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Application of Biosorption for Removal of Heavy Metals from Wastewater

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Abstract

Fresh water accounts for 3% of water resources on the Earth. Human and industrial activities produce and discharge wastes containing heavy metals into the water resources making them unavailable and threatening human health and the ecosystem. Conventional methods for the removal of metal ions such as chemical precipitation and membrane filtration are extremely expensive when treating large amounts of water, inefficient at low concentrations of metal (incomplete metal removal) and generate large quantities of sludge and other toxic products that require careful disposal. Biosorption and bioaccumulation are ecofriendly alternatives. These alternative methods have advantages over conventional methods. Abundant natural materials like microbial biomass, agro-wastes, and industrial byproducts have been suggested as potential biosorbents for heavy metal removal due to the presence of metal-binding functional groups. Biosorption is influenced by various process parameters such as pH, temperature, initial concentration of the metal ions, biosorbent dose, and speed of agitation. Also, the biomass can be modified by physical and chemical treatment before use. The process can be made economical by regenerating and reusing the biosorbent after removing the heavy metals. Various bioreactors can be used in biosorption for the removal of metal ions from large volumes of water or effluents. The recent developments and the future scope for biosorption as a wastewater treatment option are discussed.

Keywords: biosorption, heavy metal, isotherm, water, waste, pollution

1. Introduction

Water plays an important role in the world economy. Majority (71%) of the Earth's surface is covered by water, but fresh water constitutes a miniscule fraction (3%) of the total. Water fit for human consumption is obtained from the fresh water bodies. Approximately, 70% of the fresh water goes to agriculture. This natural resource is becoming scarce at many places and its unavailability is a major social and economic concern [1]. Though access to safe drinking water has improved over the last few decades, it is estimated that five million deaths per year are caused due to consumption of polluted drinking water or drought. In many developing countries, 90% of all wastewater still goes untreated into the fresh water bodies making it unfit for human consumption, which either leads to scarcity or affects the human population [2]. The concern to protect fresh water bodies for a healthy population is a challenge in recent times.

Industrialization to a larger degree is responsible for the contamination of environment especially water where lakes and rivers are overwhelmed with a large number of toxic substances. Heavy metals are reaching hazardous levels when compared with the other toxic substances [3]. Heavy metals are a unique group of naturally occurring compounds. Their continuous release leads to overconsumption and accumulation. As a result, people around the globe are exposed to adverse consequences of these heavy metals. Many industries (fertilizers, metallurgy, leather, aerospace, photography, mining, electroplating, pesticide, surface finishing, iron and steel, energy and fuel production, electrolysis, metal surface treating, electro-osmosis, and appliance manufacturing) discharge waste containing heavy metals either directly or indirectly into the water resources [4]. Toxic heavy metals, which are of concern, are chromium (Cr), lead (Pb), zinc (Zn), arsenic (As), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd), mercury (Hg), and so on. As these metals are not biodegradable, they tend to accumulate in the living organisms and lead to various diseases and disorders which ultimately threaten human life. They can cause ill health, even when present in the range of parts per billion (ppb) [5]. Biosorption has emerged as an attractive option over conventional methods for the removal of heavy metal ions from effluents discharged from various industries which ultimately reach and pollute fresh water bodies. This chapter reports the toxicity of heavy metals, the advantages of biosorption, various biosorbents used for the removal of metal ions, effect of immobilization and modifications of biosorbents, various factors affecting the process of biosorption, different bioreactors used in biosorption, and the application of biosorption for the removal of metal ions from various wastewaters like industrial effluents and contaminated water resources. The recent advances, current status, and future of the process are discussed.

2. Toxicity of heavy metals

The pathway of exposure for heavy metals is mainly through inhalation, dermal contact, and ingestion. The individual metal exhibits its own specific signs of toxicity [6]. The severity of health effects is dependent on time and dose, the type of heavy metal, and its chemical form. The nature of effect may be toxic, mutagenic, neurotoxic, teratogenic, or carcinogenic [6]. Many studies reported that heavy metals affect cell organelles and interact with cell components causing cell damage and apoptosis. Even at a low level of exposure, they induce multiple organ damage.

Intoxication of heavy metals also leads to damage to the major systems in the body and may lead to an increased risk in developing cancers [7]. Metal ion pollution is highly persistent, and most of them are nonbiodegradable. The presence of various heavy metals such as chromium (Cr), lead (Pb), zinc (Zn), arsenic (As), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd), and mercury (Hg) causes disturbances in circulatory, gastrointestinal, and nervous systems. They also affect various organs and lead to blindness, deafness, brain damage, loss of fertility, cancer, and many other severe health problems that ultimately cause death of the individual [7–9].

3. Conventional methods for heavy metal removal

Heavy metals like nickel, copper, zinc, cadmium, chromium, lead, and mercury are major pollutants that affect the fresh water reservoirs due to the discharge of large amounts of metal-contaminated wastewater from industries. Because of their persistent, non-biodegradable, and toxic nature, they accumulate in the environment such as in the food chain and cause serious health disorders. Over the last few decades, many conventional treatment methods have been used for the removal of heavy metals from contaminated wastewaters. The commonly used methods include chemical precipitation, ultra-filtration, ion exchange, reverse osmosis, electro winning, and phytoremediation, and they are introduced briefly [10–14].

Chemical precipitation is the most widely used method for heavy metal removal from inorganic effluents. The conceptual mechanism involved is that the dissolved metal ions get precipitated by chemical reagents (precipitants) and result in the formation of metal hydroxides, sulfides, carbonates, and phosphates (insoluble solid particles) that can be simply separated by sedimentation or filtration.

Ion exchange is based on the reversible exchange of ions between solid and liquid phases. An ion exchanger is a solid resin capable of exchanging both cations and anions from an electrolytic solution and releases counter-ions of similar charge in a chemically equivalent amount.

Membrane filtration is capable of removing not only metal ions but also suspended solid and organic components. A membrane is a selective layer used to make contact between two homogeneous phases with a porous or non-porous structure for the removal of pollutants of varied size.

Ultrafiltration (UF) is a permeable membrane separation process with pore sizes in the range of 0.1–0.001 micron which permeates water and low molecular weight solutes, while retaining the macromolecules, particles, and colloids that are larger in size. The removal of Cu (II), Zn (II), Ni (II), and Mn (II) from aqueous solutions was achieved by using ultrafiltration assisted with a copolymer of malic acid and acrylic acid attaining a removal efficiency of 98.8% by forming macromolecular structures with the polymers which are rejected by the membrane [15].

Microfiltration (MF) works with the same principle as ultrafiltration. The major difference between the two processes is that the solutes which are removed by MF are larger than those rejected by UF. Cross-flow microfiltration (CFMF) in yeast-based bioaccumulation process was used for the removal of metal ions from tap water artificially contaminated with Cu (II), Cd (II), Pb (II), and Cr (III). The method was efficient for the removal of metal ions with an efficiency of 31, 7, 63, and 71%, respectively [16].

Nanofiltration (NF) is used for the separation of large molecules possible by small pores when they are within the molecular weight range from 300 to 500 Da with a pore diameter of 0.5–2 nm. A commercially available nanofiltration membrane NF270 was used for the removal of Cd (II), Mn (II), and Pb (II) with an efficiency of 99, 89, and 74%, respectively [17].

Reverse osmosis (RO) is a pressure-driven membrane separation process that forces the solution to pass through a semi-permeable membrane for the removal of heavy metals from various industries. Reverse osmosis was used for the removal of Cu (II), Ni (II), and Zn (II) by using a polyamide thin-film composite membrane TW30-1812-50 [18].

Electrodialysis (ED) is a novel liquid hybrid membrane separation process used for the separation of ionized species in the solution that passes through an ion exchange membrane when electric potential is applied or due to concentration gradient. The removal of heavy metal ions in groundwater in Korea was achieved by an ED system for the removal of arsenic, lead, manganese, and nitrate nitrogen with 73.9, 89.9, 98.9, and 95.1%, respectively [19].

Photocatalysis is used for the rapid and efficient destruction of environmental pollutants by using semiconductors which are non-toxic. This method is achieved by a five-step process: transfer, adsorption to the surface of the semiconductor, photocatalytic reactions at the surface, and finally decomposition and removal of the pollutants at the interface region. The heavy metals present in the pharmaceutical waste were photocatalytically degraded and removed by using selenium-doped ZnO nanocomposite semiconductor and the removal capacity was found to be 0.421 (Cu), 0.211 (Cr), 0.147 (Pb), and 0.097 (Cd) per 0.5 g of ZnO/Se nanocomposite [20].

Besides these conventional methods, techniques like coagulation/flocculation [21], electrocoagulation [22], electro-floatation [23], and electro-deposition [24] have been used for the removal of heavy metals from contaminated water resources. However, all the above-mentioned technologies are associated with various disadvantages like incomplete metal removal, generation of sludge, high reagent and energy requirements, and aggregation of metal precipitates and fouling of the membranes.

4. Bioaccumulation and biosorption

In view of the disadvantages associated with conventional methods for metal removal, there is a need for alternative, cost-effective technologies. In recent years, biosorption/bioaccumulation processes have been considered as novel, economic, efficient, and eco-friendly alternative treatment technologies for the removal of heavy metals from contaminated wastewaters generated from various industries.

4.1. Bioaccumulation

Bioaccumulation is a metabolism-mediated active process in which the metal ions accumulate the biosorbent intracellularly in the living cells. The process occurs in two steps: the first

step is the adsorption of metal ions onto cells, which is quick and identical to biosorption, and the later step is slower which includes the transport of metal species inside the cells by active transport [25]. Unlike biosorption, it is an irreversible, complex process which depends on the metabolism of the cells. The process of bioaccumulation occurs by cultivating the biomass of a microorganism in the vicinity of the metal to be accumulated. Since the solution contains the growth medium, the organism begins its metabolic processes and activates the intracellular transport systems for the accumulation of the sorbate. However, the major limitation of the process is that the nutritive medium for growth of the microorganism contains organic carbon sources [26, 27]. Bioaccumulation is an active process which requires a living biosorbent and is mediated by the metabolism of the microorganism used. The process operates by cultivating the microbe in the presence of a metal ion which has to be removed. Part of the biosorbate accumulates inside the cell which enables the biomass to increase and bind greater amounts of metal ions. The organisms which are capable of resisting high loads of metal ions are best suited for accumulating metal species. They do not possess any mechanisms for hindering the accumulation of metal ions in large quantities [28]. They may possess special mechanisms for synthesizing special intracellular binding regions rich in thiol groups as a response to metal ions in their surviving environment. It was found that morphology and physiology of the cell changes upon increase in concentration of the metal ion to be accumulated [29]. Efficient bioaccumulation can be achieved by selecting the microbes that are screened from polluted environments [30]. *Pichia stipitis* yeast was capable of bio-accumulating Cu (II) and Cr (III) with the maximum uptake capacity of 15.85 and 9.10 mg/g, respectively, from aqueous solutions with an initial concentration of 100 ppm at pH 4.5 [31]. *Aspergillus niger* was capable of removing Cu (II) and Pb (II) with the maximum uptake capacity of 15.6 and 34.4 mg/g, respectively [32]. **Table 1** summarizes some more examples of biosorbents used for metal bioaccumulation.

