Harmful Impacts of Heavy Metals and Importance of Biosorption Technique for Their Removal from Wastewater: A Review

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ARTICLE INFORMATION

ABSTRACT

The increasing number of effluents discharged from the source of water (urban, industrial, agricultural, etc.), is resulting in a higher concentration of heavy metals in the source. Heavy metals have a density of over $5g/cm^3$ to the metals. These are toxic, mutagenic, carcinogenic, and resistant in watery and non-aquatic environments and impact water and non-water bodies seriously by substituting the basic metals of the same function. The extraction from the wastewater can be done in numerous techniques for example using an ion replacement, membrane filtration, osmosis, etc. This study discusses the adverse effects of heavy metals on the human body, the benefits of biosorption over traditional approaches for removal of heavy metals, the different biosorbents used to extract heavy metals, and concerning issues regarding its commercial use, offering a wider viewpoint for the diversity of biosorbents and utilization of biosorption technique. It is evident from the profound literature survey that pH, biosorbent particle size, contact time, initial metal ion concentration, presence of chelating ligands, etc. are some factors that affect the rate and extent of biosorption.

1. Introduction

All living beings necessitate the availability of safe drinking water. Only 3% of the water on the planet is non-salty, with the remaining 2% in the form of ice and glaciers, and less than 1% of the available water may be used for residential, agricultural, and industrial purposes. Because the aquifer is so finite, it must be preserved and kept clean. However, as urbanization and industrialization increase, so does the density of polluted wastewater deposition, resulting in the release of many toxic contaminants into the surrounding environment and a variety of negative repercussions on the ecological system and environment, e.g., contaminated water, polluted air, and soil, and so on (Malik et al., 2019). In developing countries, proper and clean water supply is a concerning challenge nowadays and more than 18 million people are dying each year due to water-borne diseases (Beatrice et al., 2019). Various industries e.g., the manufacture of batteries, steel, paper, paint, pulp, metal plating, agrochemicals, agrochemicals, petrochemicals, chemical manufacturing, mining, leather tanning, and fertilizer industries produce wastewater containing heavy metal ions and discharge their untreated or poorly treated effluents into water sources e.g., rivers, ponds, lakes, etc. These heavy metals are not compostable, unlike organic waste, and are very stable in water due to their ability to form complexes (Sathianesan et al., 2018). Once these metals are accumulated in water sources, they can also enter the food cycle that has a dangerous effect on the whole ecosystem. When these metals reach the human body, they can seed to brain damage, kidney dysfunction, bone damage, nervous system damage, the destruction of red blood cells (RBCs), neurological deformations, and even cancer (Sharma et al., 2009; Alkherraz et al., 2020).

Heavy metals are harmful even at a very small concentration and deteriorate the water standards resulting decrease in the availability of safe, clean, and freshwater (Mashkoor et al., 2018). It has indeed become vital to efficiently extract heavy metals from wastewater, for avoiding contamination of the surface and groundwater. This review will cover the dangers of heavy metal ions on the body, the importance of biosorption, biosorbent metal bonding properties, state-of-the-art of biosorbents for heavy metal ion removal, heavy metal biosorption equilibrium, kinetic, and thermodynamic studies, preventative measures, augmentations, and obstacles.

2. Heavy Metal Ions and their Harmful Effects on the Human Body

2.1. Lead

Heavy metal plum is 11.36g/cm³ heavy metal. Even in extremely small quantities, lead is recognized as very hazardous for the human body. Their possibility for human exposure is through water, food, and inhalation intake. Lead is cancerous and neurotoxic and causes damage in the human body to the kidneys, liver, and peripheral nervous system (Moyo et al., 2013). Paints, batteries, printing, production processes of glass, plating, petrochemical industries, pigments, and rubber industries are the major sources of lead (Nadeem et al., 2009). The permissible lead concentration in drinking water is 0.05 mg/L, according to the World Health Organization (WHO).

2.2. Cadmium

Cadmium (specific density 8.65g/cm³) is mostly used as an anti-corrosive agent in industries. Human exposure to cadmium can be through food, water, breathing, or smoking pathways. Long exposure to cadmium can cause anemia, kidney and bone damages, weight loss, renal disturbances, cancer, pulmonary damages, hypertension (Rose et al., 2015) Effluents discharged from batteries, electroplating, metallurgy, paint pigments, plastic manufacturing, fertilizers, and alloy industries consist of a considerable amount of cadmium (Robert et al., 2018b). The permissible amount of cadmium in drinking water is 0.003mg/L as per WHO guidelines.

