



A Review On Bioremediation Of Chromium Toxicity From Environment.

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Introduction

Heavy metals refer to substances that occur naturally and that have high atomic weight with five times more density as compared to water. They are naturally found in earth's crust in respective oxidized versions. Sometimes due to natural calamities or due to anthropogenic activities, they come in contact with the biotic components of the environment and have a toxic impact. Heavy metals have a broad spectrum of applications in fields of agriculture, medicines, industries, technology, etc. Because of rapid urbanization and industrialization, the heavy metals are carried along with the effluents let out from industries and get into air, water and soil, as these act as a sink for these recalcitrant contaminants. The intensity of heavy metal toxicity depends on many factors like dose of the toxin, route of exposure, species being exposed to the toxin, age and gender of the individuals who are exposed, and their nutritional condition (Tchounwou *et al.*, 2012). Mercury, chromium, lead, arsenic, cadmium and other such heavy metals are greatly harmful to public health, as exposure even in low dosage to these toxicants can induce multiple organ failures in humans and have a deleterious impact on flora and fauna of the environment. Hence, they are considered as priority elements. Chromium and lead need to be remediated by environmental protection agency.

Toxicity of heavy metals

Nowadays, environmental contamination by heavy metals and its hazardous impact on

human health and nature are growing drastically. As heavy metals have been increasingly used, human exposure to these metals has skyrocketed. Heavy metals from foundries, mining, and other metal-based industries have prominently contributed towards polluting the environment (Ferguson, 1990; Bradl, 2005; He *et al.*, 2005). Heavy metal exposure may also occur due to some natural processes, like metal corrosion, soil erosion, leaching, evaporation of metals from water and deposition in soil, etc. (Nriagu, 1989).

On the basis of the need for heavy metals in biological functioning, these metals can be categorized into two types: essential and non-essential heavy metals. Despite their toxic nature and below their toxic threshold, some metals like Zinc, Selenium, Nickel, Molybdenum, Manganese, Magnesium, Iron, Chromium, Cobalt and Copper are very much essential in trace amounts for different physiological activities. Some metals are an integral part of enzymes. Inadequacy of these metals might lead to deficiencies (WHO, 1996). Non-essential metals such as Lithium, Boron, Gallium, Rubidium, Strontium, Cadmium, Mercury, Lead, etc. are toxic but are not required for biological functioning. The heavy metals are also known by the name of 'trace elements', for their very low concentrations (ppb range to < 10ppm) in different environmental matrices (Pendias & Pendias, 2001). Bio availability of the heavy metals impacts their toxicity. It is dependent on various physical parameters like

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temperature, solubility, etc., chemical factors like their speciation (ability to persist in different oxidation states), and biological factors like physiological adaptation, characteristics of species, interactions between trophic levels, etc. (Verkleji, 1993).

Heavy metal toxicity on humans

There are around thirty-five elements of public health concern owing to their residential and occupational exposure. Out of these, twenty-three are regarded as heavy metals. Some of these metals form an integral part of our environment and diet (Glanze, 1996). Heavy metals are called 'systemic toxicants' as they bring about damage of vital organs like brain, kidney, composition of blood and other vital organs. They do so because they are bioavailable and easily get partitioned in the tissues (Haq *et al.*, 2015). Depending on the duration of exposure, whether it is short-term or long-term, heavy metals cause damage to various extents. Long-term exposure leads to physical, muscular and neurological disorders that are progressive. Repeated long-term exposure can also lead to cancer (Järup, 2003). Symptoms of toxicity of heavy metals are usually non-specific and retrospective but are never early warning signals or prospective (Nriagu, 1988). Awareness and knowledge of heavy metals are extremely essential to take precautions against their excessive contact (Ferner, 2001).

