



## Possible remediation of hexavalent chromium by native fungi of Sukinda mining area: a review

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ARTICLE INFO	ABSTRACT
<p>Received : 15 January 2022                      Revised : 23 March 2022                      Accepted : 04 April 2022</p>	<p>The expeditious industrialization is helping the world to give a new modern era with all sorts of amenities. But the consequences are following great risks that might result in a terrifying future. Heavy metal pollution and its hazardous effects are one of them. Though India is the 3rd largest chromium producing country and the Sukinda valley of Odisha, is the chief source for chromium, hence here the threat of chromium pollution is at a high point. Countermeasures to this problem have become of prime importance. Among several remedial measures, bioremediation is an approaching process to control the accelerated growth of heavy metal contamination including chromium. In the world of microorganisms, the congenital characteristics of fungi have great importance as they can grow easily in polluted habitats. Again, there is evidence of native fungi having the potential to bind with heavy metals and remove toxic agents from natural environments. The pathway of chromium toxicity and its possible remediation potential by fungi have been studied extensively in the Sukinda area. This study signifies some positive aspects that can be practised in the future as a convenient option for bioremediation. Fungal bioremediation improved with biotechnology tools will be suitable output for rapid remediation which is vital for this moment.</p>
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### Introduction

After the industrial revolution, the anthropogenic exploitation of chromium increased rapidly in India as well as in Odisha. Chromium is an essential metal that dominates the domestic market as it is exported to other countries for ferroalloys. Other than ferroalloys, it is also used as a chief ingredient in refractories, ceramics and the preparation of chromium-containing chemicals. As Chromium is the most demanding mineral reserve of our country hence it stands as the economical, sociological, and financial backbone of our territory. Among all the forms of chromium, Cr (VI) is referred as the most toxic form as is detrimental for all the ecosystems. Overdose of Cr (VI) results in depletion of seed germination, plant growth and yield quality by disturbing the enzymatic activity, nutrients and

oxidative balance. Whereas in case of animals it leads to mutagenesis and several genetic disorders. Odisha contributes almost 97% of India's reserve of chromium (US EPA data 2004) and Sukinda is the chief source of chromites. Several mining industry of Sukinda and their methodologies are having a great impact for contaminating the nearby natural resources and making it inappropriate for the surrounding biological system. The open cast mines raised near Sukinda escalated the concentration of hexavalent chromium which is far above the permissible limits. This leads the environment toxic for the local biotic community. It captured everyone's attention when designated as the 4<sup>th</sup> most polluted area by Blacksmith report 2007 (BI university 2007). The upcoming threat indicates that proper propaganda was essential to establish



**Figure 1: Mining sites of sukinda (Source from google map)**

a non-toxic or less toxic environment for the people of Sukinda balancing the ecological, economical and ethical status.

Detoxification of chromium should include a procedure that is inexpensive, eco-friendly and could apply on an extended version. The remedial proposal forwarded for chromium reduction includes physical, chemical and biological cleaning procedures. Almost all methods including some combinations are either having less impact on remediation or produces secondary pollutants which result in no action. In order to prepare an optimal remedial strategy, an understanding of the characteristics of chromium and its interaction with the environment focusing on its mechanism of contamination needs to be explained.

Remedial measures using living biomass or bioremediation raised is an emerging technology that has been used extensively. After analyzing the pathways of chromium contamination, conversion of chromium from a toxic form to a nontoxic form was an approachable option for remediation in mines area (Bhutiani *et al.*, 2019; Chuanhan *et al.*, 2019; Irfan *et al.*, 2022). Again, the traits of adsorption were traced in plants and in microorganisms which symbolizes utilization of these living organisms for detoxification of contaminating mining areas. The remediation using biological agents are cost effective, valuable and effortless option to be applied in the Sukinda region. Bioremediation is a cleaning process that includes a pathof investigation for molecular

