		Dhamangaon—Puyardand, Nagpur and Chandrapur district	20° 38′ 30″ N–76° 26′ 00″ E	22.81–35.15
		Pitechua, Chandrapur district	20° 38′ 30″ N–76° 23′ 00″ E	Data unavailable
	Sindhudurg	Kankavali	16° 16′ 00″ N–73° 45′ 00″ E	30.88–31.04
		Janoli	16° 17′ 00″ N–73° 42′ 00″ E	Data unavailable
		Vagda	16° 14′ 00″ N–73° 45′ 00″ E	34.21
		Gosaviwadi	16° 13′ 00″ N–73° 42′ 15″ E	39.07
Andhra Pradesh	Janaram block	Khammam district	17°18′ 00″ N–80° 24′ 00″ E	39.26
	Konayyapalem block	Khammam district	17° 10′ 00″ N– 80° 25′ 00″ E	39.55
	Linganapetta block	Khammam district	17° 15′ 00″ N– 80° 25′ 00″ E	27.22–36.84
	Sriramgiri block	Khammam district	17° 20′ 00″ N–80° 24′ 00″ E	38.12
	Kondapalli block	Krishna district	16° 37′ 00″ N–80° 32′ 00″ E	22.81–51.94
Karnataka	Nuggihali	Hassan district	13° 06′ 00″ N–76° 25′ 00″ E	22.78–49.09
	Sindhuvalli—Talur	Sindhuvalli block in Mysore district	12° 11′ 30″ N–76° 38′ 00″ E	37.5–46.95
		Dodkatur block in Mysore district	12° 10′ 40″ N–76° 36′ 30″ E	38.64
		Talur block in Mysore district	12° 11′ 30″ N–76° 36′ 30″ E	19.92–40.05
Tamil Nadu	Karunglapatti and Sitampundi	Salem district and Namakkal district	11° 14′ 10″ N–78° 00′ 00″ E	9.75–27.16
	Solavanur-Mallanayakkan-palaiyam—Karapaddi	Coimbatore district	11° 24′ 30″ N–78° 13′ 40″ E	21.79–27.87

of Mines and Waste Recoveries’ and prepared a Regional Environmental Impact Assessment (REA) report. The monitoring report generated by REA observed that the surface water quality exceeded the drinking water standards in the Damsala nallah. Most of the groundwater samples investigated were found to have water quality exceeding the quality standards for drinking purposes. The fauna and flora of the region were also found to be highly contaminated. In all the sampling points, Cr(VI) was found to be present at a higher concentration (IBM 2013) (Table 3). We attribute the release of high loads of Cr(VI) to intensive mining activities in the region. It leads to environmental deformation.

Impacts of chromite mining on the environment

Reports portray the metal mining process as one of the major contributors to the pollution of the natural environment, especially the water bodies (Moncur et al. 2005). The fine heavy metal particles have all the chances of being adsorbed to the ground surface, flow off to nearby lakes and rivers, and as well as leach into the groundwater (Mulligan et al. 2001). Chromium is regarded as a very important metal

Table 3 Concentration of Cr(VI) at various sampling point in the Sukinda valley. *Source*: IBM (2013)

Samples	Cr(VI) concentration
Sediment of Damsala nallah	30–104 mg/kg
Sediment of paddy fields	6–190 mg/kg
Leachate of nallah sediment	2–12 mg/l
Leachate of paddy field sediments	0.7 mg/l
Surface water	Up to 3.4 mg/l
Groundwater	Up to 0.6 mg/l
Dust	0.01–0.08%
Paddy	< 0.001–142 mg/kg
Fruits	5–28 mg/kg
Fish	14–115 mg/kg

