



## **Effect of chromium generated by solid waste of tannery and microbial degradation of chromium to reduce its toxicity: A review**

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### **ABSTRACT**

*Leather industries releases large amount of wastes which are in solid and liquid form. One of the likely solid wastes produced as of leather industry is chrome-tanned leather shavings(CTLS) hides, etc. Wastes releases from tannery industries contain major toxicity of chromium which releases into the environment directly or indirectly. Chromium (Cr) into the environment creates unfavorable outcomes by altering the normal physiochemical properties of soil and water. It is determined that Chromium is the principle threat of tannery industry. Cr is extremely venomous and carcinogenic to humans, animals, vegetation and as well as overall environment. Effective management of tannery waste is the necessity of the time. Although lot of alternative treatments were assessed to reduce the toxic effect of Cr on environment but none of them forced out Cr completely. In some cases researchers however successful enough working biotechnological methods to reduce the toxic effect of chromium (Cr VI). Hence treatments are either complex, expensive or not applicable worldwide due to proficient work force environment. Consequently, to tackle these challenges demanding environmental ordinance which can be practiced and approved widely over the world. This problem can be overcome by microbial degradation process which uses plants like hyper-accumulators, microbes for the treatment of contaminants. Though, it is time consuming this helps in complete restoration and pollution free process.*

**Keywords:** Leather Industry. Solid waste, microbes, environment.

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### **INTRODUCTION**

Environment is getting fragile and environmental pollution is one of the disagreeable side effects of industrialization, urbanization, population growth and irrational approach towards the environment. Wastes produced from industries are generated from different processes and the quantities, features of produced effluent and wastes vary from industry to industry depending upon the raw material used, water consumption and average daily production [1]. The mutual problems associated with unauthorized management and discarding of wastes include infections, disease transmission, soil and water pollution[2]. Due to industrial expansion, large amounts of industrial wastes are gathering in environment and cannot be disposed without prior special treatments. Due to industrial enlargement, enormous amounts of industrial wastes are gathering in environment and can't be disposed while not previous special treatments[3]. In specific, waste products from the mining, tanneries and metal refining industries, sewage sledges, etc contain heavy metals at high concentrations. Generally, these heavy metals can be leaked from the soil to the surface water system[4, 5] at concentrations higher beyond acceptance (CEC, 1986).Environmental pollution from heavy metals and minerals can arise from natural as well as anthropogenic sources.

Natural sources are: seepage from rocks into water, volcanic activity, forest fires etc. In anthropogenic activity the pollution occurs both at the level of industrial production as well as end use of the products and run-off[6]. From the research conducted by Blacksmith Institute, it estimates that close to 125 million people are at risk from industrial pollution worldwide.

The chief hazardous metals which are of great concern for India in terms of their environmental load and health effects are lead, mercury, chromium, cadmium, copper and aluminium.

These metals exist in soil leads to severe threat and needs to be treated. Data of Central pollution control board (CPCB) display that Maharashtra, Gujarat and Andhra Pradesh subsidize to 80% of hazardous waste in India (Press information Bureau, Govt. of IndiaPib.nic.in/release/9.11.2011).

Waste disposal into the environment generates adverse effects by changing the normal physicochemical properties of soil and water[5]. However several conventional physicochemical methods are currently being practiced but biological methods are better alternatives, because they are economical as well as eco-friendly.

