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A review of chromite mining in Sukinda Valley of India: impact and potential remediation measures

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ABSTRACT

Sukinda Valley, one of the highly polluted areas of the world is generating tons of mining waste and causing serious health and environmental issues in its surroundings. Several reports are available reporting the severity of hexavalent chromium, yet little efforts have been made to address the pollution and its remediation due to a lack of proper remedial measures. The review highlights the pros and cons of various physical, chemical and biological techniques used worldwide for the treatment of chromium waste and also suggests better and reliable bioremediation measures. Microbes such as *Acidophilium* and *Acidithiobacillus caldus* (Bioleaching), *Pseudomonas, Micrococcus* and *Bacillus* (Bioreduction), *Aereobacterium* and *Saccharomyces* (Biosorption), are widely used for bioremediation of hexavalent chromium owing to their unique metabolic activities, ionic movement through an extracellular membrane, and other cellular adsorptions and reduction properties. The use of native and hybrid combinations of microbes supported by organic supplements is projected as a fast and efficient technique that not only reduces chromium quantity but also maintains the integrity of the microbial sources. Innovation and emphasis on nano-based products like nanocomposite, nano adsorbent, nanoscale zerovalent iron (nZVI) particles and multifunctional plant-growth-promoting bacteria (PGPB) will serve as the next generation environmental remediation technologies in the near future.

Introduction

Mining is one of the most ancient practices carried out across different parts of the world since the growth of human civilization (Hartman and Mutmansky 2002). With ever-increasing demands for minerals and advances in ore-extraction techniques, it had only escalated with times. Currently, mining activities cover more than 2% of the earth's surface in the form of opencast and underground mining (Coelho *et al.* 2011). Mining can be considered as a "Necessary Evil" as on one side it provides several benefits like employment, raw materials for industries, petroleum, natural gas, petrochemicals, and precious metals/stones, but is also a significant source of environmental pollutions, adverse health effects and biodiversity loss (Jaishankar *et al.* 2014). The use of nonscientific mining activities has further added to its severity leading to degradation of land, disturbance of water table, topographic disorder, and alteration to land use patterns in and around mining sites (Bridge 2004; Saviour 2012).

Chromium is a vital metal occurs significantly in the earth's crust, and in trace quantities ($<1,000 \mu g \ g^{-1}$) on rocks and soils surface. Naturally, chromium occurs in water as a result of weathering and erosion processes or even due to windblown dust particles. Chromite, the core ore of the element chromium is an oxide of chromium (Cr) and Iron (Fe) containing about 68% of Cr_2O_3 and 32% of FeO with Cr to Fe ratio of about 8:1. Thus, Cr_2O_3 is the major ore mineral of chromium and is an accessory phase in many ultramafic rocks (Matrosova *et al.* 2020). As per the World Mining Data, the world's chromite production is about 13 billion metric tonnes, enough for human usage for hundreds of years (Reichl *et al.* 2016). Currently, mining activities cover more than 2% of the earth's surface as opencast and underground mining, of which 90% of the resources are in South Africa, Kazakhstan, Turkey, India, and Finland as shown in Figure 1a (Coelho *et al.* 2011). India, with a geographical area of about 328 million hectares has 0.14% of its land use for mining activities (Ministry of Mines 2017). India ranked 4th in terms of volume of production from mining sources and stands 3rd for the production of chromate ores in the world (Soni and Vyas 2015).

Sukinda Valley in Odisha of India produces about 99% of the total chromite ores of the country. Karnataka contributes 0.6%, while states like Nagaland, Manipur, Maharashtra, Jharkhand, Tamil Nadu, and Andhra Pradesh cumulatively for the rest of 0.4% (Indian Bureau of Mines 2016) (Figure 1b). The Sukinda Valley spread in over $200 \ km^2$ holds an estimated 183 million tons of raw chromium deposits (Das *et al.*
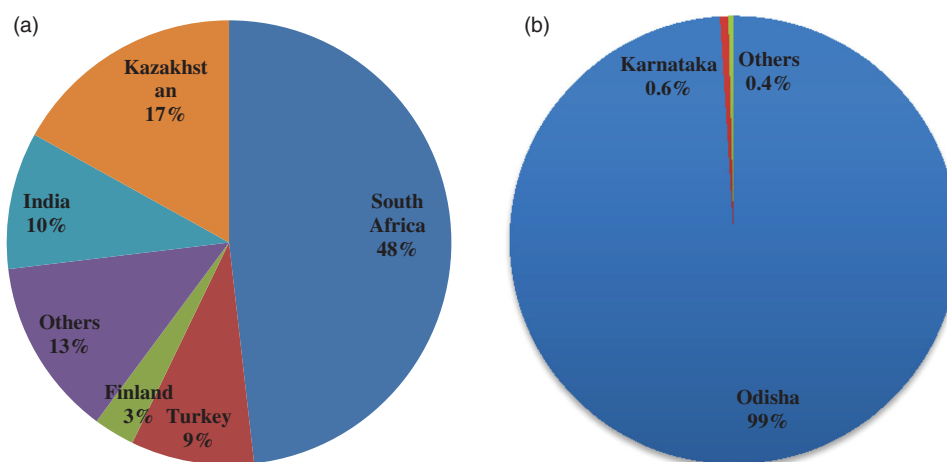
Figure 1. (a) Country-wise chromium production (%) during 2016–17 (U.S. Geological Survey, 2018), (b) Chromium production (%) in India during 2016–17 (Indian Bureau of Mines 2016).

Table 1. Occurrence of chromium and its industrial applications.

Forms of Cr	Sources	Applications	Ref.
Cr(0)	Does not occur naturally	Primarily used in making steel and other alloys	(De Oliveira Andrade and Mattje 2012)
Cr(II)	$CrBr_2$, CrC_{I2}, CrF_2, CrSe, Cr_2Si	Used in chromizing and in the preparation of chromium metal and internal medicine	(Choppala et al. 2013)
Cr(III)	CrB, CrB_2, $CrBr_3$, $CrC_{I3}.6H_2O$, CrC_{I3}, CrF_3, CrN, $KCr(SO_4)_2$ $12H_2O$, $FeCr_2O_4$	Widely applied in tanning, green paints, inks, text dyes, and ceramics	(Zayed and Terry 2003)
Cr(IV)	CrO_2, CrF_4	Data tape applications for enterprise-class storage systems and magnetic tape emulsion	(De Oliveira Andrade and Mattje 2012)
Cr(V)	CrO_4^{3-}, KCr_3O_8	Mutagenic and carcinogenic agent	(Zayed and Terry 2003)
Cr(VI)	$(NH_4)_2CrO_4$, $BaCrO_4$, $CaCrO_4$, K_2CrO_4, $K_2Cr_2O_7$, $PbCrO_4$. Wolman compounds from NaF and $C_6H_4N_2O_5$ with $Na_2Cr_2O_7/K_2Cr_2O_7$, $CrCuO_4$, copper–chromium–arsenic (CCA) formed by combining $CuSO_4$, $Na_2Cr_2O_7$ and As_2O_3, composites of copper–chromium–boron (CCB), copper–chromium–fluoride (CCF) and copper–chromium–phosphate (CCP)	Used as preservatives for chrome plating, wood, leather and as coolant	(Saha and Orvig 2010)

2013). Currently, 20 opencast and two underground mines are operational in the valley generating about 160 million tons (MT) of overburden. It also releases 11.73 tons of Cr(VI) to the environment every year, making it the fourth-worst polluted places in the world. Chromium mining in Sukinda Valley had, therefore, resulted in major biodiversity loss and severe health impact for locals human population inhabiting around the belt (Dhal et al. 2011; Mishra and Sahu 2013; Biswas et al. 2017; Das and Singh 2011; U.S. Geological Survey (USGS) 2015).

