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REVIEW ARTICLE

Macroalgae as a Potentially Low-Cost Biosorbent for Heavy Metal Removal: A Review

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ABSTRACT

Biosorption is a promising technology not only for the removal of heavy metals but also for the recovery of precious metals from solution phases. The conventional methods available for removal of heavy metal are costly and also produce some toxic sludge. This has lead to the invention of new technology like biological removal of heavy metal. This paper reviews some practical aspects of the application of algal biomass for the biosorption of heavy metals from wastewater. The ability of different algal species to remove metals varies with algal group and morphology, with the speciation of specific metals and their competition with others in wastewater, and with environmental or process factors. The scattered literature on the uptake of heavy metals by dead algal biomass of macroalgae has been reviewed, and the uptake capacity and efficiency of different species, as well as what is known about the mechanisms of biosorption, are presented.

Keywords*:* Macroalgae, biomass, biosorbent, heavy metal, mechanism.

INTRODUCTION

Currently environmental pollution is one of the issues of serious concern in the whole world since industrial activities contribute to the growth of the economy at the expense of the environment especially in developing countries. Huge amount of wastewater is discharged to the environment above the level that nature can eliminate as a result of increasing population and industrial developments such as the textile industry which discharges huge amount effluents with abnormal physicochemical properties particularly from its wet processes which demands environmental monitoring [1]. The Indian environmental mangers and researchers have recently explained the condition of freshwater resources in India and their management as a serious environmental problem which includes nutrition enrichment, acidification and domestic waste, agricultural waste, sewage and industrial effluents toxic substances identified as major impacts [2]. A study has revealed that almost in India 70% of surface water resource and ground water reserves have been contaminated by biological, organic and inorganic wastes [3]. A number of studies on heavy metal removal from solution have been launched because of the ecological effects of toxic metals released into the environment [4].

Environmental pollution from man-made sources can easily create local conditions of elevated metal presence and this case could lead to some hazardous effects on animals and humans [5]. Various methods have been employed in the removal of heavy metals from industrial effluents. Among them, include ion exchange, chemical precipitation, membrane filtration, reverse osmosis, evaporation, oxidation, electro dialysis, solvent extraction, activated carbon adsorption [6]. Hence the cost-effective and efficient naturally abundant alternatives to the conventional methods of metal contaminated industrial waste water treatment are required [7].

Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution. This implies that the removal mechanism is not metabolically controlled. In contrast, the term bioaccumulation describes an active process whereby removal of metals requires the metabolic activity of a living organism. In recent years research on the

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mechanisms of biosorption has intensified since biomass can be employed to sequester heavy metals from industrial effluents (e.g. from the mining or electroplating industry) or to recover precious metals from processing solutions [8]. Recent biosorption experiments have focused attention on wastes, which are by-products or the waste materials from large-scale industries. For e.g. the waste mycelia available from fermentation processes, olive mill solid residues [9], activated sludge from sewage treatment plants [10], biosolids [11], aquatic macrophytes [12], etc.

One of the most abundant and highly available natural resources in tropical ecosystems is alga. Along with its industrial valorization in the cosmetics, pharmaceutical and food industries, the use of alga for environmental decontamination is an interesting field of research and development. Indeed, based on their rich biochemical composition, the algal biomass is a very promising material to be used as adsorbent to remove various kinds of pollutants from contaminated water and wastewaters [13].

Marine algae, popularly known as seaweeds, are biological resources, which are available in many parts of the world. Algal divisions include red, green and brown seaweed; of which brown seaweeds are found to be excellent biosorbents. This is due to the presence of alginate, in gel form and their macroscopic structure offers a convenient basis for the production of biosorbent particles that are suitable for sorption process applications. N umerous approaches have been made for the development of low-cost sorbents from industrial and agricultural wastes. Of these, crab shells, rice husks, activated sludge, egg shell and peat moss deserve particular attention [14].

Seaweeds offer several advantages for biosorption because of their larger surface area. This offers a convenient basis for the production of biosorbent particles suitable for sorption process. They contain many polyfunctional metal-binding sites for both cationic and anionic metal complexes. Potential metal cation-binding sites of algal cell components include carboxyl, amine, imidazole, phosphate, sulphate, sulfhydryl, hydroxyl and chemical functional groups contained in cell proteins and sugars. Brown algae stand out as very good biosorbent of heavy metals [15]. Seaweeds are widely available source of the biomass. Annually, 2 million tonnes of algae is harvested from seas and oceans or are cultivated in artificial systems [16].