2.3. Zinc

Zinc functions in numerous enzymes as a cofactor and is thus important for the human body, but its concentration over a permissible amount is also harmful. Its specific density is 7.13g/cm³, indicating that it is stable in aqueous media. Zinc can cause vomiting, anemia, stomach cramps, skin irritations, nausea, coughing, and a decrease in oxygen uptake efficiency if consumed over a permissible amount (Nawaz et al., 2009 Zwain et al., 2014). Zinc is released into the environment because of discharged effluents of galvanizing plants, municipal wastewater treatment plants, acid mine drainage plants, and natural ores also (Kumar et al., 2006). According to WHO guidelines, the permissible amount of zinc in drinking water is 5.0 mg/L per day (Kumar et al., 2006b).
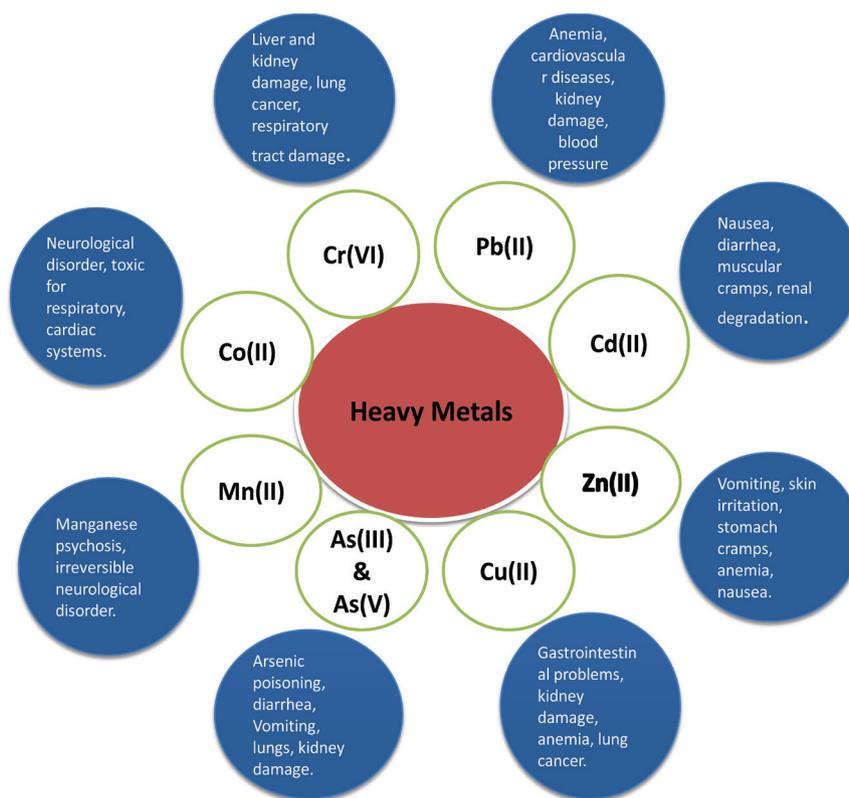
Figure 1: Diagrammatic representation of heavy metals and associated diseases.

2.4. Copper

As copper (specific density of 8.96g/cm³) is an important trace ore for humans, due to its contribution to enzyme function, tissue, and bone growth. The usage of Cu(II) over acceptable levels leads to deposition of copper in the liver, causing headache, nausea, vomiting, respiratory conditions, insufficiency in the liver and kidneys, and gastrointestinal bleeding (Bilal et al., 2013) and incessant inhalation of copper-containing sprays lead to lung cancer also (Bhatia et al., 2015). There is also a possibility of a very rare and life-threatening but inherited disorder called Wilson's disease due to too much accretion of copper in organs. Copper makes its way through electroplating, steel and iron production, mining, printing, electronics and metal sectors, and photography industries, electrical and electronics (Bhatia et al., 2015). The permissible Cu(II) level is 1.5 mg/L in drinking water, as per the guidelines of the WHO.

2.5. Arsenic

Poisoning with arsenic is among the most daunting groundwater quality problems in India as well as in the world. Its particular density is 5.72g/cm³ and is also naturally prevalent in groundwater. Approximately 300 million individuals worldwide suffer from groundwater arsenic toxicity (Tariq et al., 2019). The chronic, severe poisoning from long-term, continuous arsenic exposure has been linked to vomiting, abdominal pain, skin cancer, diarrhea, cardiovascular disease, damage to lungs and kids, cutaneous pigments (Blackfoot's disease), urine bladder. (Kamsonlian et al., 2012; Rodríguez et al., 2013). It is noticeable that 70% of the arsenic production is used as copper chrome arsenate (CCA) for treating timber and 22% of the remaining is used in agricultural chemicals, and the remaining 8% is used in non-ferrous alloys, pharmaceuticals, glass industries (Ranjan et al., 2009)biosorbent dosage, initial metal ion concentration and temperature were studied. Langmuir, Freundlich and Dubinin-Radushkevich (D-R. Many natural phenomena also are responsible for arsenic concentration in the environment such as volcanic eruption, weathering, fire, etc (Nigam et al., 2013). As per WHO guidelines, the permissible amount of arsenic is 0.01mg/L which indicates the extent of its toxicity.

2.6. Manganese

Manganese is an indispensable metal for the human body (specific density 7.43 g/cm³). It is active in numerous ingredients, but it may also be a dangerous heavy metal if ingested to an acceptable extent. Industries including fertilizer, petrochemical, dry battery cells, electrical coils, tanning metal processing alloys, and the mining industry release manganese into the environment (Suguna et al., 2010; Rangnani et al., 2017). Intake of high quantities of manganese can lead to the psychosis of manganese, gastrointestinal buildup, low levels of hemoglobin, and permanent neurological illness (marked by uncontrolled laughing, impotence) (Parvathi et al., 2007; Suguna et al., 2010). The permissible amount of manganese is 0.1mg/L.

2.6. Cobalt

Cobalt is an integral component of vitamin B12 that occurs naturally within the body (8.90 g/cm³ specific density) (Vilvanathan et al., 2016). It may also be harmful, though, above the permissible level. Cobalt comes from wastewater in various industries, e.g., electricity plating, pigments, petrochemical facilities, alloys, and nuclear reactors cobalt comes from wastewater (Robert et al., 2018a; Vilvanathan et al., 2018). Extensive and chronic exposure to cobalt, heart and immune, lung, cardiac and Immune effects, neurotoxicological problem, pulmonary congestion and bleeding even cancer also (Vilvanathan et al., 2016). The daily permissible amount of cobalt is not specified by WHO.

2.7. Chromium

Chromium in two oxidation states +3 and +6 are available (specific density 7.19g/cm³), although Cr (VI) is believed to have toxicity as compared to Cr (III). Through the air, food, water, or even skin chromium may enter a body. Chromium is in use in several industries, including manufacturing, metallurgy, metalworking, chromium mining, painting and pigment making, tanning, anodizing, trimming tools, and the manufacture of basic chrome sulfate (Rahman et al., 2017; Singanan et al., 2017). Cr(VI) may induce liver damage, edema, vomiting, diarrhea, lung congestion, corrosion of skin and edema, and is thought to be cancerous and mutagenic. (Chandrakala et al., 2015; Sharma, 2018). The permissible amount of Cr(VI) is specified at 0.05mg/L by WHO.

