Chapter 13
Microbial Remediation Technologies for Chromium Removal: Mechanism, Challenges and Future Prospect

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Abstract Heavy metal (HM) exposure is regarded as one of the greatest environmental concerns worldwide due to their non-biodegradability, high bioaccumulation in the food chain, and most importantly, human carcinogenicity. The industrial uses of chromium (Cr) are diverse and include metallurgy, paint, leather tanning, and electroplating. Because of inadequate waste discharge regulations, toxic amounts of Cr are released into the environment, severely damaging the ecosystem. It is now understood that Cr has some advantages for humans in its trivalent oxidation form [Cr(III)] as a micronutrient. However, its hexavalent form [Cr(VI)] is a strong carcinogen and has no recognized biological functions. Over the years, a number of physico-chemical, and biobased techniques have appeared in the effort to eliminate Cr from the environment. Bioremediation of Cr have several advantages over the conventional physical and chemical treatment methods due to its low cost, environment friendly practices and sustainability. Bacteria employs several mechanisms such as biosorption, efflux, bioreduction and bioaccumulation that they possess either inherently or have acquired to counter the toxic effects of Cr with time. This chapter focuses in detail on microbial mechanisms and responses against Cr toxicity, their applications and challenges in real time applicability of these. Further, the latest strategies and solutions in developing bioremediation applications are also discussed in this chapter. Nanobioremediation, immobilization techniques and use of enhancers have immense scope in improving the bioremediation efficiency and also in metal recovery. This information will be helpful in understanding the current status of research of Cr pollution remediation and bridging the gap between lab scale findings and its real time applicability in the environment.

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13.1 Environmental Pollution

Natural resources are being consumed quickly due to the rapid development of society. Although heavy metals are used in a variety of industrial processes, some of them have the potential to seriously harm the environment. Heavy metals are hard to break down and have a long half-life. They will obstruct specific protein and nucleic acid processes after entering the body (Bartlett 1991; Chen and Tian 2021). One of the biggest environmental problems today is the discharge of dangerous heavy metals into wastewater from industry and human activity. Many academics and experts are paying attention to water pollution because it poses a serious threat to people, land animals, and aquatic animals and plants. This is mostly due to a growth in various industrial operations, which contribute significantly to the global production of waste and untreated water (Ayele and Godeto 2021). In addition to its undesirable side effects, industrial and technological advancements also damage and pollute the environment. Xenobiotics, poisonous, and other gases are unintentionally and intentionally released into the environment as a result of these revolutions (Verma and Kuila 2019). Water pollution induced from release of unregulated and large amounts of untreated or partially treated industrial effluents is a major threat to all life forms (Munjur et al. 2020). For instance, drinking water polluted with atorvastatin (a medication used to treat cardiovascular conditions) has indeed been related to serious health complications like myopathy, renal problems, amnesia and memory lapses, pancreatic and hepatic malfunction, etc. (Ali et al. 2019). Many other kinds of wastes from industrial, agricultural or domestic when dumped into water bodies untreated over the years can severely pollute and the contaminants can cause a variety of ailments including cutaneous, gastrointestinal, and vector-borne illnesses as well as blindness, paralysis, and renal (Chowdhary et al. 2017). Broadly, several drugs from pharmaceuticals (Ali et al. 2019), inorganic pollutants and polysaccharides from distillery industries (Chowdhary et al. 2017), organic wastes from pulp and paper industries (Zainith et al. 2019) and heavy metals that are continuously released from electroplating, chemical, metallurgy, tannery, textile industries etc. (Chowdhary et al. 2020) are of great concern as they present a very big environment challenge and threatening health of humans.

13.2 Heavy Metals

Metals with a weight greater than 5 g/cm^3 are classified as heavy metals (HMs) (Fulke et al. 2020). Chromium (Cr), cobalt (Co), copper (Cu), cadmium (Cd), arsenic (As), gallium (Ga), iron (Fe), mercury (Hg), lead (Pb), nickel (Ni), and manganese (Mn) are

a few of the more well-known heavy metals (Pandey and Madhuri 2014). With high molecular weight, atomic number, and specific gravity, they include the majority of transitional metals, basic metals, some metalloids, and lanthanides (Ayele and Godeto 2021). Due to their non-biodegradability and prolonged atmospheric persistence, these toxic pollutants—which are commonly present in industrial effluents (Lian et al. 2019; Prasad et al. 2021); are detrimental even at extremely low concentrations. This makes them a significant environmental risk and one of the most challenging and complex environmental issues posing risks to both the ecosystem and public health (Kapahi and Sachdeva 2019; Monga et al. 2022a). HMs are naturally components of earth's crust that more than five times denser than water (Karimi-Maleh et al. 2021; Elgarahy et al. 2021; Cuellar et al. 2022). These elements can be found in nature in different forms such as hydroxides, acids and bases or as chemical complexes; can neither be destroyed or degraded from the environment (Cuellar et al. 2022). Due to their non-biodegradability, high bio accumulation in food chain and most of all human carcinogenicity, heavy metal exposure is considered one of the biggest environmental concerns globally (He and Chen 2014). Few metals are required by living beings to undertake certain metabolic activities, but several of these metals can be detrimental to human health at even very low concentration (Zhang et al. 2016a, b; Cuellar et al. 2022). Ideally, heavy metals when used in industries must undergo a regulated processing start from their sourcing extractions from ground deposits to their smelting and refining stages with a proper disposal of the resulting products. Instead, the heavy metal containing industrial wastes are released in the environment during each of these stages (Cuellar et al. 2022). Numerous industrial sectors, including electrochemical, pulp and paper industries, textile, metallurgies, mineral extraction, and the dye and paint chemical industries, employ various types of metals extensively for a variety of purposes (Igiri et al. 2018; Sun et al. 2019a; Ayele and Godeto 2021). Environmental deterioration is mostly brought on by unplanned industrial and urban expansion, which disregards the importance of a healthy environment. Due to these acts, heavy metal pollution has significantly increased, upsetting the natural balance (Wang et al. 2018). According to a WHO study, over 1.7 million children under the age of five die as a result of exposure to dangerous pollutants, particularly heavy metals (Xu et al. 2018). As a result, heavy metal environmental pollution is a major problem that necessitates immediate action (Pushkar et al. 2021).

13.3 Cr Contamination/Menace in India

The chromite deposits in India constitute around 2% of the world load. Of this, Odisha alone is responsible for 98% of the total chromite with 97% found in Sukinda valley (Mishra and Sahu 2013). In accordance with survey conducted by the Ministry of Environment, Forest, and Climate Change (MoEFCC), the Government of India (GOI), states—Andhra Pradesh, Maharashtra, Tamil Nadu, Karnataka and Gujarat—produce 80% of the metal-enriched toxic waste (Singh et al. 2020). Leaching and natural weathering of chromite from chromite mines into water bodies is a severe

cause of concern for soil and water pollution (Das and Mishra 2009; Prasad et al. 2021). In these Indian states, Ranipet in Tamil Nadu, Kanpur in Uttar Pradesh, Sukinda valley in Odisha), and Vadodara in Gujarat were identified as having the highest levels of contamination (Mishra and Sahu 2013; Jamshed and Vamit 2017; Singh et al. 2020). For example, the Cr(VI) and total Cr levels reported pin the Ranipet were 142 mg/L and 158 mg/L, respectively (Jeyasingh et al. 2011). Cr(VI) concentrations of up to 80 mg/L have been reported from the Kanpur region (Singh et al. 2013). According to studies by the Regional Research Laboratory (RRL) of the Council for Scientific and Industrial Research (CSIR) in Sukinda Valley, 7.6 metric tonnes of excess and overloaded waste were being dumped annually with the potential to release 11.3 tonnes of Cr(VI) in the ecosystem. Orissa Voluntary Health Association (OVHA) furthermore investigated the human mortality rates in the vicinity of such mining areas and found that 86.42% of the population in nearby villages were affected due to chromite mine related disorders (Gupta et al. 2019; Prasad et al. 2021). Also, around 80% of Indian tannery industries are majorly involved in chrome tanning. Tannery industry produce about 1500 metric tonnes of chrome sulphate per year as effluent that is discharged in the environment. A report on heavy metal contamination and risk analysis in water and sediments of the Ganga River between Kanpur and Pryagraj India, was recently published by Aggarwal et al. In 2022. In most of the samples, sediment Cr levels were higher than the averages for the Indian River System (IRS) and the planet's surface rocks, which were 87 and 71 mg/L, respectively. Sediment Cr levels ranged from 31.4 to 100.2 mg/L on average (Aggarwal et al. 2022). Cr pollution in the Ganga River is also to be blamed on by the usage of paint components containing Cr use for vehicular refurbishment. Cr concentrations in some of the samples have reached an alarming level due to the lethality that it can cause to some of aquatic species in the river (Aggarwal et al. 2022). In Yamuna River, Pb and Cr levels have exceeded the WHO permissible limits and most of the samples tested were extremely contaminated and unfit for the purposes of drinking, cooking or washing (Singh Sankhla et al. 2021).

13.4 Chromium (Cr): Occurrence, Speciation, and Fate into the Environment

The French chemist Louis Vauquelin made the discovery of Cr in 1797. Due to the various colours seen in the Cr-containing substances, Cr was given the Greek term "chroma" (Barnhart 1997). The transition metal Cr has atomic number of 24, an atomic weight of 51.996 amu, and an electronic structure of 4d5s1. It is a member of group VI-B of the periodic table. With well almost all naturally occurring Cr being in the trivalent state [Cr(III)], it is also the 21st most abundant component in the Earth's crust and quite prevalent in river waters, lakes, seawater, and underground waters naturally. It is typically combined with Fe or other inorganic materials (Barnhart 1997). Chromite (Fe, Mn) is the most important ore of chromium being found

in nature (Focardi et al. 2012). The zero [Cr], trivalent [Cr(III)], and hexavalent [Cr(VI)] forms are the most significant in industrial products and the environment due to their stability, even though it exists in multiple valence states (ranging from −2 and +6). (Barnhart 1997; Karthik et al. 2017). However, their chemical properties are contradictory, display differences in physicochemical characteristics, and exhibit biological reactivity, which has diverse effects on living cells (Bharagava and Mishra 2018; Sanjay et al. 2017; Pushkar et al. 2021). Some species need Cr(III), which is less harmful and functions as a supplement, for development and some metabolic pathways (Ma et al. 2019a, b). Moreover, due to its high bioavailability and dispersion rates in natural systems, Cr(VI) is more hazardous than Cr(III). The cellular membrane is quickly penetrated by Cr(VI), which can easily react with the proteins in the cytoplasm of the host cell (Bharagava and Mishra 2018; Pushkar et al. 2021). Also, Cr's ionic state is regulated by the pH and electrochemical state of the aqueous environment that it is present in. Table 13.1 lists some of the basic characteristics of different forms of Cr.

In the environment, Cr(III) is most stable and requires a considerable amount of energy to get converted into lower or higher valency states. Cr(II) is only stable in the absence of any oxidizing agent since otherwise it easily oxidizes to Cr(III) under anaerobic conditions. The Cr(III)/Cr(II) metal ion couple's negative standard potential (Eo) also supports this. On the other hand, Cr(VI) is unstable and strongly oxidizing in the presence of electron donors because of its extremely favorable redox potential in acidic solution (Eo between 1.33 and 1.38 V). The acidity drops as a result of the H^+ being used up during the reduction of $HCrO_4^-$ (Eq. 13.1), further lowering the chemical potential. When CrO_4^{2-} is reduced within a more basic solution, OH^- is produced in the face of a redox gradient (Eo = −0.13 V). When a result, Cr(III) is less stable than Cr(VI) and has a lower potential as basicity rises (pH > 4). However, in weakly/slightly acidic and weakly basic conditions, E versus pH has a steeper slope than Eq. (13.2) because di- and mono-hydroxy species are formed. A Pourbaix diagram has thus helped significantly in illustrating the pH and redox potential parameters that all the species must meet in order to be thermodynamically stable (Fig. 13.1) (Kotaś and Stasicka 2000).

$$HCrO_4^- + 7H^+ + 3e^- - Cr^{3+} + 4H_2O \tag{13.1}$$

Table 13.1 Physical properties of the various forms of Cr

Properties	Melting point (°C)	Boiling point (°C)	Solubility in water (g/L)	Density (g/cm^3)
Cr	1185	2672	Insoluble	7.14
$CrCl_3$	1152	–	Slightly soluble	2.76
K_2CrO_4	968.3	–	790	2.73
Cr_2O_3	226	4000	Insoluble	5.21
CrO_3	196	–	624	2.70

Adopted from WHO (1996), Pushkar et al. (2021)

$$CrO_2^- + 4H_2O + 3e^- - Cr(OH)_3 + 5OH^- \quad (13.2)$$

Gorny et al. (2016) extensively reviewed the existing literature concerning the redox pathways of Cr(III and VI) in aquatic habitats and their respective transposition to the surface sediments, where the speciation data is particularly limited and scarce. The main governing factors in Cr speciation in aquatic settings involve Mn(III, IV) hydroxides for Cr(III) oxidation, dissolved Fe(II) and HS-acting as Cr(VI) reducing species along with ferrous and sulfide minerals as Cr(VI) reducing phases as well as Fe(II) bearing minerals. Nonetheless, the redox conversion of Cr(VI)–Cr(III) is also a result of microbial action, and this conversion occurs either through detoxifying or dissimilatory reductions. The indirect conversion/oxidation of Cr(III)–Cr(VI) is also known to occur by Mn(II) oxidizing bacteria, though the mechanisms are not clearly identified yet. Moreover, Mn(II) and ammonium ions are not known to encourage reduction of Cr(VI). After it is reduced to Cr(III), the mobility of Cr(III) ions in the sediment fractions gets very restrictive and is only regulated by precipitation and sorption mechanisms (Gorny et al. 2016).

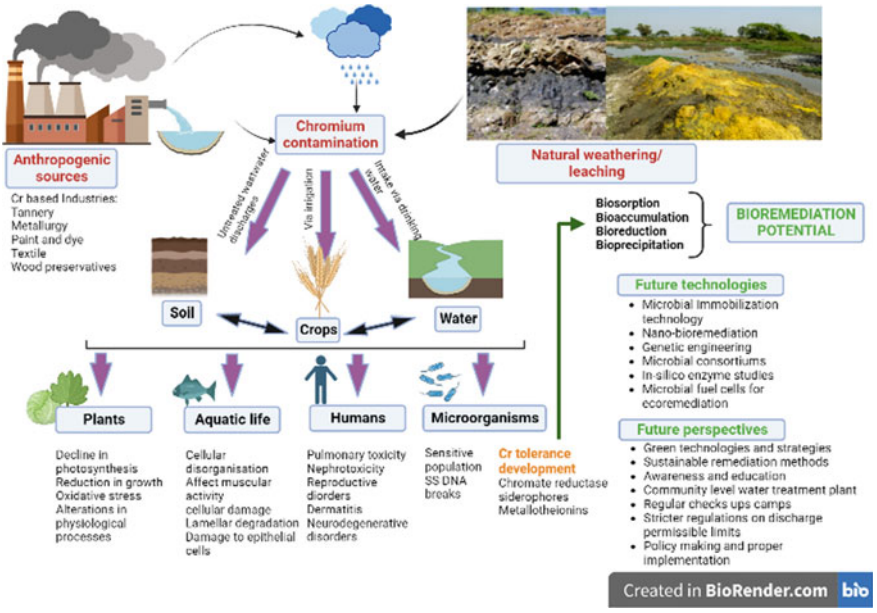

Fig. 13.1 An overview of environmental Cr contamination due to natural and anthropogenic sources; its effects on plants, aquatic life, microorganisms, and humans; future remediation technologies and perspectives

13.5 Essentiality of Cr(III)

With completely distinct reactivity in its two most abundant oxidation states, Cr(III) and Cr(VI), Cr stands out among other HMs as an intriguing exception (Genchi et al. 2021; Monga et al. 2022a, b). While Cr(VI) has a far higher bioavailability than Cr(III) due to its high solubility in water and transmembrane permeation, Cr(III) is less hazardous because it cannot easily pass through cell membranes. As consequence of this, Cr(VI) disseminates easily away from the innate site of contamination and is highly toxic even at low concentrations (Gorny et al. 2016; Nakkeeran et al. 2018). The Cr(VI) species being principally dominant in natural aquifers while the Cr(III) species being widespread in municipal wastewater rich in organics (Cheung and Gu 2007). The redox potential of Cr affects both its knietics and its dynamics (Moffat et al. 2018; Monga et al. 2022a, b). From being a vital trace element to a physiologically inert element (metallic Cr) to a strong endocrine disruptor to being genotoxic and carcinogenic, Cr exhibits a variety of traits (DesMarais and Costa 2019). It is now understood that the Cr(III) is necessary for both normal human and animal development. It has been identified as a pharmacologically active element due to its significance in the maintenance of nucleic acid (NA) structural integrity as well as glucose and lipid metabolism (Zayed and Terry 2003; Vincent 2017). Absorbed from dietary Cr, Cr(III) is now known to be a constituent of glucose tolerance factor (GTF) which is responsible for glucose clearance from the blood via an insulin stimulating mechanism. Also, Cr(III) ions contribute to the activation of the insulin receptor tyrosine kinase, which increases and enhances the insulin action threefold. Therefore, a lack of Cr(III) ions might lead to ailments and weight loss related with carbohydrates (Monga et al. 2022a). IARC (International Agency for Research on Cancer) in 1990 classified Cr(VI) as a class 1 carcinogen. Due to human activities, Cr(VI) is now widely spread in the environment and acts using complex mechanisms of generating reactive oxygen species leading to oxidative stress, epigenetic changes, chromosomal and DNA aberrations, and mutagenesis (Genchi et al. 2021; Monga et al. 2022a, b).