Biosorbent type	Metal ion	Uptake capacity ^a (mg/g)	Reference
<i>Pichia guilliermondii</i>	Cu (II)	20	[29]
<i>Aspergillus niger</i>	Pb (II)	172.25	[33]
<i>Aspergillus flavus</i>	Cu (II)	93.65	[34]
<i>Bacillus circulans</i>	Cr (VI)	34.5	
<i>Bacillus megaterium</i>		32	
<i>Saccharomyces cerevisiae</i>	Cr (III) & (VI)	11.3, 3.3	[35]
<i>Drepanomonas revolute</i>	Zn (II), Cd (II), Cu (II)	22.1, 0.75, 0.2	[36]
<i>Uronema nigricans</i>	Zn (II), Cd (II), Cu (II)	24.3, 0.37, 0.95	
<i>Euplotes</i> sp.	Zn (II), Cd (II), Cu (II)	71.5, 0.83, 0.25	

^aSince the process of bioaccumulation is achieved with the living organisms, the uptake capacity was determined with the wet weight of the biosorbent.

Table 1. Use of microorganisms for bioaccumulation of metal ions.

4.2. Biosorption

Biosorption can be defined as a simple metabolically passive physicochemical process involved in the binding of metals ions (biosorbate) to the surface of the biosorbent which is of biological origin [25]. Biological removal includes the use of microorganisms, plant-derived materials, agriculture or industrial wastes, biopolymers, and so on. It is a reversible rapid process involved in binding of ions onto the functional groups present on the surface of the biosorbent in aqueous solutions by means of various interactions rather than oxidation through aerobic or anaerobic metabolism [37]. The advantages of this process include are simple operation, no additional nutrient requirement, low quantity of sludge generation, low operational cost, high efficiency, regeneration of biosorbent, and no increase in the chemical oxygen demand (COD) of water, which are otherwise the major limitations for most of the conventional techniques [27]. Biosorption can remove contaminants even in dilute concentrations and has special relevance with respect to heavy metal removal owing to toxicity at ppb levels. Microorganisms (live and dead) and other industrial and agriculture byproducts can be used as biosorbents for the process of biosorption.

The first stage in biosorption is that biosorbent should be suspended in the solution containing the biosorbate (metal ions). After incubation for a particular time interval, equilibrium is attained. At this stage, the metal-enriched biosorbent would be separated [27]. The process of biosorption is advantageous because it is reversible, does not require nutrients, a single-stage process, of quick range, has no danger of toxic effects and cellular growth, allows intermediate equilibrium concentration of metal ions, and is not controlled by metabolism [26].

Biosorption capacity (mg/g) of the biosorbent can be defined as the amount of biosorbate (metal ions) biosorbed per unit weight of the biosorbent and can be expressed by using the following mass balance equation:

$$q_e = \frac{(C_i - C_e) V}{m} \quad (1)$$

The percent biosorption (R%) known as biosorption efficiency for the metal was evaluated from the following equation:

$$R \% = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where q_e is the amount of adsorbed metal ions of the adsorbent (mg g^{-1}), C_i is the initial concentration of metal ion in the solution (mg L^{-1}), C_e is the equilibrium concentration of metal ion in the solution (mg L^{-1}), V is the volume of the medium (L), and m is the amount of the biomass used in the adsorption process (g).

5. Mechanism of biosorption

The mechanism of biosorption is a complex process which involves the binding of sorbate onto the biosorbent. Many natural materials can be used as biosorbents which involve the

binding of metal ions by physical (electrostatic interaction or van der Waals forces) or chemical (displacement of either bound metal cations (ion exchange) or protons) binding, chelation, reduction, precipitation, and complexation (refer **Figure 1**). Biosorbents contain chemical/functional groups like amine, amide, imidazole, thioether, sulfonate, carbonyl, sulfhydryl, carboxyl, phosphodiester, phenolic, imine, and phosphate groups that can attract and sequester metal ions. The key factors controlling and characterizing these mechanisms are [38, 39]:

- the chemical, stereochemical, and coordination characteristics of metal ions like molecular weight, ionic radius, and oxidation state of the targeted metal species;
- properties of the biosorbent, that is, the structure and nature (in case of microorganism—living/non-living);
- type of the binding site (biological ligand)
- the process parameters like pH, temperature, concentration of sorbate and sorbent, and other competing metal ions; and
- availability of the binding sites.

The combined effects of the above parameters influence the metal speciation (the formation of new forms of metal as a result of biosorption).

5.1. Complexation

It is defined as the formation of a complex by the association of two or more species. Mononuclear (monodentate) complexes are formed between the metal ion and the ligands in which the metal atom occupies the central position. Polynuclear (multidentate) complex is formed by more than one metal ion in the center and the metal atom may carry a positive,

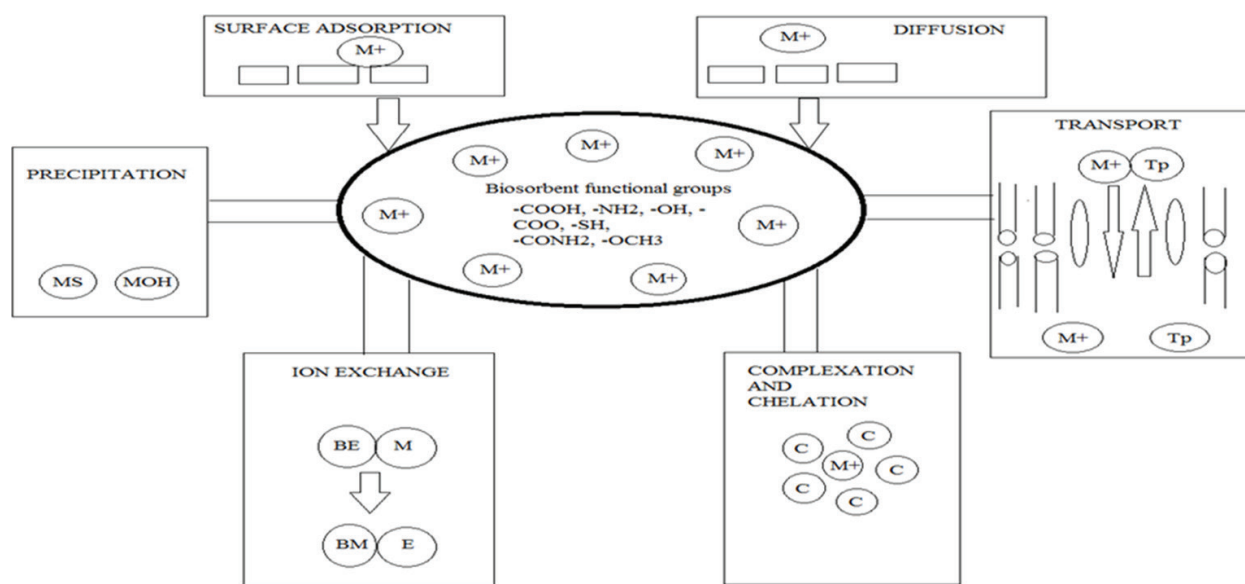


Figure 1. Hypothesis of different mechanisms of biosorption. M+: heavy metal ions, C: chelating agents, BE: molecules with exchangeable ions, BM: molecules with metal ions, Tp: transport protein.

negative, or neutral charge depending on the number of binding ligands involved. The complex formation to the monodentate ligand is more preferable than multidentate because the latter contains multiple ligands which may lead to multiple species binding. The metal ion interacts with the ligands by covalent bonds. The attenuated total reflection infrared spectral (ATR-IR) analysis of *Cyanobacterium microcystis* after the biosorption of antimony (III) suggested the involvement of carboxyl, hydroxyl, and amine groups through surface complexation [40]. A similar mechanism of biosorption was reported by other studies by using *Acidiphilium*, *Termitomyces clypeatus*, and alkali-modified sewage sludge for the removal of Cd (II), Cr (VI), and Cd (II), respectively [41–43].

5.2. Chelation

It refers to the process in which a chelating agent binds to the metal ion at more than one place at a time in order to form a ring structure and the complex is known as chelate. Mostly polydentate ligands participate in the reaction to form stable structures by multiple bonding. An increase in binding sites of the ligand increases the stability of the structure. Chelates are more stable than complexes because of multiple binding with the metal ion in more than one place. Rice straw was used as a potential biosorbent for the removal of Cd (II) from the effluent. The biosorbed Cd (II) chelates with the functional groups such as C=C, C–O, and O–H and carboxylic acids which are present on the surface of the biosorbent [44]. A similar mechanism of biosorption was reported in the removal of Cr (III) and Cu (II) by carboxyl and hydroxyl groups present on the surface of soybean meal waste [45].

5.3. Coordination

The metal atom in the complex is bound to its immediate neighbors by a coordinate covalent bond by accepting a lone pair of electrons from the non-metal atom. The non-metal atom is known as the donor (coordinating atom) and the metal atom which accepts the electron pair is known as the acceptor. Compounds having such types of bonds in their structure are known as coordinate compounds. Some examples of coordinating groups are =O, -NH_2 , -NH , -N= , -OH , -S- , -O-R , and =NOH .

5.4. Ion exchange

Ion exchange is an important concept in biosorption which involves the exchange of binary metal ions during biosorption with the counter-ions present on the surface of the biosorbent. Most of the purification process works on the mechanism of ion exchange. Ion exchange can take place either by cation or anion exchange. Carboxyl groups can be a good example of cation exchangers while amino/imidazole groups represent anion exchangers. The process of biosorption of Cr (III), Cd (II), and Cu (II) by *Spirulina* was studied. Three functional groups capable of cation exchange were identified on the surface: phosphate, carboxyl, and hydroxyl groups [46]. Ion exchange mechanism of biosorption was reported in other studies using rice straw for the removal of cadmium by exchange with K^+ , Na^+ , Mg^+ , and Ca^+ and for the removal of Cu (II), Zn (II), and Pb (II) using watermelon rind [44, 47].

5.5. Precipitation

The metal ions form precipitates with the functional groups present on the surface of the microbial cells and remain intact or penetrate into the microbial cell. Most cases involve the formation of insoluble inorganic metal precipitates. Organic metal precipitates may be formed when microbial cells are used. Most of the extracellular polymeric substances excreted by the microbes are involved in the formation of organic precipitates. Precipitation of Cu (II) onto *Mesorhizobium amorphae* causes deformation, aggregation, and damage to the cell surface as shown by scanning electron microscope-energy dispersive X-ray (SEM-EDX) analysis [48]. This mechanism of precipitation for biosorption of metal ions was reported by other studies using soybean meal, watermelon rind, and green tomato husk (*Physalis Philadelphia lam*) for the removal of Cr (III) and Cu (II); Cu (II), Zn (II), and Pb (II); and Fe and Mn, respectively [45, 47, 49].