Naturally chromium occurs in various oxidation states, but Cr (III) and Cr (VI) are of remarkable worry biologically. Chromium is a necessary metal that is involved in the metabolism of glucose in humans and animals, but its hexavalent form is very toxic and carcinogenic[7]. Demand for Cr(VI) is increasing day by day due to its extensive use in numerous industrial and chemical processes such as film and photography, galvanometric and electrical procedures, metal cleaning, plating and electroplating, leather, and mining[8]. These industrial processes produce toxic waste in a large amount that contains hexavalent chromium with concentrations ranging from tens to hundreds of milligrams per liter along with other forms of chromium [9]. Hexavalent chromium is often found in soil and ground water due to its wide spread industrial use in several process industries [10], such as tannery, electroplating, steel industries etc. Cr(VI) are highly toxic[11] pollutant even at very low concentration[12, 13]. As many aerobic and anaerobic microorganisms are capable of reducing Cr(VI) to Cr(III), bioremediation may play an important role for the detoxification from Cr (VI) even at very low (ppm or ppb) level. It has already been reported that because of the presence of some enzymes called chromium reductases [14], completely different microorganisms belonging particularly to the genus, *Pseudomonas* can reduce Cr(VI) to Cr(III). The reduction of transformation capacity of Cr(VI) by microorganisms at higher initial concentration of Cr(VI) has been observed by other researchers [15] and the phenomenon has been explained by the presence of inhibitory effect of Cr(VI) at high concentration level [16].

## **2. Tannery wastes and chromium contamination:**

In tannery industries tanning are performed by two methods, Vegetable tanning and Mineral tanning. Vegetable tanning uses tannin (a class of polyphenol astringent chemical) which are present naturally in the bark and leaves of many plants. Mineral tanning usually uses chromium in the form of basic chromium sulfate. Chrome tanning is faster than vegetable tanning (less than a day for this part of the process) and produces a stretchable leather which is excellent for use in handbags and garments.

Chromium-based tanning process is predominantly followed worldwide[17, 18]Leather industry produces chromium-based waste both in liquid and solid form such as chromium sludge, chrome-tanned leather shavings (CTLSS), and chrome leather trimmings. These wastes are unavoidable due to adaptability of chromium, and possess a serious threat to the environment. It has been estimated that 0.02 million tons of chromium shaving is generated in India per annum. Nearly, 0.8 million tons of CTLSS could be generated per year globally [19]. Among heavy metals presents in tannery waste, Chromium is one of the most common pollutant. Chromium is found in several oxidation states ranging from -2 to +6, among which chromium (IV) and chromium (III) are the most significant as of their persistence and stability. Chromium (VI) catches its place in the priority list arranged by the Agency of Toxic Substances and Diseases Registry (ATSDR). Chromium compounds can cause mutation and cancer, and hinder enzymes and nucleic acid synthesis. In comparison, chromium (III) is less toxic and less mobile[20] than Cr (VI).Cr(VI)penetrate cells 1000 times more than Cr(III).Chromium contamination of the environment is of concern because of the mobility and toxicity of Cr (VI). Trivalent and hexavalent chromium differ widely in physicochemical properties and biological reactivity. While Cr (VI) species and dichromate's are extremely water-soluble and mobile in the environment.

### 3. Chromium toxicity:

Industries like electro plating, metallic cleansing and dyeing processing, cement, and leather tanning industries are the major source and play role in discharging chromium into the environment. Hexavalent chromium is the main chromium species used in industrial processes, including manufacturing of metallic alloys (the most important use of Cr), chrome leather tanning, metal cleaning processing, electronics and wood preservation and so on, and is therefore the most common pollutant in a wide variety of industrial wastes [15]. Cr in the hexavalent phase (Cr-VI) is more toxic than in trivalent state (Cr-III). Moreover, Cr (VI) is recognized to be highly toxic, mutagenic and carcinogenic for mammals including humans whereas Cr (III) is an essential trace element which is required for lipid, glucose and amino-acid metabolism as well as a general dietary supplement. Studies have revealed that Cr (VI) is approximately 100 times more toxic and 1000 times more mutagenic than Cr (III). Chronic inhalation of hexavalent chromium compounds increases risk of lung cancer. The accumulated chromium in soil can also be reason of acute and long term toxic effects on soil ecosystems. Non occupational exposure to the metal happens via the ingestion of chromium-containing food and water, while occupational exposure arises via inhalation [21]. Humans and animals confine chromium in the liver, lung, spleen, kidney, bone marrow, and red blood cells (RBC) (ATSDR, 1989). The central paths for the excretion of chromium are via the kidneys/urine and the feces/bile [21]. Cr VI i.e. Hexavalent chromium compounds are genotoxic carcinogens in nature. Inhalation of hexavalent chromium compounds increases risk of lung cancer (lungs are especially susceptible, tracked by fine capillaries in kidneys and intestine). It's quite challenging that polluted arena by industrial wastewater exhibit a mobilization ratio of less than 5 (possibly poisonous) for selected plant species. The deployment ratios for weeds turn out to be greater than 5 (Fig. 1), which shows healthy morphology in the early flowering stage [5]. The work done by Marchese and his coworkers [22] about accumulation of Chromium in four fresh water clams, crabs, plant species and fishes showed that, all the four fresh water species and animals were found with high concentration of Chromium which means there is well-known accumulation occur. The release of heavy metal poses large threat to the environment and public health because of their toxic nature, bio-accumulation within the organic phenomenon and persistence in nature (Ceribasi and yetis, 2001).