13.6 Origins of Cr Pollution

13.6.1 Natural Sources

The Earth's crust naturally contains Cr (Srivastav et al. 2018). It can be released naturally, primarily in Cr(III) and Cr(VI) form, from sources of Cr by processes of weathering (McCartor and Becker 2010; Stambulska et al. 2018; Prasad et al. 2021) (Fig. 13.2). According to Oze et al. (2007), the Earth's crust has Cr concentrations of over 200 mg kg^{-1} in ultramafic (ultrabasic) rock formations and ophiolite serpentinites structures, which make up about 1% of the landscape of the terrestrial environment, mostly found in the densely populated Mediterranean and Pacific regions

(Prasad et al. 2021). The sole valence state identified in the serpentine soil solids is Cr(III), however Cr(VI) has been found in the serpentine soil solutions from New Caledonia and California at quantities <30 M. The presence of Cr-spinels, specifically chromite and Cr-magnetite, has a direct impact on the concentration and range of Cr levels in serpentine sediments. However, oxidation of Cr(III) from Cr-spinels by high-valent Mn oxides or other potent oxidants has been found as a potential source of Cr(VI) in serpentine soil solutions. These phases are weather resistant and are maintained in the soil ecosystem (Oze et al. 2004). Chromite ore bodies could generate toxic Cr(VI) levels from inert chromites and contribute towards Cr pollution in waterbodies as shown in a study made on chromite bearing oxidized rocks in Orissa, India (Godgul and Sahu 1995). Cr(VI) is a toxin typically originating from anthropogenic activity (Bartlett and James 1988). However, both ground and surface waters from California, Italy, and Mexico have recorded naturally existing aqueous Cr(VI) concentrations up to 73 g/L, values exceeding the WHO's limit for drinking water of 50 g of Cr(VI) per litre, or 960 nM Cr(VI) (Oze et al. 2007). In the presence of birnessite, an ubiquitous manganese rock, Oze et al. (2007) observed rapid dissolution of chromite and subsequent conversion of Cr(III) to aqueous Cr(VI), explaining the production of Cr(VI) by a Cr(III)-bearing material regarded to be geochemically inert. Natural events may cause the Cr(III) in ultramafic- and serpentinite-derived soils and sediments to be oxidised and absorbed, resulting in dangerously high amounts of Cr(VI) in both surface and groundwater (Oze et al. 2007).

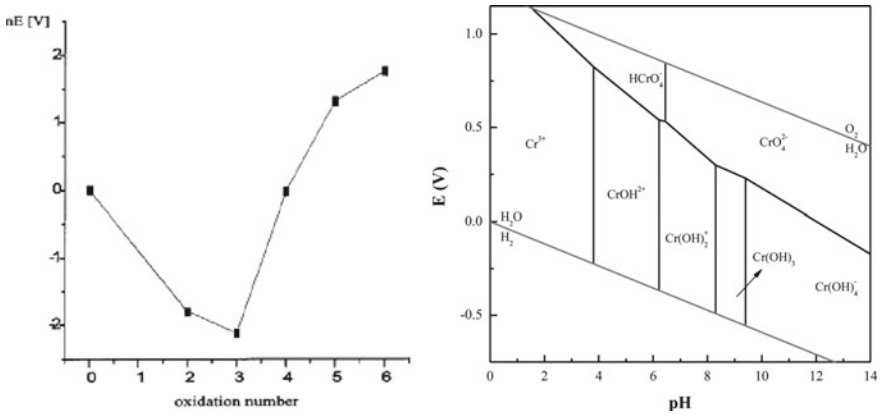

Fig. 13.2 Left: The Cr Species Frost diagram in an acidic condition. Right: A schematic Pourbaix diagram for the dominant Cr species in dilute, aerated aqueous solutions in the absence of any other agents for complexing Cr, except water or OH^-. Adapted from Kotaś and Stasicka (2000)

13.6.2 Human Activities

The global Cr reservoir is impacted by anthropogenic and natural events (Coetzee et al. 2020; Singh et al. 2020; Guo et al. 2021). The human population has been exposed to Cr through pollution exposure or drinking contaminated water (DesMarais and Costa 2019) (Fig. 13.2). Due of Cr's negative impacts on health, many laws have been put in place for monitoring and discharge. Over 100 locations release Cr, according to a Pure Earth survey from 2019, putting approximately 1.5 million individuals at risk of exposures to Cr and other contaminants (Singh et al. 2020). Effluent and sludge dumped from industrial facilities like chrome plating, metal polishing, leather tanning, and textiles are the principal sources of Cr(VI) pollution (He and Li 2020; Prasad et al. 2021; Jobby et al. 2018). Table 13.2 mentions the various industrial effluent and wastewater sources and the Cr content they usually carry. These industries contribute significantly to Cr(VI) toxicities and contamination in water and soil (Lian et al. 2019; Prasad et al. 2021). This hampers plant growth, agriculture, animal health, damaging human health eventually (Mitra et al. 2017). The USEPA and the European Union (EU) currently advise that the acceptance limit for surface wastewater should be less than 0.05 mg/L, with the total concentration of Cr [Cr(III), Cr(VI), and other forms] use around to below 2 mg/L (Labied et al. 2018; Ukhurebor et al. 2021; Monga et al. 2022a). A threshold of 0.05 mg/L of Cr in drinkable water and 0.1 mg/L for industrial effluent emission into groundwater have been set by the Central Control Board in India. Further to set criteria for controlled Cr emissions under the Clean Air Act of 1990, the USEPA increased the threshold to 0.1 mg/L (USEPA 2010). Governments and individuals all over the world are still very concerned about the presence of Cr in both natural and artificial ecosystems (Singh et al. 2020; Chen and Tian 2021). In Mexico, for instance, there are 769 tonnes of Cr(VI) waste being produced annually (Cuellar et al. 2022).

Table 13.2 Type of Cr(VI) salts used in various industries

Cr used in industries	Chemical forms
Chrome plating	Barium chromate, zinc chromate, Strontium chromate, sodium chromate
Leather tanneries	Ammonium dichromate
Wood chemical additives/preservatives	Chromium trioxide
Stainless steel factories	Potassium chromate, ammonium dichromate, potassium dichromate
Paints and pigments	Barium chromate, calcium chromate, lead chromate, zinc chromate, potassium dichromate

Adopted from Prasad et al. (2021)

13.7 Toxicity of Cr(VI)

13.7.1 Humans

The main toxic heavy metals- Pb, Cd, Hg and Cr stand out (Ozden et al. 2018; Cuellar et al. 2022) with the latter being a fascinating case due to its entirely different reactivities in its two most prevalent oxidation valence states of Cr(III) and Cr(VI) (Genchi et al. 2021; Monga et al. 2022a, b). The EPA has included Cr(VI) in the list of toxic substances (USEPA 2014) and has received a classification as a carcinogenic agent by the US Department of Health and Human Services with lung cancers being the most commonly associated with Cr(VI) intoxication (Cueller et al. 2022). Notably, high concentrations of Cr can substitute other metals in biological systems and have negative effects like cancer, kidney failure, neurodegenerative diseases (ND), and death (Monga et al. 2022a). On oral consumption, a part of Cr(VI) is extracellularly converted to Cr(III) as a protective mechanism (Proctor et al. 2002; De Flora et al. 2006). As soon as Cr(VI) enters the cells, it combines spontaneously with intracellular reducing substances such ascorbic acid, glutathione, cytochrome, etc. to produce short-lived intermediaries like Cr(V) and Cr(IV), free radicals, and ultimately Cr(III) (Costa 2003; Cheung and Gu 2007). The primary toxicity mechanism of Cr(VI) is explained by the fact that Cr(III) has a relatively low penetration, is largely trapped inside of cells, accumulates, and interacts with DNA (Zhitkovich 2011). Also, Cr(V) can undergo a redox cycle ton regenerate Cr(VI) along with generating ROS that could interact with DNA-protein multiplexes, creates oxidative stress and triggers multiple apoptosis signaling pathways compromising the cellular functions (De Flora et al. 2006; Wu et al. 2020). Then by producing ROS in excess and depleting physiological antioxidant molecules, Cr(VI) can change redox balance via Fenton reaction (Wang et al. 2007; Li et al. 2019a; Monga et al. 2022a). Cr and its related toxicity has been a point of contention of several decades now. Cr(VI) exposure can cause cellular injuries and dangerous health consequences in several ways. Genchi et al. (2021) have extensively reviewed Cr toxicity on human health. According to many investigations, long term exposure to Cr(VI) can lead to neurodegeration, renal damages, dermal sensitivities, genotoxicity, cytotoxicity and immune system disorders (Sun et al. 2015; Fu et al. 2020). Cr exposure triggers specific kinds of cellular responses in the vital organs of human bodies (Monga et al. 2022a) (Fig. 13.3) including epigenetic modifications, gene regulations, DNA modifications etc. For instance, one of the most active transcriptome responses to Cr(VI) in mouse lung cells was eukaryotic translation initiation factor (eIF2) signalling (Rager et al. 2019). EIF2 pathway is frequently up-regulated in tumor cells and is involved in cell proliferation and growth (Watkins and Norbury 2002; Sonenberg and Hinnebusch 2009). Also, Cr(VI) sensitive genes such as MLH1and RAD51 were down regulated displaying a decrease in DNA replication, recombination and repair (Rager et al. 2019). In liver cells, Cr(VI) interferes with mitochondrial functions: diminished my copy number, respiration and redox equilibrium and retarded my electron transport chain (Yang et al. 2020). Normal mt fusion and proliferation occur

in a dynamic equilibrium, but Cr(VI) has the power to upset this balance and produce fission, which affects cellular homeostasis and leads to oxidative stress and cellular death (Li et al. 2019a; Monga et al. 2022a). In addition, Cr(VI) causes morphological and functional damage to the immune system's crucial organs, including the thymus, spleen, lymph nodes, and bone marrow (Hultman and Pollard 2022). Wistar rats were given Cr(VI) orally for 135 days, during which time Karaulov et al. (2019) observed morphological and functional changes in the lymphoid tissue, including lymphoreticular hyperplasia and plasma cystic macrophages. Studies in Cr-exposed individuals and laboratory animals, abnormal Cr(VI) deposition and ROS induced oxidative stress in brain tissue and motor function impairment (Travacio et al. 2000). Brain cells are much more prone to oxidative stress damages as compared to other cells due to: (1) they require aerobic respiration and use a lot of oxygen, (2) their cellular membranes contain relatively high quantities of Polly saturated fatty acids, and (3) their levels of antioxidant enzymes like GSH are quite low (Ferreira et al. 2015). They are therefore more vulnerable to the oxidation of proteins, lipids, and membrane pores, which reduces MMP and causes neuronal death (Zhao et al. 2019). For instance, exposure to Cr(VI) resulted in abnormal behaviors and symptoms such as increase in surfing and darting movements and impaired locomotion in Fish and Drosophila (Singh and Chowdhuri 2017). Evidence for developmental toxicity of Cr(VI) was found in a study on pregnant rats by Pribluda (1963). Rats given 1 mg/kg Cr demonstrated poor bone formation in their embryos. When compared to the control group, the group that received 2 mg/kg of Cr(VI) also demonstrated the lack of the sacral vertebrae (Marouani et al. 2017).

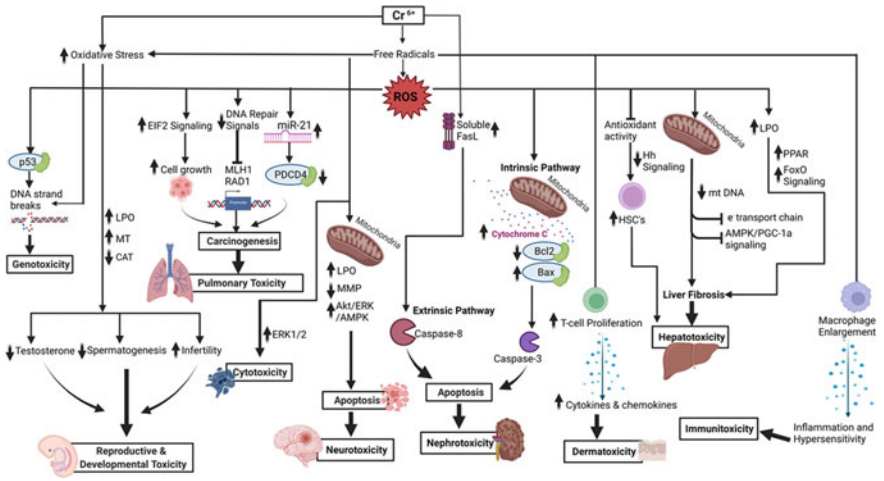

Fig. 13.3 Specific cellular responses with Cr(VI) toxicity. Adapted from Monga et al. (2022a)

13.7.2 Plants

The solubility of Cr(III) is much lower than Cr(VI), preventing its mobility in leaching into groundwater, thus affecting its bioavailability and absorption by plants (Cervantes et al. 2001). $HCrO_4^-$ and CrO_4^{2-} are the two most common forms of Cr(VI) in soils are that are quite easily absorbed by plants and travel rapidly downwards into deeper layers of soil and groundwater (Elahi et al. 2020). Cr(VI) levels above 5 mg/kg in soils and 0.5 mg/L in solution can be extremely dangerous for plant growth and metabolism (Elahi et al. 2020; Ayele and Godeto 2021). Jobby et al. (2018) have extensively listed some of the major effects of Cr(VI) toxicity in plants such as reduced uptake of nutrients, stunted growth, necrosis, chlorosis, decline levels of physiological and metabolic pathways etc. (Jobby et al. 2018). Leaves are the main organs for photosynthesis in plants; increasing Cr(VI) concentrations in soil leads to reduction in leaf area and biomass, suppression of chlorophyll production, loss of Mg^{2+} ions from chlorophyll molecules, inhibition of photosynthetic electron transport chain and thus photosynthesis failure leading to leaf necrosis and chlorosis (Stambulska et al. 2018). The oxidative stress generated in the plant cells due to Cr(VI) leads to lipid peroxidation, DNA strand breaks and chromosomal aberrations leading to cell death (Guo et al. 2021).

13.7.3 Microorganisms

Similar to its effects in plants and animals, due to requirement of Cr as an essential nutrient in trace amounts (Monga et al. 2022a); microorganisms are sensitive to both deficiency and excessive levels of Cr ions (Mishra and Bhargava 2016). HMs can have a significant effect in shaping microbial community structures in various ecosystems according to some reports (di Cesare et al. 2020). For instance, sedimentary microbes are vital for nutrient cycling, energy flow and organic matter remineralization. Under the effect of pollutants, the composition, abundance, and function of these microbial communities may change due to susceptibility and lead to decoupling of biogeochemical processes (di Cesare et al. 2020). Cr(VI) stress in the sensitive population of microorganisms disturbs their metabolism by altering their nuclei acid structure, cell membrane disruption, inhibition of enzyme activities and oxidative phosphorylation leading to LPO and osmotic imbalance (Ayangbenro and Babalola 2020). It causes cell enlargement and elongation while it inhibits cell division which is necessary for cellular growth and metabolism (Mishra and Bhargava 2016). On the other hand, due to their brief life cycles and basic genetic organization, some native microbes have evolved to modify their genetic make-up, conferring them the ability to survive in polluted environments. Bacteria has evolved several mechanisms (discussed below) such as efflux, intracellular/extracellular reduction, biosorption, extracellular binding by EPS etc. in order to tolerate toxic levels of HMs (Bruins et al. 2000; di Cesare et al. 2020).

