ENVIRONMENTALLY BENIGN BIO-SORBENT MATERIALS FOR THE HEAVY METALS REMOVAL

Abstract

The incorporation of heavy metals in the water sources due to rapid industrial development has steered the contamination of water resources. The toxic pollutants from the contaminated water are eliminated by cost-effective, environmentally friendly, efficient, and recyclable bio-sorbents having lesser chemical oxygen demand. Bio-sorption is the emerging process of physicochemical adsorption of lethal heavy metals using the biological origin materials from such as micro-organisms, biomass, agro-forest waste, plant materials, industrial wastes, etc. The mechanism of bio-sorption is fastened by the presence of functional groups such as –OH, -C=O, -P=O, -S-, -NH2, etc. on the cell wall of biomaterials. The bio-sorbent convoyed by these functional groups with certain chemical modifications showsa higher adsorption capacity over the other conventional adsorbents. The bioremediation of wastewater encompasses the adsorption of heavy metals using the bio-sorption process, which entails precipitation, complexations, ion exchange, etc. This chapter details the various bio-sorbent materials and their implications in the bio-sorption of lethal heavy metals from contaminated water.

Keywords: Bio-sorption, Adsorption, Heavy metals, Eco-friendly, bioremediation, biomass.

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I. INTRODUCTION

Environmental stability is vital for the survival of the living organism in the ecosystem. But, the loss of biodiversity and habitats of the living speciesled to a disruption in the ecological balance. The health of the environment is under threat due to anthropogenic actions such as exhaustive quarrying, manufacturing, electroplating, mineral extraction, agronomic practices, excavating oil and gas in the ocean, the release of wastewater effluents, emissions and dumping of metal by-products, and natural climatic change[1][2][3]. However, this is accountable to hasty urbanization and growing industries on a global platform. There may have several causes but mainly the heavy metals discharge into the aquatic system evokes environmental concern. Thus, industrial development upraised the incorporation of heavy metals in the aquatic sources and polluted the water habitat eventually. Indeed, this deteriorates the environment, habitats, and human health. This resulted in a negative impact on our ecosystem[4].

Due to their extreme toxicity, obstinacy, and incremental hazards heavy metals constitute environmental risk noteworthy. The polluted aquatic system led to the incorporation of heavy metals in the food chain that triggers a depraved influence on health. Heavy metals accumulate in the ecosystem as persistent toxicants, which then contaminate the food chain and lead to the collapse of the ecosystem equilibrium[5][6]. Persistent heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn are frequently present in the aquatic ecosystem which enters into the food chain through aquatic species[7][8].

Consequently, de-contamination of heavy metals from the waste-water effluent before release into the stream is much more important for the sake of human health and to save aquatic life. In the literature, various strategies have been devoted to the remediation of wastewater. These methods such as adsorption, membrane filtration, chemical, electrodialysis, photocatalytic degradation, etc, have been implemented. There are also traditional methods such as precipitation, complexation, ionexchange, coagulation, etc. employed for the removal of heavy metals from the contaminated water. Adsorption is considered a sophisticated technique for water remediation. But, it involves controlling the major parameter such as the nature of the adsorbent, percent efficiency, operating conditions, retention time, etc. while performing the water bioremediation. But the conventional methods are tedious, low precise, and expensive that could not be afforded[9][10]. Nowadays, nanotechnology is an emerging advanced research area and a promising strategy to accomplish the task to clean the environment. There are various materials have been employed such as carbon nanotubes, graphenes, magnetic nanoparticles, metal oxide nanoparticles, etc.to remove the heavy metals from the water[11][12]. But, research should focus on the inexpensive, sustainable, and environment-friendly method for the bioremediation of wastewater.

On account, biosorption is an emerging technology used for heavy metal bioremediation very efficiently. This method is socioeconomically viable and could be the finest substitute. The biosorption process is rapid and reversible that may be metabolism-based or metabolism independent. This encompasses the binding of metal ions on the cell surface through functional groups present on the cell composites of the cell wall. The biological adsorbents such as bacteria, fungi, yeast, algae, etc. for the removal of heavy metals[13]. The different forms of biomass (live or dead, modified or immobilized) are also used in the biosorption process[14]. Apart, this technique offers a cost-effective substitute

that utilizes renewable or waste biomass materials owing less operating parameters for the removal of heavy metals[15][16].