According to the specification of the Bureau of Indian Standards (BIS) the drinking water standards for heavy metals are mentioned in Table 1:

Table 1: 10500-2012 Drinking water standards under Bureau of Indian Standards (BIS).

Heavy Metals	BIS Desirable Limit (mg/L)	BIS Permissible Limit (mg/L)
Lead	0.01	NR
Cadmium	0.003	NR
Zinc	5	15
Copper	0.05	1.5

Arsenic	0.05	NR
Manganese	0.1	0.3
Cobalt	-	-
Chromium	0.05	NR

3. Importance of Biosorption

Heavy metals' concentrations have to be reduced in the direction of increasing legislative standards so that clean and fresh water would be provided for drinking, irrigation, animals, and thus the whole ecosystem (Bhatti et al., 2009). Different traditional methods are known for the extraction of polluted water heavy metal ions, e.g. ion-exchange, chemical precipitation, reverse osmosis (Bilal et al., 2013; Dodbiba et al., 2015; Kavitha & Arunadevi, 2018; Rahman et al., 2017; Ahmad et al., 2012; Rotimi & Okeoghene, 2014; Mashkoor et al., 2018), oxidation, ozonation, photocatalysis, electro flotation (Mashkoor et al., 2018; Moyo et al., 2013), irradiation, chemical coagulation, flocculation, nano-filtration, solvent extraction, membrane process and ultrafiltration, adsorption (Ahmad et al., 2012; Moyo et al., 2013; Bilal et al., 2013). Adsorption includes many sub-sections dependent on the adsorbate nature and process, for example, carbon nanotubes, carbon activated, nanoparticles designed, bio-sorbents, etc (Bilal et al., 2013). However, biosorbent use is a somewhat better cost, availability, and results in choice. Figure 2 shows the comparative analysis of conventional methods with biosorption, which represents their shortcomings and advantages.
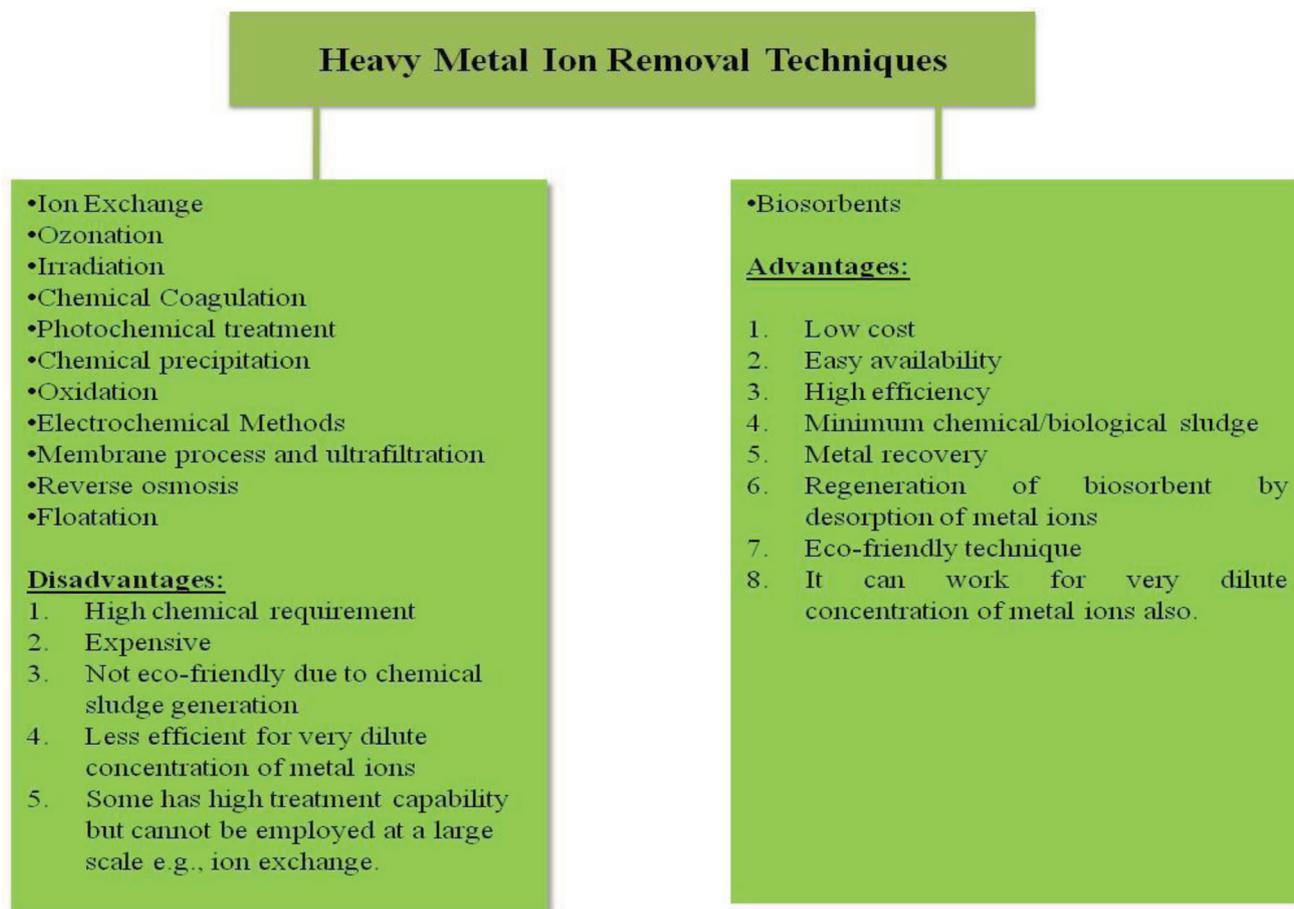
Figure 2: Flow chart representing the comparison between conventional methods and biosorption.