13.8 Cr Pollution Remediation Measures and Practices

13.8.1 Wastewater Treatment

Eradication of toxic HMs such as Cr from industrial and domestic wastewater's is very essential in order to protect and maintain the standards of water streams, aquatic systems, and groundwater aquifers. Several technologies have been developed over the last decades with the goal of successful treatment of wastewater contaminated with HMs, particularly Cr. High solubility, bioavailability, and toxicity of Cr(VI) necessitates its removal from wastewater before discharged into the environment (Ukhurebor et al. 2021). More conventionally, Cr removal technologies were based on physical and chemical treatments such as chemical reduction, precipitation, membrane separation (ultrafiltration, nanofiltration, reverse osmosis, ion exchange membranes), flotation, solvent extraction, electrochemical methods (electrolysis, electro coagulation, electrodialysis) and ion-exchange (Srivastava et al. 2016; Ukhurebor et al. 2021) while the latest methods are more biotechnology based using bacteria (living and dead biomass), fungi, agro-industrial waste materials etc. that create less toxic byproducts, are sustainable and economically viable (Cuellar et al. 2022). The two main processes used in these procedures are reduction, where Cr(VI) is changed to Cr(III) at an acidic pH, and precipitation, where Cr(III) is formed at an alkaline pH. Addition of iron can reduce this two-step process into one (Mitra et al. 2017; Ukhurebor et al. 2021):

$$CrO^{-2} + 8H^{+} + 3Fe + 2 \rightarrow Cr^{+3} + 3Fe^{+3} + 4H_2O$$

According to Malaviya and Singh (2011), reduction and precipitation procedures are frequently used to remove Cr from wastewater, but they also utilize a lot of chemicals and produce too much secondary waste. On the other hand, membrane-based methods (ion exchange etc.) are better in a way that they don't produce secondary pollution but they are very expensive, consume high energy and ineffective at low Cr concentrations (Malaviya and Singh 2011; Ukhurebor et al. 2021). In a recent study, Liu et al. (2022) combined the flocculation and membrane separation processes to treat wastewater from a tannery containing Cr. They used flocculation ultrafiltration (UF) to pre-treat the wastewater before transferring the generated water directly into nanofiltration (NF) for concentration treatment. When the salt contents of the main and secondary freshwater were 200–500 mg/L and 800–1000 mg/L, respectively, the NF multistage treatment was utilised to control the freshwater recovery rate to 90%. Finally, the effluent was desalinated using electrodialysis (ED) (Liu et al. 2022). By modifying a standard polyacrylonitrile (PAN) UF membrane, Mantel et al. (2022) was able to combine UF and ion exchange into a combined filtration process. By using this technique, adsorptive dead-end filtering was used to remove particulate particles and dissolve Cr(VI) (Mantel et al. 2022). In addition to precipitation and reduction, adsorption has emerged as a cost-effective and a simpler method to treat Cr

containing wastewater. Adsorbents before were manly composed of chemical materials such as activated carbon, chitosan, zeolites etc. (Owlad et al. 2009) with diverse adsorptive abilities and majority of the functioning at low pH. Carbamoyl chitosan, a derivatized form of chitosan, has however demonstrated remarkable results for the adsorption of Cr, with an adsorption efficiency as high as 438.8 mg/g (Chauhan et al. 2012). Moreover, carbon-based nano-materials such as graphene have shown good adsorption properties in its oxidized state (Agarwal and Singh 2017). As reviewed by Singh et al. (2020) several new derivatized nano materials like Polyaniline nanorods dotted on grapheme oxide, Polypyrrole/Fe_3O_4 Nanocomposite, Phosphonium-coated (MNPs) and carbon nano anions in recent years have shown promising results for Cr removal. Additionally, carbon nanotubes have become an effective adsorbent that may be used alone or in conjunction with any metal, such as FeO. Because of the larger surface area, this combination has been found to boost the adsorptive capacity for Cr. It also has the added benefit of enabling total metal removal by easy magnetic methods (Luo et al. 2013; Singh et al. 2020).

13.8.2 Soil Remediation

In all aquatic systems, the sediment is the part where dissolved constituents and contaminants tend to gather due to scavenger representatives and adsorptive components (Peng et al. 2009). Conventional remediation techniques like in-situ capping and relocation actions were widely practiced but are now becoming unsustainable due to various problems associated with land space, budget, contaminant conveyance paths and ecological compatibility. The majority of soil treatment technologies rely on physiochemical techniques like sediment washing (which involves dissolving metal contaminants in aqueous chelating agent solutions), electro-chemical treatment (which involves separating metal cations using an electro-magnetic field), and thermal treatment of the sediment (Akcil et al. 2015). Since Cr can be absorbed into plants from the soil, plants can be utilized for phytoremediation. Phytoremediation is a green technique that utilizes plants to remove non-degradable toxic metal ions from the soil (Anju 2017). It is a better technique as compared to conventional physical and chemical methods since it does not harm the ecosystem, in-situ treatment volume can be achieved since it involves both dissolved and sorbet pollutants (Genchi et al. 2021). Cr hyperaccumulation plants, including *Spartina argentinensis, Amaranthus dubius, Convolvulus arvensis*, and others, have already been reported in the literature (Guo et al. 2021). It is suggested that the hyperaccumulator grade requirement be set at 300 g/g given the extremely low Cr concentrations in plants, both in normal (1 g/g) and metalliferous (ultramafic) soils (50 g/g). *Pycnandra acuminata* exhibits leaves with a metal content that is at least 2–3-fold better than other plants that grow in typical soils and significantly higher than the plants that grow in soil that are metalliferous (Van der Ent et al. 2013). Mangrove afforestation zones at designated locations in The Vai River watershed of Vietnam were recently advised to be employed for their phytoremediation prospects (Nguyen et al. 2020; Monga

et al. 2022a). Leeching, often referred to as soil washing, is a technique that treats contaminated soil using principles of physical separation, chemical extraction, or a combination of both. Particles made of soil differ physically from particles made of heavy metals. Physical separation therefore takes advantage of this distinction to concentrate these heavy metals into smaller amounts that may then be eliminated (Ukhurebor et al. 2021). Testing for the removal of Cr from soil using chemicals like acetic acid, ethylenediamine tetra acetic acid (EDTA), and HCl on samples of pond sludge demonstrated that the highest removal efficiency of Cr was achieved using 0.3 M of HCl with 82.69%, accompanied by EDTA at 72.52%, and the lowest efficiency was recorded by 3 M of acetic acid with 46.96%. (Abumaizar and Smith 1999). Oxalic acid (OA), citric acid (CA), and HCl had also been utilized in the elimination of Cr, with oxalic acid showing the highest potency in this regard (Sun et al. 2019b). It was concluded that while oxalic acid can be used to remediate soil for Cr, it must be careful not to leach vital minerals or reduce soil fertility (Ukhurebor et al. 2021).

13.9 Microbial Remediation Mechanisms and Technologies

Conventionally, ion-exchange, membrane filtration, and reduction-precipitation are the three most often used techniques for removing Cr(VI). However, operating these processes at a large-scale are very expensive (Cheung and Gu 2003), especially for developing countries. Due to their relatively high removal efficiency, low cost, and environmentally safe or sustainable practice, biological remediation approaches using microbial strains (bioremediation) or plant species (phytoremediation) have grown significantly in popularity as the preferred choice for chromium removal technologies (Nakkeeran et al. 2018; Lian et al. 2019; Prasad et al. 2021). Due to their incapacity to degrade, HMs can build up in the environment, causing a serious threat to human health and poisoning the food chain (Genchi et al. 2021). Thus, bioremediation has evolved as one of the safer and more effective alternatives for treating HM pollution as compared to conventional physical and chemical methods (Singh et al. 2020).

13.9.1 Bioremediation

The elimination and reduction of HMs from contaminated environments is possible with the help of the innovative technology known as bioremediation. Microbes are crucial to the bioremediation of metals. *Flavobacterium, Pseudomonas, Bacillus, Arthrobacter, Corynebacterium, Mycobacterium, Methanogens, Aspergilus niger, Rhizopus arrhizus, Azotobacter, Alcaligenes, Ganoderma applantus,* and others are among (Verma and Kuila 2019). Through bioremediation, a metal site can be rehabilitated to its prior state without compromising the ecosystems (Jobby et al. 2018).

Living organisms such as bacteria, fungi, yeast, algae, and plants have the ability to clean up after themselves, however bacteria and fungi have been demonstrated to be more proficient at it. These technologies have a number of benefits, including minimal energy requirements, low operating costs, no environmental or health risks, high efficiency, the potential for reuse, and metal recovery (Garbisu and Alkorta 2003). Metal is frequently used by microorganisms as a nutrition or energy source to meet their growth requirements (Tang et al. 2007) and metabolise these pollutants through enzymatic/or non-enzymatic mediated reactions into less toxic or harmless compounds such as CO_2 or CH_4, water and biomass (Vidali 2001; Jobby et al. 2018). Bioremediation is made of two terms: "bios" meaning life and "remediate" means to solve the issues. So 'bioremediation' refers to solving environmental issues with the use of living organisms. Bacteria, for instance can remove/accumulate/precipitate or reduce toxic pollutants into less toxic forms. Though mostly these processes need the right combination of nutrients, time, temperature, ph etc. for carrying out effective bioremediation of the contaminants. Bioremediation has emerged as a new sustainable technology for decontamination of polluted ecosystems (Nur-E-Alam et al. 2020).

13.9.2 Types of Bioremediations

There are primarily three kinds of bioremediation:

(1) **Biostimulation**: Chemicals or nutrients that activate microorganisms are used to stimulate them to start the cleanup process. Biostimulation was chosen as the treatment option in 1999 at the Ace Services Superfund Site, a chrome processing plant in Kansas (Jobby et al. 2018).
(2) **Bioaugmentation**: This procedure introduces bacteria to the surface of the contaminated area, where they are then allowed to proliferate. It is mostly used to remove soil contamination. Though Cr(VI) contaminated soils naturally contain organisms that have adapted to the environment and are therefore better bioremediators, bioaugmentation is typically not used as a method (Jobby et al. 2018).
(3) **Intrinsic bioremediation**: This technique uses the indigenous microorganisms to transform hazardous toxins into inert ones.
(4) **Mycoremediation**: This type of bioremediation uses fungus, not bacteria or other microorganisms, for remediation purposes. Effective bioremediation of soil depends on a number of parameters, including the elemental composition of the pollutant, the soil's moisture content and pH, the microbial comunities present at the contaminated site, and temperature (Asha and Sandeep 2013; Jobby et al. 2018). Here I t is essential to comprehend the precise mechanism of action for metal removal by microorganisms in order to develop an efficient microbial-based treatment approach since remediation activity is closely linked to microbial metabolism (Singh et al. 2020).

13.10 Fungal Bioremediation

Fungi can actively participate in the bioremediation of Cr(VI) due to their special ability to tolerate HM. Such fungi bioremediate Cr(VI) through a variety of processes, including biosorption, bioaccumulation, and bioreduction (Ghosh et al. 2021) (Table 13.3). These mechanisms depend on fungi genetics, metal ion and environmental factors (Hassen et al. 1998; García-Hernández et al. 2017). Shan et al. (2022) in a recent report, isolated a Cr(VI) reducing fungal strain, Fusaium proliferated S4 from polluted soils near a chemical plant in China. Additionally, they evaluated the diverse Cr(VI) removal capacities of distinct cellular components and listed the following cell components in order of strength: cytoplasmic, cellular secretions, and cell debris (Shan et al. 2022). Various fungal strains have been reported in the literature: Fusarium chlamydosporium (Sharma and Malaviya 2014); Aspergillus and Rhizopus sp. (Ahmad et al. 2005); Aspergillus flavus, Fusarium sp., Helminthosporium sp., Aspergillus niger, and Aspergillus versicolor (García-Hernández et al. 2017). According to reports, certain Aspergillus sp. are frequently utilised as biosorbents to remove and sequester Cr(VI). Galactosamines, chitin, glucan, and certain lipids and amino acids in the cytosol are polysaccharides that are significant in the fungal metabolism of Cr(VI).

13.11 Algal Bioremediation

Algae has been shown previously to prevent eutrophication in wastewaters. For bioremediation, algae utilises the mechanism of photochemical reduction (Table 13.3). Algae has potential for Cr(VI) biodegradation because it produces oxygen during photosynthesis that is used by heterotrophic bacteria to generate biomass (Ghosh et al. 2021). Algae specifically uses its secondary metabolites such as phytochelations, metallothioneins and its cell wall constituents such as glucuronic acid, alginates, and other cell wall functional groups like $-OH$, NH_2, SO_4^{2-}, $-COH$ for the biosorption of Cr(VI) ions (Elahi et al. 2020; Ghosh et al. 2021). Cr(VI) then bioaccumulates in the algal cell wall as a result of this. After 27 days of incubation period, algae including *Euglena sp., Chlorella vugaris, Spirulina sp., Spirogyra sp., Scenedesmus sp., Cladophora sp., Ceranium sp., Selenastrum sp.*, and *Nosctoc linkia* demonstrated a Cr(VI) detoxification efficacy of 97% from the culture system (Ghosh et al. 2021). I In another article, authors proposed that thylakoid membrane of Chlorella vulgaris in the presence of sodium alginate (SA) hold a capacity to reduce Cr(VI)–Cr(III) with 70% effectiveness in 4 days of incubation (Lee et al. 2017; Ghosh et al. 2021). Transgenic algae perform better than raw algae, according to more recent research. Genetic engineering can be used to improve the genes that express metal-binding proteins on algal membrane surfaces (Cheng et al. 2019).

Table 13.3 List of microorganisms (Bacteria, fungi and algae) with Cr(VI) bioremediation potential along with their mechanism of removal and optimum experimental conditions. NB = Nutrient broth; BM = Broth medium; ZMB = Zobell marine broth; LB = Luria Bertani broth; PDB = Potato Dextrose broth

Microbial strain	Source of isolation	Mechanism studied	MIC (Mg/L)	Initial Cr(VI) conc^n	Media	Optimum pH; T (°C)	Reduction ability (%)	Incubation/ contact time	References
Bacteria									
Bacillus sp. AKVCRR04	Marine sediment, Versova creek, Mumbai	Bioflocculation/ biosorption	2000	400	NB	7; 37	96.08	48 h	Monga et al. (2022b)
Pseudomonas aeruginosa AKVCRR02	Marine sediments of Versova creek, Mumbai	Bioflocculation/ biosorption	2000	400	NB	7; 37	95.15	120 h	Monga et al. (2022b)
Lactobacillus plantarum MF042018	Marine samples from Alexandrian Mediterranean Seacoast, Egypt	Bioaccumulation	100	100	Broth medium		30.2 ± 0.5%		Ameen et al. (2020)
Marinobacter hydrocarbonoclasticus	Equatorial Indian Ocean and Arabian Sea coastalwaters	Siderophore production, exopolysacharides Aerobic/anaerobic reduction	–	55.15	NB	32 ± 2 °C	88% aerobically; 89% anaerobically	5 days	Vijayaraj et al. (2019)
Enterobacter cloaceae (AK-I-MB-71a)	Marine	Exopolysaccharide sequestration		25, 50, 100			60–70		Iyer et al. (2004)

(continued)

Table 13.3 (continued)

Microbial strain	Source of isolation	Mechanism studied	MIC (Mg/L)	Initial Cr(VI) conc^{n}	Media	Optimum pH; T (°C)	Reduction ability (%)	Incubation/ contact time	References
Bacillus licheniformis	Marine samples from Tamil Nadu, India	Enzymatic reduction, extracellular surfactants interactions	1500	20	ZMB		100	24–72 h	Kavitha et al. (2011)
Bacillus sp. MTCC 5514	Marine samples from Tamil Nadu, India	Enzymatic reduction, extracellular surfactants interactions	2000	20–2000	ZMB		100	24–96 h	Gnanamani et al. (2010)
Exiguobacterium Indicom MW1	Marine water of Paradip fort, Odisha		1500	100	AMM and M9	8; 35	91% in AMM; 92% in M9	192 h	Mohapatra et al. (2017)
Brevibacillus laterosporus	Marine water of Paradip fort, Odisha		2100	100		8; 35	92	120 h	Mohapatra et al. (2017)
Bacillus subtilis SHBB	Sediment		1000	100		7; 37; 4% NaCl	98	72 h	Swapna et al. (2016)
Pseudochrobactrum sp. B5	Marine	Bioreduction	2000	1000	LB		100	96 h	Ge et al. (2013)
Proteus sp. H24	Marine	Bioreduction	1500	1000	LB		100	144 h	Ge et al. (2013)
Klebsiella pneumoniae	Soil and water samples from phillipines	Biosorption	550	100	LB	7; 30	87	7 days	Bennett et al. (2013)

(continued)

Table 13.3 (continued)

Microbial strain	Source of isolation	Mechanism studied	MIC (Mg/L)	Initial Cr(VI) conc^n	Media	Optimum pH; T (°C)	Reduction ability (%)	Incubation/ contact time	References
Bacillus firmus	Soil and water samples from Phillipines	Biosorption	550	100	LB	7; 30	96	7 days	Bennett et al. (2013)
Mycobacterium sp.	Soil and water samples from Phillipines	Biosorption	750	100	LB	7; 30	91	7 days	Bennett et al. (2013)
Bacillus Amyloliquefaciens	Sediment	Biosorption				7	82.10	60 min	Ramachandran et al. (2022)
Pseudomonas chengduensis PPSS-4	Marine sediment of Paradip fort, Odisha	Biosorption by EPS, biofilm	2000	10	LB	6; 37; 4% NaCl	72.29	4 h	Priyadarshanee and Das (2021)
Halomonas sp. TA04	Marine sediments, southern Italy	Bioreduction (DPC method)	4.0 mM	0.5 mM	YEPG-NaCl	7–8, 28	81.5	24 h	Focardi et al. (2012)
Sporocarcina saromensis M52	Sediments from intertidal zone in Xiamen, China	Bioreduction (DPC method)	500	100	Modified LB	7–8.5; 35	100	24 h	Ran et al. (2016)
Sphingopyxis macrogoltabida SUK2c	Marine water of Sukinda valley, Odisha	Biosorption and extracellular reduction		4	NB	1; 30	55%	2 h	Prabhakaran et al. (2019)

(continued)

Table 13.3 (continued)

