Futuristic Trends in Biotechnology
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IIP Series, Volume 3, Book 11, Part 1, Chapter 3
A COMPREHENSIVE REVIEW ON THE BIOSORPTION OF HEAVY METALS
AND DIVERSE BIOSORBENTS USED FOR EFFECTIVE MITIGATION OF
HEAVY METAL POLLUTION FROM THE CONTAMINATED SITES

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Abstract

Heavy metals are defined metallic elements characterized by their high density and these metals have a specific gravity that is at least five times greater than that of water (5 g/cm^3). Metals like zinc, nickel, and copper are needed for cellular growth of all the living beings in low concentration but at higher concentration all the heavy metals are toxic and cause negative effect in beings. Heavy metals are mainly discharged from the varied industrial sources including, metal smelting, coal combustion, mining, foundry and chemical manufacturing industries into the air, water and soil. Other than industrial discharge, domestic activities and agricultural practices may also accumulate heavy metals in the environment. Due to its toxicity, discharge of heavy metals should be closely monitored and regulated to protect human health and environment. Furthermore, to remediate the contaminated site, lots of conventional methods are employed, but due to its high cost, less effectiveness and the accumulation of large chemical wastes, an alternative method is needed for effective remediation of heavy metal from the environment. Thus, the important alternative method for the remediation of heavy metals is biological remediation (bioremediation). One of the principle and sustainable method in bioremediation is the biosorption method in which living or non-living biological materials, such as bacteria, fungi, algae and yeast were used for binding of heavy metal ions present in the environment. The

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biosorption process is influenced by a variety of factors that can affect its efficiency and effectiveness which includes pH, temperature, contact time, biomass dosage and initial heavy metal ion concentration. Hence, heavy metal biosorption is of great interest for researchers as it offers an eco-friendly and efficient method for mitigating heavy metal pollution from various industries, agricultural fields and natural environment. Thus, this review mainly focuses on biosorption process and its efficiency in the removal of heavy metals.

Keywords: Heavy metal, Biosorption, Biosorbent, Bioremediation, Conventional method.

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I. INTRODUCTION

Heavy metals are naturally present in the environment, but it poses severe threat to human health and the environment. These elements have high atomic weight and specific density of 5 g/cm^3, and thus designated as "heavy" metals. Based on the biological and ecological significance of heavy metals, it can be categorized into two main groups, essential and non-essential. Essential heavy metals includes copper, ion, magnesium, selenium are those that are required in a trace quantity for the proper functioning of biological systems of humans, animals and plants. Besides which they also serves as co-factors for various physiological processes [1]. However, non-essential heavy metals have no known biological functions and found to be toxic to living organisms even at low concentrations. Exposure to the non-essential heavy metals like lead, cadmium, mercury can lead to various adverse health effects and environmental pollution [2], [3].

Heavy metals can enter into the environment from various natural and anthropogenic sources. Natural sources of heavy metals refer to the one which is not primarily accumulated by human activities for instance, geological weathering, volcanic emissions, forest fires, geysers and deep-sea vents. However, anthropogenic sources of heavy metals that are released into the environment through human activities, like mining, smelting, casting, abundant usage of chemical fertilizers and pesticides, coal and oil combustion, vehicle emissions and urban runoff [4]. These anthropogenic sources often lead to heavy metal contamination and pose environmental and health risks. Primarily, these heavy metals can enter the human body through various means, including ingestion, inhalation or skin contact and it can accumulate over time, leading to various health problems. The severity of heavy metal poisoning depends on the factors like type of heavy metal, level and duration of exposure to heavy metal and the medical history of the person who is exposed to heavy metals [5], [6], [7].

Over past few decades, to abolish heavy metal contaminants distinct chemical and physical methods were used. However, these conventional methods possess a large number of disadvantages, like producing secondary contaminants, high cost and less efficiency in heavy metal removal. Hence research was focused on discovery of new technologies for the enhanced and effective removal of heavy metals from the environment. In this context, bioremediation could be used as an effective and potential substitute for conventional techniques in managing heavy metal pollution and thus minimizing its impact on human health and the ecosystem [8]. Among various bioremediation strategies, biosorption is considered as a predominant method used to remediate heavy metals from the metal polluted sites. Biosorption could be defined as the potential capacity of biological materials to aggregate and bind with the heavy metals from contaminated water or soil onto its cellular structure. Bacteria, fungi, yeast and algae are potential biological material or biosorbents which can effectively remediate metals from contaminated sites by biosorption process. Due to the beneficial properties like low cost and high efficiency, biosorption technique is highly recommended compared to other conventional methods [9].

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II. BIOSORPTION MECHANISMS

Biosorption mechanism is classified based on the type of interaction between heavy metals and microbes [10], [11], [12]. Biosorption mechanisms are categorized into two processes,

- Metabolism dependent biosorption
- Non -metabolism dependent or Metabolism independent biosorption.

