Chapter 12
Toxicity of Rhizospheric Chromium Contaminated Soil and Its Phytoremediation

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Abstract The chromium is a common ingredient of industrial products for providing tensile strength, corrosion inhibition and shining ability to metals. The overuse of chromium during industrial production is one of the factors responsible for rhizospheric soil chromium contamination and phytotoxicity. Billion dollars of chromite resources are present across the world. The chromite mining and release of hexavalent chromium from industrial refuges, augment the risk associated with rhizospheric soil chromium contamination. The hexavalent chromium is recognized by USEPA, as a hazardous metal. Selection of hyper-accumulators for operation of phytoremediation is a possible solution for this burning environmental problem. The hyperaccumulator, associated soil biota and available chromium, interactions in rhizospheric soil decides the fate of phytoremediation. The disposal of hyperaccumulators biomass used during phyto-remediation may have dire consequences but found to be sustainable, economical, and advantageous, as compared to possible physico-chemical processes. The present approach of biomass use, during rhizospheric remediation of chromium contaminated soil is gaining acceptance over the years. For process efficiency improvisation, it is required to optimize the operating conditions, during pilot and field scale applications. The successful operation of phytoremediation using selected chromium hyperaccumulators, at pilot and field stages of application could help in promoting the detoxification of environmental components like soil and minimization of adverse impacts of chromium on public health and environment. It is a step towards up-gradation of environmental quality and protection of living society on a sustainable basis.

Keywords Chromium · Hyperaccumulators · Phytoremediation · Rhizosphere · Toxicity

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12.1 Introduction

The application of chromium (Cr) individually or in combination with other heavy metals, like nickel-based alloys, improves the strength and corrosion resistivity of manufactured steel products. It is also commonly used as an ingredient during commercial activities like metal plating, leather tanning, wood keeping, painting, dyeing and chemicals manufacturing. The excessive use of Cr with industrialization and urbanization is one of the prime factors behind degradation of environment by Cr rich effluents, sludge and solid wastes. The contamination of soil profile has increased the human health risk around the mining and industrial sites. The soil toxicity of Cr contaminated sites is correlated with the proportionate distribution of Cr(VI) (hexavalent chromium), Cr(III) (trivalent chromium), and TCr (total chromium), in its structural horizons.

The contaminated soils, rich in Cr(VI) are extremely toxic and removal of toxicity is possible by enriching its rhizospheric segments with organic carbons, during phytoremediation. It may get channelized by the possible reduction of hydrophilic Cr(VI)–Cr(III), with the decrease in its stability and water solubility (USEPA 1998; Zayed and Terry 2003). The soil Cr kinetics during phytoremediation is possibly modulated by the locally involved abiotic and biotic components of the soil environment (Eco-USA 2001).

The detoxification of Cr contaminated soils can be possible with the application of physical and chemical principles, but unlike biological principles, are responsible for secondary environmental pollution, at many instances. The physico-chemical techniques like soil flushing, solidification, stabilization, vitrification, redox reactions, excavation and off-site disposal were attempted earlier with different degrees of success, but not free from disadvantages (USEPA 1993). These techniques are either proved to be costly or inappropriate for successful detoxification of Cr contaminated soils. The operation of phytoremediation is a viable option under the present context for successful detoxification of Cr contaminated industrial and mining sites.

12.2 Speciation of Chromium and Toxicity

In its natural state, Cr is a hard silvery metal, ranked as the 17th top most hazardous substance (USEPA 1999, 1998). The two stable forms of this toxic metal are Cr(III) and Cr(VI). The intermediate unstable forms like Cr(IV) and Cr(V) are formed during conversion of Cr(VI) and Cr(III), following redox reactions. During intracellular reduction in tissues of living organisms, the concentration of TCr may be same as the concentration of Cr(III), if, all Cr(VI) gets reduced to Cr(III), in the system,

The hazardous Cr(VI) is extremely toxic to biological cells, beyond threshold limits. Its high toxicity is more pronounced with increase in solubility, permeability and mobility, as compared to those under trivalent conditions (Das et al. 2021a, b). It may be due to the variation in configuration and confirmation of specified chemical species. The Cr(III) is mostly non-toxic within the threshold limits and much required for living cells, as a trace dietary supplement (Panda and Choudhury 2005; Nematshahi et al. 2012).

12.3 Hexavalent Chromium as a Toxic Heavy Metal

The Cr(VI) is a commercially useful heavy metal, required during industrial production. Besides its tensile strength and corrosion resistance, some other features attract its presence, as an adjunct during industrial processing. The ability of Cr salts to change colour at different concentrations is another aspect for its consideration as a colouring agent, during industrial requirements (Augustynowicz et al. 2020). The production and post-production processes released wastes, rich in Cr(VI) to surroundings and responsible for occurrence of soil pollution, directly or indirectly. The enrichment of soils with Cr(VI), leads to expression of its adverse effects on components like resident biota. The excessive accumulation of Cr(VI) in living cells, sourced from contaminated soils, expresses its toxicity in affected cells.

The industrial effluents, from metals finishing, leather tanning, cement production and similar processes cause Cr(VI) based water pollution. Besides surface water pollution, the Cr based contamination of bore well water is an example of groundwater pollution (Zaidi et al. 2014). The soil pollution, directly from Cr rich industrial wastes or indirectly through contaminated surface water or harvested groundwater shows wide range of variation in Cr(VI) contamination. The spectrum of Cr rich wastes from industries, mines and urban sectors are released in solid, liquid or gaseous phases. The Cr(VI) from these wastes, directly or indirectly, channelized into the soil and responsible for wide range of Cr(VI) led soil pollution.

The post-contamination changes caused by Cr(VI), includes, irreversible alterations in the genomic constituents, errors at the levels of transcription, translation and post-translation, anomalous cell division, and activity of proteins inside exposed tissues, and subsequently, direct or indirect interruption of the cellular development (Das et al. 2017, 2018).