Chromium

French chemist, Nicholas-Louis Vauquelin, discovered the heavy metal chromium in 1797. He hypothesized chromium as a distinct element. He isolated the oxides of chromium (Cr) from crocoite (PbCrO₄). In 1798, he was successful in isolating metallic chromium by reducing chromic oxide (Cr₂O₃) with charcoal. The new element that was formed was given the name 'Chroma' in Greek, meaning colour. In 1800, Tassaerat, a German chemist discovered that chromium was present in chromite ore (Guertin *et al.*, 2016). Since the time of its discovery, chromium has become a vital metal in industries for its broad spectrum of plating and coating applications (Papp & Lipin, 2000). A thorough knowledge of chemistry of chromium is essential to remediate the chromium which is released as a pollutant from industries.

Redox chemistry of chromium

Through strong bonds, chromium (III) reacts and thus forms various complexes with hydroxides. Chromium exists as Cr (OH)₂⁻ at acidic pH levels 2 - 6.3. Cr (OH)₃ is a dominating species from pH 6.3 to alkaline range of 11.5. At a pH more than 11.5, it exists as Cr (OH)₄⁻ form (Rai *et al.*, 1987). CrO₄²⁻ along with HCrO₄⁻ is the dominant species of Cr (VI). Naturally occurring chromium, as well as the anthropogenically released chromium, changes its oxidation state on alteration of redox condition of its environment. Cr (VI) is a powerful oxidizing agent along with being highly unstable. Its reaction with the available reducing agents is spontaneous in the environment (Rai & Szelmeczka, 1989). The organic content of the environment readily reduces Cr (VI) (Bartlett, 1991; Schroeder & Lee, 1975). Consequently, Cr (VI) gets converted into Cr (III). Since the hexavalent to trivalent chromium couple has high redox potential, very few oxidizing agents like dissolved oxygen and manganese in nature enable Cr (III) to get oxidized into Cr (VI). But it is an extremely slow reaction according to a study (Schroeder & Lee, 1975).

Natural source of chromium

Chromium never occurs in nature in its elemental form. Fe₂Cr₂O₃ is a major commercial chromium mineral. The statistical review of worldwide trace elements emissions from natural sources estimates that chromium from windblow will have emission factors of 100 mg/kg of chromium windblown dust and 390 mg/kg of chromium volcanic particles (Pacyna & Nriagu, 1988). The varying concentrations of chromium in different soils and rocks influence the atmospheric emission of chromium (Påhlsson, 1989). Chromium is involved in processes at air-sea interface (Buat-Menard & Chesselet, 1979). Fortunately, very less amount of chromium present in soil or water will be in equilibrium with air. Else, the entire earth's chromium could have got oxidized to toxic chromium (VI). Small concentration of chromium in soil is due to oxidation of trivalent chromium. But chromium pollution in soil is mostly from anthropogenic source. Chromium cycle is a very slow cycle. The stagnation of chromium as Cr (III) or activation of chromium as Cr (VI) is dependent on redox..... conditions and solubility of Cr (III). Simultaneous



oxidation and reduction are a unique feature of chromium cycle in soil (Bartlett, 1991). Chromium that is added to soil or water has the tendency to persist latently unless it is removed by processes like adsorption, leaching or precipitation (Bartlett, 1991; Ross *et al.*, 1981). Chromium enters the biological membranes of plants, microbes or humans as Cr (VI) which is toxic in high doses.

Anthropogenic source of chromium

Chromium utility and toxicity at the same time is a tricky situation to handle. The chemical properties that make chromium as an important industrial choice over other heavy metals, control its environmental fate and toxicity (Barnhart, 1997). Chromium and compounds of chromium have a broad spectrum of applications in industries, and hence, their excessive use contributes greatly to the burden of chromium in the atmosphere. Chromium finds applications in both hexavalent and trivalent forms in various industries. The toxicity of the hexavalent version of chromium is 100 times more than its trivalent version, as it is highly soluble. Since hexavalent chromium is an extremely good oxidising agent, it is used in leather processing (Pacyna & Nriagu, 1988). It is used in industries that deal with chemical and refractory processing, cement manufacturing industries, ore refining, brake lining and automobile catalytic converters, electroplating clearing agents, cooling tower water treatment, and wood preservatives. The effluents of these industries are laden with chromium and its compounds (Kotaś & Stasicka, 2000). Around 40% of the total chromium use for industrial purposes is contributed by the leather industry (Barnhart, 1997). The metallurgical industries consume 67% of chromium, refractories use about 18% and chemical industries utilize about 15% of the chromium produced (Saha *et al.*, 2011). Chromium is not originally hexavalent. When chromium is subjected to high temperature for melting or welding, it undergoes oxidation to be converted to hexavalent state.