5.6. Reduction

In this process, the metal interacts with the functional groups like carboxyl, gets reduced, and leads to the growth of crystals. Elements like gold and palladium have been obtained by the process of reduction. The metal gets reduced once it binds to the biosorbent at discrete places. Removal of toxic hexavalent chromium can be done by the process of reduction. Many organisms remove Cr (VI) by reduction to Cr (III) by biosorption from the aqueous solution [50–52].

The mechanism of biosorption can be studied using different techniques. The acidic and basic properties of the functional groups that are present on the material surface and ion exchange properties can be determined by Boehm method or potentiometric titration [53]. Fourier transform infrared spectrometry (FTIR) offers important information about the functional groups that are present on the surface of biosorbents like carboxyl, amino, amide, hydroxyl, sulfate, carbonyl, ether, ester, and the nature of the bond that are involved in biosorption [54]. Scanning electron microscope (SEM) is a powerful technique for qualitative evaluation of the structure and morphological changes of the biosorbent before and after metal biosorption. Energy dispersive X-ray (EDX) technique provides valuable information about the availability of various elements on the surface of the biosorbent. X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique for analyzing the surface chemistry of the biosorbent, that is, electronic state and empirical formula of the elements present and oxidative state of the biosorbed metal ion [55].

6. Types of biosorbents

Identification of biosorbents for the process of biosorption is a major challenge. It is desirable to develop/obtain biosorbents with the capacity to bind/uptake metal ions with greater affinities [56]. A wide variety of materials available in nature can be used as biosorbents for the removal of metals from contaminated water resources. Any kind of plant, animal, and microbial biomass and their derivatives; plant, industrial and agriculture wastes; and byproducts discharged from various industries can be employed as biosorbents. It is important to select a biosorbent from the large spectrum of available materials. The desired characteristics of an ideal biosorbent are [56]:

- high affinity for metals (biosorption capacity)
- low economic values (low cost)
- availability in large quantities
- easy desorption of the adsorbed metal ions and possible multiple reuse of the biosorbent

The use of different materials as biosorbents is explained in detail:

6.1. Industrial byproducts

Low-cost materials from different industries have been used for the treatment of wastewater. Many industries, especially food industries, dispose large quantities of waste and byproducts. The cost for disposal is sometimes challenging. Using these zero-cost industrial wastes as effective biosorbents for treating wastewater effluents can solve the dual problem (waste disposal and effluent treatment) [57]. Waste byproducts produced from different industries, that is, steel, aluminum, paper, fertilizer, food, mining, and pharmaceuticals, can be used as biosorbents. It is estimated that the use of biosorbents from industrial waste will grow at an annual rate of 5% [58]. **Table 2** summarizes the type and source of the biosorbent, type of biosorbate targeted, and maximum biosorption capacity/biosorption efficiency of various industrial biosorbents.

Type of biosorbent	Source of biosorbent	Biosorbate	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
Tea industry waste	Local tea factory	Cr (VI)	54.65 mg/g ^{a*}	Langmuir	-OH, -SO ₃ , C-O, -CN		[59]
Sugar industry waste (bagasse)	Food canning processes	Cd (II), Fe (II)	96.4%, 93.8% ^{a*}				[60]
Peach and apricot stones	Juice and jam industry	Pb (II)	97.64%, 93% ^{a*}	Langmuir			[61]
Antibiotic waste	Antibiotic production complex	Cationic dye (Basic blue 41)	111 mg/g ^{a*}	Freundlich		Ion exchange or complexation	[62]
Sludge	Paper mill	Ni (II), Cu (II), Pb (II), Cd (II)	13.7, 13.9, 14.1, 14.8 mg/g ^{a*}	Freundlich		Ion exchange and physico-chemical adsorption	[63]
Waste green sands	Iron foundry industry	Zn (II)	10.0 mg/g ^{a*}	Freundlich			[64]
Fly ash	Cement industry	Pb	22 mg/g ^{a*}			Precipitation	[65]

^aIndicates the dry weight of the biosorbent, ^{*}Indicates batch biosorption experiments at laboratory scale.

Table 2. Use of industrial byproducts for biosorption of metal ions.

6.2. Agricultural waste materials

A great deal of interest in the removal of pollutants from wastewaters has focused on the use of agricultural waste/byproducts as biosorbents. Agricultural wastes especially those with high percentage of cellulose and lignin contains polar functional groups like amino, carbonyl, alcoholic, phenolic, and ether groups having high potential for metal binding [66]. These groups donate a lone pair of electrons and form complexes with metal ions in the solution [67]. Due to their unique chemical composition (the presence of hemicellulose, lipids, lignin, water hydrocarbons, simple sugars, and starch having a variety of functional groups) and availability, the use of agro-wastes seems to be a viable option for heavy metal remediation. Grapefruit peel was reported to biosorb cadmium and nickel with a biosorption capacity of 42.09 and 46.13 mg/g from aqueous solutions. Equilibrium data showed the better fit with the Freundlich isotherm model with the ion exchange mechanism. FTIR analysis showed that the carboxyl and hydroxyl groups are mainly involved in the biosorption of metal ions [68]. The bark powder of *Acacia leucocephala* was used as a low-cost biosorbent for the removal of Cu (II), Cd (II), and Pb (II) with the biosorption capacity of 147.1, 167.7, 185.2 mg/g, respectively, from the aqueous solution. The biosorption mechanism involved is physico-chemical adsorption involving carboxyl, hydroxyl, and amine groups present on the surface of the biosorbent for biosorption. The Langmuir model shows the best fit than the Freundlich model [69]. **Table 3** summarizes the type of the biosorbent, biosorbate, and maximum biosorption capacity of the different agriculture wastes as biosorbents.

6.3. Microbial biosorbents

Microorganisms capable of tolerating unfavorable conditions evolved their use as biosorbents in the removal of metal ions from wastewaters. They include bacteria, yeast, algae, and fungi. Experiments focused on the use of dead and or living microorganisms offer options for the type of remediation to perform [82]. However, the use of dead microbial biomass for the binding of metal ions has been preferred over living biomass because of the absence of the requirement of nutrients and monitoring BOD and COD in effluents. Hence, the use of dead biomass is economical [83]. These biosorbents can effectively sequester metal ions in the solution and decrease the concentration from the ppm to ppb level efficiently; therefore, they are considered as ideal candidates for the treatment of complex wastewaters with high volume and low concentration of metal ions [84]. A large quantity of materials of microbial origin has been investigated as biosorbents for the removal of metal ions extensively [85]. Reports do not include the use biomass of any pathogens for water treatment. Most of the microbial groups are composed of a large number of functional groups which indicate their potential as biosorbents. Some studies which identified the functional groups involved in the biosorption of metal ions are given in **Table 4**.

6.3.1. Algae as biosorbents

The use of algae as a biosorbent has received focus due to the scarce requirement of nutrients, high sorption capacity, plentiful availability, high surface area to volume ratio, less volume of sludge to be disposed, and the potential for metal regeneration and recovery. They are considered as both economic and ecofriendly solutions for wastewater treatment [92]. Different groups of algae differ in the composition of the cell wall. The cell wall of brown algae mainly contains three components: cellulose (structural support), alginic acid (a polymer of mannuronic and

Type of biosorbent	Biosorbate	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
Rice husk	Ni (II)	51.8% ^{a*}	Langmuir and Freundlich	-OH, C=O, C-H		[70]
Cabbage, cauliflower waste	Pb (II)	60.57, 47.63 mg/g ^{a*}	Langmuir	-OH, C=O	chemisorption	[71]
Sugarcane bagasse	Ni (II)	2 mg/g ^{a*}	Langmuir		Ion exchange	[72]
Papaya wood	Cd (II), Cu (II), Zn (II)	97.8%, 94.9%, 66.8% ^{a*}	Langmuir			[73]
Green coconut shell (powder)	Cr (III), Cr (VI), Cd (II),	90%, 86%, 99% ^{a*}	Freundlich		Ion exchange	[74]
Wheat shell	Cu	99% ^{a*}	Langmuir			[75]
Peanut hull	Cu	12 mg/g ^{a*}	Langmuir		Ion exchange	[76]
Barley straws	Cu, Pb	4.64, 23.20 mg/g ^{a*}	Langmuir		Chemisorption and ion exchange	[77]
Neem bark	Pb	86.7% ^{a*}	Freundlich	O-H, C-O, N-H, C-N, C-O, S-O	Ion exchange	[78]
Iris peat	Cu (II), Ni (II)	17.6, 14.5 mg/g ^{a*}	Langmuir			[79]
Date pit	Cu (II),Cd (II)	35.9, 39.5 mg/g ^{a*}	Freundlich	-C=C, -C=N	Hydrogen bonding and electrostatic attraction	[80]
Cassava peelings	Cu (II), Cd (II)	127.3, 119.6 mg/g ^{a*}	Langmuir		Ion exchange	[81]

^aIndicates the dry weight of the biosorbent, ^{*}Indicates batch biosorption experiments at laboratory scale.

Table 3. Use of agricultural wastes for biosorption of metal ions.

guluronic acid with its corresponding salts), and sulfated polysaccharide with high contents of carboxyl groups that are involved in the process of the biosorption of metals. Red algae have received attention for biosorption due to the presence of sulfated polysaccharide made of galactans (having high contents of hydroxyl and carboxyl groups). Green algae contain cellulose with a high percentage of protein bound to polysaccharides which contain many functional groups like amino, sulfate, hydroxyl, and carboxyl [93]. Hence several authors focused on the removal of metal ions using algal biomass from contaminated water resources. It has been reported that algae can biosorb about 15.3–84.6% which is higher compared to the other microbial biosorbents [94]. The biosorption capacity of green algal species, *Spirogyra* sp. and *Cladophora* sp. for the removal of Pb (II) and Cu (II) from aqueous solutions, was studied. The capacity of *Spirogyra* was 87.2 and 38.2 mg/g and for that of *Cladophora* was 45.4 and 13.7 mg/g

Biosorbent	Biosorbate	Functional groups	Reference
<i>Mucor rouxii</i>	Cu (II)	Amino, carboxyl, phosphate	[86]
<i>Streptomyces rimosus</i>	Pb (II)	–COO, –C–O, –NH, –C=O, –OH	[87]
<i>Maugeotia genuflexa</i>	As (III)	Carboxyl, hydroxyl, amide	[88]
<i>Rhizopus cohnii</i>	Cd (II)	Carboxyl, amino, hydroxyl	[89]
<i>Oedogonium hatei</i>	Ni (II)	Carboxyl, phosphate, amide, hydroxide, thiol	[90]
<i>Bacillus subtilis</i>	Au (III)	Amino, carboxyl, hydroxyl	[91]

Table 4. Functional groups of microbial biomass involved in biosorption of metals.