Chromium is an industrial metal used in the manufacturing of stainless steel and metallurgy, chemical processing and several other commercial products (Table 1). However, considering its large-scale release to the environment and the fact that it is also a hazardous material causing numerous health disorders, an adaptation of proper remediation measures is the need of the hour. Hence, the study is an attempt to underline the impact of chromium on human health around Sukinda Valley, in India and highlights some of the potential bioremediation techniques.

Chromite pollution

There are about 35 metals found on Earth, of which 23 are heavy metals. Chromium can be found in six different forms and is readily released to the environment. It is of immense concern for human health due to their residential or occupational exposure (Jaishankar et al. 2014). The most significant and hazardous impact of chromium is from the mining projects. It affects the soil, air and water resources within the mining sites through acid drainage, erosion of soils and mine wastes, and contaminant leaching (Sharma et al. 2012). Chromium enters the ecosystem through anthropogenic activities such as untreated industrial discharge, dumping of solid waste, electroplating, dye, and pigment manufacture, wood preservations, refractory wastes solar cells, and leather tanning industries, etc. (Sharma et al. 2012). The generation of chromium and its presence in different ecological niches (Air, water and soil) around Sukinda along with their permissible limits set by various health agencies across the globe are listed in Table 2. The potential hazardous impacts

Table 2. Chromium concentration in Sukinda Valley and their permissible limits.

Components	Maximum permissible limits of Cr	Observed Chromium conc. in Sukinda Valley	Units	References
Air	100 as Cr and 10 in an insoluble form	130	µg m^{-3}	(Ministry of Mines, Government of India 2013)
Dust (Work zone)	120	20000		(Ministry of Mines, Government of India 2013)
Workplace	10	52–187		(WHO 2012; Mishra et al. 2016)
Fresh water	0.0001–0.05	5–11	mg l^{-1}	(WHO 2012)
Ground water	<0.001	0.023–1.35		(WHO 2012)
Surface water	0.001–0.01	0.012–3.4		(Mishra and Sahu 2013; Naz et al. 2016)
River water-sediment	200	30–104		(Ministry of Mines, Government of India 2013)
Soil	10–50	47	mg kg^{-1}	(Ertani et al. 2017)
Paddy fields soil segments	350	6–190		(Ministry of Mines, Government of India 2013)
Paddy	1	0.001–142		(Ministry of Mines, Government of India 2013; Qu et al. 2015)
Fish	0.15	3–37.93		(WHO 2012)
Milk	0.01	<0.001–0.69		(Ministry of Mines, Government of India 2013)
Fruits and vegetables	2.3 (dry weight)	5–28		(Eslami et al. 2007; Ministry of Mines, Government of India 2013)
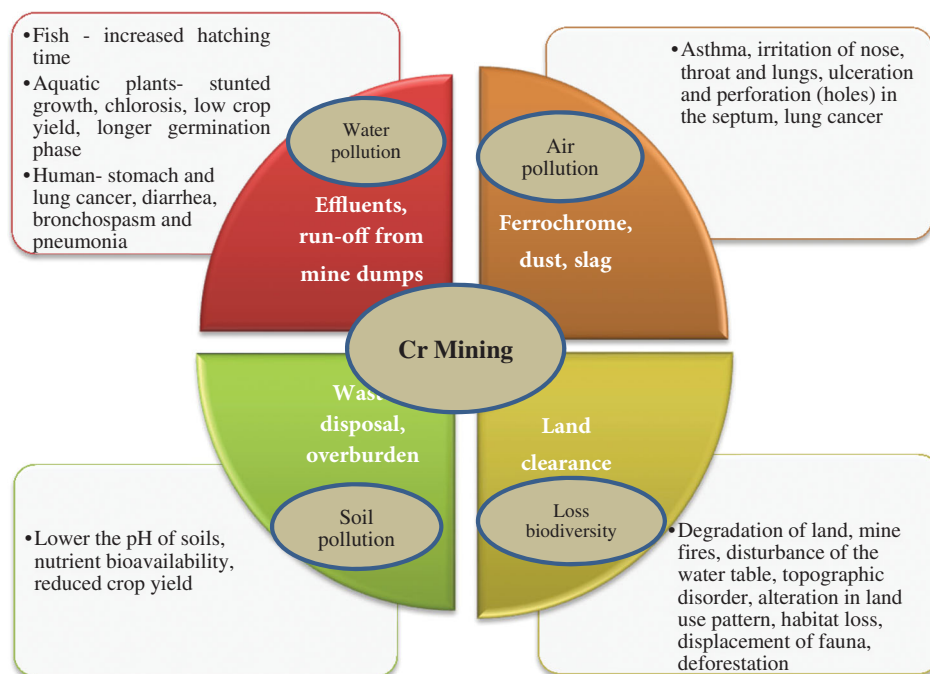
Figure 2. Various environmental impacts of chromite mining.

of toxic Cr forms on all aspects of biodiversity are described in Figure 2.

Chromium in all of its forms is highly toxic and is associated with several diseases in humans and plants. Cr(VI) causes respiratory and mucous irritant related diseases and disorders that include irritation of nose and throat, asthma, ulcer in lungs, and perforation (holes) in the septum. The minimal exposures about 0.09–2 µg m^{-3} of Cr can cause ulcers, septal perforations, and reversible impairment of lung function (WHO 2012; Ertani et al. 2017).

Workers in mines and Cr-based industries are exposed to airborne Cr(VI) with high exposures frequently occurring via inhalation and dermal contact (Ashley et al. 2003). The Odisha Voluntary Health Association reported that 86.42% of deaths in villages surrounding Sukinda Valley are results of excess exposure to Cr(VI) (Das and Singh 2011). While the presence of Cr in the atmosphere is a serious issue,

pollutants contaminating the water sources around Sukinda Valley, i.e., the Dharamsala and the Brahmani rivers regarded as more severe (Das and Singh 2011; Mishra and Sahu 2013).

The soil quality around the Sukinda Valley is slightly better than the other environmental variables (air and water). Chromium concentration in soil and segments of crop fields (paddy) in the valley was lower than their legitimate values of 47 mg kg^{-1} and 6–190 mg kg^{-1} (Ministry of Mines, Government of India 2013; Ertani et al. 2017). However, an elevated level of soluble Cr, bioavailable of Cr (III) and other forms can dent the soil quality and its infertility (Jaishankar et al. 2014; Reijonen and Hartikainen 2016).