having uses in various industrial processes, thus leading to its increased demand. Excessive demand for the metal has also led to an increase in the mining activities of chromite ores. Though chromium is present in the non-toxic trivalent form in the earth's surface, due to open cast mining activities the trivalent Cr(III) comes in contact with atmospheric air and water and has maximum chances of oxidizing to the toxic hexavalent(Cr(VI)) form. Separation of chromite ores from hard rocky surfaces involves techniques like blasting and drilling followed by crushing. A huge amount of fine ore particles and dust generated get blown away through the air to nearby localities, thus posing chances of causing Cr(VI) contamination through atmospheric deposition (Rosas et al. 1989). Mines also use water to control dust during drilling and other mining operations. These mine wash water can seep into the groundwater or flow to the nearby water bodies thereby contaminating them (Das 2018). Accumulation of rainwater in the open mining pits and drainage from such pits also bear the same consequences. Dewatering of open pits during the rainy season to enable continuous mining activities may also heavily contaminate nearby places or water bodies into which the excess water is discarded. The chromite mining process is largely related to the generation of a huge amount of wastes and rocks in the form of overburden (Dhakate and Singh 2008). Drainage from such overburdens may also bear the possibility of leaching out a large number of heavy metals into the soil and nearby water systems. High levels of Cr(VI) in the soil and water bodies may result in the toxic heavy metal being accumulated in the plants and crops, thus easily getting transferred through the food chain. Some of the beneficial microflora of the soil may get affected due to the presence of Cr(VI), thus leading to 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 (Das and Singh 2011). Inhalation of air dispersed with Cr(VI) particulates that arise from mining activities is a serious threat to human health and may lead to several ailments of the lungs and the respiratory tract. Consumption of contaminated water or food crops also possesses the chances of various diseases of the stomach and the alimentary canal. Several other human activities like the use of the Cr(VI)-contaminated water of rivers and ponds present nearby the mining localities for purposes like bathing, cleaning, and washing may also lead to various skin diseases.

Chromite mining activities expose the heavy metal Cr(VI) to the surrounding environment. Cr(VI) being a proven environmental carcinogen, expresses its toxicity on the biological entities. Several pieces of research have been carried out to study the toxicological impact of this heavy metal on plants, animals, microbes, and humans. In the following section, we discuss in brief about the toxicological implications of Cr(VI) on the living biota residing in and near the mining sites.

Hexavalent chromium (Cr(VI)) has been reported to impart its toxicity on various parameters related to plant growth and development (Table 4) like germination (Lopez-Luna et al. 2009; Dey et al. 2009), radical growth (Corradi et al. 1995), growth of roots (Sundaramoorthy et al. 2010; Rout et al. 1997; Samantary 2002; Barcelo et al. 1985), shoot length (Mallick et al. 2010; Lopez-Luna et al.2009), leaf growth (Dube et al. 2003) and yield (Sundaramoorthy et al. 2010). Cr(VI) has also been reported to impact various physiological processes in plants like photosynthesis (Panda and Choudhury 2005; Paiva et al. 2009; Liu et al. 2008), mineral uptake (Singh et al. 2013; Sundaramoorthy et al. 2010; Liu et al. 2008; Gopal et al. 2009; Gupta et al. 2000), enzymatic activities (Samantary 2002; Zaimoglu et al. 2011), protein activities (Vajpayee et al. 1999, 2000), electron transport (Dixit et al. 2002; Vranova et al. 2002). The toxicity of Cr(VI) affects the overall health of the plants, thereby leading to plant death. Loss of plants due to Cr(VI) toxicity at industrial and mining sites largely contributes toward biodiversity loss and may bring about a perturbance in the 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. Crop loss may further prove to be a deterrent toward the financial and economic growth of farmers of the region.

Besides causing severe plant toxicity, Cr(VI) is found to have an impounding effect on humans (Fig. 3) either through inhalation, oral intake, or dermal contact (Das and Singh 2011).

Laborers working in the chromite mines are always at a high risk of being affected by Cr(VI) contamination and its toxic effects. Cr(VI) is a proven sensitizer of the skin as well as the respiratory tract. It induces nasal irritation and upon continuous exposure may lead to the formation of nasal perforations (Menezes et al. 2004; Holland and Avery 2009). Cr(VI) also leads to skin ulcers only when there is an existing cut or abrasion on the skin and may even further lead to the formation of 'chromium holes' (Beyersmann and Hartwig 2008; Zhitkovich 2005). Cr(VI) has also been reported to cause cancer of the lungs in humans and animals. The probable mechanism behind the carcinogenesis has been discussed herein.

