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Role of Bacteria in Bioremediation of Chromium from Wastewaters: An Overview

[1]Mukesh Kumar
[2]Tapan Kumar Mukherjee
[3]Indu Sharma
[4]Sushil Kumar Upadhyay*
[5]Raj Singh

Author's Affiliation:
[1,2,3,4,5]Department of Biotechnology, Maharishi Markandeshwar (Deemed to be University), Mullana-Ambala, Haryana133207, India

***Corresponding Author:**
Sushil Kumar Upadhyay
Department of Biotechnology, Maharishi Markandeshwar (Deemed to be University), Mullana-Ambala, Haryana133207, India
E-mail: dr.rajsingh09@gmail.com

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ABSTRACT

Chromium exists in many forms according to their valence from 0 to VI. Most dominant and stable valences of Chromium are III and IV. Chromium is non degradable, harmful and toxic pollutants which negatively affect the environment. It transfers to one trophic level to another via the food chain and continues their cycle in the nature. Bacteria, fungi, algae and plants are the best constituents of biomass which reduces the toxicity of heavy metals in the ecosystem. Bioremediation is a natural process for waste treatment in an industrial area. This comprehensive review article describes the sources of chromium contamination in wastewater and soils, various treatment technologies for the removal of chromium from water/ wastewater and different bacteria dependent possible bioremediation of this metalin aneco-friendly and cost effective manner.

KEYWORDS: *Bioremediation, Chromium, Technology, Pollutant, Bacteria.*

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INTRODUCTION

Untreated wastewater from industries, factories and meals containing highly toxic heavy metals affect environment and health of animals as well as plants. These heavy metals are Cr(Chromium), Pb(Lead), Hg(Mercury) and Cd(Cadmium) (Igiri et al., 2018). Chromium is the earth's 21st most abundant element and the sixth most abundant transition metal. Chromium is found naturally in rock, soil, plants, animal, sediment, air contaminant and water of various sources such as surface, ground, freshwater and seawater (Krishnamurthy and Wilkens, 1994). The trivalent forms of this metal are relatively immobile, more stable and much less toxic than hexavalent forms (Ross et al., 1981, Katz and Salem, 1994; Losi et al., 1994). Chromium exists in many forms according to their valence from 0 to VI. Most dominant and stable valences of chromium are III and IV (Landrot et al., 2012). Chromium is non degradable and harmful toxic pollutant and affect to environment and transfer to one step to another via food chain and continue its life cycle in nature (Jobby et al., 2018).

Chromium occurs in 2^+, 3^+ and 6^+ oxidation states but Cr(II) is unstable and very little is known about its hydrolysis. It produces mononuclear species $CrOH^{2+}$, $Cr(OH)^{2+}$, $Cr(OH)^{4-}$, neutral species $Cr(OH)_3^0$ and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$ (Radovic et al., 2000, Mohan et al.,2005; Mohan et al.,2006). The main aqueous Cr(III) species include $Cr(OH)^{2+}$, $Cr(OH)_3$ and $Cr(OH)_4^-$. The Cr(III) species predominate at pH < 3.6 (Francoise and Bourg, 1991), whereas $Cr(OH)_4^-$ predominates at the pH >11.5 (Rai et al., 1987). At a slightly acidic to alkaline pH, ionic Cr(III) species precipitates as amorphous $Cr(OH)_3$ (Francoise and Bourg, 1991). Cr(III) can also be chelated by organic molecules that are adsorbed to mineral surfaces (James and Bartlett, 1983).

Chromium compounds are widely used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection, chemical manufacturing, brass, electrical, electronic equipment and catalysis (Kimbrough et al., 1999). Cr(III) hydroxide trihydrate is used as green pigment, as mordant, as a tanning agent and as a catalyst (Patnaik, 2003). Microorganisms like bacteria, fungi, yeast, algae and plants are utilized for eradicating these heavy metals from contaminated areas. Microbial bioremediation of heavy metals is very much dependent on the nature of the site and the chemicals present in the surrounding ecosystem (Whiteet al., 1997). The table 1 describes the sources and toxicity of various heavy metals.

