Chapter 7
Biological and Nonbiological Approaches for Treatment of Cr(VI) in Tannery Effluent

Asma Kalsoom and Rida Batool

Abstract Leather tanneries are major source of hexavalent chromium contamination in the biosphere. Chromium (Cr) is being considered as an essential heavy metal extensively used in different industrial sectors for example, leather, paint, textile, and electroplating. A characteristic feature of chromate is its environmental mobility and consequently is a cause of environmental risk. Cr(VI) belongs to group A human carcinogen due to its mutagenicity, carcinogenicity, and teratogenicity in plants, animals, and humans, therefore causing serious health issues in all living beings. Conventional methods for chromate removal includes ion exchange, chemical precipitation, reverse osmosis, and electrochemical from tannery effluents. These procedures are effective but require high energy and chemical consumption that may produce secondary problems such as corrosion, spillage, and toxicity. So, the need of the hour is to develop eco-friendly techniques for efficient Cr(VI) removal. Therefore, bioremediation is an effective alternate for reclamation of contaminated sites. Bioremediation is the biological approach to degrade heavy metals using indigenous microorganisms. Microbes such as bacteria, fungi, yeast, and algae have the ability to survive under harsh environmental conditions. These microbes are proficient to reduce toxic Cr(VI) into less toxic Cr(III) by various cellular mechanisms. Therefore, environment friendly, economical, and effective strategies are needed to reduce chromate pollution in the surroundings. Thus, this chapter gives detailed information on production and properties of tannery effluent, environmental pollution, and health hazards of tannery effluent, biological and nonbiological methodologies for the effluent remediation. Moreover, the pros and cons of current processes have also been briefly discussed in this chapter.

Keywords Tannery effluent · Hexavalent chromium · Environmental and health issues · Bioremediation · Conventional methods

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7.1 Introduction

Chromium (Cr) is a heavy metal naturally present in two oxidation states i.e., Cr(III) and Cr(VI). Cr is generally dispersed in fresh water, rocks, and oceans (Krishnamurthy and Wilkens 1994; Saxena et al. 2019; Mishra and Bharagava 2016). Nutritionally, trivalent chromium is an essential part of balanced diet for humans and animals that maintains and inhibits adverse effect on metabolic processes of fats, carbohydrates, and protein synthesis (such as raised fasting insulin, reduced glucose tolerance, high cholesterol and triglycerides, and hypoglycemic symptoms) (Raman et al. 2018; Anderson 1989, 1997). Cr is also used for production of cement, stainless steel, paint pigments, wood preservatives, leather, etc. The dissemination and concentration of Cr in different environmental samples is summarized in Table 7.1. For freshwater life, the recommended guidelines are 8 µg/L for Cr(III) and 1 µg/L for Cr(VI), for marine life 50 µg/L for Cr(III) and 1 µg/L for Cr(VI), for irrigation water 5 µg/L for Cr(III) and 8 µg/L for Cr(VI), and for drinking water is 50 µg/L for Cr(VI) (Krishnamurthy and Wilkens 1994; Pawlisz 1997).

For the past few years, anthropogenic activities have contributed to ecological contamination, causing an increase in concentration of various heavy metals for example, chromium, selenium, lead, cadmium, mercury, etc. Industrial waste is disposed of in the nearby water bodies and ultimately absorbed in the surroundings. These heavy metals are utilized in several industries such as tanneries, electroplating, mining, textiles, pesticide industries, etc. (Vendruscolo et al. 2017; Kishor et al. 2019). Environmental pollution has affected various illnesses as they have crossed the recommended threshold limit value given by WHO (World Health Organization) (Witek-Krowiak et al. 2011; Mishra and Bharagava 2016; Saxena et al. 2017; Joshi

Table 7.1 The distribution and recommended concentration of chromium in various environments (Krishnamurthy and Wilkens 1994)

Sample type	Concentration
Natural soils	5–1000 mg kg^{-1}
	5–3000 mg kg^{-1}
	5–1500 mg kg^{-1}
	30–300 mg kg^{-1}
	Trace to 5.23%
Serpentine soils	634–125,000 mg kg^{-1}
World soils	200 mg kg^{-1} (mean)
	100–300 mg kg^{-1}
	10–150 mg kg^{-1} (mean 40 mg kg^{-1})
Sediments	0–31,000 mg kg^{-1}
Fresh water	0–117 µg L^{-1} (average 9.7 µg L^{-1})
Sea water	0–0.5 µg L^{-1}
Air	1–545,000 ng m^3
	100 ng m^3
Plants	0.006–18 mg kg^{-1}
Animals	0.03–1.6 mg kg^{-1}

2018). Cr (VI) pollution is of utmost concern worldwide, as it is considered extremely toxic, mutagenic, and carcinogenic for living organisms. For the last 15 years, chromium has been classified among the 20 most lethal environmental contaminants (Chrysochoou et al. 2012).

Effluents of manufacturing industries such as textiles, tanneries, electroplating, tanneries, paint, etc., contains large percentage of Cr(VI) (Mohapatra et al. 2017; Kishor et al. 2019). These industries are releasing their effluents continuously in their surroundings, which is a leading threat to environmental safety. Because chromium is a nondegradable pollutant as it persists in the environment (Ran et al. 2016).

Hexavalent chromium can cause severe infections such as, skin and lung cancers, hepatic diseases and bronchial tract infections, etc. (Ali et al. 2016). However, trivalent chromium is less toxic and exists in oxides and hydroxides which is insoluble at pH >5 (Mohapatra et al. 2017). As a result, Cr(III) is not capable of entering into the cells and removed easily. Hexavalent to trivalent chromium reduction can be achieved by physiochemical, electrochemical, and biological processes (Habibul et al. 2016). Several physiochemical techniques are used such as chemical precipitation, membrane separation, solvent extraction, and ion exchange (Witek-Krowiak et al. 2011). These methods are inadequate and ineffective for chromate removal, due to high cost and energy consumption, incomplete removal and formation of other toxic compounds.

Cr(VI) removal has also being carried out through biological techniques. These techniques are environment friendly, cost-effective, safe, and free from toxic side products formation (Eccles 1995; Shakoori et al. 2000). Various studies have investigated plants, yeasts, fungi, and bacteria for remediation. Microbes are being exploited for beneficial purposes. Bacteria develop different mechanisms to overcome metal toxicity such as intracellular and extracellular reduction of Cr(VI), metal efflux, DNA repair enzymes, and detoxification enzymes for reactive oxygen species (ROS) (Thatoi et al. 2014). Heavy metal ions accumulate in bacterial cells in both soluble as well as in particulate form (Devi et al. 2017). Microbes convert toxic hexavalent chromium into less toxic trivalent chromium either by direct method that involves enzymatic reduction or by indirect process that consist of formation of complex compounds with metabolites (Bento et al. 2005; Pei et al. 2009; Soni et al. 2013; Chandra et al. 2011). Several bacteria such as *Agrobacterium*, *Bacillus*, *Deinococcus*, *Enterobacter*, *Escherichia*, *Pseudomonas*, *Shewanella,* etc., are reported to show high Cr(VI) reduction potential (Thatoi et al. 2014). Cr(VI) reduction greatly depends on temperature, pH, and chromium salt concentrations (Wani et al. 2018).

The process of removal of heavy metals through biological materials is termed as biosorption. This technology is very operative for detoxification of toxic industrial effluents. Agricultural wastes are efficient biosorbent materials and have low cost such as rice husk, exhausted coffee, peat moss (Dakiky et al. 2002), rice hulls and soybean hulls (Marshall and Champagne 1995; Tarley and Arruda 2004), and wheat bran (Iqbal et al. 2002). These biosorbent materials are used in combination with Cr(VI) reducing bacteria for efficient removal of chromate from environment.

Thus, this chapter describes the properties of tannery effluents, hexavalent chromium as major pollutant, health risks, and effect of Cr compounds on the biosphere and remediation of tannery effluents by biological and nonbiological methodologies. The purpose of this chapter is to give complete information about tannery effluents and related issues that are required for further research and development.

7.2 Production and Properties of Tannery Effluent

In Pakistan, tanning industries are the leading cause of pollution due to disposal of unprocessed wastes in water bodies and on land. Developing countries have been observed with an increase in leather production as compared to developed nations. Pakistan has gained an increase in leather export from US$ 672 million to US$ 1.13 billion, indicating a cost increase of 68% in a 5-year span (2002–2007) (Haydar and Aziz 2009). Currently, there are about 2500 leather manufacturing units in Pakistan. From year 1999 to 2015, number of tanning units have raised from 529 to 800 (Padda and Asim 2019; Bharagava et al. 2018). In tanning process, animal hides are transformed through various chemical reactions to leather. Four major steps are involved for production of leather i.e., beams house operation (pre-tanning), lanyard processes, retaining, and finishing (US EPA 1986; Tunay et al. 1995; Cooman et al. 2003; Saxena et al. 2017) (Fig. 7.1). The hide is processed through various chemicals such as NaOCl, NaOH, H_2SO_4, chlorides, enzymes, lime, formic acid, chlorobenzene, ammonium salts, kerosene, tenso-active compounds to remove fat, meat, and hair. The hide is then subjected to mineral salts, chromium [Cr(III)], and dyes to leather. Thus, effluent generated has a large quantity of Cr(III), sulfates, sodium, and chlorides. However, the end products of each step produce different kind of waste materials and concentration may vary (Tunay et al. 1995). Basaran et al.