Algae are special interest for and the development of new biosorbent material due to their high sorption capacity and ready availability in practically unlimited quantity. According to statistical review on biosorption, algae have been used as biosorbent material 15.3% more than other kinds of biomass and 84.6% more than fungi and bacteria. Brown algae among the three groups of algae (red, green and brown) received the most attention. Higher uptake capacity has been found for brown algae than for red and green algae [17]. Brown algae stand out as very good biosorbent of heavy metals [18]. Their cell walls contain fucoidin and alginic acid. The alginic acid offers anionic carboxylate and sulfate ions at neutral pH. There are several chemical groups that could attract and sequester the metals in biomass like acetamido groups of chitin, amino and phosphate groups in nucleic acids, amino, sulfhydryl and carboxyl groups in amino acids and proteins, hydrohyls in polyaccharides etc. The presence of some functional group does not guarantee their accessibility for sorption, perhaps due to the steric, conformational or other barriers [19].

It seems likely that algae do not form a homogeneous group within the vegetal kingdom. They are divided into several evolutionary pathways completely independent: a ‘‘red pathway’’ with red algae (Rhodophyta), a ‘‘brown pathway’’ with brown algae (inter alia, Chromophyta) and a ‘‘green pathway’’ that includes green algae (Chlorophyta) along with mosses, ferns and several plants. Differences between these types of algae are mainly in the cell wall, where sorption takes place. The cell walls of brown algae generally contain three components: cellulose, the structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium and calcium; and sulphated polysaccharides. As a consequence, carboxyl and sulphate are the predominant active groups in this kind of algae [20].

The biosorption of the heavy metal ions on the cell surface occurs by ion exchange process. Brown marine alga *Sargassum vulgaris* was found to uptake metals like Cd, Ni, Pb by the main chemical groups on their surface such as carboxyl, amino, sulfhydryl and Sulfonate [21] studied the biosorption of zinc metal ion by *Anabaena variabilis*.

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Table 1: Three algal divisions and significant characteristics

Division	Common name	Pigments	Storage product	Cell wall	Flagella
Chlorophyta	Green algae	Chlorophyll a,b; a-b- and g-carotenes and several xanthophylls	Starch (amylose and amylopectin) (oil in some)	Cellulose in many (b-1,4-glucopyroside), Hydroxyproline glucosides; xylans and mannans; or wall absent; calcified in some	Present
Phaeophyta	Brown algae	Chlorophyll a,c; b-carotene and fucoxanthin and several other xanthophylls	Laminaran (b-1,3-glucopyranoside, predominantly); mannitol	Cellulose, alginic acid, and sulfated mucopolysaccharides (fucoidan)	Present
Rhodophyta	Red algae	Chlorophyll a (d in some Florideophyceae); R- and C-phycocyanin, allophycocyanin; R- and B-phycoerythrin. a- and bcarotene and several xanthophylls	Floridean starch (amylopectin-like)	Cellulose, xylans, several sulfated polysaccharides (galactans) calcification in some; alginate in corallinaceae	Absent

Information in this table is from a similar, more extensive table compiled by [22].

The cell wall of algae consists of chitin, lipids, polysaccharides and proteins. These macromolecules provide different functional groups, such as thioether, carboxyl, imidazole, hydroxyl, carbonyl, phosphate, phenolic, etc., which can form coordination complexes with heavy metals. Algal biomass can be used for biosorption process in live or dead form. However, in applications, the use of nonliving biomass is more practical and advantageous because living biomass cells often require the addition of fermentation media which increases the biological oxygen demand or chemical oxygen demand in the effluent. In addition, non-living biomass is not affected by the toxicity of the metal ions, they can be subjected to different chemical and physical treatment techniques to enhance their performance. Physical treatment methods such as heat, acid and base treatments have usually shown an increase in biosorption capacity of biomass due to re-organization of cell wall structure [23]. Typical algal cell walls of Phaeophyta, Rhodophyta, and many Chlorophyta are comprised of a fibrillar skeleton and an amorphous embedding matrix. The most common fibrillar skeleton material is cellulose (**Fig 1**).