The chapters discuss the utility of different types of biosorbents and recent advances in the biosorption of heavy metals to date and possible outcomes of this innovative technique with its future perspective.
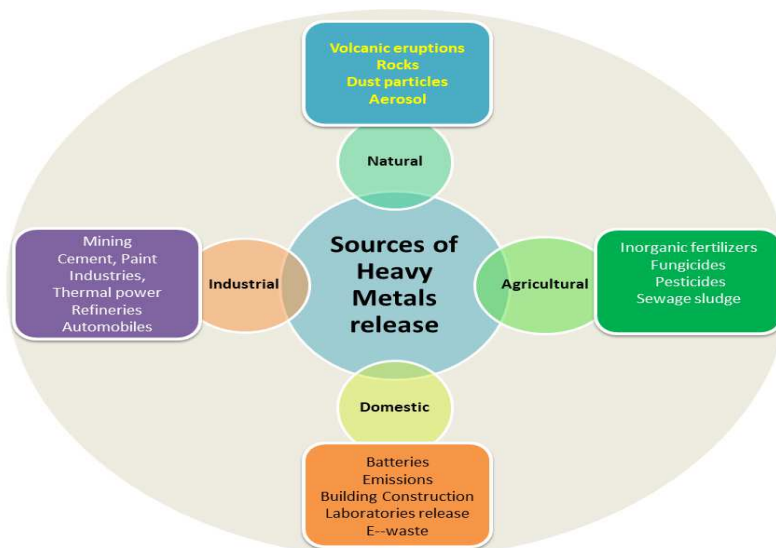

Figure1: The sources of heavy metals released in the water system

II. CONVENTIONAL METHODS

The wastewater effluents are treated before being streamed into the water resources. The removal of heavy metals from contaminated water comprises conventional methods such as electrochemical, physiochemical, and adsorption methods. In several circumstances, conventional methods are fast, low-efficiency, and expensive.
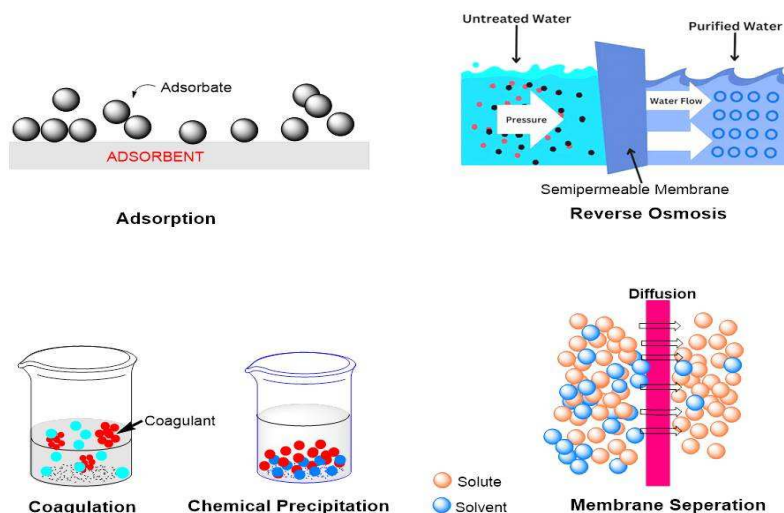

Figure 2: Conventional methods of heavy metal removal

1. **Electrochemical Methods:** The electrochemical methods of heavy metal removal include electro coagulation, elctrofloatation, and electro dialysis. The electrochemical methods are eco-friendly, quick, and cost-effective that do not generates sludge in the huge amount[17].Electro coagulation is characterized by the precipitation of heavy metals by applying the electrical field between aluminium or Iron electrodes The electro coagulation system works by neutralizing the charged particles and destabilized ions get precipitated[18][19].