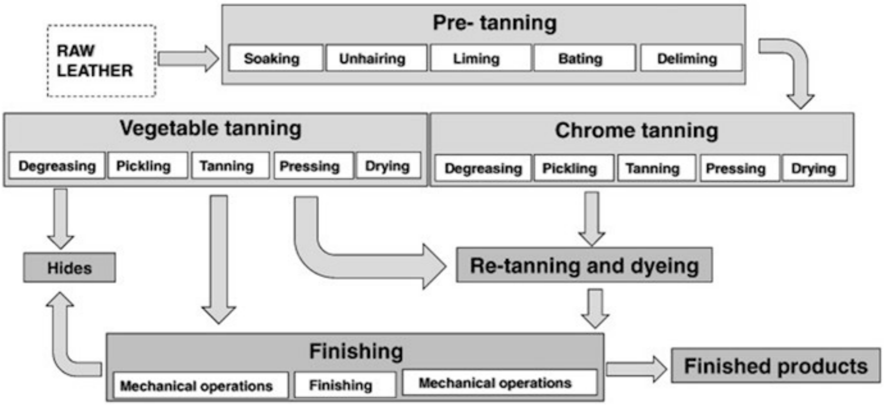

Fig. 7.1 Flow sheet of leather tannery industry (Lofrano et al. 2013)

(2008) and Saravanabhavan et al. (2004) described similar procedures for leather tanneries situated in Turkey and India, respectively.

7.3 Environmental Pollution and Health Hazards of Tannery Effluent

Anthropogenic activities are causing heavy metal contamination in the environment globally and are one of the primary sources of metal ion uptake in the food chain leading to serious diseases. In Pakistan, heavy metal contamination has created a serious situation regarding human health, environment, and economy. The disposal of untreated industrial effluent from leather tanneries has caused an accumulation of chromium (Cr) compounds in the areas near tanneries. Previous studies by Pakistan EPA has reported Cr values in the tannery waste, which are significantly higher than the safe limits established by nation standards (EPA 1990). Tannery wastewater is a potential noxious waste. It has created severe ecological problems that are linked to high concentration of chrome together with its rich coloration and high chemical oxygen demand (COD). Cr(III) is extensively utilized as tanning agent in leather tanneries as it forms complex compounds with proteins and amino acids (Song et al. 2000). This trace element is necessary for normal development of human and animals. In the pure state, Cr(III) has no harmful effect. When present in large quantity, it shows little toxic effect. Generally, Cr is not completely integrated into the leather and comparatively large quantity of Cr is discharged into the effluents. About 2% Cr is present in hide dust in the effluent and other wastes. Effluents from leather tanneries end up in the surroundings and large quantity of Cr is accumulated that are converted into more toxic and insoluble form with time because of complex structures formation with hydroxyl ions (Khan 2001).

Hexavalent chromium compounds are responsible for both acute and chronic toxicity. The interaction of Cr(VI) compounds by contact, ingestion, or inhalation causes severe illnesses such as eczematous and allergic skin reactions, dermatitis, damage to the nasal septum, mucous and skin ulcers, bronchial infections, allergies, hepatocellular deficiency, inflammation of stomach and intestines, etc. (Khan 2001; Chandra et al. 2009).

7.4 Cr(VI) as a Major Pollutant in Tannery Effluent

Environmental damage caused by tannery discharge has created a critical problem in Pakistan and signifies a technical challenge for an efficient and safe cleaning process. Chromium, a brittle,, and shiny metal is present in environment in combined form around 0.1–0.3 mg/kg of earth's surface. It exists in several oxidation states (−2 to +6) and the most stable are Cr(III) and Cr(VI) (Molokwane et al. 2008).

Cr(III) solubility is affected by the formation of oxides and hydroxides. Chromium is mainly employed in the metallurgy industry, particularly stainless steel production. Other Cr salts are used for manufacturing of pigments, leather tanning, metal finishing, etc. Tanned hide is approximately 80–90% made from chromium compounds (Papp 2004). Discharged effluents from tanneries contain about 40% of Cr as Cr(III) and Cr(VI). For each 200 kg of hide, more than 600 kg of waste is produced by a tannery (Khan 2001). Cr chemicals have also been used for the production of metal castings and mortars, refractory bricks, and as wood preservative.

Conversely, the US Environmental Protection Agency (US EPA) has prohibited the use of Cr(VI) compounds as a wood preservative regarding health issues. Because of wide applications, huge amount of Cr wastes is released into the environment each year. In 2003, US EPA declared about 32,589.6 metric tons of Cr compounds was disposed of and half of the quantity was landfilled in the surroundings (US Environmental Protection Agency 2005). Potable water guidelines by the WHO states 0.05 mg/L as the maximum permissible limit for total chromium. Cr is hazardous, but also spreads fast over aquatic systems and underground waterways. Consequently, Cr has been recognized as toxic environmental pollutant by US EPA (Narayani and Shetty 2013).

7.4.1 Impact of Chromium Compounds on Environment

Chromate is present naturally but anthropogenic activities give rise to Cr(VI) pollution in the environment. Natural sources contribute 54,000 tons of chromium. Studies showed that atmospheric Cr comes back to soil and water bodies by rain. Cr estimated time to reside in the atmosphere is less than 10 days (Agency for Toxic Substance and Disease Registry (ATSDR) 2015). Chromate present in soils can seep into surface water because of its highly soluble and mobile nature (Coetzee et al. 2018). It is a common practice to irrigate agricultural land by wastewater. Tannery effluents has large content of valuable nutrients, however it also contains toxins such as Cr that might damage soil quality and crop production (Alvarez-Bernal et al. 2006). High percentage of Cr in soils can prevent germination of seeds and growth of seedling. The toxic effects of Cr are less apparent on seed development than on growth of seedling. Barley seeds were able to germinate in soil under chromate stress of 100 mg/kg. However it showed slow growth due to Cr(VI) inhibition of diastase that is necessary for mobilizing the starch reserved for early growth (Zayed and Terry 2003).

In plants, the toxicity of Cr is greatly dependent on ionic species of element. Hauschild (1993) analyzed the effect of Cr(VI) toxicity in barley and rape plants provided in hydroponic culture. Cr(VI) and Cr(III) were supplied in the range of 0–100 mg/kg. When chromate (100 mg/L) stress was applied to plants, up to 3000–5000 mg/kg of Cr(VI) was accumulated and was up to 300–400 mg/kg when Cr(III) (100 mg/L) stress was applied in hydroponic culture. These high levels of chromium caused leaf chlorosis, reduced root and shoot growth, stimulation of chitinase activity, and low levels of water content in leaves (Zayed and Terry 2003).

7.4.2 Health Hazards of Chromium Compounds

A characteristic feature of chromium is its environmental mobility and consequently is a cause of environmental risk. Cr(VI) belongs to group A human carcinogen due to its mutagenicity, carcinogenicity, and teratogenicity nature in plants, animals, and humans (Narayani and Shetty 2013) (Fig. 7.2).

The ingestion of Cr(VI) leads to severe illness and can even causes death. Oral toxicity (LD_{50}) of Cr(VI) was reported to be 50–100 mg/kg and for C(III) 1900–3300 mg/kg in rats (NIOSH 1977). Cr(VI) ions readily solubilize in water and hence can pass through the cell permeability barriers (Thacker et al. 2006). In the living cells, oxyanions of heavy metals has impact on the metabolism of structurally associated nonmetals. Hexavalent chromium toxicity is linked to its capability to induce oxidative stress and damage DNA in cells (Reynolds et al. 2009). Previous studies have extensively described the development of oxidative stress that led to membrane damage for example, loss of membrane potential or inhibition of electron transport chain (ETC) both in prokaryotes and eukaryotes.