Chromium pollution from electroplating effluents

Electroplating refers to a process wherein a layer of metal coating is deposited on an object. In this process, an electric current is passed through a solution that consists of dissolved

metal ions and the metal object required to be plated. In an electrochemical cell, the metal that needs to be coated acts as cathode that attracts metal ions from solution. The electroplating industries generate a lot of liquid wastes as effluents which are both acidic and alkaline in nature. The acidic effluents are laden with chromium and other heavy metals, while the alkaline effluents contain heavy metals and calcium chloride. The sludge from electroplating industries is rich in chromium (Gomes & Asaeda, 2009). Electroplating effluents carry significant quantities of chromium. To comply with the safety standards of environmental agencies, the effluents need to be treated so that the toxicity of chromium can be brought down.

Chromium toxicity

The oxidation state of chromium reflects the toxicity of the chromium compound. Elemental chromium and Cr (III) have the features of being stable and non-toxic, while Chromium (VI) has the features of being highly toxic and unstable. Chromium (VI) is very mobile in environmental compartments like soil and groundwater, as it is highly soluble; once chromium enters the environmental matrices in hexavalent form, it dissipates into several ecosystems where it undergoes speciation (Dahab *et al.*, 1990). When hexavalent chromium is in the form of chromates, it is structurally similar to phosphates and sulphates of the physiological system. Because of this molecular mimicry, in the cell membrane, they easily enter the cells through sulphate transporters (Ksheminska *et al.*, 2005). Chromium is considered as class A carcinogen and is identified as the most hazardous among 17 chemicals hazardous to human and environmental health, thereby creating a pressing need to remediate chromium and minimize the risk (Zhitkovich, 2011). Beyond permissible limits, it is reported that chromium causes a number of environmental and health hazards (Ullah *et al.*, 2018; Bakshi & Panigrahi, 2018).

Permissible limits of Chromium

World Health Organisation, Environmental Protection Agency (EPA), and other such world organisations have imposed a strict regulation by specifying permissible limits of chromium. If an exposure level goes beyond this limit, it is considered toxic to life forms. This is shown



below:

Sl. no.	Environment component	Chromium levels (ppm)
1.	Primary Drinking Water Standard	0.1
2.	Soil	1- 1,000
3.	Livestock Water	1
4.	Surface Water	0.05
5.	Industrial effluents	2
6.	Sewage Sludge	3000

The acceptable guideline value of chromium is 0.05 mg/L as stated by the World Health Organisation (WHO). According to OSHA (Occupational Safety and Health Administration), 5 µg/m³ for an 8 hour time-weighted average is the permissible exposure limit for hexavalent chromium and for all hexavalent chromium compounds. As per the regulations of NIOSH (National Institute of Occupational Safety and Health), 15µg Cr (VI) /m³ is the IDLH (immediately dangerous to life or health) condition for chromate and chromic acid (Eller, 1994). The recommended exposure limit of Cr (VI) compounds as per NIOSH is 0.2mg Cr (VI) / m³ on a time-weighted average of 8 hours. The new Threshold Limit Value (TLV) for chromium and its compounds, according to the American Conference of Governmental Industrial Hygienists (ACGIH), is 0.002mg/ m³; for inhalable hexavalent chromium compounds, the short term exposure limit (STEL) is 0.0005 mg/ m³.

Analytical techniques for chromium estimation

A number of techniques are employed for the purpose of detecting chromium at trace levels as low as 0.001 mg/kg. Some important ones are Flame atomic absorption spectroscopy (FAAS), Atomic absorption spectroscopy (AAS), Inductively coupled plasma techniques, such as ICP, etc. Biochemical estimation using diphenyl carbazide assay is a cost-effective alternative to analytical technique. In an acidified medium, diphenyl carbazide reacts with hexavalent chromium to turn into a deep pink coloured complex, the absorbance of which is read at 540 nm using a spectrophotometer. Selection of a method is based on its versatility, cost effectiveness, and application feasibility on a large scale.

