Review Article

Bio-sorbents: A novel technology to mitigate Heavy metal pollution

Abstract

The toxicity and bioaccumulation tendency of heavy metals in the environment is a serious threat to the health of living organisms. Unlike organic contaminants, heavy metals cannot be broken down by chemical or biological processes. Hence, they can only be transformed into less toxic species.Contamination of the environment with heavy metals has increased beyond the recommended limit and is detrimental to all life forms.Microbial remediation is described as the use of microorganisms to perform the absorption, precipitation, oxidation, and reduction of heavy metals in the soil.Bio-sorption can be defined as "the ability of biological materials to accumulate heavy metals from waste water through metabolically mediated or physico-chemical pathway of uptake.Fungi, yeast, algae and bacteria have proved to be potential metal –biosorbents.The sustainable approach needs to be developed in order to select the most appropriate bio-sorbent, operating conditions, and efficient mechanism of heavy metal removal in industrial effluent, to sufficiently address the major challenges involved.

Keywords:*Bio-accumulation, bio-sorbents, Heavy metals, Toxic species*

Introduction

Heavy metal pollution is currently a major environmental problem because metal ions persist inenvironment due to their non-degradable nature. The toxicity and bioaccumulation tendency of heavy metals in the environment is a serious threat to the health of living organisms. Unlike organic contaminants, heavy metals cannot be broken down by chemical or biological processes. Hence, they can only be transformed into less toxic species.The build-up of heavy metals and metalloids in soils and waters continues to create serious global health concerns, as these metals and metalloids cannot be degraded into non-toxic forms, but persist in the ecosystem. Contamination of the environment with heavy metals has increased beyond the recommended limit and is detrimental to all life forms (Gaur *et al*., 2014;Dixit *et al*., 2015; Tak*et al*., 2013). The standard for soil, as established by the Indian standardsfor heavy metals, is 3–6, 135–270, 75–150, 250–500, and 300–600 mg/kg for Cd, Cu, Ni, Pb, and Zn, respectively (Nagajyoti*et al*., 2010).

The majorities of the heavy metals are toxic at low concentrations and are capable of entering the food chain, where they accumulate and inflict damage to living organisms. All metals have the potential toexhibit harmful effects at higher concentrations and the toxicity of each metal depends on the amount available to organisms, the absorbed dose, the route and the duration of exposure (Mani and Kumar, 2014). Thus, it is imperative to remove or reduce heavy

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metal contamination in order to prevent or reduce contaminating the environment and the possibility of uptake in the food web.To achieve this,bioremediation is employed in order to increase metal stability (speciation), which in turn reducesthe bioavailability of metal (Abbas *et al*., 2014).

Bioremediation is an environmentally friendly and cost-effective technique for heavy metal removal/recovery, when compared to the conventional chemical and physical techniques, which are often more expensive and ineffective, especially for low metal concentrations. In addition, these conventional methods generate significant amounts of toxic sludge. Microorganisms possess astonishing metabolic pathways which utilize various toxic compounds as a source of energy for growth and development, through respiration, fermentation, and cometabolism. Due to their characteristic degradative enzymes for a particular contaminant, they have evolved diverse mechanisms for maintaining homeostasis and resistance to heavy metals, in order to adapt to toxic metals in the ecosystem (Brar*et al*., 2006). So, microbial remediation is described as the use of microorganisms to perform the absorption, precipitation, oxidation, and reduction of heavymetals in the soil (Su, 2014). Microorganisms have various mechanisms to mitigate heavy metal contamination i.e., bioaccumulation, biomineralization, biosorption, and biotransformation. Due to these abilities, they have been effectively used as biosorbents for heavy metal removal and recovery. Majority of the heavy metals destroy the microbial cell membranes, but microbes have the capacity to defend and overcome the toxic effect. In this article, the the capacity of the microbes to act as as microbial bio-sorbents to mitigate heavy metal pollution in order to protect human and animal health and environment is described briefly.

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Toxicity of heavy metals to humans, plants and microbes

The heavy metals which are naturally occurring are typically present as insoluble forms, like in mineral structures, or in precipitated or complex forms that are not readily available for plant uptake.The adsorptioncapacity of naturally occurring heavy metals is very high in soil. The natural and anthropogenicprocesses that bring about the occurrence of heavy metals are given below in the Table 1. Heavy metals from anthropogenic sources are having high bio-availability due to their soluble and mobile reactive forms.

Table 1: Sources of Heavy metals

Natural Sources	Anthropogenic sources
Comets	Alloy production
Erosion	Atmospheric deposition
Volcanic eruptions	Battery production
Weathering of minerals	Bio-solids and improper stacking of industrial solidwaste
Rock sedimentation	Coating and explosive manufacturing
Volcanic dust	Leather tanning and mining
-	Photographic materials and printing pigments
-	Smelting, steel and electroplating industries
-	Textiles, dyes and wood preservatives
-	Pesticides, phosphate fertilizers and sewage irrigation

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Heavy metals affect all life forms badly and its effect on humans, plants and microbes are given below in the Table 2.