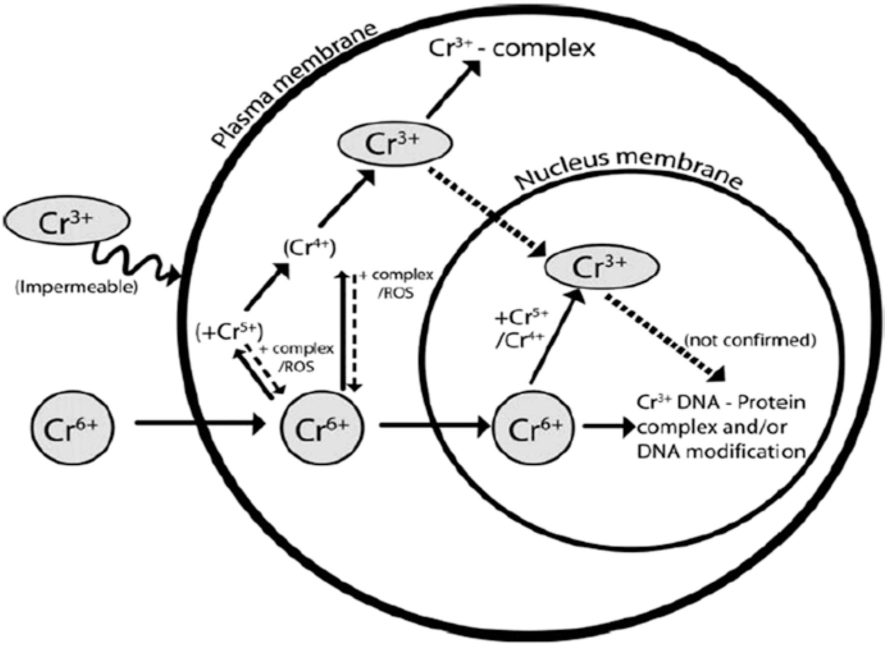

Fig. 7.2 A schematic diagram showing mutagenicity and toxicity of chromate ions (Narayani and Shetty 2013)

Hexavalent chromium is a carcinogen based on studies regarding respiratory cancer in individuals that are occupationally exposed to it (Mishra and Bharagava 2016; Chandra et al. 2011; Langard 1983). A temporary exposure levels of Cr(VI) beyond maximum contaminant level can lead to skin irritation or ulceration also called as chrome holes. Whereas, long-term exposure beyond maximum contaminant level can contribute to nerve tissue damage, kidney circulation, damage to the liver, and death (Kotas and Stasicka 2000). Individuals exposed to Cr(VI) could also suffer from nasal septum lesions. The improper waste disposal, poor storage, and leakage have made chromate as one of the most commonly recorded pollutant at waste areas (Narayani and Shetty 2013).

7.5 Nonbiological Methodologies for Effluent Remediation

Environmental protection agencies have concerns about waste treatment. Industrial effluents have bad impact on the surroundings, if strict regulatory standards are enforced then it will surely contribute to increase waste removal costs. Therefore, effluent processing is essential for long-term organization benefit. For controlling Cr pollution in countries where leather is produced at large-scale, tannery effluent treatment has become a critical issue, because of its substantial toxic content. Various leather fabricating activities and procedures bring about the generation of different types of fluid discharge. A difference in fluid volume will cause a significant effect on toxin concentrations (Springer 1994; Song et al. 2000).

Usually, tannery effluents containing high concentration of Cr (VI) compounds are processed by different physiochemical approaches for example, ion exchange, reduction, adsorption, precipitation, and electrodialysis and reverses osmosis that is expensive and has other disadvantages. These disadvantages include high reagent consumption, partial metal removal, energy requirements, and production of toxic sludge. Moreover, the majority of these strategies has some limitations and only applied at high/moderate concentration of heavy metals as compared to low concentrations (1–100 mg/Z) (Addour et al. 1999; Narayani and Shetty 2013).

Few of these methods are described below;

7.5.1 Chemical Precipitation

Chemical precipitation is a commonly used technique for removal of heavy metals from waste water. In this technique, dissolved pollutants are transformed into insoluble compounds, thus enabling subsequent removal of contaminant from the effluent by physical methods, for example, filtration (NEESA 1993). In precipitation process, precipitants particles (also known as flocculants and coagulants) size is increased by aggregation. The treatment process is directly dependent on alkalinity and pH of effluent as this will determine the amount of chemical that will be used for metal removal. Generally, sodium hydroxide or lime is used to precipitate heavy metals in water in neutralization process. But this process is not effective (incomplete precipitation) particularly when complexing agents are present (EPA 2000; Xu and Xu 2008).

For many years, chemical precipitation has been utilized as a prime technique for heavy metal removal. Groundwater contaminated with heavy metals has been remediated by chemical methods in column and pilot scale experiments. In one such analysis, calcium carbonate and granulated lime were used as coagulants (Lee et al. 2007). Moreover, a few researchers have created and specifically utilized 1, 3-benzenedaimidoethathiol dianion (industrially known as Metx) that irreversibly binds metals in aqueous solutions. In an investigation by Matlock et al. (2002), Metx showed more than 90% removal of toxic metals from acid mine wastes. Precipitation with sulfide is described to be one of the most effective processes. This is a due to its low solubility to destabilize solvent complexes. Regardless of the simplicity, this process is not suggested for use since lethal compounds could be discharged in acidic pH, subsequently leads to great risks in case of occurrence of accidental discharge or over dosage.

The best alternative recommended to conventional sulfide treatment is dithiocarbonate precipitation (Metalsorb 2004). Metals chemical precipitation methods have low costs and could be done by a pH alteration. Irrespective of these advantages, compound precipitation of metals in water still has few limitations such as production of large volume of sludge, leading to additional up to 50% effluent disposal costs (EPA 2000). Each dissolved heavy metal consists of different pH level for hydroxide precipitation. This procedure requires corrosive chemicals, therefore causing safety concerns (EPA 2000; Metalsorb 2004).

7.5.2 Ion Exchange

A reversible chemical reaction in which the ions from wastewater are exchanged by a similar charged species attached to an immobile solid particle. These exchanged particles are either synthetically manufactured resin or naturally present inorganic salts. This process is primarily similar to biosorption therefore the latter is known to work mainly on basis of ion exchange. Ion exchange mostly uses hydrocarbon-derived polymeric resins (Volesky 2003). This method has been effectively used for removal of heavy metals from waste water. Vaca et al. (2001) have described the interactions of chromium, cadmium, and lead, while competing for ion exchange active sites in naturally present clinoptilolite. Their investigation showed efficient removal of dissolved metals within 18 h in batch reactors, with the percent removal of more than 95% in acidic pH.

7.5.3 Reverse Osmosis

Reverse osmosis consists of a membrane that functions as a molecular filter to eliminate 99% of all dissolved heavy metals in a solution. In this procedure, the water goes through the film while the dissolved and particulate compounds are filtered out. This procedure is very efficient for ionic species removal from aqueous solutions. The subsequent by-product solutions make it more feasible for effective recovery of heavy metals. Regardless of the adequacy, these membranes are generally expensive. This technique is costly due to the use of elevated pressure, which makes it sensitive to working conditions.

An important advantage of reverse osmosis as compared to other effluent treatment systems is the capability to reduce the other ionic pollutant concentrations as well as dissolved organic compounds (Volesky 2003; Pawlak et al. 2005). Reverse osmosis has been used in small and large-scale experiments for heavy metal removal. Pawlak et al. (2005) conducted a study in which they checked reverse osmosis membrane module for removal of total arsenic concentration in feed water over a period of 30 days. The concentration of arsenic was reduced from 60 ppb on average to 1 ppb in the treated water.

7.5.4 In Situ Chemical Sorption

In situ chemical sorption (ISCS) is also a significant method for immobilization of Cr(VI). Activated carbon displays a significantly high adsorption capability for Cr (VI) with two mechanisms of adsorption and for other inorganic compounds. Firstly, Cr(VI) ions are adsorbed on the inner carbon surface, subsequently reduced to Cr(III), later these Cr(III) ions move to outer carbon surface (Mohan and Pittman Jr 2006). GAC (granular initiated carbon) in permeable reactive barrier (PRB) systems is extremely appropriate for hexavalent chromium removal from ground waters (Han et al. 2000). If treating naturally occurring zeolites with cationic surfactants, they can gain a positive charge on its surface, bringing about an enhanced sorption affinity for anionic metals, such as chromate. They are known as surface-modified zeolites (SMZs) and can be effectively used for chromate immobilization. PRBs filled with SMZ have been successfully used for remediation of a Cr(VI) polluted aquifer.

Another effective material for chromate ions adsorption from solutions is unrefined tamarind fruit shells (CTFS) and pretreated with hydrochloric acid. Moreover, peat has been used in commercial applications for reduction and removal of chromate from polluted groundwater (Theologou et al. 2013). Ferrous materials can also be utilized for ISCS such as mixed magnetite and maghemite nanoparticles. The use of magnetite-maghemite nanoparticles is an efficient method for chromate adsorption from aqueous solutions and can also be used for treating ground water (Chowdhury and Yanful 2010). They also demonstrated that under controlled (acidic) pH conditions, the chromate ion take-up ranges between 96 and 99%.

7.5.5 Electrochemical Technique

Electrochemical techniques give a different approach for remediation of Cr(VI) contaminated sites as it represents both electrical and chemical reactions simultaneously. Electrochemical treatment procedures have considered well due to their adaptability and ecological compatibility, which makes the removal of heavy metals from solids, liquids, and gases possible. Actually, the fundamental reagent is the electron, which is a clean reagent (Barrera-Dıaz et al. 2003). Electrochemical Cr (VI) removal strategies can be utilized in various ways depending upon the electrode material, pH of the aqueous solution, and the intensity of the current density employed. In this way different chemical reactions can occur simultaneously on electrode surface or in the aqueous solution (Barrera-Díaz et al. 2012). Electrochemical treatment was considered as rapid, need few chemicals, giving high removal and selectivity of metals, and produce less secondary compounds. Conversely, this technique requires high initial capital cost and production of spongy deposits (Madhavi et al. 2013).