The rapid uptake of Cr(VI) has been reported to occur in human and animal cells via the sulfate carriers (Sugiyama 1992). The Cr(VI) further gets reduced to Cr(III) by the action of several cellular reductants, thus causing genotoxicity (Bianchi et al. 1983). The reduction process of Cr(VI) to Cr(III) generates several intermediates like Cr(V), Cr(IV), and reactive oxygen species (ROS). The intermediates, especially Cr(V), lead to the formation of bulky

Table 4 Impacts of Cr(VI) on various plant parameters

Plant parameters	Impact of Cr(VI)	Possible reasons	Reference(s)
Germination	Reduction in germination percentage	Decrease in amylase activities leading to decreased availability of sugar to the developing embryos	Dey et al. (2009)
Radical growth	Inhibition of growth of radicals	May be due to the toxic effect of Cr(VI)	Corradi et al. (1995)
Root growth	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. Extension of the cell cycle	Barcelo et al. (1985) and Sundaramoorthy et al. (2010)
Shoot length	Reduction in shoot length	Reduced root growth and subsequently reduced transport of water and nutrients to shoots. Chromium also affects the cellular metabolism of shoots	Oliveira (2012), Mallick et al. (2010) and Lopez-Luna et al. (2009)
Leaf growth	Reduction in leaf numbers and leaf area	Reduction in the number of leaf cells and the cell size of the leaves. Loss of turgidity. Necrosis, permanent wilting, drying, etc.	Nieman (1965) and Dube et al. (2003)
Yield	Decreased plant yield	Decreased leaf numbers, surface area, and functions may be responsible	Sundaramoorthy et al. (2010)
Photosynthesis	Inhibits photosynthesis	Ultrastructural changes in the chloroplast. Affects pigment synthesis by competing with Mg and Fe for assimilation and transport to leaves Increases production of reactive oxygen species (ROS) leading to pheophitinization and deformation of thylakoid membranes	Panda and Choudhury (2005), Vernay et al. (2007) and Juarez et al. (2008)
Mineral uptake	Decreases uptake and translocation of essential micronutrients	Displacement of the nutrients from the physiological binding sites	Liu et al. (2008)
Enzymatic activities	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	Samantary (2002)
Protein activities	Degradation of proteins	Binds to the protein or displaces metals from the protein's active center	Vajpayee et al. (1999, 2000)
Electron transport	Blocks electron transport chain	Binds to the cytochrome a_3 inhibiting cytochrome oxidase activity Generates toxic oxygen free radicals in the mitochondria	Dixit et al. (2002) and Vranova et al. (2002)

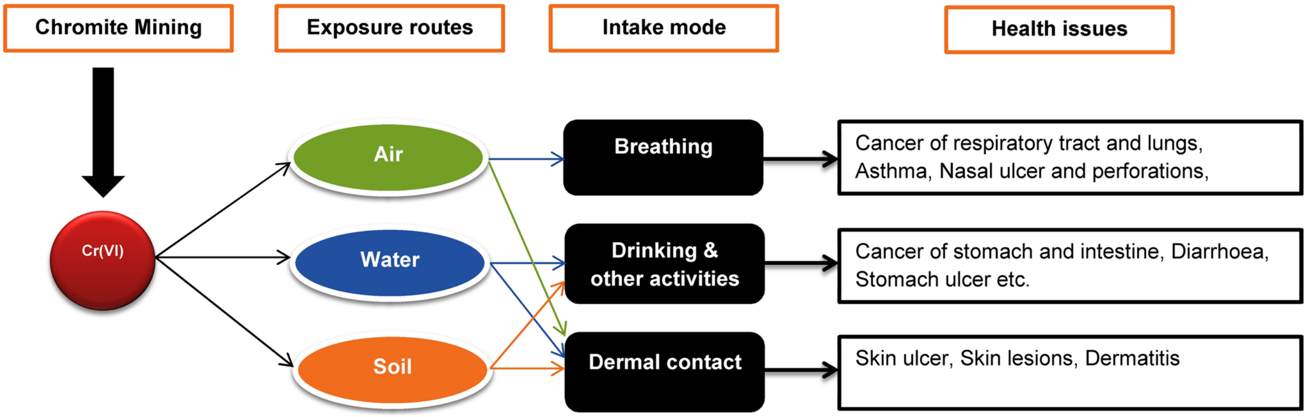

Fig. 3 Exposure routes, mode of intake and associated health issues of Cr(VI) in humans. Cr(VI) or hexavalent chromium released from the chromite mines is exposed to the aerial, water, and soil environment by leaching or as dust particles. Humans come in contact with the toxic heavy metal either through breathing, consumption of polluted water, or by penetration through skin. Unintended intake of the toxic heavy metal in humans leads to occurrence of several health issues