biology and ecological balance (Kumar *et al.*, 2011). It's a cleaning process in which microbes are used to transform harmful substances to achieve a contamination-free nontoxic environment. The whole phenomenon of bioremediation is accompanied by several sub-processes like biosorption, bioabsorption, bioaugmentation, bioaccumulation, biosolubilization, bioreduction, bio precipitation, mineralization and methylation. For the removal of heavy metals methods like biosorption, bioaccumulation, bio leaching, biomineralizations are applicable. Here the emphasis has been given to adsorption and accumulation. Presently bioremediation incorporation with nano-technology in a voyage for remediation of heavy metals (Karmacharya *et al.*, 2016; Bhutiani *et al.*, 2021; Bhutiani and Ahamad, 2018). The results showing positive symptoms in the field of heavy metals (Tyagi *et al.*, 2017). Evidences show that Heavy metals like arsenic, aluminium and nickel remediated from the respective contaminated system with this technology (Dehghani *et al.*, 2015). Even nanoparticles have certain impact on chromium also (Gupta *et al.*, 2016). So more exploration in this field can be proved as beneficiary for both bioremediation and nano technology field. Fungi are the dominating microorganism of the biotic community. Fungal biotechnology is now on a voyage to explore the absorbance capacity of metallic ions from contaminated soils in order to give a solution to the leading pollution problem.

**Table 1: Mines of Sukinda and their overburden generation in Sukinda valley**

Name of the mines	Overburden generation in million /year	Over burden dump area in ha	Reference
Saruabil,M.L. Mines Pvt. Ltd.	10.37	62.02	Mishra and Sahoo, 2013
TISCO Sukinda	5.4	79.8	
Kaliapani , OMC	3.0	48.1	
Sukinda , IMFA	0.60	45.0	
South Tailangi , IDCOL	0.54	9.995	
Kaliapani, Balasore Alloys	0.48	22.41	
Ostapal FACOR	0.47	17.18	
Mahagir , IMFA	0.20	4.49	
Kamarda, B.C. Mohanty & Sons	0.2	17.74	
Kaliapani ,OMC	0.1	-	
Sukrangi , OMC	0.03	-	
Kathpal , FACOR	0.03	27.25	
Chingudipal , IMFA	-	4.38	

**Table 2: Role of microorganisms in remediation of heavy metals**

Micro organisms	Compound	Reference
<i>Saccharomyces cerevisiae</i>	Heavy metals,Pb, Hg and Ni	[chen <i>et al.</i> ,2007,kilar <i>et al.</i> , 2009 ,infante 2014]
<i>Cunninghamella elegans</i>	Heavy metals	[tiginiv <i>et al</i> 2010]
<i>Pseudomonas fluorescens and Pseudomonas Aeruginosa</i>	Fe <sup>2+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup> ,Mn <sup>2+</sup> and Cu <sup>2</sup>	[paranthaman <i>et al</i> 2015]
<i>Lysinibacillusphaericus CBAM5</i>	Co, Cu, Cr and Pb	[Montengro <i>et al</i> 2015]
<i>Microbacteriumprofungi strainShh49T</i>	Fe	[Wu <i>et al</i> 2015]
<i>Geobacterspp</i>	. Fe (III), U (VI)	[Mirlahiji <i>et al</i> 2014]
<i>Bacillus safensis (JX126862) strain (PB-5 and RSA-4)</i>	Cd	[Rajesh <i>et al</i> 2014]
<i>Pseudomonas aeruginosa, Aeromonas sp.</i>	U, Cu, Ni, Cr	[Sinha <i>et al</i> 2011]
<i>Microorganisms Compound Reference Aerococcus sp., Rhodopseudomonas palustris</i>	Pb, Cr, Cd	[Sinha <i>et al</i> 2014, Sinha <i>et al</i> 2014]