Kinetics of chromium a Eco kinetics of chromium

In the atmosphere, chromium always exists in particulate form, and very rarely it is found in gaseous form (Cary, 1982; Kimbrough *et al.*, 2010). The size and density of the particulate matter determine its transport in the environmental matrix. In urban areas, owing to the pollution, deposition of particulate matter on land is more. The chromium aerosols released from industries have the ability to remain airborne for around 10 days and can be subjected to large- range transport (Kimbrough *et al.*, 2010). It is unlikely that the chromium compounds get transported from water to the atmosphere except transport by sprays that are windblown, due to the non-volatility of these compounds. Chromium that is released into water will finally deposit as sediment. In water column, very less amount of chromium is found in both soluble and insoluble forms. In an aquatic system, Cr (III) is bound to organic matter (King, 1988). Since Cr (III) is bound, it is not bioavailable, and hence, will not magnify in the food chain of the aquatic system. Biomagnification of Cr (III) is not evident along terrestrial food chain (Cary, 1982). In soil, the mobility of chromium depends on its speciation. Here, Cr (III) is mostly found that is stable. Upon the occurrence of oxidising conditions, Cr (III) gets transformed into Cr (VI); and in hexavalent form, Cr(VI) has much solubility and mobility, while Cr (III) has no mobility (Lin *et al.*, 1996; Robson, 2003). Chromium leaches from soil by the formation of insoluble complexes. Chromium mobility increases when there is a flooding of soil and anaerobic decomposition of plant materials. Chromium that is irreversibly adsorbed onto soil will not be bioavailable. Chromium that is unadsorbed leaches into groundwater, and thus, it increases the pH of the soil.

b Toxicokinetics of chromium

The nature of the ligands of chromium atom and its valence state determine the toxicokinetics of compounds of chromium. Exposure to chromium may be of two types — occupational or non-occupational. *Toxicokinetics of chromium* exposure by ingestion of chromium is non- occupational, which is usually via intake of food and water, while the exposure that takes place through inhalation is occupational (Langard & Vigander, 2008).



Occupational exposure of industrial workers to chromium is of prime concern, as they come under high-risk category (Guertin *et al.*,2016). Both occupational and environmental exposures to chromium cause multiple toxicities as it enters the human body (WHO, 1996).

Less water-soluble compounds get deposited in lungs, and their retention time is more than their soluble forms. Once it is absorbed, chromium gets circulated in all tissues. Liver and kidney have the highest concentration of chromium deposit. Bone is also a rich depot for retention of chromium. Chromium that is absorbed by mother is transferred to the foetus via placenta and later passed to infant via breast milk. Excretion of chromium from the system is predominantly through urine. Elimination of chromium can also occur by deposition of chromium in hair or nails. Chromium causes various health effects once it enters the human system (Guertin *et al.*,2016).

Various Effects on Humans

A) Gastrointestinal effects:

The gastrointestinal mode of absorption is usually < 10% of the ingested dose. Cr (VI) gets converted into Cr (III) in the stomach, and thus, it leads to decreased levels of Cr (VI) absorbed in the body. The chances of absorption of Cr (VI) are higher when dietary intake is lower. In humans, severe exposure to harmful doses of chromium orally results in adverse gastrointestinal effects, like nausea, ulcers, necrosis, abdominal discomfort and pain, hemorrhage, and diarrhea (Guertin *et al.*,2016).

B) Dermal effect:

Some individuals are very sensitive to chromium and its compounds. It triggers allergic reactions, resulting in severe redness and also swelling of the skin. Construction workers inhale chromium present in cement and usually develop dermatitis. The most commonly encountered forms of chromium in tanning and electroplating industries are chromic acid and alkaline chromate. These are corrosive, and when they gain entry into the skin through mild cuts or wounds, the exposure results in the formation of chromic lesions which are ulcerative and are called chrome holes. These lesions occur on fingers, hands or forearms and the dorsal side of the feet (Guertin *et al.*, 2016).

