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RESEARCH ARTICLE

STRATEGIES OF TOXIC CHROMIUM (VI) MITIGATION FROM TANNERY EFFLUENTS: A REVIEW

Ayesha Zafar, Sayanee Sarkar, Sourav Paul, Bishal Das, Deepika Biswas and Jigisha Roy Panda
Guru Nanak Institute Pharmaceutical of Science and Technology, Department of Life Science.

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Abstract

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Hexavalent chromium i.e., Cr (VI) is highly toxic and carcinogenic; it enters the environment through several anthropogenic activities. It is spuriously used in various industrial operations (leather tanning, electroplating, paint and pigment production etc.) because of its hardness and stability. It is found in industrial effluents in concentrations much above the prescribed limit of the World Health Organization (50 µg/L). Detection and remediation of chromium has been the subject of research of many scientists but many previous review works have been insufficient in comprehensive information. This review conveys the basic knowledge of chromate toxicity leading to physical discomfort and sometimes life-threatening illness including irreversible damage to the vital body system in humans. Conventional methods for removing toxic chromium ions (by chemical reduction followed by precipitation, ion- exchange and adsorption on activated coal, alum, kaolinite and ash) are costly for large-scale treatment. Microbial uptake followed by reduction of toxic Cr (VI) has become very successful due to its cost-effectiveness and use as a non-toxic agent. This is referred to as bioremediation. This review emphasises various strategies for hexavalent chromium bioremediation from contaminated water. This review article, therefore, tries to highlight this aspect of bioremediation of Cr (VI) from industrial effluents by native, indigenously resident chromate-resistant bacteria.

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Introduction:-

Heavy metal pollution on the environment has catastrophic impacts on aquatic animals, plants, and people (Yin et al., 2019) and has drastically impacted the natural world (Dabir et al., 2019). Unexpected industrial and urban growth, which ignores the vitality of a safe environment, is the primary cause of pollution in the environment. These actions have greatly increased the pollution levels of heavy metals, breaking the ecological equilibrium (Posthuma et al., 2019). Over 1.7 million children under the age of five passed away as a consequence of being exposed to hazardous substances, including heavy metals, as stated in one of the reports in WHO (Xu et al., 2018). As a result, heavy metal pollution of the environment is a serious problem that demands rapid action. Most dangerous heavy metals, which include lead (Pb), mercury (Hg), zinc (Zn), copper (Cu), nickel (Ni), chromium (Cr), cadmium (Cd), zinc (Zn), and others, are frequently used in a variety of industrial processes that eventually end up in natural resources like land, soil, rivers, and seas. Around the globe, numerous studies (Fan et al., 2019) have demonstrated the presence of heavy metals in the environment above the minimum levels set by various environment monitoring

Corresponding Author:- Dr. Jigisha Roy Panda
Address**:-** Assistant Professor Guru Nanak Institute of Pharmaceutical Science and Technology.

agencies. The name Chromium is derived from the Greek word "chrōma" (χρώμα), meaning colour, since it forms intensely coloured compounds. It was discovered in 1797 by Louis Nicolas Vauquelin in the crocoite (chromate system) mineral. Chromium (Cr) is a heavy metal with atomic number 24 (Pradhan et al., 2019), located in the 6th group of the periodic table. Chromium is the most abundant of the Group VI A family of metallic elements. At a concentration of nearly 400 parts per million in the earth's crust as various minerals, it is the 13th most common element. Chromium has become an increasingly prevalent environmental pollutant due to its increasing utilization in industry (Sanjay et al., 2020). It is one of the world's most strategic, critical and highly soluble metal pollutants having a wide range of uses in the metals and chemical industries. In superfund-managed contaminated sites around the country, chromium is among the top 20 hazardous materials. Since it has high solubility, Cr easily penetrates both surface and groundwater systems and enters plant tissues, where its mutagenic and oncogenic qualities leave it extremely dangerous to both plants and animals (Lunardelli et al., 2018). Several rules and regulations have been put in place for the monitoring and elimination of Cr in various sectors related to the hazardous health effects of Chromium. In general, the bioavailability of an element is determined by its chemical form. Oxidation state and solubility are particularly important factors for bioavailability. For this reason, it is frequently necessary to establish the trace element composition of agricultural, biological, clinical and environmental materials in both qualitative and quantitative terms (Banerjee et al.,2019). Though chromium exists in nine valence states ranging from -2 to +6, trivalent chromium or Cr (III) and hexavalent chromium or Cr (VI) are of major significance because of their stability in the natural environment. In contrast, essential oxidation and great solubility are displayed by Cr (VI) species, which consist of the chromate and dichromate compounds, like, $CrO4^{-2,}$ $HCrO^{-4}$and $Cr_20_7^{-2}$ (Sanjay et al,.2020). In light of its high concentration in soil and wastewater from both anthropogenic and natural processes, environmental pollution with Cr has recently drawn public attention such as fertilizer application, pesticides, herbicides, antibiotics, sewage water, metal ore extraction, waste from the municipal dump, industrial throw away (Ashraf et al., 2017). Chromium is used in electroplating (such as chrome plating), in stainless steel (e.g., stainless steel), leather tanneries and dye productions (Vimercati et al., 2017) DNA can be degraded by Cr^{6+} at ≥ 0.2 mg/mL and Cr^{3+} at ≥ 1.0 mg/mL (Hsu et al., 2015).The US Environmental Protection Agency therefore considers Cr^{6+} as a Class A human carcinogen (US-EPA, 1998). Chromium is an important metal due to its high corrosion, resistance and hardness. In this reference frame, chromium is of special interest since it is an essential nutrient and at the same time a carcinogen (Novotnik et al., 2016). Dietary deficiency of trivalent chromium has been as Ashraf et al., 2017) associated with faulty sugar metabolism in humans, and inhalation of some moderately soluble hexavalent chromium compounds has been correlated with increased incidences of lung cancer, ulceration of the skin, perforation of the nasal septum, inflammation of the larynx, as well as damage to the kidneys (Pei et al., 2018).

Table 1:- Physical properties of different forms of chromium (WHO, 2021).

Properties	**Melting Point (°C)**	**Boiling Point (°C)**	**Solubility of water (g/L)**	**Density (g/cm^3)**
Cr	1185	2672	Insoluble	7.14
$CrCl_3$	1152	_	Slightly soluble	2.76
K_2CrO_4	968.3	_	790	2.73
Cr_2O_3	226	4000	Insoluble	5.21
CrO_3	196	_	624	2.70

Chromium's ionic state depends on the pH and redox state of the aqueous solution where it is found. Figure 1 shows a schematic picture of the production of free radicals during Cr (VI) reduction inside the cell via Haber-Weiss reactions (Cys, as cysteine; Asc as ascorbate; GSH is reduced glutathione) by (Elahi and Rehman., 2019), Cr^{3+} is insoluble at neutral to alkaline pH values, so its solubility is dependent on pH. Cr^{3+} is more common at pH values below 5, while Cr6+ is more concentrated at pH values above 5 (Ma et al., 2019). Strong oxidizing agent Cr^{6+} is found in aqueous systems as hydrochromate ($HCrO_4^-$), chromate (VI), and dichromate (VI). All three oxoanionic forms are present. Since the discovery of the first microbe capable of reducing Cr (VI) in the 1970s, the search for Cr (VI)-reducing microorganisms (both aerobic and anaerobic) has been enthusiastically pursued, with numerous strains being isolated (Bearcock et al., 2019). Numerous attempts have been made by researchers to maintain Cr (VI) concentrations below the advised threshold. In recent years, physical remediation such as soil replacement, soil isolation, vitrification, and electro-kinetic remediation, as well as chemical remediation such as immobilization techniques, encapsulation, and soil washing, have been used to remediate Cr pollution in soil and wastewater. These methods can be applied in-situ or ex-situ, on-site or off-site (Kanagaraj and Elango, 2019).