Paddy grains from contaminated sites in the Sukinda region were reckoned to exceed the WHO recommended limit (1 mg kg^{-1}) by a margin of 16–740 mg kg^{-1}. Similarly, milk, fruits, and other vegetables were found to contain up
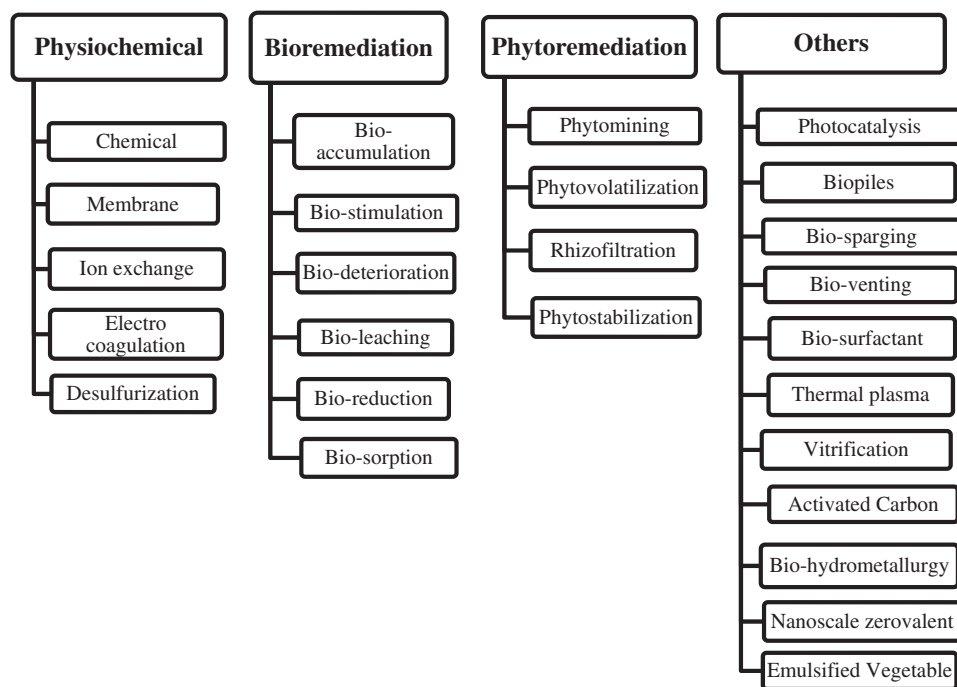
Figure 3. Flowchart representation of some of the most commonly used remediation techniques.

to 5 times higher amount of chromium than their consumable permits (<0.001–0.69 mg/kg for milk, 10–112 mg kg^{-1} for fruits and vegetables) (Eslami et al. 2007; Ministry of Mines, Government of India 2013). In plants, excess quantity of Cr is known to have an impact on plant's metabolism and development resulting in dwarf growth, chlorosis, low crop yield, deferred germination period, senescence, premature leaf fall, abrasion, alter enzymatic and biosynthesis production of growth hormones (Zayed and Terry 2003; Mohanty et al. 2009). Cr(VI) is also responsible for carcinogenic effects in human leading to ulcers in stomach and lung, and other health ailments like diarrhea, bronchospasm, pneumonia, skin irritation and gastrointestinal diseases (Dubey et al. 2001; Beaumont et al. 2008; Das and Singh 2011)

## Treatment methods for Cr (VI) pollution

To date, several methods or techniques had been developed to curb pollution caused by chromium. Some of the commonly employed techniques for treatment of Cr waste includes reduction precipitation (Enniya et al. 2018), membrane filtration (Yang et al. 2003), membrane ion exchange (Yang et al. 2014) biological adsorption and reduction (Sahinkaya et al. 2012) (Figure 3). Factors like the mobility, distribution, concentration, and speciation of chromium in the sources are known to govern the choice of the best-suited method for remediation of Cr (Zayed and Terry 2003).

Physical and chemical remediation processes though were once primarily used for reduction of Cr heavy metals, problems associated with it such as high capital investment and generation of large volume of secondary waste had restricted their use in recent times (Dhal et al. 2013; Pradhan et al.

2017; Xia et al. 2019). Physicochemical treatment technologie such as adsorption is quite implemented in many instances. However, various factors such as adsorbent characteristics and experimental conditions (equilibration time, solution pH, initial Cr(VI) concentration, ionic strength) play key role in determining the overall treatment efficiency (Islam et al. 2019). Biological remediation measures are time taking although; considering its eco-friendly approach and easy bioavailability of host sources, it is the first choice for chromium treatment. However, bioremediation is still a challenging technique and most studies remain at the laboratory stage to date (Xia et al. 2019). Some of the commonly employed biological approaches for remediation of Cr heavy metals are discussed in this section.

Bioleaching

Bioleaching is a biochemical process that uses both chemical substances and environmental microbes for the extraction of metal ions (Figure 4a). Conversely, with some modification, the process now involves the pretreatment of waste materials with acid and subsequently with iron- and sulfur-oxidizing microbes native to the sludge. Bioleaching can be achieved through direct leaching and indirect leaching. For direct leaching, non-soluble metal sulfides are oxidized to their water-soluble forms by chemolithotrophic bacteria while in the indirect route, elemental sulfur (S) is oxidized first to sulfuric acid by sulfur-oxidizing bacteria followed by the dissolution of metals by strong acid. The equations are as follows:
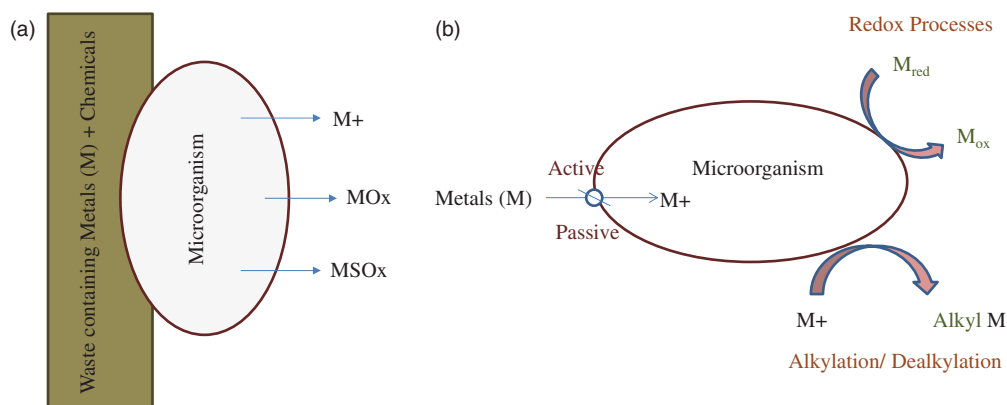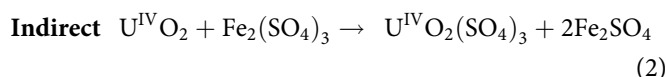
$$\textbf{Direct } 4F_eS_2 + 15O_2 + 4H_2O \xrightarrow{\text{Bacteria}} 2Fe_2(SO_4)_3 + 2H_2SO_4$$

$$(1)$$
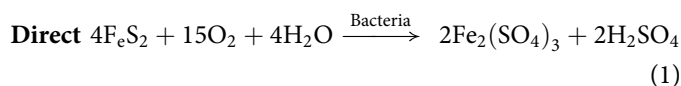
Figure 4. (a) Bioleaching of heavy metals by using microorganisms, (b) Microbial reduction of chromium.

Indirect $U^{IV}O_2 + Fe_2(SO_4)_3 \rightarrow U^{IV}O_2(SO_4)_3 + 2Fe_2SO_4$ (2)

Parameters that influence the leaching efficiency of Cr are contact time, slag/sludge composition, the concentration of competing ions, and type and concentration of leaching agents (Rastegar et al. 2014). Bioleaching of Cr heavy metal via Thiobacillus neapolitanus, Alicyclobacillus ferripilum, A. pomorum, A. ferrooxydans, A. aeris (Bharadwaj and Ting 2013), Acidithiobacillus thiooxidans, Bacillus sp. (Chen and Lin 2010), Clostridium sp., and Thiobacillus thioparus (Zeng et al. 2016) have successfully been reported for different forms of industrial waste.

