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Review paper (NS-I)

BIOSORPTION : AN APPROACH FOR BIOREMEDIATION OF HEAVY METALS

Sharma Richa[1] and Gupta Mahendra K.*[2]

1. School of Studies in Microbiology, Jiwaji University, Gwalior (INDIA)
2. School of Studies in Botany, Jiwaji University, Gwalior (INDIA)

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ABSTRACT

Expansion of industrial activities generates huge amount of toxic substances in the environment including heavy metals, which is responsible for toxicity in animals and human beings. Thereby, it is necessary to remove these pollutants from industrial effluents before discharging it into the environment. However, there are many methods for example ion exchange, ultra filtration, electrodialysis, sedimentation and reverse osmosis are used for the treatment of heavy metals containing industrial effluent but they turned out more expensive and less effective when the pollutants are present at lower concentrations. Thus, cheaper and more effective method should be searched for decontaminate targets. Bioremediation involves use of different microorganisms that employ biosorption process to decontaminate heavy metals. For this, Seaweed, fungi, microbial biomass and agricultural waste could be used as excellent source of biosorbents. Besides this, recovery of valuable sources also possible through biosorption. Today, biosorption is one of the important bioresource technology for removal of metal pollutants. The aim of this review is to focus the mechanism of biosorption, various biosorbent, advantage and disadvantages of biosorptionto remove heavy metals from different sources because of its effective, economical and eco-friendly nature.

Key Words : Biosorption, Biosorbents, Heavy metals, Bioremediation, Decontaminate

INTRODUCTION

Heavy metal contamination is a serious threat for human health as well as for environment. Environmental contamination with heavy metals results from the use of pesticides and fertilizer, industrial activities such as metal processing, mining, electroplating, smelter, tanning, carpet washing and dying. "Heavy metal" is the group of metals and metalloids with atomic density greater than 4000 kg m^{-3}or 5 times more than water.[1] Fe, Ni, Zn and Cu are essential heavy metals in trace amount for various metabolic processes but may be toxic at higher concentration, while few for example Hg, Cd, Pb etc. are toxic even at low concentration. Presence of heavy metal pollutants in soil, water and air influences the activity of microflora, plants and human. Heavy metals are non-biodegradable and persist in the environment.[2] Tyagi et al.[3] reported that in industrial area of India, the concentration of heavy metals is higher than the permissible limit of World Health Organization. Introduction of heavy metals in food chain either ending up in food chain or affect life adversely. It has been assessed that species extinction between 1975-2015 happened at a rate of 1-11% per decade.[4]So removal of these substances is necessary for living beings. Chemical precipitation or coagulation are most used techniques for the treatment of adsorptive pollutants like heavy metals but these are more expensive and less effective when the pollutants present at lower concentration.[5] Ion exchange resins and active-ated carbon are most widely used adsorbent for heavy metals remediation of industrial waste water but their high cost and low efficiency highlight the use of cheaper adsorbents. Development and implementation of cost-effective process for removal or recovery of metals is essential in order to minimize the environmental hazard of toxic metal-containing effluents. Biosorption is an environmental friendly method which uses living and nonliving biomass. Biosorption is

*Author for correspondence

still in developing phase to improve the performance and minimize the cost.

DISCUSSION

Sources and adverse effects of heavy metal contamination

Severity of toxicity from heavy metals exposure depends on various factors such as type and form of heavy metals, route of exposure, duration of exposure and susceptibility of individuals. In order to minimize exposure of heavy metals in human beings, treatment of industrial waste water is necessary. Different sources of heavy metals and their health effects associated with human beings mentioned in **Table 1**.

Table 1 : Sources and harmful effects of heavy metals

S/N	Heavy metals	Sources	Harmful effects
1.	Cadmium	Rechargeable batteries, industrial emissions, sewage and application of fertilizers	Affect kidney and causes bone demineralization hence increase the chances of fracture and bone fragility.[6]
2.	Mercury	Industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer, batteries, thermometers, fluorescent light tubes, pesticides, cosmetics and pharmaceuticals	Affect nervous system and brainmay result in irritability, shyness, and tremors etc., Exposure to high levels can permanently damage the brain, kidney and developing fetuses etc.[7]
3.	Lead	Contamination of drinking water with lead may result from the corrosion containing plumbing, Other sources: Mines, smelter and welding of lead painted metals, batteries	Highly toxic metal that shows neurotoxic effects. High level of exposure associated with the brain and kidney damage, miscarriage in pregnant women, damage the organs responsible for sperm production in man.[7]
4.	Nickel	Mining, refining, municipal waste incineration, coal and oil combustion and electroplating industries	Drinking water contains nickel higher than normal level creates stomach aches andincreased red blood cells and affect kidneys.[8]
5.	Zinc	Mining, combustion of coal and waste material and through steel industries.	Causes stomach cramps, skin irritations, vomiting and nausea, also may cause anemia and damage the pancreas.[9]
6.	Copper	Coal-fired power stations, metal production, waste incinerators, sewage treatment processes and with the application of agricultural chem.-icals, leaching of copper from water pipes.	Drinking high level of copper containing water creates nausea, vomiting, stomach cramps or diarrhea, high intakes of copper can cause liver and kidney damage and even death.[10]