Table 1: Sources and toxicity of trace elements

Heavy metal	Source of discharge	Toxicity
Arsenic	Mining and pesticide	Highly carcinogenic
Boron	Coal industries, soap and detergent manufacturing	Toxic to some plants
Cadmium	Batteryindustry, mining waste, water pipes	Causes RCC (renal cell carcinoma), destroys testicular tissue and red blood cells, disturbance in calcium metabolism, skeletal deformation, impaired reproductive function and also harmful to aquatic biota
Chromium	Electroplating industries, leather tanneries usually found as Cr(VI)in contaminated water	It leads to cancer, anuria, nephritis, gastrointestinal ulceration, puncture in portion of nose
Fluorine	Natural geological sources	Causes molted teeth and bone damage when concentration is above5mg/l
Iron	Corroded metal, industrial wastes, acid mine drainage	It leads to fast respiration, blocking of blood vessels, and dizziness
Lead	Mining, plumbing and battery industry	Anemia and kidney disease
Mercury	Mining and pesticide	Acute and chronic toxicity
Selenium	Natural geological sources, sulfur	Leads to “alkali disease” and “blind staggers” in cattle.

TREATMENT TECHNOLOGIES FOR CHROMIUM CONTAINING WASTEWATERS

In the last few years many studies and research developed on the treatment strategies /technologies and bioremediation of chromium from wastewater (Ohtake et al., 1990; Ohtake and Silver, 1994; Saha and Orvig, 2010; Pradhan et al., 2017). Several conventional treatment technologies have been developed to remove chromium from water and wastewater including chemical precipitation (Atkinson et al., 1998), ion exchange (Tiravanti et al., 1997; Rengaraj et al., 2001; Rengaraj et al., 2002; Rengaraj et al., 2003; Petruzzelli et al., 1995), membrane separation (Kozlowski and Walkowiak, 2002; Shaalan et al., 2001), ultrafiltration (Ghosh and Bhattacharya, 2006), flotation (Matis and Mavros, 1991), electrocoagulation (Parga et al., 2005), solvent extraction (Salazar et al., 1992), sedimentation (Song et al., 2000), precipitation (Roundhill and Koch, 2002), electrochemical precipitation (Roundhill and Koch, 2002), soil flushing/washing (Roundhill and Koch, 2002), electrokinetic extraction (Roundhill and Koch, 2002), phytoremediation (Roundhill and Koch, 2002), reduction (Chen and Hao, 1998), reverse osmosis (Ozaki et al., 2002), dialysis/electrodialysis (Mohammadi et al., 2005), adsorption/filtration (Mohan et al., 2005; Mohan et al., 2006; Gupta et al., 1997; 1999; 2001; Babel and Kurniawan, 2003), evaporation, cementation, dilution, air stripping, steam stripping, flocculation, and chelation (Tels, 1987; Rich and Cherry, 1987). The following paragraphs describe some of the treatment strategies of chromium from wastewater of various sources:

Reverse osmosis
Very briefly, it is a process in which heavy metals are separated by a semipermeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is an expensive procedure (Ozaki et al., 2002).

Ion exchange
Cell wall of microbes contains lipopolysaccharide and ions. For example, the alginate of marine algae occurs as salts of K^+, Na^+, Ca^{2+} and Mg^{2+} ions. These ions can exchange with counter ions such as Co^{2+}, Cu^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} resulting in the biosorptive uptake of heavy metals (Kuyucak and Volesky, 1989).

Electrodialysis
In this process, the ionic components (heavy metals) are separated through the use of semi-permeable and ion selective membranes. Application of an electrical potential between the two electrodes causes migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane (Mohammadi et al., 2005).

Ultrafiltration
Ultrafiltration is a pressure driven membrane operation which uses porous membranes for the removal of heavy metals. Metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantage includes high cost, partial removal of certain ions and generation of sludge (Ghosh and Bhattacharya, 2006).