   In the electro flotation technique, a flotation cell is used to form the bubbles of hydrogen and oxygen gas on passing electric current. Thus, floating metals ion on the liquid phase in an upward direction adheres to bubbles and are collected on the corresponding electrodes[20][21]. Electro dialysis is a modest and effectual membrane-based dialysis technique used to separate metal ions from the solution using charged ion exchange membranes. In this method, films or membranes composed of specific anions and cations are employed between cathodes. Thus, under the influence of the current cation channels allow to pass of anionically charged particles or metal ions and prevent the passage of the cations while the anion channel allows the cations to pass through but hinders the anions to pass through[22][23][24].

2. **Physiochemical Methods:** The chemical precipitation method proceeds with the formation of the precipitate by adding precipitating reagents such as soda lime, soda ash, sodium sulfide, magnesium hydroxide, etc. to the inorganic metal ions solution of wastewater. The insoluble particles generated in the solution are allowed to precipitate. This encompasses the formation of an un dissolved substance by chemical reactions that occurred in the solution and allowed it to precipitate[25][26]. The ion exchange method is considered to be a fine option for the uptake of the metal ions from the wastewater by using different resin beads and eluted from the column. Removal of Ni(II) and Cu(II) ions was performed with ion-exchange resin LewatitMonoPlus SP 112 and Purolite C100-MB cation exchange resin respectively[27][28]. Similarly, metals such as lead and nickel were eliminated by using a spurted bed with AMBERJET 1200 Na resin from wastewater[29].The heavy metals from the wastewater are removed by using the coagulant such as alum, polyaluminum chloride, and $MgCl_2$ to coagulate the metal ions such as Cu(II), Pb(II), Zn(II), and Fe(II) in the solution. The floccules formed are sedimented and water is decontaminated from the heavy metals[30][31][32].

3. **Membrane Filtration:** The membrane separation method possesses some of its great properties, such as high efficiency, easy operation, and low space requirements, which have been considered promising methods for heavy metal removal. ultra filtration, Nanofiltration, and reverse osmosis are the three main membrane filtration technology used in the decontamination of water from heavy metals[33]. Ultra filtration utilizes the pressure-mediated separation of heavy metals through a suitable MWCO semipermeable membrane. it ensures the higher efficiency of the removal of heavy metals[34].Nanofiltration technology is also accompanied by the separation of heavy metals by pressure driven through the semi permeable membrane[35]. While the reverse osmosis (RO) process allows the forceful water passage through the membrane against the osmotic pressure resulting in the separation of ions. Due to huge pressure the movement of the molecules is fastened through the membrane and the solution containing the salt is left[36].

III. BIOSORPTION

Biosorption is an adsorption process that adheres to the principles of green chemistry. It contributes to the sustainable approach towards the development of the socioeconomic aspects. This technique of wastewater treatment is efficient and cost-effective which limits the concentration of the pollutants such as heavy metals in the water systems[37][38][39].
Biomass is the key parameter of the adsorption of heavy metals. Biomass is accompanied by the biologically origin materials whether it is living or non-living or derived wastes. Biosorption is mechanistically classified into metabolism-dependent and metabolism independent. The nature of heavy metals determines biosorption through intracellular accumulation, extracellular accumulation, and adsorption at the cell surface. The use of bio-origin materials in the adsorption technique provides the platform to rectify the ecosystem and environmental issues because it provides the recycling of the bio-waste produced from different sources. The details of the bio-adsorbents have been discussed in this chapter[40].

1. **Types of Bio-Sorbent Materials:** The absorbent materials can be categorized into cellular living or non–living materials owing capacity to uptake heavy metals from the wastewater. The living bio sorbents include a microorganism, algae, yeast, fungi, etc. while non-living comprises wastes from plant-derived materials, industrial wastes, agricultural waste, sludge, etc. They are considered a significant adsorbent of heavy metals at an affordable cost[41]. We will see in detail about bio sorbent materials and their different sources.

   - **Agricultural Waste as Biosorbent:** Agro-wastes composed of major concentrations of cellulose were found to be more potent in the adsorption of heavy metal ions. Agricultural biomass contains lignin, starch, hemicelluloses, proteins, sugars, etc. The various functionalities present in agricultural biomass wastes show great affinity towards the metal ions. The low cost, easy availability, abundant, source of the many functional groups, and economical and greater adsorption capacity made agricultural waste a prominent bio sorbent material for environmental bioremediation[42][43]. Table1 shows the list of agricultural waste as bio sorbents.