12.4 Sources of Chromium Release to Rhizospheric Soil

The main source of Cr required for industrial purposes is chromites. It is one of the main reasons behind wide scale geological activities and chromite mining. The anthropogenic causes are not the only route of soil Cr pollution, as has been caused by multiple natural sources, also. Naturally, it is caused by sources like volcanic eruptions, soil erosion, rocks disintegration, sands and dusts dispersion by blowing of wind (Memon and Schröder 2009; Apte et al. 2006; Das et al. 2022a, b, c). The impacts from anthropogenic causes of soil Cr pollution is more than the impacts of pollution caused by natural phenomena (Fig. 12.1).

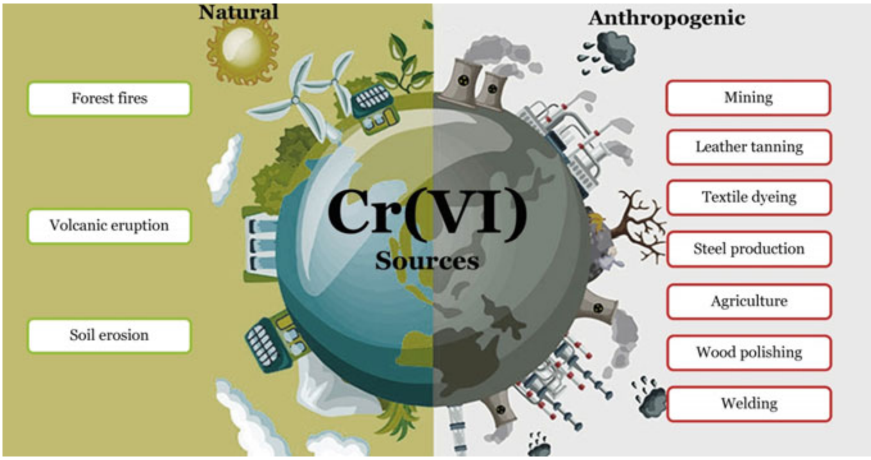

Fig. 12.1 Sources of release of Cr(VI) as a soil pollutant

The Cr as a pollutant is directly or indirectly, expressing its adverse impacts on the exposed environmental components. The activities like tanning of leather, electroplating of metals, processing of timber, dyeing of textiles, smoking of tobacco, leaching of toxicants from improper sanitary landfills, refining of ferrochrome ores, production of cement and stainless steel are noteworthy examples from anthropogenic sources of soil pollution by Cr. It imparts hazardous effects on components of ecosystems (Das et al. 2021a; Saha et al. 2011; Guidotti et al. 2015). Even, the application of phosphate fertilizers can be able to cause Cr based soil pollution, as 30–3000 mg kg^{-1} of Cr was found in it (Singh et al. 2013).

12.5 Mechanism of Rhizospheric Soil Chromium Toxicity

The chromium toxicity at the soil rhizosphere is governed by few abiotic and biotic factors prevalent at the site. This toxicity resulted due to the interactions of relative proportion of chromium species and the associated environmental components present there. The Cr forms like Cr(VI) and Cr(III) are stable and have attended high residence times as compared to its unstable forms. At a point of time, the relative proportion of Cr species present in the rhizospheric soil systems are determined by the residence times of available chromium forms.

The environmental factors determining the rhizospheric soil chromium toxicity are abiotic and biotic in nature. The abiotic factors influencing the rhizospheric soil Cr toxicity levels include texture, pH, precipitation, redox potential and nutrient status of the soil systems, and the biotic factors include soil microorganisms, organic carbon contents of the soil system.

12.5.1 Abiotic Factors Determining Rhizospheric Soil Chromium Toxicity

Texture of soil

It is determined by particle size, porosity, and water holding capacity of soil. These characters determine the type, concentration, affinity and leaching ability of the Cr species and ultimately its toxicity level in the rhizospheric soil.

Soil pH

It determines the inter-conversion of Cr(VI) and Cr(III), at a point of time in soil. Mostly, the presence of Cr(VI), makes the soil more acidic by decreasing its pH due to the induction of deprotonation.

Precipitation at the site

It is required for determining soil Cr toxicity, as Cr(VI) is hydrophilic. Its concentration is influenced by the fluctuation in soil Cr dilution coefficient.

Soil Redox potential

Specific chromium forms play significant role in determining net soil Cr toxicity. The redox potential determines the presence of specified chromium forms and fluctuations in the relative proportion of those forms.

Soil nutrient status

The sequestration of chromium from soil to flora by living cells reduces its concentration and toxicity in rhizospheric soil. The chromium is not an essential element for plants growth and survival. Specific channels are absent in plants for chromium absorption and translocation. The soil nutrient status is an important factor, as chromium species utilizes the path of specific nutrients for absorption and translocation in plants. It follows the path of nutrients sharing similarities with the structure of chromium species during the absorption and translocation in plants.

12.5.2 Biotic Factors Determining Rhizospheric Soil Chromium Toxicity

Soil microorganisms

The microbial populations present in soil, helps the plants during adsorption, absorption and translocation of Cr species from soil. It ultimately reduces the Cr toxicity in that soil. The microorganisms like species of algal, fungal and bacteria population are quite useful for inducing phytoremediation, during soil Cr detoxification. Besides, production of Cr reductase by specified microorganisms, helps in the net reduction in Cr toxicity, at rhizospheric soil systems.

Soil organic carbon content

It is required for minimization of Cr toxicity in soil. It helps in soil Cr toxicity reduction, following a series of protonation and deprotonation reactions.