7.6 Biological Methodologies for Effluent Remediation

Immensely growing population, industrialization, and deforestation have led to serious ecological problems. One of them is improper waste disposal of toxic effluents of industries into the environment. These toxic effluents mainly consist of complex mixtures of heavy metals that greatly affect living beings. Cr is major heavy metals chemical toxin, present in effluents of paint, textile, dying, and leather industries. Manufacturing and industrial activities discharged more than 0.17 million tons of Cr waste in the biosphere. Due to the relatively less toxic nature and thermodynamic stability of Cr(III) than Cr(VI), discharge of tannery effluents in water bodies and on land has created high levels of Cr (30,000 mg/kg or more) (Naidu et al. 2000).

Cr is one of the micronutrient essential for proper growth and development of human body. However, exceeding a certain limit has led to various health issues. Chromium is considered toxic in its hexavalent form and can cause skin ulcers. Prolong exposure can possibly lead to lung cancer and asthma. Hence, the regulatory authorities have emphasis on rehabilitation and remediation of Cr polluted sites (Kamaludeen et al. 2003; Chandra et al. 2009). Various strategies have been developed for removal of heavy metals from the environment. Conventional remediation treatment processes for heavy metals removal includes flocculation, chemical precipitation, evaporative recovery, coagulation, electrodialysis, floatation, reverse osmosis, nano-filtration, ion exchange and ultrafiltration, etc. These procedures are effective, however, high chemical and energy requirement makes them inefficient for remediation of polluted areas. Moreover, production of highly toxic by-products and sludge makes them even more ineffective. Therefore, environment friendly, economical, and effective strategies are needed which can reduce chromate pollution in the surroundings.

Bioremediation is the biological approach to degrade heavy metals using indigenous microorganisms (Xie et al. 2010; Bharagava et al. 2014; Raman et al. 2018). The fundamental principle of bioremediation is the use of microbes (mostly bacteria) for the removal or transfer of hazardous contaminants to less toxic forms. These microbes can only destroy harmful compounds when minerals and nutrients are available to them for growth and development of cells. Microbes have the ability to produce oxidized or reduced species that precipitate the metals (National Research Council 1993).

Microorganisms including bacteria, yeasts, fungi, and algae are capable of reducing Cr(VI) (Cervantes et al. 2001). Microbial reduction of Cr(VI) to Cr(III) has been extensively studied (Cheung and Gu 2007). Two different processes are followed by microbes for Cr (VI) reduction, i.e., direct and indirect reduction. The former process comprises various reductase bacteria that obtain electrons from reduced organic substrates (nucleotides, sugars, amino acids, vitamin, organic acids, or glutathione) (Ramírez-Díaz et al. 2008). While in the indirect process bacterial metabolism produced reducing agents (Fe^{2+} and HS^{-}) that causes Cr(VI) to reduce to Cr(III) (Prevot et al. 2018).

7.6.1 Bacterial Removal of Chromate Ions

Hexavalent chromium is known for its strong oxidizing ability and toxicity to living cells (Kotas and Stasicka 2000). Bacteria can survive and grow under harsh environmental conditions. Cr(VI) toxicity causes development of various resistance mechanisms in bacteria. Several studies reported Cr(VI) resistant bacteria that gain resistivity growing in chromate contaminated sites. *Pseudomanas* sp., was the first Cr(VI) reducing bacterial species isolated by Romanenko and Koren'kov (1977) from industrial effluents. Since then many chromium reducing bacteria have been isolated from various sources and could be applied in remediation processes (Chen and Hao 1998; Chandra et al. 2011; Narayani and Shetty 2013; Coetzee et al. 2018). Many bacterial species are known to have enhanced Cr (VI) reduction potential under aerobic and anaerobic conditions (Cheung and Gu 2007).

Microorganisms, especially bacteria, exhibit various metabolic pathways that use different toxic chemical compounds as energy source through fermentation, respiration, and co-metabolism for growth and development (Ayangbenro and Babalola 2017). These resistance mechanisms includes active efflux system, formation of complexes with thiol-containing molecules, mobilization/immobilization of heavy metals, DNA repair enzymes, intra or extracellular sequestration, detoxifying enzymes for reactive oxygen species (ROS), and transformation of toxic heavy metals into less toxic compounds (Fig. 7.1) (Bento et al. 2005; Pei et al. 2009; Soni et al. 2013).

Bioremediation involves Cr(VI) to Cr(III) reduction by microorganisms and involves an additional mechanism i.e., chromate resistance. Different bacterial species are reported for chromate reduction for example, *Escherichia*, *Deinococcus*, *Arthrobacter* spp., *Bacillus cereus*, *Burkholderia* spp., *Sporosarcina ginsengisoli*, *Kocuria flava*, *and Pseudomonas veronii* (Chandra et al. 2011; Thatoi et al. 2014).

For evaluation of chromate resistant bacteria for bioremediation purposes, Salunkhe et al. (1998) took sewage sludge sample and isolated *P. mendocina* and investigated Cr(VI) reduction potential in soil microcosm study. Their investigation showed that *P. mendocina* has the potential to immobilize 100 mg/kg Cr(VI) in 8 h. After treating Cr(VI) polluted soil with bacteria, wheat seedling growth was supported without giving any toxic effects. These findings clearly exhibited the beneficial use of bacterial treatment in remediating Cr(VI) sites (Salunkhe et al. 1998; Zayed and Terry 2003). Schematic diagram of isolation of chromate resistant bacteria from tannery wastes is shown in Fig. 7.3 (Narayani and Shetty 2013).

7.6.1.1 Bacterial Biomass Used for Bulk Removal of Metal Ions

Bacteria, algae, fungi, agricultural wastes, etc. are commonly used as biosorbent materials and possess strong ability for reclaiming heavy metals contaminated sites. These materials have wide variety of sorption sites that retain metal ions and other compounds (San Keskin et al. 2018). This technology is very effective for detoxification of toxic industrial effluents. Agricultural wastes are efficient biosorbent materials and have low cost for example, straw, coconut husks, rice husk, exhausted coffee, peat moss (Dakiky et al. 2002), coconut fiber, walnut skin, waste tea (Jouraiphy et al. 2005), rice hulls, defatted rice bran, cotton seed hulls and soybean hulls (Tarley and Arruda 2004), mustard seed cakes, and wheat bran (Iqbal et al. 2002). These materials are also processed with strong alkali to increase metal binding capacity from aqueous solutions. The binding/uptake of metals to cellular compartments is usually termed as biosorption.

Biosorbents are naturally occurring ion exchange materials which mostly comprise of weak acidic and basic functional groups. Metals can be reclaimed from the matrix by treating with HCl or H_2SO_4, NaOH/complexing agents, on dead biomass or live bacteria (Coelho et al. 2015).

Plants are also capable of heavy metal removal from polluted sites. Under metal stress condition, they produce peptide molecules that are rich in cysteine amino acids for example, metallothioneins (MTs), glutathione (GSH), and phytochelatins (PCs) that readily bind and remove metal ions in biologically inactive forms. A study showed MTs over expression in recombinant bacterial cells that increase metal ions uptake, therefore giving an opportunity to develop microbial-based biosorbents for reclamation of polluted sites (Zayed and Terry 2003).

