

## Review Article

# Bioremediation of Chromium by Microorganisms and Its Mechanisms Related to Functional Groups

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Heavy metals generated mainly through many anthropogenic processes, and some natural processes have been a great environmental challenge and continued to be the concern of many researchers and environmental scientists. This is mainly due to their highest toxicity even at a minimum concentration as they are nonbiodegradable and can persist in the aquatic and terrestrial environments for long periods. Chromium ions, especially hexavalent ions (Cr(VI)) generated through the different industrial process such as tanneries, metallurgical, petroleum, refractory, oil well drilling, electroplating, mining, textile, pulp and paper industries, are among toxic heavy metal ions, which pose toxic effects to human, plants, microorganisms, and aquatic lives. This review work is aimed at biosorption of hexavalent chromium (Cr(VI)) through microbial biomass, mainly bacteria, fungi, and microalgae, factors influencing the biosorption of chromium by microorganisms and the mechanism involved in the remediation process and the functional groups participated in the uptake of toxic Cr(VI) from contaminated environments by biosorbents. The biosorption process is relatively more advantageous over conventional remediation technique as it is rapid, economical, requires minimal preparatory steps, efficient, needs no toxic chemicals, and allows regeneration of biosorbent at the end of the process. Also, the presence of multiple functional groups in microbial cell surfaces and more active binding sites allow easy uptake and binding of a greater number of toxic heavy metal ions from polluted samples. This could be useful in creating new insights into the development and advancement of future technologies for future research on the bioremediation of toxic heavy metals at the industrial scale.

## 1. Introduction

The leakage of serious heavy metals from human and industrial activities into wastewater has become a major environmental issue. Water pollution is a major threat to human, land, and aquatic animals and plants, and it is attracting the attention of many researchers and scientists. The main reason for this may be traced back to the increase in different industrial activities which takes great part in producing plenty of waste and untreated water throughout the world. It has been emphasized that the water pollution induced from the large amounts of industrial effluents without proper treatment before disposing to the water bodies is causing a serious threat to the entire human health

[1], for example, water contaminated with atorvastatin (a drug used as cardiovascular ailments) has been causing adverse health effects such as myopathy, rhabdomyolysis, memory loss, forgetfulness and confusion, liver and muscle problems, diabetes, cognitive loss, neuropathy, pancreatic, and hepatic and sexual dysfunctions [2]. Various industrial, agricultural and domestic wastes dumped to water bodies can seriously pollute, and the potential contaminants can cause different diseases such as diarrheal diseases, vector borne diseases, cutaneous diseases, blindness, paralysis, and liver diseases (Chowdhary et al.). In general, organic dyes from textile and painting industries [1, 3], different drugs from pharmaceuticals [2], inorganic pollutants and polysaccharides from distillery industries [4], smoke and organic

wastes from pulp and paper industries [5], and wide varieties of heavy metals produced from metallurgical and electroplating, chemical, refractory brick, tanneries, wood preservation, pigments and dyes, textiles, etc., [6] are getting great environmental challenge and threatening the health of humans. Hence, great emphasis has been given by many researchers to heavy metals as they are highly toxic even at very lower concentration and continuously discharged to water bodies due to growing industrial activities.

Typically, heavy metals are those metallic elements and some metalloids with density higher than  $5 \text{ g cm}^{-3}$  [7]. Chromium (Cr), cobalt (Co), copper (Cu), cadmium (Cd), arsenic (As), gallium (Ga), germanium (Ge), iron (Fe), mercury (Hg), lead (Pb), nickel (Ni), thallium (Tl), selenium (Se), and manganese (Mn) are some commonly known heavy metals [8]. They cover most transitional metals, basic metals, some metalloids, lanthanides, and actinides, having high molecular weight, atomic number, and specific gravity. Various industrial sectors such as electroplating, tanneries, pulp and paper, textile, metallurgies, mining sectors, and dyeing and painting industries extensively consume different heavy metals for diverse purposes [9–11]. These and other heavy metals are being continuously discharged from the manufacturing industry into living environments, especially water bodies at concentrations in excess of the limits set by regulatory agencies. Heavy metal exposure has been one of the big global concerns due to its high toxicity, high bioaccumulation in the human body and food chain, the essence of nonbiodegradability, and most likely human carcinogenicity [12].

Heavy metals are reported to pose toxic effect in humans (causing different cardiovascular, inflammatory, and respiratory diseases) and other animals [8, 13]; plants (disturb photosynthesis, production, and slow the growth) [14]; microorganisms (affect morphology, metabolism, and growth) [15]; and aquatic lives (affect reproduction and even death) [8]. Among toxic heavy metals, chromium is ranked among the top sixteen toxic contaminants that have adverse effects on human health as an essential metal [16]. Chromium is being used in various manufacturing sectors, such as the metallurgical, steel, tannery and cement industries, textiles, dyeing industries, which are major sources of pollution. Chromium can exist in various oxidation states among which, hexavalent Cr(VI) and trivalent Cr(III) states are most stable one and are most commonly discharged in to water bodies from industrial activities [17, 18]. The hexavalent form is especially one of the most significant sources of environmental contamination and is documented for its nephrotoxic malignant neoplastic disease and is well known for its toxic, carcinogenic, and mutagenic effects on humans and other living organisms [19, 20].

Various water treatment technologies have been reported for the removal of toxic substances from the water bodies. Some of which include biofiltration, membrane filtration, biological activated carbon, advanced oxidation process, ion-exchange resins, and iminodiacetic acid-carbon nanotubes [21–23]. To date, adsorption technologies such as covalent organic frameworks- (COFs-) based materials [24], metal organic framework (MOF) [25], porous geopolymers

[26], biochar [27], chitosan-based adsorbents [28], 3D porous aerogels [29], agricultural and industrial wastes [30], nanomaterials [31], and biosorption [32] have been studied to remove toxic heavy metal contaminants from wastewater. More recently, efficient removal of Cr(VI) from the contaminated solutions has been reported. To mention, Zhu et al., [33] reported efficient removal of Cr(VI) using magnetite immobilized with *Lysinibacillus* sp. (a Gram-positive, mesophilic, rod-shaped bacterium commonly found in soil) and studied the mechanisms and performance to be applied in large scale. On other hand, magnetic chitosan modified with graphene oxide nanocomposite has been employed for the removal of Cr(VI) from waste water where the synthesized adsorbents exhibited varied removal efficiency at solution pH of 2 [34].

The simple, inexpensive, and ecofriendly solution that can be performed over a wide range of experimental conditions for the detoxification and elimination of Cr-pollutants is bioremediation, which uses indigenous microorganisms [32]. Most bioremediation technologies such as biosorption produce less or no secondary wastes during removing toxic heavy metal ions [35] as secondary wastes may require further technologies to be managed. The processes by which microorganisms deal with toxic metals are biosorption, bioaccumulation, and enzymatic oxidation/reduction [36]. Among bioremediation techniques, biosorption process using microbial biomass is reported to be simple, fast, economical, efficient, and also effective at industrial scales. Hence, this review work is focused on hexavalent chromium removal by biosorption using microorganisms, the mechanism involved in the removal process and the functional groups participating in the uptake of hexavalent chromium ions. In addition, an emphasis has also been given to some factors that affect haste, efficiency, and effectivities of biosorption process. In general, wide varieties of toxic heavy metals are continuously discharged into water bodies due to growing industrial and agricultural activities, and different emerging treatment technologies have been adopted to overcome such problems.

## 2. Overview of Heavy Metals

*2.1. Industrial Heavy Metals as Major Water Pollutant.* Most commonly, wastes can be discharged into the aquatic environment as domestic, agricultural, industrial, and radioactive wastes. Among these, industrial operation accounts for the largest portion of either emission of gases and discharge of different effluents. One of the main sources of water contamination is industrial wastewater, which contains high levels of heavy metals and other permanent hazardous substances. The rapid development of science and technology has taken the sector to a new stage of growth [37]. The key reasons for high pollution problems in the waste disposal field of the industry are waste toxicity and postdisposal behavior, inadequate treatment procedures, insufficient disposal, bad planning, and management of disposal sites. Wide varieties of heavy metals have been continuously discharged from industrial processes into water systems (both surface and underground waters) in

different ways (as shown in Figure 1). Most commonly, Cr, Hg, Cd, and Pb from tanneries [9]; Cu, Pb, Zn, Hg, etc., from mining [40], Hg, Pb, Cd, Zn, Cu, Cr, As, and Ni from coal production [11]; Cd, Cr, Cu, Fe, Mn, Ni, etc., from textile manufacturing [39]; Fe, Zn, Cu, Cr, Cd, Mn, Ni, and Pb from pulp and paper [38], and others such as metal refining, electroplating, petroleum production, fertilizer, pesticide, and painting industries [10] also generate heavy metals which are discharged into environment with concentration higher than the proclaimed level by regulatory organizations.