REMOVAL OF HEAVY METALS BY MICROORGANISM

Microorganisms play a vital role in nature and governing to the biochemical behavior of chromium in soil and wastewater (Fernandez et al., 2018).Chromium treatment with the help of living microorganisms is considered as a cheap and permanent solution to chromium toxicity. Biomass originated by bacteria, fungi, algae and plants are highly useful in reducing the toxicity of chromium (Vendruscolo et al., 2017; Pradhan et al., 2017). Direct use of microorganisms derived enzymes with distinctive features not only boost the efficiency of bioremediation of various metals but also reduce their toxicity (Le et al., 2017). Microbial remediation refers to the sorption, accumulation, and transformation of microbial activity to remove Cr(VI) in wastewater and immobilize it in soils (Bolan, et al., 2013) Kafilzadeh & Saberifard, 2016; Sivakumar, 2016). There are various mechanisms by which microbes bind to heavy metals. They are methylation, chelation, adsorption and complexation, intracellular uptake of heavy metals by microorganisms (bioaccumulation), extracellular uptake of heavy metals-biosorption (Sun et al., 2021). Micro-organisms can be good machination for separation of heavy metals from wastewater due to their abundant presence in the planet earth and rapid rate of multiplicity. Additionally, microorganisms are primarily found in the habitat where concentration of metal is high (Trudinger and Swaine, 1979). Fig. 1 describes various processes through which various microorganisms interact with different heavy metals.

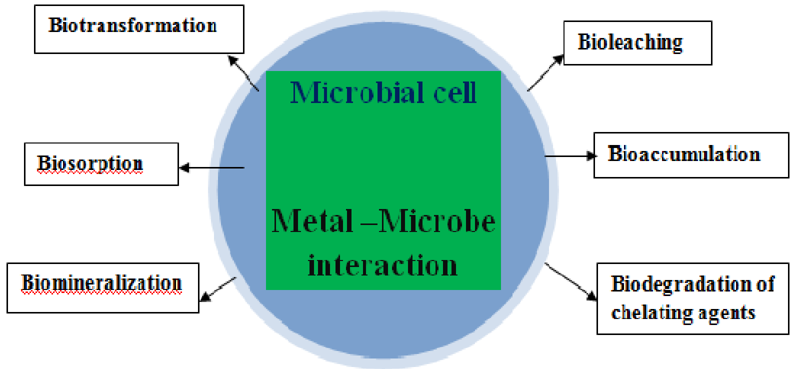

Figure 1: Metal microbe interactions

CHROMIUM REMOVAL BY BACTERIA

A wide range of microorganisms including *Enterobacter* sp. (Wang et al., 1990), *Escherichia coli* (Shen and Wang, 1993), *Bacillus* sp. (Compos et al., 1995), *Pseudomonas* sp. (Oh and Choi, 1997) *Microbacterium* (Pattanapipitpaisal et al., 2001), *Desulfovibrio* (Michel et al., 2001), *Streptomyces griseus* (Ashwini et al., 2009) and several other bacteria (Losi et al., 1994a) exhibit an exceptional capacity to detoxify Cr(VI) by converting it into less soluble and much less toxic Cr(III) (Michel et al., 2001). Most of these microorganisms have been isolated from tannery sludge, industrial sewage, evaporation ponds and discharge water (Losi and Frankenberger, 1994). Gram-positive bacteria, capable of reducing Cr(VI) as a terminal electron acceptor and with a relatively high level of resistance to chromate were isolated from tannery effluents (Shakoori et al., 1999). A chromate resistant strain of the bacterium *Serratia marcescens* was isolated from tannery effluent, which was able to reduce Cr(VI) to Cr(III), and about 80% of chromate was removed from medium. Feasibility of biotransformation of hexavalent chromium by immobilized *Bacillus coagulans* was observed in reactor with an influent hexavalent chromium concentration of 26 mg/L and retention time 24 hours (Philipet al., 1998). A number of chromium-resistant microorganisms such as *Arthrobacter* (Chaturvedi, 1992) and *Pseudomonas aeruginosa* (Ganguli and Tripathi, 2001) were reported for treatment of the tannery effluent. *Bacillus circulans, Bacillus megaterium* and *Bacillus coagulans* strains capable of bioaccumulation of Cr(VI) were isolated from treated tannery effluent of a common effluent plant (Srinath et al., 2002; 2003). *Arthrobacter* sp. and *Bacillus* sp. isolated from soil contaminated with tannery effluent were examined for their tolerance to hexavalent chromium Cr(VI) and their ability to reduce Cr(VI) to Cr(III) (Megharaj et al., 2003).