Recent development has highlighted the use of mixture or hybrid combination of native microbial strains supported by organic supplementary as most competent for bioleaching processes (Pathak et al. 2008a; Dhal et al. 2013). These efficiencies by mixed or hybrid combinations are credited to the availability of diverse functional groups present in their cell walls and other metabolic cycles. Microbial bioleaching using Thiobacillus sp. and Acidithiobacillus thiooxidans had shown leaching efficiencies as high as 95% in a reducible fraction, and 60.9–97.9% in oxidizable and residual fractions (Zeng et al. 2016). Biosurfactant from plant sources like aescin and saponin in the aqueous medium is reported to have a catalytic effect in leaching of heavy metal from contaminated soil (Hong et al. 2002).

Bioreduction

Hexavalent chromium is regarded as more toxic compared to trivalent chromium as the former has a labile center and bears structural similarity with sulfate, thus can easily penetrate into the living cell. Further in solution trivalent chromium undergoes precipitation as hydroxide, but the hexavalent chromium due to its inert nature remains stable (Saha et al. 2011). Thus, the reduction of Cr(VI), which is highly water-soluble and mobile into a less toxic form is essential for reducing its harmful effects. Bioreduction of chromium can be defined as the process of breaking down of chromium molecules from its hexavalent Cr(VI) forms into less toxic trivalent (Cr III) state (Figure 4b). The traditional method was the treatment of Cr(VI) with acids followed by precipitation with alkaline ferrous sulfate, sodium

sulfite, sulfur dioxide gas or sodium bisulfite and are still in use in some studies (Barrera-Díaz et al. 2012; Lu et al. 2019). The reduction mechanism for chromium, (i.e.,) traditional, electrocoagulation and microbial are summarized in Table 3.

Although traditional and electrocoagulation reduction are quite successful in the reduction of Cr, primary constraints associated with the methods are a large amount of residual sludge, secondary pollutants, etc. Microbial bio-reduction is preferred over other reduction measures as they are saved to the environment, easy and requires less effort. It is carried out mostly by the enzyme chromate reductases ChrR and YieF commonly found in Aeromonas, Escherichia, Pseudomonas, Bacillus, and Enterobacter (Chen et al. 1998). The alkalic amino acids present at the loop of the enzyme provide sites for binding of NAD(P)H and chromate ions. Under aerobic condition Cr(VI) reduces to Cr(III) through a soluble reductase enzyme that serves as an electron donor for NAD(P)H. Whereas in anaerobic conditions, the reduction of Cr(VI) takes place during the electron transport pathway of cytochrome (Cyt B & C) along the respiratory chains inside the intracellular membrane of the microbial cells (Ahemad 2014).

In aerobic conditions, ChrR catalyzes the reduction of Cr(VI) in two or three stages. Initially, a one-electron shuttle reduces Cr(VI) to a short-lived intermediate of Cr(V) or Cr(IV) followed by a two-electron transfer to reduce it to the thermodynamically stable product Cr(III). The reductase YieF from E. coli reduces Cr(VI) directly to its trivalent form by transferring four electrons, wherein three electrons are used up in reducing Cr(VI), while one electron is added to oxygen to produce hydrogen peroxide through hydrogen bonding (Chen et al. 1998; Ackerley et al. 2004; Zou et al. 2013).

The anaerobic reduction of Cr is carried out by Sulfate-reducing bacteria (SRB) Desulfovibrio vulgaris. In this conditions, Cr(VI) serves as a terminal electron acceptor in the respiratory chain for a vast array of electron donors, including nitroreductase, flavoprotein, glutaredoxin, NAD(P)H and endogenous electron reserves (Ibrahim et al. 2012). Sulfide produced by cytochromes of SRB almost entirely reduced Cr(VI) to Cr(III) and precipitated other metal ions (Losi and Frankenberger 1994). SRB's ability to reduce

Table 3. Different Bio-reduction methods of Cr (VI) and their mechanism.

| Methods of Cr(VI) reduction	pH	Multi-step mechanism	Ref.
Traditional	2.5	Step-I: 3 kg of sodium bisulfite added with 2–3 kg of sulfuric acid, reduces 1 kg of Cr(VI) to its trivalent form $4CrO_4^{2-}(aq) + 6NaHSO_{3(aq)} + 3H_2SO_{4(aq)}8H^+_{(aq)} \rightarrow 2Cr_2(SO_4)_{3(aq)} + 3Na_2SO_{4(aq)} + 10H_2O$ Step-II: Further addition of sodium hydroxide precipitates Cr (III) as indicated as $Cr_2(SO_4)_{3(aq)} + 6NaOH_{aq} \rightarrow 2Cr(OH)_{3(s)} + 3Na_2SO_{4(aq)}$ Step-III: After precipitation of Cr (III) hydroxide, the resulting effluent will contain little or no residual chromium. $4CrO_4^{2-}(aq) + 3SO_{2(g)} + 4H^+_{(aq)} \rightarrow Cr_2(SO_4)_{3(aq)} + 2H_2O$	(Barrera-Díaz et al. 2012)
Electro coagulation	6–8	Step-I: Anodic reaction: $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$ Step-II: Cathodic reaction: $2H_2O + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$ Step-III: Overall reactions in bulk solution $Cr_2O_7^{2-}(aq) + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \rightarrow 2Cr^{III} + 6Fe_3^+(aq)7H_2O$	(Barrera-Díaz et al. 2012)
Aerobic Bacterial reduction	2–4	Step − I : $Cr^{VI} + e^- \xrightarrow{Bacteria} Cr^{5+}$ Step − II : $Cr^{5+} + 2e^- \xrightarrow{Bacteria} Cr^{III}$	(Singh et al. 2011)
Anaerobic Bacterial reduction	7–9	Step − I : $CrO_4^{2-}(aq) + 8H^+_{(aq)} + 3e^- \xrightarrow{Bacteria} Cr^{III}_{(aq)} + 4H_2O$ Step − II : $Cr^{III}_{(aq)} + 4H_2O \xrightarrow{Bacteria} Cr(OH)_{3(S)} + 3H^+_{(aq)} + H_2O$ Step − III : $C_6H_{12}O_6 + 8CrO_4^{2-}(aq) + 14H_2O \xrightarrow{Bacteria} 8Cr(OH)_{3(s)} + 10OH^-_{(aq)} + 6HCO^-_{(aq)}$	(Cheung and Gu 2007; Singh et al. 2011)

chromate is due to its structural similarities with chromate. The reaction kinetics of bioreduction as purposed by Kim et al. (2001), involves the formation of chromate sulfide intermediate complex $\{H_2O4Cr^6S\}^{2-}$, followed by intramolecular electron transfer to form Cr(IV) species, and subsequently fast reactions with Cr(III) as the final product. The energy kinetic required by ChrR reductase to reduce each molecule of Cr is given as K_m of 374 μM and V_{max} of 1.72 μmol/min/mg.