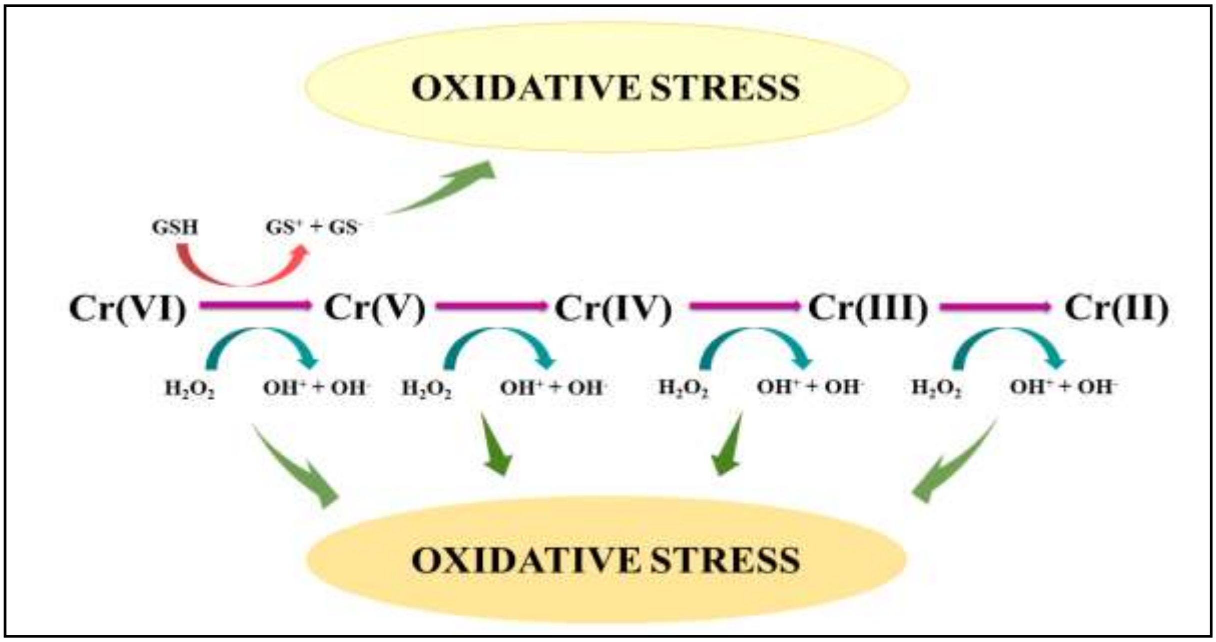

Figure 1:- Haber-Weiss production of free radicals during in-vivo Cr (VI) reduction.

The benefits of bioremediation over physical and chemical remediation include minimal or no soil disturbance, low cost, no secondary pollution, in-situ remediation, and ease of use (Khalid et al., 2017). Bioremediation techniques are the most dependable approaches for treating Cr and offer significant advantages in terms of ecology, economy, and society (Velez et al., 2017). Bioremediation focuses on organisms that are alive (plants, algae, fungi, bacteria, and forestry wastes), as well as biologically accomplished products (biochar used and raw materials from forestry and agriculture). The bioremediation of Cr (VI) involves two primary pathways (Malaviya and Singh, 2016): (i) Biosorption is the process by which biologically generated materials and live organisms sorb and enrich Cr (VI), lowering the concentration of Cr (VI) in the surrounding environment (Jobby et al., 2018); and (ii) biotransformation, which transforms highly hazardous and mobile Cr (VI) into Cr (III), making it harmless for the surrounding environment (Vendruscolo et al.2017). Regarding the application of biologically produced materials and live organisms for Cr remediation, there are currently very few published reviews. Most of the general mechanisms and processes that rely on, bacteria, fungi, algae, plants, and raw materials from forestry and agriculture, as well as their combined impacts on numerous pollution scales, are still not well understood (Fleming et al., 2019). This review also conveys the basic knowledge of chromate toxicity leading to physical discomfort and sometimes life-threatening illness to vital body systems in humans. This review emphasises various strategies for hexavalent chromium bioremediation from contaminated water. Various biopolymeric adsorbents are also used in modified forms by incorporating relevant bacterial biomass in them (Tiwari et al, 2019) to remediate chromium by adsorption. Various biopolymeric adsorbents are also used in modified forms (by incorporating relevant bacterial biomass in them) to remediate chromium by adsorption. This review paper describes in depth the toxic effects of Cr (VI), various bioremediation strategies to combat Cr (VI) pollution and future course of action (Fallahzadeh et al., 2018).

Genotoxicity of Cr (VI)

Chromium Transport and Accumulation

Cr (VI) is a toxin typically originating from anthropogenic activities. Natural or manufactured sources of chromium can enter the ecosystem, and the geochemical cycle regenerates it to maintain environmental equilibrium. A spike in chromium released due to human activity has engulfed the ecosystem and disturbed the regular chromium geochemical cycle. As a result, higher concentrations of chromium are found in soil, sources of water, groundwater, the sea, etc. Chromium enters the ecosystem naturally through weathering and rock leaching from chromite mines and other natural sources (Bharagava and Mishra, 2018). There are various valence states for chromium, spanning from 0 to VI. In the natural world, Cr (III) and Cr (VI) are the most prevalent and stable valence state species. By co-precipitating with iron (Fe), manganese (Mn), and/or aluminium (Al) oxides and hydroxides, which typically get sorbed on soil particles and combined with soil organic compounds, Cr (III) could remain in the original minerals

(Zhang et al., 2019). As a result, Cr (III) has comparatively lower bioavailability and toxicity than Cr (VI). Chromate or dichromate acts as potent oxidants to release Cr (VI), which can also be found as CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$.

These substances are more difficult for soil to absorb because of their high solubility in the environment and ease of transportation in the water present in the pores of the soil colloids, leaving them hazardous to living things (Hsu et al., 2015). Heavy metal oxyanions interfere with the metabolism of the structurally related non-metal (chromate with sulfate) and the reduction of heavy-metal oxyanion leads to the production of radicals. Effluents from textile, leather, tannery, electroplating, galvanizing, dyes and pigment, metallurgical and paint industries and. These metal ions pose problems to the water environment (Zhang et al., 2020). Remove water and runoff from surface charges/drains contaminating nearby waterways. The potential impacts of leaching operations on the environment are changes in surface and groundwater quality. The principal pathways by which leached contaminants may enter groundwater are leakage or spills from storage ponds, seepage path liners, after immersion in groundwater, drainage/drainage of rainwater, uncontrolled flow through the pile and subsequent sedimentation. These toxic metal ions not only cause potential human health hazards but also affect other life forms. Cr (VI) is toxic, carcinogenic and mutagenic to animals and humans and plays a role in reducing plant growth and altering plant characteristics (He et al., 2020). They cause physical discomfort and sometimes life-threatening illness including irreversible damage to the vital body system; in humans. A slight elevation in the level of Cr (VI) elicits environmental and health problems because of its high toxicity, mutagenicity and carcinogenicity.

Whereas its reduced trivalent form, (Cr (III)) is less toxic, insoluble and a vital nutrient for humans. 1nM of Cr (III) is required as a trace element in humans. This binds to a low molecular mass binding substance, a small polypeptide at a ratio of 4 Cr/peptide. The resulting chromium-containing peptide can activate specifically the insulin receptor tyrosine kinase (Khan et al., 2020). Hence, Cr (III) starvation in men leads to reduced glucose tolerance with a physiological condition similar to diabetes. One of the eight most toxic chemicals to the human body, Cr (VI) is also known worldwide as one of the metals that causes cancer (Jaishankar et al., 2014). In India, there are over 3000 tanneries, mostly in Tamil Nadu, West Bengal, Uttar Pradesh, Andhra Pradesh, Bihar, Gujarat, and Maharashtra. These tanneries produce about 1,75,000 m^3 of wastewater every day. It uses a lot of water, and it also produces a lot of wet waste that contains chromium. The amount of chromium found in tannery effluent ranges from 2000 to 5000 mg/L, which is significantly more than the allowed amount in wastewater (Jin et al., 2016).

Chromium-containing wastewater that has not been treated from these industries influences several water resources features, including colour, total suspended solids (TSS), chemical oxygen demand (COD), and biological oxygen demand (BOD). Additionally, it contaminates water for irrigation and agricultural field soils, which could facilitate the entry of chromium into the food chain; (Vijayaraj et al., 2018). Another way for chromium to enter the food chain is through the consumption of poultry feed, which has also been discovered to be contaminated with the metal. Chromium is then further stored in the body parts of the chicken (Yaashikaa et al., 2019). Chromium generally interacts with aquatic organisms' enzymatic and physiological functions. As a result of its neurotoxic effects, which also decrease total weight, it additionally affects how much food is consumed (Hashem et al., 2017).