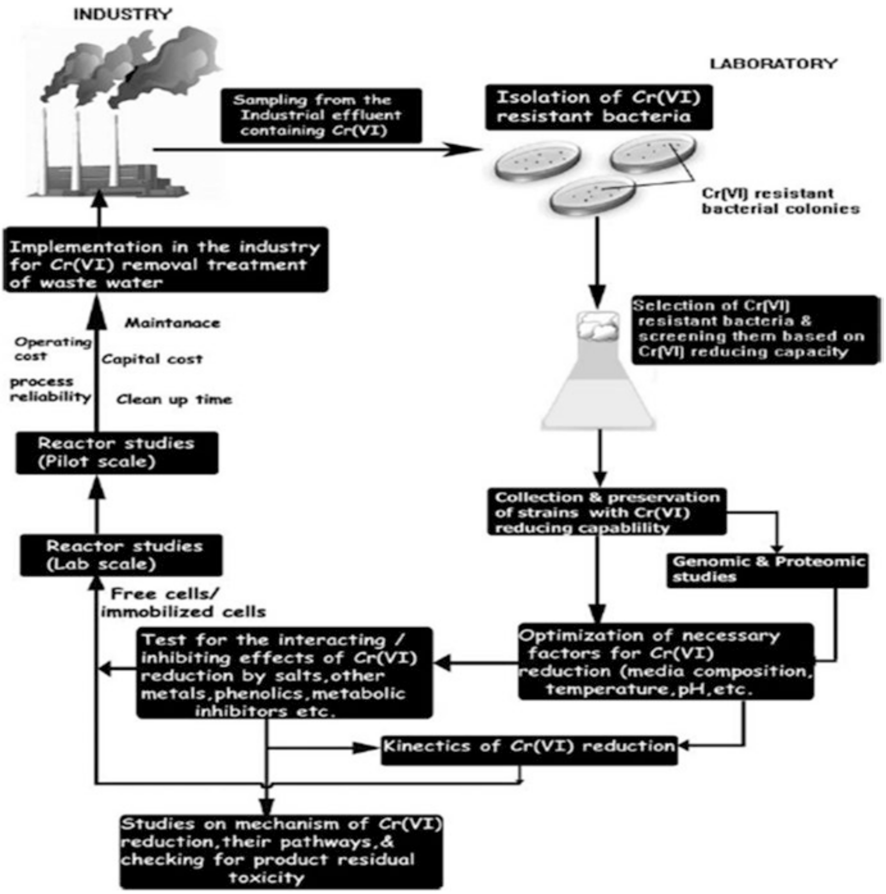

Fig. 7.3 Schematic diagram of isolation of Cr(VI) resistant bacteria from tannery wastes (Narayani and Shetty 2013)

7.6.2 *Fungal and Yeast Removal of Chromate Ions*

Fungi and yeasts have been equally known for Cr(VI) removal from contaminated environments. The beneficial characteristics of fungi are its high variability and ranging in size form microscopic molds to mushrooms. They easily grow and produce significant amount of biomass (Coelho et al. 2015). Various fungal species are reported for Cr(VI) biosorption such as *Aspergillus niger* (Srivastava and Thakur 2006), *Aspergillus oryzae* (Igwe and Abia 2006), *Trichoderma* sp., (Vankar and Bajpai 2008), *Fusarium oxysporum* (Amatussalam et al. 2011), *Aspergillus fumigatus, Aspergillus versicolor*, *Penicillium canescens* (Coelho et al. 2015), and dead fungal biomass for example, *Rhizopus oryzae, Aspergillus niger, Saccharomyces cerevisiae,* and *Penicillium chrysogenum* (Park et al. 2005). The protein molecules present on fungal cell surface comprise different functional groups that adsorb

Cr(VI) by forming chemical bonds. FTIR analysis of fungal cell wall surface showed occurrence of hydroxyl, carboxyl, amino, and carbonyl functional groups that help in the binding of chromate ions (Vankar and Bajpai 2008; Amatussalam et al. 2011).

Various studies have developed biosorbents material by using fungal strains and examined their efficiency for Cr(VI) removal. In a study, *Carica papaya* plant dry stem was used as biosorbent matrix and *F. oxysporum* cells were colonized with it. About 90% chromate biosorption was achieved using this material by the end of fifth day of incubation (Amatussalam et al. 2011). Singh et al. (2016) established *Aspergillus flavus* biosorbent material, incorporated with ferrous ions, improved removal of Cr(VI) along with the adhesiveness of biosorbent material. A study was performed with fungal strains *A. flavus* and *A. niger* associated marine seaweed to investigate for Cr(VI) resistance and accumulation. The results showed that both strains were capable of accumulating more than 25% of Cr provided to them. *Aspergillus flavus* showed maximum accumulation potential (Gupta et al. 2000). Other organisms such as *Hypocrea tawa* (Morales-Barrera et al. 2008) and *Trichoderma inhamatum* (Morales-Barrera and Cristiani-Urbina 2008) were reported for chromate reduction after biosorption process (Jobby et al. 2018). Fungal removal of hexavalent chromium generally depends on anionic biosorption.

However, other studies have suggested the use of fungal mycelia as biosorbent material that involves adsorption-coupled reaction, adsorbing Cr(VI) on biomaterials followed by reduction through non-enzymatic reactions to trivalent chromium with help of electron donors contained by the biomaterial (Park et al. 2007). Cr(VI) reduction by yeast was studied by Martorell et al. (2012). They isolated *Pichia jadinii* M9 and *Pichia anomala* M10 yeast strains from dye industry discharge. These strains also transformed Cr(VI) into Cr(III) by chromate reductase activity. Mahmoud and Mohamed (2017) showed Cr(VI) biosorption by utilizing biomass/polymer matrices beads (BPMB). They synthesized BPMB by immobilizing *Saccharomyces cerevisiae* biomass in 3% alginate extract. Approximately, 85% Cr(VI) reduction was achieved at 200 ppm initial chromate concentration and optimized cultural conditions (Jobby et al. 2018).

7.6.3 Algal Removal of Chromate Ions

Algal biomass are also used for biosorption of Cr(VI) from aqueous solutions such as tannery effluents, contaminated wastewaters, etc. Cr(VI) remediation is achieved by occurrence of functional groups for example, hydroxyl, amino, sulfate, and carbonyl in association with specific molecules phytochelatins, metallothioneins, guluronic acid, alginates, and sulfated polysaccharides solutions. Algal cell surface adsorbs Cr(VI) and then accumulates it intracellularly (Sen and Dastidar 2010; Jyoti and Awasthi 2014). Several biosorbent materials has been established and assessed for maximum Cr(VI) removal by applying biomass of *Euglena*, *Cladophora crispata*, *Dunaliella* sp., *Laurencia obtuse*, *Pachymeniopis* sp., *Scenedesmus incras-*

satulus (Ahluwalia and Goyal 2007), *Ceramium virgatum* (Sari and Tuzen 2008), *Spirogyra* sp., (Gupta et al. 2001), *Nostoc linckia* (Mona et al. 2011), *Spirulina* sp., (Rezaei 2016), *Chlorella vulgaris* (Sibi 2016).

Different studies are reported for batch cultures optimization of different physiochemical parameters (pH, temperature, adsorbent concentration, agitation time, initial chromate concentration, adsorbent dose, and contact time) to achieve maximum chromate adsorption on algal biomaterials. *Cladophora* biomass showed maximum Cr(VI) accumulation i.e., 72% after 15 min, it was followed by *Chlorella vulgaris* 34–48%, and *Selenastrum* with 39% chromate accumulation. *Spirulina* biomass accumulated up to 82.67% of Cr(VI) under optimized conditions at 10 mg/L initial chromate concentration (Rezaei 2016; Jobby et al. 2018).

7.6.4 Phytoremediation of Chromate Ions

Chromium is the second most abundant heavy metal that enters into the agricultural systems by application of Cr contaminated wastewater (Saxena et al. 2017; Gupta et al. 2018). Phytoremediation technique includes the use of plants to remediate heavy metal polluted water and soils through biochemical degradation, uptake, accumulation, or sequestration of heavy metals. The vascular plants are capable of up taking heavy metals, accumulate, and store large amounts through their root systems. The uptake of chromium contaminants in plant has been conducted through various laboratory studies and small-scale field trials (Fruchter 2002). The metal tolerance is greatly influenced by plant species and genotype.

Phytoremediation of Cr(VI) has been investigated in several plants such as *Agave lechuguilla*, *Atriplex canescens*, *Larrea tridentata, Thuja* orientalis, and *Pinus sylvestris* (Madhavi et al. 2013). Romero-González et al. (2006) used *Agave lechuguilla* biomass for chromate biosorption. Cr(VI) absorption was maximum at pH 2.0 either due to electrostatic attraction of positively charged ligands for example, protonated amines to Cr(VI) oxyanions or through Cr(VI) to Cr(III) reduction, consequently resulting in the binding of Cr(III) to the biomass (Romero-González et al. 2006; Madhavi et al. 2013).

Plants are reported to produce specific enzymes that have similar function as chromate reductase produced by bacteria and mediate in chromate reduction (Lytle et al. 1998). Early efforts for phytoremediation of Cr(VI) contaminated sites of Ranipet Tanneries in Tamil Nadu was performed with *Sorghum* by Revathi et al. (2011). They examined the effect of chromate ions on content of chlorophyll and biomass. Increased concentration of Cr(VI) showed significant reduction in plant biomass. The plant biomass was effectively increased by supplementation of vermicompost to the polluted soil, creating more space for accumulation of chromium. Various other plants have been reported for their ability of accumulating Cr includes *Barringtonia acutangula* (Kumar et al. 2014), *Callitriche cophocarpa* (Jobby et al. 2018), *Pterocarpus indicus*, *Jatropha curcas* (Mangkoedihardjo et al. 2008), *Jasminum sambac, Jasminum grandiflorum, Polianthes tuberosa, Nerium oleander,* and *Helianthus* sp. (Jobby et al. 2018). *Callitriche cophocarpa* was reported as best Cr(VI) accumulator showing 27 times greater chromate concentration in fresh shoots as compared to the older ones (Jobby et al. 2018).