Biosorption is a cheaper process for sequestration or removal of heavy metal ions as the biosorbents are prepared from the abundant and waste biomass or agricultural waste whereas techniques like adsorption by activated carbon, ozonation, irradiation, membrane filtration, etc are comparatively expensive. Biosorbents are easily available, as they are created from natural plant materials widespread in the surroundings but different approaches can be required every

time certain components are not available, e.g. radiation requires dissolved oxygen in a good amount, which may not be available always (Yagub et al., 2014). A biomaterial may show diverse selectivity, depending on its kind and functioning groups in various active sites, etc. for several distinct types of metals, the metal biosorbent is capable of showing different selectivity (Yagub et al., 2014). Metal ions can be retrieved from a biosorbent surface following adsorption. After desorption or elimination of heavy metal ions, biosorbents can also be reused. Biosorption doesn't result in sludge or secondary waste, unlike oxidation, membrane filtration, coagulation generating vast amounts of sludge, as is seen in a majority of other processes also. Biosorption is an environmentally benign technology, no harm is done towards environment. In biosorption, no by-product is created while the photochemical process produces by-products. While there is no biosorbent available, a biosorbant may be created and saved for use.

In biosorption, biological materials are used as adsorbents which introduce the term biosorbent. The process of biosorption involves a biosorbent (in solid phase) and a solvent (in liquid phase i.e., water) which is contaminated by heavy metals. The biosorbent is particularly high in affinity for the biosorbate species owing to the presence of several activity sites in biosorbents (i.e., heavy metal ions). Thus, biosorption is a mechanism in which heavy metal ions (present in the wastewater sample) bind rapidly and reversibly onto binding sites (present on the sorbent's surface).

4. Metal Bonding Characteristics of Biosorbents

From various studies, the common process of biosorbent formation can be represented as shown in Figure 3.
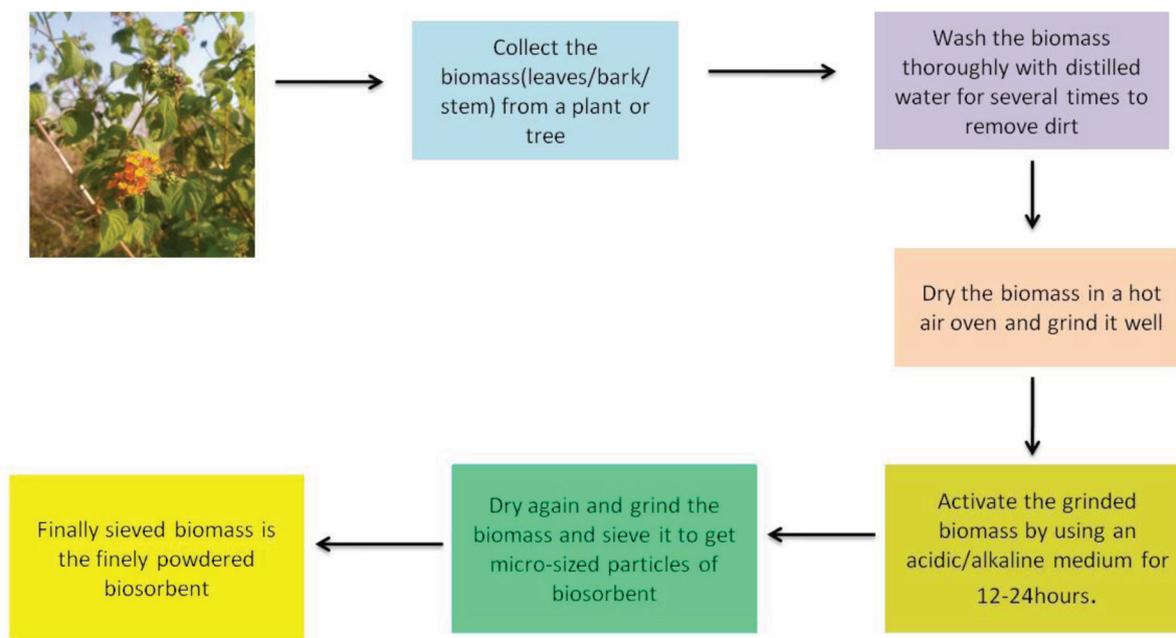
Figure 3: A representative diagram of preparing biosorbent from biomass.

The active binding groups on biosorbent surfaces are identified by FT-IR (Frontier-Transform Infrared Spectroscopy) technique. The active binding sites on a biosorbent's surface have various functional groups e.g., hydroxyl(-OH) group, carbonyl(-C=O) group, carboxy (-COO-) group, amine(-NH2) group, oxygen lone pair, alkenes, alkynes, sulfinyl(S=O) group, nitrile(C≡N) group, etc (El-araby et al., 2017; Singanan et al., 2017; Moyo et al., 2013; Nigam et al., 2013; Ravulapalli et al., 2018; Lucaci et al., 2020; Wang et al., 2015). The adsorption

proceeds until equilibrium is attained between the solid-bound biosorbate metal ions and the rest of its portion in the solution (Ingole et al., 2004). Carboxyl and hydroxyl functional groups on the biosorbent surface have a strong binding ability for heavy metal ions (Johnson et al., 2008). The changes in wave numbers before and after the adsorption of metal ions indicate that those functional groups involved bond strength changes during the whole process of metal binding.

4. Biosorbents used for Removal of Heavy Metals - State of Art

In the 18th and 19th centuries, the potential of live microorganisms was already well-known to remove metals from aqueous systems. Previously, the term biosorption was used for both living and non-living organisms but now for living organisms, the word bio-accumulation is used and for non-living organisms, biosorption word is found to be suitable (Vijayaraghavan & Yun, 2008). Biosorbents may include the leaves, fruit peels, stem or bark of various plants and trees, fruits and fruit peels, algae, fungi; which means that all types of renewable biomass have appropriate binding sites for metal ions can be used as biosorbent. The low-cost adsorbents such as agricultural wastes, products, and byproducts are frequently being used as biosorbents (Ingole et al., 2004). Agricultural wastes are porous and lightweight due to their fibrous nature and therefore are considered to be good enough for metal adsorption. Physical-chemical improvements to waste can increase the surface area, active sites, porosity, etc., thus increasing the extra capability, which can make up for extra processing costs (Johnson et al., 2008). Many studies have described biosorption pathways, which may be one or more combinations, such as ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation, and microprecipitation (Volesky and Schiewer, 1999; Vijayaraghavan & Yun, 2008).