Step I:

$$H_2S + CrO_4^{2-} \leftrightarrow \{H_2O_4Cr^{VI}S\}^{2-} \qquad (1)$$
$$HS^{\mp} + CrO_4^{2-} + H^+ \rightarrow \{H_2O_4Cr^{VI}S\}^{2-} \qquad (2)$$

Step II:

$$\{H_2O_4Cr^{VI}S\}^{2-} \leftrightarrow Cr^{VI}O_3^{2-} + S^0 + H_2O \qquad (3)$$
$$\{H_2O_4Cr^{VI}S\}^{2-} + H_2S \leftrightarrow Cr^{VI}O_3^{2-} + HSSH + H_2O \qquad (4)$$

Step III:

$$Cr^{IV} + Cr^{VI} \leftrightarrow 2Cr^{V} \qquad (5)$$
$$2Cr^{IV} \leftrightarrow Cr^{III} + Cr^{V} \qquad (6)$$
$$Cr^{V} + S^{-II} \leftrightarrow 2Cr^{III} + S^0 \qquad (7)$$

Nitroreductase, an inducible chromate reductase dimer, isolated from *Shewanelleoneidensis* poses the potential for chromate reduction activity under both aerobic and anaerobic conditions. It uses a two-electron transfer mechanism and is induced by nitrate instead of chromate on being cultivated in a nitrite containing medium (Ackerley et al. 2004). Another novel enzyme oxidoreductase isolated from *Thermus scotoductus* is a flavoprotein capable of reduces chromate under similar conditions as nitroreductase (Opperman et al. 2010). However, its reduction efficiency increases to 180 times and 50 times than quinone reductase and nitroreductase respectively in the supply of excess oxygen.

In thermophilic methanogens, the extracellular reduction of Cr(VI) is attributed to the presence of ferredoxins-dependent reactions in the electron transport chain. While for intracellular it occurs through NADPH-dependent FMN reductase. The reduction process occurs as a result of diversion of electrons from H_2 to Cr(VI) instead of CO_2 to make CH_4. Stoichiometric consumption of H_2 in the production

of Cr(III) supports the Electron diversion hypothesis. The enzyme exhibits a V_{max} value of 59.89 μM/min/mg and K_m of 86.5 μM, signifying its feasibility in laboratory conditions when $K_2Cr_2O_7$ is used as a substrate (Mala et al. 2014; Singh et al. 2015). Mass balance studies by Singh et al., (2015) on *Methanogens thermautotrophicus* suggest the Cr(VI) to cell ratio is also responsible for the reduction process. The calculation of stoichiometric ratio shows that for the reduction of every mole of Cr(VI), three moles of H_2 are required that produce two moles of stable Cr(III).

$$3H_2 + Cr_2O_7^{-2} + H_2 O \rightarrow 2Cr^{III} + 8OH^- \qquad (8)$$
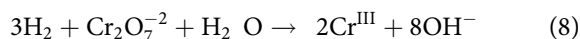
Incorporation of biogenic iron (Fe) (oxy-hydro)oxides (BIOS) with organic carboxylate complex was recently reported to enhance Cr(VI) adsorption and reduction (Whitaker et al. 2018). The study discovers that BIOS would substantially reduce Cr(VI) to Cr(III) as evident from X-ray absorption near edge structure (XANES) images. However, the lack of a 3:1 reaction stoichiometry between Fe(II) and Cr(III) suggests the roles of organic matter for auto reaction with Cr(V) and production of organo-Cr(III) complexes (Gong et al. 2018). The mass to product ratio indicates a higher accumulation of reduced Cr complexes on cell walls with time rather than inside of the cells. The organo-Cr(III) complexes formed by *Geobacter sulfur reducens* were also found to be more stable than the aqueous Cr(III) or $Cr(OH)_3$ solution (Gong et al. 2018).

Biosorption

Biosorption is a passive and irreversible independent metabolic process performed by microorganisms (refer Figure 5). Adsorption of heavy metals by microbes can be ascribed to the interaction of metals ions with functional groups such as carboxyl, hydroxyl, sulfhydryl, phenolic and extracellular polymeric substances (EPS) that are present on the cell surface of different microbes (Dehghani et al. 2016; Enniya et al. 2018; Pakade et al. 2019). These anionic ligands along
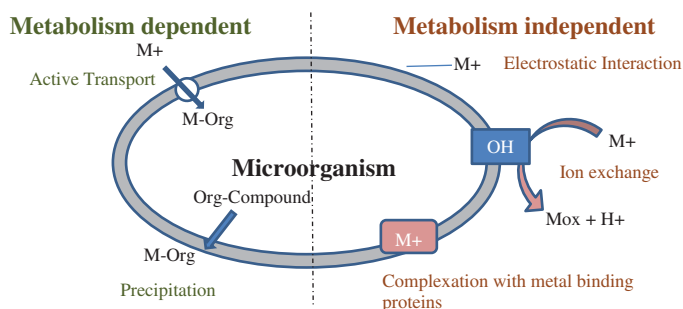
Figure 5. Mechanisms of biosorption of heavy metals by microorganism: metabolic dependent and independent metabolic methods.

with D-galactosamine polymers and polyuronides are greatly considered as heavy metal-binding sites contributing to the biosorption processes in microbes (Vendruscolo et al. 2016). The amino groups present in the microalgal species such as *Chlorella miniata* and *Spirulina platensis*, are responsible for their biosorption potential (Han, Shan, et al. 2007).

In fungi, chitosan, a compound derived from deacetylated chitin is responsible for synergistic or antagonistic effects resulting in the absorption of Cr heavy metal. Species including but not limited to *Candida sp.* (Vendruscolo et al. 2016), *Paecilomyces lilacinus* (Sharma and Adholeya 2011), *Aspergillus sp.* (Rezaei 2016), *Rhizopusar rhizus* (Arunbabu et al. 2017), *Penicillium sp.* (Zhang et al. 2017) are prominent in biosorption of Cr(VI).

Yeasts are a complex group of microbes capable of growing in various environments conditions. The species *Saccharomyces* has been an excellent absorbent agent for biosorption of Cr (Rezaei 2016). However, *Cyberlindnera fabianii* isolated from industrial effluent is by far the best-known yeast species to effectively remove 100% of chromium from after 48 h of treatment. Factors that directly impact biosorption are sources of energy (electron donors), nutrients, pH, temperature, and inhibitory substrates or metabolites concentration, etc. (Vendruscolo et al. 2016). According to the Box- Behnken design, the ideal parameters for biosorption is a biosorbent dose of $2 \, g \, l^{-1}$, Cr(VI) concentration of $67.8 \, mg \, l^{-1}$ and a reaction time of 37.5 min (Vendruscolo et al. 2016). The optimum pH for biosorption in fungal species is pH 3.0, while for bacterial species it usually ranges from 7 to 9.

Other miscellaneous sources used as low-cost adsorbents include waste newspapers (Dehghani et al. 2016), sugarcane bagasse (Garg et al. 2007), activated carbon of apricot kernel (Demirbas et al. 2004), longan seed (Yang et al. 2015), immobilized sugarcane bagasse (Ullah et al. 2013), and animal charcoal (Hyder et al. 2015). Activated carbon is an emerging entrant for adsorption of Cr(VI) considering its high specific surface to spore area (Yang et al. 2015).

Phytoremediation

Phytoremediation, often referred to as "green remediation" is a comparatively new technique where plant species or materials are applied for *in-situ* reduction, detoxification and stability of pollutants from different sources (Figure 6). Phytoremediation is advantageous over conventional remediation techniques because of cost efficiency, comfort, and large-scale applicability against a variety of contaminants while keeping the biota intact (Zayed and Terry 2003; Diwan et al. 2008; Shams et al. 2010).

