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Toxicity of Chromium and its Green Remedies

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Abstract- Chromium pollution is concerned as a major environmental issue due to its wide use in different sectors. It has received special attention because chromium is known to be toxic to human, animals and plants. Chromium toxicity depends on its two valance state one is Cr (III) and another one is Cr (VI). Cr (VI) is highly toxic and mobile where Cr (III) less toxic. The purpose of this study was to assess the toxicity of chromium compounds on the ecosystem and how to take steps for the remediation of chromium by using green plant which one is ecofriendly and cost-effective.

Keywords- Chromium, remediation, ecofriendly.

1. INTRODUCTION

Heavy metals in the environment originate from two sources; one is human activity and the other concerned with the natural circulation of the metals throughout nature. The reason of environmental pollution is not merely due to the presence of the metals themselves, but when their natural concentrations have been exceeded. The problem of chromium contamination in the environment is seriously ecological due to their bioaccumulation can enter food chains and the biological cycle. Due to anthropogenic activities, the elevated level of heavy metals which exist in nature represents serious environmental, ecological as well as financial issues [1]. Human and animals directly depends upon plants for their survival but plants are affected by number of natural phenomenon. The environmental factor affects plants productivity and among them heavy metal plays a major role. Animals and plants including humans are eventually affected by heavy metals [2, 3]. But certain metals such as iron, copper, zinc are considered as essential nutrients to plants. For the growth and development of plants chromium acts as a toxic agent among the heavy metals [4].

2. WHAT IS CHROMIUM?

In the Earth's mantle, Chromium is the 17th most abundant element. It is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases. Chromium is found in several different forms including trivalent chromium and hexavalent chromium. Chromium is one of the most toxic heavy metals and is discharged into the environment through various human activities. Extensive use of Cr in industry as plating, alloying and tanning of animal hides, inhibition of water corrosion, textile dyes and mordant, pigments, ceramic glazes, refractory bricks and pressure-treated lumber [5] results in discharge of chromium containing effluents. The consequent environmental contamination increased due to the wide anthropogenic use of Cr, and has become an increasing concern [6]. Heavy metals such as chromium are not destroyed by degradation and are therefore accumulating in the environment. The World Health Organization [7] has notified the toxic threats of chromium (Cr^{+6}) and has listed it as a human carcinogen [8]. Cr^{+6} are a threat due to its toxicity at low concentrations [9] among the toxic metal ions.

Chromium exhibits a range of oxidation states such Cr (0), Cr (III), Cr (VI) which have different toxicities and transport characteristic [10]. Out of which there are two stable forms, i.e., trivalent chromium or Cr (III) and hexavalent chromium or Cr (VI). Hexavalent chromium (Cr^{+6}) is the most toxic form of Cr. Trivalent chromium (Cr^{+3}) is referred as Chromium (III) and is considered to be an essential nutrient for the body. Generally hexavalent chromium is produced by industrial process which is a form of the metallic element chromium. Cr^{+6} is not only more toxic than Cr^{+3}, the latter form of element is also act as a essential trace element connected glucose tolerance factor [11].

3. USES OF CHROMIUM

Chromium compounds, such as hexavalent chromium are well known as laboratory reagents and as manufacturing intermediates. Major industries using chromium are the metallurgical, chemical and refractory brick industries. Widely hexavalent chromium, are used in electroplating, stainless steel production, leather tanning, textile manufacturing, and in wood preservation [12]. In the environment some other important anthropogenic sources of chromium are fuel combustion, cement production and sewage incineration/deposition [13]. One of the world's leading producers of chromium compound is the United States.