Various biosorbents are found in the literature for the removal of heavy metal ions from wastewater samples including tea waste, *Elaeis guineensis* (oil palm) biomass, bagasse, *citrus limetta, cucumis sativus, prosopis cineraria*, titania-silica, zeolite, *Theobroma grandiflorum* (cupuassu) shell, chitosan (Mashkoor et al., 2018), *Aspergillus and Trichoderma, Neocosmospora sp., Sordaria sp., Rhizopus sp., Penicillium sp., and sterile mycelia* strain fungal groups (Rodríguez et al., 2013), *Paulownia tomentosa Steud.* Leaf (Suguna et al., 2013), *Hydrilla verticilata* (Nigam et al., 2013), *Phoenix dactylifera L.* (date palm) (Ahmad et al., 2012), *Carica papaya* (papaya) wood, maize (Bhatnagar et al., 2010), Chitosan (Gerente et al., 2007), *tectona*

grandis (teak) leaf powder (Kumar et al., 2006; Ngah et al., 2008), *Imperata cylindrica* (lalang) leaf powder, *Hevea brasiliensis* (rubber) leaf powder, *Coriandrum sativum, Arachis hypogaea L.* (peanut) hull pellets, sago waste, *Atriplex canescens* (salt-bush) leaves, *Cyatheales* (tree fern), rice husk ash and neem bark, *Vitis* (grape) stalk wastes (Ngah et al., 2008), vineyard pruning waste (Karao et al., 2010), jelly fungus *Auricularia polytricha* (Huang et al., 2012), Water Hyacinth (Buasri et al., 2012), *Lantana camara* (Ravulapalli et al., 2018; Waoo et al., 2014; Girish et al., 2015; Singanan et al., 2017; Sathianesan et al., 2018), *Streptomyces fradiae* (G. Kirova et al., 2015), *Streptomyces fradiae* (Kirova et al., 2015), *Sesamum indicum* (sesame) husk (El-araby et al., 2017), *Arachis hypogaea* (groundnut) shell (Adesola Babarinde & Gloria Onyiaocha, 2016), *Cymbopogon citratus* (Lemongrass) (Babarinde et al., 2016), scale of *Genyonemus lineatus* (croaker fish) (Nkiko et al., 2013), *Pleurotus ostreatus* spent mushroom compost (Kamarudzaman et al., 2013) *Eupatorium Adinoforum* & *Acer Oblongum* leaves *(Vishwakarma et al., 2018), Tamarindus indica seeds, Corylus* (hazelnut) and *Prunus dulcis* (almond) shell (Pehlivan et al., 2009), rice polish (Ranjan et al., 2009), *Pleurotus ostreatus* (Javaid et al., 2011)*, Lawsonia Inermis* plant leaves (Bhatia et al., 2015), *Cocos nucifera* (coconut) shaft (Ofudje et al., 2015), *Olea europaea* (olive) wastes, *Prunus armeniaca* (apricot) stones, *Prunus avium* (cherries) wastes resulting from the production of cereals such as *Oryza sativa* and *Zea mays* as well as sugar cane bagasse and coir pith (Bhatnagar et al., 2010), waste shell dust of fresh water *Mussel lamellidens marginalis* (Hossain et al., 2015)*, dairy sludge based adsorbent (Rose et al., 2015), *Ipomoea batata* (sweet potato peels) (Chidi et al., 2018)*, coffea (coffee) and *Plantae* (tea) powder (Elsherif et al., 2018), marine red algae *Callithamnion corymbosum sp.* (Lucaci et al., 2020) etc. have been studied to be used as biosorbents.

There are many biosorbents as mentioned in the available literature which is used as the key factors in biomass efficacy studies performed on the information analyzed from batch tests. Primary batch tests (pH, absorbing dose, the concentration of ion, contact times, temperature, etc) and balance, kinetic and thermodynamic studies have been conducted.

The range of biosorbents accessible shows the capacity and wide range of bio-sorption techniques for wastewater decontamination. Biosorbents are discussed in the context of several adsorption methods in the elimination of heavy metals with their respective maximal adsorption capacity (Langmuir, Freundlich & Temkin models) in tabular form in table 3. In Table 3, Q_{max} indicates the amount of maximum monolayer adsorption for metal ions on biosorbent in mg/g.

Table 2: Heavy metals, biosorbents, and their respective maximum adsorption capacities.