C) Immunological effect:

Hexavalent chromium sensitises the individuals and triggers a cascade of allergic reactions. The sensitisation can be by Type I (immediate Ig E mediated) or Type V (delayed type hypersensitivity). Subsequent exposures trigger dermatitis and asthma (Guertin *et al.*,2016).

D) Hematological effects:

Cr (VI) accumulates in RBC. When chromium enters RBCs, it rapidly reduces to Cr (III) via reactive intermediates. where it hooks to hemoglobin other ligands. The stable chromium-hemoglobin complexes are sequestered within the RBCs and remain so till the end of lifespan of RBCs. It results in microcytic hypochromic anemia, which is indicated by mean cell volume (Guertin *et al.*, 2016).

E) Reproductive effects:

Chromium causes adverse reproductive effects. It increases morphologically abnormal sperms, decreases sperm count and sperm motility. It causes complications in women during pregnancy and childbirth.

F) Ocular effects:

If industrial workers are exposed to chromium and there is a direct contact of chromium (VI) with eyes, cornea gets affected, and it will result in conjunctival discharge and burns (Guertin *et al.*,2016).

G) Genotoxic effects:

Conversion of Cr (VI) into Cr (III) leads to the creation of free radicals and reactive intermediates that form adducts with DNA and protein, thereby bringing about genotoxicity. It induces DNA strand breaks and chromosomal aberrations (Guertin *et al.*,2016).

Significance of chromium remediation

Since chromium and its compounds are toxic and have a deleterious impact on environmental health as well as health of mankind, there is a need to detoxify chromium by remediating it. Since chromium (VI) is toxic and soluble, it gets partitioned into environmental matrices and enters the food chain, thereby having its deleterious impact across the different strata of food chain. Since chromium has a vast industrial application because of its oxidising



nature, the atmospheric burden of chromium from anthropogenic sources is very high. Since chromium is highly soluble, the contamination from effluents has a major impact on the ecosystem. When Cr (VI) gets converted into Cr (III) in the anthropogenic contaminants released into the environment, it is beneficial to the environment, as chromium (III) is non-toxic unlike Cr (VI) (Madhavi *et al.*, 2013). There are various techniques to remediate chromium and its compounds. A technique is considered feasible to be applied if it is cost-effective, user-friendly and eco-friendly without causing any other damage to the ecosystem or to human health. There are various conventional techniques that can be employed to remediate chromium (Madhavi *et al.*, 2013).

Treatment technologies for Chromium and Lead remediation

The effluents from the industries are subjected to various treatment technologies that are employed to reduce the chromium and are proved to be successful. The choice of treatment technology is based on the site-specific condition and nature of the contaminant. A thorough knowledge of chromium chemistry, its state of occurrence in the contaminant, behaviour of chromium in that particular environment is needed to address the remediation of chromium (Madhavi *et al.*, 2013). These treatment technologies can be classified based on the approach of treating chromium. These are as follows:

Chromium and Lead removal technique

This is a technique by which the chromium will not be reduced but physically removed from the effluents (Hawley *et al.*, 2004). This technique aims at removing the chromium as such from the effluents being treated, but it does not reduce or detoxify the chromium. The chromium and lead will be either precipitated or filtered by various techniques. These techniques pave the way for secondary contamination where the chromium being separated from the effluents needs to be further treated before disposal (Madhavi *et al.*, 2013).

A) Membrane filtration

A membrane is a semi-permeable barrier that is designed to control the traffic of molecules

between two phases across it in a specific manner. The movement of molecules across a membrane is dependent on the size, diffusion co-efficient, charge, and solubility of the molecule. The membranes that are employed can be either ultra-filters or nano filters (Madhavi *et al.*, 2013).

B) Ultrafiltration

It employs a membrane that is permeable to separate the macromolecules of heavy metal contaminants and other solids from the inorganic industrial effluent. The substances get separated based on the size and molecular weight of the compound. The main advantage of using ultrafiltration is that it provides a driving force of low intensity and a small space because of its high packaging density (Vigneshwaran *et al.*, 2005).