Phytoremediation is a low energy, inexpensive, and eco-friendly technique. It causes fewer disturbances in soil ecosystem. It prevents excavation and is generally acceptable and easily maintained. However, this technology is slow and time consuming due to slow growth rate of plants. After remediation, plant biomass needs proper disposal. A change in agro-climatic conditions directly affects phytoremediation. The pollutants can enter soil again by litter formation of these heavy metal accumulating plants. The solubility of contaminants may be increased by root exudates of hyper-accumulating plants and led to dissemination of heavy metals into the soil. Therefore, to improve and make phytoremediation a sustainable technology, plants with high growth rate are required with extensive root system for accumulating high concentration of pollutants. These plants should be able to produce large quantity of biomass and along with that recombinant technology could be used to engineer common plants with hyper accumulating genes (Khan et al. 2009).

7.7 Emerging Trends and Future Prospects

Biotechnological approach such as in situ remediation is applied to reduce or eliminate toxic heavy metals that have led to environmental hazard and risks. In situ remediation involves direct inoculation of microbes and reagents into the polluted aquifer and is becoming progressively a common technique. The cost effectiveness, simplicity of procedure, and least interference of the site give further advantage for the application of this technique. The removal processes that utilize permeable reactive barriers is also gaining acceptance. No single technique is adequate for the removal of majority of the pollutants that might exist at a site or to accomplish compliance with cleanup standards. To accomplish the goals, the use of treatment train strategy is frequently required.

For instance, inorganic reductants might be applied for mass removal of chromate contaminants, followed by the use of anaerobic bioremediation and/or to additionally check natural reduction. This strategy is gaining commercial acceptance and application, particularly at complex sites. On commercial ground, new reagents/chemicals are also added for both bioremediation and inorganic pathways. In various remediation systems, nanotechnology is applied particularly nZVI that is rapidly developing field and an effective approach for reclamation of chromate polluted environments. These materials are costly as compared to conventional materials. However, using nanoparticles in areas where conventional material may not be applied such as fractured rock aquifers. Other nanoparticles such as carbon nanotubes were used for reduction of hexavalent chromium that showed very promising results (Gu et al. 2013). Different reports are available on combination of bioremediation and electro-kinetics with significant outcomes (Fonseca et al. 2011).

Hexavalent chromium reduction can also be achieved by immobilizing microbial cells combined with nanotechnology such as, C-nanotubes impregnated into calcium alginate, significantly improved Cr(VI) reduction and enzyme stability. Nanomaterials donate electrons in enzymatic hexavalent chromium reduction and immobilization (trivalent chromium precipitates) can likewise be applied at chromate contaminated sites for remediation purposes (Igiri et al. 2018).

7.8 Conclusion

The use of biological systems for example, microbes and plants for remediation of Cr(VI) polluted sites is significantly developing and has proven a considerable progress in situ, further combined with field trials at various agro-climatic zones all over the world. Biosorption have been established as an eco-friendly, efficient, and cost-effective technique for reclamation of Cr(VI) polluted environments. Bacterial, algal, fungal, and plant biomass are considered effective for hexavalent chromium transformation. This chapter provides a detailed understanding of Cr(VI) removal through various processes. Therefore, helping in improving current technologies to be more proficient for Cr(VI) remediation.

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References

Addour L, Belhoucine D, Bouldries N, Comeau Y, Pauss A, Mameri N (1999) Zinc uptake by *Streptomyces rimosus* biomass using a packed bed column. J Chem Technol Biotechnol 74:1089–1095

Agency for Toxic Substance and Disease Registry (ATSDR) (2015) Toxicological profile for chromium. U.S. Department of Health and Human Services, Public Health Services, ATSDR, Atlanta

Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresour Technol 98(12):2243–2257

Ali A, Saeed K, Mabood F (2016) Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent. Alex Eng J 55(3):2933–2942

Alvarez-Bernal D, Contreras-Ramos SM, Trujillo-Tapia N, Olalde-Portugal V, Frías-Hernández JT, Dendooven L (2006) Effects of tanneries wastewater on chemical and biological soil characteristics. Appl Soil Ecol 33(3):269–277

Amatussalam A, Abubacker MN, Rajendran RB (2011) In situ *Carica papaya* stem matrix and *Fusarium oxysporum* (NCBT-156) mediated bioremediation of chromium. Indian J Exp Biol 49(12):925–931

Anderson RA (1989) Essentiality of Cr in humans. Sci Total Environ 86:75–81

Anderson RA (1997) Chromium as an essential nutrient for humans. Regul Toxicol Pharmacol 26:S35–S41

Ayangbenro AS, Babalola OO (2017) A new strategy for heavy metal polluted environments: a review of microbial biosorbents. Int J Environ Res Public Health 14(1):94

Barrera-Dıaz C, Urena-Nunez F, Campos E, Palomar-Pardavé M, Romero-Romo M (2003) A combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater. Radiat Phys Chem 67(5):657–663

Barrera-Díaz CE, Lugo-Lugo V, Bilyeu B (2012) A review of chemical, electrochemical and biological methods for aqueous Cr (VI) reduction. J Hazard Mater 223:1–12

Basaran B, Ulaş M, Bitlisli BO, Aslan A (2008) Distribution of Cr (III) and Cr (VI) in chrome tanned leather. Indian J Chem Technol 15:511–514

Bento FM, Camargo FA, Okeke BC, William FT (2005) Comparative bioremediation of soils contaminated with diesel oil by natural attenuation, biostimulation and bioaugmentation. Bioresour Technol 96(9):1049–1055

Bharagava RN, Yadav S, Chandra R (2014) Antibiotic and heavy metal resistance properties of bacteria isolated from the aeration lagoons of common effluent treatment plant (CETP) of tannery industries (Unnao, India). Ind. J Biotechnol 13:514–519

Bharagava RN, Saxena G, Mulla SI, Patel DK (2018) Characterization and identification of recalcitrant organic pollutants (ROPs) in tannery wastewater and its phytotoxicity evaluation for environmental safety. Arch Environ Contam Toxicol 75(2):259–272

Cervantes C, Campos-García J, Devars S, Gutiérrez-Corona F, Loza-Tavera H, Torres-Guzmán JC, Moreno-Sánchez R (2001) Interactions of chromium with microorganisms and plants. FEMS Microbiol Rev 25(3):335–347

Chandra R, Bharagava RN, Yadav S, Mohan D (2009) Accumulation and distribution of toxic metals in wheat (*Triticum aestivum* L.) and Indian mustard (*Brassica campestris* L.) irrigated with distillery and tannery effluents. J Hazard Mater 162:1514–1521

Chandra R, Bharagava RN, Kapley A, Purohit HJ (2011) Bacterial diversity, organic pollutants and their metabolites in two aeration lagoons of common effluent treatment plant during the degradation and detoxification of tannery wastewater. Bioresour Technol 102:2333–2341

Chen JM, Hao OJ (1998) Microbial chromium (VI) reduction. Crit Rev Environ Sci Technol 28(3):219–251

Cheung KH, Gu JD (2007) Mechanism of hexavalent chromium detoxification by microorganisms and bioremediation application potential: a review. Int Biodeterior Biodegradation 59(1):8–15

Chowdhury SR, Yanful EK (2010) Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphate on removal. J Environ Manag 91:2238–2247

Chrysochoou M, Johnston CP, Dahal G (2012) A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron. J Hazard Mater 201:33–42

Coelho LM, Rezende HC, Coelho LM, de Sousa PA, Melo DF, Coelho NM (2015) Bioremediation of polluted waters using microorganisms. In: Advances in bioremediation of wastewater and polluted soil, Naofumi Shiomi, IntechOpen. https://doi.org/10.5772/60770

Coetzee JJ, Bansal N, Chirwa EM (2018) Chromium in environment, its toxic effect from chromite-mining and ferrochrome industries, and its possible bioremediation. In: Exposure and health. pp 1–12

Cooman K, Gajardo M, Nieto J, Bornhardt C, Vidal G (2003) Tannery wastewater characterization and toxicity effects on *Daphnia* spp. Environ Toxicol Int J 18(1):45–51

Dakiky M, Khamis M, Manassra A, Mer'Eb M (2002) Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. Adv Environ Res 6(4):533–540

Devi BD, Thatheyus A, Ramya D (2017) Bioremoval of hexavalent chromium, using *Pseudomonas fluorescens*. J Microbiol Biotechnol Res 2(5):727–735

Eccles H (1995) Removal of heavy metals from effluent streams—why select a biological process? Int Biodeter Biodegr 35(1–3):5–16

EPA (1990) Draft report Government of Punjab, Lahore. Environment Protection Agency, Government of Punjab, Lahore, p 127

EPA (2000) Wastewater technology sheet: chemical precipitation. United State Environmental Protection. EPA 832-F-00-018. http://www.epa.Gov/own/mtb/chemical_precipitation.pdf. Accessed 7 July 2010

Fonseca B, Pazos M, Sanroman MA (2011) Removal of hexavalent chromium of contaminated soil by coupling electrokinetic remediation and permeable reactive biobarriers. Environ Sci Pollut Res Int 19:1800–1808