Table 2. Toxicity of heavy metals to humans, plants and microbes

Metal	Humans	Plants	Microbes	References
Antimony	Cancer, cardiovascular diseases, conjunctivitis, dermatitis, liver diseases, nasal ulceration, respiratory diseases etc.	Decreases synthesis of somemetabolites, growth inhibition, inhibitchlorophyll synthesis	Inhibit enzyme activities,reduced growth rate	Blais*etal*., 2008
Arsenic	Brain damage, cardiovascular and respiratory disorder, conjunctivitis, dermatitis and skin cancer	Damage cell membrane, inhibition of growth, inhibits roots extension and proliferation, interferes with critical metabolic processes, loss of fertility, yield and fruit production, oxidative stress, physiological disorders	Deactivation of enzymes	Blais*etal*., 2008
Beryllium	Allergic reactions, berylliosis, cancer,	Inhibits seed germination	Chromosomal aberration,	Blais*etal*., 2008

	heart diseases, lung diseases etc.		mutation	
Cadmium	Bone disease, coughing,emphysema, headache, hypertension, itai-itai,kidneydiseases, lung and prostate cancer, lymphocytosis, microcytic hypochromic anemia, testicular atrophy and vomiting	Chlorosis, decrease in plant nutrient content, growth inhibition, reduced seed germination	Damage nucleic acid, denature protein, inhibit cell division and transcription, inhibits carbon and nitrogen mineralization	Fashola*et al*., 2016
Chromium	Bronchopneumonia, chronic bronchitis, diarrhea, emphysema, headache, irritation of the skin, itching of respiratory tract, liver diseases, lung cancer, nausea, renal failure, reproductive toxicity, vomiting etc.	Chlorosis, delayed, senescence, wilting, biochemical lesions, reduced biosynthesis germination, stunted growth, oxidative stress	Elongation of lag phase, growth inhibition, inhibition of oxygen uptake	Barakat*et al*, 2011
Copper	Abdominal pain, anemia, diarrhea, headache, liver and kidney damage, metabolic disorders, nausea, vomiting etc.	Chlorosis, oxidative stress, retard growth	Disrupt cellular function, inhibit enzyme activities	Fashola*et al*., 2016
Mercury	Ataxia, attention deficit, blindness, deafness, decrease rate of fertility, dementia, dizziness, dysphasia, gastrointestinal irritation, gingivitis, kidney problem, loss of memory, pulmonary edema, reduced immunity and	Affects antioxidative system, affects photosynthesis, enhance lipid peroxidation, induced genotoxic effect, inhibit plant growth, yield, nutrient uptake and homeostasis, oxidative stress	Decrease population size, denature protein, disrupt cell membrane, inhibits enzyme function	Wang *et al*., 2012

	sclerosis			
Lead	Anorexia, chronic nephropathy, damage to neurons, high blood pressure, hyperactivity, insomnia, learning deficits, reduced fertility, renal system damage, risk factor for Alzheimer's disease, shortened attention span etc.	Affects photosynthesis and growth, chlorosis, inhibit enzyme activities and seed germination, oxidative stress	Denatures nucleic acid and protein, inhibits enzymes activities and transcription	Wuana*et al*., 2011
Nickel	Cardiovascular diseases, chest pain, dermatitis, dizziness, dry cough and shortness of breath, headache, kidney diseases, lung and nasal cancer, nausea etc.	Decrease chlorophyll content, inhibit enzyme activities and growth, reduced nutrient uptake	Disrupt cell membrane, inhibit enzyme activities, oxidative stress	Malik, 2004
Selenium	Dysfunction of the endocrine system, gastrointestinal disturbances, impairment of natural killer cells activity, liver damage etc.	Alteration of protein properties, reduction of plant biomass	Inhibits growth rate	Germ *et al*., 2007
Silver	Argyria and argyrosis, bronchitis, cytopathological effects in fibroblast and keratinocytes, emphysema, knotting of cartilage, mental fatigue, nose, throat and chest irritation and rheumatism	Affects homeostasis, decrease chlorophyll content, inhibits growth	Cell lysis, inhibit cell transduction and growth	Qian*et al*., 2013
Thallium	Alopecia, ataxia, burning feet syndrome, coma,	Inhibits enzyme activities, reduced growth	Damages DNA, inhibits enzyme activities	Babula*et al*., 2008

	convulsions, delirium, fatigue, gastroenteritis, hair fall, hallucinations, headache, hypotension, insomnia, nausea, tachycardiaand vomiting		and growth	
Zinc	Ataxia, depression, gastrointestinal irritation, hematuria, Icterus, impotence, kidney and liver failure, lethargy, macular degeneration, metal fume fever, prostate cancer, seizures and vomiting	Affects photosynthesis, inhibits growth rate, reduced chlorophyll content, germination rate and plant biomass	Death, decrease in biomass, inhibits growth	Gumpu*et al*., 2015

<u>Bio-sorption and Bio-sorbents</u>

In the 1990s, a new scientific areai. e., bio-sorption developed whichaimed at recovering heavy metals. It is based on the metal-bindingcapacities of various biological materials. Biosorption can be defined as “the ability of biological materials to accumulate heavy metals from waste water through metabolically mediated or physico-chemical pathway of uptake.” Fungi, yeast, algae and bacteria have proved to be potential metal - biosorbents (Volesky, 1986). The major advantage of biosorption over conventional treatment methods includes (Kratochvil and Volesky, 1998): (i) low cost; (ii) high efficiency; (iii) minimization of chemical or biological sludge; (iv) no additional nutrient requirement; (v) regeneration of biosorbent; and (vi) possibility of metal recovery.