Table 1: Agricultural waste as biosorbents

Agricultural waste	Metals	Adsorption capacity(mg/g)	References
Mango Peel	Cd(II)	68.92	[44]
	Pb(II)	99.05	
Peanut husk	Pb(II),Mn(II), Cd(II)Ni(II), Co(II)	50-100%	[45]
Eucalyptus sheathiana bark	Zn(II)	250	[46]
Coffee Husk	Pb(II)	37.04	[47]
	Mn(II)	58.1	[48]
	Co(II)	23.5	
	Pb(II)	23.7	

Cucumber peel	Pb(II)	133.60	[49]
husk of lentil	Cd(II)	107.31	[50]
Mixed waste tea	Cr(VI)	94.34	[51]
coffee ground	Cr(VI)	87.72	
Persimmon leaves	Cu2+, Cd2+, Pb2+	19.42 18.26 22.59	[52]
Lemon peel	Cu2+	13.2	[53]

- **Industrial Waste as Biosorbent:** On a global scale, many industries are working in the food sector and manufacturing. They produce huge amounts of bio waste and discards. But the waste from the food industries is utilized as bio sorbent materials for heavy metal removal. Apart from this, by-products of other industries such as paper and pulp, fertilizers, alloys, brewing, and rice mills produce a huge amount of waste and at zero cost these can be used as biosorbents for water bioremediation[54].Agrofood industries produce the byproducts of the processing of plant products in the manufacturing of juices, ayurvedic medicines, protein powder, liquors, dairy, marine, etc. These contain major functional groups that uptake the metal ions significantly. The tannery Industry sludge was employed as a composite bio sorbent for the removal of Ni(II), Co(II), Zn(II), and Cd(II)[55]. The paper mill industrial wastewater was treated in an up-flow anaerobic sludge blanket reactor and selenite was reduced in the presence of anaerobic granules to form biogenic selenium nanoparticles. This biogenic selenium nanoparticle is used to adsorb the Zn2+ ion with the maximum adsorption capacity of 60mg/g from wastewater[56].The sludge was also considered significant in the removal of, metal ions such as Ni2+, Cu2+, Pb2+, and Cd2+. Additionally, fermentation industries producing the waste biomass of Corynebacterium glutamicum were used as efficient biomass adsorbent for the elimination of Cr(VI)[57].Thus, there are many examples such as the removal of lead and mercury by activated sludge[58],Cd2+ using organo-fulvic composites[59], Pb2+ using fruit waste[60], etc.

- **Microbial Organisms as Biosorbent:** Bacteria are excellent bio sorbents due to the high surface area to volume ratio and the wide availability of potential active sites, which can act as sorption sites[25]. ChrR and YieF are two soluble enzymes that have been extracted and purified from Pseudomonas putida MK1 and Escherichia coli, respectively; these are capable of effectively reducing Cr^{6+} to Cr^{3+} under both aerobic and anaerobic conditions[61].Bacterial groups that contribute to HM removalinclude Bacillus sp., Pseudomonas sp., Arthrobacter sp., Alcaligenes sp., Azot obacter sp., Rhodococcus sp., and methanogens[62]. Among them, Bacillus sp. is considered a potential agent for removing various HMs, especially Gram-positive bacteria[63].

  The presence of organic ligands or functional groups (carboxyl, hydroxyl, sulfate, phosphate, and amine group) in structural components of algal cells makes it a potential biosorbent. Sultana et al have conveyed the capability of Chlorella kessleri microalgae biomass as a biosorbent for the elimination of lead, cobalt, copper, cadmium, and chromium from wastewater[71].