C) Nanofiltration

Nanofiltration is a reliable, advantageous, easily operable, low-energy consuming technique used for heavy metal and other pollutants removal. The separation mechanism of nanofilters is the electric effect between the membrane and the ions that co-exist in the effluent to reject the ions existing in the effluent (Religa *et al.*, 2011). Even at very low pressure, the efficiency of separation of molecules is very high in case of nanofilters, and thus, it is considered as the best technology of all the other membrane systems (Muthukrishnan & Guha, 2008). Though nanofiltration is very beneficial for filtering drinking water as well as industrial waste waters, it has its drawbacks and limitations when applied on a large scale. It is difficult to prevent the passage of solute particles across the membrane. The lifespan of the membrane is limited. The rate at which the pollutants are rejected is low, and there is always a need for simulating tools.

D) Ion Exchange resin

Ion exchange resin refers to a physical technique in which an ion having a lower affinity that has previously been bound to the resin gets replaced with an ion having a higher affinity for the resin of the ion exchange column. For the separation of chromium from industrial waters, as water flows through the ion exchange column, the hexavalent chromium ions get bound to the ion exchange resin, displacing the previously bound chloride or



hydroxyl ions. The resin that is used to sequester chromium is either natural or synthetic. Once the resins are saturated with chromium accumulation, they need to be regenerated. The main advantage of employing ion exchange resins is that they are effective in removing chromium, which is even less than the detection limits. At the same time, they have some practical disadvantages, like they contribute to the secondary contamination, are not very cost-effective, and need to be stored and disposed of (Rengaraj & Moon, 2002).

E) Granular activated carbon

In order to eradicate heavy metals and other organic contaminants from wastewater, a common technique of granular activated carbon is used. Granular activated carbon has a vast internal surface area of around 1000 m²/g. Hexavalent chromium gets adsorbed onto granular activated carbon by electrostatic force of attraction, which is in turn pH dependent. The main disadvantage of using granular activated carbon is that it is dependent on pH, and prior treatment of the effluents with chemical is a prerequisite to lower the pH which is not eco- friendly. Also, while the granular carbon is regenerated, it slowly releases the adsorbed contaminant that is not safe. (ATSDR, 2008)

Toxicity reduction methods

These are the methods wherein the hexavalent chromium gets converted into a trivalent form. Based on the means of chromium reduction, the toxicity reduction methods are further classified into chemical methods and biological methods (Madhavi *et al.*, 2013).

A) Chemical reduction

The technique of chemical reduction is non-biological or abiotic method of reducing chromium in the contaminated effluent. The notion behind this is the redox reaction of chromium from hexavalent to its trivalent form by electron donors, such as Sulphur, Fe (0) or Fe (II). The Cr (III) thus formed is precipitated out of the solution. Both reduction and removal of chromium prevalent in aqueous solution are achieved by this mechanism (Qin *et al.*, 2005).

B) Bioaccumulation

Some living cells are innately capable of taking up heavy metals and accumulating them in

their cells. The cells take up toxicants either actively by intracellular mechanism or passively by extracellular mode. This active and passive process of intake is referred to as bioaccumulation. (Hughes & Poole, 1989). In some microbes, both essential and non-essential metals can be accumulated (Cooksey & Azad, 1992).

C) Biosorption

This is the most dependable and cost-effective method of removing heavy metals from a contaminated source. In order to eradicate heavy metals from the contaminated site, both living or dead biomass can be used. Spirulina is used as a natural bio adsorbent of chromium (Rezaei, 2016). Pistachio hull waste is used as biomass to adsorb chromium (Moussavi & Barikbin, 2010). *Opuntia* biomass is used as an adsorbent to remove chromium (Fernández *et al.*, 2014).