Elemental chromium (Cr) is not found in nature but is found in minerals, especially chromite ($FeOCr_2O_3$). Hexavalent chromium is the main form of chromium used in (mostly) industrial processes, including the production of metal oils an important use of Cr, chrome leather tanning, metal cleaning processing, wood preservation, ceramics, pyrotechnics, electronics and so on, and is therefore the most common pollutant in various industrial wastes. Non-occupational exposure to the metal occurs via the ingestion of chromium-containing food and water, whereas occupational exposure occurs via inhalation (Sumaiya et al., 2023). Workers in the chromate industry are exposed to chromium concentrations of 10-50 µg/m3 for Cr (III) and 5-1000 µg/m3 for Cr (VI). Humans and animals localize chromium in the lungs, liver, kidney, spleen, adrenals, plasma, bone marrow, and red blood cells (RBC). The main routes of chromium excretion are kidneys/urine and bile/feces. Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate concerning their structure and charge (Mathur et al., 2016). Once developed, chrome sensitivity can be persistent. In such cases, contact with chromate-dyed textiles or wearing chromate-tanned leather shoes can cause or exacerbate contact dermatitis. Vitamin C and other reducing agents combine with chromate to give Cr (III) products inside the cell (Abreu et al., 2018). Cr (VI) compounds are genotoxic carcinogens. Chronic inhalation of Cr (VI) compounds increases the risk of lung cancer (lungs are especially vulnerable, followed by fine capillaries in kidneys and intestine). According to some researchers, the damage is caused by hydroxyl radicals, produced during reoxidation of Cr VI by hydrogen peroxide molecules present in the cell. Zinc chromate is the most widely used chromate in industry. Soluble compounds, such as chromic acid, are much weaker carcinogens. The accumulated chromium in soil can also cause acute and long-term toxic effects on soil ecosystems (Banu et al., 2018). The Cr (VI) concentrations in wastewater produced by industries are estimated to be between 0.1 and 200 mg/L. Stringent regulations have been imposed by various organizations. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for Cr (VI) and total chromium (including Cr (III), Cr (VI) and other forms) are 0.05 and 2 mg/L, respectively. According to the Safe Drinking Water Act, the Maximum Contaminant Level (MCL) is 0.1 mg/L (total chromium). The maximum permissible level of chromium in bottled water is 0.1 mg/L. Specific colour additives may contain chromium at levels no greater than 50 mg/L. Chromium may be used in hydrolyzed leather meal used in feed for animals provided it contains chromium at levels below 2.75% of the total by weight. According to (Baaziz et al., 2017), chromium is a toxic contaminant that is non-degradable, persists in nature, builds up in the food chain, and can eventually reach harmful levels in living systems. Occupational Safety and Health Administration (OSHA) prescribes the Permissible Exposure Limit (PEL) for Cr (VI) as 0.1 mg/m^3 (based on chromic acid and chromates listing). The National Institute for Occupational Safety and Health (NIOSH) indicates an Immediately Dangerous to Life and Health (IDLH) limit of 15 mg/m^3 as Cr (VI) (For chromic acid and chromates listing). The recommended Exposure Limit (time-weighted-average workday) is restricted to 0.001 mg/m^3 (for chromic acid and chromates and chromyl chloride listings).

Table 2:- Acceptable limit and lethal impacts of Cr (III) and Cr (VI).

Agencies	**Bureau of Indian Standard (BIS)**	**United State Environmental Protection Agency (USEPA)**	**World Health Organization (WHO)**	**European Union Standards (EU)**	**Reference**
Freshwater	0.5mg/L	0.011mg/L	_	_	Banerjee et al. (2019)
Drinking water	0.5mg/L	0.1mg/L	0.5mg/L	0.5mg/L	(WHO,2022)
Industrial discharge	2.0mg/L	_	2.0mg/L	_	Banerjee et al. (2019)

Chromium exposure in many countries has increased at an alarming rate which is having a disadvantageous effect on living organisms. Table 3 refers to the studies of chromium pollution in various countries confirming the harshness of the issue.

Chromium Toxicity

As for its hardness and stability, chromium (in hexavalent form) is widely used in industrial operations such as leather tanning. Chromium-tanned leather may contain 4-5% of chromium (Chai et al., 2019). The following lists the physical, chemical, and biological techniques used in Cr remediation. Conventional methods for removing toxic chromium ions from wastewater include chemical reduction which is followed by precipitation, ion exchange and adsorption on activated carbon, alum, kaolinite and ash. However, the costs to set up the required equipment and to operate these processes are prohibitively high for large-scale treatment (Li et al., 2019). Microbial uptake and reduction of toxic Cr (VI) have practical importance because biological strategies provide cost-effective green technology (Banerjee et al., 2019).

Microbial diversity resistant to chromium

Many microbes by their cellular activities significantly contribute to these biogeochemical cycles. The way microbes interact with toxins allows them to be eliminated and recovered are biosorption, bioaccumulation and biotransformation by enzymatic reduction (WHO, 2022). Transport of chromate via the sulfate transport system was demonstrated for the first time in Salmonella typhimurium and later in Escherichia coli, Pseudomonas fluorescens and Alcaligenes eutrophus (Table 4). Unlike other metals, which are primarily cationic species, Cr exists primarily in the oxyanion form (e.g., CrO_4^{2-}) and thus cannot be trapped by the anionic components of bacterial envelopes. However, cationic Cr (III) derivatives bind tightly to Salmonella lipopolysaccharides, Bacillus subtilis and E. coli cell walls, and capsular polymers of Bacillus licheniformis (Liu X et al., 2018).

Table 3:- Concentrations of Cr (III) and Cr (VI) above permissible limits in various countries.

Sr No	Cr^{3+}/Cr^{6+} reported areas	Country	Concentration	Any other heavy metal present	Source of contamination	References
1.	Xiu district, near Yellow River	China	506.58 mg/kg in soil sample	Copper and Zinc	Industrial effluent	Pei et al. (2018)
2.	Bandeirantes do Norte River	Brazil	47.49 mg/kg in sediment sample	Other metals in the limit	Tannery effluent	Lunardelli et al. (2018)
3.	Clyde River catchment	Scotland	971 mg/L	Lead	Naturally occurring ore minerals	Bearcock et al. (2019)
4.	Tarnaveni	Romania	525.8 mg/kg total chromium	Lead and Manganese	Chemical industry	Mihaileanu et al. (2019)
5.	Aosta Town	Italy	0.165 mg/L	Dolomite and calcite	Superficial slag deposits by a steel company	Tiwari et al. (2019)
6.	Birjand	Iran	0.132 mg/L	NM	extraction of chromite mines and its drainage	Fallahzadeh et al. (2018)
7.	Palar river	India	0.060 mg/L	Fluoride	Tannery effluent and hydrogeochemical processes	Kanagaraj and Elango (2019)
8.	Tannery Waste, Uttar Pradesh	India	5.7 ± 0.2 mg/L	Zinc, PCP, phenol	Tannery industry	Bharagava & Mishra (2018)
9.	Jharia, Uttar Pradesh	India	761 mg/L	NM	Tannery industry	Baaziz et al. (2017)
10.	Chinnavarikkam, Vellore	India	52.91 mg/kg	NM	Tannery effluent	Karthik et al (2017)

Table 4:- Comparative study of the efficiency of heavy metal reduction of diversity of bacteria.