Amidst various manufacturing industries, the tanning industry is an important contributor to the economy and, in particular, provides large-scale job opportunities to unskilled and/or trained individuals. Despite the great role of the leather industries in the social and economic development of the world, it is also the leading contributor of water contamination by heavy metals, mainly chromium. Wastewater from tanneries is primarily characterized by high levels of chemical demand for oxygen (COD), biochemical oxygen demand (BOD), turbidity, suspended solids (SS), sulfides, and chromium [41]. Huge quantities of heavy metals have been released worldwide into rivers or freshwater due to rapid global population growth, the expansion of global industrial and domestic activities, and agricultural development [42]. Heavy metals released into water bodies by waste have an incorrigible effect on the aquatic environment and damage the ability of an aquatic body to self-purify [43, 44].

Among several heavy metals generated from different industrial activities, the toxicity and health effects of chromium (Cr), which is the dominant heavy metal from tanneries, attracted the attention of researchers. Chrome tanning is one of the leather tanning industry's most commonly used methods since it provides a product with the highest value at a fair price. As a result, this process accounts for about 8% of the weight of the leather as chromium salt is applied [45]. Although the tanning process is highly important in improving the quality and acceptability of leather products, it comprises several chemical compounds such as acids, vegetable tannin, mineral salts, such as chromium sulfate, and fish or animal oil, some of which are reported to be potentially toxic to human, plants, and aquatic lives [43, 46–48]. Generally, industrial activity takes higher part in producing toxic heavy metals as waste, which directly or indirectly enter into water bodies, and Cr(VI) highly produced from tanneries is getting great challenges to be easily removed from water bodies.

## 2.2. Definition, Sources, Speciation, and Properties of Chromium

**2.2.1. Definition and Properties of Chromium.** Chromium is a steely-grey, lustrous, hard and brittle transitional metal symbolized Cr, having atomic number 24, molecular weight  $51.9961\text{ gmol}^{-1}$  and density  $7.19\text{ g/cm}^3$  at 20, melting and boiling points at 1,907 and 2,672, respectively. In the modern periodic table, Cr is the first element of group 6 and

corresponds to period 4, a d-block element with an electronic configuration of  $[\text{Ar}]3d^54s^1$  and is located between vanadium and manganese. Naturally occurring chromium is composed of three stable isotopes:  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$ , and  $^{54}\text{Cr}$ , with  $^{52}\text{Cr}$  being the most abundant (83.789% natural abundance) and is the 21<sup>st</sup> commonly abundant element in Earth's crust at around a hundred ppm [49, 50]. Cr(III) and Cr(VI) are the most commonly occurring oxidation states of chromium and are reported to be more toxic to animals, plants, and humans among its several oxidation states [50–54].

In a very simple and oxidizing medium, the trivalent chromium cation occurs only in a strongly acidic and decreasing medium, while hexavalent chromium occurs as  $\text{CrO}_4^{2-}$  anion [55]. Chromium metal with various oxidation states exhibit different characteristics, including a metallic luster, brittle and tough, steely-grey color, tarnish resistance, and high melting and boiling points (1907 and 2671, respectively) [56]. Also, chromium belongs to the refractory metal group, which includes all metals with a melting point higher than platinum ( $1,772^\circ\text{C}$ ). As a whole, chromium, the most known transition metal located in the 6<sup>th</sup> group and 4<sup>th</sup> period of the periodic table is abundant in the Earth crust and occurs as different stable isotopes and the various oxidation states of the metal determine its properties and characteristics.

**2.2.2. Sources of Chromium.** Chromium and associated chemical compounds can mainly originate naturally or anthropogenically.

(1) *Natural Sources.* From the two most stable oxidation state of chromium (i.e., Cr(III) and Cr(VI)), the trivalent one exists naturally in a complex form with the chromite ore ( $\text{FeCr}_2\text{O}_4$ ), a mineral which exists in mafic and ultramafic rocks and is a complex of varying proportions of magnesium, iron, aluminum, and chromium [57–60]. The naturally released Cr(III) ion can most probably oxidize into a highly toxic form (i.e., Cr(VI)) through microbial intervention and geochemical processes [57, 60]. Also, geologic parent materials or rock outcroppings and volcanoes are the most significant natural source of chromium pollution in the environment [61]. Chromium in rocks, mineral soils, and freshwater is usually a dispersed geochemical component. Cr is also present in all sorts of environmental elements, including air, water, and soil, of course, but in limited amounts [46, 62, 63].

(2) *Anthropogenic Sources.* Besides the existing natural process, various industrial activities produce chromium into the water bodies which have been a great threat for aquatic and terrestrial life and continued to be a concern of many researchers worldwide. Accordingly, many industrial processes employ chromium and its compounds for varied purposes. Among those manufacturing industries metallurgical, refractory, oil well drilling, metal plating, mining, textile, pulp, petroleum, chemical production, and leather consume chromium in varied amounts for different applications [64–69]. Among the most commonly existing oxidation states, Cr(VI) concentrations have increased dramatically in both marine and terrestrial ecosystems over



FIGURE 1: Different industrial activities discharging various heavy metals to the water systems [9, 11, 38, 39].

the past few centuries. It originates mainly from dyeing, textiles, steel fertilizers, photography, electroplating, manufacturing, packaging, and leather tanning and finishing [70].

In general, the most stable species of chromium, Cr(III) and Cr(VI), are produced both naturally and anthropogenically. The former one is mainly produced naturally by rock weathering, volcanic activities, and other geologic process, which gets oxidized to highly toxic Cr(VI) form by microorganisms in the environment. The hexavalent form highly produced through anthropogenic process by human activities rather than natural process.

**2.2.3. Oxidation States of Chromium.** Chromium may exist between 0 and VI in a variety of chemical varieties; however, trivalent and hexavalent chromium alone is sufficiently stable to occur in the environment [71, 72]. Chromium occurs in various chemical forms in soil (primarily as chromite (Cr(III)) and chromate (Cr(VI)), which vary greatly in terms of their biogeochemical actions [50]. Chromium species are commonly present in environmental water in two separate oxidation states, especially Cr(III) and Cr(VI), with contrasting physiological effects. Cr(III) is considered to be an important trace element for the maintenance of the efficient metabolism of glucose, lipids, and proteins in mammals. Chromium at 0 oxidation state does not exist naturally in the Earth's crust and biologically inert, while Cr(II) can be easily oxidized into Cr(III) in the

presence of air and is chemically unstable [73, 74]. This implies that different oxidation states of chromium have possessed varied properties and toxicity. On the other hand, Cr(VI) may be toxic and cancerogenic to human biological systems. Therefore, speciation of Cr(VI) and Cr(III) is important to determine toxicological actions [75, 76]. In general, though chromium exists in various oxidation states (0 to VI), only the trivalent and hexavalent forms are relatively more stable, and the difference in the oxidation state led to variation in properties and toxicity of the metal.

**2.2.4. Importance of Chromium.** Despite their toxicity, carcinogenicity, and environmental threats at elevated concentrations, chromium and its compounds at a limited amount are applied for various purposes in different units. For instance, Cr(VI) and its compounds have been employed as pigments for photography and pyrotechnics, electroplating, tanning, textile production, coloring, painting, inks, wood preservation, and plastics [77, 78]. Besides, chromium and its preparations are widely used in many industrial processes such as chrome plating, wood preservation, textile dyeing, pigmentation, chemical production, paper, and tanning [79–81]. As laboratory reagents and as production intermediates, chromium compounds, such as hexavalent chromium, are documented. The metallurgical, chemical, and refractory brick industries are major industries that use chromium. Chromium is distinguished by its high resistance to corrosion and its hardness. Thus, the

invention that steel could well be made to be extremely resistant to corrosion and discoloration by adding Cr to render stainless steel was a serious advancement. Besides Cr electroplating, this application is the highest volume user of the metal. The ore produces Cr and ferrochromium. Cr(VI) salts are used for timber preservation because of their toxicity [71]. In general, Cr in the industry is commonly used in plating, alloying, animal hide tanning, water corrosion inhibition, textile dyes and mordants, pigments, ceramic glazes, refractory bricks, and pressure-treated lumber [82].