4. TOXICITY OF CHROMIUM

4.1. *Chromium as an environmental contaminant*

Chromium exist in the environment as trivalent and hexavalent, out of which hexavalent chromium is a carcinogen and a potential soil, surface water and ground water contaminant, while trivalent chromium is much less toxic, insoluble and a vital nutrient for humans. Cr (III) occurs naturally in the environment and is an essential nutrient required by the human body [14]. Cr ranges from 10-50 mg kg^{-1} in naturally occurring soil. In fresh water, the concentration of chromium is 0.1-117 µg L^{-1}, whereas 0.2 to 50 µg L^{-1} in sea water. The occurrence of chromium in soils is generally dependent on its content in bedrock. The average range of chromium concentrations is 7-150 mg kg^{-1}, is generally as follows for the following types of soils: sandy, 30 ppm; clay, 40 ppm; limestone soil, 83mg kg^{-1}. The natural range of chromium in the atmosphere is from 0.01-1 mg m^{-3}. This element occurs in various concentrations of from 0.01 in unpolluted areas

There are multifarious industrial uses of Cr and its compounds. Chromium play an important role in leather processing and finishing [15], in the production of refractory steel, drilling muds, electroplating cleaning agents, catalytic manufacture and in the production of chromic acid and specialty chemicals. In industry hexavalent chromium compounds are used for metal plating, cooling tower water treatment, hide tanning and, until recently, wood preservation. These anthropogenic activities have led to the wide spread contamination that Cr shows in the environment and have increased its bioavailability and biomobility. Number of worker has published detailed review on the critical assessment of Cr in the environment [16, 17]. The leather industry is the major cause for the high influx of Cr to the biosphere, accounting for 40% of the total industrial use [18]. From tanning industries about 2000–32,000 tons of elemental Cr annually escapes into the environment. Even if the recommended limit for Cr concentration in water are set differently for Cr (III) (8 µg L^{-1}) and Cr (VI) (1 µg L^{-1}), it ranges from 2 to 5 g/L in the effluents of these industries [19]. In the United States, 14.6 g L^{-1} in ground water and 25.9 g. kg^{-1} in soil have been found in the vicinity of chrome production sites [6].

4.2. *Effect of Cr on human health*

Chromium as a heavy metal is ranked among the top sixteen toxic pollutants which have harmful effects on human health [20]. Chromium-III and VI are accumulated in human tissues. Chromium-VI has greater ability to enter cells and its strong oxidation potential than Cr-III so Cr-VI is more toxic than Cr-III. It has been reported that human kidney and liver are damaged due to high chromium dosage [21] and in low doses it cause skin irritation and ulceration [22]. Once inside cells, Cr-VI is reduced and produces free radicals, Cr-V, Cr-IV and eventually Cr-III, which are believed to be responsible for toxic and carcinogenic effects. Cancer in the digestive tract and lungs also occur in high chromium concentration. Many studies identified that 10 ppm Cr-VI as the threshold at which no more than 10% of exposed individuals developed skin sensitization where the same threshold was 500 ppm for Cr-III. Health effects observed in a human population chronically exposed to approximately 20,000 µg L^{-1} Cr-VI/L in drinking water contaminated by a ferrochrome plant included mouth sores, diarrhea, stomach pains, indigestion, vomiting, and higher levels of white blood cells than the reference population. Environmental Protection Agency has concluded that the only chromium (VI) should classify as a human carcinogen [23, 24]. Exposure to chromium (VI) may result in complications during pregnancy and child birth.

4.3. *Effect of Cr on aquatic ecosystem*

Cr^{+6} are the more toxic to fresh water biota in comparatively soft and acidic waters. Chromium toxicity to aquatic biota is significantly influenced by abiotic variables such as hardness, temperature, pH, and salinity of water; and biological factors such as species, life stage, and potential differences in sensitivities of local populations. In aquatic ecosystems chromium is known to bioaccumulate in algae, aquatic plants, invertebrates and fish [25, 26]. Species, organism size, sex and developmental stage of aquatic ecosystem influenced the uptake, accumulation and effects of chromium. There is little information on chromium uptake and effects in freshwater species found by some researcher [25]. At low concentrations of hexavalent chromium (parts per billion and parts per million) observed toxic effects are reduced growth and photosynthesis in algae and aquatic plants; and lethal toxicity, behavior changes and decreased growth, reproduction and survival in invertebrates. Freshwater fish can regulate different range of ambient concentrations of chromium. When fish are exposed to hexavalent chromium there are some changes in physical and bio-chemical conditions, increased hatching time, DNA damage and reduced survival but it seems that chromium-III is more toxic to fish than chromium-VI. Chromium-III decreases reproductive success, deposits on the gills and can cause death at relatively low doses where as chromium-VI does not deposit on gills but enters the fish body and affects internal organs such as the liver and kidney [27].