12.6 Focus on Soil Chromium Toxicity in India

About 2% of the world's chromium resources come from Indian chromite reserves. The Sukinda mines playing pivotal role in chromite distribution map, as it acquires 97% of India's chromite deposits (Mishra and Sahu 2013). The main chromite reserves are located in the states of Odisha (Sukinda), Karnataka (Nuggihalli), Maharashtra (Nagpur and Sindhudurg), Jharkhand (Jojohau), Andhra Pradesh (Jannaram), and Tamil Nadu (Namakkal and Thiruchengoddu). The Cr pollution from chromite mining, leaching, effluents discharge, improper Cr waste disposal, mine-tailing infiltration, and other growing industrial operations, primarily contribute to pollution in India (Prasad et al. 2021).

The Sukinda Valley, one of the top ten polluted locations on earth, is well known for major chromite reservoirs of India. It generates a substantial chunk of mining waste, which worsens the health of those exposed to it and causes severe environmental problems (Yadav et al. 2018). The chromite mining activities have ruined the topography, soil and water resources of the site and threatened the associated public health. The Cr emission from these mines to environmental components ranges in between 10 and 4000 mg Kg^{-1} (Vijayana and Nikos 2010). In Sukinda, the surface and groundwater have Cr(VI) levels much above the threshold limit, 0.05 mg L^{-1}. The Blacksmith Institute's (2007), found an alarming level of Cr(VI) in the surface water of mining area. In the Damsala nala, Cr(VI) concentrations were ranging in between 0.018 and 0.172 mg L^{-1}, throughout the summer. In contrast, it exceeded the threshold limit (0.05 mg L^{-1}) for B and C category surface water at village Ostapa, reaching up to 0.201 mg L^{-1}, during monsoon season. The Cr(VI) and TCr concentration varied from 12–311 mg Kg^{-1} to 3589–14,486 mg Kg^{-1}, respectively (Mishra et al. 2009). The adverse effects of chromite mining are observed more, within 1 km radius from the centre of mining and industrial activities. The adjacent villages are not even free from its adverse effects. The mortality rate is 86.42% in adjacent villages, due to diseases associated with chromite mining activities. The acute pollution and health risks associated with Cr(VI) result in irreversible damage to the exposed organisms (Gupta et al. 2019).

The tanneries in India use chrome tanning methods. It is a leading contributor to soil pollution specifically in states having numerous leather tanning industries. These industries release 2000–3000 tonnes of Cr per annum, thereby contaminating soil and water bodies. The states like Tamil Nadu, Gujarat, Uttar Pradesh, and West Bengal are home to majority of these industries. The tanneries generate almost 1500 metric tonnes of chromium sulphate per annum, as trash (Down to Earth 2005). The untreated effluents have Cr concentrations up to 2000–5000 mg L^{-1} and being released to nearby lakes, rivers, and streams (Dhal et al. 2013). The tanneries discharged significant amount of untreated effluents into the river Ganges (Mohan et al. 2011). The Cr(VI)-containing sludge is potentially toxic and is anticipated to have detrimental impacts on human health, when it seeps into groundwater, subsoil, and rivers. This sludge releases hazardous pollutants and volatile methane into the environment and occasionally catches fire during summer. The assessment of water quality of Kanpur revealed, groundwater with Cr(VI) content of 6.2 mg L^{-1} against the threshold limit of 0.05 mg L^{-1}. It was observed that a steady increase in the Cr concentration from upstream (0.039 ± 0.02 mg L^{-1}) to downstream (4.47 ± 1.85 mg L^{-1}) of the river, with summer being the optimal season and declining during the monsoon period (Khatoon et al. 2013). It may occur due to the increase in dilution factor during monsoon period.

Tonnes of garbage containing Cr have been piling up within the shuttered offices of an industrial complex, at Ranipet, for almost three decades. Besides, the high level of soil pollution may be due to the presence of hundreds of tanneries and small chemical companies (Rao et al. 2013). The environmental experts believe that, within a 30 km radius the groundwater has already been poisoned by Cr wastes. The study of soil and groundwater qualities at Ranipet was done in 2016. It revealed serious contamination of those environmental components. As per the Geological Survey of India, Cr(VI) contamination has a southward spread up to 2–2.5 kms. The assessment of Thandalam and Manianpattu lakes confirmed heavy contamination with Cr and thus making the water unfit for human use (Madhavan 2020). The TCCL was responsible for the production of chromium sulphate, sodium bichromate, and sodium sulphate tanning powder. The TCCL factory was shut down for environmental issues, including soil and water pollution, in 1996. A serious health risk is posed, by the estimated 1,50,000 tonnes of Cr-containing wastes, dumped there. The irresponsible dumping of waste containing Cr(VI) over a long period of time has resulted in the accumulation of trash to a height of 3–5 m over 2–4 ha. During the rainy season, Cr(VI) leachate infiltrates through the subsurface, hence, affecting the groundwater quality (CPCB 2016).

According to an assessment report, an industrial unit released, about 77,000 tonnes of hazardous Cr wastes into the environment at Gujarat (Rao et al. 2009). The area of the abandoned industrial unit is heavily contaminated with chromate salts covering an area of 15,000 square feet. The unauthorized Cr waste dumping sites are located along roadways close to the factory. Workers, exposed to Cr were shown serious health effects, including yellow discoloration of the affected parts.