Mechanism of aerobic Cr(VI) reduction

In the presence of oxygen, bacterial Cr(VI) reduction commonly occurs as a two- or three-step process with Cr(VI) initially reduced to the short-lived intermediates Cr(V) and/or Cr(IV) before further reduction to the thermodynamically stable end product, Cr(III). Nevertheless, it is at present unclear as to whether the reduction of Cr(VI) to Cr(V) and Cr(IV) to Cr(III) was spontaneous or enzyme mediated (Czakó-Véret al., 1999). NADH, NADPH and electrons from the endogenous reserve are implicated as electron donors in the Cr(VI) reduction process.

Anaerobic reduction of Cr(VI)

Early investigations on the biotransformation of Cr(VI) focused on the facultative anaerobes such as *Pseudomonas dechromaticans, P. chromatophila* and *Aeromonasdechromatica.* A number of chromium resistant microorganisms were subsequently isolated such as *B. cereus, B. subtilis, P. aeruginosa, P. ambigua, P. fluorescens, E. coli, Achromobacter eurydice, Micrococcus roseus, Enterobacter cloacae, Desulfovibrio desulfuricans* and *D. vulgaris* (Lovley, 1994). Sulfate-reducing bacteria (SRB) have been extensively studied for reduction of metals, including Cr(VI). For instance, Cr(VI) reduction by *D. vulgaris* was found to be involved as a soluble c3 cytochrome (Lovley, 1995). In *Desulfomicrobiumnorvegicum*, a hydrogenase and a c-type cytochrome catalyzed Cr(VI) reduction (Chardin et al., 2002; Michelet al.,2001). Table 2 describes chromium removing various biosorbent bacteria.

Table 2: Biosorbents for removal of chromium

Biosorbent(Bacteria)	Metal	Reference
Enterobacter cloacae	Cr(VI)	Yamamoto et al., 1993
Desulfovibrio vulgaris	Cr(VI)	Lovley and Phillips, 1994
Staphylococcus cohnii	Cr(VI)	Saxena et al., 2000
Pseudomonas aeruginosa	Cr(VI)	Ganguli and Tripathi, 2001
Acinetobacter sp.	Cr	Shrivastava and Thakur, 2003
Acinetobacter sp.	Cr(VI)	Shrivastava and Thakur, 2007

Biomass generated by the live and death bacteria is utilized for the removal of various metals from various wastes. The sources of heavy metals includes wastewater, uranium mine waste, zinc decantation tank, electroplating industry, heavy metal contaminated soils etc. Table 3 describes various microorganisms that are involved in removing metals from different sources.

Table 3: Live and dead biomass of various bacterial spp. reported for removal of heavy metal