D) Biotransformation

Biotransformation is a process where the living cells take up toxic heavy metal and convert it into non-toxic form by various intracellular and extracellular processes. *Serratia sp* has the ability to absorb and bio transform hexavalent chromium which is toxic into trivalent form which is non-toxic (Srivastava & Thakur, 2007). Some organisms, like *Pseudomonas fluorescens* LB 300, take up hexavalent chromium and reduce it (Desjardin *et.al.*, 2002).

E) Phytoremediation

Phytoremediation involves using live plants for *insitu* degradation or removal of contaminants found in sludge, sediments, soil, surface water, and groundwater. It is an economical technique, as solar energy is used for clean-up. There are five different techniques of phytoremediation (Madhavi *et al.*, 2013).

F) Phytostabilisation

When the toxic heavy metals are absorbed by plant roots or adsorbed onto the surface of the roots, it is referred to as phytostabilisation. On absorption, certain biochemicals are released by these plants into the soil and groundwater present in the immediate surrounding area of roots, which will naturally sequester, precipitate or immobilise nearby contaminants. Phytostabilisation is considered to be a



suitable, economical and eco-friendly technique to remediate trace elements (Aguado *et al.*, 2015). Various plants are found to possess the innate ability to phytostabilise chromium. *Cynodon dactylon* and *Pluchea indica* accumulate a very high content of 152 mg/kg of chromium at an input of 100mg/kg of soil. The uptake is noticed within the span of 30 days (Sampanpanish *et al.*, 2006).

G) Rhizodegradation

This is a process that occurs around plant roots in the soil and also groundwater. The rhizosphere bacteria are stimulated by exudates from plants to facilitate biodegradation of soil contaminants. Rhizodegradation is used for wastewater remediation by aquatic or terrestrial plants (Henry, 2000). Terrestrial plants that are capable of rhizodegradation are rye, sunflower, tobacco, and mustard. Rhizodegradation is more commonly used for Zn, Ni, Cu and Cr, which are primarily retained in roots (Chaudhry, 1998). It has been used to remediate groundwater containing chromium (Emsley, 2011). The major advantage of this technique is its applicability to multiple metals. But the disadvantage is that the plants that are used to remediate need to be grown first in greenhouses, hardened, and then introduced in the contaminated area to be bioremediated.

H) Phytoextraction (phytoaccumulation)

With the help of their roots, plants sequester the contaminants and then store them in their stem or leaves. On harvesting the plants, the contaminants are removed from the environment, but not necessarily degraded. This is an extremely useful strategy for the eradication of metals from soil. In some cases, the plants are incinerated via a process called phytomining to recover the metals for reuse. The plants get affected by chromium toxicity. When plants are under stress, the microbes associated with plants will come to the rescue. *P. putida* (ATCC 39123) in *E. sativa* seedling significantly increased chromium uptake and plant growth (Kamran *et al.*, 2017). Some chelating agents like citric acid increased chromium accumulation in *Zea mays*.

(Prakash *et al.*, 2016). *Portulaca oleracea* (an indigenous plant of UAE) demonstrated high extraction of Cr (VI) from soil. (Alyazouri *et al.*, 2014). *Catharethus roseus* is effective for phytoextraction of chromium (Al-Anbari *et al.*,

2016).

I) Phytovolatilisation

Some plants are capable of taking up volatile compounds and gaseous metals. They put them back into the soil via their roots and release the absorbed volatile compounds or their metabolites into the atmosphere via transpiration through their leaves. Metals like Hg, As, and Se sometimes exist in a gaseous state in the environment. Some genetically modified plant species are capable of absorbing these gaseous metals and releasing them into the atmosphere (Vara Prasad & de Oliveira Freitas, 2003). But it is dangerous when the toxic gases like Hg and Se are released, and more research needs to be done (Wilber, 1980).

J) Phytodegradation

Some plants take up the contaminants into their tissues, where either the metabolisation or biotransformation of these contaminants takes place. The site of transformation varies on the basis of the plant type. This technique is more useful for removing organic compounds like petroleum and other aromatic compounds from the groundwater (Newman & Reynolds, 2004). Many questions regarding phytoremediation are still unanswered. More light needs to be thrown to understand the effect of various compounds on the entire ecosystem of which plants may be a part.