Besides various industrial and laboratory applications, chromium, particularly trivalent chromium is nutritionally useful at the trace level. For example, a wide range of nutrients, such as coffee, nuts, green beans, egg yolks, whole-grain products, high-bran breakfast cereals, broccoli, meat, Brewer's yeast, and some brands of wine and beer are enriched with trivalent chromium [81, 83]. The recommended daily consumption of chromium according to the United State National Academy of Sciences is 50–200  $\mu\text{g}$  for adult men and women [81], but this range was recently lowered to 35  $\mu\text{g}$  and 25  $\mu\text{g}$  for adult men and women, respectively, according to Food and Nutrition Board at the Institute of Medicine [84]. However, more recently, the European Union of Food and Safety Administration had put weekly acceptable intake only, which is 300  $\mu\text{g}/\text{kg}$  of body weight per week [85]. It has been documented that chromium is important in protein, carbohydrate, and lipid metabolism, and its deficiency leads to glucose intolerance and insulin resistance [84, 86]. With this regard, daily intake of chromium at a reduced concentration (trace level) is associated with different medical applications. For instance, daily consumption of low to moderate amount of chromium helps fight against type II diabetes and obesity [83, 84, 86], and chromium-containing alloy has also dental applications such as restoration, orthodontic appliances, and implants [83]. As a whole, chromium and its compounds are extensively used in different industrial activities and as reagents in laboratories, and in trace amount, the trivalent form is important candidates in nutrition.

**2.2.5. Chromium Exposure and Toxicity.** Chromium and its compounds, particularly chromates, enter into the human body through different pathways. Accordingly, inhalation, ingestion, and dermal contacts are the major integral exposure routes for chromium, and the exposure may be acute (14 days), intermediate (75–364 days), or chronic (365 days) [47, 87]. Moreover, anthropogenically released chromium causes toxic effects in most exposed populations by inhalation of polluted air or drinking of chromium contaminated water [88, 89]. Owing to its characteristic toxicity and carcinogenicity, the United State Environmental Protection Agency (US-EPA) and US Occupational Safety and Health Administration (OSHA) have put the total chromium exposure limits for drinking water standards which are 100  $\mu\text{g}/\text{L}$  and Cr(VI)-timed weighted average for a normal workday exposure which is 5  $\mu\text{g}/\text{L}$  [89]. Furthermore, the concentration of  $0.510^{-4}$   $\mu\text{g}/\text{L}$  is the maximum permissible limit for the discharge of total chromium into the surface and portable water according to US-EPA and European Union [90].

The pattern of toxicity and accumulation of heavy metals in the atmosphere is a significant danger to the health of living organisms [15]. Heavy metal exposure has been one of the big global concerns due to its high toxicity, high bio-accumulation in the human body and food chain, the essence of nonbiodegradability, and most likely human carcinogenicity [12]. Among various heavy metals ions, the most stable chromium species (Cr(III) and Cr(VI)) are known to be toxic to aquatic and terrestrial life of which the hexavalent form is reportedly highly toxic and carcinogenic. The toxic, mutagenic, and other biological effects of chromium depend on its oxidation states. Accordingly, hexavalent chromium Cr(VI) is more harmful, cancerous, teratogenic, mutagenic, and movable than trivalent chromium Cr(III) because of its oxidizing existence [91, 92]. Even though the trivalent form is less toxic relatively, it induces its harmfulness by oxidizing into the most toxic hexavalent form in the presence of oxygen in the environment [65]. According to [47], the exposure to dichromate and chromates, which are oxyanion of chromium in +6 oxidation states and trivalent chromium released from alloys and Cr-plated objects, can cause dermatitis in humans. In synthetic pigment and industrial wastewater, Galvanometry and electricity, film and photography, plating and electroplating, metal washing, mining, and leather, chromium is the primary contaminant [93].

Chromium, especially, the hexavalent species poses its toxic effect through different mechanisms of actions. Among those, reducing activity or efficiency of the immune system; competing at enzyme activity cofactor fixation sites; inhibiting important enzymes such as oxidative phosphorylation and altering cell structures, mainly in the lipoprotein area of the membrane, are the key ones. Hexavalent chromium demonstrates high toxicity through its DNA-polymerase enzyme interface due to nasal irritation and ulceration, hypersensitivity reactions and contact dermatitis, acute bronchitis and emphysema, liver and kidney injury, internal hemorrhage, lung and skin cancer, and DNA damage [90]. Cr(VI) more readily enters the cell, but transfers multiple processes in the blood and gets reduced into Cr(III) in the human body [47]. Cr(VI) is removed from the body, while the chromate ion is transferred to the cell through a transport mechanism by which sulfate and phosphate ions also join the cell [52]. The presence of these ions in a cell can trigger oxidative stress, which is highly responsible for several chronic, neurodegenerative, cardiovascular, and other age-related diseases. In general, the augmented levels of oxidative stress, DNA adduct development, and chromosome breakups are some of the major mechanisms by which Cr(VI) cause cellular damage [89]. In due course, humans are exposed to chromium through ingestion, inhalation, and derma contact, and the exposure may be acute, intermediate, or chronic in general.

**2.2.6. Toxic Effects of Chromium in Humans.** Based on the epidemiological studies linking Cr(VI) to lung cancer, the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) classified Cr(VI)

compounds as group one human carcinogens with multiple complex mechanisms of actions [89, 94, 95]. Human exposure to Cr(VI) can cause allergies, irritations, eczema, ulceration, nasal and skin irritations, eardrum perforation, respiratory tract disorders, and lung cancer [96]. Cr(VI) exposure may lead to cytotoxicity, genotoxicity, and carcinogenicity of Cr(VI)-containing compounds, DNA mutations, and chromosomal damage at different stages, as well as to oxidative protein changes [47, 81, 97, 98]. In addition, inhaling a high level of hexavalent chromium can cause nose ulcer, irritation to the lining of the nose, anemia, irritation and ulcer in the small intestine and stomach, as well as other respiratory complications such as wheezing, coughing, nasal blockage, and facial erythema [13, 87, 99]. Eventually, repeated and high exposure of chromium and associated compounds, especially those containing hexavalent ions can severely cause several hazards, of which most are categorized under those stated in Figure 2.

**2.2.7. Toxic Effects of Chromium in Microorganisms.** Biologically, chromium ions are important nutrients as they involve in electron transport reaction in biological systems; however, microorganisms are also highly sensitive to both deficiency and excessiveness of chromium and its compounds just like plants and humans [61]. Chromium toxicity affects microbial population size, diversity, and behavior, as well as their genetic structure. Microorganism exposure to hexavalent chromium can cause alteration in morphology of both Gram-positive and Gram-negative bacteria. It disturbs the morphology, metabolism, and growth of microorganisms by altering the structure of nucleic acid, disrupting the cell membranes, causing functional damage, inhibiting enzyme activity and oxidative phosphorylation, and causing lipid peroxidation and osmotic balance [15]. Chromium causes bacterial cell elongation and cell enlargement and prevents cell division, which is essentially responsible for cell growth inhibition [61]. In general, both shortage and exorbitance of chromium can cause adverse effects in microorganisms such as disruption of the growth and cell functions are retarded.

**2.2.8. Toxic Effects of Chromium in Plants.** Chromium compounds released naturally and through different anthropogenic activities have been continuously discharged into the soil, in which different flora grow. Chromium compounds most commonly exist in the soil in the form of  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  which get easily absorbed by the plants and rapidly trickled down into the deep layers of soil, thereby endorsing surface and groundwater pollution [85]. Among various oxidation states, Cr(III) is considered to be less harmful, preventing its leaching into groundwater or its absorption by plants due to its extremely low solubility, while Cr(VI) has been shown to cause substantial harm to living cells [100]. Although some crops are not affected by low levels of Cr ( $3.810^{-4} \mu\text{M}$ ) [101], chromium compounds are highly toxic to most plants and are harmful to their production and growth. But Cr(VI) can be extremely poisonous to plants in concentrations as little as 5 mg/kg in

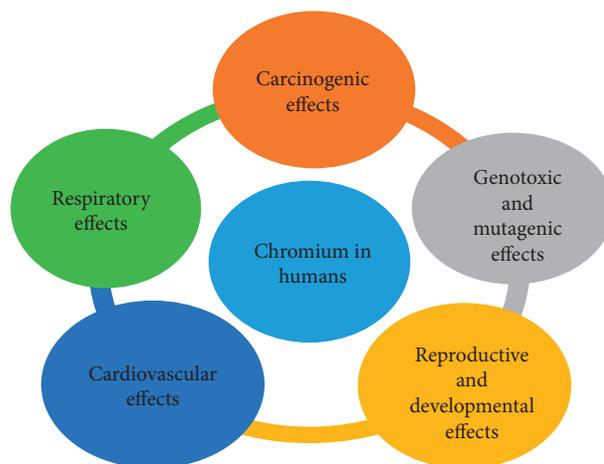


FIGURE 2: Toxicological effects of chromium on humans [61].

soils and 0.5 mg/L in solution according to Elahi et al. [85]. A reduction in nutrient uptake and photosynthesis is also correlated with Cr(VI), which contributes to slow plant growth. Several physiological, morphological, and biochemical processes are seriously disrupted and cause the production of reactive oxygen species in plant cells. Cr toxicity is indicated in the form of chlorosis and plant necrosis [62]. The major toxic effects of chromium in plants are summarized in Figure 3.