Academically and applied researches on phytoremediation techniques has unambiguously confirmed that particular plant species on suitable conditions possess the genetic prospective to reduce, metabolize or immobilize an array of hazardous heavy metals from soil and water sources (Shams et al. 2010; Ahemad 2015). A model species for Cr (VI) remediation must be fast-growing, have higher biomass, easy to cultivate and harvest and amass high concentrations of Cr in aerial component (Diwan et al. 2008). Discovery of hyperaccumulators (ability to uptake bulk quantities of toxic metal pollutants) in plants such as *Spartina argentinensis* (Redondo-Gómez et al. 2011), *Leersia hexandra* (Zhang et al. 2007) and *Prosopis laevigata* (Buendía-González et al. 2010) have further boost remediation technique. The use of rooted and submerged plant species as phytoremediation tools have additional benefits as it helps in facilitate colonization of benthic algae, invertebrates, and other microbes (Zhu et al. 1999). Apart from aquatic plant species terrestrial trees, grasses, herbs, and shrubs are actively used in phytoremediation as listed in Table 4.

Pennisetum purpureum, *Brachiaria decumbens*, and *Phragmites australis* growing hydroponically over gravel beds are the most efficient plant confiscating 97–99.6% of Cr within 24 h (Mant et al. 2006). Stinging nettle (*Urtica dioica*), Rapeseed (*Brassica napus*), Indian mustard (*Brassica juncea*) and Maize (*Zea mays*) due to their versatile nature and unexplored possibilities against several toxic heavy metals had also been incorporated to the pot experiments to explore their sensitivity toward chromium (Shams et al. 2010).

Vallisneria spiralis growing on chromium enriched nutrient medium accumulated a significant amount of chromium in different plant parts like dry weight ($1,050 \, \mu g \, g^{-1}$), leaves ($697 \, \mu g \, g^{-1}$), and rhizomes ($437 \, \mu g \, g^{-1}$) in solution containing as many as $10.0 \, \mu g \, ml^{-1}$ Cr after 72 h of treatment (Vajpayee et al. 2001). Tumbleweed (*Salsola kali*) when provided with Cr (VI), was recorded to have a varied amount of Cr distribution in different parts as for roots (2,900 mg/kg) stems 790 (mg/kg) and leaves (600 mg/kg) (Gardea-Torresdey et al. 2005).

Aquatic plants like *Eichhornia crassipes*, *Pistia stratiotes*, and *Salvinianatans* has grown on hexavalent Cr contaminated water have also confirmed experimentally to accumulate reduced Cr (III) in their leaves and roots (Sundaramoorthy et al. 2010). *Eichhornia crassipes* (water hyacinth) mount up the huge quantity of Cr in roots (5,000 to 6,000 mg/kg) on being supplied with $10 \, mg \, l^{-1}$ Cr for 14 days (Lytle et al. 1998). Poor translocation of Cr in shoots section in plants indicates that the obstruction in passes of Cr to any aerial part is not outwitted by supplying Cr as organic complexes or any other forms but is dependent on the concentration and length of exposure period (Diwan et al. 2008).
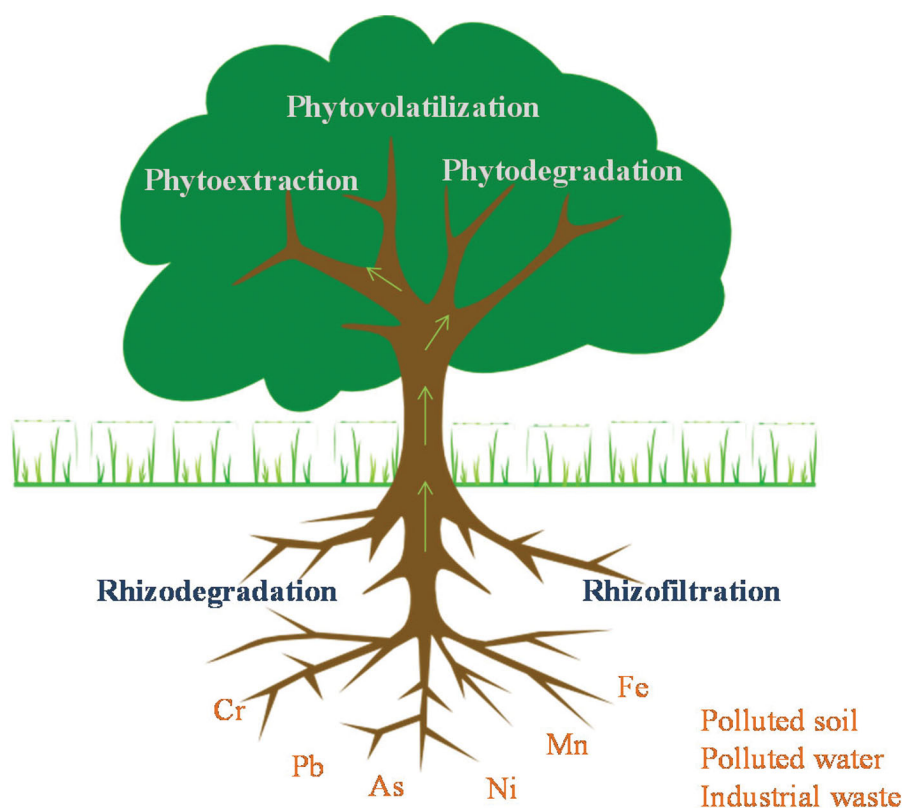
Figure 6. Phytoremediation of heavy metals.

Presence of Potassium (K) as an ingredient in salt solution $(KCr(SO_4)_2 12H_2O)$, was reported to have an unexpected positive response in growth of plants and uptake of chromium (Shams et al. 2010), while EDTA was found to serve as a hindrance agent to metal intake in hydroponic plants (Sundance sunflowers) (January et al. 2008). Genetic studies in willow species like *Salix alba*, *Salix eleagnos*, *Salix fragilis* and *Salix matsudana* had identified the gene "Expressed Sequence Tag" as an essential regulator in plants toward chromium exposure (Quaggiotti et al. 2007). Other reports suggest that an interrelated network of physiological biochemical and molecular processes can serve as an integral part, affecting the ability of a plant to accumulate heavy metals (Diwan et al. 2008).

Phytoremediation process, although are time-consuming but had proven to disintegrate and degrade chromium present in the soil. Bioinoculants (e.g., multifunctional plant-growth promoting bacteria (PGPB) along with plants) exhibit chromium resistance and reducing traits, providing a better approach for phytoremediation. PGPB improve Cr uptake ability of plants by modifying root architecture, secreting metal sequestering molecules in rhizomes, and lessen chromium-induced phytotoxicity (Ahemad 2015). The use of vermicompost prepared with cow dung using earthworm species *Eurdilus euginae* along with sorghum (*Sorghum bicolor*) was suggested as a potential source of bioremediation in Cd and Cr contaminated soil by Revathi et al. (2011).

Nanoremediation

Nanotechnology is a trending technology that had found its application in various fields including medical science, fabrics engineering, defense, space technology and many more.

Nanotechnology is also explored as possible remediation techniques with prominence in absorbance and reduction of Cr(VI) from industrial effluents when used as nano-adsorbents, nano-catalysts and nano-membranes (Lv et al. 2012; Mitra et al. 2017). Nanomaterials are an ideal candidate for environmental remediation following the characteristics features, i.e., small size, better solubility, large surface area, charges on surface area and varied surface composition (Lv et al. 2012; Kim and Roh 2019). Maitlo et al. (2019) reviewed the various nanomaterials for the sorptive removal of chromium from water.