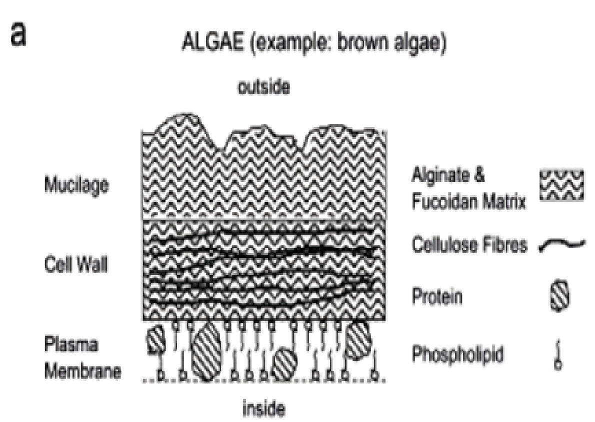

Fig 1: Cell wall structure in the brown algae [24]

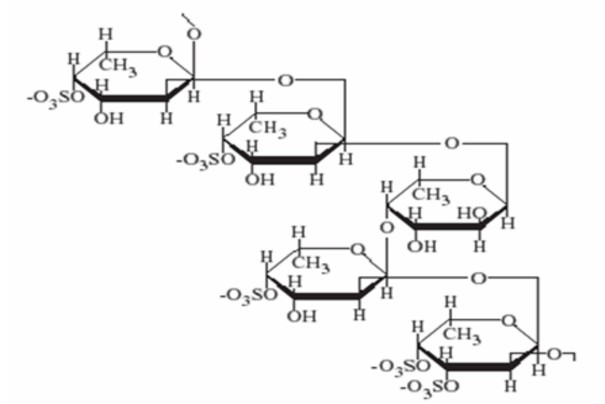

Fig 2: The structure of fucoidan, a branched polysaccharide sulfate ester with L-fucose building blocks as the major component [8]

Celulose content in *Ascoflillum* and *Laminaria* were determined as been 7 and 20% respectively. Extracelular polysaccharide as fucoidan (Fig. 2) occurs abundantly in species as *Fucus* and *Chordaria*, as well as in other brown algae from families *Laminariaceae* (which store within 5-20% of its dry weight). While alginates structural data in (**Fig 3**).

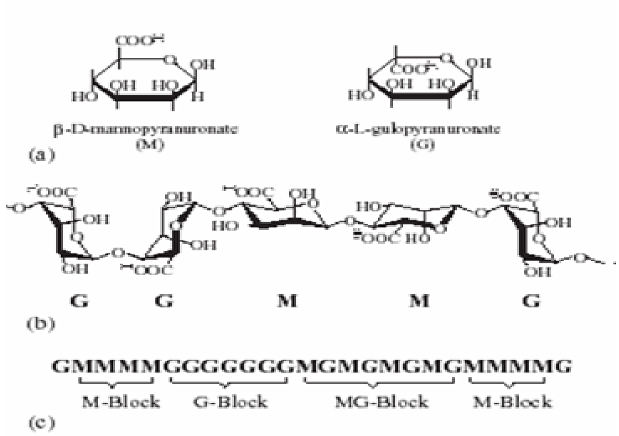

Fig 3: Alginate structural data: (a) alginate monomers (M vs. G); (b) the alginate polymer; (c) chain sequences of the alginate polymer [8]

There is an increasing amount of work being focused on heavy metal biosorption by brown seaweed [25]. Brown algae are generally known for their richness in carboxylic and sulfonate groups [4], which are mainly responsible for interactions between alga's surface and the pollutants [26]. In terms of metal sorption capacity, brown seaweed is superior to other algal species such as red and green seaweeds [27].