The cement manufacturing industries, breaking down asbestos, catalytic converter emissions and other solid organic wastes are other sources of Cr contamination. As it enters into the living organisms, it becomes the part of the food chain. Its concentration rises in tissues and eventually biomagnified in top order organisms (Mitra et al. 2017). The countries like India, Bangladesh, and Pakistan are making protein concentrates as a feed for fish and poultry from tannery wastes (skin). The high Cr content (0.3–0.4%, dry weight) in these products could be dangerous for the public health due to biomagnifications. It is a possibility that, 1 metric tonne (dry weight) of excreta, from those contaminated poultry, might expose the environment to a Cr burden of 2.94 kg. (Hossain et al. 2017). At higher concentrations, Cr is noxious

Table 12.1 Reported soil and water contamination of few Indian cities by chromium

Region	Contaminated environmental component	Causes of chromium release	Chromium concentration (in ppm)	References
Nauriyakhera (Kanpur)	Groundwater	Textile effluents, tannery effluents, chromium-rich wastes, dumpsites	16.30	Singh et al. (2009)
Pernampattu, Madhnur, Alangayam, Natrampalli (Vellore)	Groundwater	Tannery effluents	0.04	Kanagaraj and Elango (2019)
Maheshwaram watershed (Hyderabad)	Groundwater	Urban wastes, irrational waste disposal	0.011–0.418	Purushotham et al. (2013)
River Yamuna (Delhi stretch)	Surface water	Human interference	0.002–1.98	Bhardwaj et al. (2017)
Ashtamudi wetland (Kollam)	Surface water	Dumping of municipal wastes, wastes from fishing harbor, oil spillage	1.1–0.08	Karim and Williams (2015)
Ropar wetland (Amritsar)	Soil	Human interference	0.29–10.30	Sharma et al. (2018)
Ranaghat–Fulia–Shantipur area (Nadia)	Surface water	Textile effluents	0.0–4.9	Sanyal et al. (2015)

to plants and negatively impacts a variety of biological processes. In some cases, it may lead to the destruction of the entire population (Dotaniya et al. 2014). The level of Cr contamination of environmental components is variable and it depends upon the sources of Cr release (Table 12.1).

12.7 Overview of Toxic Effects of Soil Chromium Contamination

The chromium gets accumulated in soil slowly but in it maintains a long residence time. It leads to Cr based soil pollution, a burning environmental problem. The soils irrigated with sewage sludge and effluents, accumulates Cr(VI) in its surface layer (Abdel-Sabour 2007).

In the geogenic processes of chromite oxidation, the microbes interact with mafic and ultramafic rocks at the same time. It releases Cr(VI) in our natural environment.

The Cr(VI) shows opposite physical and chemical characteristics in soil colloids and has a strong affinity towards negative charge (Tumolo et al. 2020) with the pH ranges in between 4 and 8. The Cr is present in soil in low concentrations, but it may get increased in it with certain natural and manmade activities. Generally, Cr(VI) is highly reactive and toxic, as compared to other Cr forms, due to its hydrophilic structure with high oxidation state. Its small concentration in soil may be due to the result of conversion of natural Cr(III) by oxidation. In contrast, larger concentration of Cr(VI) in soil may be due to the Cr(VI) pollution or the conversion of Cr(III) by oxidation. The combustion of fossil fuels, mining, smelting of ores, amendment of sludge to soil, application of fertilizer and chemical agricultural practices are examples of major causes of soil Cr contaminations. When Cr added to sewage sludge, it may change its form but present in soil for an extended period and available to plants for many years (Dhal et al. 2013).

The Cr polluted soil samples collected from a depth of 30 cm shows variation in the levels of different forms of Cr. As an example, out of 8 km^2 sampled area, almost, 0.9 km^2 was observed to be polluted with Cr, with a high concentration up to 12 960 mg Kg^{-1} (Ayari et al. 2010). The Cr(VI) at moderate to high concentrations has been found to affect plant growth and physiology. The wilting and discoloration of leaves have been observed initially in plants during exposure to Cr toxicity (ANRCP 1998). The 0.5 ppm Cr(VI) concentration in aquatic conditions or 5 ppm of its concentration in soils, can impart phytotoxicity (Fendorf 1995).

12.8 Possible Techniques for Remediation of Soil Chromium Contamination

The widespread use of Cr in industrial installations and its extensive extraction at mining sites, pollutes the soil matrices to a larger extent. Soil being an intrinsic part of the environment is strongly related to determination of environmental health. The toxic Cr(VI) exists in soil with pH ranging from 7 to >7, as highly, moderately or sparsely soluble salts or anions, like chromate (CrO_4^{2-}). Remediation of Cr(VI) contaminated soil is extremely important to protect the public health from its adverse effects. However, the complexity of chromium compounds makes the remediation process really challenging. The stable forms of chromium are capable of conversion among stable and unstable forms in nature, due to redox reactions. It is making the soil system complicated to determine as Cr contaminated soils are hazardous or not (James 1996).

Cr is a hypertoxic and carcinogenic agent, capable of accumulation and transfer through food webs, affecting human health (Deb et al. 2022; Ding et al. 2021). Researchers worldwide are keen towards studying Cr pollution and to devise potential harmless techniques to manage the same (Zhang et al. 2021). Most of the remediation techniques, target the conversion of Cr(VI) to its least toxic and stable form in soil

(Yang et al. 2021). The remediation of Cr polluted soil can be done through physico-chemical and/or biological methods.

12.8.1 Physico-Chemical Methods for Remediation of Cr(VI) Contaminated Soils

The commonly used physico-chemical methods are land filling, soil washing, stabilization, vitrification, and chemical reduction. These methods can be used at the site of pollution or away from it, depending on the locality and contaminants load on soil.

Landfilling

Landfilling, also known as "dig and haul" is the most simple of the remediation techniques. This technique is used to remove, soil pollutants from its actual site, to a secure landfill that has been engineered with impermeable walls, drains for leachates, and other facilities. The landfill area generally located far away from urban areas and generally in isolated places. This makes the transport of the contaminated soil to the landfill site, a very costly affair. Moreover, the technique of landfilling is possible for contaminated soil over a small area. Cr(VI) pollution arising out of large sites like mines cannot be remediated using this technique.

Soil washing

Soil washing is another option that uses an aqueous solution to separate contaminants like Cr(VI) adsorbed onto the soil particles. The washing solution generally mobilizes heavy metals by making changes to soil's ionic strength, pH, complexation, oxidizing and reducing abilities (Beiyuan et al. 2017). An array of acids, alkalis and other chemicals are used in formulation of a washing solution. Despite washing, some metals and leachates tend to present in soils (Zhai et al. 2018). This technique is also not feasible for large contaminated sites.