DNA adducts in the p^{53} gene of human lung cells. The ROS formed also induce oxidative damage to the DNA of the p^{53} gene (Arakawa et al. 2012). Being a tumor suppressor gene, p^{53} works to regulate the expression of several target genes under various cellular stress conditions and helps in DNA repair. Any damage to this particular gene implies a failure of the DNA repair mechanism, leading to mutations and uncontrolled cell divisions, thus leading to lung cancer. Inhalation of Cr(VI) concentration exceeding 0.001 mg/m^3 through the mouth may also cause stomach ulcers (Lindberg and Hestidania 1983). Cr(VI) negatively affects myocardial activity. This may occur either by directly affecting the blood vessels or indirectly by reducing the pulmonary functions (Kleiner et al. 1970). Shmitova reported that transfer of Cr(VI) can occur to the fetus from the placenta of a pregnant woman being exposed occupationally to the toxic heavy metal (Shmitova 1980). We therefore conclude that upon regular and prolonged exposure, Cr(VI) may impart toxic effects and even at worse prove lethal to humans.

Chromium in small quantities is also required by the microorganisms as a nutrient. However, an excessive amount of chromium in the environment has been found to pose detrimental effect on these microorganisms (Silver et al. 2001). Cr(VI) has been found to impart toxic and mutagenic effects on most of the bacteria. Cr(VI) has been found to inhibit bacterial cell growth by causing elongation and enlargement of the bacterial cell as well as by inhibiting the cell division (Coleman 1988). Exposure to Cr(VI) has also been found to bring about morphological changes (Bondarenko and Ctarodoobova 1981) and a reduction in pathogenicity (Yamini et al. 2004) among the bacteria. Cr(VI) may bring about alterations in the cytoskeleton of algae, thus leading to loss of motility (Bassi and Donini 1984). Green algae have been found to be affected by Cr(VI), which inhibits the photosynthesis process (Corradi et al. 1995). The toxicity of chromium in microbes is also highly dependent on the oxidation states. Cr(VI) being highly soluble and mobile can easily penetrate through the bacterial cell membrane and into the cytoplasm, thus exerting toxic effects (Katz and Salem 1993). Microbes being an essential part of the biotic environment, we raise the concern that Cr(VI) pollution may disturb the microbial biodiversity that will further create environmental imbalance.

Phytoremediation for decontamination of Cr(VI) mining sites

The rise in population coupled with large-scale urbanization and industrialization has led to severe pollution of the soil. Improper disposal of wastes generated from various industries and mines enriched with heavy metals is the main factor behind soil pollution (Ye et al. 2017; Kumar et al. 2019; Bali et al. 2020). Soil is a very precious natural resource and forms the base for several agricultural activities. Hence, its contamination by heavy metals like hexavalent chromium (Cr(VI)) must be prevented. Taking into consideration the several serious consequences posed by heavy metals like Cr(VI) on the soil, several remediation techniques have been developed and applied (Liu et al. 2018). These include various physicochemical methods and some biological methods like bioremediation and phytoremediation. The physicochemical methods are although sometimes effective, but in the process affect several soil parameters like fertility and biodiversity (Khalid et al. 2017). Biological techniques are advantageous over other techniques in being cost-effective, and eco-friendly in their approach (Megharaj and Naidu 2017). The use of microorganisms (bioremediation) to clean-up contaminated soil is although a quick method, but it is still a daunting task as far as its feasibility is concerned when applied on a large scale. Hence, the current paper argues in favor of using plants (phytoremediation) for the decontamination of Cr(VI) polluted soils at mining areas. Phytoremediation is a widely accepted technique for its feasibility and eco-friendly nature (Muthusaravanan et al. 2018). In the process of phytoremediation, plants are used to remove pollutants from the environment or to contain them within their system, thus reducing those pollutants (Jensen and Gujarathi 2016; Vamerali et al. 2010). Plants having the ability to withstand the toxicity and grow in high concentrations of Cr(VI)-polluted mining sites should be selected for the remediation (Das et al. 2017). Therefore, we highly suggest proper selection of plant species for successful remediation of Cr(VI) contaminated soils.

The most interesting and important thing about phytoremediation is that it not only uses plants but also takes into account other parameters like soil characteristics, nature of the heavy metal, and microorganisms present in the soil (Das et al. 2018) (Fig. 4).