**Table 3 : Microbial Contribution To Chromium Remediation**

Organisms	Mode of Action	Reference
<i>Pseudomonas fluorescens</i>	LB300 Uptake of Cr <sub>2</sub> O <sub>4</sub> <sup>-</sup> by the strain with plasmid	[Ohtakeet <i>al.</i> , 1987]
<i>Schizosaccharomyces pombe</i>	Lysine and leucine auxotrophic and heterothallic strains of this microbe were used to obtain Cr-sensitive and tolerant mutants by UV radiation-induced and nitrosoguanidine induced mutagenesis	[czako-veret <i>al.</i> , 1999]
<i>Pseudomonas ambigua G-1</i>	Bioreduction of the Cr-concentration from 150-35mgL <sup>-1</sup> in 36hr in liquid media	[losi <i>et al.</i> , 1994]
<i>Bacillus firmus</i>	Capable of absorbing Cr <sup>6+</sup> efficiently into their biomass	[Bennett <i>et al.</i> , 2013]
<i>Klebsiella pneumoniae</i>	Capable of absorbing Cr <sup>6+</sup> efficiently into their biomass	[Bennett <i>et al.</i> , 2013]
<i>Mycobacterium sp.</i>	Capable of absorbing Cr <sup>6+</sup> efficiently into their biomass	[Bennett <i>et al.</i> , 2013]
<i>Bacillus cereus IST105</i>	Absorption of chromate on the bacterial cell wall takes place through surface functional groups like carboxyl, amide, phosphoryl and hydroxyl	[Naik <i>et al.</i> , 2012]
<i>Bacillus megatarium TKW3</i>	Hexavalent chromium reduction associated with membrane cell fraction	[Cheung <i>et al.</i> , 2006]
<i>Bacillus circulans</i>	Removal of chromium by bioabsorption	[Khanafari <i>et al.</i> , 2008]
<i>Bacillus subtilis</i>	Able to reduce chromate at concentrations ranging from 0.1 to 1 mM K <sub>2</sub> CrO <sub>4</sub>	[Garbisu <i>et al.</i> , 1998]
<i>Bacillus methylotrophicus</i>	Chromate reduction activity was found to be 91.3% at 48hrs	[Mala <i>et al.</i> , 2015]

Fungi, the dominating organisms found in Sukinda area are variably capable to survive and retrieve in the highly concentrated heavy metal fields, so recovery of precious metallic ions using fungal based cleaning approaches is one of the best solutions that can be applied for detoxification.

The study gives an idea that bioremediation using fungal isolates present in the Sukinda soil are possibly able to start a new methodology in the world of remediation.

#### **Sukinda and its environmental scenario:**

In India, Odisha state is blessed with vast deposits of mineral reserves like coal, iron, manganese and bauxite but chromium is the principal ore element that stabilizes its economy. Major share of chromite deposits (98.6%) associated with ultramafic complexes are in Sukinda and Baula Nuasahi region. Sukinda chromium valley is the largest chromium deposits of Odisha (Pattnaik *et al.*, 2016) that counts almost 195 million tons of reserve which is 98% of the total chromium in India (Mishra and Sahu., 2013). The valley encloses 200 sq. Km area bounded by latitudes 20°53' and 21°05' and longitudes 85°40' and 85°53' surrounded from Tomka-Daitari Range, North to Mahagiri Range in the South with a general slope of 18-20° towards South-West (Figure 1.)

#### **Status of chromite mines**

Chromite is chiefly used and exported in the form of ferroalloys, which accounts for about 85% of the total chromites demand of Odisha state. Some chromites are also utilized for refractory, ceramics and chromium containing chemicals. Due to demands as key industrial raw materials 17 mining leases granted for chromites mining in Jajpur district from which 12 are operating smoothly while others have some statutory clearance problem ([www.orissaminerals.gov.in](http://www.orissaminerals.gov.in)). Among these mines most are open cast mining except two, engaging anthropogenic activities which causes negligence in environmental controls posing major hazards to the flora and fauna in and around

#### **Toxicity of Sukinda area**

Blacksmith Institute USA has declared Sukinda as the fourth most polluted place (BI report 2007) of the world. The reason of pollution is the exceeded level of hexavalent chromium as particulate matter

in the airwater and soils affecting severely the nearby population (Das *et al.*, 2011.). Due to open cast mining, overburden material generating soil waste results in damage of abiotic and biotic community (Viti *et al.*, 2014). In rainy days leaching occurs which may lead to the deterioration in quality of ground and surface water (Mohanty and Patro 2011). The water also washed out with chromium from mining sites and reaches to nearby water reservoir. This causes harm to the aquatic organisms and to human society both directly and indirectly (Kumari *et al.*, 2017). Due to exploitation high amount of chromium dust generates and fuses in the air and inhalation of this polluted air may have carcinogenic effector can cause cardiac arrest (Das *et al.*, 2010). The state pollution board conducted tests for Sukinda area in October 2018 and the report reveals the presence of hexavalent chromium far from permissible limit. According to another prevailing report 70% of water and 28% of soil are inappropriate for irrigation due to high concentration of Cr(VI) (EPA 1998a). This data signifies a red alert to nearby 75 villages and 40 perennial streams.