Sr no	Name of bacteria	MIC	% Of heavy metal reduction	Optimum pH	Optimum temperature	Reference
1.	Cellulosimicrobium sp.	800 mg/L	99.33% at 50 mg/L And 62.28% at 300 mg/L	7	37 ◦C	Bharagava and Mishra, (2018)
2.	Pseudomonas stutzeri	1900 mg/L	27.47 mg/g of adsorbent	2	30 ◦C	Yaashikaa et al (2019)
3.	Bacillus cereus	2000 mg/L	100% at 200 mg/L	7.5	37 ◦C	Banerjee et al. (2019)
4.	Bacillus aerius S1	1820 mg/L	2703.48 mg/g	8	37 ◦C	Elahi and Rehman (2019)
5.	Brevibacterium iodinum S2	1820 mg/L	2600 mg/g	8	37 ◦C	Elahi and Rehman (2019)

Chromium Bioremediation

Pollution caused by heavy metals is increasing at an alarming rate which is having a disastrous effect on human beings Table 3 thus illustrates chromium pollution reported by various studies. Various methods have been aligned for remediation of chromium by physical, chemical and biological means. Physical remediation methods like soil washing, flushing, landfilling, ultrafiltration, and excavation are some techniques used for heavy metal remediation (Xia et al., 2019) Chemical bioremediation includes usually precipitation, solvent extraction, oxidation in an advanced form, ion exchange, adsorption and chemical reduction. The chemical and physical remediations both are highly expensive, economically feasible and lethal to the environment (Sumiahadi and Acar, 2018). These often cause the formation of more hazardous chemicals which cause more environmental pollution. These methods are not usually cost-effective and the problem faced while disposing of them makes these methods inevitable (Jin et al., 2016). On the other side bioremediation by biological means is more appropriate which involves biological mechanisms and processes. One such biological treatment refers to bacterial bioremediation which is a process using microbes or their enzymes to return the natural environment, that had been previously altered by contaminants (like heavy metals etc), to its original condition. The striking features of bio remediations technology and their cost effectiveness make it a favorable method adopted by many scientists around the world for the remediation of chromium and many heavy metals. Many studies have conducted bioremediation of chromium from industrial effluents using isolated bacteria from infected areas generating bacterial bioremediation (Fan et al., 2019).

Mechanism of chromium detoxification in microorganisms

Various microorganisms having chromium-resisting capacity have been studied and their mechanism of interaction with chromium has been researched (Venkatesan and Subramani, 2019). Chromium-resistant bacteria use a variety of strategies to overcome the stress produced by chromium to survive. These processes include bioaccumulation, biosorption, biotransformation, efflux, enzymatic reduction, reduction, precipitation, cytosolic binding, non-enzymatic, biofilm formation, etc.

Different Mechanisms of Bacteria

Interaction in the cell surface

The first site for interaction is the cell surface for various molecules that surround the outer surface of the cell. It transmits signals within the cell and acts as the first line of defense against the foreign particles. The bacterial envelope consists of the anionic lipopolysaccharides (LPS), phospholipids and membrane proteins. The Gram-negative bacteria have a thin peptidoglycan layer present under the LPS layer and these two layers play an important role in heavy metals interaction, while gram-positive bacteria have a thick peptidoglycan layer present on their cell surface (Baldiris et al., 2018). According to reports (Table 4), these functional groups actively participate in the cell surface absorption and interaction of chromium on the cell surface. When bacteria are exposed to chromium, their cell surface molecules change in composition as a result of their association with chromium.

Table 5:- Bio-mitigation strategies of various Cr (VI) resistant bacteria.

Sr no	Name of bacteria	Mechanism involved	Taxonomy of bacteria	Reference
1.	Azotobacter beijreinckii MTCC 2641	Exopolysaccharide (EPS) secretion	Azotobacteraceae	Chug et al. (2016)
2.	Bacillus strain TCL	EPS secretion, Cr^{6+} reduction, and efflux	Bacillaceae	Pei et al. (2018)
3.	Cellulosimicrobium funkei	I) extracellular reduction and II) intracellular reduction	Promicromonosporaceae	Karthik et al. (2017)
4.	Stenotrophomonas maltophilia	Cr6+ reduction	Xanthomonadaceae	Baldiris et al. (2018)
5.	Shewanella oneidensis	Efflux and reduction	Shewanellaceae	Baaziz et al. (2017)
6.	Pannonibacter phragmitetus	BB Reduction, efflux, Reactive oxygen Species Detoxification	Rhodobacteraceae	Chai et al. (2019)
7.	Bacillus sp.	CRB-1 Cr6+ reduction, efflux	Bacillaceae	Zhu et al. (2019)

Interaction of chromium with functional groups

Most of the functional groups that chromium interacts with on the surface of bacteria are C- and O-based. At alkaline pH (pH 9), cell surface functional groups like N–H, –CONH–, and C–NH_2 cannot interact with chromium since they are electrostatically neutral; however, COOH and OH groups are negatively charged at this pH and can therefore interact electrostatically with chromium. Nevertheless, by electrostatic contact, Cr^{3+} interacts with protonated functional groups found on the surface of bacteria (Fang et al., 2018). One of the responses and an offensive strategy against chromium toxicity is the clumping of cells, which is triggered by charges on the bacterial surface that tend to neutralize in the presence of chromium (Li et al., 2019). In addition, Cr^{6+} can combine to produce insoluble Cr^{3+}, a colloid of chromium hydroxide that is absorbed on the surface of bacteria and modifies the overall protein composition of the cell surface. When everything is considered, the bacterial cell surface plays an essential part in both chromium remediation and resistance Bacillus sp. is the most common type of Gram-positive chromium-resistant bacteria (Table 4), whereas a broad range of gram-negative bacteria (Table 5) are found to be resistant to chromium (Karthik et al., 2017).Gram-negative bacteria are more able to decrease Cr^{6+} extracellularly than Gram-positive bacteria because their outer membranes contain lipopolysaccharides, lipoproteins, and phospholipids. Shaw and Dussan claim that lineages I and II contain the efflux pumps and regulators of both Gram-positive and Gram-negative bacteria. These clusters' amino acid alignment analysis revealed that each lineage has distinct amino acid signatures and conserved areas. Lineages I and II comprise Gram-positive and Gram-negative efflux pumps and regulators, respectively (Bansal et al., 2019). A schematic representation of the similarities and differences between the responses of Gram-positive and Gram-negative bacteria to Cr^{3+}/Cr^{6+} can be found in Figure 2.

Biosorption

Biosorption is a metabolically passive process, meaning it does not require energy and the number of contaminants in the sorbent can be removed depending on the composition of the sorbent cells and the kinetic balance. Infections are recorded on a cellular basis. Biosorption is the biophysical interaction of bacteria with heavy metals that results in the adsorption of heavy metals on the surface of the bacteria, it is a non-specific reaction of bacteria to harmful heavy metals and entails the binding of chromium with the active functional groups on the cell surface. The passive process of biosorption is dependent on both the external environment and the physicochemical characteristics of the cell wall. The ability of different species of bacteria to biosorb heavy metals varies, and it is also dependent on the composition of their cell walls (Vendruscolo et al., 2017). The process of biosorption contains two stages. Passive physical adsorption, the first stage of biosorption, occurs on the surface of the bacterium through complexation, ion exchange, coordination, adsorption, chelation, and precipitation. The type of bacterium and its surroundings determine whether these physical adsorption processes of biosorption work in collaboration or separately from one another. Furthermore, it can be accomplished by both living and non-living bacterial cells because it is not dependent on bacterial metabolism. Slower-moving bioaccumulation is the second stage of biosorption, involving active chromium transport into the bacterial cell that is dependent on metabolism. Chromium that has been bioaccumulated is then internalized using binding to metallothionein, localization into specific organelles, and particle accumulation (Dutta et al., 2022).

According to (Elahi and Rehman, 2019), chromium can be absorbed as reduced Cr3+ ions or as Cr^{6+} ions. Extracellular polysaccharide compounds are said to biosorb chromium, resulting in changes to its cell shape and an increase in size (Jin et al., 2016). Proton exchange (H+) facilitates chromium biosorption through a variety of functional groups on the cell surface, including amines, carboxyl, phosphate, and hydroxyl groups (Shaw and Dussan, 2018). Cr^{6+} exists as $HCrO_4^-$ and CrO_7^{2-} at lower pH levels (Raman et al., 2017), and there is an increase in the protonation of carboxyl and amino groups on the cell wall. This causes an anionic Cr^{3+}/Cr^{6+} to be attracted to the cell surface electrostatically. Consequently, a lower pH promotes greater chromium biosorption. However, as pH rises, the deprotonation of functional groups increases the negative charges on the cell wall. This results in repulsion between the negatively charged Cr^{3+}/Cr^{6+} and the cell surface, which lowers total biosorption. Furthermore, the precipitation of metals at higher pH levels diminishes the solubility and affinity of metal ions, thereby slowing down the biosorption process.