Biosorbent type	Metal ion	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
<i>Stoechospermum marginatum</i>	Cr (VI)	32.63 mg/g ^{a*}	Freundlich		Ion exchange	[97]
<i>Ulva lactuca</i> sp.	Cd (II)	35.72 mg/g ^{a*}	Langmuir	Amido, hydroxyl, C=O, C–O	chemisorption	[98]
<i>Spirulina platensis</i>	Cu (II)	90.6% ^{a*}				[99]
<i>Oedogonium hatei</i>	Ni	40.9 mg/g ^{a*}	Langmuir and Freundlich	–OH, –CH, C=O, –CN, =C–N		[90]
<i>Maugeotia genuflexa</i>	Ar (III)	57.48 mg/g ^{a*}	Langmuir	Carboxyl, hydroxyl, amide	Ion exchange	[88]
<i>Spirulina platensis</i>	Cu	67.93 mg/g ^{a*}				[100]
<i>Palmaria palmate</i>	Cr (VI)	33.8 mg/g ^{a*}	Langmuir	–NH, C=O, C–O, –S=O	Ion exchange and complexation	[101]
<i>Fucusvesiculosus</i>		42.6 mg/g ^{a*}				
<i>Enterobacter</i> sp.	Pb (II), Cu (II), Cd (II)	50, 32.5, 46.2 mg/g ^{a*}	Freundlich			[102]
<i>Cladophora</i> spp	Pb (II), Cu (II)	46.51, 14.71 mg/g ^{a*}	Langmuir		Physical adsorption or ion exchange	[95]
<i>Laminaria japonica</i>	Zn (II)	91.5 mg/g [*]				[37]
<i>Spirogyra</i> sp	Pb (II)	140 mg/g ^{a*}	Langmuir	Carboxyl, amino, amide, hydroxyl		[103]
<i>Ecklonia</i> sp	Cr (VI)	60% ^{a*}		Amino and carboxyl	Chemisorption and Ion exchange	[51]

^{a*}Indicates the dry weight of the biosorbent, ^{*}Indicates batch biosorption experiments at laboratory scale.

Table 5. Algal biomass used for biosorption of metals.

for Pb (II) and Cu (II), respectively. The biosorption process showed the better fit with the Langmuir model, and the mechanism involved for biosorption is physical or ion exchange [95]. A marine algae *Sargassum filipendula* was used as a biosorbent for Cu (II) and Ni (II) ions with biosorption capacity of 1.324 and 1.070 mmol/g. An ion exchange mechanism was involved in biosorption with the Langmuir isotherm model showing the better fit [96]. **Table 5** summarizes some more examples of algae as biosorbents.

6.3.2. Bacteria as biosorbents

THE cell surface structure plays a vital role in biosorption. The cell wall of bacteria is primarily made up of peptidoglycan. Different species of bacteria can be classified based on cell wall composition. Two major types of bacteria are present. Gram-positive bacteria contain thick peptidoglycans bridged by amino acids. The teichoic acids present in the cell wall are linked with the lipids of the cytoplasmic membrane by forming lipoteichoic acids which are responsible for strong bonding with the membrane. The presence of phosphodiester bonds between the teichoic acid monomers gives an overall negative charge and hence are involved in the biosorption of divalent cations (metal ions). Gram-negative bacteria have a thin cell wall containing a less amount of peptidoglycan. However, the presence of an additional outer layer composed of phospholipids and lipopolysaccharides confers an overall negative charge facilitating metal binding [104]. Most bacteria develop many resistance mechanisms and efficient systems for the removal of metal ions for their survival. Some bacteria produce slime or a capsule-like layer on the surface of cell wall. These are mostly composed of polysaccharides which are charged and help to detoxify metal ions from wastewaters [105]. Because of their high surface to volume ratio and high content of potential active sorption sites, bacteria make excellent biosorbents for sequestering metal ions from industrial effluents. *Enterococcus faecium*, a lactic acid bacterium, was able to biosorb Cu (II) ions from aqueous solutions with the maximum biosorption capacity of 106.4 mg per gram of dry biomass and showed better fit with the Freundlich isotherm model [106]. The dead cells of *Bacillus subtilis* biosorb Cu (II), Fe (II), and Zn (II) from its solutions by 25.86, 21.30, and 26.83%, respectively [107]. **Table 6** summarizes some more examples of bacteria as biosorbents.

6.3.3. Fungi as biosorbents

Fungi are also considered as economic and ecofriendly biosorbents because of characteristic features, that is, easy to grow, high yield of biomass, and ease of modification (chemically and genetically) [120]. The cell wall of fungi shows excellent binding properties because of distinguishing features like chitin, lipids, polyphosphates, and proteins among different species of fungi [121]. The cell wall of fungi is rich in polysaccharides and glycoproteins which contain various metal-binding groups like amines, phosphates, carboxyls, and hydroxyls. The fungal organisms are used in a wide variety of fermentation processes. Hence, they can be easily produced at the industrial level for biosorption of metal ions from a large volume of contaminated water resources. Besides, the biomass can be easily and cheaply obtained from inexpensive growth media or even as byproducts from many fermentation industries. Further, fungi are less sensitive to the variations in nutrients and other process parameters like pH, temperature, and aeration [122]. Because of their filamentous nature, they are easy to separate by means of simple techniques like filtration.

Biosorbent type	Metal ion	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
<i>Bacillus cereus</i>	Zn (II)	66.6 mg/g ^{a*}	Langmuir and Freundlich	Amino, carboxyl, hydroxyl, carbonyl	Physic-chemical adsorption and ion exchange	[108]
<i>Bacillus pumilus</i>	Pb (II)	28.06 mg/g ^{a*}	Langmuir			[109]
<i>Trametes versicolor</i>	Cu (II)	140.9 mg/g ^{a*}	Langmuir	-NH ₂ , -OH, -C=O	chemisorption	[110]
<i>Lactobacillus delbruckii bulgaricus</i> , <i>streptococcus thermophilus</i>	Fe (II), Zn (II)	100%, 90% ^{a*}		Carboxyl and hydroxyl		[111]
<i>Bacillus coagulans</i>	Cr (II)	39.9 mg/g [*]				[112]
<i>Bacillus thuringiensis</i>	Ni (II)	15.7% ^{a*}	Langmuir			[113]
<i>Bacillus thioeparans</i>	Cu (II), Pb (II)	27.3, 210.1 mg/g [*]	Langmuir			[114]
<i>E. coli</i>	Ni (II)	6.9 mg/g ^{b*}	Redlich-Peterson	C-H	Ion exchange	[115]
<i>Pseudomonas putida</i>	Zn	17.7 mg/g ^{a*}				[116]
<i>Arthrobacter sp</i>	Cu (II)	32.64 mg/g ^{a*}	Langmuir			[117]
<i>Bacillus licheniformis</i>	Cr (VI), Fe (II), Cu (II)	95%, 52%, 32% ^{b*}				[118]
<i>Rhizobium spp</i>	Cd (II), Co (II)	135.3, 167.5 mg/g ^{a*}	Langmuir			[119]

^aIndicates the dry weight of the biosorbent; ^bIndicates the wet weight of the biosorbent; *Indicates batch biosorption experiments at laboratory scale.

Table 6. Bacterial biomass used for biosorption of metals.

Yeasts are unicellular. Most of the yeast biomass either biosorb a wide range of metals or strictly are specific to a single metal ion. *Saccharomyces cerevisiae* biomass has been widely studied as a yeast biosorbent, with high biosorption capacity [123, 124]. Yeast is also reported to have high bioaccumulation capacity and hence can be used as a suitable biosorbent for the removal of metal ions by growing them in metal-laden solutions. Many works reported that ion exchange was the key mechanism for fungi metal biosorption experiments. When *Saccharomyces cerevisiae* is grown in the media containing zinc in the concentration of 1.4372 g/L, the maximum amount of zinc found in the yeast cell was 1699 g/g of the biomass [125]. The filamentous industrial fungus *Rhizopus cohnii* was used as a biosorbent for the removal of cadmium from wastewater with the maximum biosorption capacity of 40.5 mg/g and the functional groups

Biosorbent type	Metal ion	Biosorption capacity Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
<i>Penicillium canescens</i>	As (III), Hg (II), Cd (II), Pb (II)	26.4, 54.8, 102.7, 213.2 mg/g ^{a*}				[126]
<i>Penicillium chrysogenum</i>	Ni	82.5 mg/g ^{a*}				[127]
<i>Aspergillus niger</i>	Cu (II)	9.53 mg/g ^{b*}				[128]
<i>Pencillium purpurogenum</i>	As (III), Hg (II), Cd (II), Pb (II)	35.6, 70.4, 110.4, 252.8 mg/g ^{a*}	Langmuir			[129]
<i>Pencillium simpliccium</i>	Cd (II), Zn (II), Pb (II)	52.50, 65.60, 76.90 mg/g ^{a*}	Redlich-peterson and Langmuir		Chemical ion exchange	[130]
<i>Saccharomyces cerevisiae</i>	Pb (II), Ni (II), Cr (VI)	270.3, 46.3, 32.6 mg/g ^{a*}	Langmuir		Physical adsorption	[131]
<i>Lentinus sajor</i>	Cr (VI)	18.9 mg/g ^{a*}	Langmuir	C–O, N–H, C–H	Physic-chemical adsorption	[132]
<i>Pleurotus ostreatus</i>	Cr (VI)	20.71% ^{b*}		–COOH, –NH ₂		[133]
<i>Aspergillus terreus</i>	Cu (II)	180 mg/g ^{a*}	Freundlich			[134]
<i>Phanerochaete chrysosporium</i>	Ni (II), Pb (II)	55.9, 53.6 mg/g ^{b*}			Ion exchange	[135]
<i>Pleurotus ostreatus</i>	Cu (II), Ni (II), Zn (II), Cr (VI)	8.06, 20.4, 3.22, 10.75 mg/g ^{a*}	Langmuir	–COOH, –NH ₂	Ion exchange, surface complexation and electrostatic interaction	[121]
<i>Trametes versicolor</i>	Ni (II)	212.5 mg/g ^{a*}	Langmuir	Carboxyl, hydroxyl, amine	Physico-chemical interaction	[136]

^aIndicates the dry weight of the biosorbent; ^bIndicates the wet weight of the biosorbent; *Indicates batch biosorption experiments at laboratory scale.

Table 7. Fungal biomass used for biosorption of metals.

involved in biosorption was carboxyl, amino, and hydroxyl groups. The Langmuir isotherm model showed the better fit with an ion exchange mechanism for biosorption [89]. **Table 7** summarizes some more examples of fungi as biosorbents.