Sukinda environmental situation creates a major health hazard to the residents and workers of the Sukinda valley (Pattnaik *et al.*, 2012) as well as to the floral population. Increased number of open cast mining is the prime reason for promoting the contamination of the nature (Mishra *et al.*, 2010). The solid waste (Around 7.6 tons) deposited in the boundaries of mining areas facilitates the contact of hexavalent chromium with the soil and air (Das *et al.*, 2011). Again because of drilling, blasting and transportation a large amount of dust is produced and the dust is nothing but particulate matter of hexavalent chromium that has a lethal effect to the biomes. Also, the dumping of the overburden in the nearby area interrupts the natural balance of that ecosystem causing disturbance in the plant and animal diversity.

Utilizing better mining technologies for ore exploitation is a progressive step for the development of mankind but simultaneously destroying our own environment is the major drawback. Time already alarmed us to investigate on more sustainable methods for a better future for all living beings for a better future because all creatures have their rights to live and evolve in future.

**Chromium chemistry and its toxicity:**

Chromium can easily locate in rock, soil, volcanic dust and in living organisms but in trace amount. Chromium is the first element in group 6 with atomic number 24. This element derives from only ore complex, chromites, discovered first from United States nearly about 1808. It is the chief and most indispensable industrial metal because of its significance characteristics like resistance to corrosion, hardness and high melting point. Chromium is a lustrous steel grey metal used in plating on steel and other nonferrous alloys and also owned as raw materials by the chemicals and leather industries. These properties of chromium are responsible for its huge demand in the market

Valance of chromium vary from -II to VI, whereas the only possible stable forms are III and VI available as ores, such as ferrochromite. Hexavalent chromium is produced due to anthropogenic activity (EPA 1984a) (ATSDR 2017). Because of various utilizations in different commercial field its demand in this present world has achieved in its peak. Today's modernized world demands chromium in several industries for electroplating, timber preservation and in leather tanning etc (Madhavi *et al.*, 2013). Chromium also has a significant role in living bodies but its increased concentration may lead to toxic, mutagenic, carcinogenic and teratogenic (Kilic *et al.*, 2011).

**Chromium and its utilization**

Chromium and its derivative compounds are important raw material for industries like metallurgical, chemical, and refractory. Metallurgical industries utilizes for preparation of steel and other non alloys, chemical industries for preparation of different chemicals and Refractory uses for metallurgical furnace linings and granular chromites for production of heat resistant appliances. It is also a vital agent for the living world as it stimulates fatty acid and cholesterol synthesis essential for brain and nerve systems and other metabolic reactions (Kumari *et al.*, 2017). Organ meats, mushrooms, wheat germ, and broccoli are examples of rich sources of chromium. Chromium also involves in several metabolic processes and can acts as a catalyst when taken as supplement.

**Negative impact of chromium**

The valence of chromium determines the intensity of its toxic nature (Tchounwou *et al.*, 2012). Chromium with valance VI more harmful than chromium valance with III for its high oxidizing potential, greater solubility and smaller size as compare to another valance state (Liang *et al.*, 2017). It easily enters in to the cells causing mutation or apoptosis. Hexavalent chromium is so harmful that inhalation, ingestion or even dermal contact can cause severe damage to the living body. Hence US EPA has set a limitation value i.e., beyond 0.1 milligram per litre or 100 ppb of chromium forms will be considered toxic to all form. The toxicity of chromium for many agronomical fields varies from five to one hundred mg/kg in soil (EPA 1984) (Bakshi *et al* 2022). The issued limit for chromium or hexavalent chromium for potable drinking water is up to 0.05 mg/L and drinking water near industries ranges from 2-5 g/L in the effluents (Indian standard specification for drinking water). Excess of chromium leads to yellow impacts on water and unfit for drinking (Dhal *et al.*, 2013). So hexavalent chromium above its permissible limits originates some incurable health hazards in plants and animals.