Microbial strain	Source of isolation	Mechanism studied	MIC (Mg/L)	Initial Cr(VI) conc^{n}	Media	Optimum pH; T (°C)	Reduction ability (%)	Incubation/ contact time	References
Acinetobacter calcoaceticus	Marine samples	Aerobic reduction	500	100	LB	7; 30	67.14% at pH 7; 70.53 at pH 8	24 h	Mishra et al. (2010)
Bacillus sphaericus OT4b31	Marine samples	–		30		4; 30	25% with living biomass; 44.5% with dead biomass	24 h	Velásquez and Dussan (2009)
Exiguobacterium sp. GS1	Water	–		8	TSB	7–8; 35–40	91	8 h	
Fungi									
Penicillium janthinellum P1 living biomass	Marine sediments	Biosorption	–	250	PDB	1; 30	87	8	Chen et al. (2019)
Penicillium janthinellum P1 dead biomass	Marine sediments	Biosorption	–	100	PDB	1; 30	58.6	12	Chen et al. (2019)
Aspergillus sydowii	Marine sediments from Mandovi estuary	Reduction	1000	300	Liquid broth	5; 28	26	7 days	Lotlikar et al. (2018)
Aspergillus flavus	Marine seaweeed associated	Bioaccumulation	100	100	Potato dextrose (PDB)	RT	25%	15 days	Vala et al. (2004)

(continued)

Table 13.3 (continued)

Microbial strain	Source of isolation	Mechanism studied	MIC (Mg/L)	Initial Cr(VI) conc^{n}	Media	Optimum pH; T (°C)	Reduction ability (%)	Incubation/ contact time	References
Aspergillus niger	Marine seaweed associated	Bioaccumulation	100	100	Potato dextrose	RT	25%	15 days	Vala et al. (2004)
Trichoderma viride	Seawater from Egypt	Biosorption and bioaccumulation	1000	125	–	6	98%	45 min	El-Kansas and El-Taher et al. (2009)
Aspergillus flavus	Soil and water samples from Phillipines	Bioreduction	600	150	PDB	2; 30	98	7 days	Bennett et al. (2013)
Aspergillus sp.	Soil and water samples from Phillipines	Bioreduction	600	150	PDB	2; 30	99	7 days	Bennett et al. (2013)
Aspergillus niger	Soil and water samples from Phillipines	Bioreduction	600	150	PDB	2; 30	98	7 days	Bennett et al. (2013)
Algae									
P. tricornutum CCY0033 (microalgae)	North Sea beach, Netherlands	Biosorption to EPS	1 mg/L	1 mg/L	MDV	23	35	3 days	Hedayathkhah et al. (2018)
N. pelliculosa CCMP543/ CCY0399 (microalgae)	Oyster pond, Masacheusetts, USA	Biosorption to EPS	1 mg/L	1 mg/L	MDV	23	32	3 days	Hedayathkhah et al. (2018)
Dunaliella salina (Microalgae)	Sambhar salt lake, Rajasthan, India	Biosorption	–	25		8.6	66.4	120 h	Kaushik and Raza (2019)

13.12 Bacterial Bioremediation

Due to its toxicity, Cr contaminated soil comprises a lower microbial population as compared to the soil non-contaminated by Cr (Viti et al. 2003). The bacterial species that are present are the ones that are able to tolerate/resist chromium toxicity. As per Gadd (1992), "tolerance" is the "capacity of a microbes to survive metal toxicity by means of basic components and/or ecological modification of toxicities," whilst "resistance" is the "ability of microbes to survive toxic effects of metal exposure through a detoxifying process designed in direct reaction to the metal species involved." Various researches have reported bacteria with the ability to bioremediate Cr(VI) and investigated an array of mechanisms that these bacteria adopt for their own survival (Banerjee et al. 2019; Baldiris et al. 2018; Li et al. 2021; Elahi et al. 2022; John and Rajan 2022; Kookhaee et al. 2022; Yakasai et al. 2022). These bacteria could use single or a group of these strategies to counteract the toxicity of Cr(VI) (Bharagava and Mishra 2018). Most commonly these mechanisms include bioreduction/biotransformation/enzymatic reduction, biosorption, bioaccumulation, efflux, precipitation, cytosolic binding etc. (Banerjee et al. 2019), though microbes differ in their potential to utilize these strategies. Cr(VI) bioreduction and biotransformation have been extensively studied in bacterial system as compared to other microorganisms (Elahi et al. 2022) (Table 13.3). Numerous tolerance mechanisms for bacteria to cope with the HMs have been postulated. Examples of fundamental strategies used by bacteria to survive and thrive in metal-stressed environments include active efflux, intracellular sequestration, enzymatic transformation, and oxidation/reduction of harmful metal ions (Zeng et al. 2020). Kathiravan et al. (2011) isolated Bacillus sp. from tannery effluent contaminated site and studied bioremediation process in batch and continuous operations. Nine strains that could withstand chromium up to 700 mg/L were reported by Park et al. (2000). Camargo et al. (2003) reported the optimal pH of 7–9 and temperature of 30 °C for maximum chromium reduction activity by *Bacillus sp.* Megharaj et al. (2003) examined the potential for *Arthrobacter sp.* and *Bacillus sp.* to reduce Cr(VI) and discovered that *Arthrobacter sp.* could do so up to 50 g/ml while Bacillus sp. could only do so to the extent of 20 g/ml. Cr resistant bacterial train *Bacillus cereus S-6* was isolated from effluents of tannery with the ability to reduce Cr(VI) to less toxic Cr(III). The cytosol and membrane preparations of the bacteria could reduce upto 67 and 43% of Cr(VI) within 24 h of incubation. Turick et al. (1996) reported various bacteria from different soil types for Cr(VI) reduction potential. Cheung and Gu (2003) studied the reduction of Cr(VI) to less toxic Cr(III) using *Pseudomonas putida PRS2000* for which the chromate reductase activity was instituted to be linked with soluble protein rather than membrane fraction. According to Costa (2003), bacterial strains *CrT-11, CrT-12, Brevebacterium sp. CrT-13, CrT-14* isolated from tannery effluents could tolerate upto 40 mg/ml of K_2CrO_4 on nutrient agar.

13.13 Molecular Mechanisms for Bacterial Bioremediation of Cr(VI)

13.13.1 Adsorption by Functional Groups on the Surface of the Cell

The biosorption of the metal is mostly caused by the cell wall of bacteria because it is the first to come into contact with the metal ions (Wang and Chen 2009; Gutiérrez-Corona et al. 2016). This interaction mainly depends upon the functional groups present on the bacterial cell wall and the physiochemical conditions of the medium (Karthik et al. 2017). Bacterial cell surface comprises various functional groups like hydroxyl (−OH), carboxyl (RCOOH), carbonyl (−COOH), amide (CO–NH), sulfonate, phosphonate, phosphodiester etc. that form larger compounds like lipopolysaccharides (LPS) and peptidoglycans (Karthik et al. 2017). They interact with the metal ions through a chemical bond. Maximum Cr(VI) binding efficiency occurs at acidic pH because of the electrostatic attraction between the protonated (H^+) bacterial surface and Cr(VI) (as $HCrO_4^-$). However, with increase in pH, the $HCrO_4^-$ ions convert to CrO_4^{2-} and $Cr_2O_7^{2-}$ ions. With an increase in OH^- ions in the solution, the adsorption efficiency of Cr(VI) drops at basic pH (Yaashikaa et al. 2019; Pushkar et al. 2021). Next, the adsorbed Cr(VI) either bioprecipitates on the microbial cellular surface or is biotransformed into Cr(III) which is either enzymatically catalyzed by a chromate reductase or occurs spontaneously (Thatheyus and Ramya 2016; Jobby et al. 2018).

Under the LPS layer in Gram negative bacteria is a thin coating of peptidoglycan, and these two layers interact with HMs on the cell surface in significant ways. However, the cell membrane of Gram positive bacteria only has a substantial coating of peptidoglycan (Fang et al. 2018). Under Cr(VI) stress, gram-negative bacteria secrete more LPS, which acts as a metal chelator and facilitates Cr's attachment to the cell surface (Kiliç et al. 2010). In a research study between *E. coli* and *Staphylococcus epidermidis*, Quiton et al. (2018) found that Gram negative *E. coli* bacteria had a stronger biosorption capacity due to the negative charge of LPS structures on the cell wall. Nonetheless, in case of Gram positive bacteria, the presence of a high amounts of anionic polymers in the cell wall primarily made up of peptidoglycan teichoic or teichuronic acids, helped them perform Cr biosorption. Several cell surface ligands on Gram positive cell wall such as phosphoryl, carbonyl (COO−) etc. had a strong affinity towards metal ions such as Cr(VI) (Pushkar et al. 2021). Various analytical techniques, such as Fourier transformed infrared spectroscopy (FTIR) and scanning/transmission electron microscopy with energy X-ray spectroscopy (SEM-EDX/TEM-EDX), have been used to discover the functional groups on the cell walls of the bacteria participating in Cr(VI) metal-microbial interaction as well as the process of Cr(VI) adsorption, absorption, and reduction (Batool et al. 2014; Gutiérrez-Corona et al. 2016; Elahi et al. 2022; Li et al. 2021). EPS for instance, are functional high molecular weight organic polymers found on bacterial cell surfaces

in either capsular or secreted forms (Kumar et al. 2019). They typically possess functional groups like phosphate, carboxyl, hydroxyl, amide etc. that are responsible for chelation and detoxification of metal ions (Mangwani et al. 2016). Li et al. (2021) isolated a novel bacterium *Stenotrophomonas acidaminiphila* 4-1that secreted EPS under Cr(VI) stress. They were the binding sites of adsorption of Cr(VI) on surface of cells as depicted by TEM. The adsorption was mostly mediated by electrostatic or complexing bonds as reported in various studies (Hussein et al. 2019). In a separate report, FTIR identified the amine, hydroxyl, and carboxyl chemical groups involved in Cr(VI) interaction in the cell walls of the bacteria Streptomyces werraensis LD22 (Latha et al. 2015).

FTIR analysis of untreated [without Cr(VI)] cells can reveal the possible functional groups involved in metal-microbe interaction (Elahi et al. 2022). However, under Cr(VI) stress significant shifts were observed in peaks of the FTIR spectra of the treated cells (Karthik et al. 2017; Banerjee et al. 2019; Elahi et al. 2022), validating the involvement of functional groups in Cr(VI) binding on bacterial cellular surface. Shifts in the FTIR peaks mostly involved amino, carboxyl, nitrogen, peptide (oxygen) that are all mostly C and O based (Banerjee et al. 2019).

In context to resistance to Cr(VI), a wider group of Gram negative bacteria have been documented in comparison to gram positive bacteria. Bacillus sp. Predominates among the Gram positive bacteria known to be resistant to Cr(VI) (Shaw and Dussan 2018; Pushkar et al. 2021). This observation was also reported by Satarupa and Amal (2010), in their study on chromate mine seepage water that showed prevalence of Gram negative bacteria. Despite the fact that Gram positive and negative bacteria differ from one another due to variations in the composition of their cell walls, they nevertheless have the same gene for chromium resistance (Fig. 13.4). This is mostly due to the selection of Cr resistant bacteria over time and horizontal gene transfer among bacterial groups (Pushkar et al. 2021). This was also corroborated by another study by Patra et al. (2010). They showed >99% similarity between the test Gram positive bacterial strains namely *Arthrobacter aurescens* strain MM10, *Bacillus atrophaeus* strain MM20, and *Rhodococcus erythropolis* strain MM30 with the already documented Gram Positive *E. Coli* and *Shigella* sp. (Patra et al. 2010). Gram positive involves hydroxyl groups present on their surface during Cr(VI) biosorption at pH 1–4 (Prabhakaran and Subramanian 2017). Gram negative bacteria, on the other hand, can reduce Cr(VI) extracellularly due ton the presence of LPS, lipoproteins and phospholipids present in their outer membrane (Pushkar et al. 2021) (Fig. 13.4). According to Shaw and Dussan, lineages I and II can be used to group together the efflux pumps and regulators of both Gram-negative and Gram-positive bacteria. Aligning the amino acid sequences of these clusters revealed the presence of several amino acid signatures and conserved regions in the respective lineage (Shaw and Dussan 2018; Pushkar et al. 2021). The development of microbial methods for the reduction, elimination, and retrieval of metals from aqueous solution depends on our ability to understand how bacteria acquire metals. In the case of non-living biomass, the only mechanism is metal binding to cell walls and external surfaces that is independent of metabolism. Adsorption techniques including ionic, chemical, and physical adsorption are mostly used in metabolism-independent uptake (Ahluwalia

and Goyal 2007). One of the responses and a self-defense strategy against Cr toxicity is the clumping of cells, which is caused when like charges on the bacterial surface tend to neutralise in the presence of Cr (Karthik et al. 2017). Insoluble Cr(III), a colloid form of Cr hydroxide that can form from Cr(VI), can also be absorbed on the surface of bacterial cells. This alters the total protein composition of the cell surface (Asatiani et al. 2004). Wang and Cui (2019) reported the formation of protrusions on the cell surface of the bacteria after Cr(VI) treatment (520 mg/L) which was due to absorption of Cr(III) and the changes it caused to the protein composition on the cellular surface. Additionally, due to their similar structure, sulfate transporters present on the surface of the cells also aids in the transport of chromate ions (CrO_4^2). Thus Cr(VI) competitively inhibits sulfate uptake, which is compensated by increasing the uptake of cysteine-containing molecules by cell (Gang et al. 2019). Thus, the bacterial cell surface plays a crucial role in Cr(VI) resistance and removal.

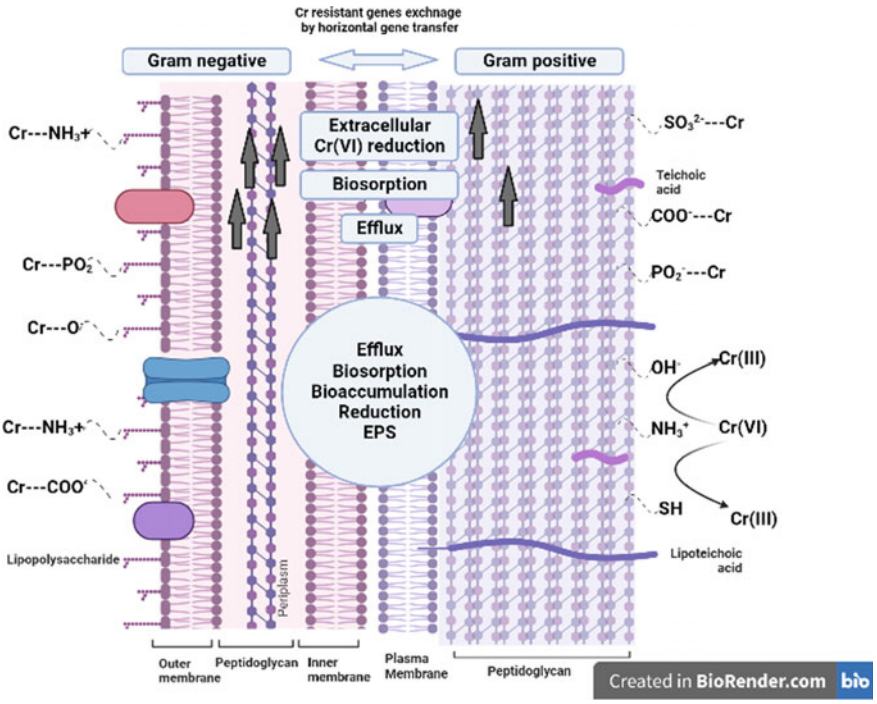

Fig. 13.4 A comparative diagram to depict Cr(VI) response of gram positive and gram negative bacteria

13.13.2 Extracellular Precipitation/Reduction: Role of Extracellular Biopolymers

Some microbial species have been observed to create extracellular biopolymers that facilitate flocculation (Monga et al. 2022b; Ayanbenro et al. 2019). Bioflocculation or biosorption is the process of any compound being absorbed by biological materials through metabolically independent or dependent absorption processes (Fourest and Roux 1992). Flocculants or surfactants are a class a amphipathic molecules that are eco friendly and aid in the HM removal from contaminated soil and sediments (Banerjee et al. 2015). They are also quite efficient at low HM concentrations because of which they are quite ideal for the treatment of effluents and wastewaters (Lin and Harichund 2011). Furthermore, in order to achieve a high bioflocculant yield at low costs and high flocculation activity efficiency, bioprospecting of strains with such capabilities is indispensable (Nwodo and Okoh 2013; Monga et al. 2022b). Numerous heavy-metal removal bacterial bioflocculants have been studied because they are non-toxic, environmentally safe, and biodegradable (Lin and Harichund 2011). Numerous bacteria, including *Bacillus, Pseudomonas, Acinetobacter*, and *Arthrobacter*, are well-known for producing bioflocculants (Banerjee et al. 2015). Though fewer studies on the biosorption of Cr(VI) with a bioflocculant have been reported. In a recent study conducted, a very effective bioflocculant, NaBsp, was successfully developed against kaolin particles utilising a tolerant Bacillus sp. strain with a high flocculant efficacy of $97.69 \pm 0.61\%$ and Fe^{3+} as a cofactor. On the surface of the bioflocculant, hydroxyl, carboxyl, and amine groups may have led to strong interactions with heavy metals. Cr(VI) has an adsorption capacity of 384.6 mg g^{-1} (Hua et al. 2021). According to a another recent study, the bioengineered strain F2-exoY-O recovered Cr(VI) more effectively than the wild strain because it produced more polysaccharide in its EPSs (Pi et al. 2021). An efficient and long-lasting method of removing chromium from contaminated habitats was provided via chelation between functional groups on EPS and Cr(VI), with a little conversion of Cr(VI) into Cr(III) on EPSs (Monga et al. 2022b). The bioflocculant synthesis of Bacillus sp. AKVCRR04 and AKVCRR05, which were isolated from the surface sediments of Mumbai's polluted Versova Creek, was also examined using the Kaolin clay assay. By the 5th day of incubation, the isolates displayed substantial flocculation activity (89.75 and 89.88%, respectively). Additionally, the growth profile of the isolates and the final pH in relation to the flocculation activity assay showed that the synthesis of bioflocculants peaked either in the late stationary phase or during the stationary phase (Monga et al. 2022b).