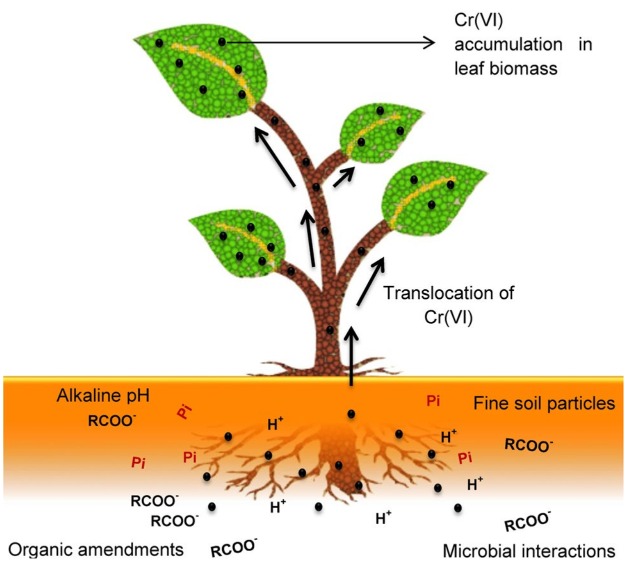

Fig. 4 Factors responsible for increasing phytoextraction of Cr(VI) from the soil. Organic amendments lead to release of organic acids that donates proton (H^+) to the soil. The released proton helps in intake of anionic inorganic phosphate (Pi) through an energy driven active process leading to alkalinization of soil. This possibly increases the accumulation of Cr(VI), a structural analogue of Pi, in hyperaccumulators. Microbes referred to as plant growth promoting rhizobacteria have been found to enhance the phytoremediation process by several means like methylation, alteration of soil pH, favoring redox reactions, and by secreting siderophores, biosurfactants, and several organic acids. The size of soil particles (fine particles) also positively influences the phytoavailability of Cr(VI) and its translocation into plants

Hyperaccumulators in the translocation of Cr(VI)

To reduce the availability of toxic hexavalent chromium (Cr(VI)) at off-site environmental components is one of the emerging fields of soil remediation. It includes the stabilization of this toxic element in the soil rhizosphere and/or its accumulation in foliar tissues of plants employed for remediation purposes. In this context, the role played by translocation is gaining importance. Translocation is a vital physiological process for plants to collect macro- and micronutrients from the soil along with water. The used xylem tissues for this purpose have the potential to extract Cr(VI) from the contaminated soils of industrial and mining belts. The functioning of these xylem tissues in conducting strands ultimately loads Cr(VI) in the intracellular vacuoles of foliar regions in addition to its deposit in the root and stem cells.

Plants uptake hexavalent chromium (Cr(VI)) from the soil via the root system and translocate to the aerial parts. Cr(VI) uptake by plant roots can either occur by apoplastic transport system or the symplastic transport system. In the case of apoplastic transportation, Cr(VI) is carried through the intercellular spaces of the roots. Symplastic transportation involves specific ion channels or carriers like sulfate or phosphate for the uptake (Chaudhary et al. 2018). Unlike non-hyperaccumulating plants that store metals in the vacuoles, the hyperaccumulator plants efficiently translocate these metals from the roots to shoots through xylem using the symplastic pathway. Transfer through the xylem is facilitated by several membrane proteins like P-ATPase (P-type ATPase), HMT-ATPase (Helminthosporium maydis T ATPase), MATE (Multi-antimicrobial extrusion), and oligopeptide transport proteins (Chandra et al. 2018). Upon translocation, the hyperaccumulator plants sequester the toxic metals in the vacuoles of the leaf cells (Sharma et al. 2016). In this mechanism, the toxic metals are chelated with specific ligands and these metal–ligand complexes are then sequestered in the vacuoles by various families of transporter proteins like CAX (cation exchangers), HMA (heavy metal ATPases), ABC (ATP-binding cassette), NRAMP (natural resistance-associated macrophage protein), CDF (cation diffusion facilitator), ZAT (zinc transporters) and many more (Chandra et al. 2018). We hereby underline the importance of different pathways and the involvement of various proteins and ligands for efficient translocation of Cr(VI) into plants.