Table 2: Biosorbents used in some biosorption purposes

S.No	Metal	Biosorbent	Reference
1	Sm and Pr	*Sargassum* sp.	[28]
2	Cu	*Sargassum* sp.	[29]
3	Co and Ni	*Sargassum ilicifolium*	[30]
4	Cd, Zn, and Pb	*Sargassum muticum*, and *Fucus spiralis*	[31]
5	La, Nd, Eu, and Gd	*Sargassum* sp.	[32]
6	Pb and Zn	*Phanerochaete chrysosporium*	[33]
7	Ni	*Sargassum wightii*	[34]
8	Cr	*Sargassum* sp	[35]
9	Pb, Zn, Cd, and Ce	*Laminaria japonica*	[36]
10	Dy, Ho, Yb, and Lu	*Sargassum honeri*, and *S. hemiphyllum*	[37]
11	Cd, Pb, Cu, Ag	*Cladophora crispata*	[38]
12	Pb	*Cladophora fascicularis*	[39]
13	Cd	*Codium fragile and Corallina officinalis*	[40]
14	Cu, Ni	*Colpomenia sinuosa*	[26]
15	Pb	*Sargassum hystrix* and *Sargassum natans*	[41]
16	Cr	*Ecklonia sp*	[42]
17	Cd, Zn, Pb, Cu	*Fucus vesiculosus*	[25]
18	Cd	*Fucus ceranoides* and *Fucus serratus*	[43]
19	Cu	*Fucus spiralis* and *Palmaria palmata*	[25]
20	Cd, Cu	*Gracilaria fischeri*	[44]
21	Pb, Cu, Cd, Zn, Ni	*Gracilaria sp.* and *Padina sp*	[27]
22	Cd, Ni	*Padina pavonia*	[45]
23	Pb, Cu, Cd, Zn, Ni	*Sargassum sp.*	[46]
24	Cd, Ni	*Sargassum vulgaris*	[45]
25	Pb	*Turbinaria conoides*	[47]
26	Zn	*Ulva reticulata*	[48]
27	Pb, Cu, Cd, Zn, Ni	*Ulva sp*	[25]
28	Cr, Co, Ni, Cu, Cd	*Laurencia obtusa*	[49]
29	Pb	*Jania rubrens*	[49]
30	Pb	*Ulva lactuca*	[49]
31	Cu, Ni	*Ulva fascia*	[26]
32	Cu	*Palmaria palmata*	[25]
33	Cu, Ni	*Petalonia fascia*	[26]
34	Al, Cd, Co, Cr, Cu, Fe, Ni, Zn,	*Pilayella littoralis*	[50]
35	Cd	*Porphyra columbina*	[40]
36	Pb	*Sargassum asperifolium*	[49]
37	Cu, Ni	*Sargassum hemiphyllum*	[26]
38	Pb	*Sargassum hystrix,*	[41]
39	Pb	*Sargassum natans*	[41]
40	Pb	*Laminaria japonica*	[51]

Among different brown seaweeds, it has been noted that Sargassum spp. possesses a relatively high metal binding capacity [52]. *Sargassum* sp. can be used for metal adsorption and to clean waste Water from the environment [53]. *Sargassum* sp. is a widespread and common kind of marine brown algae that has been used for metal recovery, due to the high content of polysaccharides in the cell wall, which are responsible for the high sorption capacity [54].

Mechanisms involved in biosorption can be classified taking into account various criteria that are, based on cell metabolism, they are classified

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as metabolism dependent and non- metabolism dependent while based on location of the sorbate species it is classified as extra cellular accumulation/precipitation, cell surface sorption /precipitation and intra cellular accumulation. The adsorbed ions are transported across the membrane in the same mechanism by which metabolically important ions such as potassium, magnesium, and sodium are conveyed [55].

Biosorption removes metal ions by biological materials and biomaterials and have been considered as potentially important sorbents for heavy metal removal. Sorption is widely used and several materials have been studied, recently, surface modification has been explored with intense interest in order to improve surface area, sorption kinetics and specifications of sorbent [56].