Biosorption

Modern industries are responsible for large degree of metal contamination in environment. It is necessary to reduce bioavailability, mobility and toxicity of heavy metals to minimize this problem. In modern era, biosorption became an effective method for removal of heavy metals from industrial effluents with the use of biological material. Naturally available biomass such as sea weeds, molds, yeasts, bacteria can be used for this purpose and are called as biosorbant. It may be specific for certain types of metals or shows no specific priority.[11] A biomass should be a cheaper source for metal remediation, easily available in nature and have fast growing capacity.[5,12] Non-viable biomasses possess a property of metal sequestering which makes it suitable for heavy metals removal even from low metal concentration solution.[13] Various chemical groups viz. hydroxyl, carbonyl, car-boxyl, sulfhydryl, thioester, imine, amide, imidazole and phosphodiester, present on bacterial, algal and fungal cell wall contribute to biosorption.[14,15] Importance of any given group for biosorption of a certain metal by certain biomass depends on the no. of sites in the biosorbant material, accessibility, chemical state of the site (availability) and affinity (binding strength between site and metal).[5]

Mechanism of biosorption

Biosorption is a property of certain types of living and nonliving biomass to bind and concentrate heavy metals from even very dilute aqueous solution. These biomass acts as an ion exchanger. The biosorption process comprises a solid phase (biosorbant or sorbent) and a liquid phase which contains a dissolved species to be sorbed (Sorbate or metal ion). Sorbent possess high affinity for the sorbate, the sorbate is attracted and removed from the solution. The process continues till equilibrium is established between the amount of solid bound sorbate and its portion remaining in the solution.[16] Microorganism uptake metals either actively (bioaccumulation) or passively (biosorption).[17,18] Biosorption with nonliving biomasses is more feasible than bioaccumulation (by living organisms) because active uptake of metal often require the addition of nutrients and complicated bioreactor system.[19] In addition, problem of maintaining the healthy microbial population due to the metals toxicity also occurred in bioaccumulation. Difficulty in recovery of valuable metals by living organism due to the intracellular binding also focused the use of nonliving biomass in biosorption.[19,20] Mechanisms of biosorption includes complexation, chemisorption, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces etc.[19] The process depends on different factors e.g. type of biomass, type of metal, concentration of metal ions and environmental condition such as pH, temperature etc.

Biomass for biosorption

Origin of biomass is the major factor to be taken into account. Capacity, affinity and specificity of the biosorbents and their physical and chemical conditions in effluents influence the efficiency of biosorption. Biosorption by living cells completed in two steps, first, metals are absorbed to the surface of cells with the help of functional group present on cell wall of organism, which is passive phen-omenon. Polysaccharide and protein content of cell wall possess a number of active sites that have capability to bind with the metals. In second step, which is active biosorption, metal ion penetrate the cell membrane and enter into the cells.[16] Algae, fungi, bacteria, mushroom, waste material and many other biosorbents reported for biosorption given in **Table 2**.

Algae

Use of algal biomass as a biosorbent is economical and more attractive due to low nutrition requirement. They are autotrophic thus, produce large quantity of biomass and do not produce toxic substances. Biosorption capacity of different red, green and brown algae has been studied by Romeraet al.[21] suggested use of algal biomass in recovery of cadmium, copper, zinc, nickel and lead from aqueous solution. Study revealed that pH 6 was optimum for recovery of Cd, Ni and Zn while less than 5 pH was suitable for Cu and Pb. In the study the best results were obtained with *Fucusspiralis*.

Fungi

Waste fungal biomass from industrial ferm-enter provides an ecofriendly and cost effective material for metal biosorption on large scale. Presence of high percentages of cell wall material in the fungi make it suitable for biosorption which shows excellent metal binding properties.[22] Sugasiniet al.[23] studied the biosorption potential of *Aspergillus*sp. from tannery effluent and observed that four *Aspergillus*sp. namely*A. terreus, A. tamarii, A. flavus*and *A. niger*have biosorption capacity for chromium. In this study, both live and alkali pretreated fungal biomass was compared for their biosorption capacity and revealed that alkali pretreated fungal biomass exhibit more biosorption capacity than the living once.

