

Review Article

Bio-sorbents: A novel technology to mitigate ~~Heavy~~ 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 wastewater through a metabolically mediated or physio-chemical pathway of uptake.” Fungi, yeast, algae, and bacteria have proved to be potential metal—biosorbents. ~~The~~ A sustainable approach needs to be developed 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: Bioaccumulation, bio-sorbents, ~~H~~heavy metals, ~~t~~toxic species

Introduction

Heavy metal pollution is currently a major environmental problem because metal ions persist in the environment 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; Taket *et al.*, 2013). The standard for soil, as established by the Indian standards for heavy metals, is 3–6, 135–270, 75–150, 250–500, and 300–600 mg/kg^{\supset} for Cd, Cu, Ni, Pb, and Zn, respectively (Nagajyotiet *et al.*, 2010).

~~The~~ ~~of the~~ Many heavy metals are toxic at low concentrations and can enter the food chain, where they accumulate and inflict damage ~~to~~ on living organisms. All metals have the potential to exhibit harmful effects at higher concentrations and the toxicity of each metal depends on the amount available to organisms, the absorbed dose, the ~~route~~ 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 to increase metal stability (speciation), which in turn reduces the 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 co-metabolism. 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 heavy metals 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. Most 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 capacity of microbes to act as microbial bio-sorbents to mitigate heavy metal pollution to protect human and animal health and the environment is described briefly.

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 adsorption capacity of naturally occurring heavy metals is very high in the soil. The natural and anthropogenic processes that bring about the occurrence of heavy metals are given below in Table 1. Heavy metals from anthropogenic sources are having high bio-availability due to their soluble and mobile reactive forms.

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Table 1: Sources of ~~h~~Heavy metals

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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 ~~is~~their effect on humans, plants, and microbes are given below in ~~the~~Table 2.

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

Metal	Humans	Plants	Microbes	References
Antimony(Sb)	Cancer, cardiovascular Cancer, cardiovascular diseases, conjunctivitis, dermatitis, liver diseases, nasal ulceration, respiratory diseases etc.	Decreases synthesis of somemetabolites, growth inhibition, inhibitschlorophyll synthesis	Inhibit enzyme activities, reduced growth rate	Blaiset <i>al.</i> , 2008
Arsenic (As)	Brain damage, cardiovascular and respiratory disorder, conjunctivitis, dermatitis 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	Deactivation of enzymes	Blaiset <i>al.</i> , 2008

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		stress, physiological disorders		
Beryllium	Allergic reactions, berylliosis, cancer, heart diseases, lung diseases etc.	Inhibits seed germination	Chromosomal aberration, mutation	Blais <i>et al.</i> , 2008
Cadmium	Bone disease, coughing, emphysema, headache, hypertension, itai-itai, kidney diseases, 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, inhibit carbon and nitrogen mineralization	Fashola <i>et al.</i> , 2016
Chromium	Bronchopneumonia, chronic bronchitis, diarrhea, emphysema, headache, irritation of the skin, itching of the 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 <i>et al.</i> , 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 <i>et al.</i> , 2016
Mercury	Ataxia, attention deficit, blindness, deafness, decrease rate of fertility, dementia, dizziness, dysphasia, gastrointestinal irritation, gingivitis ,	Affects the antioxidative system, affects photosynthesis, enhances lipid peroxidation, induced genotoxic effect, inhibit plant	Decrease population size, denature protein, disrupt the cell membrane, inhibits enzyme function	Wang <i>et al.</i> , 2012

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	kidney problem, loss of memory, pulmonary edema, reduced immunity and sclerosis and sclerosis	growth, yield, nutrient uptake, and homeostasis, oxidative stress		
Lead	Anorexia, chronic nephropathy, damage to neurons, high blood pressure, hyperactivity, insomnia, learning deficits, reduced fertility, renal system damage, a 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 <i>et al.</i> , 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 <i>et al.</i> , 2007
Silver	Argyria and argyrosis, bronchitis, cytopathological effects in fibroblast and keratinocytes, emphysema, the knotting of cartilage, mental fatigue, nose, throat and chest irritation	Affects homeostasis, and decrease chlorophyll content; inhibits the growth	Cell lysis, inhibit cell transduction and growth	Qian <i>et al.</i> , 2013

	and rheumatism			
Thallium	Alopecia, ataxia, burning feet syndrome, coma, convulsions, delirium, fatigue, gastroenteritis, hair fall, hallucinations, headache, hypotension, insomnia, nausea, tachycardia, and vomiting	Inhibits enzyme activities, reduced growth	Damages DNA, inhibits enzyme activities and growth	Babula <i>et al.</i> , 2008
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	Gumpuet <i>et al.</i> , 2015

Bio-sorption and Bio-sorbents

In the 1990s, a new scientific area, i.e., bio-sorption developed which aimed at recovering heavy metals. It is based on the metal-binding capacities of various biological materials. Biosorption can be defined as “the ability of biological materials to accumulate heavy metals from [waste water](#) through a metabolically mediated or [physio](#)-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 actively transported across the cell membrane. Various microbial biomass have different biosorptive abilities, which also vary considerably within each group. However, the biosorption capacity of each biosorbent depends on its prehistory and 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 bioreactor configuration, as well as physical and chemical conditions to enhance biosorption (Fomina *et al.*, 2014).

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Bacteria have been used as biosorbents owing to their ubiquity, size, ability to grow ~~under controlled~~ under controlled 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 high surface-to-volume ratios and their numerous ~~potentially~~ potentially active chemisorption sites, such as the teichoic acid on the cell wall (Mosaet al., 2016).

~~Yeasts~~ Yeast and ~~molds~~ mold 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 industrial fermentation 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 for the removal of toxic metals from polluted wastewaters, with excellent abilities for metal uptake and recovery (Dursun et al., 2003). They have developed a complex defense system to neutralize heavy metal toxicity, ~~prominence~~ prominent as good biosorbents because of their high sorption capacity. Red, green, and brown algae have been used for adsorption studies and are all readily available in marine and freshwater environments (Srivastava et al., 2015).

Algae are autotrophic, thus ~~require~~ requiring a low number of nutrients and ~~produce~~ producing a large biomass compared to other microbial biosorbents. They have a high sorption capacity and 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 sorb 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 the cytoplasm, 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, and biological mechanisms. These factors include intracellular and ~~extra~~ extra-cellular processes, where bio-sorption plays a limited and ~~ill-defined~~ 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., the 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 sufficiently address the major challenges involved.

Conclusion

Bio-sorbents are a boon to the environment as it is a low-cost technology for the remediation of harmful heavy metals from the environment. There are passive as well as active mechanisms for the removal of heavy metals from the environment by micro-organisms. Heavy metals got accumulated in the environment both by natural and anthropogenic processes. Heavy metals are toxic to humans, animals, plants as well as the environment. The process of bio-sorption includes electrostatic interaction, ion exchange, precipitation, redox process, surface complexation, etc. A 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.

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