As mentioned above, for various molecules present in the extracellular environment, cell surface acts as the first line of defence and also transmits signals inside the cell. This is important in deciding the fate of the molecule as it enters the cellular environment (Pushkar et al. 2021). The EPS production is believed to be crucial protective strategy for bacteria to thrive and survive in environments polluted with HMs (Zeng et al. 2020). The EPS matrix mainly consists of negatively charged functional groups that aids in chelating metal ions and avoiding the direct contact of cells

and the toxic pollutants (Wu et al. 2019; Zeng et al. 2020; Li et al. 2021). When Cr(VI) interacts with protonated biomass in an acidic pH environment, it is reduced to Cr(III) in the aqueous phase or in the biomass (Park et al. 2006). Using analytical methods including XPS, XAS, and SEM-EDX/TEM-EDX, this process has been established to occur in both bacteria and fungus (Park et al. 2007). Nevertheless, numerous studies have also shown that some bacterial species, including Cyanobacteria (Ozturk and Aslim 2008), Azotobacter (Joshi and Juwarkar 2009), Arthrobacter (Shuhong et al. 2014), Bacillus (Dogan et al. 2015), as well as fungal species, including Trichoderma and Schwanniomyces, produced EPS with the ability to remove Cr(VI) by an adsorption coupled reduction mechanism. Metal ions can be bioabsorbed by bacteria that naturally produce an EPS coating, keeping them from interfering with important biological components. These bacteria's EPS coating may offer sites where metal cations can be attached (Scott and Palmer 1990; Bruins et al. 2000). Several bacterial species, including Klebsiella aerogenes, Pseudomonas putida, and Arthrobacter viscosus, exhibit the capacity to bind metals extracellularly (Bruins et al. 2000).

Metal chelation by EPS is an interesting property that makes it important in the field of Cr(VI) remediation (Chug et al. 2016; Saba et al. 2019a, b). There are three different forms of EPS: soluble (S-EPS), loosely bound (L-EPS), and tightly bound (T-EPS). Briefly, the protein and the polysaccharide content of EPS act as electron donors in Cr(VI) reduction. The N and O groups on the LB and TB LBS transfer electron for this reduction. Cr(III) then immobilises onto the negatively charged groups on the EPS surface such as −OH, −ROOH (Pushkar et al. 2021). For non-enzymatic reduction, FTIR analysis revealed the role of −OH groups of polysaccharides and −NH groups of membrane proteins (Srinath et al. 2002). In *Bacillus sp.* MRP-3, functional groups of T-EPS played important role in Cr(VI) adsorption in comparison to LB-EPS in Cr(VI)/Cr(III) attachment (Shao et al. 2019). According to findings from a different study, Pseudochrobactrum saccharolyticum LY10 increases T-EPS expression when Cr(VI) levels increase (Long et al. 2019). As a cellular response mechanism, it has been observed that in activated sludge, bacteria produce more of the −N component of S-EPS in the presence of Cr(VI)/Cr(III) (Liu et al. 2020). Thus, EPS aids bacteria in removing chromium in a number of ways. The method of bioremediation of chromium and other heavy metals can be further improved with future study concentrating on the stimulation of EPS synthesis by bacterial cells (Pushkar et al. 2021).

13.13.3 Accumulation of Cr(VI) and Cr(III) on Cell Envelope: Biosorption and Bioaccumulation

Microorganisms adopts a variety of strategies and mechanisms to be able to survive in heavy metal polluted environment. Biosorption, bioaccumulation and biotransformation are frequently used by microbes to detoxify Cr(VI) to comparatively less

harmful forms (Jobby et al. 2016). These techniques form a crucial part of bioremediation process. The superiority of biobased remediation methods over conventional physical and chemical methods are now well known (Jobby et al. 2018). There are two ways by which microorganisms incorporate metals into their cellular processes, first one is known as "passive uptake", more popularly known as "biosorption". This is a metabolism-independent uptake of metals that can take place in both living and dead microbial cell biomass. The other one is "active uptake" which involves energy and metabolism for the metal transport and can occur only in living biomass. These two modes of metal transport combined together are called "bioaccumulation" (Wang and Chen 2009; Gutiérrez-Corona et al. 2016). Biosorption being a passive process varies among different bacteria and depends largely on the cell wall composition, its physicochemical characteristics and that of the surrounding medium (Bharagava and Mishra 2018; Jobby et al. 2018). The physicochemical interaction between the metal pollutants and the surface of dead or live bacterial biomass that leads to adsorption of heavy metals on bacterial surface. It's a natural response of bacteria that is non-specific in nature and involves a formation of a chemical bond (Pushkar et al. 2021). Bioaccumulation on the other hand, utilizes the respiration energy of the metabolic pathway of bacteria to accumulate Cr(VI) within the cell wall (Wang et al. 1989; Jobby et al. 2018).

In first stage of biosorption, the physical adsorption may take place by forming a chemical bond, ion-exchange, adsorption, or precipitation on the surface of the bacteria. Depending on the type of bacterium and its environment, these physical adsorption processes of biosorption may function independently or in concert. It can also be accomplished by live and non-living bacterial cells because it is independent of bacterial metabolism (Jarosławiecka and Piotrowska-Seget 2014). Bioaccumulation is the second stage of biosorption; it is a slower procedure that involves active Cr transport into the bacterial cell that is regulated by metabolism. After bioaccumulation, Cr is released intracellularly by a number of pathways, such as localization to particular organelles, association with metallothionein, accumulation as a particulate HM, extracellular precipitation, or complexation (Srinath et al. 2002; Bharagava and Mishra 2018; Elahi and Rehman 2019a, b). According to Ma et al. (2019a, b) chromium is biosorbed either as Cr(VI) ions or as its reduced form, Cr(III) ions. Based on numerous biosorption studies on various bacteria that have been published in the literature, it can be assumed that biosorption is influenced by factors such as pH, temperature, biomass dosage, initial Cr concentration, contact time, etc. (Jobby et al. 2018). Cheng et al. (2021) used single-factor studies to understand the impact of Cr(VI) and RSM based on Box-Behnken design (BBD) to study the biosorption behavior of strain *Shewanella putrefaciens.* They could achieve Cr(VI) bio-removal with an efficiency of up to 85.68% under the optimized conditions of 16.57 h of contact time, a pH of 8, and 0.42 g/L of biomass (Cheng et al. 2021). The ability of *B. paraconglomeratum* ER41 to decrease Cr(VI) was demonstrated by Harboul et al. (2022). It could grow, totally biosorb, and bioreduce 100 mg/L of Cr(VI) in 48 h at pH 8 and 30 °C and demonstrated strong resistance to Cr(VI) (700 mg/L). The factors pH, temperature, chromium concentration, and contact time all play a significant role in the Cr(VI) reduction process. Additionally, the composition of bacteria's cell

walls varies depending on the growth conditions and medium type. As a result, the same bacteria isolated from several sites exhibited diverse biosorption rates (Rizvi et al. 2020; El-Naggar et al. 2020). According to the research data, biosorption is a successful chromium bioremediation technique. The process of heavy metal bioremediation will benefit tremendously from additional study aimed at improving the biosorption capacity of microorganisms (Pushkar et al. 2021). Pulimi et al. (2012) employed statistical design tools such as Plackett-Burman design, Central Composite design etc. in order to optimise physical and chemical variables for Cr(VI) biosorption and biotransformation by strain *Acinetobacter junii* VITSUKMW2. A maximum of 99.95% of Cr(VI) removal was achieved in 12 h under optimised parameters of initial Cr(VI) levels (54 mg/L). El-Naggar et al. (2020) investigated biosorption based removal of Cr(VI) using *Pseudomonas* sp. NEWG-2. A statistical model based on RSM (response surface methodology) of face-centered central composite design was applied to the growth studies of P. alcaliphila NEWG-2 (FCCD). According to their FCCD test findings, the bacteria could proliferate and remove of 96.60% of 200 mg/L of Cr(VI) in the presence of yeast extract (5.6 g/l), glucose (4.9 g/l), and pH 7 for the duration of the 48 h incubation period. Furthermore, monolayer chromium ion adsorption on homogeneous sites on the bacterial surface was modelled as following both the pseudo-first-order model and the intraparticle diffusion model, demonstrating that the Langmuir model well explains chromium ion biosorption by *B. paraconglomeratum* (Harboul et al. 2022). In another report, the biomass of the metal tolerant *B. amyloliquefaciens isolated from a marine soil was optimized for biosorptions conditions.* Acidic pH and long contact times inhibited the effectiveness of biosorption. At pH 7 and 60 min of contact, the highest biosorption was 82.10% and 80.12%, respectively (Ramachandran et al. 2022). The authors further reported that the biosorption efficiency when declined at acidic pH and longer contact times. They identified the adsorption mechanism as monolayer and a favourable adsorption as indicated from the Freundlich model.

According to Srinath et al. (2002), *B. circulans, B. megaterium,* and *B. coagulans* were outstanding strains that were able to adsorb 34.5 mg, 32.0 mg and 39.9 mg Cr of dry weight respectively. The biosorption ability of the living and dead biomass of *Bacillus. coagulans* and *Bacillus. megaterium* was also evaluated by the authors, and they discovered that the dead cells were more efficient. *B. coagulans* dead cells absorbed 39.9 mg Cr g^{-1} dry weight while living cells only adsorbed 23.8 mg Cr g^{-1} dry weight. In the case of *B. megaterium*, similar outcomes were attained (15.7 and 30.7 mg Cr g^{-1} dry weight by living and dead cells, respectively). Inactive/dead cells perform better than active/living cells because they are more vulnerable to the harmful effects of metal ions, which can cause cell death during the metal removal process (Jobby et al. 2018). In comparison to other bioremediation methods, biosorption processes is reported to have various advantages because the metal is binding to the various multifunctional uniformly distributed binding sites on the cell surface; additional nutrients or chemicals are not required; simple and low cost to implement with high efficiency and re usability of the biosorbent. Additionally, the potential for metal recovery has drawn much research into the use of diverse biomass, including bacteria, fungus, and microalgae, for the removal of HMs, particularly Cr(VI) (Ayele

and Godeto 2021). The following are additional benefits and drawbacks of non-living biomass (Modak et al. 1996; Ahluwalia and Goyal 2007):

- **Advantages**
  - Because dead biomass is growth independent, toxicity of cells and physiological constraints are not a limitation. So the problems related to nutritional requirements for optimised growth, aseptic conditions and disposal of by-products are not present. A wider range of operating conditions are possible in terms of pH, temperature, initial metal concentration etc.
  - Biomass in this case can be easily procured from several industries, biomass is essentially a waste for fermentation sectors.
  - Non-living biomass also behaves as an ion exchange, so the entire process is fast and efficient because of high metal loading capacity and desorption (recovery) abilities.
- **Disadvantages**

  Another drawback of employing dead biomass is that metal desorption is required before the biosorbent can be used again due to early saturation of the metal interaction sites.
  Because the cells are not metabolically active, any potential for biological process improvement like genetic engineering is limited.
  Also there is no biological control over the characteristic of the biosorbent or in altering the metal ionic state.

13.13.4 Biotransformation/Bioreduction

"Bioreduction" is a potential method for decreasing the level of Cr(VI) contamination. It involves conversion of Cr(VI) into Cr(III) using living systems (Wang et al. 1989; Jobby et al. 2018). Cr(VI) is 10–100 times more harmful than Cr(III) since it is a known carcinogen, a strong oxidant, and has a higher bioavailability in ecosystems (Costa 2003; Chang et al. 2019). The mechanism of biotransformation and reduction of Cr(VI) to lesser toxic Cr(III) has been thoroughly investigated in bacteria as compared to fungi, yeasts or actinomycetes (Elahi et al. 2022). As discussed previously, microbes are compelled to adopt a variety of strategies for their own survival under chromium stress. Cr tolerance/resistance and reduction are two independent phenomena employed by microbes in order to combat Cr(VI) stress. Strains that are able to resist Cr(VI) may not necessarily have the molecular capacity to reduce it also (Elahi et al. 2022). Bacterial strains with the ability to reduce Cr(VI) are popularly known as chromium-reducing bacteria (CRB) (Elahi and Rehman 2019b; Elahi et al. 2022). Various CRBs have been isolated from Cr(VI) contaminated soils (Karthik et al. 2017; Chang et al. 2019; Li et al. 2020, 2021), tannery sewage waste water (Elahi et al. 2022), and industrial effluents (Baldiris et al. 2018). Due cell membrane's impermeability to Cr(III) complexes, biotransformation mechanism of

conversion of Cr(VI)–Cr(III) has been regarded as a potential solution for treatment of polluted wastes and reduce Cr toxicity in the environment (Karthik et al. 2017; Chang et al. 2019). Contrary to some metal ions in wastewater, such as Cu^{2+}, Cd^{2+}, Pb^{2+}, and Ni^{2+}, which can only be eliminated by biosorption, certain microorganisms can also detoxify Cr(VI) by reducing it to the less dangerous Cr(III) (Karthik et al. 2017; Chang et al. 2019). This method offers better prospects as a bioremediation process for Cr(VI) detoxification since Cr(VI) can be completely removed by microbial reluctant so after a certain operating time but still, the adsorption sites on these biosorbents are limited in number and prone to saturation (Vijayaraghavan and Yun 2008; Jobby et al. 2018; Chang et al. 2019). Until recently majority of studies had focused on Cr(VI) tolerance levels and basic bioreduction capabilities. Relatively, little is known with regards to the Cr binding sites involved in biosorption, intercellular accumulation and extracellular precipitation (Karthik et al. 2017). Moreover, these studies were mainly dependent on an indirect method of Cr(VI) elimination and did not consider Cr(III) compounds in their bioreduction evaluation. The validity of this methodology may be questioned in future (Baldiris et al. 2018). Because both reduction and adsorption can be used to eliminate Cr(VI), a basic examination of Cr(VI) elimination can scarcely confirm the true Cr(VI) reducing activity, and the valence state of the reduced Cr must be determined directly (Karthik et al. 2017; Baldiris et al. 2018). Cr(VI) tolerant Pseudomonas sp. DC-B3 isolated from a contaminated mine-soil demonstrated a strong ability to reduce Cr(VI) to less harmful (III) without any exogenous electron donor at pH 2. With increasing Cr(VI) concentration, both the reduction capacity and reduction rate increased linearly, achieving a reduction capacity of 32.0 mg Cr(VI)/g over a 75 h period at an initial concentration of 135.0 mg/L (Chang et al. 2019).

Following steps are involved in intracellular Cr(VI) reduction (Fig. 13.5):

1. **Cr(VI) biosorption on the surface of the cell**—As indicated in the previous sections, Cr(VI) ions form chemical bonds with bacteria's cell surface by making use of functional groups such amide, alkane, and amines.
2. **Cr(VI) transport**—Because there are no transport channels for Cr(VI) ions to enter the cells, they use SO_4^{2-} and phosphate channels instead due to their structural similarities (Mala et al. 2015; Elahi et al. 2022; Wang et al. 2017; Pushkar et al. 2021). Since Cr(VI) and SO_4^{2-} ions share a significant degree of similarity, Cr(VI) can pass through cellular membranes conveniently due to active sulphate transporters (Cervantes et al. 2001; Ayele and Godeto 2021). Once inside the cell, Cr(VI) is reduced to Cr(III), which is ultimately released from the cell (explained later). Cr(VI) intracellular reduction promotes chromate accumulation in the extracellular environment and ensures a low cytosolic concentration (Joutney et al. 2014).
3. **Cr(VI) reduction**—(1) Intracellular enzymatic reduction: The intracellular levels of Cr(VI) is reduced to insoluble Cr(III) by cytoplasmic molecules enzymatically or non-enzymatically (Thatoi et al. 2014; Gutiérrez-Corona et al. 2016; Singh et al. 2020); (2) Extracellular reduction by secreted enzymes: The cell benefits from this process because it saves energy by not having to carry Cr(VI)

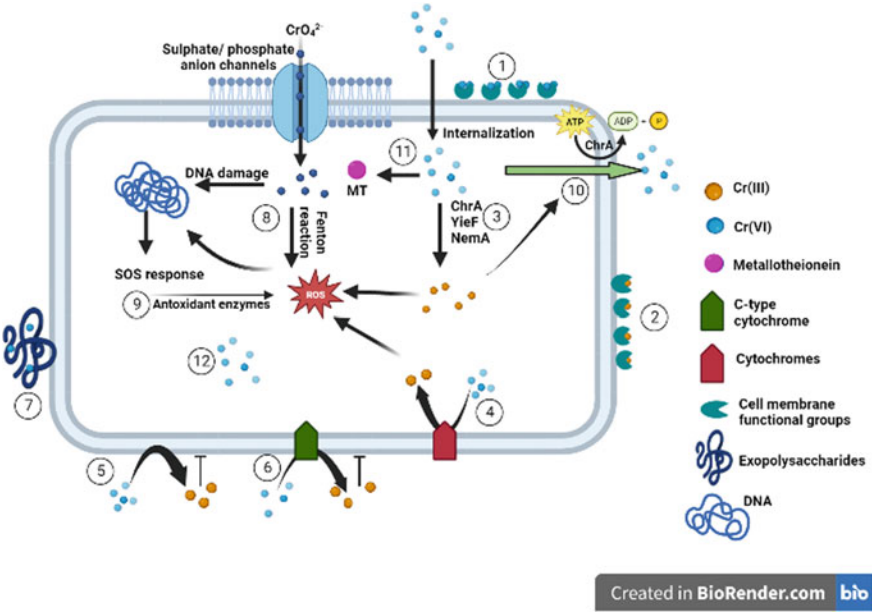

Fig. 13.5 Schematic diagram to illustrate various mechanisms employed by bacteria in response to Cr(VI) stress: (1) Biosorption of Cr(VI); (2) Biosorption of Cr(III); (3) Intracellular enzymatic reduction of Cr(VI)–Cr(III); (4) Reduction of Cr(VI)–Cr(III) by cytochrome in cytoplasm; (5) Cr(VI) reduction by cell membrane; (6) Cr(VI) reduction by c-type cytochrome under anaerobic conditions; (7) Cr(VI) entrapment by EPS; (8) Fenton reaction and SOS cellular response due to Cr(VI) stress with subsequent generation of ROS leading to cell damage; (9) Activation of antioxidants in as a defense response to ROS; (10) energy dependent efflux of Cr(VI) from cell; (11) complexation of Cr(VI) with metallotheioneins; (12) Bioaccumulation. Adapted from Pushkar et al. (2021)

into the cell and subsequently Cr(III) out of it. For instance, this mechanism for gram negative bacteria is predominated by NADH-dehydrogenase pathway under aerobic conditions. Since this an energy-intensive process, these enzymes are secreted only under Cr(VI) stress (Cheung and Gu 2007; Ayele and Godeto 2021). (3) Non- enzymatic extracellular reduction.