Metals	Biosorbents	Qmax (mg/g)	References
Pb(II)	Macrofungus *Ganoderma carnosum*	22.79	(Akar et al., 2006)
	Gossypium hirsutum (Cotton)	45.01	(Riaz et al., 2009)
	H_3PO_4- modified *Cicer arientinum*	171.28	(Nadeem et al., 2009)
	Corylus (Hazelnut) shell	28.18	(Pehlivan et al., 2009)
	Prunus dulcis (Almond) shell	8.08	(Pehlivan et al., 2009)
	Talinum triangulare (Water Leaf).	142.86	(Babalola et al., 2009)
	Phanerochaete chrysosporium	87	(Marandi et al., 2010)
	Jelly fungus *(Auricularia polytricha)*	221	(Huang et al., 2012)
	Raw and oxalic acid-modified *Zea mays L.* (maize husk)	7.38 and 9.33	(Adeogun et al., 2013)
	Durio (Durian) tree waste	20.37	(Yusoff et al., 2014)
	Cocos nucifera (Coconut coir)	37.04	(Yusoff et al., 2014)
	Elaeis guineensis (Oil palm) empty fruit bunch	37.59	(Yusoff et al., 2014)
	Streptomyces fradiae pretreated with NaOH	138.88	(Kirova et al., 2015
	Phytolacca americana L.(PAL), HNO_3- modified *P. Americana(HPAL)*	10.83(PAL), 12.66(HPAL)	(Wang et.al., 2015)
	Tephrosia purpuria Leaf (TPL) biomass	90.6	(Madala et al., 2015)
	Mirabilis jalapa	38.461	(Begum et al., 2015)
	Cymbopogon citratus (Lemon grass)	50	(Babarinde et al., 2016)
	Dicliptera bupleuroides Leaves	1.76	(Tiwari et al., 2017)
	Urtica dioica Leaves (UDL)	1.493	(Tiwari et al., 2017)
	Lantana camara leaves' biomass	10.849	(Robert et al., 2018)
	Olive (*Olea europaea*) branches activated carbon	41.32	(Alkherraz et al., 2020)
	Pyrus pashia leaves' biomass	5.73	(Sharma et al., 2020)
	Rubus ellipticus leaves' biomass	3.38	(Kumar et al., 2020)
Cd(II)	*Cocos nucifera* (Green coconut) shell powder	285.7	(Pino et al., 2006)
	Talinum triangulare (Water Leaf).	100	(Babalola et al., 2009)
	Heartwood powder of *Areca catechu*	10.660	(Chakravarty et al., 2010)
	Jelly fungus (*Auricularia polytricha*)	63.3	(Huang et al., 2012)
	Water Hyacinth (*Eichhornia crassipes*)	104	(Murithi et al., 2014)
	Parkia biglobosa chaff biomass (PBC)	157.98	(Ogbodu et al., 2015)
	Parkia biglobosa pulp biomass (PBP)	16.70	(Ogbodu et al.,2015)
	Waste shell dust of fresh water mussel *Lamellidens marginalis*	18.18	(Hossain et al., 2015)
	Mirabilis jalapa	38.461	(Begum et al., 2015)
	Dairy sludge-based adsorbent	24.75	(Rose et al., 2015)
	Lemon grass (*Cymbopogon citratus*)	40	(Babarinde et al., 2016)
	Ipomoea batata (Sweet potato peels)	125	(Chidi et al., 2018)
	Lantana camara leaves' biomass	7.80	(Robert et al., 2018)
	Olea europaea (olive) branches activated carbon	38.17	(Alkherraz et al., 2020)
	Pyrus pashia leaves' biomass	3.83	(Sharma et al., 2020)
	Rubus ellipticus leaves' biomass	4.48	(Kumar et al., 2020)

Zn(II)	*Tectona grandis* (teak) L.f. leaves biomass	16.42	(Kumar et al., 2006b)
	Phanerochaete chrysosporium immobilized Ca-alginate beads (OPCFCA)	168.61	(Lai et al., 2008)
	Citrus X sinensis (orange) peel cellulose immobilized Ca-alginate beads (OPCCA)	147.06	(Lai et al., 2008)
	Phanerochaete chrysosporium (F)	125.0	(Lai et al., 2008)
	Citrus X sinensis (Orange) peel cellulose (OPC)	108.70	(Lai et al., 2008)
	Plain Ca-alginate bead (PCA)	98.26	(Lai et al., 2008)
	Gallus Domesticus shell powder	46.05	(Kalyani et al., 2009)
	Valonia tannin resin	35.51	(Şengil et al., 2009)
	Phanerochaete chrysosporium	57.21	(Marandi et al., 2010)
	Pleurotus ostreatus	3.22	(Javaid et al., 2011)
	Water Hyacinth	83.01	(Buasri et al., 2012)
	Acid treated *Zeamays* leaf powder	74.0741	(Tichaona et al., 2013)
	Durio (Durian) tree sawdust (DTS)	22.78	(Yusoff et al., 2014)
	Cocos nucifera (coconut) coir (CC)	24.39	(Yusoff et al., 2014)
	Elaeis guineensis (oil palm) empty fruit bunch (EFB)	21.19	(Yusoff et al., 2014)
	Waste shell dust of fresh water mussel *Lamellidens marginalis*	10.64	(Hossain et al., 2015)
	Dicliptera bupleuroides Leaves	1.06	(Tiwari et al., 2017)
	Urtica dioica Leaves (UDL)	1.039	(Tiwari et al., 2017)
	*Olea europaea (*olive) branches activated carbon	34.97	(Alkherraz et al., 2020)
Cu(II)	*Tectona grandis* L.f. leaves powder	15.43	(Kumar et al., 2006a)
	Enterococcus faecium, (a lactic acid bacterium)	106.4	(Yilmaz et al., 2010)
	Pleurotus ostreatus	8.06	(Javaid et al., 2011)
	Fungal *Pleurotus ostreatus*	3.59	(Tay et al., 2012)
	*Pleurotus ostreatus spent mushroom compost(*PSMC)	3.87	(Tay et al., 2012)
	Lawsonia Inermis plant leaf biomass	6.06	(Bhatia et al., 2015)
	Sesamum indicum L. (Sesame Husk)	10.83	(El-araby et al., 2017)
	Dicliptera bupleuroides leaves	2.55	(Tiwari et al., 2017)
	Urtica dioica Leaves (UDL)	1.490	(Tiwari et al., 2017)
	Eclipta Alba leaf biosorbent	9.2	(Kavitha et al., 2018)
	Activated *Eupatorium adinoforum* (AEA)	5.008	(Vishwakarma et al., 2018)
	Activated Acer oblongum (AAO)	3.358	(Vishwakarma et al., 2018)
	Olea europaea (Olive) branches activated carbon	43.10	(Alkherraz et al., 2020)
	Pyrus pashia leaves' biomass	4.73	(Sharma et al., 2020)
	Rubus ellipticus leaves' biomass	2.80	(Kumar et al., 2020)
As(III) and As(V)	*Fungus Penicillium purpurogenum*	35.6 for As(III)	(Say et al., 2003)
	Lessonia nigrescens	45.2for As(V)	(Hansen et al., 2005)
	Chitosan-coated biosorbent	56.50 for As(III) and 96.46 for As(V)	(Boddu et al., 2008)
	Oriza sativa L. (Rice polish)	0.13888 for As(III) and 0.14705 As(V)	(Ranjan et al., 2008)