Chromium also affects the growth of leaves, the main photosynthetic plant organ. Increasing chromium concentration leads to a significant reduction in the leaf area and leaf biomass, which is accompanied by decreased photosynthesis and induction of chlorosis and necrosis of leaves. Under Cr exposure, many destructive processes take place in leaves. These include suppression of chlorophyll synthesis, disruption of chloroplast ultrastructure, inhibition of photosynthetic electron transport, and release of magnesium ions from the molecule of chlorophyll [102]. Symptoms of Cr(VI) poisoning in plants include reduced plant growth, leaf deformation and necrosis, chlorosis, decreased enzyme activity and nutrient absorption and transport, damage to root tissue, decreased photosynthesis, lipid peroxidation, DNA strand break, and chromosome aberration [81, 103]. Thus, chromium can inhibit photosynthesis, seed germination, and nutrient uptake and affect the growth and functionality of its parts in general.

### 3. Chromium Removal Methods

Several methods of removing heavy metals from polluted water have been used [104–107]. Heavy metals such as chromium have been removed from polluted environments such as wastewater via several conventional physicochemical procedures such as chemical precipitation, electrolysis, ion exchange, floatation, coagulation and flocculation, membrane filtration, reverse osmosis, adsorption, and photocatalysis [56, 108–114]. The removal of chromium by such traditional methods are inefficient during the reduction of heavy metals at very low concentrations of 10–100 mg/L so that the metal ions are not completely removed and also the

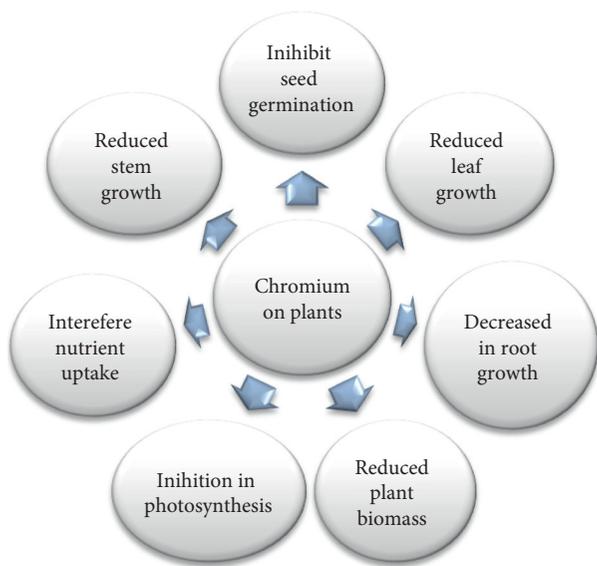


FIGURE 3: Toxic effects of chromium in plants [50].

methods are very costly [109, 115, 116]. In addition, these conventional methods generate large quantities of secondary waste (sludges) and other toxic products that may require other technologies to be brought to nontoxic, biodegradable, and environmentally benign forms.

Consequently, the focus has been shifted to biological remediation approaches having relatively high removal efficiency, less cost and environmentally benign. Biotransformation and biosorption are widely used technologies that utilize the ability for heavy metal transformation or adsorption by microorganisms or plants [56, 117]. Technologies for the biological removal of heavy metals use biomass to remove chromium from industrial waste and are cost-effective, environmentally safe and easy to operate [56, 118]. The alternative and environmentally sustainable form of chromium biosorption is the biological one. Potential biological methods (i.e., biosorption, bioaccumulation, oxidation/reduction, leaching, precipitation, volatilization, decay, and phytoremediation) have been employed to remove and detoxify toxic heavy metals from contaminated water and sediments. In addition, the options for the recovery of metals sequestered by biosorbents (use of suitable desorbing agents) and microbial biomass are identified [119]. Though different chemical and physical methods have been applied as removal technique, the biological remedy using microorganisms attracted the attention due to economic feasibility, simplicity, efficiency, and production of less or no secondary wastes in general.

**3.1. Biological Method of Chromium Removal.** The biological method of heavy metal removal involves the decomposition and/reduction of toxic heavy metal ions to relatively less and/nontoxic forms by using the living and/or dead biomass of microorganisms (such as bacteria, fungi, algae, and yeast), industrial or agricultural wastes, naturally occurring materials (such as clay, chitin, chitosan, lignin, and zeolite), and different parts of plants. A potentially useful method for the

detoxification of Cr contamination and bioremediation of polluted waste is the biological reduction of Cr(VI) to Cr(III) [100]. Chromium removal by microbial species is a sustainable development solution that is healthy and environmentally friendly. These techniques are conceivably employed by using different microbial biomass mainly bacteria, fungi, and algae. The biosorption of Cr(VI) using fungal, algal, or bacterial biomass (growing, resting, and dead cells) and biological and agricultural waste materials has been described as a possible alternative to the current conventional methods of industrial wastewater detoxification [20]. Chromium-resistant microorganisms are responsible for/to the biological reduction of Cr(VI) to less mobile Cr(III), and their consequent precipitation may be an important method of detoxification of polluted Cr(VI) sites and have a possible application for bioremediation [96]. Microorganisms remove heavy metals in such a way that they utilize metal ions for their advancement and by converting them into carbon dioxide, methane, water, and biomass through enzyme-catalyzed metabolism of poisonous substances [120].

In the microbial remediation process, microorganisms (such as bacteria, fungi, algae, and yeasts) are stimulated to readily degrade the environmentally toxic pollutants to eco-friendly or safe levels in soil, subsurface materials, water, sludge, and residues [35]. It has been reported that different microbial remediation techniques such as biosorption, bioaccumulation, biotransformation, and bioleaching have been employed to remove chromium and other heavy metals from industrial wastewaters [92]. The bioremediation process recently reported as the dominant friendly mechanism for heavy metal removal from a polluted environment is summarized in Figure 4. Bioaccumulation, also called active biosorption, is a metabolism-dependent mechanism in which hexavalent chromium (Cr(VI)) is transported across the membrane into the cell by cellular energy in living biomass only [92]. The bioaccumulation process occurring in living microorganisms involves the following steps [56, 121]. Initially, potentially toxic heavy metal ions get attached to the surface ligand of the cell. Then, the metal-ligand complex formed at the surface of the cell is transported inside the cell by transporter protein. Finally, transported complexes intracellularly interact with metal-binding proteins (such as metallothionein and phytochelatins), where precipitation, methylation, and other process takes place. However, the process is limited to the living cells only and inhibits microbial cell growth at a relatively higher metal concentration [92]. Finally, the living and dead microbial biomass, mainly that of bacteria, fungi, and algae ecofriendly degrade and remove toxic chromium ions by the process of biosorption, biotransformation, and bioaccumulation.