7. Effect of pretreatment on biosorption

Since the process of biosorption relies on the number and availability of functional groups on the surface of the biosorbent, modification by changing the surface characteristics can greatly influence the capacity of biosorbent used for the removal of metal ions [137]. Microbial-derived

biosorbents are amenable for modification in order to increase the available binding sites and enhance the biosorption capacity leaving low residual metal concentration. A number of methods have been employed for surface modification of microbial biomass. The physical methods of pretreatment include heating, autoclaving, freeze drying, thawing, and lyophilization. Various chemical methods used for the pretreatment include acid or alkali treatment, washing with detergents, treatment with organic chemicals such as formaldehyde, sodium hydroxide, dimethyl sulfoxide, and cross-linking with organic solvents [3]. Physical- or chemical-treated microbial biomass show altered properties of metal biosorption compared to the original biomass. If the biomass is large in size, they are grounded into fine granules and are treated further for efficient biosorption [8]. The characteristic feature of pretreatment is to modify the surface groups either by removing or masking or by exposing the greater number of binding sites [3]. It is also observed that the longer duration of pretreatment can

Type of biosorbent	Type of treatment	Metal ions	Biosorption capacity/ efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
<i>Saccharomyces cerevisiae</i>	Ethanol	Cd (II), Pb (II)	15.63 and 17.5 mg/g ^{a*}	Langmuir			[140]
<i>Bacillus subtilis</i>	Supercritical CO ₂ , autoclaving	Ni (II)	98.54%, 99.2% ^{a*}		Carboxyl, phosphate amino, hydroxyl		[141]
<i>Penicillium lanosa</i> <i>coeruleum</i>	Heat, NaOH, detergent Gulteraldehyde	Pb (II), Cu (II) Ni	127%, 106%, 95%, 162% 72% ^{a*}				[142]
<i>Mucor rouxii</i>	0.5 N NaOH	Pb (II), Cd (II), Ni (II), Zn (II)	66%, 76%, 189%, 120% ^{a*}				[143]
<i>Termitomyces clypeatus</i>	Acid and alkali	Cr	100% ^{a*}	Langmuir and Freundlich	Amino, carboxyl, phosphate, hydroxyl, carbonyl	Physical adsorption, ion exchange, complexation, electrostatic attraction	[144]
<i>Aspergillus niger</i>	0.5 N NaOH	Pb (II), Ni (II)	80%, 60% ^{a*}				[145]
<i>Aspergillus versicolor</i>	DMSO	Pb (II)	30.6 mg/g ^{a*}	Redlich-Peterson	N-H, C-H, C=O, COO-	Ion exchange	[146]
<i>Pencillium chrysogenum</i>	Alkali	Cr (III), Ni (II), Zn (II)	27.2, 19.2, 24.5 mg/g ^{a*}		Amino, carboxyl, hydroxyl		[147]
<i>Anabaena variabilis</i>	Acetic acid	Cr, Ni	84.60%, 83.10% ^{a*}				[148]

^aIndicates the dry weight of the biosorbent, ^{*}Indicates batch biosorption experiments at laboratory scale.

Table 8. Use of chemically modified (treated) biosorbents for the biosorption of metals.

further enhance the biosorption capacity. *Saccharomyces cerevisiae* treated with glutaldehyde increased the biosorption of Cu (II) ions [138]. The autoclaving of cells increases the surface area caused by cell rupture resulting in higher binding capacity compared to the normal cells. The treatment of autoclaved *Aspergillus niger* biomass treated with various chemicals increased the biosorption capacity for chromium from 2.16 to 86.88% when compared with the untreated biomass [139]. Hence, different pretreatments modify the surface functional groups (by masking or exposing) that influence biosorption capacity. The masking of carboxylic and amine groups present on the surface of *Saccharomyces cerevisiae* biomass by esterification and methylation decreased the biosorption capacity for Cu (II) ions which indicates that those functional groups are involved in the biosorption of metal ions and the study showed the better fit with the Freundlich isotherm model [138]. Various studies reported the use of treated biomasses for the removal of metal ions with high absorption rates was given in **Table 8**.

8. Immobilization of biosorbent

A major consideration for any biosorption is the separation of solid and liquid phases. Centrifugation and filtration are the routinely used techniques but not recommended at the industrial level. A continuous system with the biosorbent attached to a suitable bed is advantageous [149]. The use of free microbial cells as a biosorbent in continuous system is associated with many disadvantages such as the difficulty in separation of biomass, loss of biosorbent after regeneration, low strength, and little rigidity [150]. Microbial biomass can be immobilized by using a biopolymeric or polymeric matrix. The technique of immobilization is a key element that improves the performance of the biosorbent by increasing the capacity, improving mechanical strength and resistance to chemicals, and facilitating easy separation of biomass from a solution containing pollutants [151]. The process of immobilization is well suited for non-destructive recovery. Immobilization of the biosorbent into suitable particles can be done by using techniques like entrapment (in a strong but permeable matrix) or encapsulation (within a membrane-like structure) [152]. A number of matrices have been employed for immobilization including sodium or calcium alginate, polyacrylamide, silica, polysulfone, and polyurethane. It is very important to use a suitable immobilization matrix since it determines the mechanical strength and chemical resistance of the biosorbent particle targeted for biosorption while the matrix should be cheap and feasible to operate [153]. The use of an immobilized biosorbent is also associated with some disadvantages like increase in the cost of the biosorbent and an adverse effect on the mass transfer kinetics. This is because immobilization reduces the number of binding sites that are accessible to metal ions as majority of the sites are embedded within the bead [154]. The live and heat-inactivated *Trametes versicolor* immobilized within carboxyl methylcellulose (CMC) beads were efficient in the removal of Cu (II), Pb (II), and Zn (II) from the aqueous solution. The biosorption capacity were found to be 1.51 and 1.84 mmol, 0.85 and 1.11 mmol, and 1.33 and 1.67 mmol for Cu, Pb and Zn of both live and heat-inactivated biosorbents, respectively. The study shows the best fit with the Langmuir isotherm model [155]. **Table 9** gives the examples of various immobilization matrices used for the biosorption of metal ions.

Immobilized matrix	Type of biosorbent	Metal biosorbed	Isotherm model	Functional groups involved	Mechanism	Reference
Silica	<i>Aspergillus niger</i>	Cr, Cu, Zn, Cd				[156]
	<i>Phaseous vulgaris</i>	Ni (II)	Langmuir	C-O, -C-S		[157]
Polyurethane	<i>Phanerochaete chrysosporium</i>	Pb (II), Cu (II), Cd(II)				[158]
	<i>Corynebacterium glutamicum</i>	Reactive yellow 2	Redlich-peterson		Chemisorption	[159]
Polyacrylamide	<i>Pseudomonas sp</i>	U	Freundlich			[160]
	<i>pseudomonas maltophilia</i>	Au	Langmuir			[161]
Calcium alginate	<i>Bacillus cereus</i>	Pb (II)	Freundlich			[162]
	<i>Trametes versicolor</i>	Cd (II)	Langmuir and Freundlich			[163]
Sepiolite	<i>Aspergillus niger</i>	Fe (II, III)				[164]

Table 9. Various immobilization matrixes used with biomass for biosorption of metals.

9. Desorption and the regeneration of biosorbents

In order to keep the process costs down and for recovery of valuable metal ions after the biosorption, it is crucial for regeneration of the biosorbent [152]. The primary objective of desorption is to retain the adsorption capacity of the biosorbent. The process of desorption should be such that the metal can be recovered in the concentrated form (in case of metals of economic value), and the biosorbent needs be restored to the original state with undiminished biosorption capacity for reuse [8]. Hence an appropriate eluent for desorption should meet the following requirements [112]

- low cost;
- environment friendly;
- non-damaging to the biomass; and
- ensure intact metal-binding capacity.

The possible eluents are dilute mineral acids (HCl, H₂SO₄ and HNO₃), organic acids (citric, acetic and lactic acids), and complexing agents (EDTA, thiosulphate, etc.) for the recovery of the biosorbent and metal recovery. Desorption efficiency can be determined by the S/L ratio, that is, solid to liquid ratio. The solid represents the biosorbent and liquid represents the eluent (volume) applied. For complete elution and to make the process economical, high S/L values are desirable [3]. Although, desorption is considered advantageous, in some instances,

Type of biosorbent	Type of eluent	Metal ion	% of desorption	Isotherm model	Functional groups involved	Mechanism	Number of cycles	Reference
<i>Spirulina sp</i>	0.1 M HNO ₃	Cr, Cd, Cu	98	Langmuir	Carboxyl, phosphate, hydroxyl, amine	Ion exchange		[46]
<i>Aspergillus niger</i>	0.1 N NaOH	Cr	90%	Freundlich	Carboxyl, amide, phosphate, hydroxide	Chemisorption		[166]
<i>Aspergillus flavus</i>	0.1 N HNO ₃ , 0.1 N NaOH	Cu (II)	80%					[167]
<i>Raw wheat bran</i>	0.01 mol/L HCl, HNO ₃	Cd (II), Pb (II)	100%, 57%	Langmuir			Four	[168]
<i>Scenedesmus sp</i>	0.1 M H ₂ SO ₄	Zn	99%	Freundlich			Five	[169]
<i>Aspergillus niger</i>	0.5 N H ₂ SO ₄	Cr				Redox reaction		[50]
<i>Montmorillonite</i>	0.1 M HCl	Ni (II), Mn (II)	92.8%, 90%	Freundlich		Physical adsorption	Three	[170]
<i>Rhizopus nigricans</i>	HNO ₃	Pb (II), Cd (II), Ni (II), Zn (II)	90%				Five	[171]

Table 10. Use of different eluents for desorption of metal ions.

a loss in the capacity of the biosorbent to retain the desired metal ion has been reported. The metal Cr (VI) was desorbed almost completely from the *Mucor hiemalis* biomass by using 0.1 N of NaOH. The biomass retained its activity of biosorption and desorption up to five cycles. Experimental data fit well with the Langmuir isotherm model, and FTIR analysis showed that the amino groups are involved in biosorption [165]. **Table 10** summarizes the use of different eluents for the desorption of metal ions from different biosorbents.

10. Factors affecting biosorption

Various factors influence the biosorption process namely, biomass concentration, initial metal concentration, and operational factors like pH, temperature, concentration of the initial metal ion, and concentration of the biosorbent.

10.1. Effect of pH

The pH of the solution is an important factor since it influences the metal chemical speciation, solubility, and the total charge of the biosorbent [82]. At low pH (acidic pH), the hydronium

ions are closely associated with the active ligands of the biosorbent and therefore, there exists a competition between the protons and metal ions for the binding sites [172]. At higher pH, there exists lower number of H⁺ ions, and the number of active sites of the functional groups is free and exposed (negative charge) which results in increased biosorption by attracting positive charged metal ions. At higher pH, the metal might begin to precipitate and form hydroxides and as a consequence hinder the biosorption process [108]. The increase in pH from 1 to 4 increased the biosorption of Cr (VI) from wastewaters by *Saccharomyces cerevisiae* biomass [173]. For biosorption of Cr by pretreated *Aspergillus niger* the optimum pH was found to be 3 [166]. An increase in pH from 2.0 to 4.5 increased the biosorption of cadmium by *Rhizopus cohnii* biomass and thereafter it reached a plateau in the pH range from 4.5 to 6.5 [89].