**Mechanisms of chromium toxicity**

Reduction is a normal phenomenon of chromium but not necessarily to less toxic form (Kawanshi *et al.*, 1986). Basically, this is the most supported mechanism of chromium involvement in biological process. It destroys the cell by producing free radicals (Fenti *et al.*, 2020). Overdose of hexavalent chromium inside a cell may mislead some important pathways like transcription, translation and DNA replication causing mutagenesis (Su *et al.*, 2014). DNA damage show miserable condition to cell as it concludes to genotoxicity. Hexavalent chromium affects the male reproductive system as well as the development of fetus (Kim *et al.*, 2012). Chromium elements are highly toxic to plants. Excess of chromium deposition affect germination and limits the growth of plant which results in reduced dry matter production and decreased yield. It also interrupts several physiological and metabolic processes causing oxidative stress to the plant. Earlier symptoms can

be identified by chlorosis and necrosis effects (Oliveira *et al.*, 2012).

Hexavalent chromium is unable to act directly with the DNA. It enters into the cells through various transport systems. As it has similarities with sulphate oxyanions ( $\text{SO}_4$ ), it can affect the cells either by creating oxidative stress or by attaching to the DNA in its reduced form. When it enters into the cells it immediately reduces to an intermediate form i.e Cr (V)/(IV) due to the presence of biological ascorbate and thiol group. The intermediate stage forms hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and free radicals that causes oxidative stress and leads to cell proliferation and mutation. The intermediate forms are unstable so it further converts to trivalent chromium (Cr (III)) which inserts into the structural DNA forming chromium DNA adduct which interrupts the central dogma of life (Shahid *et al.*, 2017).

#### Effect of chromium on Animal cells

Carcinogenic effects of the chromium have been studied from years with sufficient evidence which clarifies the toxicity and mutagenicity in animal and plant cells (Narayani *et al.*, 2013). Animal cells encountered by chromium through dermal contact, inhalation and ingestion and each of these aspects create a threat to different part of animal cells. Chromium exposure to epidermis of animal cell can cause dermatitis and dermatosis while inhalation can cause irritation, itchiness and nose bleed in nasal septum (Alvarez *et al.*, 2021) and exceeded contact may cause respiratory disorder. Normally ingestion of chromium after a certain limit can result into cancer in gastro intestinal tract, oesophagus or may be in stomach. Studies also represent the cytogenetic impact of Cr in different biological systems (Mayotte *et al.*, 2018) which leads to point mutation, alternation of physico-chemical properties of nucleic acid and DNA damage (Mayotte *et al.*, 2018), but mechanism responsible for Cr oxidation specially with genetic material is still doubtful (Masinire *et al.*, 2021). Depending on the proportion of exposure the toxicity can show minimum to lethal effect in animal body.

A survey on the workers related to chromium Industries confirms that Chromium causes Carcinogenic effect on human (den Braver-Sewradj *et al.*, 2021). An experiment on workers of

chromite mines in the United States reports that lung cancer was initiated with 1,445 workers, those who are directly involved in extraction from chromite mines from 1930 to 1947 (Clementino *et al.*, 2018). Further study shows that hexavalent chromium can cause skin ulceration, lesion and other allergies through dermal contact. It can result into asthma or perforation in nasal septum by extreme inhalation of hexavalent form. (Halasova *et al.*, 2009). Ingesting Cr (VI) causes abdomen and viscous injury which will cause cancer (Langård *et al.*, 2019)

#### Chromium toxicity on Plant cells

Plant Physiology and metabolisms gets affected by Chromium. Although the chromium absorption is still uncertain but it was assumed that depending on the valence of Chromium it gets absorbed by various methods. Active absorption of chromium is found in case of hexavalent chromium as it attached with a carrier ion like sulphate for its translocation (Singh *et al.*, 2013). Hexavalent chromium also has affinity towards Fe and P ion for carrier binding. In case of trivalent chromium passive absorption takes place which requires no energy for its translocation in plants. Again there is a lack of reports that justify the enzymes for reduction or gaining of electrons to the valence of chromium within a plant. Thus metal speciation is the only responsible factor to exert its path for accumulation or translocation as well as intensity of virulence.