4.4. *Effect of Cr on animals*

Acute and chronic adverse effects of chromium to warm-blooded organisms are caused mainly by Cr^{+6} compounds. The effects of chromium observed on animals in experimental doses through food, water or injection include: cancers, reproductive harm, behavioral changes, reduced growth and survival. Metallic Cr and Cr^{+3} are non-toxic [28], whereas compounds of Cr^{+6} are dangerous to animals. However, workers are exposed to water solubilized Cr^{+3} that cause cancer as well as dermatitis and toxicity found in rabbits also [29]. There are many laboratory studies to analyzed chromium toxicity to animals, but very few field studies were conducted to study the effects of environmental chromium pollution on wildlife.

4.5. *Effect of Cr on plants*

Plants can accumulate Cr-III and VI and deposited on leaves from soil, sediment, water and atmosphere. Exposure to excess Cr-III or VI can negatively affect plant health and survival. When plants exposed to excess chromium, toxic effects are: reduced growth, decreased chlorophyll production causing yellow leaves, narrow leaves, small root systems, decreased or complete inhibition of seed germination, delayed growth, decreased seed yield, wilting and death [30, 6]. Excess chromium damages root membranes and a plant's ability to take up water. It also alters uptake and translocation of essential elements such as nitrogen, iron, potassium, magnesium, manganese, phosphorous, calcium, sulphur, copper and zinc [6, 30]. This is not only affecting plant health but a change occurs in plant nutrition which affect wildlife as well as human health. Sensitivity and effects vary between species, making toxicity predictions difficult without extensive plant studies. When plants uptake chromium the amount of chromium varies among species due to differences in absorption, transportation and storage of metals [31]. In most studies it is found that plants majority of chromium store in their roots, translocation to all other parts of a plant does occur in proportions that vary across plant species. There are many studies which show that low plant ability to transport chromium from roots to other plant parts but some studies also stated chromium concentrated greater amount in leaves than in roots [30].

5. REMEDIES OF CHROMIUM AND PHYTOREMEDIATION

Review shows a few workers who reported the toxicity of Cr in crop plants, because most of the research has been focused on phytoaccumulation of Cr by plants for its use in phytoremediation. There are several species that have ability to accumulate over 1000 mg Cr/kg in their above ground parts have been identified and are classified as hyperaccumulators. Khan (2001) [32] reported the potential of mycorrhizae in protecting tree species *Populus euroamericana*, *Acacia arabica* and *Dalbergia sisso* against the harmful effects of heavy metal and phytoremediation of Cr contamination in tannery effluent-polluted soils. In a study it is confirmed that Cr was poorly taken up into the aerial tissues in temperate trees but was held predominantly in the root [33]. These findings mean that the prospects for using trees as phytoremediators on Cr-contaminated sites are low, their main value being to stabilize and monitor a site [34]. This has suggested to research with the prospects of increasing Cr translocation by adding chemical and biological amendments to soil. Srivastava et al. (1999b) [35] found that increasing concentrations of organic acids resulted in increased uptake of Cr without affecting the distribution in plant parts. Source-to plant transfer coefficients of Cr tended to increase with increasing concentrations of organic acids in wheat.

5.1. *Phytoremediation*

Phytoremediation is a technology which is used to remove pollutants from the environment through green plants. The term phytoremediation contents the Greek prefix phyto (plant), attached to the latin root remedium (to remove an evil). This technique is cost effective approach for removal of heavy metals from soil and ground water [36]. It is best applied at shallow contamination sites of organic, nutrient or metal. Phytoremediation technique can be success when there is much availability of plant species- mainly those native to the region of the interest which are able to tolerate and accumulate high concentration of heavy metals [37]. For the phytoremediation technology the major hurdle is poor translocation of Cr from roots to shoots in using plants and trees. In this article phytoremediation technology deals with the problem of chromium toxicity which has been shown that if chromate is reduced to chromic oxide by chemical or biological methods, the inertness and insolubility of chromic oxides in soil limited the formation of chromate and reduced environmental risk [38]. Mycorrhizae and organic acids (citric and oxalic acid) have been reported to play an important role in phytoremediation of Cr-contaminated soils by enhancing Cr uptake and increasing translocation to shoot [39, 40]. There are several techniques like chemical, physical and biological for metal contaminated soil but phytoremediation is the most appropriate technique which may be determined by studding the particular category of contamination. Remediation of metal contaminated soil can be grouped into two type's i.e. in situ method and ex situ method [41, 42].