10.2. Effect of temperature

Temperature deals with the thermodynamics of the process and kinetic energy of the metal ions [82]. The temperature can have a positive or negative effect on biosorption at certain intervals. An increase or decrease in temperature causes a change in the biosorption capacity of the biosorbent. High/increasing temperature enhances the biosorptive removal of biosorbates but it is associated with the limitation of structural damage to the biosorbent [38]. Hence, optimum temperature for efficient biosorption has to be chosen for the maximum binding of metal ions. In this context, a maximum biosorption of 86% for cadmium ions was achieved with *Saccharomyces cerevisiae* at 40°C [173]. A rise in incubation temperature from 25 to 40°C sharply increased the biosorption rates of Cr (VI) by *Streptococcus equisimilis* [174].

10.3. Effect of initial metal concentration

The mass transfer resistance between the liquid and solid phases can be overcome by the initial concentration of metal ion [175]. The biosorption capacity (quantity of biosorbed metal ions per unit weight of the biosorbent) of the biosorbent increases initially with the increase in metal ion concentration and then reaches a saturation value. However, the biosorption efficiency of the biosorbent decreases with increase in metal ion concentration. The higher biosorption efficiency at low metal concentration is due to the complete interaction of ions with the available binding which sites results in higher rates of efficiency. At higher concentrations, the number of metal ions remaining unbound in the solution is high due to the saturation of available binding sites [176]. The effect of different initial concentration (25–500 mg/L) of Cd ions on the biosorption of *Hypnea valentiae* was studied. It was found that highest biosorption efficiency (86.8%) was observed with a Cd concentration of 25 mg/L from simulated wastewaters [177]. The biosorption efficiency of the cashew nut shell decreased from 86.03 to 76.17% with the increase in copper ion concentration from 10 to 50 mg/L [178].

10.4. Effect of biosorbent dose

Biosorbents provide the binding sites for metal biosorption, and hence its dosage strongly affects the biosorption process [179]. The increase of the biosorbent dose at a given initial metal concentration increases the biosorption of metal ions due to greater surface area which in turn increases the number of available binding sites [179]. At lower concentrations of the biosorbent, the amount of metal biosorbed per unit weight of the biosorbent is high. Conversely, at high concentration of the biosorbent, the quantity of metal ion biosorbed per unit weight decreases.

This is because of lower adsorbate to binding site ratio due to the insufficient amount of solute present for complete distribution onto the available binding sites and possible interaction between binding sites. The biosorption of Cd and Pb ions by *Anabaena sphaerica* was increased with an increase in the biosorbent dose from 0.025 to 0.25 g/100 ml but stabilized at higher biomass dosages because of the formation of aggregates which reduce the effective surface area for biosorption [180]. The biosorption efficiency of *Parthenium hysterophorus* for Cr biosorption increased from 61.28 to 80.81% with an increase in biomass concentration from 0.1 to 1 g because of the availability of more binding sites but the biosorption capacity decreased from 9.43 to 0.37 mg/g due to decreased metal to biosorbent ratio [181]. A similar trend was observed in many other studies in respect of the effect of biomass concentration.

10.5. Effect of contact time

The time required to attain maximum biosorption depends on the type of biosorbent, metal ion, and their combination. The rate of biosorption is rapid initially (within an hour) with almost 90% of the metal binding because all the active sites are vacant and available for metal ion biosorption. But with increase in time the rate of biosorption decreases due to increase in percentage saturation by metal ions remaining in the solution [182]. Most of the Cd and Zn ions are biosorbed onto *Aspergillus niger* biomass within the first 6 h and there is no further biosorption after 24 h [183]. *Bacillus cereus* and *Pseudomonas aeruginosa* biosorb Zn ions with an equilibrium contact time of 30 min [108].

10.6. Effect of agitation speed

The increase in agitation speed increases the biosorption capacity of the biosorbent by minimizing its mass transfer resistance. While the added turbulence enhances the sorption of the metal ions [184], it may also lead to the destruction of the physical nature of the biosorbent. A moderate speed ensures the best homogeneity for the suspension with a high capacity of biosorption. High agitation speeds result in the occurrence of vortex phenomenon which results in the loss of the homogenous nature of the suspension. Excessive turbulence may also reduce the time of interaction between the biosorbate and biosorbent, thus decreasing the extent of biosorption [183]. The optimum speed of agitation for the biosorption of Cd and Zn by *Aspergillus niger* was found to be 120 rpm [183]. With an increase in agitation speed from 0 to 80 rpm, the biosorption efficiency also increased from 32.4 to 65% [62].

11. Biosorption equilibrium isotherms

Sorption isotherms explain the equilibrium relationships between biosorbent and biosorbate and the mass of the biosorbed component per unit mass of biosorbent and the concentration of biosorbate in the medium under a given set of conditions (temperature and concentration). It also determines the equilibrium distribution of metal ions and how selective retention takes place when two or more biosorbent components are present [185]. The term “isotherm” can be defined as a curve explaining the retention of a substance on a solid at various concentrations

[82]. The determination of equilibrium parameters is the basic requirement for designing a good biosorption system. For determination of the best-fitting sorption isotherm, linear regression is frequently used. In order to predict the isotherm parameters, the method of least squares is applied.

The biosorption capacities of different biosorbents for different pollutants can be best explained by biosorption equilibrium isotherms. Several isotherm models are available to describe the mechanism of the biosorption process and the equilibrium biosorption distribution. Some of the isotherms used in biosorption studies are Langmuir, Freundlich, and Temkin isotherms. However, the biosorption process may show better fit with a specific isotherm.

Biosorption isotherm data of Pb (II) and Cu (II) ions onto green algal species, *Spirogyra* and *Cladophora*, were in good agreement with the Langmuir isotherm demonstrating the formation of the monolayer coverage of metal ions on the outer surface of the biosorbent [95]. The Langmuir model fitted well with the biosorption of Pb (II), Zn (II), and Ni (II) ions onto *Bacillus subtilis* [186]. Freundlich isotherm showed the best fit for the biosorption of Cu (II) ions onto lactic acid bacterium, *Enterococcus faecium* [106]. Biosorption of Cr (VI) ions onto *Bacillus thuringiensis* also shows the better fit with Freundlich isotherm [187].

12. Bioreactors used for biosorption

Various types of bioreactors have been investigated for application at the industrial level. A bioreactor is a system used for the production of microorganisms or desired metabolites employing defined and controllable factors. The typical categories of bioreactors used for the biosorption are stirred tank bioreactors (STRs), air lift bioreactors (ALRs), fluidized bed bioreactors (FBRs), and fixed bed bioreactors (FXRs). These reactors can be operated either in batches or in continuous modes or both (fixed bed and stirred tank bioreactors). Factors (pH, temperature, mixing and agitation, and nutrient availability) affecting the process of biosorption in the bioreactor have to be optimized and controlled by using cooling jackets (temperature), baffles/agitators (mixing), feed lines (supplies nutrients), and acid/base addition (pH) [188].

12.1. Fixed bed bioreactors

It is designed with the biosorbent fixed onto a bed and a container having the bed within. During biosorption, the water contaminated with heavy metals is passed through the column. The biosorbents biosorb the metal ions until the maximal capacity is reached. The biosorbent is then regenerated for the release of heavy metals. In order to ensure continuous working conditions, the presence of two columns is employed. Biosorption is performed on one column while the regeneration of spent biosorbent on the other by rinsing with a suitable chemical reagent. Most of the biosorption processes have used fixed bed bioreactors. Its advantages include simplicity in construction and operation and possibility to carry out process in a countercurrent flow (a current flowing in opposite direction) [189]. However, it is necessary to examine the pressure drop and the effect of column dimensions when operated in a continuous mode [190].

Type of reactor	Biosorbent	Metal species	Biosorption efficiency	Reference
FBRs	<i>Pseudomonas aeruginosa</i>	Cd (II), Cr (VI)	67.17%, 49.25% ^{a*}	[191]
	Sand grains	Cu (II), Pb (II), Ni (II)	96%, 93%, 98% ^{a*}	[193]
ALRs	<i>Trichoderma viridae</i>	Cr (VI)	94.3% ^{b*}	[194]
	<i>Scenedesmus incrassatulus</i>	Cr (VI)	43.5% ^{a#}	[195]
STRs	<i>Rhizopus arrhizus</i>	Cr (VI)	70.5% ^{a#}	[196]
	<i>Trichoderma viridae</i>	Cr (VI)	60% ^{b*}	[194]
PBCs	<i>Aspergillus niger</i>	Cu (II)	83.96% ^{a#}	[197]
	<i>Ulva reticulata</i>	Cu (II), Co (II), Ni (II)	56.3%, 46.1%, 46.5% ^{a#}	[198]
	Sewage sludge	Cr (VI), Ni (II)	90% ^{a#}	[199]
	<i>Microcystis aeruginosa</i>	Pb (II), Cd, (II), Hg (II)	80%, 90%, 90% ^{a#}	[200]

^aIndicates the dry weight of the biosorbent; ^bIndicates the wet weight of the biosorbent; *Indicates batch biosorption experiments at laboratory scale; and [#]Indicates continuous biosorption experiments.

Table 11. Use of different bioreactors for biosorption of metal ions.

12.2. Fluidized bed and air lift bioreactors

These two reactors almost work on the same principle of separation and can be operated in the batch mode. The reactor contains liquid, gaseous, and solid phases. The solid phase is a biosorbent on solid particles used for the retention of metals. The reactor operates with the idea that the gas allows the liquid containing the metal species to be removed to rise. The liquid then flows upward through the middle of the reactor and comes back down through the edges resembling a fountain [191]. In this the liquid is in continuous movement and moves the entire volume of the column. The metal species then adhere to the biosorbent. Once the biosorbent is harvested, the target molecule is separated. Since the particles are in continuous movement, it is preferred and also reduces the clogging effect of the biosorbent. Fluidized reactors are associated with the low mass transfer [38].

12.3. Stirred tank bioreactors

Liquid phase can be separated from the solid phase by a membrane system. Though the process is simple, the cost of operation is high due to high energy requirements [192].

The efficiency in the removal of metal ions largely depends on the type of bioreactor, type of biosorbent, and operating conditions. Recent studies evaluated the efficiency of different biosorbents in the removal of metal ions by using various types of bioreactors (**Table 11**).

13. Application of the biosorption process at pilot scale

Many researchers have attempted pilot-scale studies to make the technology of biosorption available at the industrial scale. A small pilot plant with a three-zone contact settling was developed in a single vessel using anaerobically digested sludge as the biosorbent for the removal of Cu (II) ions. The efficient metal removal (similar to the batch experiments) of 90 mg/g of the

biosorbent was observed [201]. Flotation is a separation process that can effectively separate the metal-loaded biosorbent suspended in the aqueous solution. The technique of biosorptive flotation was applied for the removal of nickel, copper, and zinc ions from the aqueous solutions using grape stalks as the sorbent. Two feed solutions containing different metal concentrations were prepared. The dilute metal solution was applied followed by the concentrated metal solution in the counter-current mode in order to improve the performance of the biosorbent. The experiments were conducted in 10 L columns and satisfactory metal removal was observed (Cu—95%; Zn—98%; Ni—70%; Ca—82%). The biosorbent after regeneration by using an aqueous mixture of sodium sulfate and sodium citrate can be used for the second cycle [202]. A two-step operation for biosorption and sedimentation was operated in a 200 L pilot plant for the removal of pollutants using biomass of *Cunninghamella elegans* and the obtained results proved that the biosorption process is effective in treating wastewaters efficiently [203].