Once bound to the cell wall of living microbes, metals are activelytransported across the cell membrane.Various microbial biomasseshavedifferent biosorptive abilities, which also vary considerablywithin each group. However, the biosorption capacity of each biosorbent depends on its prehistoryand pretreatment, as well as the experimental conditions. The biosorbent should be cheap, effective,and easy to grow and harvest. The organism should also lend itself to alteration of the bioreactorconfiguration, as well as physical and chemical conditions to enhance biosorption (Fomina*et al*., 2014).

Bacteria have been used as biosorbents owing to their ubiquity, size, ability to grow undercontrolled conditions, and resilience to an extensive range of environmental conditions (Wang, 2009).Various heavy metals have been tested on bacteria species such as *Pseudomonas*, *Enterobacter*,*Bacillus*, and *Micrococcus* sp. Their excellent sorption capacity is due to their highsurface-to-volume ratios and their numerouspotentialyactive chemosorption sites, such as the teichoicacid on the cell wall (Mosa*et al*., 2016).

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Yeasts and molds are easy to cultivate, can be genetically and morphologically manipulated,and can produce a high biomass yield. They are widely used in a variety of large-scale industrialfermentation processes, producing ferrichrome, gallic and kojic acid, and enzymes like lipases, glucose,isomerase, pectinases, amylases, and glucanases(Wang *et al*., 2009). They are extensively used as biosorbents forthe removal of toxic metals from polluted wastewaters, with excellent abilities for metal uptake andrecovery (Dursun*et al*., 2003). They have developed a complex defense system to neutralize heavy metal toxicity, prominence as good biosorbents because of their high sorption capacity. Red, green, and brownalgae have been used for adsorption studies and are all readily available in marine and fresh waterenvironments (Srivastava*et al*., 2015).

Algae are autotrophic, thus require a low number of nutrients and producea large biomass compared to other microbial biosorbents. They have a high sorption capacityand are readily available in large quantities (Abbas *et al*., 2014).

Mechanisms of Heavy Metal Uptake by Microorganisms

Microbes can trap heavy metal ions through the cellular structure of a microorganism and subsequently sorbs them onto the binding sites of the cell wall (Malik, 2004). This process is called biosorption or passive uptake,and is independent of the metabolic cycle. The amount of metal sorbed depends on the kinetic equilibrium and composition of the metal at the cellular surface. The mechanism involves several processes, including electrostatic interaction, ion exchange, precipitation, the redox process, and surface complexation (Yang *et al*., 2015). The process is fast and can reach equilibrium within a few minutes. Biosorption can be carried out by fragments of cells and tissues, or by dead biomass or living cells as passive uptake via surface complexation onto the cell wall and other outer layers (Fomina*et al*., 2014).

The other method is a process in which the heavy metal ions pass across the cell membrane into thecytoplasm, through the cell metabolic cycle. This is referred to as bioaccumulation or active uptake.Bioaccumulation is a process of a living cell that is dependent on a variety of physical, chemical, andbiological mechanisms.These factors include intracellular and extra cellular processes, where bio-sorption plays a limited and ill-defined role (Fomina*et al*., 2014). The microbes that can accumulate heavy metals should have a tolerance to one or more metals at higher concentrations. These organisms exhibit transformational abilities i.e., capacity to change toxic chemicals to harmless forms that allows the organism to lessen the toxic effect of the metal. The organism of choice may be native to the polluted environment or isolated from another environment and brought to the contaminated site (Sharma *et al.*, 2000).

A sustainable approach needs to be developed in order to select the most appropriate biosorbent, operating conditions, and efficient mechanism of heavy metal removal in industrial effluent, to sufficientlyaddress the major challenges involved.

Conclusion

Bio-sorbents are boon to environment as it is a low cost technology for the remediation of harmful heavy metals from the environment. There is passive as well as active mechanisms are there for the removal of heavy metals from environment by micro-organisms.Heavy metals got accumulated in environment both by natural and anthropogenic processes. Heavy metals are toxic to human, animal, plants as well as environment. The process of bio-sorption includes electrostatic interaction, ion exchange, precipitation, redox process; surface complexation etc.Thesustainable approach needs to be developed in order to select the most appropriate bio-sorbent, operating conditions, and efficient mechanism of heavy metal removal in industrial effluent, to sufficiently address the major challenges involved.

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