5.1.1. *In situ Methods*

Remediation occurs without excavation of a contaminated site according to this method. *In situ* method defined as transformation or destruction of the contamination, immobilization to reduce bioavailability and separation of the contaminant from the bulk soil [43]. *In situ* methods are cheaper and effective in reducing ecological impacts. This technique can be applied to both organic pollutants as well as inorganic pollutants that are found in soil, water and air. The technique involves the ability of plants to absorb and concentrate elements of heavy metals from contaminated environmental media.

5.1.2. *Ex situ Method*

This method is used for the removal of contaminated soil for treatment either on or off site, and then returning the treated soil to the restored site. This type of treatments may either destroy or may result in the contaminant being immobilized or otherwise solidified. The *ex situ* technique is to excavate heavy metal contaminated soil and then rebury it at a landfill site [44, 45].

In phytoremediation pollutants that are amenable to one of the five applications; phytodetoxification, rhizosfiltration, phytostabilization, phytoextraction and phytovolatilization.

5.1.3. *Phytodetoxification*

This process is an *in situ* method, which involves detoxification of heavy metals through plant based chelation, oxidation and reduction mechanism. Several species of algae have been used in the reduction of Cr (VI) to Cr (V) and also to Cr (III). Metal chelators like EDTA, organic acid, DTPA and glycine are useful for removal of heavy metals [46].

5.1.4. *Rhizofiltration*

This process can remove contaminants from flowing water and aqueous waste streams through extensive root system of plants. This can be used in both *in situ* and *ex-situ* application and also with non–hyperaccumulator plant species. Several plants have the ability to remove contaminants through rhizofiltration e.g. duckweed.

5.1.5. *Phytostabilization*

This the process in which plants are used to transform soil metals to less toxic forms, without removing metal from soil. Phytostabilization mainly used in remediation of soil, sediments, sludge and depend upon plant roots. This technique can occur through sorption, precipitation or metal valence reduction [47]. It is very effective when rapid immobilization is needed to preserve ground water and surface water.

5.1.6. *Phtoextraction*

In this technique the plants are used which are capable to accumulating metals from contaminated soils, sediments and water at high concentrations into their tissue [48]. It is the best method to remove soil contaminants without destroying soil structure and fertility. Phytoextraction is best suited for the remediation of areas that are polluted at low concentrations. Hyperaccumulator plants are mainly used in this process. To make this process feasible, plants extract large concentration of heavy metals into their roots; translocate the heavy metals to the surface biomass and produces large amount of plant biomass. The removed heavy metal can be recycled through phytomining. One species that showed high tolerance to Cr is *Typha angustifolia* [49].

5.1.7. *Phytovolatilization*

It is another type of phytoremediation which uptake contaminants from soil through plants transform them into a volatile form then transpire them into the atmosphere. In this technique contaminants can pass by using plant membranes then to leaves, where contaminatants can volatilize into the atmosphere comparatively low concentration [50].

6. CONCLUSION

Due to the increasing developmental activities this element is responsible for toxicity in the environment. On another hand in certain defined limits Cr is essential to life for performing important functions in the metabolism of living organisms but after exceeding certain limits it become toxic and destroy the ecosystem, pathogen to living organisms and carcinogenic for animals and human beings. One common approach, polluted soils are shifted to landfills is expensive and impose environmental risk and health hazard. Therefore some approaches are needed which could be used in cleaning chromium polluted area and eco-friendly, out of which Phytoremediation techniques used to reduce heavy metals contaminations and to minimize the hazards of heavy metal toxicity. Hyperaccumulator plants are needed to enhance the phytoremedition technique which is effective, affordable and ecofriendly to clean-up of metal contaminated sites.

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