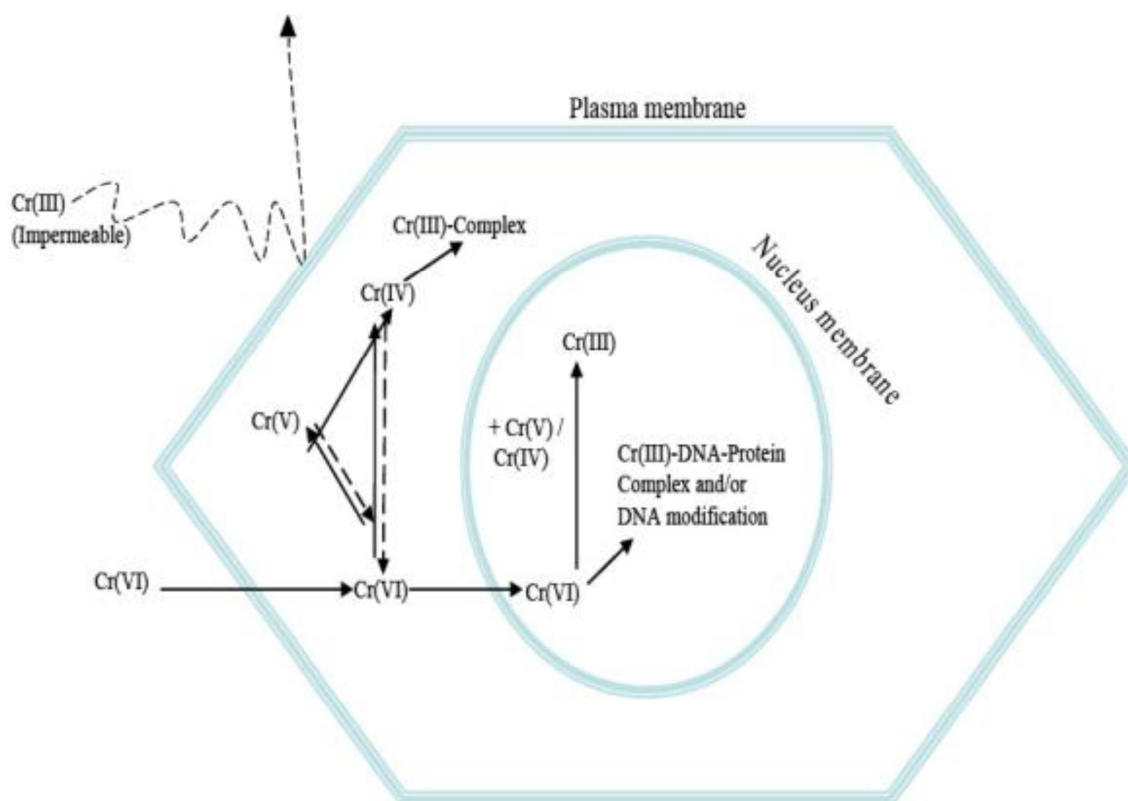


Fig 1: Schematic diagram of the toxicity and mutagenicity of Cr (VI) (Cheung *et al.*, 2007)