Vitrification

The process of vitrification uses thermal energy in order to melt the soil so as to bring physical or chemical stabilization. Heavy metals like Cr in the soil are isolated in glass material wherein they remain chemically bound (Shao et al. 2022; Shu et al. 2020). This process in particular is highly energy demanding and therefore a costly option.

Stabilization

Stabilization of Cr(VI), a toxic metal in contaminated soils is mostly carried out by the use of types of stabilizing agents. The stabilizing agents react with heavy metals through a sequence of reactions like adsorption using suitable adsorbents, precipitation, and reduction using requisite redox agents, to reduce the mobility, toxicity, or biological efficiency of contaminants (Xu et al. 2021; Mei et al. 2022).

Adsorption

It is a common technique, used for decontamination of soils polluted by metals (Wadhawan et al. 2020). Agricultural residues and charged carbons from organic sources are excellent adsorbents, having metal removal ability from soil. Hence, it is being used as natural adsorbents (Cheng et al. 2019). Chitosan, a natural polymeric nanoparticle has high adsorption properties, may be attributed to the reactive amino and hydroxyl groups present as functional groups on it. Recent uses of chitosan in nanofiltration of metal contaminants from contaminated soil have been done, successfully (Wadhawan et al. 2020). Biochar is also considered to be a good adsorbent on the basis of its economy, easy availability, and optimum water retention capacity. Biochar also helps in cycling of nutrients during crop growth, along with reduced uptake of heavy metals from soils by engaged plants (Fu et al. 2021; Kavitha et al. 2018). A dose of 10 g Kg^{-1} of biochar-nZVI was found to successfully remove 86.55% Cr(VI) from polluted soil along with increasing the abundance and diversity of indigenous bacterial species (Yang et al. 2022). In a recent study, double hydroxides of magnesium (MgAl) and calcium (CaAl), calcined with temperature variation, to immobilize Cr(VI) in soil. The use of MgAl at 500 °C and CaAl at 900 °C were found to adsorb Cr at a rate of 13.89 mg g^{-1} and 33.78 mg g^{-1}, respectively. It indicates that, the double hydroxides could stabilize Cr(VI) better in soil and thus prevent its movement from soil to plants (Zhao et al. 2021). The use of appropriate adsorbents for remediation of Cr contaminated soil is not a long-term solution, as heavy metals like Cr(VI) will eventually undergo decomplexation over time and leads to the release of several secondary pollutants (Lin et al. 2022).

Precipitation

The process of precipitation, makes use of certain chemicals, referred to as 'precipitants'. These chemicals have the ability to react with heavy metals, to form insoluble complexes. Soil pH and metal concentration are two major factors to determine success of the process. Cr is more soluble and mobile at low pH and can be precipitated by increasing the pH of soil matrix. Sludge rich in Cr generated from industries is first digested, followed by addition of specific salts and hydroxides (Pham et al. 2019). However, precipitation does not work out all alone. It needs certain secondary techniques, like exchange of ions, adsorption or both in sequence, for complete metal removal.

Chemical Reduction

Chemical reduction makes use of chemicals to reduce the metal from its toxic to least toxic form. This process is generally used to reduce Cr(VI) to least toxic, Cr(III). Several industries generate huge amount of Cr(VI) rich effluents, and commonly treat them by the process of chemical reduction. The chemicals like ferrous sulphate, sodium bisulphite, sulphur dioxide, and ferrous ammonium sulphates are some of the reluctant, used for the reduction of toxic Cr(VI), in industries. Soil mixing equipment, injection wells are some of methods to introduce reducing agents to sub-surface soils, at metal polluted sites. The drawbacks of the process include, occurrence of several side reactions, making the soil Cr(VI) treatment an arduous task (Higgins et al. 1997).

12.8.2 Biological Approaches for Remediation of Cr Contaminated Soil

The technique of bioremediation uses organisms like microbes for microbial remediation and plants for phytoremediation. These organisms, remove toxic metal contaminants, like Cr(VI) from soil (Leong et al. 2019; Khoo et al. 2021). A major advantage of bioremediation lies in the fact that in certain cases the remediation of the environment can be easily carried out without the need for any human intervention. Bioremediation can be carried out as in-situ (on-site) and ex-situ (off-site), for detoxification of Cr contaminated soils. The in-situ technique involves processes such as Biosparging (Hussain et al. 2021), Bioventing (Anekwe and Isa 2021), Bacterial remediation (Dhaliwal et al. 2020), Fungal remediation (Srivastava et al. 2015), and Phytoremediation (Lakkireddy and Kües 2017). Similarly, the ex-situ techniques include Land farming (Mosa et al. 2016), Composting (Dhaliwal et al. 2020), and Bio-piling (Gogoi et al. 2021). The ex-situ mode of remediation involves excavation of soil from polluted sites and its shifting to an off-site condition for treatment of pollutants. At the post-treatment stage the disposal of treated wastes have to be done at some pre-approved sites. It makes the whole process more tedious and expensive (Fasani et al. 2018).

12.9 Phytoremediation as a Technique for Soil Chromium Remediation: Opportunities and Challenges

The soil Cr remediation is an arduous task and needs proper attention, keeping in mind the several lethal impacts it poses on environment as well as on its components. There are several methods, being employed worldwide for the remediation of Cr contaminated soil and water, as discussed in the previous section. However, it is quite important to select an appropriate method that is not only feasible, cost-effective, but also environmentally sustainable. Phytoremediation is one such environmentally sustainable technique that makes use of flora, soil conditioners, and rhizospheric microbes to reduce the toxicity of environmental contaminants (Das 2018). Plants like hyperaccumulators, can withstand and accumulate high concentrations of soil Cr(VI) during remediation (Das et al. 2017).

