REVIEW ARTICLE *Al Ameen J Med Sci (2009)2(2) Special:57-63*
ISSN 0974-1143

Bioremediation Of Heavy Metal Toxicity-With Special Reference To Chromium

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Abstract: All metals are toxic and our bodies require special transport and handling mechanisms to keep them from harming us. The toxicity occurs in humans due to environmental pollution via soil or water contamination or due to occupational exposure. Some of these metals are useful to us in low concentrations but are highly toxic in higher concentrations. These metal toxicity cause serious morbidity and mortality. Among these heavy metals chromium toxicity can cause serious carcinogenic, genotoxic and immunotoxic effects in humans and animals. Of the two oxidative states in which chromium can be present Cr (III) and Cr (VI), Cr (III) is essential for the human system whereas Cr (VI) has harmful effects. So, one of the ways of reducing Cr-toxicity in Cr-contaminated soil and water is to reduce soluble Cr (VI) to insoluble Cr (III). This can be achieved by microbial activity and is a cost-effective and environment friendly method. Many genera of microbes like *Bacillus*, *Enterobacter*, *Escherichia*, *Pseudomonas* and also some yeasts and fungi help in bioremediation of metals and chromium-contaminated soil and water by bio-absorption and bioaccumulation of chromium. The potential of bioremediation of metal toxicity and its impact on the environment is discussed.
Key-words: Metal-toxicity, Chromium-toxicity, Bio-remediation, common effluent treatment plants.

Introduction:

Metals when present in our body are capable of causing serious health problems, by interfering with, our normal body functions. Some of these metals are useful to the body in low concentrations like arsenic, copper, iron and nickel but are toxic at high concentrations. Other metals like aluminum, beryllium, cadmium, lead and mercury have no biological functions and are highly toxic disrupting bodily functions to a large extent. They disrupt bodily functions by accumulating in vital organs and glands in the human body such as in the heart, brain, kidney, bone and liver. They also displace vital nutritional minerals from their proper place in the body to provide biological functions e.g., lead or cadmium displaces calcium in an enzyme reaction disrupting the enzyme reaction to a large extent. As their impact in the body, is at such basic levels that they are the causal factors in multiple health problems. Metal causes genotoxicity as they affect the DNA and immunotoxicity as they are major irritants to the body. The genomic instability by these metals induces cancer [1]. When we look at the immense impact of these metals in our body we wonder as to how these heavy metals enter our body. We get exposed to these metals from our surroundings whether our immediate environment or our place of work. These toxins can be present in foods and beverages, they might be present in the air we breathe and the exposure can also be through our skin. We can protect ourselves by wearing gloves, using protective breathing apparatus and eating food grown organically. But all the above protective mechanism do not let us fully escape from being exposed to heavy metals. Hence the question is not that whether we have been exposed or not but it is a matter of how much and how often. As these heavy metals are natural component of the Earth's crust we can be easily exposed to them. Once they enter the human body they cannot be degraded or destroyed but tend to bioaccumulate.

Toxicokinetics of metals: We should be aware of the ways by which our body gets exposed to heavy metals, the mechanism by which they cause toxicity. Of some of the common heavy metals we will discuss the following - aluminum is present in antacids, baking powder, beer, cigarette filters, dental amalgams, toothpaste etc. is causes neurofibrillary degeneration and neuro-degeneration. This can lead to diseases like Alzheimer's, anemia, dementia, N-M disorders, and Parkinson's disease, kidney and spleen disorders. Arsenic is used as coloring agent in wall paper and toys, in insecticides and rat poisons and to protect timber and hide from termites. Its toxicity increases the permeability of small blood vessels, causes necrosis of intestinal mucosa and interferes with mitochondrial enzyme system. The effect of arsenic toxicity is abdominal pain, anorexia, vomiting, liver / lung/ skin cancers. Napolean Bonaparte, emperor of France was rumored to have been effected by arsenic poisoning. Cadmium is found in batteries, cigarette smoke (1 cigarette contains 1-2 micrograms of cadmium), incineration of tyres / rubber / plastic, vending machine soft drinks. Their toxicity causes liver and kidney damage, prostate dysfunction, bone diseases and cancer. Mercury enters the body to dental amalgams, felt, laxatives, tattooing etc. and can cause adrenal dysfunction, damage to the central nervous system, hypothyroidism and nerve fiber degeneration. Nickel is present in hydrogenated fats and oils, stainless cookware, tea, tobacco smoke. Nickel toxicity causes kidney dysfunction, disruption of hormone and lipid metabolism and intestinal cancer. Lead is present in auto exhaust, hair dyes, in paints, in sindoor (vermillion), in surma (collyrium), glazing of pottery and enamel ware . Lead toxicity causes co-ordinatioin and concentration lost, decreases I.Q, causes infertility, memory loss , specially long term memory , causes mood swing and sterility. Heavy metal overload in the environment causes growth of stealth pathogens and also combinations of certain metals increases toxicity while other combinations reduces it e.g., lead makes mercury 100 times more toxic, while Zn and Mg reduces cadmium toxicity [2,3]. One of the major mechanisms behind heavy metal toxicity has been attributed to oxidative stress. The metals are capable of interacting with nuclear proteins and DNA causing oxidative deterioration of biological macromolecules [1]. Studies show that heavy metal possesses the ability to generate reactive radicals resulting in cellular damage to lipid bilayer and DNA. These reactive radicals' species include a wide variety of radicals and chelate of amino acid, peptides and proteins complexed with toxic metals [4]. The risk assessments for an essential metal such as Mn, Zn, Fe, Se presents a challenge because of the need to consider the balance between essentiality and toxicity. For each metal there are two ranges of intake associated with adverse health effects. Intakes that are too low and can lead to nutritional toxicity and intakes that are too high and can lead to genotoxicity and immunotoxicity.