Effect of chromium toxicity has been studied in different stages of plants. Hexavalent chromium creates some serious problem in plant tissues at higher concentration. With increase concentration of chromium symptoms of chlorosis and necrosis is progressively visible with a sharp decline in protein production and nitrogenase activity. (Paiva *et al.*, 2014) Also reduced shoot and root growth with wilted leaves observed at early stage (Rai *et al.*, 2014). The morphological parameters severely affected by the application of chromium correspondingly the yield and production is also affected that may lead to no harvest condition. Again, the biochemical and physiological parameters are also disturbed by the increasing chromium concentration (Pattnaik *et al.*, 2022). Again Rosko & Raclin (1977) showed hexavalent chromium concentration affect growth, photosynthesis, morphology and enzyme activities

in algae and is toxic in concentrations ranging from 20 -10,000 ppb . Thus, the effect of chromium toxicity has a direct impact on plant growth and yield.

#### **Remedial measures and bioremediation:**

Contamination of chromium toxicity at the manufacturing sites is due to hexavalent chromium that is stable by nature. So, it is our prime importance to dive into the detailed information of chromium and its chemistry of conversion to its stable state. Excess disposal of waste products from mining industries decreases the capacity of self-cleaning, for which soil, water, air and crops get affected. Consequent contamination in these biotic elements with hazardous metals and toxic chemical led this area into jeopardy. Hence development of new technology is essential which should emphasize on conventional approach for disposal of pollutants without producing any secondary pollutant and without disturbing the ecological food chain. (Asha *et al.*, 2013).

#### **Remediation proposals and their incapacities**

While a lot of environmental investigation and remediation work involves chemical and physical protocols, it is important to remember that this type of methods is just one of the hundreds that can have impact on particular or limited areas (Bahi *et al.*, 2012). Physical procedures like excavation solidification/stabilization, filtration, reverse osmosis, membrane technology, evaporation and electrochemical treatment were introduced earlier for complete removal of pollutants. But it is unable to give a persistent solution to this problem. These proposals are not acceptable due to the complicated application procedure which is difficult when it comes to large quantity remediation and second is its high cost.

Chemical detoxification includes chemical precipitation, oxidation or reduction ion-exchange and other sulphur or iron-based compounds, such as Fe (II) [Jagupilla *et al.*, 2009], amorphous FeS<sub>2</sub> [Li Y *et al.*, 2016], calcium polysulphide (CaS<sub>x</sub>) [Chrysochoou *et al.*, 2015] and sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) [Li *et al.*, 2011]. Again, as hexavalent chromium is water soluble; it can never be separated by means of physical separation (Pradhan *et al.*, 2020). These detoxification procedure

produces huge secondary pollutants so application of this procedure may be possible for industries but not for mining sites as Sukinda.

Now the bioremediation process has become a prime importance to deal with chromium pollution issue using microorganisms to detoxify the hazardous component from a particular area (Vargas *et al.*, 2019). The microbes may be indigenous or may be exported to the contamination site (Kumar *et al.*, 2011). Some varieties of bioremediations are phytoremediation, bioventing, bioleaching, land farming and biostimulation etc. (Verma *et al.*, 2008). As living organisms are involved to reduce pollutant concentration and a maintain biodiversity balance hence bioremediation can be used as a better clean-up programmed for metal contaminated and polluted ecosystem (Park *et al.*, 2011).

#### **Bioremediation**

Microbes prove to be the best remedial agents as they are able to degrade the contaminants with less energy as well as less costly ways. Again, aerobic microbes shows better results than the anaerobe (Arshi *et al.*, 2021). Biological agents like yeast, bacteria and fungi take part in the cleaning programme called, Bioremediation (Kumar *et al.*, 2011). Usually, microorganisms use the contaminants as their nutrients and utilizes in their metabolisms (Asha *et al.*, 2013). Initially the interest was on anaerobes like *aeromonas*, *micrococcus* and *aerococcus* (Sharma *et al.*, 2021). There was a success found in *Thermus scoductus* and in certain *achromobacter sp.* In case of fungi the experiment starts with *actinomyces*. Now several bacteria and fungi have been reported to reduce or adsorb, transform or bioaccumulate heavy metals from different contaminated soils. Bioremediation can be natural or intervention processes (Asha *et al.*, 2013). Metals has a significant role in microbial metabolism and bioremediation is perfect approach to utilize it as a treatment facility.