Table 2: Bacteria as biosorbent

Bacterial biosorbent	Metal	Adsorption capacity	References
Tenotrophomonasmalto philia	Cr	99.2 %	[64]
Aeribacillus pallidus MRP280	Pb	96.78 %	[65]
Arthrobacterviscosus	Pb	97 %	[66]
Bacillus sp. Q3	Cd	93.76 %	[67]
Pseudomonas aeruginosa FZ-2	Hg	99.7 %	[68]
Klebsiella sp. USL2S	Hg Pb Cd Ni	85 % 97.13 % 73.33 % 86.06 %	[69]
Pseudomonas azotoformans JAW1	Cd Cu Pb	98.57 % 69.76 % 78.23 %	[70]

Table 3: Algal Biomass as Biosorbent

Algal biosorbent	Metals	Adsorption capacity	References
Spirogyra sp.	Pb(II)	30 %	[72] [73]
Sargassummuticum	Sb(II)	50 %	[74]
Cystoseirabarbata	Cd(II)	68 %	[75]
Scenedesmus obliquus AS-6-1	Cd(II)	93.39%	[76]
A. junii-coconut fiber	Cr (VI)	30 %	[77]
Lessonianigrescens	As(I)	76 %	[78]

The application of the fungus as biosorbent material is the most effective way to capture the heavy metals from the wastewater due to its efficient uptake capacity. Fungi very vital role in cleaning up heavy metals from wastewater through the process of bioaccumulation and biosorption. Thus, limiting the concentration of heavy metals in the water. The cell wall of the fungus is characterized by the presence of chitin, proteins, lipids, and polyphosphates. The cell wall of the fungus is composed of a chain of polysaccharides and glycoproteins accompanied by functionalities such as –NH2, -COOH, and –OH groups. These have been prominent in capturing the

heavy metals at their site easily[79][80]. The fungi tolerant towards the heavy metals are investigated for the adsorption of the heavy metals Viz. Cd, Pb, Ni, and Cr. The results have depicted that A. terreus, T. viride, T. longibrachiatum, and A. niger are very efficient in the adsorption of metal ions from wastewater effluents[81]. Thus, adsorption through fungal culture is cost-effective, efficient, and eco-friendly.
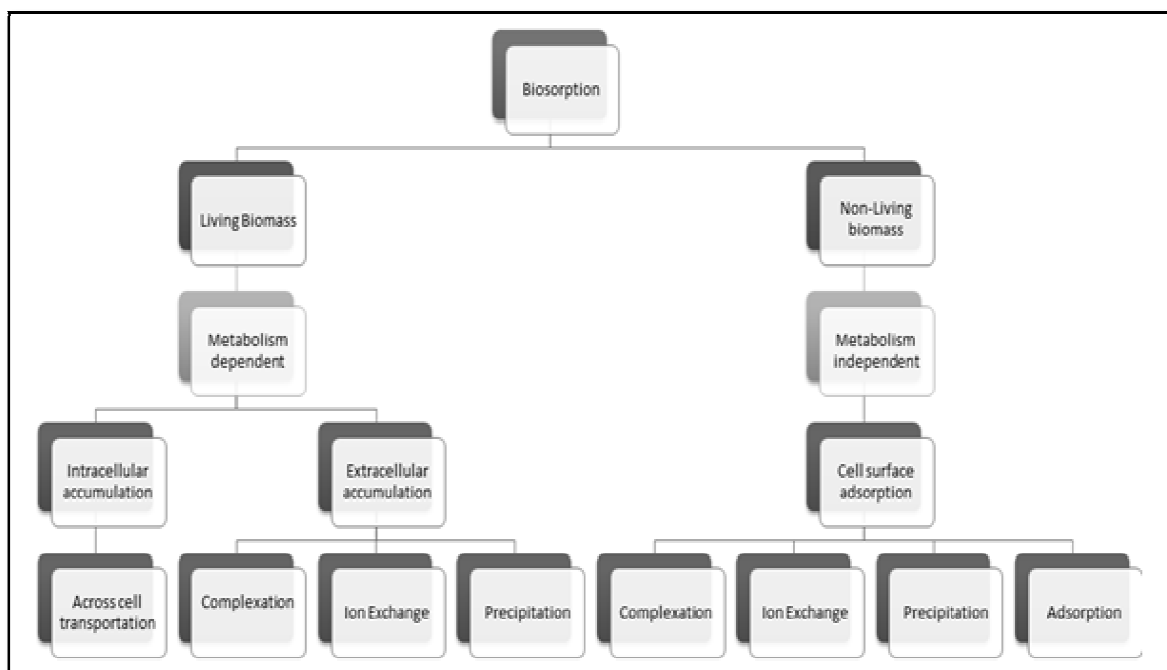
2. Mechanism

Figure 3: Schematic representaion of mechanism of heavy metal adsorption by biosorbents.