Phytoremediation as a whole is comprised of many techniques which includes phytoextraction (Ali et al. 2013), phytostabilization (Lone et al. 2008), phytodegradation (Pilon-Smits 2005), phytostimulation (Dzantor 2007), phytovolatilization

(Limmer and Burken 2016), rhizofiltration, and phytodesalination (Ali et al. 2013). Reduction of soil Cr(VI) through phytoremediation, mainly employs stabilization of metal in rhizospheric soil and/or its translocation to aerial plant biomass. Plants generally utilize the xylem tissues to translocate Cr(VI) from contaminated soils into their tissues. Plants generally uptake Cr(VI) through their roots by either the apoplastic or the symplastic systems of transport. Apoplastic transport of Cr(VI) is an energy independent pathway and occurs using intercellular spaces in roots. However, the symplastic pathway is energy dependent and takes into account the involvement of sulphate or phosphate ion channels/carriers (Chaudhary et al. 2018). The non-hyperaccumulators among plants tend to accumulate heavy metals in vacuoles of roots whereas, the hyperaccumulators among plants transfer metals from roots to different portions of shoots through vessels of xylem using symplastic pathway (Chandra et al. 2017). Several membrane proteins facilitate, the transfer of the metal through the tissues of xylems (Chaudhary et al. 2018). The metal moves to aerial parts of plants, especially to foliar tissues for accumulation. Once inside those tissues, the Cr is sequestered to vacuoles present in foliar cells, with the action of several transporter proteins.

The detoxification of Cr contaminated soil systems is possible using physico-chemical and biological principles. Analysis of these methods indicates that, phytoremediation is an economical and sustainable technique for detoxification of Cr contaminated rhizospheric soil (Schnoor 1997; USEPA 2000). The plant species engaged for phytoremediation purpose is decided by its ability to detoxify the Cr polluted soil systems, in an economical, optimal and sustainable manner. The quantity of Cr uptake by those plants, engaged for phytoremediation, is variable and species specific.

The roots and stems of cruciferous plants like, *Brassica juncea* has the ability for efficient accumulation of toxic Cr(VI) from polluted soil or aquatic systems (Salt et al. 1997). Besides *B. juncea*, other crucifers like *B. nigra*, *B. oleracea*, *B. campestris*, *B. carinata*, and *B. napus* have the ability for efficient metals accumulation (Kumar et al. 1995). Similarly, aquatic species like *Eichhornia crassipes* are useful for remediation of oxidation pond designed for the loading of discharges from industrial units. In an earlier study, the *Eichhornia crassipes*, were allowed to grow on Cr(VI) polluted systems, but it shows the accumulation Cr(III) in tissues of roots and stems (Lytle et al. 1998). The *Eichhornia crassipes* was not only a hyperaccumulator of Cr, but can accumulate cadmium to a certain extent. It shows poor accumulation of arsenic and nickel under polluted conditions (Zhu et al. 1999). The preference for bioaccumulation of heavy metals is species specific. The plant species *Helianthus annuus* accumulates heavy metals in the order of cadmium > nickel > chromium which is reverse to the trend shown by *Brassica juncea* (Zavoda et al. 2001). It is an indication towards transformation of Cr species with the reduction of its toxicity level during phytoremediation. All the plant species are not equally capable of heavy metals remediation. The plant species shows gradation, with respect to heavy metal remediation.

The roots are the main region for Cr accumulation in plants (Das et al. 2022a, b, c). The X-ray absorption spectroscopy revealed that, Cr(VI) entered into the roots of *Prosopis* sp. was completely reduced to Cr(III) during its movement from root to leaves and being present in Cr(III) in foliar biomass (Aldrich et al. 2003). The interest concentrates on the point of conversion of Cr(VI)–Cr(III) during phytoremediation. An earlier study reflected that, the Cr(VI) was converted to Cr(III) during its presence in lateral roots of plants engaged for phytoremediation, and then the Cr (III) was moved into the foliar tissues (Lytle et al. 1998).

A specific plant species is not equally capable of reducing the toxicity of a number of heavy metals. The *Brassica sp* is capable of effective extraction of Cr from soil as compared to the extraction of other heavy metals like zinc, cadmium, copper and nickel present in soil systems (Kumar et al. 1995).

The chelators induced bioaccumulation of heavy metals is not so encouraging. The chelating agents can induce the accumulated metal concentration in plants but the overall metal detoxification by plants from soil, decreased significantly. The metal detoxification in soil decreases due to the tissue necrosis of plants engaged for phytoremediation purpose (Chen and Cutright 2001).

The dicotyledonous plants are more suitable for phytoremediation as compared to monocotyledonous plants, as these two groups of plants have differences in the structure and composition of root systems. The dicotyledonous plants with network of taproot system are preferable for phytoremediation as compared to the fibrous root systems of monocotyledonous plants. The extensive network of celluloses and hemicelluloses in dicotyledonous taproot system, provides more polar hydroxyl groups, required for the transport of Cr from soil to cellular systems of flora present in rhizospheric soil. Presence of these polar OH^- groups helps in the lysis of water and formation of bonds between Cr and water. It may be the possible reason for more solubility and mobility of Cr(VI) inside the plants. It is supported by the earlier findings like, the buckwheat shows more Cr absorption by roots and its translocation from roots to the stems and leaves, as compared to monocot plants like corn and barley (ANRCP 1998; Das et al. 2022a).

The gradient of bioaccumulation of Cr species across plant parts may be attributed to the difference in chemical structures of those plant parts. The roots show relatively high polysaccharides fractions as compared to stems and leaves. The roots and stems have rich OH^- fractions as compared to leaves rich in proteins. It may be a possible explanation for better uptake and bioaccumulation of total chromium (TCr) in roots as compared leaves. It is strengthened by the outcomes of the study on bioaccumulation of TCr, in tissues of *Larrea tridentate* (Gardea-Torresdey et al. 1998).

The phytoremediation efficiency, not only depending on plants as hyperaccumulators, but also on parameters like, characteristics of soil, metals, and microorganisms present in the rhizospheric systems (Das et al. 2018). The multiple factors required for successful operation of phytoremediation of Cr from contaminated soils are described in brief in the succeeding sections.