Chromium: Elemental Chromium (Cr) does not occur in nature, but is present in ores, primarily in the form of chromite ($FeOCr_2O_3$). The two oxidation states of chromium, Cr (III) and Cr (VI) are stable and predominant in the environment.
Chromium plays an important role in glucose and cholesterol metabolism and is an essential element to man and animals but at higher levels is toxic to both.
Chromium Exposure: Non-occupational exposure to the metal occurs via ingestion of chromium-containing food and water, whereas occupational exposure occurs via inhalation. Cr (III) is poorly absorbed, regardless of the route of exposure, whereas Cr (VI) is more readily absorbed. Humans and animals localize chromium in the lung, liver, kidney, spleen, adrenals, plasma, bone marrow and red blood cells. Workers exposed to chromium have developed nasal irritation (at<0.01mg/m3, acute exposure), nasal ulcers, perforation of the nasal septum (at 2 g/m3, sub-chronic or chronic exposure) and hypersensitivity reactions and "chrome holes" of the skin [5]. Respiratory and dermal toxicity of chromium is well documented [5]. Many neural defects, malformation and fetal deaths have been caused by Cr (VI). The subchronic and chronic oral reference dose (Rfd) value is 1 mg/kg/day for Cr (III). The subchronic and chronic oral Rfd for Cr (VI) are 0.02 mg/kg/day and 0.005 mg/kg/day, respectively [6]. Excessive Chromium (Cr) is present in the environment due to (i) chrome plating and polishing operation (ii) inorganic chemical production (iii) cooling tower and steel mill effluents (iv)wood processing facilities (v) petroleum refineries and (vi) the tanning industries. In USA greater than 50,000 mg of chromium is used every year and 4500 kg/d of chromium is released into the environment. USA regulations say Cr that could be present in drinking water is 0.1 mg/l, 5 mg/l leached from solids and 200 mg/kg in biosolids [6], the natural soil has about 53 mg/kg of chromium.
Manifestations : Oxidation potential is a critical factor for chromium and some other metals. Cr (VI) exposure during last 24-48 hours can be found by the fluctuation of urinary level of Cr (VI), whereas the individual "base" level more generally reflects cumulative post exposure to Cr in any valence state. Currently, there is not sufficient information in literature to recommend guidelines about the levels of chromium in whole blood, plasma and urine – total chromium or Cr (VI) below which current Cr (VI) exposure may be considered as safe or hazardous [7]. Soluble Cr (VI) may be weakly carcinogenic to the lungs, but pose a significant carcinogenic risk if ingested. This is because of low pH of the stomach as particulate chromate dissolves at low pH [5].
*Management of toxicity :*In India, industrial units use common effluent treatment plants (CETPs) to varying degrees to treat and process waste streams. Common effluent treatment plants (CETPs) have been promoted in the region as a long-term, end of pipe solution to the environment problems arising from contaminated waste water disposal. Investigations by the Greenpeace International in Gujarat clearly showed that CETPs failed to deal with all the chemicals pollutants produced by the industries, specially the heavy metals and organic pollutants. Consequently waste water which are considered acceptable for discharge to surface water by the authorities can still contain high concentration of toxic and persistent chemicals [7].Tannery effluents emanating from CETP in Unnao, UP was found toxic in nature

having high Biochemical oxygen Demand BOD, Chemical Oxygen Demand COD, Total Dissolved Solids TDS and Cr content (5.88 mg.l), which supported growth of chromate-tolerant bacteria [8]. Shukla *et al* isolated four strains of chromate-tolerant bacteria from the effluent which showed multiple metal and antibiotic resistances, these strains accumulated Cr to a high extent proving that they have a great potential in recovery and detoxification of Cr [8].