Strategies for bioremediation of Cr (VI)

Bacterial Cr (VI) Reduction

Chromium reductase, an enzyme, or a natural process may transform highly poisonous and mobile Cr^{6+} into less toxic and insoluble Cr^{3+}, which is another significant and extensively researched method of chromium detoxification in bacteria. Chromium reductase activity is present in the majority of chromium-resistant bacteria: cellulosimicrobium sp., Ochrobactrum sp., Bacillus sp. JDM-2-1, Staphylococcus capitis, Cellulosimicrobium funkei, Pseudomonas putida, Lysinibacillus fusiformis ZC1, Achromobacter xylosoxidans SHB 204, Pediococcus pentosaceus, and Providencia sp. are among the bacterial species that have been reported to have chromium reductase activity (Vendruscolo et al., 2017).Depending on where chromium reduction occurs, there are two different types of chromium reductases: membrane-associated reductase and intracellular reductase Table 6. Membrane-associated reductase uses sulfate transport channels that are found on the bacterial surface to transfer Cr^{6+} into the cytoplasm and convert it to Cr^{3+} at the cell envelope during the transport process.

Figure 2:- Comparison of Cr (VI) resistance in Gram-positive and Gram-negative bacteria.

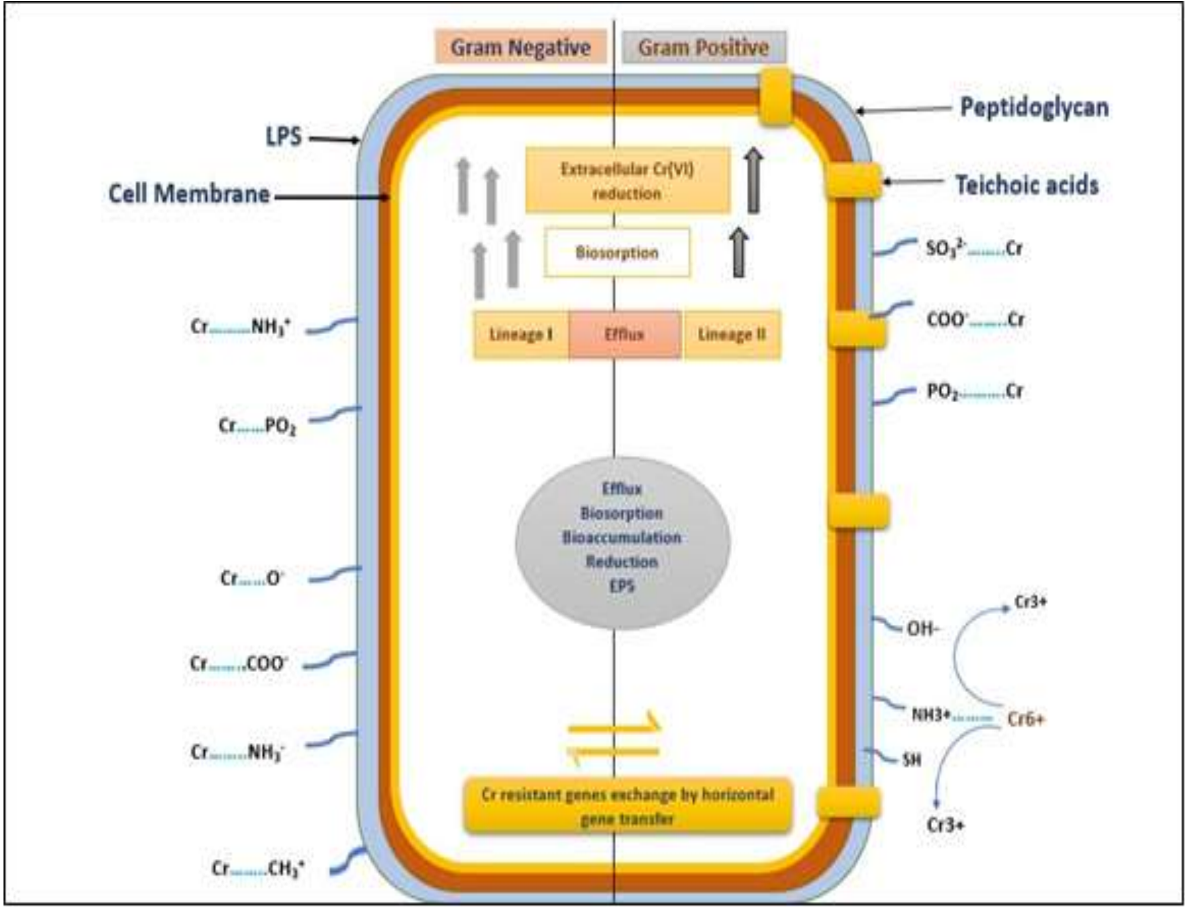

Table 6:- Chromate reductase activity of various bacteria: a comparative study.

Sr no	Name of the bacteria	Chromium reductase activity shown	Reference
1.	Bacillus strain TCL	EPS and cell membrane	Banerjee et al. (2019)
2.	Bacillus sp.M6	Cell envelope and cell cytoplasm	Zhu et al. (2019)
3.	Oceanobacillus Oncorhynchus W4	Cr^{6+} reduction by cell Envelop	Chai et al. (2019)
4.	Stenotrophomonas macrophilia	A soluble fraction of the cell	Baldiris et al. (2018)

Intracellular chromium reduction involves the following steps

1. **Biosorption of chromium on the cell surface-** Alkane, amines, amides, and other functional groups allow Cr6+ from the surrounding media to be adsorbed on the surface of bacteria.
2. **Cr $^{6+}$ transport-** Cr^{6+} is transported via $SO_4{}^{2-}$ and $PO_4{}^{2-}$ channels and exists in the tetrahedral $CrO_4{}^{2-}$ ionic form, which is an analogue of physiologically significant anions like $SO_4{}^{2-}$ and $PO_4{}^{2-}$(Kalola V, Desai C, 2020).
3. **Cr $^{6+}$ reduction-** Cytosolic molecules convert intracellular Cr^{6+} to insoluble Cr^{3+}.
4. **Cr $^{3+}$ bioaccumulation-** The cytosol contains reduced Cr^{3+} (Zhu et al. 2019)

Bacterial biomass decreases when chromium is present because bacterial energy is directed toward chromium reduction and detoxification. The mere presence of a high number of active cells with maximum enzymatic activity is likely the reason why bacteria in the logarithmic phase are substantially better at performing Cr^{6+} reduction than bacteria in any other growth phase (Wang et al., 2017). In both anaerobic and aerobic environments, chromium reduction can take place. The electron transport chain, where Cr^{6+} functions as a terminal electron acceptor, is often linked to membrane-bound reductase proteins and/or enzymes, which are implicated in the anaerobic reduction process. When the environment is anaerobic, the electrons that ubiquinone produces travel through cytochrome b to cytochrome c. Once cytochrome c is reduced, it is oxidized to decrease Cr6+ extracellularly.

Efflux mechanism inside the cell

The chromium, which is present inside the cytoplasm of a cell, can harm essential biomolecules that are necessary for cell viability. As a result, certain bacteria have evolved an effective efflux pump that functions as a cell defense mechanism by pushing harmful chromium ions out of the cell and into the periplasm or surrounding environment. The flex process is typically used by bacteria to carry out various tasks such as preserving cell homeostasis and strengthening their resistance to salt and heavy metals, antibiotics which allow them to endure harsh environments (Ikegami et al., 2020). Microorganisms that are resistant to chromium, ethidium bromide (EtBr) and chromium are reported to be efficiently effluxed by bacillus strain TCL, reducing intracellular chromium damage. Therefore, the secretion of chromium functions in combination with the excretion of other harmful compounds, and transmembrane potential drives chromium reflex and energy-dependent chemiosmotic gases process that is concentration dependent. It is proposed that it is related to the trans-electron transport chain whereby chromium efflux inhibits the chain by removing electrons from it to facilitate chromium expulsion from the cell (Pei et al., 2018). The genes are reported to be involved with chromium $^{3+}$ and chromium $^{6+}$ transport by playing a variety of roles such as generating membrane potential, electron transfer and transmembrane.