Bacteria

A number of potential bacterial species are available for biosorption of metals. High surface-to-volume ratio and a high content of potentially active chemosorption sites such as on teichoic acid in their cell wall make it excellent material for biosorption.[24] *Bacillus* sp. has been used in commercial biosorbent prepa-ration due the high potential of metal seque-stration.[22] A study by Bhaktaet al.[25] sugge-sted that heavy metals can also be removed from living system by biosorption. They reported *Lactobacillus reuteri* as a potential cadmium and lead removal Lactic acid bacteria in vivo challenge in the intestinal milieu of fish for the uptake and control of heavy metal bioaccu-mulation.

Yeast

Chemical compounds of yeast cells can also act as ion exchangers with rapid reversible binding of cations. Thippeswamyet al.[26] repor-ted that *Saccharomycescerevisiae* has showed high biosorption of Cd^{2+} (67%), followed by Pb^{2+} (61%), Ni^{2+} (64%), Cr^{6+} (63%), Cu^{2+} (57%), Zn^{2+} (53%). After elemental analysis by EDS they confirmed that bios-orption by *S. cerevisiae*mainly due to the ion exchange. The metal biosorption was found maximum in single metal system compared to multi metal ions.

Mushroom

Advance research conducted on biosorption highlights the absorption capacity of both edible and non-edible varieties of mushrooms for heavy metals. It has been resulted that heavy metals concentration is considerably higher in mushroom than in other agricultural crops. This indicates that there is an effective mechanism in mushrooms that enables them readily accumulates heavy metal from the environment.[27,28]

Kariukiet al.[29] reported biosorption of lead and copper using rogers mushroom biomass '*Lepiotahystrix*'.Presence of functional groups such as hydroxyl, carbonyl and carboxyl are responsible for binding of metal's ions. The adsorption capacity in the study was found to be 3.89 and 8.50 mg/g for Pb and Cu respectively.

Waste material from food industries and agriculture

Agricultural by product for example peat, wood, pine bark, soybean and cotton hulk, rice bran, saw dust, wool have been demonstrated to remove heavy metals from waste water.[30]

Advantage and disadvantage of biosorption

Advantages

Biosorption is the cheaper method for heavy metal remediation because biosorbent often made from abundant or waste material. Biosorption shows high efficiency because it can remove even small amount of heavy metals from the solution and it is also possible to recover metal from the aqueous solution. Unlike precipitation, biosorption does not produce high quantity of sludge.Biosorbant are regenerative thus can be reused after metal is recycled.

Disadvantages

In this process, Metal desorption is necessary prior to further usewhen metal interactive site are occupied.There is no potential for biologically altering the metal valency state.Biological process improvement e.g. through genetic engineering of the cells, is limited because cells are not metabolizing.[50]

Table 2 : Different biosorbents reported for biosorption of various heavy metals[31-46]

S/N	Metals	Biosorbent	Reported by
1	Cr(VI)	Green algae *Spirogyra*	Gupta et al.
2	Pb(II)	*Rhizopusnigricans*	Kogej et al.
3	Cu(II)	Modified cellulosic materials	Acemıoglu and Alma
4	Zn(II), Cd(II)	Coconut husk	Babarinde
5	Cu ion	Brown seaweed *Sargassum*sp.	Antunes et al.
6	Co(II)	Hazelnut shells	Demirbas
7	Cr, Pb, Cu	*Staphylococcus saprophyticus*	Ilhan et al.
8	Cr, Ni	Raw rice bran	Oliviera et al.
9	Cr(VI)	Black tea leaves	Hossain et al.
10	Cr(VI)	*Ecklonia* biomass brown seaweed	Park et al.
11	Cr(III) & Cr(VI)	*Pseudomonas aeruginosa*	Kang et al.
12	Cu(II) & Co(II)	Crab shell particles	Vijayaraghavan et al.
13	Hg(II)	Modified sunflower stalk	Hashem et al.
14	Cr	Attenuated cultures of *B.Subtilis* and *Pseudomonas aeruginosa*	Tarangini and Satpathy
15	Cu(II)	Neem leaf based adsorbents	Sethu et al.
16	Cd(II), Pb (II)	*Anabaena sphaerica* biomass	Abdel-Aty et al.
17	Cd(II), Pb(II), Ni(II)	*Aspergillus* and *Penicillium*	Pattanayak et al.
18	Pb(II)	Cashew nut shell derived adsorbent	Phromraket al.

CONCLUSION

In modern era, Biosorption becomes a useful alternative to conventional methods for the removal of toxic metals from industrial effluents. Extensive research has been made on biosorption using various species of live or inactivated biomass of bacteria, fungi, algae and yeast. Adsorption using low cost natural and waste biomasses constitutes the basis for a new cost effective technology. The application of modern molecular biotechnology to microorganisms may greatly enhance the specificity of biosorbents. Research in the field of biosorption has focused the development of microbial material with increased affinity, capacity and selectivity for target metal. In future, more attention should be given to this area.

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