The removal of Cr from contaminated water sources by nanoscale zerovalent iron (nZVI) particles employed on herb-residue biochar extracted from *Astragalus membranaceous* was credited to the presence of numerous porous structure and oxygen-rich functional groups present on its surface (Shang et al. 2017). ZVI (nZVI) has an advanced and better surface area ($182.97\,m^2g^{-1}$) enabling them to remove several pollutants like PCBs, TCE, and DDT, Pb(II) through reduction, adsorption and precipitation (Guan et al. 2015). Zerovalent iron nanoparticles, when support with resin showed Cr removal efficiency of 84.4% under optimal conditions (Fu et al. 2013). Further, the addition of carboxymethyl cellulose (CMC) as a stabilizer for nZVI improves the efficiency to 100% for solutions containing 10 mg/l of Cr (Wang et al. 2010). Polymer-nZVI composite film composed of multiple layers of chitosan, polyethylene glycol (PEG) blend, poly (sodium 4-styrene sulphonate) solution (PSS) and live biomass of Sulfate-reducing bacteria (SRB) had a Cr deduction rate of 394 mg/g under anaerobic conditions (Argulwar et al. 2018).

The novel nanocomposite of acid-treated rock wool zerovalent iron (ARWZ), when used as a membrane, is reported

Table 4. Bioremediation with their sources and other catalytic factors.

Techniques	Source of remediation	Type	pH	Temp. (°C)	Time (Days)	Others	Ref.
						Catalytic factors	
Bioleaching	Acidithiobacillus thiooxidans	Bacteria	2	30	–	–	(Nareshkumar et al. 2007)
	Acidithiobacillus ferrooxidans		1 –2.5	–	–	Fe^{3+}	(Rastegar et al. 2014)
	Geotrichum sp.		–	–	7	Magnetic field and Aerobic condition	(Qu et al. 2016; Kim and Roh 2019)
	Bacillus sp.		(Qu et al. 2016)				
Bioreduction	Antrodiavaillantii	Fungus	3	–	28	Citric acid, Oxalic acid	(Sierra-alvarez 2009)
	Brettanomyces sp.	Yeast	–	–	5	–	(Pathak et al. 2009)
	Cellulosimicrobium sp.	Bacteria	–	–	–	–	(Bharagava and Mishra 2018)
	Bacillus sp.		–	35	–	–	(Dhal et al. 2013)
	Planococcusmaritimus		7	35	1–1.16	–	(Dey and Paul 2015)
	Arthrobacter sp.		7	35	–	Glycerol and glucose	(Pal et al. 2013)
	Bacillus sphaericus		7	32	–	120rpm	(Xiao et al. 2017)
	Bacillus sp.		8	30	–	–	(Xiao et al. 2017)
	Arthrobacter sp.		7	35	–	–	(Samuel et al. 2012; Talib et al. 2019)
	Escherichia coli Acineto bacterjunii Bacillus subtilis		7.5	–	1.125	–	
	Enterobacter cloacae		–	30	1	180 rpm	(Harish et al. 2012)
	Pseudomonas sp. (P. aeruginosa and P. stutzeri)		–	37	2	Acetate minimal medium	(Ozturk et al. 2012)
	Bacillus sp.		10	35	–	Immobilized with polyvinyl alcohol, sodium alginate, and multiwalled carbon nanotubes	(Ibrahim et al. 2011)
	Pseudomonas aeruginosa		–	–	3.5	–	(Pang et al. 2011)
Biosorption	Halomonas sp.	Proteobacteria	–	37	2.25	–	(Murugavelh 2013)
	Chlorella miniata	Algae	2	–	2.41	–	(Han et al. 2017)
	Aspergillus niger, Aspergillus flavus	Fungus	2 to 9	22–40	1	–	(Park et al. 2005; Kumar and Dwivedi 2019)
	Pichia guilliermondii	Yeast	–	30	3–5	–	(Ksheminska et al. 2008)
	Saccharomyces cerevisiae		–	38	2	–	(Ksheminska et al. 2006)
	Activated carbon	Apple peels	2 to 7	10–40	0.16	–	(Enniya et al. 2018)
	Cyberlindnerafabianii	Yeast	–	–	2	–	(Joutey et al. 2015)
	Aspergillus oryzae	Fungus	5	30–35	–	–	(Congeevaram et al. 2007)
	Aspergillus niger, Aspergillus sydoni and Penicilliumjanthinellum		2	–	–	–	(Kumar et al. 2008)
	Aspergillus fumigatus Fresenius		5.5	35	5	–	(Dhal et al. 2018)
	Trichoderma sp.		5.5	–	–	–	(Vankar and Bajpai 2008)
	Micrococcus sp.	Bacteria	5	30–35	–	–	(Congeevaram et al. 2007)
	Pantoea sp.		3	–	–	–	(Ozdemir et al. 2004)
	Spirulina sp.	Algae	5	25	–	Agitation time – 120 min	(Rezaei 2016)
	Cladophora sp.		2	–	–	120 rpm	(Rangabhashiyam and Balasubramanian 2018a)
	Spirogyra species		2	18	0.083	–	(Gupta et al. 2001)
	Chlorella miniata		2	–	0.083	–	(Han, Mao, et al. 2007)
	Sargassumwightii and Caulerparacemosa		5	–	–	–	(Tamilselvan et al. 2012)
	Portulacaoleracea	Biomass	2	–	45min	–	(Shinghal 2015)
Phytoremediation	Salsola kali	Herb	5.8	–	–	Agar-based medium	(Gardea-Torresdey et al. 2005)
	Medicagosativa and Sorghum bicolor		–	–	50	–	(Karimi 2013)
	Helianthus annuus		–	–	–	EDTA, Citric Acid	(Turgut et al. 2004)
	Urticadioica		5.5 to 6.5	–	–	50– 300 mg/l N, 40 to 300 mg/l P_2O_5 and 100–500 mg/ l K_2O	(Shams et al. 2010)
	Polianthestuberosa		–	–	–	–	(Ramana et al. 2012)
	Brassica juncea		7 to 7.8	–	125	–	(Diwan et al. 2008)
	Pterocarpus indicus and Jatropha curcas	Tree	–	29–49	–	–	(Mangkoedihardjo et al. 2008)
	Pterosper mumacerifolium (shells)		2–10	25	–	phosphoric acid, Sulfuric acid	(Rangabhashiyam and Balasubramanian 2018b)
	Pinussylvestris		7 to1	25	–	–	(Ucun et al. 2002)
	Penisetum purpureum, Brachiaria decumbens and Phragmites australis	Grass	–	–	1	Gravel beds	(Mant et al. 2006)

to have an unexpectedly high removal capacity of Cr(VI) (197.69 mg/g) in 30 min from industrial effluents and soil through adsorption and reduction. The property is accredited to its vast face area and superior magnetic property (Zhou et al. 2018; Hou et al. 2019). Carbon nano-onions (CNOs) are materials used as substitute adsorbent to confiscate Cr from the water treatment industry. CNOs are highly sensitive to pH and are therefore dependent on the pH of the waste solution (Sakulthaew et al. 2017). More recently, 3 D urchin-shaped monometallic palladium along with formic acid was successfully used as nanocatalyst in detoxification Cr containing industrial effluents (Mitra et al. 2017).