Bioaccumulation

Bioaccumulation is an active metabolic process driven by energy from a living organism and requires respiration Bioaccumulation occurs when pollutants are transported to the surface and into cells. Both bioaccumulation and biosorption occur naturally in all living organisms. Bioremediation has been used for the last three decades and as a result, the laboratory process could be scaled up to a fully commercialized technology. An effective bioremediation program is based on the management of soil microbial communities capable of remediation. Heavy metals exhibit toxic effects on the soil biome, and they can affect key microbial processes and decrease the number and activity of soil microorganisms (Dutta et al., 2022). The microbial population has often been used as an easy and sensitive indicator of anthropogenic effects on soil ecology. The Cr (VI)-reducing ability found in some bacteria has raised the possibility of using these microorganisms as a biotechnological tool for the remediation of chromate-polluted zones. The main advantages of using bacterial Cr (VI) reduction are that it does not require high energy input nor toxic chemical reagents and the possibility of using native, non-hazardous strains (Habib et al., 2024). Cr (VI) has been reported to cause shifts in the composition of soil microbial populations and detrimental effects on microbial cell metabolism at high concentrations. Quite a few studies on soil contamination of heavy metal from industrial sites were reported based on recent isolation and purification of Cr (VI) reductases from aerobic bacteria and the fact that the process involved in Cr (VI) reduction occurring under anaerobic conditions is starting to be understood, biological processes for treating chromium contaminated sites are becoming very promising. Some of the emerging technologies for the mitigation and remediation of Cr (VI) include microbial strategies for in situ and on-site bioremediation.

Conclusion:-

Bioremediation in its different forms has been used in a wide variety of environmental clean-up projects. The success is dependent on the type and extent of soil or water contamination, site characteristics, environmental factors etc. Microbes that can degrade. When pollutants break down, the biodegradable population decreases. Residues from treatment are generally inert products and include carbon dioxide, water and biomass cells. Bioremediation is necessary for the destruction of many contaminants. Many things considered legitimate hazards can be turned into harmless products. This eliminates the possibility of future liability for handling and disposal of contaminated materials. Bioremediation can often be carried out in the field without causing significant disruption to existing processes. This also eliminates the need to transport large amounts of waste to different locations and the potential hazards to human health and the environment that may arise during transportation. Biological processes are generally well-defined. Testing from the test bench through trial and error to full implementation is difficult. Research is needed to develop and develop bioremediation technologies suitable for sites with mixed contaminants that do not disperse well in the environment. There is a need to promote more field bioremediation studies than just bacterial isolation in lab scale and treatment assays Very few studies have shown how waste can be treated using bioremediation. A continuous search for the new biological form is required for proper management of increasing pollution and contamination. Therefore, bioremediation is still considered an advanced technology to control daily environmental problems that threaten residents.

Future Perspective

Bacterial bioremediation can be combined with other techniques such as phytoremediation immobilization which can support the growth of bacteria, which also help in achieving maximum bioremediation Though limitations of phytoremediation lie in the fact that the process is limited to the surface plants and the area occupied by the roots. Moreover, the system is not efficient enough to put a complete check on the process of heavy metals leaching. There is always a danger of bioaccumulation and biomagnification of the contaminants into the plants and then to higher levels through food chains. The biggest hurdles lie in the fact that few plants are bigger and cannot be moved from one place to another to be used for the process of bioremediation.

Not all pollutants can be easily treated, accumulated or degraded by bioremediation using microbes, and the microbial impact of metal contamination associated with phytoremediation has so far been neglected. Thus, there is a need to search for new techniques such as genetically modified microorganisms or to combine plants, fungi and bacteria to provide interesting opportunities in the bioremediation process. Even though various sources of bioremediation such as bacteria, archaebacteria, yeasts, fungi, algae and plants are available, the biological treatment alone is not sufficient enough to treat the pollutants or contaminated sites. Every biological form has a different growth requirement (temperature, pH and nutrients) so we need to isolate those forms, which can be cultured easily in the laboratory, with minimal requirement and can be useful in treating a variety of pollutants. A detailed study of area-wise and pollutant-type databases is much needed to finalize the priority area and the need for the effective removal of the pollutants from the contaminated sites. The decontamination of these natural resources is essential for the conservation of nature and the environment using the bioremediation process.

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Conflict of interests

The authors declare no conflict of interest with anyone.

References:-

1. Yin, J., Wang, L., Chen, Y., Zhang, D., Hegazy, A. M., & Zhang, X. (2019). A comparison of accumulation and depuration effect of dissolved hexavalent chromium (Cr6+) in the head and muscle of bighead carp (Aristichthys nobilis) and assessment of the potential health risk for consumers. Food Chemistry, 286, 388-394. https://doi.org/10.1016/j.foodchem.2019.01.186
2. Dabir, A., Heidari, P., Ghorbani, H., & Ebrahimi, A. (2019). Cadmium and lead removal by new bacterial isolates from coal and aluminium mines. International journal of environmental science and technology, 16, 8297-8304. http://dx.doi.org/10.1007/s13762-019-02303-9
3. Posthuma, L., Altenburger, R., Backhaus, T., Kortenkamp, A., Müller, C., Focks, A., ... & Brack, W. (2019). Improved component-based methods for mixture risk assessment are key to characterize complex chemical pollution in surface waters. Environmental Sciences Europe, 31(1), 1-11. 10.1186/s12302-019-0246-5
4. Xu, X., Nie, S., Ding, H., & Hou, F. F. (2018). Environmental pollution and kidney diseases. Nature Reviews Nephrology, 14(5), 313-324. https://doi.org/10.1038/nrneph.2018.11.
5. Fan, X., Ding, S., Chen, M., Gao, S., Fu, Z., Gong, M., ... & Zhang, C. (2019). Peak chromium pollution in summer and winter caused by high mobility of chromium in the sediment of a eutrophic lake: in situ evidence from high spatiotemporal sampling. Environmental science & technology, 53(9), 4755-4764.https://doi.org/10.1021/acs.est.8b07060
6. Mohinuzzaman, M., Saadat, A. H. M., Mostofa, K. M. G., Islam, S. M. N., Hossain, S. M., & Tareq, S. M. (2018). Health risk assessment of chromium-accumulated fish and vegetables at Gulshan Lake of Bangladesh: a case study. Pollution, 4(3), 459-469 DOI: 10.22059/POLL.2018.246483.344