4. **Cr(VI) bioaccumulation**—The Cr(VI) that is bioreduced to Cr(III), then gets bioaccumulated in the cytoplasm (Karthik et al. 2017; Pushkar et al. 2021).

Several factors (directly or indirectly) determine the reduction potential of a bacterial strain including pH, initial concentration of chromate, presence of electron donors as well as co-existence of other metal ions in the samples (Mala et al. 2015; Singh et al. 2020; Elahi et al. 2022). The majority of the microorganisms identified have not been shown to be capable of reducing Cr concentrations by more than 60%. Additionally, the majority of the isolates perform poorly at high Cr loads (Singh et al. 2020). Under chromate stress, essential compounds produced by the bacteria during carbon oxidation for cellular growth gets utilized as electron donors for Cr(VI) reduction

(Karthik et al. 2017; Pushkar et al. 2021). In the presence of oxygen, the reduction process involves the generation of various transient toxic ions such as Cr(IV), Cr(V) and ROS that leads to oxidative stress and cellular damage (Bharagava and Mishra 2018; Elahi et al. 2022). Presence of high levels of Cr(VI) prevents normal cellular proliferation as the bacterial energy is mostly spent in reducing the Cr(VI) ions to lesser toxic forms (Parameswari et al. 2009). Bacteria in log-phase performed better Cr(VI) reduction than in any other phase mostly due to high number of active cells with maximum enzymatic activity (Ikegami et al. 2020). But the time taken form bioreduction would increase with Cr(VI) ion concentration which could be due to saturation of the enzyme (Jeyasingh and Philip 2005). Factors such as loss of microorganisms, toxicity to microorganisms, and uneven microbial growth at high Cr(VI) concentrations hamper the commercial applications of bioremediation. MIT (Microbial Immobilization Technology) is a popular research area today since has the potential to address the drawbacks of bioremediation technology (Jiang et al. 2022). Immobilization of microbial cultures has been shown to increase the stability and efficacy of organisms and to produce greater Cr adsorption/reduction than free organisms. For the purpose of immobilising Cr(VI) reducing or sorbing bacterial cells, matrices such as agar, agarose, polyethylene glycol, polyacrylamide, etc. have been investigated (Hora and Shetty 2016).

Several antioxidant enzymes such as GSH, GSSH and CAT are synthesized as a defensive mechanism to transform harmful ROS into safe compounds, thereby preventing metal generated ROS from altering the reduced environment within the cell (Elahi et al. 2022; Gu et al. 2020). Antioxidant profiling of *Bacillus cereus* b-525 k with or without 2 mM Cr(VI) stress depicted an increase in expression of all AOXs especially peroxidase (POX) with a 99% increase (Elahi et al. 2022). Because they can be produced in response to a variety of environmental stresses, including those caused by metal ions (Cd, Al, Zn, and Cu), drought, water, and gamma radiation, peroxidases are also classified as stress enzymes (Khalid and Jin 2013). The findings of Elahi et al. (2022) were well in line with those of Suthar et al. (2014), who also indicated that Cr(VI) stress causes a significant rise in all antioxidant enzymes. Elahi and Rehman (2019a) have previously emphasized on the importance of glutathione and non-protein thiols in reducing metal generated ROS toxicity. In reducing ROS toxicity, glutathione and non-protein thiols are crucial (Elahi and Rehman 2019a). Bacillithiol (BSH), a thiol molecule present in most Bacillus species, is likely involved in maintaining cellular redox balance and contributes to microbial resistance to several antibiotics, according to a 2009 study by Newton et al. (Elahi et al. 2022). Bacilli thiol (BSH) have been previously reported to in most Bacillus sp. Playing crucial roles in ROS toxicity and resistance to antibiotics (Newton et al. 2009). It was seen that *Pseudomonas brassicacearum* LZ-4 had potential to co-bioremediate naphthalene and chromate. Here, naphthalene was the sole carbon source that tremendously elevated the reduction capacity of the bacteria from 25 to 96.2%. Authors reported the upregulation of catabolic gene NahG gene in the presence of naphthalene that encodes for salicylate hydroxylase along with FAD as cofactor. FAD could be acting as the electron acceptor from NADH for subsequent Cr(VI) reduction (Huang et al. 2017).

13.13.4.1 Enzymatic Reduction

Chromate reduction in several microbial species depends upon the utilisation of Cr(VI) as a terminal acceptor catalysed by chromate reductases enzyme in their respiratory processes converting Cr(VI)–Cr(III) (Lovley and Philip 1994; Singh et al. 2020). Pseudomonas sp. was one of the earliest reported bacteria with Cr(VI) bioreduction abilities under anaerobic conditions (Singh et al. 2020). Later, E. coli was reported to biotransform Cr(VI)–Cr(III) aerobically (Shen and Wang 1993). There are two different kinds of Cr reductases: membrane-associated and intracellular, depending on where the reduction takes place. Numerous investigations have confirmed the existence of intracellular and membrane linked Cr reductase enzyme activities in the cellular membranes, cytoplasmic fractions and cell supernatants (Ilias et al. 2011). For the enzymatic Cr(VI) reduction mechanism in bacteria, either soluble cytosolic proteins or insoluble cell membrane enzymes are responsible for the catalysis. It has been widely documented that a variety of bacterial taxa, including *Pseudomonas, Bacillus*, and *Arthrobacter*, can reduce Cr(VI) enzymatically in either an aerobic or anaerobic environment, or even both (Ramírez-Díaz et al. 2008; Thatoi et al. 2014; Viti et al. 2014; Gutiérrez-Corona et al. 2016).

Indigenous species are frequently employed in the bioreduction process since they don't need extra nutrients to survive and proliferate when used in scale-up applications. This is a practical method that is affordable, secure, and generates no extra byproducts (secondary pollution). After the quick initial identification with 16S rRNA gene sequencing, the second stage in bioremediation studies is study of genomics to identify the enzymes that are involved in the reduction process (Baldiris et al. 2018). More recent reports have also determined the Cr(VI) reduction mechanism mediated by reductases present in microbial culture supernatant. Many chromate reductases such as ChrR, YieF, NemA and LpDH catalyse the bioreduction reaction by utilising electron donors like NAD(P)H, mediating the transfer of electrons to Cr(VI) and at the same time generating ROS (Reactive oxygen species) in two-step process known as Class I ("tight") and Class II ("semi-tight") (Thatoi et al. 2014). In comparison to membrane-associated chromate reductase enzymes, reductases that are soluble are better suited for protein engineering as they suit the environmental circumstances of contaminated sites. This makes them suitable for the development of biocatalysts for bioremediation (Thatoi et al. 2014; Baldiris et al. 2018). High extracellular chromate activity was reported for *Bacillus amyloliquefaciens* under optimised conditions by Rath et al. (2014), Gutiérrez-Corona et al. (2016). In a co-remediation study of pollutants chromate and pentachlorophenol, chromate reductase activity was reported in cytosolic fraction (48%) followed by culture supernatant (39.7%) and cell debris (12.3%) (Tripathi and Garg 2013; Gutiérrez-Corona et al. 2016). Baldiris et al. (2018) demonstrated the cytosolic nature of the chromate reductase responsible for chromate reduction in strain S. maltophilia. Their report was contradictory to Blake et al. (1993) who reported a membrane associated reductase responsible for chromate reduction in the same bacteria. Another study on *Bacillus sp.* TCL have reported the constitutive expression of membrane associated chromate

reductase and loosely bound EPS as sites for Cr(VI) reduction or Cr(III) immobilisation respectively (Banerjee et al. 2019). Authors correlated the enhanced activity by membrane fractions with increased expression of membrane-bound reductases under chromate stress. The shifts in FTIR peaks to amino, carboxyl and nitrogen and oxygen of peptide bonds further suggested a protein (chromate reductase) mediated metal binding on cell surface under chromate stress. Numerous studies showed that EPSs and cytoplasmic extracts both contributed to the decrease of Cr(VI) by *Bacillus sp.* (Pan et al. 2014; Das et al. 2014; Li et al. 2019a, b).

The most crucial component for overcoming the difficulties in biodegradation and bioremediation of pollutants is the isolation of microorganisms from contaminated locations (Tang et al. 2021). Since the majority of bioreduction reactions are mediated by enzymes, variations in temperature and pH may have considerable effects on the rate of ionisation, the folding of proteins, and the activity of enzymes (Zhang and Li 2011). Although several research have focused on identifying the Cr(VI) reduction sites of various bacterial strains, the number of microorganisms and the intricate mechanisms involved in Cr(VI) reduction make this effort far still from sufficient. Li et al. (2019a, b) determined the Cr(VI) reduction sites of Cr tolerant *Bacillus sp.* M6 by comparing reduction rates in permeable cells (without phospholipid bilayer) and untreated cells as control. The permeable cells exhibited higher Cr(VI) reduction ability than intact cells, which implicated the involvement of cytoplasm of bacillus sp. M6 in the reduction process. Their results were in line with previous reports on *Planococcus maritimus* VITP21 and *Bacillus sp.* G1DM22 by Sangeetha et al. (2012) and Desai et al. (2008a, b) respectively. In both the studies, Tritonx-100 treatment was used to dissolve the phospholipid bilayer of the cell membranes, that subsequently released the reductive substances from the cytoplasm resulting in higher Cr(VI) reduction rate by the respective bacteria. In addition to cytoplasmic extracts, cell envelope extract also showed higher reduction rate when compared to untreated cells (Li et al. 2019a, b). Cell membrane and cytoplasm were both involved in Cr(VI) reduction and their potentials were similar. Cell membrane reductase involved the sulfate channels that transported Cr(VI) into the cytoplasm due to structural similarity of chromate and sulfate anion; and also reduced Cr(VI)–Cr(III) during the transport at the cell envelope (Li et al. 2019a, b). Interestingly, *Providencia sp.* reduced Cr(VI) mostly in the cell cytoplasm (Thacker et al. 2006), but *Thermus scotoductus* SA-01 reduced Cr(VI) primarily in the cell membrane (Opperman and Van Heerden 2007). Researchers have shown that Cr(VI) tolerance and reduction are two distinct mechanisms. Latter is detoxification of Cr(VI) and is usually not plasmid-related (Cervantes et al. 2001; Baldiris et al. 2018). The mechanism of Cr(VI) reduction varies among microbial strains depending upon their bio-geochemical activities and nutrient utilization patterns (Megharaj et al. 2003). According to Dhal et al. (2013) three most common reduction patterns are-(1) Aerobic reduction involving soluble chromate reductases that utilizes NADP or NADPH as cofactors (Park et al. 2000); (2) Anaerobic reduction that uses Cr (VI) as terminal electron acceptor in the electron transport cycle (Tebo and Obraztsova 1998) and (3) reductions brought about by chemical processes involving substances located within or extracellularly, such

as glutathione, amino acids, nucleotides, vitamins, carbohydrates, or organic acids (Myers et al. 2000).

Aerobic Reduction of Cr(VI)

When oxygen is present, the bacterial Cr(VI) reduction process transforms into a two- or three-step process, primarily starting with the reduction of Cr(VI) species to the transient intermediates Cr(V) and/or Cr(IV) before being further reduced to Cr(III), which is known to be a thermodynamically stable end product. Here in this reduction procedure, the electron donors are NADH, NADPH and those from the endogenous reserves. The Cr(VI) reductase ChrR mentioned above reduces C(VI) to form Cr(V) followed by Cr(III) involves one-electron and a two-electron shuttle respectively (Lovley 1993). On the other hand, the enzyme YieF is unique in that it catalyses the direct reduction of Cr(VI)–Cr(III) through a four-electron transfer, where three electrons are used to reduce Cr(VI) and the fourth is transferred to oxygen (Ackerley et al. 2004). In the cytoplasm, typically aerobic reduction occurs. Aerobic Cr(VI) reduction is carried out by soluble enzymes such as flavoprotein, dehydrogenase, NADH-dependent nitroreductase, and azoreductase (Chai et al. 2019; Dong et al. 2018). *Pseudomonas sp.* GT7 was tested for four electron donors for Cr(VI) reduction (Zhang et al. 2016a, b). NADH and NADPH enhanced the Cr(VI) reduction by the soluble fraction of GT7. While NADH and NADPH portrayed similar stimulation levels; the effects were stronger as compared to citrate and succinate. Their results were in agreement with previous reports on the cytoplasmic fractions of others bacterial strains such as *Pseudomonas sp.* G1DM21 (Desai et al. 2008a, b) and T. scotoductus SA-01 (Opperman et al. 2008). Authors further suggested the to explore electron donors that are cheaper such as glucose and fructose as the ones used in their study were expensive (Zhang et al. 2016a, b).

The process of Cr(VI) resistance in *Ps. aeruginosa* has been attributed to increased or decreased efflux of Cr (VI) ions through the membrane (Nies and Silver 1995). A close relative of *Ps. Synxantha* with ability to reduce Cr (VI) was reported by Gopalan and Veeraman (1994). In contrast to the previously stated bacteria, which use reductases soluble in the cell cytoplasm, *Ps. Maltophilia* O-2 and *B. megaterium* TKW3 were shown to use reductases linked with membrane cell fractions. Several studies have reported the purification of Cr (VI) reductases from *Pseudomonads.* Also, Ishibashi et al. (1990), partially purified soluble Cr (VI) reductases from *Ps. Putida* PRS2000. Similar study was reported by Suzuki et al. (1992) from *Ps. ambigua* G1. Another soluble Cr (VI) reductase called ChrR was purified by Park et al. (2000) from *Ps. putida MK1* strain. On the basis of the amino acid sequence of purified ChrR protein, gene coding ChrR, *chrR* was recognized by Park et al. (2001). They also presented an open reading frame (ORF) *yieF* having high homology to *chrR*, ChrR showing most optimum reduction at 35 °C. ChrR was further acknowledged as a dimeric flavoprotein catalysing the reduction of Cr(VI) primarily at 70 °C (Ackerley et al. 2004). *Oceanobacillus oncorhynchi* W4 relied on biological reduction as the method of Cr(VI) removal than biosorption and the

process was enhanced by addition of electron donors like glycerine followed by NADH, glucose and lactate (Zeng et al. 2019). A model strain of dissimilatory metal reduction bacteria, *Shewanella oneidensis* MR-1, has the ability to reduce Cr(VI)–Cr(III) either aerobically or anaerobically (Gang et al. 2019). This strain is reported to utilise endogenous electron donors such as NADH under aerobic conditions. When conditions are anaerobic, electrons are acquired from donors like membrane-associated cytochromes involved in the electron transport system (Gang et al. 2019). Supply of exogenous i.e. use of external donors such as glucose, lactose, sodium acetate, glycerol have also been reported to enhance the Cr(VI) reduction abilities of bacteria (Pushkar et al. 2021). Glycerol was reported to be an efficient electron donor for Cr(VI) reduction in *Bacillus sp.* M6 by Li et al. (2019a, b). However, under anoxic conditions, lactate acts as a spectacular electron donor for reduction (Huang et al. 2019). Furthermore, ChrT protein decreases Cr(VI) via using NAD(P)H, with a preference for NADPH > NADH > non-NAD(P)H (Gu et al. 2020). Although E. coli FACU displayed a decreased level of NADH (Mohamed et al. 2020). In both aerobic and anaerobic environments, Gram negative *Ps. aeruginosa, Serratia marescens, Alcaligenes faecal*, and *Klebsiella oxytoca* reduce Cr(VI) when Fe(II) and Fe(III) are present (Bansal et al. 2019). Humic acid or Anthraquinone-2,6-disulfonate (AQDS) improved the ability of *Aeromonas hydrophila* ATCC 7966 to reduce Cr(VI). As evidenced by the MtrC deleted mutant's inability to respond to AQDS dosage, the respiratory circuit played an important role in HM reductions (Huang et al. 2019). Thus, it concluded that NADPH, carbon sources, $K_2Cr_2O_7$ and K_2HPO_4 positively impacted the Cr reductase enzyme activity while it was negatively affected in the presence of NaCl, nitrogen sources, temperature and Ni (Banerjee et al. 2019; Ma et al. 2019a, b). As per several reports, after the translocation of Cr(VI) into the cell, bioreduction of Cr(VI)–Cr(III) can be depicted as following reactions: (Suzuki et al. 1992; Pushkar et al. 2021).