Ahalya et al have proposed the mechanism of heavy metal uptake by the microbial biosorbents in three ways as (a) Extracellular accumulation/precipitation; (b) Cell surface adsorption/precipitation; (c) Intracellular accumulation. So, the biosorption mechanism is further classified as metabolism-dependent and metabolism independent[16]. This can be shown diagrammatically in Figure 3.

The biosorption takes place in both living and non-living cellular biomasses. Biosorption occurs as metabolic dependent in living biomass while metabolic independent in non-living (dead) biomass. The metabolic pathway proceeds through the intracellular and extra-cellular accumulation of heavy metals. The chemical interaction of cell gradients promotes transportation across the cell. The heavy metals accumulated outside the cell undergo complexation, ion exchange, and precipitation reaction. Thus, the mechanistic exclusion of heavy metals by algae is a result due to biosorption and bioaccumulation[16][82]. In a metabolic independent pathway, the heavy metal establishes the chemical interaction with functional groups such as carboxyl (-COOH), hydroxyl (-OH), and amidogen (-NH2) present on the cell surface of dead biomass and sorption takes place via ion exchange, precipitation, complex formation, chelation, and adsorption. The extracellular metabolites interact with metal ions to form the complex outside the cell. The cell surface possesses the binding proteins protruding outward and

interacts chemically with the metal ions and gets adsorbed onto the cell surface. Cell. Such a type of phenomenon is called active adsorption[83][84].Figure 4 shows the schematic representation of biosorption by cellular biomass.
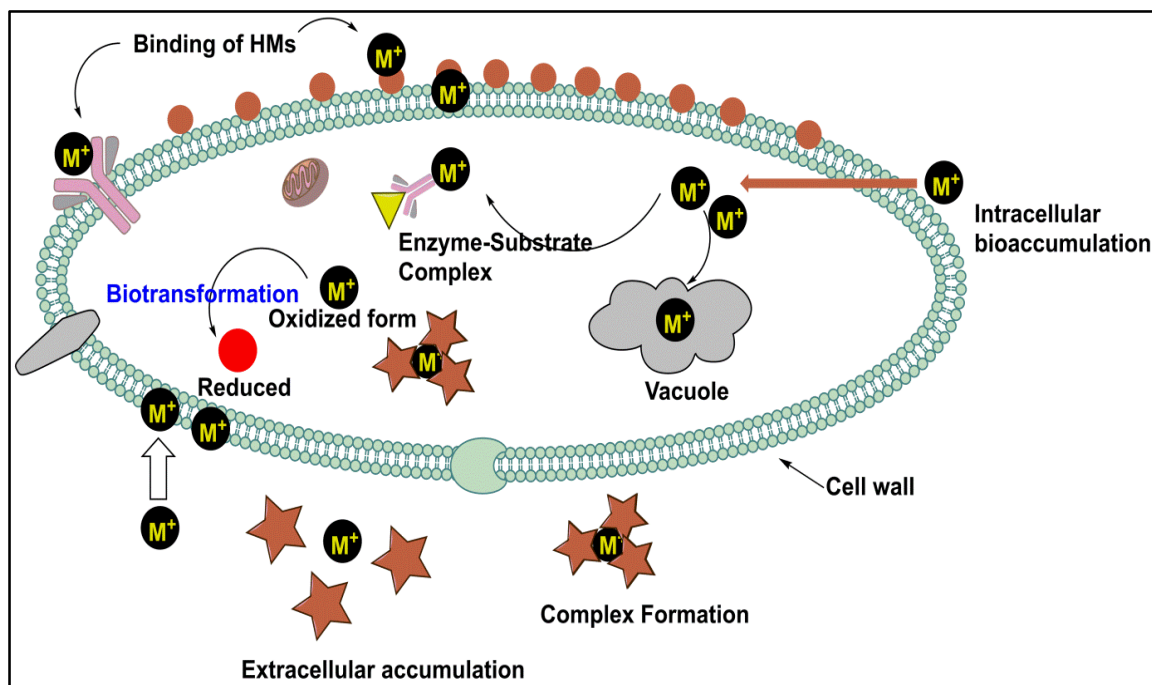