7. Pradhan, D., Sukla, L. B., Mishra, B. B., & Devi, N. (2019). Biosorption for removal of hexavalent chromium using microalgae Scenedesmus sp. Journal of Cleaner Production, 209, 617-629. https://doi.org/10.1016/j.jclepro.2018.10.288
8. Sanjay, M. S., Sudarsanam, D., Raj, G. A., & Baskar, K. (2020). Isolation and identification of chromium-reducing bacteria from tannery effluent. Journal of King Saud University-Science, 32(1), 265-271.https://doi.org/10.1016/j.jksus.2018.05.001.
9. Ashraf, A., Bibi, I., Niazi, N. K., Ok, Y. S., Murtaza, G., Shahid, M., ... & Mahmood, T. (2017). Chromium (VI) sorption efficiency of acid-activated banana peel over organo-montmorillonite in aqueous solutions. International journal of phytoremediation, 19(7), 605-613. https://doi.org/10.1080/15226514.2016.1256372
10. Vimercati, L., Gatti, M. F., Gagliardi, T., Cuccaro, F., De Maria, L., Caputi, A., ... & Baldassarre, A. (2017). Environmental exposure to arsenic and chromium in an industrial area. Environmental Science and Pollution Research, 24, 11528-11535. doi: 10.1007/s11356-017-8827-6
11. Liu, X., Wu, G., Zhang, Y., Wu, D., Li, X., & Liu, P. (2015). Chromate reductase YieF from Escherichia coli enhances hexavalent chromium resistance of human HepG2 cells. International Journal of Molecular Sciences, 16(6), 11892-11902. **https://doi.org/10.3390/ijms160611892**
12. Novotnik, B., Ščančar, J., Milačič, R., Filipič, M., & Žegura, B. (2016). The cytotoxic and genotoxic potential of Cr (VI), Cr (III)-nitrate and Cr (III)-EDTA complex in human hepatoma (HepG2) cells. Chemosphere, 154, 124-131. https://doi.org/10.1016/j.chemosphere.2016.03.118
13. Elahi, A., & Rehman, A. (2019). Comparative behavior of two gram-positive Cr6+ resistant bacterial strains Bacillus aerius S1 and Brevibacterium iodinum S2 under hexavalent chromium stress. Biotechnology reports, 21, e00307. https://doi.org/10.1016/j.btre.2019.e00307
14. Ma, L., Xu, J., Chen, N., Li, M., & Feng, C. (2019). Microbial reduction fate of chromium (Cr) in aqueous solution by mixed bacterial consortium. Ecotoxicology and environmental safety, 170, 763-770. https://doi.org/10.1016/j.ecoenv.2018.12.041
15. Kanagaraj, G., & Elango, L. (2019). Chromium and fluoride contamination in groundwater around leather tanning industries in southern India: Implications from stable isotopic ratio δ53Cr/δ52Cr, geochemical and geostatistical modelling. Chemosphere, 220, 943-953.https://doi.org/10.1016/j.chemosphere.2018.12.105.
16. Khalid, S., Shahid, M., Niazi, N. K., Murtaza, B., Bibi, I., & Dumat, C. (2017). A comparison of technologies for remediation of heavy metal contaminated soils. Journal of geochemical exploration, 182, 247-268. https://doi.org/10.1016/j.gexplo.2016.11.021
17. Velez, P. A., Talano, M. A., Paisio, C. E., Agostini, E., & González, P. S. (2017). Synergistic effect of chickpea plants and Mesorhizobium as a natural system for chromium phytoremediation. Environmental technology, 38(17), 2164-2172. https://doi.org/10.1080/09593330.2016.1247198
18. Malaviya, P., & Singh, A. (2016). Bioremediation of chromium solutions and chromium-containing wastewaters. Critical reviews in microbiology, 42(4), 607-633. https://doi.org/10.3109/1040841X.2014.974501
19. Jobby, R., Jha, P., Yadav, A. K., & Desai, N. (2018). Biosorption and biotransformation of hexavalent chromium [Cr (VI)]: a comprehensive review. Chemosphere, 207, 255-266. https://doi.org/10.1016/j.chemosphere.2018.05.050
20. Vendruscolo, F., da Rocha Ferreira, G. L., & Antoniosi Filho, N. R. (2017). Biosorption of hexavalent chromium by microorganisms. International Biodeterioration & Biodegradation, 119, 87-95. https://doi.org/10.1016/j.ibiod.2016.10.008
21. Bharagava, R. N., & Mishra, S. (2018). Hexavalent chromium reduction potential of Cellulosimicrobium sp. isolated from common effluent treatment plant of tannery industries. Ecotoxicology and environmental safety, 147, 102-109. https://doi.org/10.1016/j.ecoenv.2017.08.040
22. Zhang, Q., Amor, K., Galer, S. J., Thompson, I., & Porcelli, D. (2019). Using stable isotope fractionation factors to identify Cr (VI) reduction pathways: Metal-mineral-microbe interactions. Water research, 151, 98-109.https://doi.org/10.1016/j.watres.2018.11.088
23. Hsu, L. C., Liu, Y. T., & Tzou, Y. M. (2015). Comparison of the spectroscopic speciation and chemical fractionation of chromium in contaminated paddy soils. Journal of Hazardous Materials, 296, 230-238. https://doi.org/10.1016/j.jhazmat.2015.03.044
24. Zhang, B., Wang, Z., Shi, J., & Dong, H. (2020). Sulfur-based mixotrophic bio-reduction for efficient removal of chromium (VI) in groundwater. Geochimica et Cosmochimica Acta, 268, 296-309.https://doi.org/10.1016/j.gca.2019.10.011.
25. Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary toxicology, 7(2), 60-72.https://doi.org/10.2478/intox-2014-0009.

26. Jin, W., Du, H., Zheng, S., & Zhang, Y. (2016). Electrochemical processes for the environmental remediation of toxic Cr (VI): A review. Electrochimica Acta, 191, 1044-1055. https://doi.org/10.1016/j.electacta.2016.01.130
27. Vijayaraj, A. S., Mohandass, C., Joshi, D., & Rajput, N. (2018). Effective bioremediation and toxicity assessment of tannery wastewaters treated with indigenous bacteria. 3 Biotech, 8, 1-11.https://doi.org/10.1007/s13205-018-1444-3.
28. Yaashikaa, P. R., Kumar, P. S., Babu, V. M., Durga, R. K., Manivasagan, V., Saranya, K., & Saravanan, A. (2019). Modelling on the removal of Cr (VI) ions from aquatic systems using mixed biosorbent (Pseudomonas stutzeri and acid-treated Banyan tree bark). Journal of Molecular Liquids, 276, 362-370. https://doi.org/10.1016/j.molliq.2018.12.004
29. Ahmed, S., Fatema-Tuj-Zohra, Khan, M. S. H., & Hashem, M. A. (2017). Chromium from tannery waste in poultry feed: a potential cradle to transport human food chain. Cogent Environmental Science, 3(1), 1312767.https://doi.org/10.1080/23311843.2017.1312767
30. Chaudhary, A., gul Javaid, K., & Bughio, E. (2023). Toxic effects of chromium chloride on haematology and histopathology of major carp (Labeo rohita). The Egyptian Journal of Aquatic Research, 49(3), 291-296.https://doi.org/10.1016/j.ejar.2023.01.003
31. Jamil Emon, F., Rohani, M. F., Sumaiya, N., Tuj Jannat, M. F., Akter, Y., Shahjahan, M., ... & Goh, K. W. (2023). Bioaccumulation and bioremediation of heavy metals in fishes—A review. Toxins, 11(6), 510. doi: 10.3390/toxics11060510
32. Abreu, P. L., Cunha-Oliveira, T., Ferreira, L. M., & Urbano, A. M. (2018). Hexavalent chromium, a lung carcinogen, confers resistance to thermal stress and interferes with heat shock protein expression in human bronchial epithelial cells. Biometals, 31, 477-487. https://doi.org/10.1007/s10534-018-0093-7
33. Banu, S. K., Stanley, J. A., Taylor, R. J., Sivakumar, K. K., Arosh, J. A., Zeng, L., ... & Padmanabhan, V. (2018). Sexually dimorphic impact of chromium accumulation on human placental oxidative stress and apoptosis. Toxicological Sciences, 161(2), 375-387.https://doi.org/10.1093/toxsci/kfx224.
34. Jin, H. U., Meng, D. L., Liu, X. D., Liang, Y. L., Yin, H. Q., & Liu, H. W. (2018). Response of soil fungal community to long-term chromium contamination. Transactions of Nonferrous Metals Society of China, 28(9), 1838-1846. https://doi.org/10.1016/S1003-6326(18)64828-9
35. Zhu, Y., Yan, J., Xia, L., Zhang, X., & Luo, L. (2019). Mechanisms of Cr (VI) reduction by Bacillus sp. CRB-1, a novel Cr (VI)-reducing bacterium isolated from tannery activated sludge. Ecotoxicology and Environmental Safety, 186, 109792.https://doi.org/10.1016/j.ecoenv.2019.109792
36. Sumiahadi, A., & Acar, R. (2018, March). A review of phytoremediation technology: heavy metals uptake by plants. In IOP conference series: earth and environmental science (Vol. 142, p. 012023). IOP Publishing. Doi:10.1088/1755-1315/142/1/012023
37. Fan, Y., Li, Z., Zhou, T., Zhou, S., Wu, L., Luo, Y., & Christie, P. (2019). Phytoextraction potential of soils highly polluted with cadmium using the cadmium/zinc hyperaccumulator Sedum plumbizincicola. International journal of phytoremediation, 21(8), 733-741. DOI: 10.1080/15226514.2018.1556592
38. Venkatesan, G., & Subramani, T. (2019). Reduction of hexavalent chromium to trivalent chromium from tannery effluent using bacterial biomass. DOI:10.3923/jest.2012.142.154
39. Baldiris, R., Acosta-Tapia, N., Montes, A., Hernández, J., & Vivas-Reyes, R. (2018). Reduction of hexavalent chromium and detection of chromate reductase (ChrR) in Stenotrophomonas maltophilia. Molecules, 23(2), 406. **https://doi.org/10.3390/molecules23020406**
40. Fang, G., Li, W., Shen, X., Perez-Aguilar, J. M., Chong, Y., Gao, X., ... & Zhou, R. (2018). Differential Pd-nanocrystal facets demonstrate distinct antibacterial activity against Gram-positive and Gram-negative bacteria. Nature communications, 9(1), 1-9. 10.1038/s41467-017-02502-3
41. Li, M., He, Z., Hu, Y., Hu, L., & Zhong, H. (2019). Both cell envelope and cytoplasm were the locations for chromium (VI) reduction by Bacillus sp. M6. Bioresource technology, 273, 130-135.https://doi.org/10.1016/j.biortech.2018.11.006
42. Karthik, C., Barathi, S., Pugazhendhi, A., Ramkumar, V. S., Thi, N. B. D., & Arulselvi, P. I. (2017). Evaluation of Cr (VI) reduction mechanism and removal by Cellulosimicrobium funkei strain AR8, a novel haloalkaliphilic bacterium. Journal of hazardous materials, 333, 42-53.https://doi.org/10.1016/J.JHAZMAT.2017.03.037.
43. Bansal, N., Coetzee, J. J., & Chirwa, E. M. (2019). In situ bioremediation of hexavalent chromium in presence of iron by dried sludge bacteria exposed to high chromium concentration. Ecotoxicology and environmental safety, 172, 281-289. https://doi.org/10.1016/j.ecoenv.2019.01.094
44. Shaw, D. R., & Dussan, J. (2018). Transcriptional analysis and molecular dynamics simulations reveal the mechanism of toxic metals removal and efflux pumps in Lysinibacillus sphaericus OT4b. 31. International Biodeterioration & Biodegradation, 127, 46-61. https://doi.org/10.1016/j.ibiod.2017.11.016