**3.1.1. Reduction of Cr(VI) to Cr(III).** As it has been discussed in preceding sections, hexavalent chromium is more toxic to plants, animals, and aquatic species when compared to the trivalent species. Hence, transforming the more toxic Cr(VI) species from the solution to the less toxic one can take place

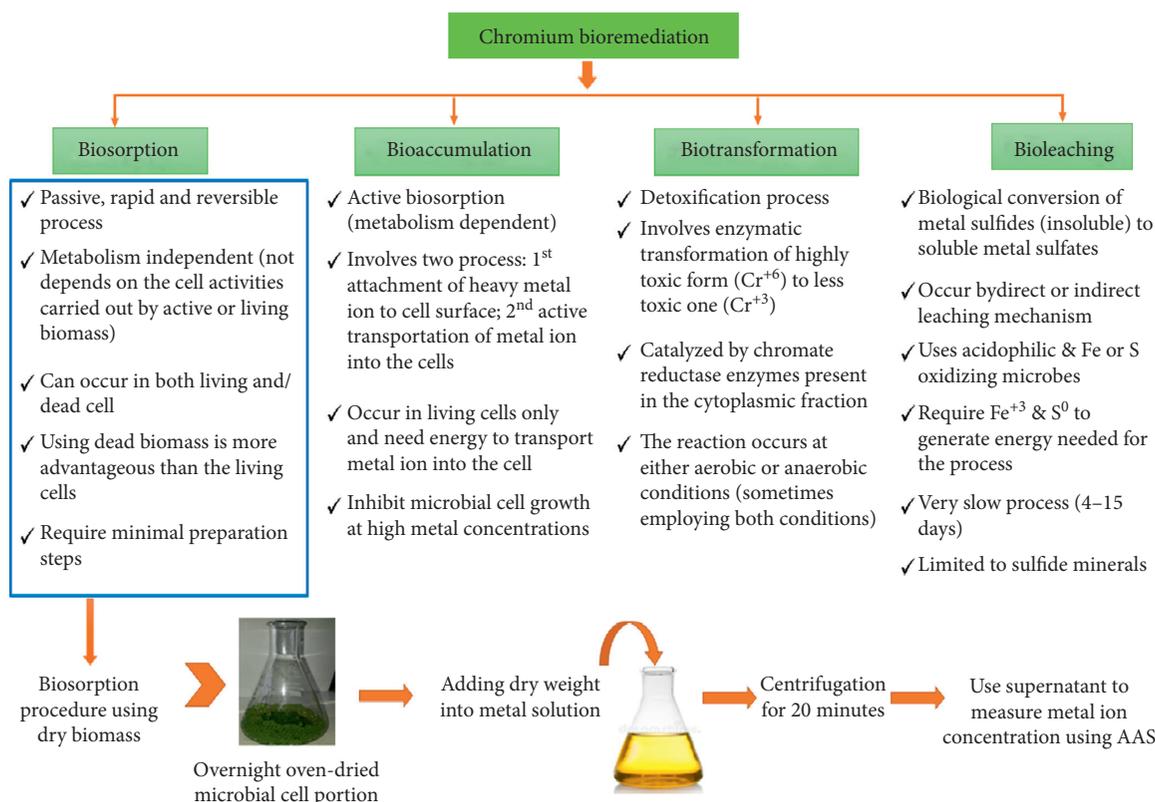


FIGURE 4: Heavy metal bioremediation processes by microorganisms [87, 92, 121–123].

by different process through varied conditions. In addition to extracellular adsorption and intracellular accumulation, Cr(VI) can importantly transform and reduce to less toxic Cr(III) species by chromium reductase enzyme [63, 124]. More importantly, the biomass surface with electron donating agents such as hydroxyl groups, amine groups, and secondary alcohol groups interact with Cr(VI) favorably at acidic pH and is reduced to Cr(III), which subsequently binds to the negatively charged functional groups (such as sulfonate group and carboxyl group) [7]. Even though the reduction of hexavalent chromium to the trivalent one most of the time takes place in living biomass, it has also been observed in nonliving microalgae biomass, which might due to the release of glutathione [63]. In this regard, Cr(VI) reduction at acidic pH condition using dead microalgae biomass is as follows [125].

Therefore, in addition to biosorption and bioaccumulation, hexavalent chromium can also be removed from aqueous solution by being enzymatically reduced and transformed in to less toxic species (such as Cr(III)) by living or dead microbial biomass at different favorable conditions.

**3.1.2. Hexavalent Chromium (Cr(VI)) Biosorption.** In contrast to the bioaccumulation process, biosorption is a metabolism-independent mechanism, which can occur in both living cells (but not depend on cell activities) and dead microbial biomass [92, 120, 121, 126]. In biosorption

mechanisms, the toxic heavy metal ions such as Cr(VI) extracellularly bind to various functional groups of the microbial cell wall (as shown in Figure 5), which are removed either by surface precipitation, ion exchange, or complexation/chelation process [92, 121, 127]. The compositions and structures of the cell wall vary across different microorganisms. For instance, the bacterial cell wall composed mainly of peptidoglycan [128], but that of fungi is glucans, chitin, glycoproteins, melanin [129], and the algae cell wall is composed mainly of alginate, mannans, and sulfonated polysaccharides [130].

Hence, the extensive mechanism for the biosorption process is very complex since it depends on the types of biomasses going to be used, the functional groups of the microbial cell wall, its structure, and extracellular polymer substances secreted by microorganisms [131–133]. The biosorption process is reported to have various advantages over other bioremediation mechanisms for toxic heavy metal removal from polluted environments. The presence of multifunctional groups and uniform distribution of binding sites on the cell surface, no need for additional nutrients (chemicals), minimal preparatory steps, low cost, high efficiency, regeneration of biosorbent, and possibility of metal recovery are some advantages of the biosorption process [90, 121]. Owing to these and other related advantages, the focus has been given to the biosorption process using different microbial biomass such as bacteria, fungi, and microalgae for the removal of heavy metals particularly hexavalent chromium. Different microbial

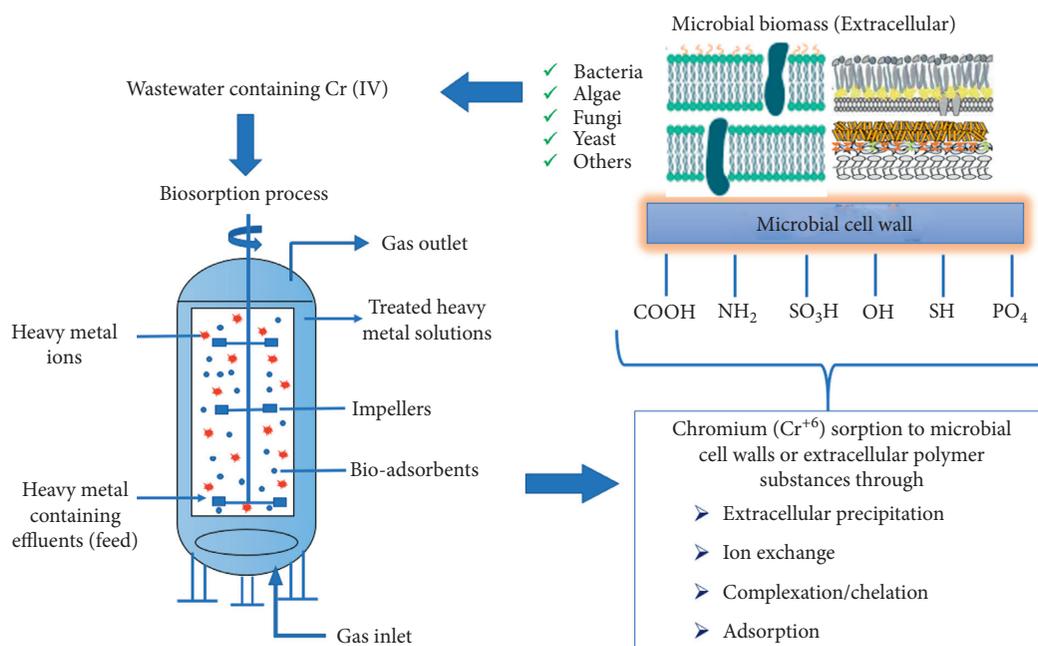


FIGURE 5: Hexavalent chromium (Cr(VI)) biosorption process by microorganisms [90].

TABLE 1: Various microorganisms used for biosorption of chromium.