#### **Mechanism of bioremediation**

Absorption of metals by microorganisms can take place actively through bioaccumulation and passively through biosorption. Several bioremediation cases were witnessed of having

impressive landmark on the field of heavy metal detoxification.

Biosorption is a type of bioremediation where that aim is to attach the toxic metals or contaminants to the surface of living organisms. The surface of the Cell walls are composed of different complexes including various catatonic and anionic properties that helps the heavy metal compound to latch on the surfaces (Fernández *et al.*, 2018). Biological complex like Polysaccharides, lipids, amino acids and other functional groups are responsible for biosorption. Again, functional group like carboxylate, hydroxyl, amino and phosphate groups are actively present in microorganisms that may shows biosorption (Rathi *et al.*, 2021). So, microbes mediated biosorption process is an affordable and large scale applicable process that can go commercial. There is also some draw backs as these are microorganisms they also have certain metabolism that requires oxygen or other gases that increase the COD and decreases the BOD in water bodies. In soil again they can release some gases that may produce secondary pollutants. The major factor is applying microorganisms may bring risk on the healthy environment of living biomass and other environmental factors.

Bioaccumulation is a process where the living entity completely engulfs the toxic materials and utilizes in its own metabolism. The mechanism of bioaccumulation is ambiguous but studies may conclude that the metabolically active uptake leads to the intercellular space and allow attaching with the protein and peptide ligands (Mishra and Malik, 2013). But it also implies that the microorganisms need to be alive for metabolic action that may imposes unique challenges like necessity of nutrition, environment for maximum propagation and most important health risk to the nearby biotic community. So, using native microorganisms could be an effective option for bioaccumulation.

Biosorption and bioaccumulation can be proved as best remedy for various polluted sites as they have the ability of regeneration. Other advantages include low cost, removal substantial quantities of metals and recovery of metals.

### Bioremediation of Chromium

Trivalent chromium is less harmful because of its impermeability larger size lack of oxidation

capacity, so conversion of Cr (VI) to Cr(III) can be a applicable process for the treatment of chromium contaminated wastes and industrial effluents. Cr (VI) at normal environmental state, get reduced in the presence of ascorbate and glutathione to form pentavalent, tetravalent free radicals and finally trivalent form. The conversion of pentavalent to hexavalent process are reversible process that under go redox reaction inside the cell membrane leading to the formation of ROS complex that can combine affect DNA directly Cr. The common physiological mechanisms inside a cell can be directly affected by Cr (IV) through mutation (Mishra *et al.*, 2019). But there are sulphate utilizing microbes absorbs hexavalent chromium through the membrane sulphate transport channels present in the cells.capacity So microbes have a capacity to intact or intake the chromium through their body again the self-replicating and cost effectiveness makes bioremediation an effective biological tool for chromium detoxification.

### Fungi in the Field of Bioremediation

The kingdom fungi comprise a vast and diversified group of organisms that are found in almost every ecosystem which makes it ubiquitous in nature. The ability of producing spore makes the fungi survive the stress conditions. Extended mycelia growth may help fungi to grow in a large effected area with low nutrient requirement. Again, these organisms don't require a special condition for their dispersal, like other microorganisms. Fungi can produce several extracellular oxido-reductase that can degrade lingo-cellulose which can be used as pollutant degrading agents without utilization of carbon and energy sources and hence are called as the cleaning agents or the decomposers of the environment. Unique properties of Fungi and the mutualistic relationship with other organisms make it an excellent experimental organism for bioremediation. However, fungi of heavy metal polluted Indian habitat aren't that exploited for bioremediation