Bioremediation

Bioremediation involves the usage of biological agents to remediate the contaminants. Biological treatment of Cr (III) polluted wastewater has increased, as it is more efficient and cost-effective than other conventional physicochemical techniques. The bioremediation also circumvents the problem of secondary contamination of chromium removal conventional techniques. There are several microbes and plants that possess an innate ability to resist and /or detoxify the contaminant. The mode of removal by the biological agents can be bioaccumulation or biosorption or biotransformation. Bioremediation processes are both cost-effective and environmentally friendly (Fernández *et al.*, 2018; Sangwan & Dukare, 2018).

Microbial remediation of chromium

Removing chromium from the environment



using microbes is a very economical and feasible approach, as chromium can be naturally detoxified in an effective way, thereby causing very less harm to the environment (Jeyasingh & Philip, 2005). Chromium reduction in bacteria occurs both in aerobic and anaerobic conditions (Wang & Shen, 1995). To sustain in chromium-laden environment, the microbes presumably be innately resistant to chromium, and thereby harbour potential metabolic pathways to counter the toxic impact of chromium. Various chromium remediating bacteria like *Bacillus plumulis*, *Alcaligenes faecalis* and *Staphylococcus spp.* (Shakoori *et al.*, 2010), *Pseudomonas sp* (Jayalakshmi & Rao, 2013), *Bacillus subtilis strain PESA* (Tharanum *et al.*, 2012) occur in nature as depicted in Figure 2.1.

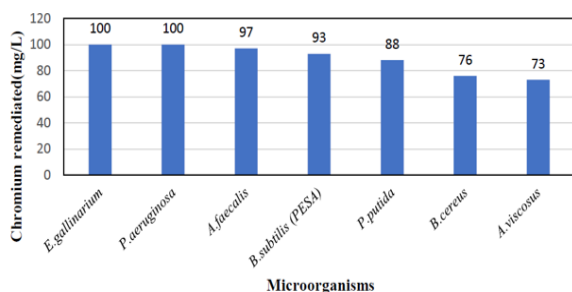


Figure 2.1 Graphical representation of chromium removal efficiency of various microorganisms

Various chromium-tolerant bacteria are capable of thriving in chromium-laden environments despite the stress induced by chromium. This is due to the different metabolic changes occurring in these microorganisms due to chromium exposure. Different mechanisms, as indicated in Figure 2.2, are present in various bacteria for reducing toxic chromium to its non-toxic version (Ahemad 2014; Yan & Chen, 2019). Schematic representation of chromium resistance and toxicology in a bacterial cell: (1) Due to its structural similarity with sulphate, chromate gets into the bacterial cell with the help of sulphate transporter encoded by the chromosomal DNA. (2) Plasmid DNA encoded efflux systems are employed so as to eject the intracellular chromates out of the bacterial cell, to resist chromate toxicity. (3) To reduce aerobic Cr⁶⁺ into Cr³⁺ soluble reductase is used which requires NAD(P)H as an electron donor while anaerobic Cr⁶⁺ reduction occurs in the electron transport pathway by cytochrome b

(cyt or cytochrome c (cyt c) along the respiratory chains in the inner membrane; As Cr³⁺ derivatives are insoluble, Cr³⁺ cannot pass the bacterial cell membranes. (4) Membrane- embedded chromate.

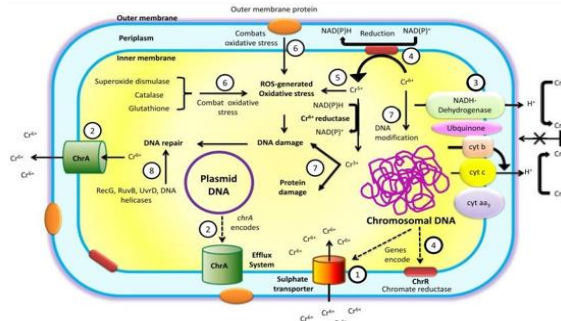


Figure 2.2 Schematic depiction of chromium resistance and toxicology in a bacterial cell

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