While the usage of nanomaterial's and nano-products are limited for remediation of Cr(VI) pollutants, it is widely in use for treatments of such as Co(II), Ni(II), Cu(II), Cd(II), Pb(II) and As(III) (Anjum et al. 2016). Manganese oxides (MnO) nanoparticles are proficient for Cd (II) and Zn (II) while Graphene Nanosheets (GNS)/§-MnO_2, Nanocrystalline titanium dioxide, and ZnS nanocrystals are capable for reduction of Ni(II), As(III) Hg(II) (Varma et al. 2013; Qu et al. 2014). Nanotechnology being a relatively new concept and a rapidly progressing technology it is only a matter of time before it will be able to address the hazardous issues in the environment including that of Cr(VI) pollution.

Others remediation techniques

Although microbial and plant sources have great potential for bioremediation of Cr(VI), modern developments in environmental research and waste management technology have underlined new techniques for the treatment of heavy metals. Some of them are Bioaugmentation, Electrocoagulation, Biosurfactants, Vitrification, Bio-hydrometallurgy, and photocatalytic technology.

Bio-augmentation or seeding involves the deposition of highly specialized and engineered microbial populations to any contaminated site with recalcitrant toxic compounds to foster the degradation rates (Tyagi et al. 2011). The technique, however, results in the loss of the indigenous bacterial population while enhancing the growth of protozoans.

Electrocoagulation (EC) is a technique where electrolytic oxidation is introduced to an aqueous medium resulting in the destabilization of suspended or dissolved contaminants and generating coagulant. Electrocoagulation has modestly thrived against Cr(VI) ions from groundwater and needs more technical improvements (Hamdan and El-Naas 2014).

Bio-surfactants are nontoxic washing agents with features of low toxicity, eco-friendly, simple fabrication, and re-useable. Bio-surfactants eliminate the production of secondary pollutants while degrading a significant amount of pollutants. The use of emulsified vegetable oil (EVO) with acetate and $Mg(OH)_2$ has led to the complete removal of Cr from simulated groundwater and also induced accumulation of microbes related to organic fermentation and iron reduction (Fu et al. 2017). The use of biosurfactants from the aqueous extracts of plant biomass in association with anionic and neutral agents has gained tremendous popularity over the years (Mukherjee et al. 2016). Nandi et al. (2017) reported a

reduction efficiency of 96% for Cr (VI) concentration using biosurfactant from blue-green algae (1 g) in combination with $3 * 10^{-2}$ M sodium dodecyl sulfate (SDS). Several studies have also reported the use of aqueous extracts from different plant biomass like Moringa oliefera, sugarcane bagasse, siris sawdust containing amino acids and sugars which has been found to reduce Cr (VI) to Cr (III) by about 99% in the presence of anionic and neutral surfactants (Mukherjee, Ghosh, et al. 2014; Mukherjee, Saha, et al. 2014; Mukherjee et al. 2015).

Vitrification is the recovery of heavy metal from electroplating sludge with a reported recovery rate of 95% (Huang et al. 2013). Chemical additives (limestone and cullet) followed by heat treatment (1,450 °C) were used for the extraction of Ni and Cu from industrial sludge.

Bio-hydrometallurgy is a relatively new concept that employs various microorganisms along with acids, alkalis or organic solvents to the recovery of valuable metal (Mishra and Rhee 2010).

Photocatalytic processes are another useful technique where solar energy is used to reduce Cr(VI) to Cr(III). The use of Tin(IV) Sulfide/Graphene Oxide photocatalyst demonstrated an increased degradation rate of hexavalent chromium in comparison to normally visible light irradiation (Han et al. 2017). The photocatalytic reduction may be applied to organic matters and acids (iron fulvic acids and humic acid) to reduce heavy metals. The photocatalytic reduction is, however, have a high cost and a complicated installation procedure. The key factors influencing the photocatalytic reduction efficiency of Cr (VI) such as pH, activity of the catalyst, adsorption of Cr on the catalyst and other additives were briefly discussed in the recent review article outlined by Zhao et al. (2019).

Conclusion

Rapid industrialization makes production and disposing of heavy metal to the surrounding environment inevitable. Chromium pollution in Sukinda Valley had adversely affected the environmental scenario, causing several diseases in humans, animals, and plants. Chromium-containing waste needs special treatment for environmental security and recovery, as available remediation measures (physical, chemical and biological) are restricted in one way or the other (Table 5).

Despite different and distinct from each other in principle, various complementary techniques (chemical, microbial and biological) are in use for the remediation of heavy metal. Detailed knowledge of the sources and chemistry along with information on its potentially toxic effects at the contaminated site are necessary for the selection of the appropriate remedial method. Bioremediation though is a successful technique for the reduction of heavy metal pollutants, may not be useful for all heavy metals in every condition.

Microbial degradation and deterioration is a fast, gentle, energy-efficient method that generates fewer byproducts, yet, time-consuming and needs expert management.

Table 5. Advantages and limitations of some of the commonly used remediation techniques.

Remediation techniques	Advantages	Limitations	Ref.
Physiochemical methods			
Precipitation	Relatively inexpensive and straightforward to operate. Easy availability, moreover, low-cost	A large volume of sludge effectiveness reduced in the presence of multiple contaminants	(Agrawal *et al.* 2006; Bvrith and Reddy 2013)
Ion exchange	High treatment capacity, high removal efficiency, and fast kinetics	A time-consuming generates significant secondary waste	(Kang *et al.* 2004; Agrawal *et al.* 2006)
Membrane separation	Purifies heavy metals, suspended solids, and other associated organic compounds	High cost, membrane fouling, limited flow rates	(Agrawal *et al.* 2006; Bvrith and Reddy 2013)
Electrochemical	The rapid process, require fewer chemicals, provide high selectivity and produce less sludge	Involve high initial capital cost, production of the dendrite, lose or spongy deposits	(Rana *et al.* 2004; Barrera-Díaz *et al.* 2012)
Bioremediation methods			
Bioleaching	Easy to operate, less secondary waste	Very slow, leached toxic materials may run-off to nearby water sources	(Pathak *et al.* 2008b; Zeng *et al.* 2016)
Adsorption	Easily available, profitable, easy to operate and cost-efficient	Metal-specific and requires chemical derivatization to improve its sorption capacity	(Bvrith and Reddy 2013; Vendruscolo *et al.* 2016; Enniya *et al.* 2018)
Bioreduction	Eco-friendly, require even fewer reagents, easy and inexpensive to operate	Need Isolation, identification, and characterization of microbes from their native soil or aqueous environment before their application, difficult to maintain	(Barrera-Díaz *et al.* 2012; Harish *et al.* 2012)
Phytoremediation methods			
	Eco-friendly, high accumulation rate	Long duration time, phytotoxic at high concentrations, the probable route for vegetation contamination in the food chain	(Bvrith and Reddy 2013)
Nanoremediation			
	Eco-friendly, effective in small quantity, large surface area, high sensitivity	Need expertise for synthesis, expensive, difficult to maintain	(Mitra *et al.* 2017)

Although the success of a mixed or hybrid combination of native bacterial strains are being advocated, physiochemical parameter and culturing medium are to be optimized for increasing the recovery percentage of Cr and other heavy metal. The development of engineered microbes and their genetic manipulation can further boost the technological advances in the treatment of Cr(VI) waste and other toxic metals. Hence, a combined approach involving nanotechnology, microbiology and biotechnology, which are currently under active research, is much needed as the next-generation technologies for environmental pollution management.

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