12.9.1 Selection of Appropriate Plants

Selection of suitable plant species as hyperaccumulators of soil Cr is the initial and crucial step for the smooth functioning of phytoremediation. It is better to select plant species for this purpose, on the basis of certain distinctive features acquired by those species (Fig. 12.2).

The term hyperaccumulator was first used for plants that can retain/tolerate >1000 mg Kg^{-1}, dry weight of heavy metals like nickel in their tissues. Plants growing in natural environment and dry vegetation with hyperaccumulation ability of 300 mg Kg^{-1} of Cr can be labelled as Cr-hyperaccumulating plants (Farooqi et al. 2022). An indigenous plant species is more preferable over other plants due to fewer requirements of management and easy acclimatization to the soil profile, native climate, and seasonal fluctuations. Besides the indigenous plants, there are certain exotic species that can outperform others in terms of accumulation. Plants with high biomass yield, tolerance to extreme climatic conditions, tolerance to variations in soil chemical profiles, and deep and branched network of roots can be considered as an effective phytoremedial species for decontamination of soil Cr(VI) (Sarma 2011). Higher biomass yield means higher capacity to retain Cr(VI) in its biomass. Similarly, tolerance to varied climatic conditions and soil chemical profiles ensures that the plant can easily be grown and thrive in most part of the globe, thus not making its use restricted to a particular geographical area. Deep and branched network of roots will ensure maximum coverage and contact with the soil, thereby making the accumulation process much efficient.

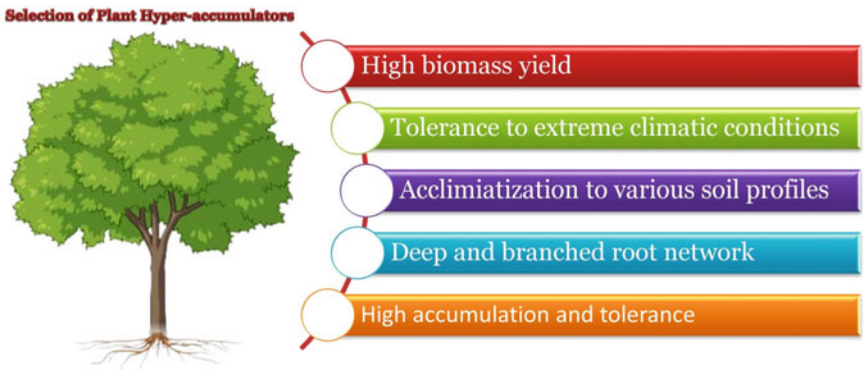

Fig. 12.2 Important factors for selecting a hyper-accumulator plant

12.9.2 Characteristics of the Rhizospheric Soil

The soil chemical features at rhizosphere, like organic carbon content, pH, and texture, to certain extent determine the local availability of metals for phytoremediation (Shah and Daverey 2020). At a low pH of <5, the Cr(VI) is present in soil as oxyanion, like CrO_4^{-2} and remained there in immobilized condition. With an increase in pH (>5), the toxic heavy metal becomes highly mobile and available in soil for absorption by plants root system. Organic amendment in soil rich in Cr(VI) results in reducing the soil pH. It forms a stable organo-metallic complex and exhibits reduced toxicity (Das et al. 2021a). Recent studies have suggested organic acids supplementation as a source of protons that may help in inducing the detoxification Cr(VI) based polluted soils (Das et al. 2021a).

The texture of soil is one of the determining factors, to estimate the efficiency of phytoextraction (Złochet al. 2017). The small sized soil particles have higher concentration of metals like Cr(VI), as compared to coarse particles. The more reactive surface area of small sized soil particles may be a factor for enhanced translocation of metals into plants, from those soils.

12.9.3 Concentration and Nature of the Metal (Cr(VI))

The concentration of metals like Cr(VI) in soil, is another factor to determine the extent of phytoremediation under the stipulated conditions. The upsurge in concentration of soil Cr(VI), beyond the metal accumulation limit of selected plant species, would not work out in favour of remediation process. Similarly, the oxidation state of Cr in soil is directly linked with the phytoavailability of heavy metal for plants. The Cr in its oxidized form, Cr(VI) is highly dynamic and can be easily moved into the root systems of hyperaccumulators from soil matrix. Contrary to it, the reduced and insoluble Cr(III) state in soil matrix, remains immobilized in soil and unavailable for plants to get absorbed.

12.9.4 Interaction of Rhizospheric Microbes

Rhizospheric microbes, also referred to as 'plant growth promoting rhizobacteria' (PGPRs) positively influence the phytoremediation of chromium (Fig. 12.3). The PGPRs are capable of producing several organic acids that can reduce the soil pH, thus enhancing the heavy metals bioavailability for phytoextraction (Yang et al. 2018). The rhizospheric microbes involved in the redox reactions of metals, present in soil, by producing certain oxidising or reducing agents. These agents stabilize the metals in soil or transform them into less toxic forms (Ma et al. 2016).