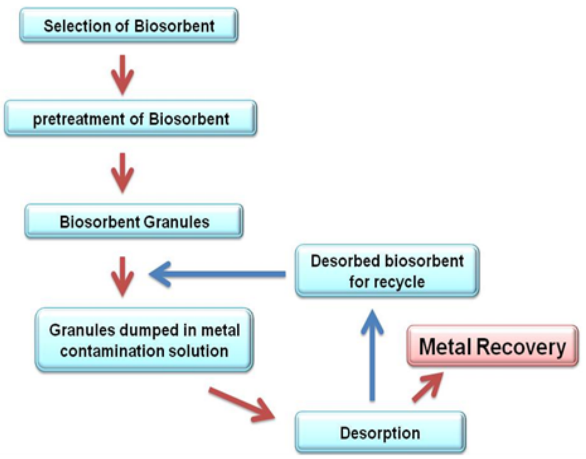

Fig 4: General schematic representation of biosorption process [55]

Overall, biosorption is defined as the capacity of a substrate to retain metallic species, ionic forms or ligand from fluids in the molecular structure of the cell wall. The biosorption mechanisms include extracellular and intracellular bonds, as well as complex interactions that depend on the type of metal and the biosorbent structure [8].

The mechanism of the metal biosorption is a complex process. The status of biomass (living or non-living), type of biomaterials, properties of metal solution chemistry, environmental conditions such as pH, influence the mechanism of biosorption [57]. The elucidation of the mechanism of metal uptake is essential to develop technologies related to the metal recovery [58]. Based on cell metabolism, mechanisms involved in biosorption can be categorized as metabolism dependent and metabolism independent, while they are classified as extra cellular accumulation/ precipitation, cell surface sorption and intra cellular accumulation on the basis of the location of the sorbate species. Other mechanisms for biosorption are transport across cell membrane, ion exchange and complexation [55].

The main substances in brown algae are alginates, which usually constitute around 20–40% of the total dry weight and fucoidans. They are likely to be the main functionalities involved in pollutant binding reactions [59]. Seaweed has been reported to be rich in other extracellular polymer on its cell wall matrix, with the alginate polysaccharide being responsible for ion exchange capacity of the brown algae due to the capacity of carboxyl group [60]. The uptake of heavy metals may differ between seaweeds species e.g brown seaweeds are considered to be better bioaccumulators of heavy metals than their green counterparts. It could be used as a universal bioindicator. Macro algae biomass has been considered as a relatively high adsorption capacity for removal of heavy metal ions has attracted attention over the last decades [61].

Mechanisms of heavy metal uptake by algae

The mechanism by which biological materials remove metals is not completely understood. The performance of the biosorbent depends on the ionic state of the biomass. The uptake of metals by biomass is a two step process, the cells of biomass contains proteins and polysaccharides which offer a lot of binding site for heavy metals. The first step is the stoichiometric interaction between the cell components and the metal ions. The second step is the accumulation of heavy metal on the binding sites [62].

Elucidation of mechanisms active in metal biosorption is essential for successful exploitation of the phenomenon and for biosorbent regeneration in multiple re-useable cycles. The main uptake mechanisms suggested are: ion exchange between protons and heavy metal ions at the binding site or light metals and heavy metals [43,63] adsorption by physical forces, electrostatic interactions [64], chelation, complexation [63], microprecipitation [65]. Extracellular polysaccharides (such as alginates and fucoidans) are the main components of cell walls responsible for metal uptake [43]. Because of their high content of such polysaccharides, brown algae may have a higher uptake capacity than other algae [43]. Theoretically, the type of sorption mechanism (physical /chemical) is given by the magnitude of of ΔH (enthalpy change) for a given sorption process calculated from sorption isotherm data obtained at different temperatures [68]. So that, thermodynamically the heat of adsorption (ΔH), ranging from 0.5 to 5 kcal/mol (2.1–20.9 kJ/mol) gives physical adsorption mechanisms, and the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions, 5– 100 kcal/mol (20.9–418.4 kJ/mol) [39]. It is supposed that biosorption on dead biomass involve a physical sorption phenomenon while biosorption on active biomass involve both physical and chemical sorption phenomena plus transmembrane and accumulation of heavy metals in the cell. Bioaccumulation occurs in two stages, biosorption where metal ions bind to the cell wall via an ion exchange mechanism and metal ion transportation into the cellular interior [67].

Ion exchange

Ion exchange has been suggested as being the dominant mechanism of biosorption by algal biomass [68,69]. Generally, the biomass if is not treated, contains light metals ions such as K+, Na+, Ca+2, Mg+2 which are bound to the acid functional group of the alga. In biosorption process these anions are exchanged with heavy metals. C ontinuous laboratory scale column to evaluate the release of light metals from stipes and blades of *Sargassum sp*. in biosorption testes for Zn uptake. After digestion, they found the amount of light metals in stipes higher than in blades. They concluded that both alkaline and alkaline-earth elements have been contributed for the biosorption of zinc [70].