Figure 4: Mechanism of heavy metal uptake by cellular biomass

Thus, biosorption of heavy metals from wastewater is much more promising, cost-effective, recyclability of waste biomass, easy availability, considerable high efficiency, and environment friendly, and implemented at very low concentrations for the uptake of heavy metals.

3. **Kinetic Study:** The nature of the biosorbent used in the removal of heavy metals determines the kinetics of the biosorption. The most frequently pseudo–first order model proposed by the Lagergren suit is perfect for biosorption. Several models have been proposed to describe the rate of adsorption of heavy metals by using biomass adsorbent. Thus, if k_{s1} (min^{-1}) is the rate constant in the first-order model The q_e is the equilibrium adsorption capacity of the adsorbent andq_t is the adsorption capacity at time 't' then,

$$-dq_t/dt = k_{s1}(q_e - q_t)$$

The total rate of biosorption can be summarized by considering the number of sites present on the adsorbent for the adsorption in the presence of adsorbate. Thus, if 'C' is the concentration of the adsorbate at time t and C_b is the apparent concentration of adsorbate at a time 't' after adsorption, then the pseudo-first-order model [85]can be represented by the following equation as -

$$\frac{-dc}{dt} = k_f C - k_b C_b$$

The adsorption isotherm such as Langmuir and Frendlich adsorption isotherm depicts the adsorption carried out by the biosorbent. The Langmuir adsorption isotherm is considered by assuming the availability of vacant active sites on the surface of the biosorbent. The heavy metals are adsorbed on the active sites forming the monolayer and further adsorption is prevented due to limiting distribution of sites. Thus, if q_m is the maximum adsorption capacity (mg g^{-1}), q_e is the adsorption at equilibrium state, K_a is the equilibrium constant of the rate of adsorption/desorption of Langmuir model, then Langmuir adsorption isotherm is given by -

$$qe = \frac{qmKaCe}{1 + KaCe}$$

The Freundlich adsorption isotherm describes that once the active sites are occupied by the heavy metal then adsorption energy declines and thus, the linear form of the Frendlich model can be expressed as

$$\log qe = \log Kf + \frac{1}{n} \log Ce$$

Where K_f is the Frendlich adsorption isotherm constant, q_e is the adsorption at equilibrium[25].

The biosorption depends upon several factors such as the nature of heavy metals, biosorbents, temperature, pH, initial concentration, and contact time. There might have been proposed several models to explain the kinetics of biosorption but the Langmuir model holds good for the adsorption of heavy metals by using biosorbents.

4. **Conclusion and Future Perspectives:** Biosorptionis a promising field to remove heavy metals from wastewater and it offers better opportunities to develop innovative adsorption technology via the use of biomass waste. The flexibility in the biosorption study provides varied applications in environmental bioremediation. This could be possible due to the availability of plenty of biomass waste emerging from different sources and the development in the technology to recycle them acquiring the purpose of bioremediation of wastewater. Biosorption utilizes biosorbent materials such as agricultural waste, algae, fungi, and microorganisms as biosorbent. The mechanism of adsorption has been provided in this chapter. The low-cost processing of biosorption is crucial for the economy and attributes to sustainable development. But, there are several reasons why this is less implemented on the industrial scale. The adsorption efficiency is considerably low for the adsorption of heavy metals.It seems difficult for the use of microbial biomass on a large scale for the sorption of heavy metals. Thus, biosorption technology requires improvement to enhance the capacity of adsorption. The use of hybrid technology must be considered for removal of the heavy metals. The immobilization of Nano based materials on biomass reveals satisfactory results but it needs to be improved further to increase the efficiency. This requires the optimization of the processing aspects of biosorbent and physicochemical conditions to be maintained.

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