1. **Metabolism Dependent Biosorption:** In metabolism dependent biosorption, ATP is essential for the binding process of metal ions on to cell wall of microorganisms. Microbial cell wall has different functional groups on the surface such as polysaccharides and proteins which act as active sites for the binding of metal ions. The ligands (functional group) such as phosphoryl, carboxyl, carbonyl, sulfhydryl and hydroxyl groups are located on the surface of the microbial cell wall which aid in metal binding. In this process, metals are taken up by living biosorbent as a result, metal ions enter into the cytoplasm of living cells and get adhered to various functional groups [13], [14]. Different strategies are employed in this technique, for instance, chelation, ion exchange etc. In metabolism dependent biosorption, biosorbents or adsorbent (microorganism) bind to the metal ions (adsorbate) at more than one place by using Van der Waals forces or covalent bonding to create a ring structure which is very strong [15]. Further, the strong binding results in the accumulation of the heavy metal on the adsorbent's surface which facilitate the removal process [16], [11], [17]

2. **Metabolism Independent Biosorption:** In a metabolism-independent mechanism, heavy metal removal occurs through passive physical and chemical interactions with non-living or inactive biological materials, such as dead microbial cells or organic materials like peat, activated carbon, chitosan, alginates, starch, pectin, sawdust and wood chips, lignocellulosic materials, soyben hulls, wheat bran and clay. Moreover, this mechanism does not rely on the metabolic activity of living organisms. Anionic ligands (carboxyl, amine, hydroxyl, phosphate, and sulfhydryl groups) are present on the surface of the microbial cell wall, which binds with metal molecules and are thus removed. Nevertheless, living cells are more preferred over dead cells because living cells continuously uptake metal molecules and possess self-replenishment property [18], [19].

III. TYPES OF BIOSORBENTS

Biosorbents are biological materials, which possess the ability to aggregate and remove heavy metal ions from contaminated environments. These biosorbents possess specific surface properties which allow them to interact and immobilize the heavy metals contaminants. Further biosorbents was divided into two types,

- Living organic materials
- Non-living organic materials

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1. **Living Organic Materials:**

- **Bacteria as Biosorbents:** Bacterial biosorbents is an essential tool in addressing heavy metal contamination in water, soil and industrial effluents due to their diversity, ability to accumulate heavy metals and cost effective nature. Among all microorganisms, bacteria are abundantly present in nature. Many different bacterial species exhibit varying levels of metal-binding capacity, which facilitate the metal binding. Bacterial cells have substantial surface areas with active functional groups that can interact with heavy metal ions. Metal ions usually attach to the functional groups present on the cell surface, following which internalization of metal ions takes place. While comparing gram positive and gram negative bacteria, gram positive bacteria possess increased biosorption capacity due to the presence of abundant glycoproteins. Because of the presence of phospholipids and lipopolysaccharide, gram negative bacteria hold less efficiency in metal biosorption technique [20], [21].

- **Algae as Biosorbents:** Algal cell walls are constructed by polysaccharides for instance, alginic acid, chitin, xylan, mannan. They possess functional groups like, sulfate, hydroxyl, phosphate, imidazole, amino group and amine. These functional groups interact with heavy metals by two ways such as ionic and covalent bonding. Carboxyl and sulfate groups of algal cell wall interact by ionic bonding whereas amino and carboxyl groups interact by means of covalent bonding with metals. This binding gradually provokes the production of phytochelatins, which facilitate the sequestration of heavy metals within the algal cell that rendering the completion of biosorption process [20], [22].

- **Fungi as Biosorbents:** Fungal cell wall exhibits admirable metal binding capacity due to its cell wall components, like chitins, mannans, glucans, lipids, polysaccharides, pigments etc. Fungal cell wall is composed of 90% polysaccharide which plays a crucial role in metal binding. Fungi have complex structures with extensive mycelium and hyphae, which provide a large surface area for heavy metal biosorption. Recent research also shows that physical and chemical treatments of fungi by using autoclaving, heat processes, dimethyl sulfoxide, laundry detergent, orthophosphoric acid, formaldehyde, glutaraldehyde and NaOH treatment can further enhance the efficiency of biosorption process [23], [20], [24].

- **Yeast as Biosorbents:** Yeast cells effectively remove heavy metal by bioaccumulation process than biosorption process because free yeast cells are not considered as a good candidate for biosorption. Physical and chemical pretreatment of yeast cells, increases the surface volume ratio for metals binding [25], [26]. Different biosorpents used for metal removal are tabulated in table 1.

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Table 1: Different Biosorbents Employed for Heavy Metal Biosorption [2], [27].