The hexavalent chromium (Cr(VI)) toxicity in the soil is reduced with the possible transformation of highly toxic Cr(VI) to trivalent chromium (Cr(III)) using the metabolism of selective groups of hyperaccumulators. The response of chromium to membrane transporters of plants used for transport of inorganic phosphates from the soil depends upon its chemical speciation and expressed through genetic or non-genetic alterations. The acceptance of the toxic Cr(VI) by those membrane transporters is possibly decided by the anionic structures of orthophosphate and chromate. After the intake, it may be channelized inside the cells, utilizing the biochemical machinery responsible for phosphate metabolism. The mobility of Cr species is variable and alters with the variation in the redox state. The high mobility of Cr(VI) is possibly linked with its chemical structure at the oxidation state. Contrary to it, the structural changes occur at the reduced state, Cr(III) changes its docking pattern, and mostly impermeable to move across the cell membrane. The quick transformation of Cr(VI) to Cr(III) is pH dependent. We have noticed the importance of chemical speciation and its behavior during sequestration of the toxic elements during phytoremediation.

Rhizospheric soil chemistry

The chemistry of rhizospheric soil also plays an important role in the phytoavailability of heavy metals like hexavalent chromium(Cr(VI)). Soil properties like pH, organic content, and texture greatly influence the availability of metals for phytoremediation (Shah and Daverey 2020). Cr(VI) mostly occurs as an oxyanion (CrO_4^{-2}) and at low soil pH (<5.0) remains adsorbed in the soil, thereby reducing its uptake in plants. However, at high pH (>5.0), Cr(VI) remains highly mobile and thereby demonstrates high phytoavailability. The reaction of metals with organic matter to form an organometallic complex in the soil is also a pH-dependent process. At alkaline pH, the free metal ions in the soil form hydroxyl products that intensify organometallic complex formation, thereby reducing their toxicity. The low soil pH limits the availability of anionic inorganic phosphates in the soil. Its intake from the soil by the hyperaccumulators is influenced by proton mediated co-transport mechanism (Ullrich and Novacky 1990). The Pht1 phosphate transporters present in the cellular membranes of hyperaccumulators are possibly guiding this movement of inorganic phosphate from the soil to plants parts through the soil–root interface (Rausch and Bucher 2002; Bucher 2007). The intake of inorganic phosphates from the soil is a proton-dependent active process (Ullrich and Novacky 1990). It leads to the alkalinization of the soil. Possibly, a similar mechanism is utilized by the hyperaccumulating plants to intake structural analog Cr(VI) from the contaminated mining and industrial sites of Sukinda. The release of organic acids from the supplemented materials can be used as a source of proton streaming to boost up the remediation of Cr(VI) from the contaminated sites.

The texture of the soil also plays an important role in the phytoavailability of heavy metals, thereby directly relating to the phytoextraction efficiency of the plants (Złoch et al. 2017). Fine soil particles having a size of less than 100 µm have higher reactivity and surface area as compared to coarse soil particles. Therefore, finer particles tend to have higher concentrations of heavy metals like Cr(VI) in them. Lotfy and Mostafa (2014) observed that fine-textured soils exhibited high bioavailability of heavy metals like Cr and enhance its translocation in plants. Hence, we consider that the physical and chemical properties of soil also have a major role to play in enhancing the translocation of Cr(VI) from soil to different plant tissues.

The plant–microbes interaction

Plant–microbes interaction plays a crucial role in the phytoremediation of heavy metals. These microorganisms are referred to as plant growth promoting rhizobacteria (Khan et al. 2009) and can efficiently enhance the phytoremediation process by several means like methylation, alteration of soil pH, favoring redox reactions, by secreting siderophores, biosurfactants, and several organic acids (Table 5). Microorganisms can produce several acids that increase the availability of metals for phytoextraction by bringing about a change in the soil pH (Yang et al. 2018). A study demonstrated the role of citric and oxalic acids in enhancing the chromium phytoremedial ability of the *Suaedavera* plant (Gómez-Garrido et al. 2018). Microbes also oxidize or reduce metals directly or via the action of oxidizing or reducing agents produced by them. The redox reactions bring about a reduction in heavy metal phytotoxicity by stabilizing these metals in the soil and also by transforming them into non-toxic forms (Ma et al. 2016). A study on *Cellulosimicrobium cellulans* revealed its ability to reduce hexavalent chromium (Cr(VI)) to less mobile and comparatively non-toxic trivalent chromium (Cr(III)) in the soil (Chatterjee et al. 2009). Nayak et al. (2018) reported a *Bacillus cereus* strain that was found to be highly efficient in the reduction of Cr(VI) and a few other metals. The strain efficiently improved the phytoremedial ability of *Vetiveria zizanioides*. The adept ability of microorganisms in biosorption of heavy metals also assists the plants to a greater extent in the process of phytoremediation. The sorption of metals by microorganisms can take place by either the passive or active mechanism. Passive sorption occurs via an interaction between the metals and the functional groups present on the surface of dead microbial cells (Fomina and Gadd 2014). The active sorption process involves the uptake of metals from the soil by living microbial cells employing different mechanisms. The metallothioneins present inside the microbial cells bind to the metals and facilitate their sequestration in particular intracellular organelles. Certain microorganisms have been found to produce amphiphilic substances known as 'biosurfactants'. The biosurfactants can desorp metals from the soil and in turn increase their solubility and mobility, making the metals bioavailable for plant uptake (Lal et al. 2018). *Bacillus subtilis* SHB13,