#### 4. Effect of Chromium on environment:

Chromium (Cr) is the topmost heavy metal contaminant found in the tannery effluent occupying 40% of the total industrial use. Cr used by the leather industry to tan hides is not used completely by leather and comparatively large amounts outflows into the effluent[23]. Cr (VI) negatively affects the environment due to its eminent solubility, mobility and responsiveness. Soils and groundwater surrounds are utmost affected by Cr (VI) pollution from spills, unlawful disposition and unguarded stock piles of new techniques chromium products. Though Cr (III) is an essential nutrient for human beings but there is no conflict that Cr (VI) compounds are more poisonous than Cr (III). Generally the effluents are extremely complex mixtures comprising of both inorganic and organic compounds that make the tanning industry possibly a pollution-intensive sphere [24]. [3] examined the total of amalgams in the monetarily considerable products and vegetables watered with tannery effluent. They've accounted that the collection of metal from soil to plant structure won't consent any particular model and veered with connection to metal, species and plant structure. In India, about 2000–32,000 tons of elemental Cr annually escapes into the environment from tanning industries. Tamil Nadu is a leading finished leather producer in India. Tamil Nadu which was considered as one of the “Critically polluted area”[6]. The contamination doubts are amplified by the under mentioned attributes of Cr (VI):

- Cr (VI) is extremely dissolvable and mobile in water. These consequences in eminent consumption rate in animal and plant cells.
- Cr (VI) is extremely available to live organisms through multiple paths of entrance such as consumption, epidermal adjoin, breathing in, and absorption (in the case of plants and root ages).
- Cr(VI) shortens seed sprouting of plants [25]. This is suspected to be due to root dalliances.
- Other analysis suggested retardation of development photosynthesis and enzyme actions in algae due to the bearing of Cr (VI) at concentration as low as 10 ppm [5, 26, 27].

#### 5. Microbial reduction of Chromium:

Chemical methods are often available for elimination of chromium in majority from industrial effluent but they often fail to meet the environmental regulations. In chemical treatment very harmful chemicals are discharged which are toxic as well as harmful to environment. So microbial treatment of CTLS may be better alternative in comparison with chemical treatment for this purpose as the chemical agents add to the environmental pollution. Microbial treatment involves all kinds of microbes like bacteria, fungus, etc. Study have conveyed potential of some species of bacteria like *Pseudomonas*, *Bacillus* and *Arthrobacter* for reducing the level of chromium[28, 29]. In polluted sites, chromium obtainability is influenced by processes like complex formation, oxidation-reduction, precipitation, which in turn depend on microbial activities. Though, exposure to chromium for a long time can reduce microbial diversity, population and activity. Many bacterial species surviving in presence of chromium for years in contaminated sites are found to be highly resistant to chromium and are measured as important for removal of chromium[30]. The current study tries to check the potential of a strain of *Bacillus subtilis* isolated from East Calcutta Wetlands for biological treatment of chromium (VI). Chromium (VI) is virulent to biological systems due to its strong oxidizing potential that causes harm cells [31]. However, some microorganisms within the presence or absence of oxygen will reduce the toxic form of Cr (VI) to its trivalent form [32]. These microorganisms are identified as chromium reducing bacteria (CRB). It was demonstrated that among CRB, gram-positive CRB are significantly tolerant to Cr (VI) toxicity at relatively high concentration, whereas gram-negative CRB are more sensitive to Cr (VI) (Coleman, 1988). Initially, researchers targeted on facultative microorganisms such as, *Pseudomonas dechromaticans*, *Aeromonas dechromotica*. A series of other diverse microorganisms were later isolated including sulfate-reducing bacteria (SRB) such as *Desulfovibrio vulgaris*[5] and Fe(III) reducing bacteria such as and *Thiobacillus ferrooxidans* [33].