Bacteria							
S.No.	Species	IC (mg/L)	Dose (g/L)	pH	Time (hr)	% Removal	References
1	<i>Bacillus salmalaya</i>	—	—	3	0.83	20.35 mg/g	[134]
2	<i>Bacillus</i> sp.	—	—	—	72	75	[135]
3	<i>Bacillus</i> spp.	1	0.25	2	5	99	[110]
4	<i>Enterobacter cloacae</i>	0.001	—	—	120	81	[19]
5	<i>Chelatococcus daeguensis</i>	15	—	7	24	94.42	[136]
6	<i>Micrococcus</i> sp.	100	—	7	24	90	[137]
7	<i>Planococcus</i> sp.VITP21	142.8	—	6.8	12	83	[138]
8	<i>Pseudomonas alcaliphila</i> NEWG-2	200	—	7	48	96.60	[139]
9	<i>Halomonas</i> sp. DK4	100	—	6	48	81	[140]
10	<i>Klebsiella</i> sp	100	—	9	72	63.08	[141]
11	<i>Sinorhizobium</i> sp. SAR1	—	7.5	1	—	285.71 mg/g	[142]
Fungi							
1	Consortium of <i>Penicillium commune</i> , <i>Paecilomyces lilacinus</i> , <i>Cladosporium perangustum</i> , <i>Cladosporium perangustum</i> , and <i>Fusarium equiseti</i>	—	—	4	24	100	[143]
2	<i>Fusarium</i> sp	—	—	—	—	100	[144]
3	<i>Aspergillus Niger</i>	18.125	4	3	168	96.3	[145]
4	<i>Aspergillus flavus</i>	18.125	4	3	168	92.8	
5	<i>Aspergillus fumigatus</i>	18.125	4	3	168	90.1	
6	<i>Aspergillus nidulans</i>	18.125	4	3	168	86.7	
7	<i>Aspergillus heteromorphus</i>	18.125	4	3	168	83.7	
8	<i>Aspergillus foetidus</i>	18.125	4	3	168	78.6	
9	<i>Aspergillus viridinutans</i>	18.125	4	3	168	74.4	
10	Consortium of <i>Aspergillus lentulus</i> , <i>Aspergillus terreus</i> , and <i>Rhizopus oryzae</i>	100	—	6.5	96	100	[146]
11	<i>Aspergillus lentulus</i>	100	—	6.5	120	83.11	
12	<i>Aspergillus terreus</i>	100	—	6.5	96	95.57	
13	<i>Rhizopus oryzae</i>	100	—	6.5	168	25.34	
14	<i>Aspergillus versicolor</i>	50	—	6	—	99.89	[147]
15	<i>Rhizopus oryzae</i>	400	—	7	72	91.15	[148]

TABLE 1: Continued.

Bacteria							
S.No.	Species	IC (mg/L)	Dose (g/L)	pH	Time (hr)	% Removal	References
16	<i>Aspergillus sp</i>	100	—	5	24	92	[137]
17	<i>Cladosporium cladosporioides</i>	504	0.5	1	288	491.85 mg/g	[149]
18	<i>Trichoderma sp.</i>	200	0.0016	5	2	96.38	[150]
19	<i>Aspergillus terreus</i>	1000	10	1	24	54	[151]
20	<i>Pleurotus ostreatus</i>	50	—	—	0.367	100	[152]
21	<i>Pleurotus ostreatus</i>	—	0.2	5	2	20.71	[153]
Microalgae							
1	<i>Scenedesmus sp.</i>	10	10%(w/v)	1	1.5	92.89	[154]
2	<i>Pseudanabaena mucicola</i>	—	—	2	—	71	[155]
3	<i>Pseudopediastrum boryanum</i>	10	2	2	—	70	[112]
4	<i>Scenedesmus sp.</i>	—	—	—	—	98	[156]
5	<i>Chlorella colonials</i>	6.07	2.7	—	108	97.8	[157]
6	<i>Chlorella sorokiniana</i>	100	0.2	6.2	72	99.6793	[158]
7	<i>Chlorella sp.</i>	—	—	—	96	34	[159]
8	<i>Chlorella vulagris</i>	100	1.2	3	1	99.75	[160]
9	<i>Scenedesmus sp</i>	10	10%(w/v)	1	2	93.1	[154]
10	<i>Spirulina platensis</i>	150	0.2	1	1.5	45.5 mg/g	[161]
11	<i>Isochrysis galbana,</i>	—	10 mL	5	2	335.27mg/g	[162]
12	<i>Chlamydomonas sp</i>	250	1.5	4	0.5	91	[163]

biomass that has been employed for biosorption of chromium is summarized in Table 1.

The ability of microorganisms, for example, bacteria, fungi, and algae to remove heavy metal ions and, or to promote their transformation to less-toxic forms, has attracted the attention of various environmental scientists, engineers, and biotechnologists for many decades [10]. This is mainly because the process is simple, rapid, economical, and environmentally benign when compared to the physical or chemical techniques. In general, biosorption is metabolism-independent process, in which both living and dead cells can be used and the Cr(VI) ion extracellularly bind to various functional groups of the microbial cell wall, which are removed either by surface precipitation, ion exchange, or complexation/chelation process as typical mechanism.

**3.2. Bacteria.** Chromium removal by using bacterial strain is characterized as relatively rapid, economic, requires less energy, and the process requires less or no chemicals [62]. Bacterial species isolated from metal-contaminated environments are highly resistant to toxic heavy metals than those isolated from none-contaminated environments. Both Gram-positive and Gram-negative bacterial strain isolated from soil, water, and another chromate contaminated environment especially, effluents from tanneries and electroplating industries, has been employed for chromium biosorption [90, 164]. However, at a relatively high concentration, Gram-positive bacteria showed significantly good tolerance to toxic Cr(VI) when compared to Gram-negative bacteria [164]. Different bacterial species recently employed for chromium biosorption are summarized in

Table 1. Due to their high surface-to-volume ratios and a high content of potentially active chemisorption sites such as teichoic acid in their cell walls, bacteria make outstanding biosorbent. Due to their small scale, their ubiquity, their capacity to grow under regulated conditions and their resistance to a broad variety of environmental circumstances, bacteria have been used as biosorbent. [165].

**3.3. Fungi.** Fungi are microbes that, due to the production of high biomass yields, are used as biosorbent for the removal of heavy metals. They are among the abundantly used microorganisms for biosorption of Cr(VI) since they are versatile, capable to adopt harsh environments, and can tolerate high hexavalent chromium concentration (above 10,000 mg/L) [90]. Fungal species are usually immune to higher metal ion concentrations [20, 165]. In fungi, Cr(VI) is adsorbed on the cell surface by forming a chemical bond with functional groups which are present on cell surface proteins [62]. The binding of hexavalent chromium to the fungal cell is owed to the chemical components, mainly proteins, lipids, and polysaccharides such as galactosamine, chitin and glycan, and the varieties of functional groups such as carboxyl ( $-\text{COOH}$ ), phosphate ( $\text{PO}_4^{3-}$ ), amine ( $-\text{NH}_2$ ), thiol ( $-\text{SH}$ ), and hydroxide ( $-\text{OH}$ ) groups [166]. Cr-fungi interactions have been extensively studied, mainly related to chromate tolerance in filamentous fungi and yeasts, and chromate reduction by yeasts. Fungi are usually less susceptible to metals than bacteria [66].

**3.4. Microalgae.** Algae are efficient and cheap biosorbents due to little nutrient requirement and their high productivities (i.e., high growth rate compared to the terrestrial

plants and can complete an entire growing cycle in every few days) [167]. Based on statistical analysis on algae potentiality in biosorption, it has been reported that algae absorb about 15.3%–84.6% which is higher as compared to other microbial biosorbents [168]. Heavy metal uptake by microalgae encompasses passive biosorption by dead biomass and active biosorption by living microalgae cells. In the process of passive biosorption, metal ions in the cationic form are physically adsorbed over the microalgal cell surface that contains functional groups such as hydroxyl (-OH), carboxyl (-COOH), amino (-NH<sub>2</sub>), and sulfhydryl (-SH). During active biosorption, the metal ions are translocated across the cell membrane into the cytoplasm [169]. The binding of heavy metal ions to microalgae biomass is owed to the presence of multiple functional groups such as carboxylic acid, ether, amide, hydroxyl, and other carbonyls [170]. Among various binding functional groups, deprotonated sulfate and carboxyl groups as well as the monomeric alcohol and laminarin, are most likely responsible for the biosorption process [171]. Depending on its speciation, there are reports of tolerance or resistance of a small number of algae to Cr. The reduction of Cr(VI) to Cr(III) and reduced Cr uptake by algal cells is not likely to be involved in Cr(III) algal resistance [66].

In winding up, dead and living biomass of bacterial, fungal, and algal species are the most important, extensively used, relatively rapid, and economic process for removing toxic and hazardous metal ions like hexavalent chromium by biosorption.

#### 4. Factors Influencing Chromium Biosorption by Microorganisms

**4.1. The Influence of pH.** It is a very important parameter. It affects the solubility of metal ions and binding sites of biomass [172]. Both biosorption and Cr(VI) reduction is dependent on the initial pH of the media. The carboxylic, phosphate, and amino groups are deprotonated at pH values greater than pK<sub>a</sub>, and therefore, negatively charged surface functional groups are able to bind positively charged metal ions, but metal ions no longer attracted to the biomass as the carboxylic, phosphate, and amino groups become protonated at pH values less than pK<sub>a</sub> [173]. Since Cr(VI) reduction is a proton consumption process, there is an increment in pH with Cr(VI) reduction. Hence, Cr(VI) reduction is generally higher at low pH values [88]. Indeed, the biosorption of chromium is highly favored as chromium anions are electrostatically get attracted to the carboxyl and amino groups on the surface of biomass, which are protonated at lower pH [110]. According to Ozer et al. [174] *Pediastrum boryanum* biosorbents showed its maximum adsorption of Cr(VI) at pH 2.0, but when the pH value raised, Cr(VI) removal efficiency was declined. This indicates that the pH of the reaction environment highly affects the heavy metal biosorption capacities of microbial biomass. The optimal conditions employed by different researchers to obtain good biosorption efficiencies by different microorganisms, mainly bacteria, fungi, and yeast biomass are given in Table 1.