$$\mathrm{Cr(VI)} + 1e^{-1} = \mathrm{Cr(V)} \tag{13.3}$$

$$\mathrm{Cr(V)} + 2e^{-1} = \mathrm{Cr(III)} \tag{13.4}$$

Overall bio reduction of Cr(VI) to insoluble Cr(III) hydroxide reaction can be shown.

as:

$$CrO_4^{2-} + 8H^+ + 3e^{-1} = \mathrm{Cr(III)} + 4H_2O \tag{13.5}$$

$$\mathrm{Cr(III)} + 4H_2O = Cr(OH)_3 + 3H^+ + H_2O \tag{13.6}$$

Anaerobic Reduction of Cr(VI)

The abundance of anaerobes with Cr(VI) reducing abilities offers excellent potential for in situ bioremediation of contaminated sediments. This only needs an additional supply of nutrients and some modifications to the existing physical environment in order to achieve the desired results (Romanenko and Koren'Kov 1977). When oxygen is absent, Cr(VI) acts as a terminal electron acceptor in the respiratory chain for a wide range of electron donors such as proteins, fats, carbohydrates, hydrogen, and NAD(P)H (Cheung and Gu 2007). The cytochrome families (like cyt b and c) were recurrently shown to be implicated in the enzymatic anaerobic Cr(VI) reduction. In anaerobic reduction process, the electrons generated by ubiquinone reduce cyt c (via cyt b) that subsequently gets oxidised to reduce Cr(VI)–Cr(III) extracellularly (Gang et al. 2019). Cr(III) then remains attached to the cell surface bound to various functional groups or is released in the surrounding environment. SRB have been extensively studied for Cr(VI) reduction. A number of Cr(VI) reducing anaerobes have identified including *B. Cereus, Ps. aeruginosa B. subtilis, Ps. ambigua, Ps. fluorescens, Micrococcus roseus, Desulfovibrio desulfuricans and D. vulgaris* (Cheung and Gu 2007). *Desulfovibrio vulgaris* was found to be involving soluble c3 cyt for Cr(VI) reduction (Turick et al. 1996). The process of Cr(VI) reduction under anaerobic situation was reported to be the result of both soluble and membrane-linked enzymes. Equation (13.5) below shows the total Cr(VI) reduction under anaerobic conditions using glucose as a carbon source. In an aqueous solution, the Cr(VI) is changed into the insoluble Cr(III) hydroxide. Other powerful electron donors can replace glucose, which makes the reduction process easier (Singh et al. 2011a).

$$C_6H_{12}O_6 + 8CrO_4^2 + 14H_2O + 3e^{-1} = Cr(OH)_3 + 10OH^- + 6CHO^- \quad (13.6)$$

13.13.4.2 Non-enzymatic Reduction

The non-enzymatic pathway for Cr(VI) reduction is carried out by chemical pathways in association with microbial metabolic compounds present in intra/extracellularly such as amino acids, sugars, antioxidants or nucleotides (Cervantes et al. 2001; Dhal et al. 2013; Gutiérrez-Corona et al. 2016). For instance, ascorbate can reduce Cr(VI). Also, riboflavin derivatives FAD and FMN are important coenzymes that can reduce chromate (Cervantes et al. 2001). *Microbacterium sp.* CR-07 bacterial supernatant was tested to reduce Cr(VI) which turned out to be was unaffected in the presence of 1% SDS solution, hot water, or pH value, showing that reaction was non-enzymatic. But glutathione was found in the supernatant in addition to the absence of reducing sugar showing that the reduction was caused by glutathione (Liu et al. 2012). Extracellular EPS caused highest Cr(VI) reduction rate in *Pseudochrobactrum saccharolyticum* LY10 (Long et al. 2019). Also, the microbial biomass in the form of other metal ion pollutants such as Fe(II) or H_2S, or organic molecules such as intracellular thiols or EPS can be utilized for non-enzymatic Cr(VI) reduction pathways

(Dwisandi et al. 2021). Moreover, Fe(II) and H_2S are the anaerobic byproducts of iron and sulfate reducing bacteria that can effectively reduce Cr(VI) individually or together under certain circumstances (Gutiérrez-Corona et al. 2016; Dwisandi et al. 2021). In *Pseudomonas stutzeri* KC, direct Cr(VI) reduction has been shown by means of siderophore pyridine-2,6-bis (thiocarboxylic acid) (pdtc) that could effectively reduce 86% of Cr(VI). The by-products of pdtc hydrolysis also reduce Cr(VI) (Zawadzka et al. 2007; Gutiérrez-Corona et al. 2016).

13.13.5 Transmembrane Efflux of Chromate

When Cr(VI) enters the cytoplasm, its interactions at the molecular level and how Cr exposure leads to cellular apoptosis, mutagenicity and carcinogenicity via oxidative stress pathways, DNA aberrations and epigenetic modifications have been extensively reviewed (Monga et al. 2022a). In order to overcome the stress, certain bacteria have evolved an active efflux mechanism as part of their cellular metabolic functions to expel harmful Cr ions into the periplasm or extracellular environment. Overexpression of these proteins thus is one of the ways of circumventing the Cr(VI) (Saba et al. 2019a, b; Mushtaq et al. 2022). Additionally, these efflux pumps are also used by bacteria to carry out other cellular functions such as in maintaining cell homeostasis, acquiring resistance to antibiotics, heavy metals, and salts, and surviving in harsh environments (Cánovas et al. 2003; Pal et al. 2020). Efflux of Cr(VI) has been documented as one of the key resistance mechanisms in various bacteria (Mushtaq et al. 2022) which is mostly conferred by ChrA protein (Ramírez-Díaz et al. 2008; Dong et al. 2018; Pushkar et al. 2021). ChrA proteins were first identified from *P. aeruginosa* and *Cupriavidus metallidurans* in relation to the efflux mechanisms. Afterwards, many of them were identified based on genome sequence analysis and grouped into a large Chromate ion transporter (CHR) family (Díaz-Pérez et al. 2007; Baaziz et al. 2017). They were further subdivided on the basis of protein lengths-short chain CHR (180 aa long) and long chain CHR (400 aa long). The several transmembrane regions of ChrA protein can be encoded by genes present on plasmid or chromosomes (Baaziz et al. 2017).

In *Pseudomonas aeruginosa*, ChrA is encoded by plasmids pUM505 (Cervantes et al. 1990; Ramírez-Díaz et al. 2008), comprises of 416 amino acid sequence and a structural configuration of 13 transmembrane segments (TMS) (Jiménez-Mejía et al. 2006; Ramírez-Díaz et al. 2008). It performs as an chemiosmotic pump to efflux Cr(VI) out of the cytoplasm with a proton motive force (Mushtaq et al. 2022). The efflux mechanism in Pseudomonas PAO1 was linked to NADH oxidation and ChrA had a Km of 0.12 mM Cr(VI), a Vmax of 0.5 nmol Cr(VI)/min per mg of protein. ChrA gene is usually found on plasmids or sometimes on chromosomes along with other genes such as ChrB, chrC, chrE, chrF in some bacterial species (Viti et al. 2014; Mushtaq et al. 2022). ChrA protein generates hydrogen ions leading to an electrochemical proton gradient across the cell membrane that expels the Cr(VI) from the cytoplasm (He et al. 2018). ChrC is involved in decreasing oxidative stress, whereas

ChrB is a regulator of Cr(VI) detection. Contrarily, ChrE has a role in facilitating the breakdown of some chromate-glutathione complexes (Viti et al. 2014; Mushtaq et al. 2022). The ChrB gene has a favourable regulatory effect by making the ChrAB protein more capable of metabolising chromate than the ChrA protein is, despite the fact that the ChrB protein cannot transport chromate from cells (He et al. 2018; Chen and Tian 2021). *Shewanella oneidensis* strain deleted of ChrA gene (genes belonging to large family of chromate ion transporters) showed lesser resistance to Cr(VI) than its wild type strain (Baaziz et al. 2017). Expression of ChrA in E.coli made the bacteria capable of resisting Cr(VI) stress and growing in the presence of high Cr(VI) concentrations. This has been reported in literature previously on plasmid encoded ChrA of *Shewanella sp.* and for multiple ChrA of *Burkholderia xenovorans* LB400 (Acosta-Navarrete et al. 2014; Baaziz et al. 2017). The pARI180 plasmid DNA carrying the respective gene was transformed into E. coli DH5 α strain that made the bacteria Cr(VI) resistant, but after the plasmid was lost E. Coli lost its resistance and became sensitive to Cr(VI) (Dhakephalkar et al. 1996; Chen and Tian 2021). Efflux of Cr(VI) can occur together with other harmful molecules. Many of the Cr resistant bacteria reported are also tetracycline resistant because both of them are transported of the cell using active efflux pumps (Pushkar et al. 2021). A Cr(VI) tolerant *Bacillus* strain TCL could effectively transport Cr(VI) and ethidium bromide (EtBr) out of the cell in order to reduce the intracellular stress (Banerjee et al. 2019; Pushkar et al. 2021). Additionally, the efflux mechanism is concentration dependent reaction since it is driven by an energy-dependent chemiosmotic homeostasis (Shaw and Dussan 2018; Pushkar et al. 2021).

13.14 Challenges in Developing Cr Bioremediation Technology

- Microbial remediation of Cr(VI) has been a subject of research for several decades now, and tremendous progress has been made so far. But still several questions needs answers especially in context of molecular cellular responses in the presence of the metal and their use in designing Cr bioremediation from the environment. For instance, *Ps. aeruginosa* PA01 has shown the involvement of oprE (responsible for outer membrane expression), rmlA (for cell LPS expression) and ftsK (cytoplasm) in tolerance to Cr (Rivera et al. 2008). But the roles of these genes are not yet documented for Cr resistance in detail. Similarly, other important genes with Cr reduction abilities but less explored are ChrT and YieF (Gu et al. 2020). Furthermore, as compared to gram negative, not many gram-positive bacteria has been reported with Cr bioremediation. There exists a clear gap in knowledge of the differences in the mechanisms that Gram positive and negative bacteria use for Cr resistance (Shaw and Dussan 2018).

- As the Cr concentrations increased, the rates of Cr(VI) elimination and reductions dropped, according to past researches on Cr(VI) bioremediation. This results from the strained metabolic pathways and impaired biological functions of the cells under severe Cr stress (Pan et al. 2014; Akkurt et al. 2022). At 200 and 300 mg/L Cr(VI) concentrations, *Bacillus sp.* CRB-B1 eliminated 86.15 and 43.1% of Cr(VI) respectively, although the reducing activity was impaired at concentrations higher than 300 ml/L. (Tan et al. 2020). Similar observations were reported by Huang et al. (2021) where *Sporosarcina saromensis* W5 strain which a novel facultative anaerobe, showed gradually decreased removal efficiency with increasing Cr(VI) levels. *Cellulosimicrobium sp.* isolated from leather industry wastewater could efficiently remove Cr(VI) up to 100 ml/L in 96 h. However, at higher concentrations of 200 and 300 mg/L the reduction ratio reduced drastically after the same amount of time (Bharagava and Mishra 2018).
- Due to lack of proper regulations, mixing of industrial wastes further complicates the problem. Varying pH affects the normal microbial growth cycle and makes the maintenance of an active and functional microbial population a challenge. In addition, the metabolic byproducts also may form complexes with the metal ions that may further complicate the desorption processes (Singh et al. 2020). Due to these complications researchers are now opting for non-living biomass, although research continues on re-usage and proper disposal methods for fully loaded adsorbents (Babangida et al. 2021).
- Biostimulation was suggested as a modification to stimulate the living biomass during bioremediation (Pradhan et al. 2017) by adding electron donors such as acetate, lactate etc. While their efficiency in Biostimulation also depended on the indigenous microbial community structure and physicochemical properties of the site; the continuous supply of nutrients was a challenge. Several reducing agents such as SO_2, H_2S, metallic Fe etc. that showed promising results in Biostimulation also created secondary pollution (Babangida et al. 2021).
- It has been emphasized in literature that HM stress will trigger bacterial EPS formation because EPSs act as the first defense of bacterial cell, preventing metals from the outer environment from interacting with essential cellular components. The potential of EPS to remove HMs from polluted environments has been comprehensively documented in the literature, with a primary focus on its biotechnological potential (Zeng et al. 2020). However, knowledge about the effects of HMs on EPS production as well as the correlation between EPS production and HM resistance in bacteria is still limited, particularly for exposure to different metals.
- The vulnerability of microorganisms to other toxins and environmental stressors present at the treatment site is one of the main bottlenecks in the bioremediation process. The majority of bioremediation research focuses on isolating Cr(VI) resistant bacteria and evaluating their bioremediation effectiveness in controlled lab settings. Therefore, future study must concentrate on the utilisation of microorganisms that can remove chromium from the actual polluted locations (Pushkar et al. 2021).

13.15 Strategies to Develop Cr Bioremediation Technology

13.15.1 Microbial Immobilization Technology (MIT)

In order to overcome issues in bioremediation treatment such as loss of microorganisms, loss of metabolic activity and toxicity at higher Cr concentrations and uneven microbial growth cycles can be overcome by MIT by chemically or physically confining the microbial cells or other biocatalysts in a specific area in the system and increase the microbial metabolism active for a longer time duration (Kathiravan et al. 2010; Jiang et al. 2022). Several carrier types has been devised over the years such as inorganic carriers (biochar, activated charcoal, diatomite etc.), organic carriers (alginate, agar, chitosan etc.), composite carriers (combination of polyvinyl alcohol and sodium alginate), and new carriers (modified carrier materials, nano materials) (Jiang et al. 2022). Biochar is an emerging material due to its large specific area, rich pore structure and functional groups for efficient absorption of microorganisms (Lehman and Joseph 2015). For instance, Zhu et al. (2021) compared the efficiencies of free (SRB6-2-1) and immobilized SRB IBXM700 using wheat straw biochar to treat Cr(VI) polluted wastewater. IBXM700 had a maximum removal efficiency of Cr(VI) of 286.54 mg g^{-1}, which was 166.3 and 30.8 mg g^{-1} greater than free SRB6-2-1 and XM700, respectively (Zhu et al. 2021; Jiang et al. 2022). Li et al. (2020) applied different formulations in the immobilization of strains *Bacillus cereus* D and *Bacillus cereus* 332 to compare the efficiencies of Cr(VI) reduction. The strongest reduction was achieved when sodium alginate (SA) was used to immobilise *B. cereus* D (66.9%) in 120 h. However, the immobilised beads of *B. cereus* 332 using SA with diatomite achieved a higher reduction rate of 88.9% in 72 h. Notably, the diatomite increased the hardness of the immobilised beads as compared to beads made with only SA that were not very hard and easily broke (Li et al. 2020). A similar study with SA was previously carried out by Samuel et al. (2013) to immobilise Acinetobacter johnsonii, E. coli, and B. subtilis for the removal of Cr(VI) from sewage water. The maximal Cr(VI) adsorption capacity (657 mg g^{-1}) was demonstrated by bacteria immobilised in the reactor using SA. The clearance rate of Cr (VI) after five adsorption and desorption tests was 74.22%. Also researchers frequently modify their composition and create a composite carrier to complement each other in order to further improve the effectiveness of bioremediation and circumvent the limitations with inorganic and organic biosorbent in a hostile environment in the actual treatment process. For instance, carbon nanotubes and SA were employed as a composite biosorbent for immobilisation of *Shewanella oneidensis* MR-1. They observed that the beads added with carbon nanotubes enhanced the Cr(VI) reduction by four times as compared to free/unfixed cells. The stability and reusability of the micro beads were both significantly enhanced by the inclusion of carbon nanotubes (Yan et al. 2013). More recently, in order to obtain a specific performance new carrier can be modified for the number of oxygen-containing functional sites, surface area, pore structure etc. to further improve the adsorption performance and immobilisation (Huang et al. 2015; Jiang et al. 2022). Modified biochar carrier materials has been recently reported using

Iron (Fe) and Zn (Jiang et al. 2022). The electrostatic interactions with the positively charged biochar enhanced the chemical adsorption capabilities of biochar, thereby improving the contact probability of microorganisms with Cr(VI) (Sun et al. 2019c). In order to devise a sustainable bioremediation technology, the recovery and regeneration of immobilized microorganisms and the carrier while removing Cr(VI) is crucial to avoid secondary pollution (Jiang et al. 2022). Researchers have tried using magnetically modified materials as immobilisation carriers and found excellent stability and reusability (Wang et al. 2021; He et al. 2020). Commercial technologies based on MIT approaches are few. AMT-BIOCLAIMTM is a commercially available product that contains immobilised *B. subtilis* cells on polyethyleneimine and glutaraldehyde. BioFIX is yet another method that has been developed. It uses a variety of biomasses like Sphagnum peat moss, algae, yeast, bacteria, and/or aquatic flora bound to a high density polysulfone. Elution cycles of more than 100 are achievable (Wang and Chen 2009; Singh et al. 2020).