Fruchter J (2002) Peer reviewed: in-situ treatment of chromium-contaminated groundwater. Environ Sci Technol 36:23

Gu H, Rapole S, Huang Y, Cao D, Luo Z, Suying W, Guo Z (2013) Synergistic interactions between multi-walled carbon nanotubes and toxic hexavalent chromium. J Mater Chem A 1:2011–2021

Gupta R, Ahuja P, Khan S, Saxena RK, Mohapatra H (2000) Microbial biosorbents: meeting challenges of heavy metal pollution in aqueous solutions. Curr Sci 78(8):967–973

Gupta VK, Shrivastava AK, Jain N (2001) Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species. Water Res 35(17):4079–4085

Gupta P, Rani R, Chandra A, Kumar V (2018) Potential applications of *Pseudomonas* sp. (strain CPSB21) to ameliorate Cr^{6+} stress and phytoremediation of tannery effluent contaminated agricultural soils. Sci Rep 8(1):4860

Habibul N, Hu Y, Wang YK, Chen W, Yu HQ, Sheng GP (2016) Bioelectrochemical chromium (VI) removal in plant-microbial fuel cells. Environ Sci Technol 50(7):3882–3889

Han I, Schlautman MA, Batchelor B (2000) Removal of hexavalent chromium from groundwater by granular activated carbon. Water Environ Res 72:29–39

Hauschild MZ (1993) Putrescine (1,4-diaminobutane) as an indicator of pollution-induced stress in higher plants: barley and rape stressed with Cr(III) or Cr(VI). Ecotoxicol Environ Saf 26:228–247

Haydar S, Aziz JA (2009) Characterization and treatability studies of tannery wastewater using chemically enhanced primary treatment (CEPT)—a case study of Saddiq Leather Works. J Hazard Mater 163(2–3):1076–1083

Igiri BE, Okoduwa SI, Idoko GO, Akabuogu EP, Adeyi AO, Ejiogu IK (2018) Toxicity and bioremediation of heavy metals contaminated ecosystem from tannery wastewater: a review. J Toxicol 2018:2568038

Igwe J, Abia AA (2006) A bioseparation process for removing heavy metals from waste water using biosorbents. Afr J Biotechnol 5(12):1167–1179

Iqbal M, Saeed A, Akhtar N (2002) Petiolar felt-sheath of palm: a new biosorbent for the removal of heavy metals from contaminated water. Bioresour Technol 81(2):151–153

Jobby R, Jha P, Yadav AK, Desai N (2018) Biosorption and biotransformation of hexavalent chromium [Cr (VI)]: a comprehensive review. Chemosphere 207:255–266

Joshi NC (2018) Biosorption: a green approach for heavy metal removal from water and waste waters. Res J Life Sci Bioinform Pharm Chem Sci 4(1):59–69

Jouraiphy A, Amir S, El Gharous M, Revel JC, Hafidi M (2005) Chemical and spectroscopic analysis of organic matter transformation during composting of sewage sludge and green plant waste. Int Biodeter Biodegr 56(2):101–108

Jyoti J, Awasthi M (2014) Bioremediation of wastewater chromium through microalgae: a review. Int J Eng Res Technol 3(6):1210–1215

Kamaludeen SP, Megharaj M, Juhasz AL, Sethunathan N, Naidu R (2003) Chromium-microorganism interactions in soils: remediation implications. Rev Environ Contam Toxicol 178:93–164. Springer, New York

Khan AG (2001) Relationships between chromium biomagnification ratio, accumulation factor, and mycorrhizae in plants growing on tannery effluent-polluted soil. Environ Int 26(5–6):417–423

Khan MS, Zaidi A, Wani PA, Oves M (2009) Role of plant growth promoting rhizobacteria in the remediation of metal contaminated soils. Environ Chem Lett 7(1):1–19

Kishor R, Bharagava RN, Saxena G (2019) Industrial wastewaters: the major sources of dye contamination in the environment, ecotoxicological effects, and bioremediation approaches. In:

Bharagava RN (ed) Recent advances in environmental management. CRC Press Taylor & Francis. ISBN-13: 978-0-8153-8314-7

Kotas J, Stasicka Z (2000) Chromium occurrence in the environment and methods of its speciation. Environ Pollut 107:263–283

Krishnamurthy S, Wilkens MM (1994) Environmental chemistry of Cr. Northeast Geol 16(1):14–17

Kumar D, Tripathi DK, Chauhan DK (2014) Phytoremediation potential and nutrient status of *Barringtonia acutangula* Gaerth. Tree seedlings grown under different chromium (CrVI) treatments. Biol Trace Elem Res 157(2):164–174

Langard S (1983) The carcinogenicity of chromium compounds in man and animals. In: Burrows D (ed) Chromium: metabolism and toxicity. CRC Press, Boca Raton, pp 13–30

Lee M, Paik IS, Kim I, Kang H, Lee S (2007) Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate. J Hazard Mater 144(1–2):208–214

Lofrano G, Meriç S, Zengin GE, Orhon D (2013) Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. Sci Total Environ 461:265–281

Lytle CM, Lytle FW, Yang N, Qian JH, Hansen D, Zayed A, Terry N (1998) Reduction of Cr(VI) to Cr(III) by wetland plants: potential for in situ heavy metal detoxification. Environ Sci Technol 32(20):3087–3093

Madhavi V, Reddy AVB, Reddy KG, Madhavi G, Prasad TNKV (2013) An overview on research trends in remediation of chromium. Res J Recent Sci 2277:2502

Mahmoud MS, Mohamed SA (2017) Calcium alginate as an eco-friendly supporting material for Baker's yeast strain in chromium bioremediation. HBRC J 13(3):245–254

Mangkoedihardjo S, Ratnawati R, Alfianti N (2008) Phytoremediation of hexavalent chromium polluted soil using *Pterocarpus indicus* and *Jatropha curcas* L. World Appl Sci J 4(3):338–342

Marshall WE, Champagne ET (1995) Agricultural byproducts as adsorbents for metal ions in laboratory prepared solutions and in manufacturing wastewater. J Environ Sci Health Part A 30(2):241–261

Martorell MM, Fernández PM, Fariña JI, Figueroa LI (2012) Cr (VI) reduction by cell-free extracts of *Pichia jadinii* and *Pichia anomala* isolated from textile-dye factory effluents. Int Biodeter Biodegrad 71:80–85

Matlock MM, Howerton BS, Atwood DA (2002) Chemical precipitation of heavy metals from acid mine drainage. Water Res 36(19):4757–4764

Metalsorb (2004) Heavy metal chelating agents. http://www.snf-group.com/IMG/pdf/Heavy_Metal_-METALSORB_E.pdf. Accessed 9 July 2010

Mishra S, Bharagava RN (2016) Toxic and genotoxic effects of hexavalent chromium in environment and its bioremediation strategies. J Environ Sci Health C Environ Carcinog Ecotoxicol Rev 34(1):1–32

Mohan D, Pittman CU Jr (2006) Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. J Hazard Mater 137:762–811

Mohapatra RK, Parhi PK, Thatoi H, Panda CR (2017) Bioreduction of hexavalent chromium by *Exiguobacterium indicum* strain MW1 isolated from marine water of Paradip Port, Odisha, India. Chem Ecol 33(2):114–130

Molokwane PE, Meli KC, Nkhalambayausi-Chirwa EM (2008) Chromium (VI) reduction in activated sludge bacteria exposed to high chromium loading: Brits culture (South Africa). Water Res 42(17):4538–4548

Mona S, Kaushik A, Kaushik CP (2011) Biosorption of chromium (VI) by spent cyanobacterial biomass from a hydrogen fermentor using Box-Behnken model. Int Biodeter Biodegr 65(4):656–663

Morales-Barrera L, Cristiani-Urbina E (2008) Hexavalent chromium removal by a *Trichoderma inhamatum* fungal strain isolated from tannery effluent. Water Air Soil Pollut 187(1–4):327–336

Morales-Barrera L, de Maria Guillen-Jimenez F, Ortiz-Moreno A, Villegas-Garrido TL, Sandoval-Cabrera A, Hernández-Rodríguez CH, Cristiani-Urbina E (2008) Isolation, identification and characterization of a *Hypocrea tawa* strain with high Cr (VI) reduction potential. Biochem Eng J 40(2):284–292

Naidu R, Kookana RS, Cox J, Mowat D, Smith LH (2000) Fate of chromium at tannery waste contaminated sites at Mount Barker, South Australia. In: Naidu R, Willett IR, Mahimairaja S, Kookana RS, Ramasamy K (eds) Towards better management of soils contaminated with tannery waste, proceedings no 88. Australian Council for International Agricultural Research, Canberra, pp 57–70

Narayani M, Shetty KV (2013) Chromium-resistant bacteria and their environmental condition for hexavalent chromium removal: a review. Crit Rev Environ Sci Technol 43(9):955–1009

National Research Council (1993) In situ bioremediation: when does it work? National Academies Press, Stockholm