**4.2. The Influence of Temperature.** The temperature of the adsorption medium could be important for energy-dependent mechanisms in metal biosorption by microbial cells [175]. The temperature is an important parameter for bacterial growth, which affects the enzymatic reactions necessary for Cr(VI) reduction [176]. Growth and reduction of Cr(VI) is negatively affected by extreme temperature which arises from the reduction in viability or due to the arrest of the physiological activity of the cell. Higher temperature results in protein denaturation and DNA damage as well as change in the structure of the membrane [177]. According to [178], with an increase in the temperature range of 30 to 40, the removal rate of Cr(VI) by strain *Desulfovibrio* CR-1 gradually increased to the same level, and the removal effect was best.

**4.3. The Influence of Contact Time.** Contact time is one of the most significant parameters for the effective use of the biosorbent for a practical application, and it has direct impact on the heavy metal removal efficiency. Metal ion removal efficiencies increase with increasing contact time and more or less remain constant after equilibrium achieved [179, 180]. Biosorption occurs rapidly if equilibrium is optimally attained within a few hours [181]. The metal adsorption of chromium (VI) by *Pantoea* sp. TEM18 increased rapidly during the first 5 min and remained nearly constant after 15 min. After this equilibrium period, the number of adsorbed metals ions did not significantly change with time [182].

**4.4. The Influence of Initial Metal Ion Concentration.** The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases [172]. At higher concentrations, more chromium ions are left unabsorbed in the solution due to the saturation of binding sites [110]. The study done by [142] confirms that an increase in metal concentration, from 100 mg/L to 500 mg/L, led to a decrease in percentage Cr(VI) removal (from 99.88% to 83.69%). But analysis of total Cr showed that uptake capacity of the biosorbent SAR1 increased (6.27 mg/g to 28.95 mg/g) with an increase in Cr(VI) concentration.

**4.5. The Influence of Biosorbent Dosage.** The increase in the biosorbent concentration favors the heavy metal biosorption because of the increase in surface area [150]. According to [167], Cr(VI) removal efficiency by microalgae *Scenedesmus* species increased rapidly from 45.9 to 92.9% with the increase of S/L from 2 to 10%(w/v), and on further increase up to 30% (w/v) is slightly increased to 96%.

**4.6. The Influence of Agitation Speed.** Agitation enhances dissolved oxygen or aeration which in turn strongly favors microbial growth and hence increases chromate reduction. However, there may be mechanical damage to microbial cells as a result of high agitation speed [88].

Generally, pH, temperature, contact time, stirring speed, and adsorbent dosages are the major factors that highly influence the removal efficiency of chromium ions from the solutions. This means that efficient and maximum biosorption can take place at specified temperature, pH, contact time, and dosage of adsorbent depending on the specific types of microbial biomass used.

## 5. Mechanisms of Chromium Biosorption by Microorganisms

Microbes are organisms that are capable of tolerating unfavorable circumstances, and these mechanisms evolved for the past millions of years. There are several protection mechanisms of heavy metal resistance by microbial cells. These mechanisms are an extracellular barrier, extracellular sequestration, and active transport of metal ions (efflux), intracellular sequestration, and reduction of metal ions [9]. The biological process of heavy metal removal can either be biosorption or bioaccumulation according to the cell's metabolism process [183, 184]. The two-bioremediation process differs mainly by the nature of sorbent, which in this case is the material of biological origin known as biosorbent. Bioaccumulation is a metabolism-dependent process in which the intracellular uptake of metal occurs due to increased membrane permeability. It can occur only with living organisms in which the contaminants are transported into the cell, and the metal ions are accumulated inside the cell of the biosorbent [183–185]. Biosorption, on other hand, is a quick, independent, and metabolically passive process responsible for the selective sequestration of heavy metal ions by dead/inactive biomaterials [183, 184]. During biosorption, the heavy metals bind to the cell walls extracellularly, while they bound to the proteins such as metallothionein once the metal ions are inside the cells in the bioaccumulation process.

The biosorption process always involves a solid phase which serves as the biosorbent (various biological materials). Due to the higher affinity of the sorbent for the sorbate species, the sorbate is attracted and bound thereby various mechanisms [181]. Biosorption is a nondirected physicochemical interaction that occurs between metal species and the cellular components of biological species. The mechanisms behind their resistance include adsorption, uptake, methylation, oxidation, and reduction of toxic, highly soluble Cr(VI) to less soluble and less toxic Cr(III) [186]. Heavy metal ions can be entrapped in the cellular structure of such organisms and subsequently be absorbed onto binding sites present on it (Figure 6). Biosorbents contain a variety of functional groups, including carboxyl, imadizole, sulfhydryl, amino, phosphates, sulfate, thioether, phenol, carbonyl, amide, and hydroxyl moieties [181].

Microorganisms interact with metal ions through cell wall-associated metals, intracellular accumulation, metal siderophore, extracellular polymeric reactions with transformation, extracellular mobilization or immobilization of metal ions, and volatilization of metals [15]. As biosorption is a process in which physicochemical interaction between the charged surface groups of micro-

organisms and ions in the solution takes place by the process of complexation, ion-exchange, micro-precipitation, adsorption [176, 187]. Metal sequestration or uptake in the case of bioaccumulation is followed by a number of processes such as localization of metal (Cr) within cell components, metallothionein binding, metal accumulation, extracellular precipitation, and complex formation [88]. Microbial Cr(VI) removal typically involves three stages: binding of chromium to the cell surface, translocation of chromium into the cell, and reduction of Cr(VI) to Cr(III). In general, Cr(VI) reduction by microorganisms may proceed on the cell surface, outside the cell, or intracellularly, either directly via chromate reductase enzymes, or indirectly via metabolite reduction of Cr(VI) [188].

## 6. Functional Groups Involved in Microorganisms during Biosorption of Chromium

The functional group is one of the major determinant factors in studying the removal of heavy metals from a contaminated environment using biological methods. Identifying functional groups responsible for the binding metal ions to the microbial biomass is very helpful in determining the biosorption mechanism and also important to decide on the plausibility of biomass for the process. Biosorbent containing multiple functional groups are more plausible for biosorption as the presence of multiple binding sites widens more contaminants binding opportunities. The type, structure, and connectivity of functional groups may considerably vary from microorganism to microorganisms and most of these groups have been characterized mainly on the microbial cell walls. The functional groups such as aldehydes, alkyl chains, amide, amine, alcohols/phenols, carboxylic, ester, organic halide compounds, phosphate, sulfoxide, and aliphatic organic chains of cellulose were identified as functional groups for the biosorption of chromium [7].

According to Javanbakht et al. [189]; the microbial biomass with oxygen (O-), nitrogen (N-), sulfur (S-), and/phosphorus (P-) containing functional groups directly participate in the binding of certain metal ions. The active functional groups present in microbial cells that are responsible for metal ion binding and the adsorption isotherm followed is given in Table 2. Different spectroscopic and microscopic techniques, such as infrared and Raman spectroscopy, electron dispersive spectroscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance (NMR), X-ray diffraction analysis, X-ray absorption fine structure spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM), have been employed for identifying some active sites involved in binding of heavy metal ions [189, 201]. However, most studies employ Fourier-transform infrared spectroscopic (FT-IR) technique to identify and characterize certain functional groups present in microbial biomass for uptake of toxic heavy metals such as hexavalent chromium. FTIR