45. Raman, N. M., Asokan, S., Shobana Sundari, N., & Ramasamy, S. (2018). Bioremediation of chromium (VI) by Stenotrophomonas maltophilia isolated from tannery effluent. International journal of environmental science and technology, 15(1), 207-216.https://doi.org/10.1007/s13762-017-1378-z.
46. Kalola, V., & Desai, C. (2020). Biosorption of Cr (VI) by Halomonas sp. DK4, a halotolerant bacterium isolated from chrome electroplating sludge. Environmental Science and Pollution Research, 27(22), 27330-27344. DOI: 10.1007/s11356-019-05942-0
47. Wang, Y., Su, H., Gu, Y., Song, X., & Zhao, J. (2017). Carcinogenicity of chromium and chemoprevention: a brief update. OncoTargets and therapy, 4065-4079. Doi: 10.2147/OTT.S139262
48. Ikegami, K., Hirose, Y., Sakashita, H., Maruyama, R., & Sugiyama, T. (2020). Role of polyphenol in sugarcane molasses as a nutrient for hexavalent chromium bioremediation using bacteria. Chemosphere, 250, 126267. https://doi.org/10.1016/j.chemosphere.2020.126267
49. Pei, Y., Yu, Z., Ji, J., Khan, A., & Li, X. (2018). Microbial community structure and function indicate the severity of chromium contamination of the Yellow River. Frontiers in microbiology, 9, 38.doi: 10.3389/fmicb.2018.00038
50. Banerjee, S., Kamila, B., Barman, S., Joshi, S. R., Mandal, T., & Halder, G. (2019). Interlining Cr (VI) remediation mechanism by a novel bacterium Pseudomonas brenneri isolated from coalmine wastewater. Journal of Environmental Management, 233, 271-282. https://doi.org/10.1016/j.jenvman.2018.12.048
51. Pei, Y., Yu, Z., Ji, J., Khan, A., & Li, X. (2018). Microbial community structure and function indicate the severity of chromium contamination of the Yellow River. Frontiers in microbiology, 9, 38. DOI: 10.3389/fmicb.2018.00038
52. Lunardelli, B., Cabral, M. T., Vieira, C. E., Oliveira, L. F., Risso, W. E., Meletti, P. C., & Martinez, C. B. (2018). Chromium accumulation and biomarker responses in the Neotropical fish Prochilodus lineatus caged in a river under the influence of tannery activities. Ecotoxicology and environmental safety, 153, 188-194. https://doi.org/10.1016/j.ecoenv.2018.02.023
53. Bearcock, J. M., Smedley, P. L., Fordyce, F. M., Everett, P. A., & Ander, E. L. (2017). Controls on surface water quality in the River Clyde catchment, Scotland, UK, with particular reference to chromium and lead. Earth and Environmental Science Transactions of the Royal Society of Edinburgh, 108(2-3), 249-267. https://doi.org/10.1017/S1755691018000397
54. Mihaileanu, R. G., Neamtiu, I. A., Fleming, M., Pop, C., Bloom, M. S., Roba, C., ... & Gurzau, E. (2019). Assessment of heavy metals (total chromium, lead, and manganese) contamination of residential soil and homegrown vegetables near a former chemical manufacturing facility in Tarnaveni, Romania. Environmental Monitoring and Assessment, 191, 1-13. DOI: 10.1007/s10661-018-7142-0
55. Tiwari, A. K., Orioli, S., & De Maio, M. (2019). Assessment of groundwater geochemistry and diffusion of hexavalent chromium contamination in an industrial town of Italy. Journal of contaminant hydrology, 225, 103503. https://doi.org/10.1016/j.jconhyd.2019.103503
56. Fallahzadeh, R. A., Khosravi, R., Dehdashti, B., Ghahramani, E., Omidi, F., Adli, A., & Miri, M. (2018). Spatial distribution variation and probabilistic risk assessment of exposure to chromium in ground water supplies; a case study in the east of Iran. Food and chemical toxicology, 115, 260-266. https://doi.org/10.1016/j.fct.2018.03.019
57. He, X., & Li, P. (2020). Surface water pollution in the middle Chinese Loess Plateau with special focus on hexavalent chromium (Cr6+): occurrence, sources and health risks. Exposure and Health, 12(3), 385-401. https://doi.org/10.1007/s12403-020-00344-x
58. Khan, A., Michelsen, N., Marandi, A., Hossain, R., Hossain, M. A., Roehl, K. E., ... & Schüth, C. (2020). Processes controlling the extent of groundwater pollution with chromium from tanneries in the Hazaribagh area, Dhaka, Bangladesh. Science of the total environment, 710, 136213. https://doi.org/10.1016/j.scitotenv.2019.136213
59. Chug, R., Gour, V. S., Mathur, S., & Kothari, S. L. (2016). Optimization of extracellular polymeric substances production using Azotobacter beijreinckii and Bacillus subtilis and its application in chromium (VI) removal. Bioresource technology, 214, 604-608. https://doi.org/10.1016/J.BIORTECH.2016.05.010.
60. Baaziz, H., Gambari, C., Boyeldieu, A., Ali Chaouche, A., Alatou, R., Méjean, V., ... & Fons, M. (2017). ChrASO, the chromate efflux pump of Shewanella oneidensis, improves chromate survival and reduction. PLoS One, 12(11), e0188516. https://doi.org/10.1371/journal.pone.0188516
61. Chai, L., Ding, C., Li, J., Yang, Z., & Shi, Y. (2019). Multi-omics response of Pannonibacter phragmitetus BB to hexavalent chromium. Environmental pollution, 249, 63-73. https://doi.org/10.1016/j.envpol.2019.03.005

62. Zheng, Q., Na, S., Li, X., Li, N., Hai, R., & Wang, X. (2019). Acute effects of hexavalent chromium on the performance and microbial community of activated sludge in aerobiotic reactors. Environmental technology, 40(14), 1871-1880. https://doi.org/10.1080/09593330.2018.1432695
63. Banerjee, S., Misra, A., Chaudhury, S., & Dam, B. (2019). A Bacillus strain TCL isolated from Jharia coalmine with remarkable stress responses, chromium reduction capability and bioremediation potential. Journal of hazardous materials, 367, 215-223. https://doi.org/10.1016/j.jhazmat.2018.12.038
64. World Health Organization. (2022). Guidelines for drinking-water quality: incorporating the first and second addenda. World Health Organization.
65. Priya, A. K., Gnanasekaran, L., Dutta, K., Rajendran, S., Balakrishnan, D., & Soto-Moscoso, M. (2022). Biosorption of heavy metals by microorganisms: Evaluation of different underlying mechanisms. Chemosphere, 307, 135957. https://doi.org/10.1016/j.chemosphere.2022.135957.
66. Nnaji, N. D., Onyeaka, H., Miri, T., & Ugwa, C. (2023). Bioaccumulation for heavy metal removal: a review. SN Applied Sciences, 5(5), 125. https://doi.org/10.1007/s42452-023-05351-6
67. Habib, S. S., Naz, S., Fazio, F., Cravana, C., Ullah, M., Rind, K. H., ... & Khayyam, K. (2024). Assessment and bioaccumulation of heavy metals in water, fish (wild and farmed) and associated human health risk. Biological Trace Element Research, 202(2), 725-735. https://doi.org/10.1007/s12011-023-03703-2.