14. Biotechnological intervention: genetically engineered microorganisms (GEM)

Most biosorbents sequester metal ions by using cell-surface moieties. However, they lack the property of specificity and affinity for metals. By using the available genetic engineering technologies specific tailoring can be done to the microbial biosorbents with required selectivity and affinity for metal ions [204]. Genetic engineering technology involves altering the genetic material of the organism in order to develop an efficient strain for the removal of metal ions against the wide range of contaminants present in the wastewater [205]. One such emerging strategy which has received increased attention in recent times is the use of metal-binding proteins such as metallothioneins and phytochelatin. For example, *E. coli* was modified to express phytochelatin 20 on its surface enhancing the accumulation of Hg by 25 times over that by wild-type strains [204]. The technology also offers the advantage of developing microbial strains that can withstand complex environmental conditions and stressful situations. A major obstacle associated with the molecular approach is that it has been applied to only limited bacterial strains like *Escherichia coli*. Hence, other microorganisms need to be explored using this molecular intervention. **Table 12** shows the list of selected genetically engineered bacteria used for the removal of metal ions.

Metal ion	Initial concentration (ppm)	Biosorption efficiency %	Genetically engineered bacteria	Expressed gene of interest	Reference
Hg	7.4	96	<i>E. coli</i>	Hg ²⁺ transporter	[206]
As	0.05	100	<i>E. coli</i>	Metalloregulatory protein ArsR	[207]
Ni	10 uM	15 µmol	<i>E. coli</i>	nixA gene	[208]
Cr	10	48–93.8%	<i>Alcaligenes eutrophus</i>	pEBZ141(Cr resistance genes)	[209]
Hg		77.58 mg/g	<i>Rhodopseudomonas palustris</i>	pSUTP+pGPMT	[210]

Table 12. Use of genetically engineered microorganisms for biosorption of metal ions.

15. Application of biosorption for real wastewaters/effluents

Efforts have been devoted to apply the process of biosorption as a waste treatment method. Instead of aqueous metal solutions, the experiments involved the effluents collected from various polluted sources. Various studies have reported high removal efficiencies.

The electroplating waste containing Cu (II), (6 mg/L) along with other ions (Zn, Cr (VI), Na, Ca, K), was treated with different agro-waste/natural biosorbents at the optimum conditions (pH ~6.0, determined by batch experiments). Removal efficiency for Cu ranged from 77 to 95%. Other metals in the effluents were also removed to various extents [211].

Industrial effluent samples were collected from El-Fayoum for chemical production company outfalls in Egypt to decontaminate Co (II), Cd (II), Cr (III), and Pb (II) by using four red seaweeds namely *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens* and *Pterocladia capillacea*. The biosorption efficiencies of the four biomasses were within the range from 57 to 94% and the highest efficiency was observed with *Galaxaura oblongata* biomass followed by *Corallina mediterranea*, *Pterocladia capillacea* and *Jania rubens* with mean biosorption efficiencies of 84, 80, 76, and 72%, respectively. The study demonstrates that the four seaweeds can be promising, cheap, efficient, and biodegradable biosorbents for lowering of metal ion pollution from the environment [212].

In related study, the efficacy of sugarcane bagasse (the immobilized and native form) for the removal of chromium from wastewater collected from the local tanning plant (Kasur, Pakistan) was evaluated. At a biosorbent dose of 0.1 g and pH of 2.0, the biosorption efficiency was found to be 411 mg/g of biomass which is equivalent to 73% of total chromium present in the wastewater. This highest efficiency was observed with the immobilized form of the biomass when compared with the other forms (native and chemically treated). At the batch level, the maximum uptake was 80.6 and 41.5% in batch mode for Cr (VI) and Cr (III) [213].

The removal efficiency with real effluents can be affected due to the presence of other components like other metals, organic matter, anions, and so on which can compete for the binding sites. The fungal biosorbent *Pleurotus ostreatus* was used for the treatment of wastewater collected from the main drain of the local electroplating industrial units situated at Shahdra, Lahore, Pakistan. A slight wane in the biosorption efficiency when the biomass was used for real wastewater treatment was observed. In case of a real effluent, the metal removal efficiencies for Cu (II), Ni (II), Zn (II), and Cr (VI) were 46.01, 59.22, 9.1, and 9.4%, respectively, while for the single synthetic metal solution, it was 52, 63.52, 10.9, and 11.8%, respectively. This moderate to slight decrease in the removal efficiency of biosorbent might be due to the competition of various contaminants for binding sites as reported in many other studies. Another compounding factor is high COD which also causes reduction in biosorption [121].

The potential of seaweed (*Sargassum*) biomass was used to decontaminate heavy metal ions from urban real storm water runoff. The biosorbent was able to remove metal ions but the efficiency was slightly lesser (90, 65, 50, and 40%) than the single synthetic solute system (80, 50, 15, and 10%) of Pb, Cu, Zn, and Mn, respectively, under similar conditions. The other contaminants like anions, organics, and other trace metals present in the runoff may compete with the existing binding sites of the biosorbent resulting in a decrease in the efficiency of biosorption [214].

However, the removal efficiency attained with real effluents may be comparable with single or simulated synthetic metal solutions.

Gooseberry fruit (*Emblica officinalis*) waste was used as the biosorbent for the removal of Cu from the real electroplating wastewater (50 ml), containing various metals including Cu, from the local electroplating plant in Aligarh city. The wastewater (pH 3.0) was freed of suspended matter, diluted 10 times to the final concentration of Cu (II) of 38 mg and the pH was then adjusted to pH 4.2 before biosorption. The efficiency of metal removal was 98.07% in the column process (1 ml/min) and 65% in batch experiments. The removal efficiency (as calculated from the data given) for mono-metallic solution batch experiments was comparable [215].

In another study, wastewater having heavy metals and textile dyes was collected from the local metal, and the textile processing industry in Turkey was treated with *Punica granatum* L. peels. Under optimum experimental conditions the removal of Pb (II) was 98.07%. Simulated water containing interfering ions also showed a removal efficiency of 98.18%. This was compared well with removal efficiencies (94% as calculated from the data) with mono-metal solutions under optimal conditions. Thus, other components of wastewater such as different metallic salts and dyes did not interfere with removal [216].

The effluent discharged from the battery industries located in the Northern region of Kolkata was treated by *Aspergillus versicolor* biomass to remove Pb (II) ions. It was observed that the efficiency for the removal of Pb (II) ions was found to be 86% which was almost similar to the value obtained by the mono-metallic synthetic system. Hence the study suggests that the presence of additional cations or anions present in the effluent does not affect the biosorption efficiency of the biomass used in the experiment [217].

Modification to the process conditions with real wastewaters may be necessary to achieve removal efficiencies comparable to those obtained with mono-metal solutions.

A *Spirogyra* granule packed column was employed for treating various industrial effluents which was done by passing wastewaters (1 L, 0.6 ml/min) from different industries namely the carpet industry, paper mill industry, and electroplating industry near Varanasi, India. The packed column achieved removal efficiency of >90% for Cu, Cd, Zn, Ni, Pb, and Cr from the three industrial wastewaters. However, this required the reduction of pH from 7.8 to 4.5 (for metals other than Cr) and 2 (for Cr) although the optimum pH of 5.0 was used with metal solutions [218].

Neem sawdust was employed as the biosorbent in a column bioreactor for the removal of Cr (VI) at 94 mg/L from 1.5 L of raw tannery wastewater collected from a common effluent treatment plant in India. The results revealed that the biosorbent of 20 g was sufficient for the removal of chromium with the removal efficiency of 99%. Batch experiments were conducted at 2 g/L dosage at initial concentrations of 150 mg/L in 100 ml shake flasks [219].

16. Commercialization and adoption of biosorption as waste treatment technology

In spite of the advantages over other conventional techniques, there is a glaring lack of adoption of biosorption as a waste treatment technology. Few commercial ventures offering

Biosorbent	Source
AlgaSORB	<i>Algal biomass</i>
B.V.SORBEX	Biomass from various sources
AMT-Bioclain	<i>Bacillus</i> sp.
Bio-Fix	Different biomass
Rahco	Different biomass
MetaGeneR	Different biomass
AquaSorb	Activated carbons
P.O.L. Sorb	Sphagnum Peat Moss
MSR	<i>Rhizopus arrhizus</i>
<i>Azolla</i> Biofilter	<i>Azolla filiculoides</i>

Table 13. Commercial biosorbents.

biosorption as a treatment have emerged. A few commercial biosorbents are available, as shown in **Table 13**. There is a dearth of field trials for a seemingly promising decade-old technology.

Volesky and Naja reported that the lack of commercialization was due to non-technical reasons—due to lack of partners. Computer models based on pilot tests can reduce the scope of field tests. Data and cases of application can attract investors, consultants, distributors, and clients [220].

The BV Biosorbex Inc. is a Canadian company, started by Professor Bohumil Volesky of McGill University, Montreal, Canada, involved in commercializing biosorption. Its services include the biosorption-based removal of heavy metals from industry waters using reactors carrying novel biosorbents as granules offered at the 1/10th the cost of ion exchange resins. The biosorbents may be made from industrial waste, algal biomass, and specialized biomass. The biosorbents are reported to function between pH 4–10 and 5–75°C with efficiencies of >99.9% at 10–50 ppb concentrations of heavy metal and organic matter (<5000 mg/L). The company can conduct lab-scale studies, consultancy, design process, and operate waste treatment plants. Pilot biosorption systems may involve column, fluidized bed, or mixed tank reactors. The company plans to capture 15% of market of ion exchange resin (<http://www.bvsorbex.net/invest.htm>).

AlgaSorb by Biorecovery Inc. has algal biomass immobilized in silica gel. In a pilot study two columns in series with different biosorbents of algae were used to remove mercury from groundwater. Algasorb 624 with high Hg retention but high leakage was used followed by AlgaSorb 620 having the opposite characteristics. Sodium thiosulphate (0.1 M) followed by deionized water (10 bed volumes) was used for regeneration. The study was successful for varying levels of mercury and in the presence of Ca, Mg, and organic matter [221]. Immobilization protects algae against decomposition by microbes. Also, a hard material suitable for packing into columns is obtained. A portable effluent treatment equipment has two columns operating in series or parallel at flow rates of 1 gallon/min and has 0.25ft³ of

AlgaSorb in each column. Equipment for operating at higher flow rates has been designed. Both metal cations and oxyanions can be bound while Ca, Mg, Na, and K ions do not interfere to a significant extent [222].

Bioclaim by Vistatech Partnership Pvt. Ltd. developed *B. subtilis* biomass obtained by treating with NaOH and immobilizing in binders like polyetheimine and glutaraldehyde. The biosorbent is stable and used for removing metals including gold from gold cyanide.