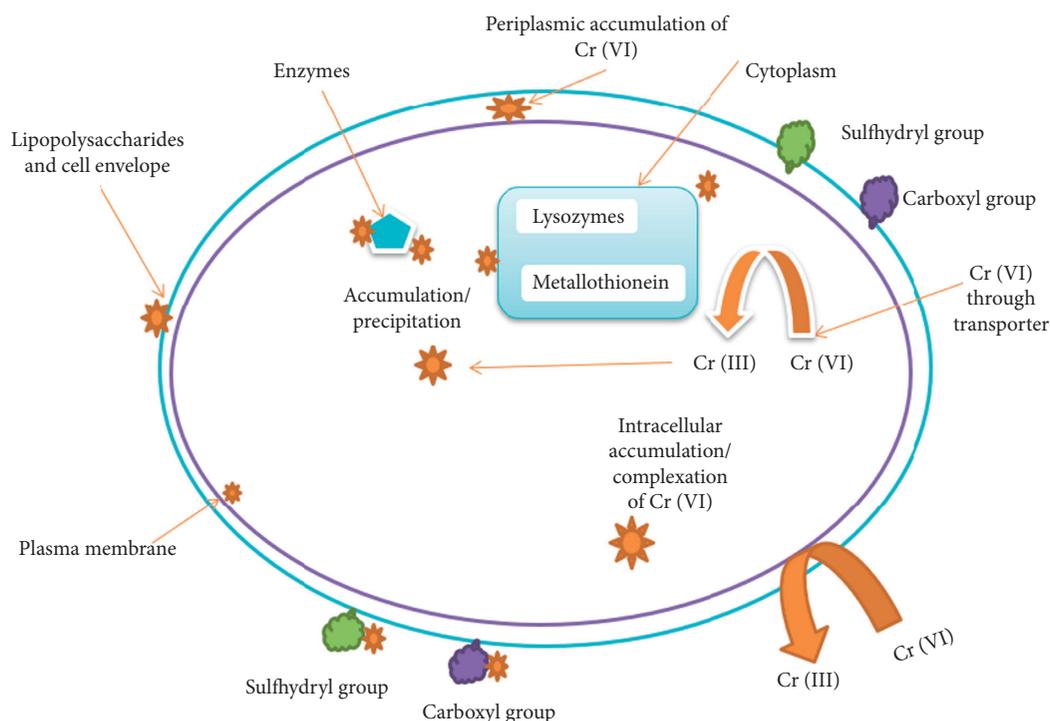


FIGURE 6: Mechanisms for Cr(VI) biosorption by microorganisms [88], [103].

TABLE 2: Involvement of various functional groups as revealed by FTIR analysis in chromium binding by different microorganisms.

FUNGI				
S/ no	Fungi	Functional groups	Adsorption isotherms	References
1	<i>Aspergillus foetidus</i>	C=O, C-Cl, PO <sub>4</sub> <sup>-3</sup> amine, N=C=S, OH, C-O	Freundlich	
2	<i>Aspergillus niger</i>	C=O, amine, C-OH, C-NH <sub>3</sub>	Freundlich	
3	<i>Aureobasidium pullulans</i>	C=O, C-H, amine, N-N=O, C=C-H	Freundlich	
4	<i>Aspergillus terricola</i>	C=C-H, C=O, C-OH, amine, C=N	Freundlich	[190]
5	<i>Cladosporium resinae</i>	C=C-H, COH, C=C-H C=C, N-N=O, CS-NH, C=S	Freundlich	
6	<i>Acremonium strictum</i>	C=O, CH <sub>3</sub> , C-NH <sub>3</sub> , C=C-H, C-Cl, C=N, C-O, COH	Langmuir	
7	<i>Phanerochaete chrysosporium</i>	C-O, C=C, C-Cl, amine, C=O, C=N, CS-NH, PO <sub>4</sub> <sup>-3</sup>	Freundlich	
8	<i>Paecilomyces variotii</i>	Amine, CC, CN, OH, PO <sub>4</sub> <sup>-3</sup> , C=S, OH	Langmuir	
9	<i>Aspergillus terreus</i>	-OH, -CH, N-H, C-O, P-O	—	[151]
10	<i>Pleurotus ostreatus</i>	NH and COOH	—	[153]
11	<i>Aspergillus niger</i>	-COOH, -OH, -NH <sub>2</sub>	—	[187]
12	<i>Arthrinium malaysianum</i>	-OH, C-O, C=O, -NO <sub>2</sub> , C <sub>x</sub> OH	—	[191]
BACTERIA				
1	<i>Bacillus marisflavi</i> and <i>Arthrobacter</i> sp	-OH, -NH acetamido group, amide bond, C=O of COO <sup>-</sup> , free phosphates, phosphate groups, -CN	—	[192]
2	<i>Klebsiella</i> sp.	-NH <sub>2</sub> , O-H, -CONH-, -COOH, C=C, -CH <sub>2</sub>	Freundlich	[141]
3	<i>Halomonas</i> sp. DK4	-OH, -CH <sub>2</sub> , N-H, P-O-C, C=O	Langmuir	[140]
4	<i>Bacillus cereus</i> Pf-1	-OH, -CH and -NH stretching, C=O, -COO <sup>-</sup> , -C-O and -C-N	Langmuir and Freundlich	[193]
5	<i>Sinorhizobium</i> sp. SAR1	N-H, O-H, C-O, P-O, C-H	Langmuir	[142]
6	<i>Pseudomonas aeruginosa</i> Rb-1 and <i>Ochrobactrum intermedium</i> Rb-2	-OH, -NH, S-H, C=C, carboxylic group, SO <sub>2</sub> O <sup>-</sup> , C-O, S=O, -C-C- and C-Cl,	—	[194]
7	<i>Bacillus cereus</i> IST105	O-H, N-H, C=C, P=O, C-O,	—	[195]
8	<i>Streptomyces werraensis</i> LD22	O-H or N-H, C-H, C-O	—	[196]
MICROALGAE				
1	<i>Spirulina platensis</i>	C=O, C-C, C-O-C, P=O groups, COO <sup>-</sup> , CH <sub>2</sub> and NHC(O) amid groups, Carboxyl groups	—	[197]

TABLE 2: Continued.

S/ no	Fungi	FUNGI Functional groups	Adsorption isotherms	References
2	<i>Chlorella miniata</i>	Carboxylate group, C-O, amide I and amide II, amino group, O-H and N-H, -CH <sub>3</sub> and $\text{>CH}_2$	Langmuir	[198]
3	<i>Chlorella miniata</i>	O-H and N-H, C-H, -CH <sub>3</sub> , COO-, P=O, C-O	—	[199]
4	<i>Spirulina platensis</i>	-OH and -NH, C=O, -C triple bond, C-H, carboxylate and phosphoryl groups	Freundlich	[161]
5	<i>Isochrysis galbana</i> ,	-OH, -COOH and C=O, -NH,	Langmuir and Freundlich	[162]
6	<i>Pediastrum boryanum</i>	-OH, -COOH, -NH, C-O, -CH <sub>3</sub> , C-OH, C-N-C,	—	[174]
7	<i>Lyngbya putealis</i>	-NH, -CH, -C≡N, and -C=C	—	[200]
8	<i>Scenedesmus</i> sp	N-H, O-H, C-H, -COOH, C-F, C-Cl, C-Br, C-O	Langmuir and Freundlich	[167]

spectroscopy analysis was carried out to obtain the characteristics of the functional groups and to identify the chemical bonds that played a significant role in the process of biosorption of chromium [141].

As a whole, the functional groups associated with the cell wall significantly vary from microorganism to microorganisms. In addition, existence of different functional groups such as amine, amide, carbonyl, and phosphate together in microbial cell widens the intracellular accumulation and extracellular adsorption of toxic heavy metal ions. Therefore, functional groups play pivotal roles in the removal of heavy metal ions from the solution and the mechanism associated can also be determined after knowing certain functional group involved in biosorption.

## 7. Conclusion

This paper reviews chromium biosorption by various microorganisms such as bacteria, fungi, and microalgae, as well as factors that influence metal removal and sorption mechanisms. Microbial remediation of Cr(VI) from the environment is one of the most viable and sustainable methods for reducing excess Cr(VI) levels in the environment. These microbes have evolved impressive mechanisms to preserve their homeostasis and resistance to heavy metals to thrive in such a toxic environment. The biosorption process is a microorganism-based technology that is cost-effective, safe, and simple to use for removing chromium from the water environment, and it has a lot of potential for future applications. Mechanisms involved in the biosorption process include transport across the cell membrane, complexation, ion exchange, precipitation, and physical adsorption. Metabolism-independent metal binding to the cell walls and external surfaces is the only mechanism present in the case of nonliving biomass. The biosorption capacity of biosorbents can be affected by the pH of the environment, temperature, contact time, biomass dosage, initial metal concentration, and other factors. Since, industrial wastewaters may contain more than one toxic heavy metal unlike laboratory solutions, simultaneous removal of many coexisting pollutants may be challenging. Hence, further research

on these topics is needed to take full advantage of microbial biotechnology in environments. [201]

## Data Availability

No data were used to support this study.

## Conflicts of Interest

The authors declare they have no conflicts of interest.

## Acknowledgments

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