Bioremediation : Microorganisms play a significant and vital role in bioremediation of heavy metal contaminated soil and wastewater. Indigenous soil microbes appear well suited for Cr (VI) transformation in highly contaminated soil. Very stable final chromium forms can be achieved as a result of microbial activity, with minimal risk of re-release of Cr (VI). In liquid treatment system, biotransformation of Cr (VI) by pure culture has been studied under a range of redox (aerobic and anaerobic), temperature (10-45^{o}C) and pH(6.5-9.5 conditions). *Escherichia coli* ATCC 33456 transformed Cr(VI) faster at 10^{o}C to 45^{o}C under anaerobic than at 10^{o}C to 35^{o}C under aerobic condition. Many genera of microbes like *Bacillus*, *Enterobacter*, *Escherichia*, *Pseudomonas* and also some yeasts and fungi help in bioremediation of metal and chromium-contaminated soil and water by bio-absorption and bioaccumulation of chromium[9-20]. Heavy metal resistant fungi and bacteria were isolated from the soil samples of tanning industry, the bioaccumulation of Cr (VI) by these isolates were evaluated and their ability to remove heavy metal like Cr (VI) from tannery effluents were found. The pH of the effluent was significant in removing the metal. The heavy metal removal by the bacteria *Pseudomonas* was attributed to the cellular growth of these organisms. Chromium (VI) can be bio-transformed by undergoing enzymatic reduction, resulting in formation of reactive intermediates and Cr (III) [21]. Chromium-resistant bacteria isolated from the soil can be used to reduce toxic Cr (VI) from contaminated environment. The mechanism of Cr-tolerance or resistance of selected microbes is of particular importance in both bioremediation and waste water treatment technology [22]. Gomes *et al* found the applicability of the charophyte, *Nitella pseudoflabellate* in the remediation of Cr (VI) contaminated water at different calcifying potentials [23]. In 2008 Rehman *et al* found that *Bacillus* sp had the ability to reduce hexavalent chromium into its trivalent form. These bacteria could reduce 91% of Chromium from the medium after 96 hours and was also capable of reducing 84% chromium from the industrial effluents in Lahore after 144 hours [24]. Morales *et al* wanted to isolate and analyze chromium-resistant microorganisms suitable for bioremediation. They found that *Streptomyces* sp tolerated heavy metals and elevated levels of chromium despite its negative effect on growth and development was efficient at removing Cr (VI) by promoting reduction to Cr (III). Hence chromium-resistant microorganisms are a promising candidate for detoxification of sites containing heavy metals [25]. More data of chromium reduction was obtained by scientists from *Pseudomonas aeruginosa* [26], *Bacillus* sp [27,28], *Streptomyces* [29], from *Pseudomonas fluorescens* [30,31],from yeasts like *Pichi guilliermondii* [32] also from *Micrococcus* sp and *Aspergillus* sp in Tamil Nadu [33]. *Aspergillus niger* biomass has been found to be very effective in bioabsorption of Cr (III) and Cr (VI) in spent chrome liquor from chrome tanning process in leather industry in Chennai. Maximum absorption of 83% for Cr (III) at 48 hours 79% of Cr (VI) at 36 hours was observed [34].

Conclusion

It is apparent that the current methods of effluent treatment plants are unable to treat the wastes they receive and discharge toxic and persistent pollutants to the rivers and estuaries. They create toxic sludge which need disposal. To stop pollution and to prevent metal-toxicity there is a clear need for an overall waste treatment strategy with the goal of elimination of priority pollutants at source. This can be achieved by indigenous microorganisms found in various industrial effluents which can be used as an indicator of pollution and can be used to resist, process, metabolize and detoxify chromate polluted waste water.

Future Scope

Chromate resistant determinants in bacteria are carried by plasmids-having potential to detoxify chromate polluted water [35] such plasmid can be transferred to make biomasses capable of reducing metal toxicity. Similar work was done by Kao *et al* using a MerP expressing recombinant *Escherichia coli*, where the MerP originated from Gram-positive (*Bacillus cereus*) and Gram-negative (*Pseudomonas* sp) were used to adsorb Ni, Zn and Cr in aqueous solution [36]. Some scientists in Varanasi used *Eichhornia crassipes* (water hyacinth) to remove heavy meals from contaminated water [37]. Others in Chennai showed that *Spirulina fusiform* can remove 93-99% of chromium from tannery effluents. Chromium pollution in the effluent can be detected by alga like *Chlamydomonas reinhardtii* [38] and water lilies (*Nymphaea spontanea*) [39]. The environmental impact of heavy metal toxicity should be rapidly handled by using the bioremediation processes to reduce the toxic levels of heavy metals [40]. We can intake good metals like selenium (200 microgam daily), zinc (20-50mg daily) and magnesium (350 mg daily) to squeeze out the bad metals [41]. Hence the importance of bioremediation of heavy metals would depend on the biogeochemistry of the water bodies or soils impacted by industries discharging effluents into them.

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