Heavy metals	Microorganism			
	Bacteria	**Algae**	**Fungi**	**Yeast**
Arsenic (As)	*Bacillus* sp. *Kocuria* sp.	*Spirogyra hyaline*	*Penicillium chrysogenum*	
Cadmium (Cd)	*Pseudomonas putida* *Enterobacter cloacae*	*Sargassum tenerrimum* *Fucus vesiculosus*	*Aspergillus cristatus* *Aspergillus niger*	*Saccharomyces cerevisiae*
Copper (Cu)	*Pseudomonas aeruginosa* *Bacillus licheniformis*	*Fucus vesiculosus* *Ascophyllum nodosum*	*Pleurotus ostreatus* *Aspergillus lentulus*	*Saccharomyces cerevisiae* *Candida pelliculosa*
Lead (Pb)	*Bacillus cereus* *Enterobacter cloacae*	*Pithophora* sp. *Fucus vesiculosus*	*Rhizopus nigricans* *Trichoderma longibrachiatum*	*Mucor rouxii*
Mercury (Hg)	*Enterobacter cloacae*	*Sargassum* sp. *Cladophora fascicularis*	*Aspergillus flavus* *Aspergillus fumigatus*	*Saccharomyces cerevisiae*
Cobalt (Co)	*Rhodopseudomonas palustris*	*Spirogyra hyaline*		*Saccharomyces cerevisiae*

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2. **Non-Living Organic Materials:** The waste materials includes lignocellulosic materials (peat, soyben hulls, wheat bran, corn cobs, soya bean hulls, cotton seeds hulls, fruit peels, sawdust and wood chips), activated carbon, chitosan, alginate, starch, pectin and clay are considered as non-living organic material. Phenolics and carboxylic group present in the cellulosic waste material acts as a active functional group for metal removal. By means of adsorption, ion exchange, surface precipitation and complexation mechanism metal ions bind with the functional groups present in waste materials. Thus non-living organic material acts as biosorbent to remove heavy metals [28], [29].

IV. FACTORS AFFECTING BIOSORPTION PROCESS

Heavy metal biosorption process mediated by microbes is depends on various factors which is discussed as follows; [30], [31].

1. **Temperature:** For efficient metal ion removal, temperature must be optimized. The impact of temperature on metal removal varies depending on the type of microorganism and heavy metal used. In general 20˚C to 35°C is suitable for metal removal but temperature higher than 45°C may damage the functional group present on the biosorbents and thus decreasing the metal removal efficiency [30], [32].

2. **pH:** The general range of pH for effective metal biosorption ranges between 2.5 to 6. In acidic conditions, the functional groups on the biosorbent are more likely to be protonated, resulting in a positively charged surface. This positive charge on biosorbent enhances the biosorption of heavy metal ions on to it that are negatively charged. In alkaline conditions, the functional groups are more likely to be deprotonated, resulting in a negatively charged cell surface. This negatively charged bacterial cell wall repels the negatively charged metal ions, reducing the metal biosorption process [30], [33].

3. **Initial Metal Ion Concentration:** The initial metal ion concentration of heavy metal can have a significant impact on the efficiency and effectiveness of the biosorption process. The biosorption efficiency tends to be higher at lower initial concentrations as there are more available binding sites on the microbial biomass relative to the number of metal ions in the solution. But when the initial metal ion concentration increases, the system may reach saturation, resulting in the decreased biosorption efficiency [30].

V. DESORPTION AND RECOVERY OF HEAVY METALS

After biosorption the next crucial step is desorption of heavy metal from biosorbent. Desorption can be defined as a process where the adsorbed metal ions on the biosorbents are removed by using chemical agents. For desorption different chemical agents (eluent) can be used which includes, complexing agents (thiosulfate, EDTA), organic acids (acetic acid, citric acid) and mineral acids (HNO_3, H2SO$_4$, HCl). Recovery agents may affect the physical properties of biosorbents such as metal binding efficiency; hence proper care is required while selecting proper eluent or recovery agents. The selected eluent should be of low cost, environment friendly and non-damaging to the biomass [30], [2]. Type of desorption agent and percentage of desorption is tabulated (Table 2).

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Table 2: Desorption Agent used for Various Biosorbents [30].

S.no	Biosorbents	Heavy metal	Eluent	Percentage of desorption
1	*Aspergillus niger*	Cr	0.1 N Sodium hydroxide	90%
2	*Aspergillus flavus*	Cu (II)	0.1 N Nitric acid 0.1 N Sodium hydroxide	80%
3	*Rhizopus nigricans*	Pb (II), Cd (II), Ni (II), Zn (II)	Nitric acid	90%
4	*Montmorillonite*	Ni (II), Mn (II)	0.1 M hydrochloric acid	92.8%
5	*Scenedesmus sp*	Zn	0.1 M Sulfuric acid	99%

VI. ADVANTAGES OF BIOSORPTION

Microbes offer several advantages over to other conventional techniques. Some of the advantages are listed below.

- The cost of production of biological materials (microorganism) is economical.
- Effective removal of multitudinous heavy metals.
- Suitable for large volumes of wastewater and soil.
- Generation of secondary waste materials is minimal.
- Recovery of heavy metals is also possible by desorption process [20].

VII. CONCLUSION

Heavy metals from polluted sites can potentially be removed through biosorption process by using microorganism. Biosorption is the most economical and eco-friendly method for removal of heavy metal from the contaminated environment when compared to other conventional methods. However, for effective biosorption the choice of appropriate biomass and optimum growth parameters are essential. Nevertheless, understanding the biosorption mechanism for heavy metal remediation and the use of diverse living and non-living biosorbents holds a promising key in mitigating the toxic heavy metal from the metal contaminated environment.

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