#### 6. Biological degradation of chromium:

Unlike organic contaminants, the metals cannot be ruined, but can be converted to a stable form or removed. The process of using microorganisms to degrade or remove hazardous pollutants from the environment is known as biodegradation or biological degradation. Even though Cr (VI) can be reduced by algae or plants, in soil microorganism has been confirmed to be most effective[10, 32, 34]. The biological processes are highly specific with culture requirements and at time are difficult to extrapolate the results from lab to field. It also often takes longer time than other treatment such as excavation and removal of soil. There are numerous factors affecting the method of bioremediation such as depletion of preferential substrates, lack of nutrients, toxicity and solubility of contaminants, chemical reaction or reduction potential and microbial interaction (Fig. 2).

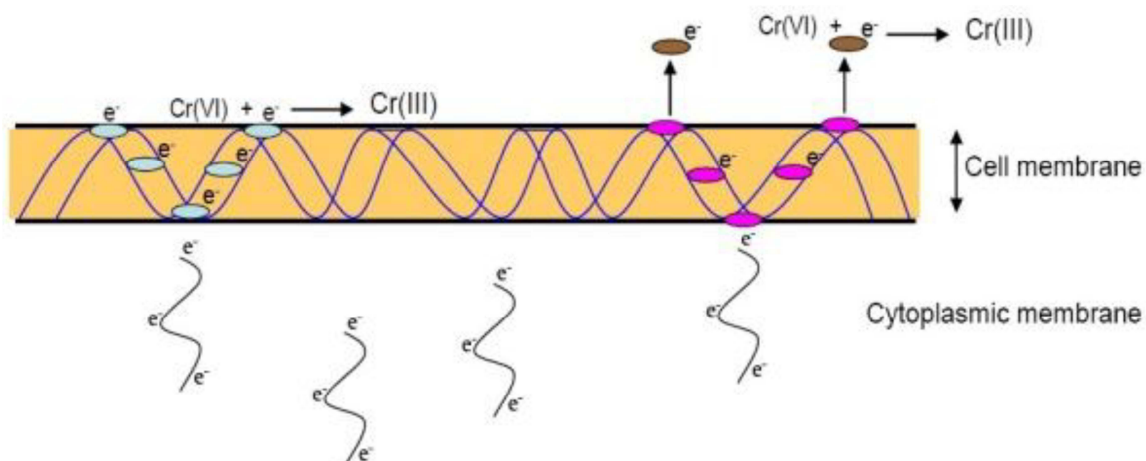


Fig 2:Cr (VI) reduction in respiratory chain involving trans membrane protein[35]

Mechanisms by which microorganisms act on heavy metals include bio sorption (metal sorption to cell surface by physicochemical mechanisms), bioleaching (heavy metal mobilization through the excretion of organic acids or methylation reactions), bio-mineralization (heavy metal immobilization through the formation of insoluble sulfides, etc), accumulation inside cell, and enzyme-catalyzed reactions (redox reactions)[36]. The major microbial processes that influence the degradation of metals are summarized in Fig 3.