### Native Fungi in heavy metal reduction:

The extremophilic nature of fungi makes mycoremediation an emerging subject and attracts attentions in recent years. Among the diversified group filamentous fungi are the significant group that used due to its low-cost values and easy

growing mycelia. Binding properties of microbes are already evident, again in fungi involving gene i.e., hydrohobin has also been described for metal tolerance. Again, microbes belong to area of extreme metal condition develops metal resistance ability by their own. There may be involvement of more than one mechanism in case of fungi Sukinda is a well-known chromium contaminated site and hence it is the ideal source for chromium tolerant fungi. There are notable indigenous fungal strain that can show tolerance to varieties of heavy metals. Filamentous fungi like *Asperigillus*, *Penicillium*, *Rhizopus*, *Tricoderma* and *Fusarium* have been reported showing tolerance to heavy metals.

### Fungal bioremediation Mechanism

Fungi can interact with different metals depending on the metal type, environmental condition and type of organisms. Possible mechanism of fungal bioremediation may include extracellular remediation or intracellular remediation. Extracellular remediation otherwise called biosorption and the intracellular remediation is called bioaccumulation. In biosorption the outer layer of cells acts as a chelating agent to bind the hexavalent chromium whereas in bioaccumulation it is uptake inside to the cell allowing reduction to the trivalent form. The aim of biosorption to prevent the chromium inside the cell whereas bioaccumulation aims to reduce the hexavalent chromium concentration inside the cell. Fungal cell wall may be the responsible bioremediating organ that chelate Cr (VI). The proteins and the peptides present on cell wall acts as chelating agent to bind chromium. In yeast it was evident that glutathione binds the hexavalent chromium, whereas it was suggested that presence of other pigment like melanin and other polymorphic materials are helping in binding the hexavalent chromium. Some FTIR report confirms that biosorption occur in the presence of functional group like Carboxyl, Amine and Hydroxyl that presumes to help in biosorption (Kumar *et al.*, 2021). Biosorption can also be performed in dead fungal biomass (Akhtar *et al.*, 2020). There are also other External environmental factors can affect the biosorption capacity. Factors like Biomass, Initial concentration (Kavita *et al.*, 2011), contact of time and Temperature (Sarkar *et*

*al.*, 2013) may disturb the biosorption capacity. The Bioaccumulation reductions have not been studied in brief. There are a number of channels through which the hexavalent chromium can enter into the cell. It can actively be transported into the body through sulphate ion channel as it has structural similarity with sulphate ion (Zhio *et al.*, 2009). As bioaccumulation can successfully observed in fungi like *Asperigillus* and *Fusarium*, its mechanism and potential need to be discovered.

### Conclusion

- Antagonistic activities of hexavalent chromium are accelerating in speed since 1990 in Sukinda area, has a serious implication on the flora and fauna. So our first priority is to regulate the environment in such a manner that its outbreak should be limited in that particular area for that a frequent surveys and continuous monitoring is essential.
- Scientists should encourage the bioremediation protocols and removal of hexavalent chromium without producing any secondary pollutants. Current situation of Sukinda reviews explains that the bioremediation is capable to fulfill the needs for detoxification. It is an attractive option to clean, manage and remediate the hexavalent chromium contamination through microbial activity.
- Recent bioremediation research activity mainly focuses on the bacterial and plant based remediation processes whereas fungi are the natural pollution cleaning agents. So scientists need to change their vision other than bacteria and plants.
- Again, the over qualifying properties of fungi makes it a perfect bioremediation tool for Sukinda. Novel species of fungi family should be explored by which the speed of remediation can be elevated with great potential. Presently an increase in fungal research has been noticed, but only a few are towards their destination.
- Again now a days, the use of biotechnology is at its peak, so exploration and editing in fungal genes using biotechnological tools is essential to constitute a better promising candidate for removal of chromium toxicity.
- Although the speed of remediation depends on the environmental condition that may not favor to the

organisms to Sukinda again while working with microorganisms there is a risk of infection or mutation whose results can't be ignored. Bioremediation has been accepted and used in different corner of world.

- The diversified characteristics of fungal species incorporated with biotechnological techniques can be applied as an improved tool for bioremediation against chromium toxicity after further investigation.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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