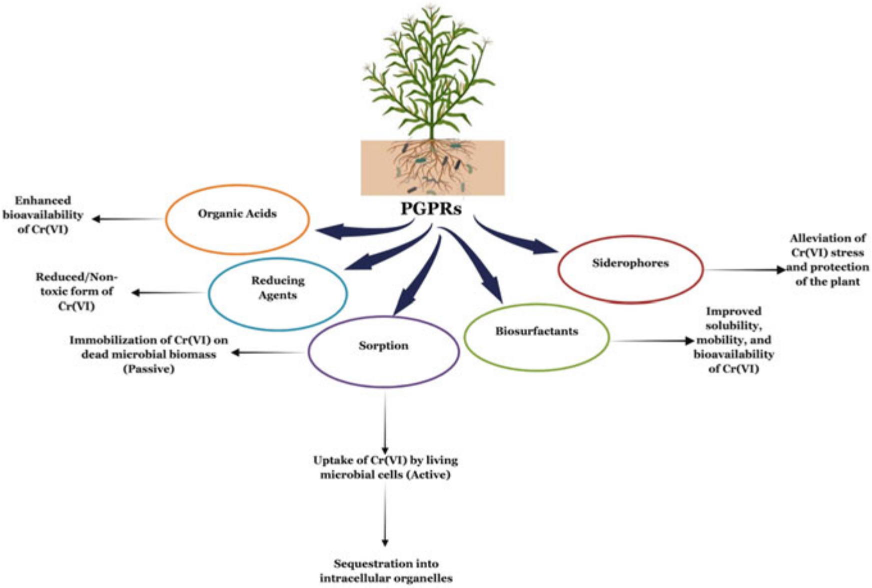

Fig. 12.3 Role of PGPRs in the phytoremediation of Cr(VI)

Specific microbes have an inherent capability for biosorption of heavy metals from soil, following passive or active mechanism, and thereby help in phytoremediation. Passive sorption immobilizes heavy metals by attaching to functional groups present on the surface of dead microbes. In active sorption process, the heavy metals are trapped by the living microbial cells. These metals then sequestered within the intracellular organelles by binding with metallothioneins, present in cells (Das et al. 2021a).

Some microorganisms have the ability to produce amphiphilic compounds, known as 'biosurfactants'. These compounds can make desorption of heavy metals from soil. They also improve the solvation and dynamism of metals, thus making them available for intake by plant hyperaccumulators (Lal et al. 2018). Rhizospheric microbes can also produce 'siderophores' (compounds having low molecular weight), capable of protecting plants under heavy metal stress conditions. The siderophores are basically iron chelators and thus alleviating the biosynthesis of chlorophyll pigments with healthy growth of the plants under metal stress conditions (Ahemad 2015). Many rhizospheric microbes can be utilized for Cr(VI) remediation in soil (Table 12.2).

Table 12.2 Application of rhizospheric microbes for Cr(VI) remediation in soil

Microorganism	Mechanism	Remediation effect	References
Bacillus subtilis MAI3	Production of antioxidants and reductase enzymes	Reduction of Cr(VI)–Cr(III), promoted growth and production of photosynthetic pigments in soybean	Wani et al. (2018)
Paenibacilus konsidensis SK3	Rhizospheric interactions, lowering of pH, secretion of organic acids in soil	Decrease in soil Cr(VI) and increase in phytoremedial ability of *Pongamia pinnata*	Das et al. (2022b)
Klebsiella sp. CPSB4	Secretion of organic acids for phosphate solubilization	Plant growth promotion, 95% reduction of soil Cr(VI)	Gupta et al. (2018)
Cellulosimicrobium cellulans $KUCr_3$	Production of IAA, and solubilization of phosphate	Reduction of Cr(VI)–Cr(III), promoted growth of chilly plant and reduced the uptake of Cr	Chatterjee et al. (2009)
Microbacterium sp.	Cr(VI) reduction	Reduced Cr(VI) toxicity and improved biomass in fenugreek	Soni et al. (2023)
Sphingomonas sp.	Upregulation of antioxidant system	Increase in plant biomass, reduced translocation of Cr(VI), and reduced oxidative stress in soybean	Bilal et al. (2018)
Cellulosimicrobium funkei	Promotion of plant growth promoting substances	High Cr(VI) tolerance up to 1200 µg/ml, enhanced root length in *Phaseolus vulgaris* L	Karthik et al. (2017)

12.10 Socio-economic Aspects of Phytoremediation of Chromium Contaminated Rhizospheric Soil

The good health of common people is intricately linked with sustainable development, and rational land use practices. The soil toxicity due to Cr enrichment breached these notions and not only affecting the public health but also have some adverse impacts on the economic development of a country. The leachable Cr(VI), is a hazardous and Group I human carcinogen (IARC 1990), released from industrial activities. To obtain a sustainable economic development, it is required to take steps for detoxification of Cr based polluted soils, using phytoremediation. Primary target of phytoremediation is to restore the quality of Cr contaminated lands by restricting the Cr content of soil. It is essential to restrict the Cr toxicity of soil, caused by anthropogenic activities, as this toxicity is increasing with time. The toxicity caused by release of Cr(VI) from natural sources is highly insignificant, as compared to its release from anthropogenic sources.

The use of edible plant species for phytoremediation purpose may create havoc for the society. The consumption of those species is significantly fatal due to bioaccumulation of toxic products. As a bio-safety measure, it is better to engage non-edible plant species or weeds for the remediation of soil Cr level. Post-remediation measures require safe disposal of used plants, to prevent secondary environmental pollution and to establish sustainable development.

The phytoremediation is an economical and user friendly technique for land detoxification. It can be suitable for use by all the sections of society, at pilot and field scale levels. It can bring reclamation of hectares of land, which is essential for sustainable socio-economic development at the regional and global levels.

12.11 Conclusion

The release of chromium from multiple sources is degrading the quality of land resources. The high concentration of chromium in soil is making it unfit for productive uses. To protect the living systems and their associated environment from chromium adverse effects, it is better to use the phytoremediation to control Cr based soil pollution. It is advantageous to use phytoremediation for redressal of soil chromium toxicity, as compared to other physico-chemical techniques. It is an economical, user friendly and effective technique. The use of dicotyledonous plants for phytoremediation is preferable, as compared to the use of monocotyledonous plants for this purpose. The efficiency of soil Cr phytoremediation can be upgraded with proper regulation of hyperaccumulators rhizosphere. The active and passive mechanisms involved in this phytoremediation are step towards restoration of healthy state of degraded environment. To a certain extent, it can prevent the emerging socio-economic disruptions caused by toxic pollutants, at different levels. Further study on this aspect is essential to bring improvement of phytoremediation process.

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