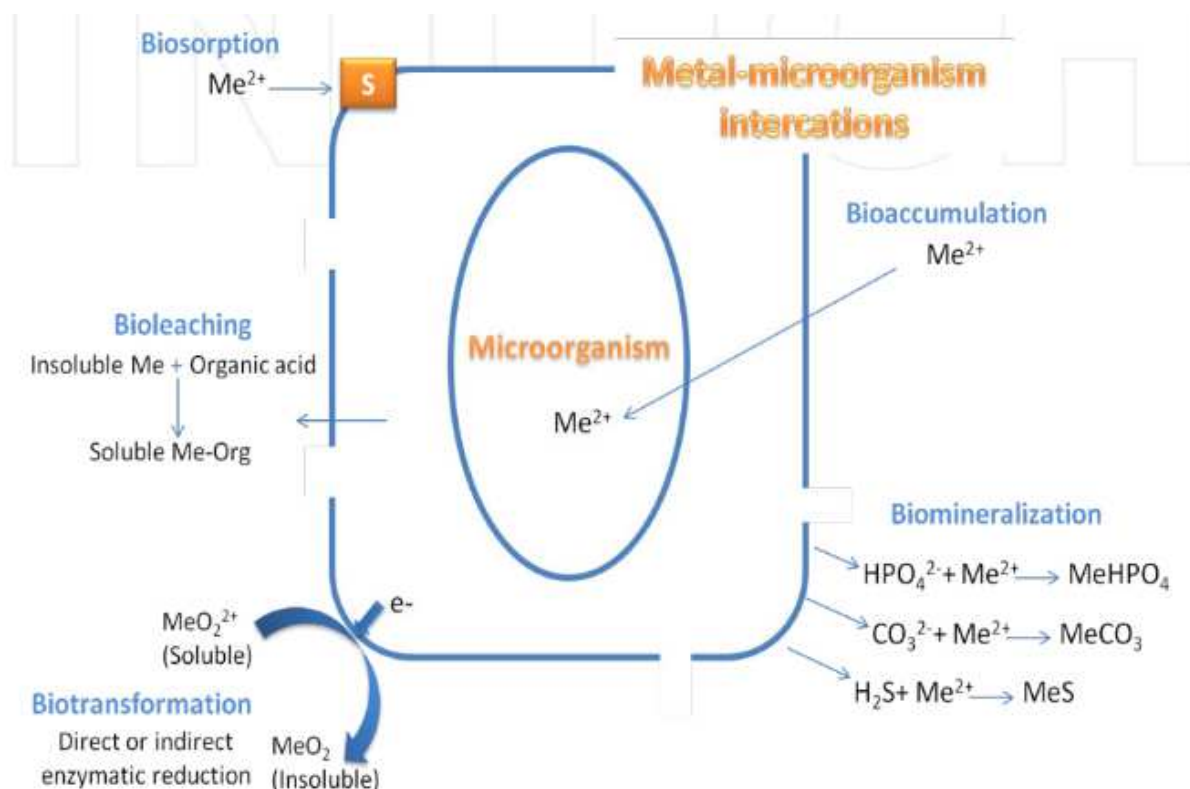


Fig 3: Microbial processes used in bioremediation technologies modified from Lloyd and Lovley

### 6.1. Bacterial degradation of chromium:

Hexavalent Chromium is toxic to bacteria that are existing in the contaminated soil or waste water. The bacterial species are capable to nurture in the toxic conditions and are commonly supposed to be tolerant/resistant to chromium[30, 37]. *Pseudomonas sp.* was the first hexavalent chromium to be recognized from waste water.



Resistance is explained as the capability of a microorganism to persist toxic effects of metal exposure by means of a detoxification mechanism formed in direct response to the metal species concerned. Tolerance is explained as “the capability of a microorganism to endure metal toxicity by means of intrinsic properties and or environmental modification of toxicity[38]. Bacterial strain that are isolated from electroplating industry displayed higher reduction rate paralleled with the procured one[39]. *Bacillus coagulans* isolated from electroplating industry was capable of reducing Cr (VI) by using soluble enzyme and using malate as external electron donor. The biological reduction of Cr (VI) was found similar to sulfate reduction process. Thus we can say that bacteria which are isolated from highly chromium contaminated soil are helpful in reducing the chromium level[40].The bio-degradative pathways have also been reported in bacteria from the genera *Corynebacterium*, *Mycobacterium*, *Aeromonas* and *Bacillus*[41]. Although many bacteria are able to metabolize various organic pollutants, a single bacterium does not hold the enzymatic capability to degrade all or even most of the organic compounds in a polluted soil. Mixed microbial populations have maximum powerful bio-degradative potential because the genetic information of more than one organism is necessary to degrade the complex mixtures of organic compounds present in contaminated areas[42].Microorganisms have developed the capabilities to protect themselves from heavy metal toxicity by various mechanisms, such as adsorption, methylation, oxidation and reduction. Reduction of metals can occur through dissimilarly metal reduction [42], where bacteria utilize metals as terminal electron acceptors for anaerobic respiration. Along with this, bacteria may having reduction mechanisms that are not attached to respiration, but in its place are supposed to be metal resistance. For example, reduction of Cr(VI) to Cr(III) under aerobic [43] or anaerobic conditions [44].