	Momordica charantia	0.88 for As(III)	(Pandey et al., 2009)
	Fe(III)-treated biomass of *Staphylococcus xylosus*	54.35 for As(III) and 61.34 for As(V)	(Aryal et al., 2010)
	Algae *Maugeotia genuflexa* biomass	57.48 for As(III)	(Sari et al., 2011)
	Living cells of *Bacillus cereus*	32.42 for As(III)	(Giri et al., 2012)
	Arthrobacter sp. biomass	74.91for As(III) and 81.63 for As(V)	(Prasad et al., 2013)
	Hydrilla verticilata	11.65 for As(III)	(Nigam et al., 2013)
	Pretreated biomass of psychrotolerant *Yersinia* sp. strain SOM-12D3	159 for As(III)	(Asadi Haris et al., 2018)
Mn(II)	*Aspergillus niger*	19.34	(Parvathi et al., 2007)
	Saccharomyces cerevisiae	18.95	(Parvathi et al., 2007)
	Glutaraldehyde Cross-linked Chitosan Beads	278	(Suguna et al., 2010)
	Raw *Euphorbia mammillaris* (corncob) biomass	6.54	(Adeogun et al., 2011)
	Acid-treated corncob biomass	7.87	(Adeogun et al., 2011)
	Raw and oxalic acid-modified *Zea mays* (maize husk)	8.52 and 9	(Adeogun et al., 2013)
	Nigerian kaolinite clay	111.11	(Dawodu et al., 2014)
	Rice (*Oriza sativa*) husk ash	3.21	(Adekola et al., 2016)
	Saccharum bengalense	21.72	(Imran et al., 2018)
Co(II)	PFBI (Fungal based biosorbent developed in the lab)	190	(Suhasini et al., 1999)
	Crab shell particles	322.6	(Vijayaraghavan et al., 2006)
	Citrus limon (lemon) peel as biosorbent	22	(Bhatnagar et al., 2010)
	Tectona grandis (teak) leaves powder	29.48	(Vilvanathan et al., 2016)
	Lantana camara leaves' biosorbent	8.32	(Robert et al., 2018)
	Camellia sinensis (tea) and *Coffea* (coffee) powder	244	(Elsherif et al., 2019)
Cr(VI)	*Pleurotus ostreatus*	10.75	(Javaid et al., 2011)
	Brassica napus (canola) biomass	10.67	(Balarak et al., 2014)
	Tamarindus indica (tamarind) pod shell	40	(Desai et al., 2014)
	Ageratum conyzoides leaf powder	21.505	(Chandrakala et al., 2015)
	Mirabilis jalapa	23.255	(Begum et al., 2015)
	Phoenix dactylifera L. (date palm) fiber	62.5	(Rahman et al., 2017)
	Application of immobilized *Musa paradisiaca* L. (banana peels) into calcium alginate beads	109.890	(Sharma et al., 2018)
	Stems of *Lantana camara* plant	26.25	(Ravulapalli et al., 2018)
	Dan- iellia oliveri stem bark	5.455	(Adebayo et al., 2020)
	Goethite particle	6.627	(Adebayo et al., 2020)

The heavy metal ion affinity of biosorbents is found to be enhanced by modifications on their surface, e.g., raw and oxalic acid-modified maize husk for adsorption of lead (II) (in table 2). It is found that using agricultural wastes as biosorbents in their natural form may cause the addition of lignin to the effluent and consequently increases BOD (Biological Oxygen Demand) and this is where the modifications of biosorbents are considered to be better. Therefore, some biosorbents can be seen with respective modifications in table 2 to improve the metal uptake. Notably, acid-modified biosorbents are more capable than unmodified biosorbents (de Freitas et al., 2019)**.** It is noticeable that the biosorbents listed in table 2, have a significant amount of Q_{max}, which indicates the importance of using biosorbents to remove the heavy metals.

6. Equilibrium, Kinetic, and Thermodynamic Studies of Heavy Metal Biosorption

6.1. Adsorption Isotherm Models

Langmuir and Freundlich models are the most used isotherms to identify the effective modeling for the dynamic adsorption process by varying the concentrations of stock solutions.

Langmuir adsorption model

This model is premised on a presumption that solutes are adsorbed in a monolayer onto the adsorbent's surface with a definite number of identical binding sites and uniform adsorption energy without any interactions between adsorbed molecules (Lesmana et al., 2009). Langmuir adsorption model is expressed as follows:

$$Q_e = Q_{max} \frac{K_L C_e}{1 + K_L C_e} \qquad (1)$$

Where C_e is the metal ion concentration at equilibrium (mg/L), Q_e is the number of metal ions removed (mg/g), K_L is Langmuir isotherm constant (L/mg) and Q_{max} is the maximum adsorption capacity(mg/g).

Freundlich adsorption model

This isotherm model consists of an empirical equation that proposes multilayer adsorption on the heterogeneous surface. It is expressed mathematically as follows:

$$Q_e = K_F C_e^{1/n} \qquad (2)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3)$$

Where, K_F is the Freundlich isotherm constant related to the adsorption capacity of the adsorbent and n is an empirical constant. If the value of 1/n is between 0 and 1, then it implies that the adsorption process is favorable.

6.2. Adsorption Kinetics Models

The dynamic adsorption process is often described by pseudo-first-order and pseudo-second-order kinetic models for varying time intervals.