US Bureau of Mines devised bio-fix beads by immobilizing biomass in porous polysulfone beads. Immobilized *Sphagnum* biomass has 4-5-5.0 meq cations per gram capacity comparable to ion exchange resin, with an operational pH range of 3.0–8.0, and metal affinity in the order of $\text{Al} > \text{Cd} > \text{Cu} > \text{Zn} > \text{Fe} > \text{Mn} > \text{Ca} > \text{Mg}$. Majority of equilibrium sorption occurred in 20 min. Bio-fix was used for four onsite field trials. The regeneration by sulfuric acid and subsequent neutralization is done by Na_2CO_3 . The beads were stable to physical and environmental deterioration and displayed over 95% removal over 250 cycles of regeneration. The source of wastewater and the presence of organic matter below 50 mg/L did not inhibit metal removal. Such promising results encouraged field trials.

A three column-circuit (lead, scavenger and elution) was used to remove metals from wastewater from taconite operation. Several metals (Ni, Co, Cu, Zn) were removed (98%) with 20 min residence time and 40–50BV of solution at low temperatures of water (1–3°C) or air ($\leq 0^\circ\text{C}$). The metals were precipitated by treating the elute with MgO and evaporating to obtain residue.

Employing a similar setup, 90–95% of removal was obtained for Zn, Fe, and Mn. However, the presence of suspended solids interfered with the operational efficiency.

In a low maintenance circuit, beads filled in bags made of Polymax B material were placed in troughs or in buckets in the flow of wastewater discharge. Over a 11-month period, Fe concentration of wastewater from an abandoned silver mine was reduced to below 1 ppm level from 20 to 60 ppm levels. This involved 2300 L of beads placed in troughs. Both bucket and trough circuits were used to treat discharge for abandoned mine containing Cd, Cu, Fe, Pb, and Zn. Drinking water standards were (85–89% removal) met with either system at flow rates of 0.3–0.5 L/min with weekly replacement of 50% of beads. Operating cost with bio-fix beads compared well with lime precipitation treatment for similar wastewaters [223].

BIOS process by the Noranda technology center utilized a bed of sawdust, algae and sphagnum moss near seepage. The metal-saturated biomass is later disposed of (as tailings or sent to smelter) or washed for recovery of metals. The bed contained bark (20 years old), wood pulp, and sawdust. Total void volume was 7 L. A Plexiglas reactor was used in 30 L capacity to treat acid mine drainage (AMD). Over a 7-day residence time at room temperature, pH was not effected but Cu (100%) and Zn (65%) were removed. Better metal removal (95–100% for Al, Cu, Zn, Fe) was achieved for a 14-day residence time. The pH did not increase and stabilized at 3 over 12 bed volumes. At lower temperature of 10°C (as compared to 20°C), the removal of metal (except for Cu) ions was reduced. The process compared well with lime organic mixture (LOM) and the anoxic lime stone drain (ALD) methods and was better compared to the Biotrench method in terms of metal removal [224].

Later, different combinations of treatments (LOM/BIOS/ALD, BIOS/ALD and LOM/ALD) were executed to treat AMD. The volume of the initial reactor was 30 L except in the case of LOM/ALD (20 L). The downstream reactors were of 4 L. With LOM/BIOS/ALD, As, Cd and Cu were removed beyond detection. Fe and Zn were also reduced by 93 and 50%, respectively. The pH was increased to 6.3. With the BIOS/ALD system, pH increased to 6.3 and As, Cd, and Cu were removed beyond detection. Metal Al was reduced to 0.7 ppm while Fe and Zn were removed at 99 and 38% efficiency. BOD and COD were negligible. There was no influence of low temperature. The LOM/ALD was referred as the best treatment, achieving the removal of all metals including Zn (99%) and Mn (68%), not attained with other combinations, along with negligible BOD and COD [225].

AquaSorb is a granular, powdered, and extruded activated carbon used primarily for the treatment of water, waste liquid streams and the recovery and recirculation of process liquors. The source of carbon which is activated for water treatment is from coconut shell, coal, and wood raw material by chemical or steam activation. Specially designed AquaSorb for the use in liquid phase adsorption systems in the range of granular, ground, and extruded (pelletized) form can be supplied by Jacobi Carbons. It can be applied as home water filters for the dechlorination of water, in order to reduce chloramines and produce water with good taste, more pure and palatable than the normal municipal water (<https://www.wateronline.com/doc/aquasorb-activated-carbon-0001>).

The highest grade of Sphagnum Peat Moss is used for the development of P.O.L. Sorb which acts as a superb adsorbent for solutions due to the inherent capillary action of the activated peat which provides powerful wicking action that encapsulates oils, solvents, heavy metals, pesticides, herbicides, and so on which are in contact. It is manufactured by The ARK Enterprises, Inc. The raw material of POL Sorb is leafy, stem free, and least an abundant part of the peat in its natural or partial biodegraded state (<http://www.arkent.com/POL%20Sorb%20Flyer.pdf>).

MSR is a biosorbent produced by immobilizing the inactivated cells of *Rhizopus arrhizus* with the desirable particle size of 0.5–1.2 mm. The characteristic features of the biosorbent are that it is resistant to chemicals, compression and abrasion, high porosity, and is with good wetting ability. These proprietary immobilized particles (MSRs) were used for the recovery of uranium from ore leaching operations [226].

17. Conclusions

One advantage of biosorption is the removal of residual or minute concentrations of contaminants. Conventional water treatments may not completely remove contaminants. Hence, biosorption may be integrated downstream of other conventional water treatments. This is especially relevant in the case of pollutants like heavy metals whose effects are felt even at ppb levels.

The efficiency for the removal of specific metals is hindered by the presence of other contaminants. This may be important during the recovery of specific metals of economic value. In

this regard, biosorption may be applied to wastes and effluents before it enters the sewage or natural discharge streams like rivers, seas and so on.

However, with the aim of treating effluent/remediating water resources of all/most contaminants, it may be an advantage to have all pollutants (metal or contaminants) removed simultaneously using a non-specific/non-selective biosorbent and reducing the number of operations/steps. Multiple biosorbents of different specificities/selectivities can also be used.

The strains or biomass used as the biosorbent should be of safe origin especially for water treated for human or animal consumption. Hence, pathogens and toxin-producing organisms need to be avoided. In this regard biomass from food-grade microorganisms like lactic acid bacteria and (wine/beer yeast) and agro-waste is of significance.

Regeneration and immobilization of biomass in order to reduce the cost of biomass involve the use of hazardous solvents which can lead to pollution. Hence, the use of harmless chemicals may be explored.

The existing waste can be classified as solid (degradable and non-degradable) and liquid in nature. A lot of solid non-biodegradable wastes (plastic) can be recycled to form chemically and mechanically robust and inert matrices to hold the biosorbent. Degradable wastes or biomass (agricultural/domestic/industrial) can be employed as biosorbents. A compatible biosorbent-matrix combination can then be employed to treat liquid discharge/effluents. This can make the waste treatment economical and sustainable while addressing the problems of solid and liquid effluents simultaneously.

Nature provides a diversity of biomass varying in binding specificity, efficiency, and ruggedness. This diversity can be tailored to site-specific waste treatment needs by applying the advanced techniques of recombinant DNA technology, synthetic biology and so on. Strains can be modified to express single/multiple metal-binding proteins on the cell surface. Chimeric proteins with multiple metal-binding domains having suitable binding and regeneration conditions can be engineered and expressed. Binding and regeneration conditions for the biosorbents can also be manipulated. Strains tolerant to harsh waste environments, and/or able to accumulate the toxic metals can be developed. However, laws regulating the dispersal or release/containment of genetically modified organisms will need to be considered. Techniques like genome shuffling are considered natural and can be employed for the modification of microorganisms. Confusion exists on the Crispr-Cas9 technology if it can be considered a genetic modification. Also, biosorption processes involving dead biomass may be a convincing argument against such regulations.

Nanotechnology is a cutting-edge technology involving the development of novel materials through the manipulation at nanoscale. The use of biomass has been explored to produce nanometal particles of silver, Cu, gold and so on. This novel use of biosorption linking the wastewater treatment to synthesis/the recovery of metals/nanometals from wastewater makes economic sense for capital investment.

The development of novel efficient biosorbents (nanocellulose, nanocomposites like pectin/TiO₂, nano Fe₃O₄/*Sphaerotilus natans*, ostrich bone waste-zero valent iron, polyaniline-modified nanocellulose) has also been obtained by varied treatments including solvents, heat, and so

on. This may be the answer to optimizing and economizing biosorption-based waste treatment by improving stable efficient biosorbents.

Biosorbents carrying metals can be included into feeds or fertilizers as metals bound to organic ligands have greater bioavailability. Also, they can enhance the shelf life of the feed involved.

However, biomass may also bind hazardous chemicals (like dyes) when used with industrial effluents. The use of such biomass into feeds is not recommended.

Biosorption is beneficial over conventional techniques. The potential has been demonstrated at laboratory and pilot scales even with actual effluent/discharges. But there is a dearth of examples in the real scenario at organized levels like municipalities/cities/pollution treatment centers/industries. Few commercial ventures have been made. This might be because of the diversity of pollutants and their chemical and biological waste background. A set of promising biosorbents/processes may need to be optimized or standardized for specific effluent types. The cost and feasibility in terms of large-scale applications may be evaluated.

Routine adoption at municipal and industrial levels requires success stories at field studies. Better metal removal efficiencies at lower costs and labor when compared to other conventional treatments can convince the industry/state to adopt biosorption. However, there is a lack of field experiments. Executing field studies needs great coordination, capital, manpower, and infrastructure.

State intervention is needed to assist the scientific community to not only fund and coordinate such large studies in terms of manpower/infrastructure but to also access the industry(s) concerned. The general indifference of the industry toward waste treatment may be an issue.

The state can act as bridge for informing and facilitating the availability of biomass from different sources to different polluting units. Such efforts will create a mutually sustainable waste treatment scenario. For example, the disposal of agro-waste from the rural setup to polluting units in order to treat effluents is a win-win for both parties.

An environment encouraging start-ups based on biosorption technology needs to be created.

Stringent norms and scrutiny against effluent discharge can convince the industry to view waste treatment as a necessary investment rather than an avoidable overhead cost. Under this scenario start-ups like Biosorbex, investing in eco-friendly waste treatment technologies, can flourish.

Efforts may be devoted to also apply biosorption at domestic (household) or community levels rather than awaiting the installation of large centralized water treatment setups.

Techniques like response surface methodology, artificial neural networking, boosted regression tree, and genetic algorithm may be used for process optimization. Modeling should be done in solutions with multiple metals and organic matter simulating the real wastewater conditions. Pilot and field studies should be conducted comparing biosorption with the conventional techniques. The use of computer-based simulations or modeling can reduce the number of field trials.

The challenges encountering biosorption are similar to those faced by membrane filtration technology before achieving relevance and popularity as today. This includes the cost and stability of the biosorbent (membrane), the decrease in binding sites (fouling), and poor understanding and general reluctance to adopt new technologies etc. Hence, given its eco-friendly nature and other merits, it will find its place as a routine water treatment process.

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