Coordination or complex formation

The metal removal from solution can also take place via complex formation onto the cell surface as result of interaction between metal and active groups. This phenomenon involves covalent coordination and links electrostatic forces. Studying biosorption of Cu by *Chlorella vulgaris*, one of the mechanism of Cu removal is formation of coordination bonds between metals and amino and carboxyl groups of the cell wall polysaccharides [71].

Microprecipitation

Precipitation can take place when pH of solution varies in process due cellular metabolism and/or even when concentration of ionic species in wastewater increases up to their saturation index. The metal removal from solution is sometimes associated with active defence of biomass producing compounds which favours precipitation. More or less simultaneously can take place precipitation dependent or not by biomass metabolism. Microprecipitation can produce a distortion of sorption results and hinder determination of the amount of metal uptake [72].

Chelation

Bases contain more or one ligand atom, a multidentate complex, can occupy more than one coordination position in the complex. Chelates are complex formation with multidentate ligands and the phenomenon has been called chelation. The terms inner-sphere and outer-sphere complex are used to distinguish between binding which is, respectively, largely covalent in character or chiefly electrostatic in nature. In the first case, the interacting ligand is immediately adjacent to the metal cation. In the second case, ions of opposite charge are attracted and approach each other within a critical distance and effectively form what is termed an ion pair. In outer-sphere complexes, the metal ion or the ligand or both generally retain their coordinated water when the complex is formed. In other words, the metal ion and the ligand are most often separated by one or more water molecules [8]. Some live microalgae (e.g. *Chlorella miniata*) can also bioreduce the metal from its high valence state (e.g. Cr (VI)) via complexing with polysaccharides as reductants, then transported and accumulated inside the cell [64].

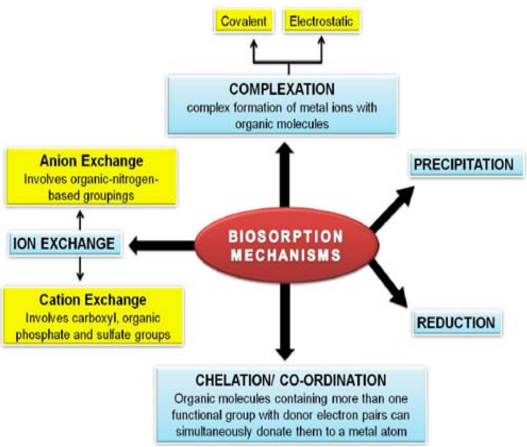

Fig 5: Mechanism of Biosorption [55]

This material presents a high organic leaching when used for metal waste treatment. The organic leaching can be many and would hinder its industries applications. This can lead to a secondary pollution and also to a decrease in the adsorption performance in water and wastewater treatment [54]. Therefore, it is important to modify the material before its application in biosorption processes. This modification can be done by using base, acid, calcium, or aldehyde [73].

Applications of biosorption

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The process of biosorption offers several benefits than bioaccumulation since there is no need of providing the growth conditions, no growth media is required and these materials are available as wastes or by-products. Research in biosorption suggests the following advantages over other techniques [74]:

1. The materials are usually wastes or by-products and at almost no cost.
2. There is no need of costly growth media and aseptic conditions.
3. The process is independent of physiological constraints of living cells.
4. Process occurs at a very rapid rate because the ion exchange resins behavior of the material, metal loading is very high.
5. Reversible process, after metal desorption the material can be subjected for the further recycle.
6. The formation of chemical or biological sludge is minimized.

CONCLUSION

Algal biomass is a useful alternative to conventional adsorption products for heavy metal uptake from industrial effluents. Metals can be removed over broad range of pH, temperature and initial concentration. The cost of the process is lesser compared to other techniques. Low concentration of heavy metals in effluents can be easily and effectively removed using biosorbents. Literature review reveals that a particular biosorbent can be used to remove a wide range of metals. Algae are found to have more metal removal capacity than bacteria. Biological sorbents are applicable for all kinds of industrial effluents, the biggest advantage is that their ability to remove heavy metals from effluents containing low concentrations of metals.

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