Microbes	Metals	Source
Pseudomonas aeruginosa	Cd, Cr and Ni	Wastewater
Pseudomonas sp. and *Bacillus* sp.	U	Uranium mine waste
Ralstonia metallidurans	Zn	Zinc decantation tank
Bacillus sphaericus	Cr	Soil of Andaman Islands
Micrococcus sp. and *Aspergillus* sp.	Cr and Ni	Electroplating industry waste
Pseudomonas fluorescens and*Microbacterium* sp.	Pb	Rape roots of Pb contaminated soil
Burkholderia sp.	Pb and Cd	Heavy metal-contaminated soils
Bacteria CCNWRS33-2	Cu, Cd, Zn and Pb.	Root nodule of *Lespedeza cuneata*
Acidobacteria, Actinobacteria, Bacteroidetes, Gemmatimonadetes	Ni, Cd, Zn, Co and Cd	Soil samples near farmland
B. arsenicus, B. pumilus, B. arsenicus, B. indicus, B. clausii, P. maritimus and *Staphylococcus pasteuri*	As, Hg, Co, Cd, Pb, and Se.	Soil of Eloor (India)
Graphium putredinis, Fusarium solani, Fusarium sp. and *Penicillium chrysogenum*	Cd, Cr, Ni, Pb and Zn	Horticulture waste, sewage sludge and municipal solid waste compost
Achromobacter sp. strain AO22	Cd and Zn	Soil near *Crotolaria juncea*

CONVENTIONAL TREATMENT AND DISADVANTAGES

The classical or conventional techniques like precipitation, ion exchange etc. gives rise to several problems such as unpredictable metal ions removal and generation of toxic sludge which are often difficult to dewater and require extreme caution in their disposal (Xia and Liyuan, 2002). Besides that, most of these methods also present some limitations whereby they are only economically viable at high or moderate concentrations of metals but not at low concentrations (Addour et al., 1999), meaning diluted solutions containing 1 to 100 mg/L of dissolved metal(s) (Cossich et al., 2002).

FACTORS AFFECTING BIOSORPTION

Several factors which influences and limit bioremediation efficiency include temperature, pH, redox potential, nutritional status, moisture, and chemical composition of heavy metals (Shukla et al., 2013)

Temperature seems to have no influence on the biosorption performances in the range of 20-35°C (Aksu et al., 1997). pH seems to be the most important parameter in the biosorptive process as it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Galun et al., 1987). Biomass concentration in solution seems to influence the specific uptake of metals. For example, lower values of biomass concentrations enhance their specific uptake (Fourest and Roux, 1992). Biosorption is mainly used to treat wastewater where more than one type of metal ions would be present and the removal of one metal ion may be influenced by the presence of other metal ions (Tsezos and Volesky, 1982; Sakaguchi and Nakajima, 1991). Fig. 2 Factors affecting bioremediation.

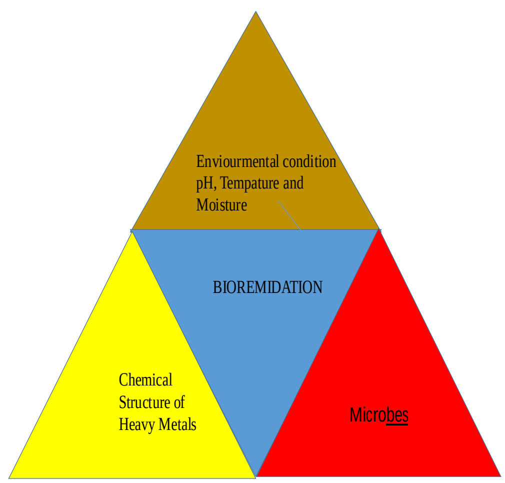

Figure 2: Factors affecting Bioremediation a Triangle

CONCLUSION

High levels of various metals in the environment including wastewater and soils are toxic to human health and physiology and need to be removed from the contaminated sources. This review article describes various treatment strategies including bioremediation of various metals with special focus on chromium sourced from different industrial and factories wastewater, sludge and contaminated soils. Chromium exists in many forms according to their valence from 0 to VI. Most dominant and stable valiances of Chromium are III and IV. Bacteria, fungi, algae and plants are constituents of biomass and utilized for the bioremediation of chromium. Various microorganisms play a vital role in nature and governing the biochemical behavior of chromium in soil and wastewater. Enzymes generated by various microorganisms are highly useful to remove different metals from various industrial effluents and therefore may be utilized to clean the environment and reduces the chances of toxicity to the human health and physiology generated by these metal contaminated materials.

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