Table 5 Role of plants–microbes interactions in enhancing the phytoremediation of chromium contaminated soils

Plants under Cr(VI) stress	Associated microorganisms	Effects	References
Sesbania sesban	*Bacillus xiamenensis* PM-14	Plant growth promotion, increase in chlorophyll content, antioxidant activities, relative water content, chromium uptake, Reduction in proline, malondialdehyde and electrolyte leakage	Din et al. (2020)
Tagetes erecta	*Bacillus cereus* CK 505 *Enterobacter cloacae* CK 555	Accumulation of high level of chromium within 35 days	Chitraprabha and Sathyavathi (2018)
Prosopis laevigata	*Bacillus* sp. MH 778713	Increased phytoremediation of chromium	Ramírez et al. (2019)
Veteveria zizanioides	*Bacillus cereus*	Production of 1-aminoacyclopropane 1-carboxylate synthase (ACC), indole acetic acid (IAA), siderophore and solubilization of phosphate, increased phytoremediation capacity	Nayak et al. (2018) and Shah and Daverey (2020)
Triticum aestivum	*Azotobacter* sp.	Production of Extracellular polymeric substance (EPS) and immobilization of chromium in the soil	Joshi and Juwarkar (2009)
Capsicum annuum	*Cellulosimicrobium cellulans*	Reduction of Cr(VI) to Cr(III) in the soil	Chatterjee et al. (2009)
Helianthus annuus L.	*Rhizobacteria SS6*	Enhancement in plant morphological characters, grain yield, oil content of seeds, total biomass and chromium accumulation	Bahadur et al. (2017)
Oxalis corniculata	*Kocuria rhizophila*	Adsorption of Cr(III)	Lal et al. (2018a, b)

isolated from the marine source, was found to produce the biosurfactant ‘surfactin’, which efficiently reduced 98% of 100 ppm chromium and 74% of Cr(VI) within 72 h of action (Swapna et al. 2016). Microorganisms present in the plant rhizosphere produce several organic acids reportedly enhancing the phytoremedial ability of plants by increasing heavy metals and nutrients uptake (Yang et al. 2018). Gómez-Garrido et al.(2018) reported the active involvement of citric and oxalic acid toward enhanced phytoremediation of chromium in *Suaedavera* plant. Rhizospheric microorganisms especially bacteria secrete low molecular weight compounds called siderophores that act as an iron chelator and supply iron to plants under metal stress soil conditions. The supply of a sufficient quantity of iron ensures in alleviating chlorophyll biosynthesis that remains suppressed in plants due to heavy metal-induced iron deficiency. Siderophores via chelation bring about a reduction in the formation of free radicals around the zone of plant roots and shields the microbial phytohormones from oxidative damage induced by the heavy metals. This not only ensures enhanced phytoextraction efficiency in plants but also protects the plant from pathogenic microorganisms in the soil (Ahemad 2015). We the authors acknowledge the importance of microbes and their involvement as a facilitator in the Cr(VI) remediation process. Besides, we hereby profoundly state that the microbial populations act as a first line of defense for the plant against various pathogens and stress as reviewed from several literature sources.

Conclusion

Chromium is an important metal that finds wide applicability in several industrial sectors. Chromite mines provide raw materials for several industrial establishments and are important as far as the economic growth of a country like India is concerned. However, economic growth should not be at the cost of the environment. Cr(VI), the toxic form of the element and a proven carcinogen, imparts adverse effects on the environment and its living entities. The widespread contamination of areas like Sukinda valley in India due to excessive chromite mining activities in the region has drawn the attention of several researchers toward possible clean-up efforts. In this context, phytoremediation appeals to be the most sustainable measure for cleaning the contaminated sites. Proper selection of plants along with physicochemical soil parameters and the study of plant–microbe interaction could help in devising efficient remediation strategies for the mining areas.

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