### 6.2. Fungal degradation of chromium:

Fungus behave as bio-absorptive material to eliminate hexavalent chromium. Bio-sorption mechanism is done by two methods- metabolism dependent and non-metabolism dependent. The chemicals get attach to the functional groups on the surface and get absorbed. Several fungus can be treated as a natural bio-sorbents to absorb hexavalent chromium in environment. Bio-sorption of the chromium ion Cr (VI) from the cell surface of *Trichoderma* fungal[45]species in aerobic condition was investigated. The extreme efficiency of 97.39% was found at 5.5pH. The results of FT-IR analysis proposed that the chromium binding sites on the fungal cell surface were most likely carboxyl and amine groups. The absorption isotherm calculated fit to Freundlich models.

Fungi are an important part of degrading microbes because, like bacteria, they are able to metabolize organic matter; they are principal organisms responsible for the decomposition of carbon in the environment. Unlike bacteria, fungi can grow in low moisture areas and in low pH, which helps them in the breaking of organic matter. Equipped with extracellular multi-enzyme complexes, fungi are most efficient, especially in breaking down the natural polymeric compounds. By means of their hyphal systems they are also able to colonize and penetrate substrates rapidly and to transport and redistribute nutrients[42]. The attributes that distinguish filamentous fungi from other life forms determine why they are good biodegrades. First, the mycelial growth habit gives a competitive advantage over single cells such as bacteria and yeasts, especially with respect to the colonization of insoluble substrates.

### 6.3. Yeast degradation:

Yeasts are known for playing an important role in the removal of heavy metals which are toxic. There are many information on bio sorption of heavy metals by yeasts. In the case of hexavalent chromium (Cr(VI)) we found that *P. anomala* is able to remove Cr(VI)[46].The capability of yeast to reduce hexavalent chromium was considered. The in vitro decrease of hexavalent chromium using Crude Chromate Reductase (CChR) of *Pichia jadinii* M9 and *Pichia anomala* M10, isolated from a textile-dye factory effluent[47].

## CONCLUSION

Microbial activities are very essential for the renewal of our environment and maintenance of the global cycle. These happenings are included in the term biodegradation. Among the substances that can be degraded or transformed by microorganisms are a huge number of synthetic compounds and other chemicals having ecotoxicological effects like hydrocarbons and heavy metals.

Microorganisms might be considered excellent pollutant removal tools in water, soil and sediments, generally due to their benefit over other bioremediation procedures. Biodegradation represents a highly profitable process, but still affordable tool of removing pollutants, hence a very feasible process to be applied. The capacity of a microbial population to degrade pollutants can be enhanced also by stimulation of the indigenous microorganisms by addition

of nutrients. The ever increasing concern about the getting worse of the environmental condition could be a driving force to evaluate and remediate pollutant from the ecosystem. Chromium is very virulent to human wellness, beasts and the environment (land, water system, deposits plants and so on). There are some species of microbes which are able to decrease or we can say that remove the chromium content up to 90%. The strain of *Bacillus subtilis* isolated from East Calcutta Wetlands removed chromium from growth medium under laboratory condition up to 90%. Thus by treating with microbes we can reduce the chromium level as well as this process does not involve any kind of chemicals thus this study shows that the biological treatment helps in full reduction or removal of hexavalent chromium in the environment.

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