NEESA (1993) Precipitation of metals from ground water. NEESA Document Number 20.2-051.6. Novel Energy and Environmental Support Activity, Port Hueneme

NIOSH (1977) Registry of toxic effects of chemical substances. DHEW (NIOSH) Pub. 78-104-B. National Institute for Occupational Safety and Health, Cincinnati 2:296, 590

Padda IUH, Asim M (2019) What determines compliance with cleaner production? An appraisal of the tanning industry in Sialkot, Pakistan. Environ Sci Pollut Res 26(2):1733–1750

Papp JF (2004) Chromium use by market in the United States. In: Paper presented at 10th international ferroalloys congress. Cape Town, South Africa, pp 1–4

Park D, Yun YS, Park JM (2005) Use of dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics. Process Biochem 40(7):2559–2565

Park D, Lim SR, Yun YS, Park JM (2007) Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction. Chemosphere 70(2):298–305

Pawlak Z, Zak S, Zablocki L (2005) Removal of hazardous metals from groundwater by reverse osmosis. Pol J Environ Stud 15(4):579–583

Pawlisz AV (1997) Canadian water quality guidelines for Cr. Environ Toxicol Water Qual 12(2):123–161

Pei QH, Shahir S, Raj AS, Zakaria ZA, Ahmad WA (2009) Chromium (VI) resistance and removal by *Acinetobacter haemolyticus*. World J Microbiol Biotechnol 25(6):1085–1093

Prevot AB, Ginepro M, Peracaciolo E, Zelano V, De Luca DA (2018) Chemical vs bio-mediated reduction of hexavalent chromium. An in-vitro study for soil and deep waters remediation. Geoderma 312:17–23

Raman NM, Asokan S, Sundari NS, Ramasamy S (2018) Bioremediation of chromium (VI) by *Stenotrophomonas maltophilia* isolated from tannery effluent. Int J Environ Sci Technol 15(1):207–216

Ramírez-Díaz MI, Díaz-Pérez C, Vargas E, Riveros-Rosas H, Campos-García J, Cervantes C (2008) Mechanisms of bacterial resistance to chromium compounds. Biometals 21(3):321–332

Ran ZH, Bi WA, Cai QT, Li XX, Min LI, Dong HU, Guo DB, Juan WA, Chun FA (2016) Bioremediation of hexavalent chromium pollution by *Sporosarcina saromensis* M52 isolated from offshore sediments in Xiamen, China. Biomed Environ Sci 29(2):127–136

Revathi K, Haribabu TE, Sudha PN (2011) Phytoremediation of chromium contaminated soil using sorghum plant. Int J Environ Sci 2(2):417

Reynolds MF, Peterson Roth EC, Bespalov IA, Johnston T, Gurel VM, Menard HL, Zhitkovich A (2009) Rapid DNA double-strand breaks resulting from processing of Cr-DNA cross-links by both MutS dimers. Cancer Res 69:1071–1079

Rezaei H (2016) Biosorption of chromium by using *Spirulina* sp. Arab J Chem 9(6):846–853

Romanenko V, Koren'kov V (1977) Pure culture of bacteria using chromates and bichromates as hydrogen acceptors during development under anaerobic conditions. Mikrobiologiia 46:414–417

Romero-González J, Peralta-Videa JR, Rodríguez E, Delgado M, Gardea-Torresdey JL (2006) Potential of *Agave lechuguilla* biomass for Cr(III) removal from aqueous solutions: thermodynamic studies. Bioresour Technol 97(1):178–182

Salunkhe PB, Dhakephalkar PK, Paknikar KM (1998) Bioremediation of hexavalent Cr in soil microcosms. Biotechnol Lett 20:749–751

San Keskin NO, Celebioglu A, Sarioglu OF, Uyar T, Tekinay T (2018) Encapsulation of living bacteria in electrospun cyclodextrin ultrathin fibers for bioremediation of heavy metals and reactive dye from wastewater. Colloids Surf B Biointerfaces 161:169–176

Saravanabhavan S, Thanikaivelan P, Rao JR, Nair BU, Ramasami T (2004) Natural leathers from natural materials: progressing toward a new arena in leather processing. Environ Sci Technol 38(3):871–879

Sari A, Tuzen M (2008) Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies. J Hazard Mater 160(2–3):349–355

Saxena G, Chandra R, Bharagava RN (2017) Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants. Rev Environ Contam Toxicol 240:31–69

Saxena G, Purchase D, Mulla SI, Saratale GD, Bharagava RN (2019) Phytoremediation of heavy metal-contaminated sites: eco-environmental concerns, field studies, sustainability issues and future prospects. Rev Environ Contam Toxicol 249:71–131

Sen M, Dastidar MG (2010) Chromium removal using various biosorbents. Iran J Environ Health Sci Eng 7(3):182–190

Shakoori A, Makhdoom M, Haq R (2000) Hexavalent chromium reduction by a dichromate-resistant gram-positive bacterium isolated from effluents of tanneries. Appl Microbiol Biotechnol 53(3):348–351

Sibi G (2016) Biosorption of chromium from electroplating and galvanizing industrial effluents under extreme conditions using *Chlorella vulgaris*. Green Energy Environ 1(2):172–177

Singh R, Kumar M, Bishnoi NR (2016) Development of biomaterial for chromium (VI) detoxification using *Aspergillus flavus* system supported with iron. Ecol Eng 91:31–40

Song Z, Williams CJ, Edyvean RGJ (2000) Sedimentation of tannery wastewater. Water Res 34(7):2171–2176

Soni SK, Singh R, Awasthi A, Singh M, Kalra A (2013) In vitro Cr(VI) reduction by cell-free extracts of chromate-reducing bacteria isolated from tannery effluent irrigated soil. Environ Sci Pollut Res 20(3):1661–1674

Springer H (1994) Treatment of industrial waste of the leather industry-is it still a major problem? J Am Leather Chem Assoc 89:153–187

Srivastava S, Thakur IS (2006) Evaluation of bioremediation and detoxification potentiality of *Aspergillus niger* for removal of hexavalent chromium in soil microcosm. J Soil Biol Biochem 38:1904–1911

Tarley CRT, Arruda MAZ (2004) Biosorption of heavy metals using rice milling by-products. Characterization and application for removal of metals from aqueous solutions. Chemosphere 54(7):905–915

Thacker U, Parikh R, Shouche Y, Madamwar D (2006) Hexavalent chromium reduction by *Providencia* sp. Process Biochem 41:1332–1337

Thatoi H, Das S, Mishra J, Rath BP, Das N (2014) Bacterial chromate reductase, a potential enzyme for bioremediation of hexavalent chromium: a review. J Environ Manag 146:383–399

Theologou E, Panagiotakis I, Dermatas D, Chrysochoou M, Toskos T (2013) Remediation technologies for hexavalent chromium contaminated aquifers. In: Proceedings of the 13th international conference on environmental science and technology, Athens, Greece.

Tunay O, Kabdasli I, Orhon D, Ates E (1995) Characterization and pollution profile of leather tanning industry in Turkey. Water Sci Technol 32(12):1

U.S. Environmental Protection Agency (2005) Guidelines for carcinogen risk assessment. EPA/630/P-03/001. US EPA, Washington, DC

U.S. EPA (1986) U.S. EPA Guidelines for the health risk assessment of chemical mixtures (PDF) EPA/630/R-98/002 (1986)

Vaca MV, Callejas RLP, Gehr R, Cisneros BJN, Alvarez PJJ (2001) Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. Water Res 35(2):373–337

Vankar PS, Bajpai D (2008) Phyto-remediation of chrome-VI of tannery effluent by *Trichoderma* species. Desalination 222(1–3):255–262

Vendruscolo F, da Rocha Ferreira GL, Antoniosi Filho NR (2017) Biosorption of hexavalent chromium by microorganisms. Int Biodeter Biodegr 119:87–95

Volesky B (2003) Sorption and biosorption. BV-Sorbex, Inc., St. Lambert (Montreal). (ISBN 0-9732983-0-8) Quebec, Canada

Wani PA, Wahid S, Singh R, Kehinde AM (2018) Antioxidant and chromium reductase assisted chromium (VI) reduction and Cr (III) immobilization by the rhizospheric *Bacillus* helps in the remediation of Cr(VI) and growth promotion of soybean crop. Rhizosphere 6:23–30

Witek-Krowiak A, Szafran RG, Modelski S (2011) Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. Desalination 265(1–3):126–134

Xie X, Fu J, Wang H, Liu J (2010) Heavy metal resistance by two bacteria strains isolated from a copper mine tailing in China. Afr J Biotechnol 9(26):4056–4066

Xu Y, Xu T (2008) Heavy metal complexes wastewater treatment with chelation precipitation. In: 2nd International conference on bioinformatics and biomedical engineering, IEEE, pp 2789–2793

Zayed AM, Terry N (2003) Chromium in the environment: factors affecting biological remediation. Plant Soil 249(1):139–156