13.15.2 Genetic Engineering

Most researches have focused on isolating indigenous/wild bacteria from contaminated sites for their potential use in the bioremediation processes as they are already adapted to complex environmental conditions. However, selective binding of metals and ability to remove them from polluted environments is lacking in these wild bacteria (Singh et al. 2011b; Ayangbenro and Babalola 2020). Now, it is widely accepted that molecular biology and genetic engineering of indigenous strains has a better potential application in designing bacteria for remediation tasks. They have been successfully demonstrated to have better remediative abilities, selective removal and metal binding capacity than wild type strains for degradation of pollutants under defined conditions (Singh et al. 2011b; Akkurt et al. 2022). Al Hasin et al. (2010) reported a genetically manipulated methanotroph *Methylococcus capsulatus* that could bioremediation Cr(VI) over a wide range of concentrations. In another study, Valls et al. (2000) in order to boost its affinity to metal ions, manipulated a mouse MT protein to be expressed onto the surface of the cell of a HM tolerant *Ralstonia eutropha* CH34 which was already adapted to survive in HM polluted soils. MTs are low-molecular-weight proteins that aid in detoxify HMs, protects cells from the oxidative damage by scavenging free radicals due to their high think content. Two human MT genes, MT2A and MT3, were recently cloned into E. Coli Jm109 by Akkurt et al. (2022). Due to the expression of the MT gene, which improved the reduction of Cr(VI) compared to wild type, these transformed strains were able to capture Cr ions inside the cells in addition to surface binding.

13.15.3 Enhancement of Bioremediation

13.15.3.1 Microbial Consortium for Bioremediation

Actual heavy metal polluted areas have much different environmental conditions as compared to laboratory conditions, thus the applications of pure cultures kept in sterile conditions in a laboratory are limited in the real world. A consortium of bacteria is more likely to sustain and survive in field conditions due to their competitiveness among each other (Tang et al. 2021). A mixed bacterial consortium attached to phosphate minerals and alginate improved the bioreduction efficiency of Cr(VI) and subsequent removal of Cr(III) (Ma et al. 2019a, b). Benazir et al. (2010) immobilised a consortium of *B. subtilis, Ps. aeruginosa* and *S. cerevisiae* using SA. The consortium demonstrated improved remediation efficiency and decreased Cr(VI) from initial concentration of 770–5.2–5.7 mg/L in the tannery effluent as when compared to individual cultures. In another study, Cr(VI) reducing bacteria *Morganella morganii* STB5 demonstrated improved reduction efficiencies of 70.41 and 68.27% when immobilised on electro spun polystyrene and polysulfone web respectively, beginning from an initial Cr(VI) level of 25 mg/L. These may be incorporated into setups for continuous treatment of Cr-contaminated discharge waters because they were reusable for at least five cycles (Sarioglu et al. 2016). The mixed microbial consortium of *Geotrichum sp.* and *Bacillus sp.* exhibits alternating growth and synergy. They have a significantly higher Cr(VI) bioremediation efficacy (Qu et al. 2018). Arshad et al. (2017) observed that the presence of 5% biochar and the microbial consortium reduced the toxicity of Cr to wheat plants (*Pseudomonas japonica* and *B. cereus*). The availability of hazardous Cr in the food chain was reduced due to the conversion of Cr(VI)–Cr(III), which limited its absorption by plants and resulted in a decrease in Cr toxicity. Such an amendment-based strategy might be useful in the case of significant Cr(VI) contamination of soil habitats. Additionally, it was discovered that this addition enhanced the physicochemical qualities of the soil. Therefore, using a combination of biochar and microorganisms to treat soils that are contaminated with Cr will result in soil conditioning in addition to Cr remediation.

13.15.3.2 Addition of Enhancer

The bioremediation activity can be enhanced by using a wide range of substrates, some of which may serve as nutrition sources or as co-donors of electrons. Also, Tang et al. (2021) have listed several minerals in Cr(VI) polluted sites that can contribute in enhancing the bioremediation under appropriate conditions. Magnetite can act as cytochrome OmcS to enhance extracellular electron transport. In both aerobic and anaerobic environments, Fe(II) could increase the removal efficiency of Cr(VI); on the other hand, Fe(III) displayed an inhibitory effect under anaerobic conditions and high concentrations during aerobic conditions (Bansal et al. 2019;

Tang et al. 2021). Phosphorus minerals were also suggested to be added to increase the removal of Cr(VI) because they could promote the formation of antioxidant enzymes and microbial resistance to Cr(VI). In addition to strengthening the genes involved in reducing Cr(VI), it also increases the capacity to absorb nutrients to lessen cell damage. The negatively charged and rough surface also aids in the removal of Cr(III) (Ma et al. 2020). Sulfur and its compounds can also be used as an electron donor for heterotrophic Cr(VI) reducers like *Desulfovibrio* and *Desulfuromonas*, and volatile fatty acids (VFAs) produced from abiotic sulphur oxidation can also be used to support bioreduction. This is due to the common coexistence of organic compounds and reduced sulphur compounds in groundwater aquifers (Zhang et al. 2020).

13.15.4 Bacterial Biofilm and Sequestration Through EPS for Cr(VI) Removal

A number of strategies have been developed by nature to counter the toxic levels of Cr(VI) in the environment, but nature was at its best when it manifested biofilms (Bhunia et al. 2022). The formation of biofilms, auto-aggregation in response to environmental conditions, and host colonisation are all facilitated by the various surface elements and cell surface derivatives expressed in bacteria, such as flagella, EPS, LPS, etc., in conjunction with various environmental signals, such as quorum sensing (Ghosh et al. 2021). In addition, high sorption capabilities, feasibility and low production cost are some of the main advantages of biofilms documented in HM removal. The positively charged cat ionic HMs accumulated in the environment adsorbs to the negative charges of the biofilms with electrostatic bonds. Thus, biofilms of various microbes can be regarded as efficient adsorbents for HMs (Priyadarshanee and Das 2021). EPS for instance, as mentioned before, acts as a resistance mechanism in HM toxicity such as Cr(VI). The two most commonly found forms of EPS are LMW (low molecular weight fractions) and HMW (high molecular weight fractions). While LMW is an inactive form of EPS produced under regular conditions, HMW form of EPS is produced under stress and the two combined gives rise to biofilms as a protective shield against Cr(VI). The biofilm acts by retarding the diffusion of Cr(VI) within the cellular membrane and helps the bacteria thrive b under stress (Ghosh et al. 2021). A marine bacterium strain called *Pseudomonas chengduensis* PPSS-4 was discovered by Priyadarshanee and Das (2021) from contaminated soils at Paradip Fort in Odisha, India. When compared to free planktonic cells, the bacteria demonstrated a significantly greater uptake of multiple-metals [Pb(II), Cr(VI), and Cd(II)] in biofilm mode. These findings were consistent with a prior work by Black et al. (2014), which found that a biofilm-forming bacterium eliminated Pb(II) at a rate of 83.7% compared to 72.6% with free cells. Contrary to this, in a recent report by Wadood et al. (2021), *Staphylococcus equorum* KS1 and *Staphylococcus equorum* KW1 isolated from contaminated soils and wastewater were more efficient in Cr(VI)

reduction in their planktonic form (free cells) as compared to their biofilms in 24 h. Thus, for faster Cr(VI) reduction in wastewater planktonic cells are probably more suited than planktonic forms according to authors. Additionally, these bacteria were isolated from wastewater, and since flowing water and toxic pollutants are a common feature of wastewater environments where bacteria can live, these organisms have evolved to perform more efficiently in this type of environment (Elahi and Rehman 2019a; Wadood et al. 2021). On the other hand, S. equorum KS1 isolated from soil formed the firmest and thick biofilm in both presence and absence of Cr(VI) showing the biofilm forming character of soil-borne bacteria (Wadood et al. 2021).

13.15.5 Microbial Fuel Cells (MFCs) for Eco-Remediation of Cr(VI)

MFCs are another emerging technology to bioremediate Cr(VI) from soils and subsurfaces. A major problem faced in conventional bioremediation strategies is the generation of electron acceptor that reoxidizes the contaminant. Alternatives include inserting MFCs into soil sediments, where the anode will serve as the electron acceptor through biodegradation (Ghosh et al. 2021). MFCs are a unique technology of simultaneously generating renewable energy and Cr(VI) remediation making it an environmentally sustainable approach and has attracted many researchers (Ali et al. 2018; Yu et al. 2022). Dual-chamber of MFC was applied in a study by Tandukar et al. (2009) that completely removed Cr(VI) from polluted wastewater in operating time of 300 h and generated power of 55.5 mW/m^2 where Cr(VI) existed in hydroxide precipitated form. The organic and inorganic components of wastewater were decomposed by microbes in the anode. The electrons generated were transmitted to the cathode through an external circuit that reduced Cr(VI)–Cr(III) in a bio-electrochemical reaction and generated electricity (Tandukar et al. 2009). *Aeromonas, Pseudomomas* and *Thiuomonas* are some of the bacteria that could metabolise anoxic substrates to generate electrons thus, promoting catholic reduction of the target pollutants (Huang et al. 2008). However, still the effective mechanisms, optimizations of different influencing factors and the practical application of MFCs in different contaminated sites are still a long way. Yu et al. (2022) in a recent review have extensively the state-of-the-art experience of using MFCs for eco-remediation of Cr(VI), their performance and challenges associated with the technology. Proton exchange membranes (PEM) for instance, are ver important in maintaining anaerobic environment and in proton migration top cathode chamber. However, PEM needs to be cleaned every 6–7 months to avoid biological fouling which is a laborious process that makes the on-site and long-term application of MFCs a challenge (Xu et al. 2012; Yu et al. 2022).

13.15.6 Nano-Bioremediation (NBR) of Cr(VI): a Green Technology

When a substance is scaled down to the nanoscale, the surface area per unit mass ratio rises; as a result, more of that substance can interact with other particles and impact the levels of reactivity. Also, with NMs lesser activation energy is spent in chemical reactions or in other words, NMs show quantum effect. Another attribute of nanoparticles (NPs) is 'surface plasmid resonance' which can be used to detect toxic metal ions. Various metallic and non-metallic NMs of different shapes and sizes are available for custom environmental remediations: (1) NPs are capable of diffusing into contaminated areas where micro particles cannot; (2) they have stronger reactivity to redox amenable pollutants (Rizwan et al. 2014). Zero-valent iron NPs (nZVI) are one of the most commonly used and effective adsorbents NPs for Cr(VI) remediation from aqueous solutions (Mitra et al. 2017). Nano-bioremediation is a unique combination of nanotechnology and bioremediation. With the use of nanotechnology, this technology uses nano particles developed from prokaryotes (gram-negative rods, actinobacteria, etc.) and eukaryotes (fungi, algae, and plants) (Rajput et al. 2021; Hidangmayum et al. 2022). Le et al. (2015) reported dechlorination and biodegradation of biphenyls using Zn NPs and *Burkholderia xenovorans*. NPs derived from plant extracts such as, *Noaea mucronata* have been reported for the bioremediation of HMs from polluted water bodies (Mohsenzadeh and rad 2012). There have been several reports published on the toxicity of nZVI, however it is still unclear how nZVI might affect the ecosystem. Ravikumar et al. (2016) used biologically (BS-nZVI) and chemically (CS-nZVI) synthesised nZVI to test the cytotoxicity of five native isolated strains and their consortia. Cell membrane damage and a reduction in cell viability were observed. However, it was discovered that BS-nZVI had a less harmful impact on the consortium than CS-nZVI (Ravikumar et al. 2016). Fresh neem leaves (*Azadirachta indica*) extract was used to synthesise NPs in this study. Zhang et al. (2022) biosynthesized palladium nano particles with *Shewanella oneidensis* MR-1 (bio-Pd) under aerobic conditions for the subsequent bioreduction of Cr(VI). They could achieve the smallest average particle size of 6.33 ± 1.69 nm by maintaining a high cell: Pd ratio. The small size and uniform distribution of extracellular bio-Pds could completely reduce 200 mg/L of Cr(VI) within 10 min and also maintained high activity for five operating cycles much higher than commercial Pd/Cs. To overcome the slow electron, transfer rate in conventional wastewater treatment methods, Qian et al. (2022) evaluated the non-enzymatic Cr(VI) reduction mediated by SRB especially by speeding up the electron transfer by in-situ developed FeS- NPs. The Cr(VI) removal rate was one magnitude higher than without FeS NPs in addition to improved reduction efficiency via non-enzymatic reactions with sulfide. The bio-FeS NP@SRB functioned as an electronic bypass that improved the electron flux substantially and switched the reduction process from the cytosolic to extracellular environment, which had a greater detoxifying effect on microbes and eventually stimulated the electron transfer extracellularly and eventual Cr(VI) reduction (Qian et al. 2022).

Use of anti-oxidants as biomaterials for nano bioremediation: Several organic compounds possess strong potential for reducing Cr(VI) ions to less toxic Cr(III) in the presence of phenolic and −OH groups. Cr(VI) readily accepts a proton from the phenolic −OH groups and is converted to Cr(III) and the phenolic group to a quinone subsequently (Babangida et al. 2021). The challenges faced with conventional biosorption processes such as secondary pollution due to overloaded biosorbets are mentioned above. In contrast to the use of chemicals like zero-valent iron and others, the use of antioxidant compounds is currently the subject of intense research for its potential use in Cr(VI) detoxification. But physical state of the system or the bacteria can degrade natural antioxidants. Therefore, advancements in nanoscale technology are essential for protecting antioxidants from other hazardous co-contaminants, undesirable byproducts, and microbes. In addition, ti protection, NPs also provides stability and a controlled release of their contents for a long lasting efficacy (Babangida et al. 2021). Mystrioti (2014) reported on the application of green tea in the fabrication of Zn NPs for the reduction of chromium (VI) in a column design. They also looked into the efficiency of five plant juices and extracts, including red wine, *Mentha spicata*, *Syzygium aromaticu*m, and *Camellia sinensis*, for producing suspensions of Fe NPs and using them to reduce the amount of Cr(VI) in the environment. Green tea, pomegranates, and red wine were discovered to be three of these plants that are more efficient at reducing Cr(VI) (Mystrioti et al. 2016). Additionally, it was demonstrated that palladium nanoparticles (PdNPs) serve an important role as a catalyst in the elimination of Cr(VI) utilizing formic acid (Omole et al. 2007). They observed that the reduction is sensitive to temperature, pH, PdNP concentrations, as well as formic acid levels and that it exhibits first-order kinetics with respect to the reactant. When polyamic acid was used as the reducing agent in a previous study by the same author, they discovered a promising potential. They came to the conclusion that the strategy offers a significant advantage over traditional approaches, which frequently take more time to achieve complete reduction. According to Sadik et al. (2014), PdNPs in soil resulted in a 93 4% conversion of chromium (VI) to (III), compared to a 15% conversion when formic acid was applied alone. Such findings support the majority of the rationales for immobilizing antioxidants as micro- and NPs, including safety from microbial action and prolonged release for improved efficacy. The function of −OH and ROOH groups in biodegradable polymers and metal ions in metal-based NPs is explained by the synergistic effect that the immobilization compounds have on the conversion of Cr(VI).

13.16 Conclusion and Future Prospects

This chapter extensively highlights on the issue of environmental chromium pollution that the world is facing and the current technologies that exist for Cr remediation. Microbial remediation or bioremediation offers several advantages over the conventional chemical and physical methods. Bacterial bioremediation mechanisms and technologies have been discussed in detailed in this chapter. This extensive analysis

on this subject suggests the need of a better understanding of the microbial molecular mechanisms, responses and pathways in order to design an efficient bioremediation system for a particular contaminated site. Also, it is crucial to know the indigenous microbial community structure, their metabolic potential and the physicochemical conditions of the site in order to achieve a 'designer microbial approach'. Literature also indicates the lack of practical on-site use of bioremediation approaches that seem to be mainly limited to lab scale. Toxicity at higher metal concentrations, presence of co-contaminants in the system, compromised microbial growth, saturation of adsorption sites, secondary pollution etc. are some of the challenges faced while developing effective bioremediation technologies. In parallel, several researchers are working on developing new strategies such as immobilization, nano-bioremediation to achieve sustainable and efficient bioremediation. For instance, biochar and biosurfactants in combination with algae or duckweeds have emerged as attractive sorting agents that are not only sustainable but also aid in the abatement of global warming (Singh et al. 2020). When paired with other methods like phytoremediation and immobilization that can encourage the growth of the bacteria, bacterial bioremediation is faster, more economical, and much more sustainable (Pushkar et al. 2021; Singh et al. 2020). Nonetheless, the in-silico strategies to Cr(VI) remediation must continue analyzing novel genes, genomes, from cultured or uncultured novel strains to diversify the taxonomy and fill gaps in the existing literature (Bhunia et al. 2022).

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