Pseudo-first-order kinetic model

$$Q_t = Q_e \left(1 - \exp(-K_1 t)\right) \qquad (4)$$

Where, Q_e and Q_t are the amount of metal ion adsorbed (mg/L) onto the biomass at equilibrium and at any time

t (min) respectively, K_1 is the rate constant of the pseudo-first-order model (min^{-1}).

Pseudo-second-order kinetic model

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + K_2 t \qquad (5)$$

Where K_2 is the rate constant of the pseudo-second-order kinetic model (g/mg/min) and all other terms have their usual meanings.

6.3. Thermodynamic Study of Adsorption

Thermodynamic parameters such as a change in Gibbs free energy (G^o), enthalpy (ΔH^o) and entropy (ΔS^o) are calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_c \qquad (6)$$

$$K_d = \frac{Q_e}{C_e} \qquad (7)$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (8)$$

Where, R is the universal gas constant (8.314 J/mol/K), T is the temperature (K), Q_e is the concentration of adsorbed metal ions (mg/L), C_e is the metal ion concentration in solution (mg/L) and K_c is equilibrium constant.

A negative value of change in enthalpy indicates that the biosorption process is exothermic while positive value implies it to be endothermic, while the change in Gibb's free energy is relatable to the spontaneity of the process. The negative and positive values of imply spontaneous and non-spontaneous biosorption processes respectively.

7. Limitations, Precautions, Improvements and Future Scopes

More than 15,000 peer-reviewed journal articles have covered the biosorption process over its 69-year history, but it hasn't been widely used in industrial applications until now (Michalak et al., 2013). The poor mechanical resistance and low stability of the biomass could have been a hindrance to the industrial implementation of this technique. There appeared to be problems with the regeneration of the sorbent and its subsequent degradation, even with its high capacity for ion exchange capacity during the biosorption process. Biosorption success is dependent on the concept of recovering and reusing sorbents; in that sense, ion exchange conquers out biological sorption. Otherwise, municipal wastewater management will be a challenge, and fresh sorbent-biomass will be required regularly. But, various

researches are done on the removal of various industrial effluents, fertilizers etc. to enhance the future possibilities of using biosorption on a commercial scale. A few points to be considered regarding the precautions, improvements and challenges to use this technique on a commercial scale can be discussed as follows:

1) The biomass should be plentiful, readily accessible and can be collected free of charge.

2) In deciding biosorption treatment, transportation, maintenance, management, and the final disposal of biosorbent regeneration are the major factors that should be properly considered. Depending on the type and quality of the wastewater to be operated, the costs can vary. Therefore, Financial evaluations are essential for the deployment of biosorption technology on an industrial scale to determine the overall cost of the sorbent and biosorption process to treat a significant volume of wastewater.

3) Laboratory experiments are performed based on optimum pH values, but a mixture of different wastewaters of different pH will be generated in actual industrial effluents, and the administration of the pH in these conditions will be a difficult task.

4) Removal of some particular ions can be interrupted by some essential metal ions which will further deteriorate the quality of water e.g., (Vijayaraghavan et al., 2010a) used HCl pretreated crab shells to avoid excessive leaching of Ca^{2+} and Mg^{2+} ions but the results still were not satisfactory. Therefore, before using a biosorbent on a commercial level, its capabilities and affinities towards different ions must be known. On this premise, the numerical simulations entangled should also be enhanced and simplified.

5) For the feasibility of biosorption process many other factors must also be considered including effluent characteristics like volume, contaminant form, competing ion, solution's chemical characteristics, pH, and temperature change, biomass features e.g., available capacity, mechanical stability, regeneration potential, pollutant sensitivity, and kinetic reactions.

6) It is worth realizing that a bio-sourced can be utilized for numerous cycles but that the ability of the material is reduced after several cycles and becomes a waste again after continuous usage. Therefore, proper waste disposal will also be a problem that needs to be addressed before commercial expansion.

7) More emphasis should be placed on the use of biosorption techniques in the separation, purification, and recovery of biomolecules from mixtures.

8) Before implementing any biosorption procedure, it is important to establish the rational biosorption mechanism related to the type of biosorbent.

8. Conclusion

The preceding studies show that a diverse variety of bioassortments can be employed for removing heavy metal ions from industrial water, such as diverse industrial bacterial biosorbents, agricultural by-products or biomass-based adsorbents. The following points can be drawn from this literary review:

• Several biosorbents can be employed as a synthetic solution for removal of more than one metal which means that with more than one type of heavy metal, a single biosorbent may be used according to their ability to bind to a biosorbent functional group on the biosorbent surface.

• The activated biomass is more efficient than the non-activated biomass activated or changed under acidic and fundamental conditions.

• Many metals rush at higher pH values (in the basic media), hence the optimal pH value for the majority of them is usually between 4 and 7.

• The presence of other metal ions can create a competitive situation for biosorption, this fact also should be considered before using the biosorbents practically on an industrial scale.

• The biosorption rate becomes slow and the amount of adsorbed metals reduces if there is the presence of a complex-forming ligand. The stronger the ligand, the stable will be the complex which will not fit in the active sites and thus the metal adsorption becomes difficult.

• The adsorbed metal ions can be eliminated and the biosorbent can be utilized for further cycles of adsorption-desorption.

• Smaller particle sizes lead to better performance of biosorbent.

From a wide number of published literature (reviewed here), it can be concluded that various kinds of biomass are useful for purifying the wastewater samples, but further work is yet to be done on their capacity in terms of high adsorption rate, high efficiency and shortening of reaction time to use them on a big or industrial scale. Further advancement is required to turn this highly efficient method into functional implementations of this skill. In specific, continuous large-scale activity horizons the extension of biosorption processes to different types of wastewater. Biosorption can find potential uses in areas where heavy-metal solutions like laboratory effluents, mine effluent, or dilute solutions such as municipal runoffs and green roof runoffs have to be removed. More studies should therefore be based on biosorption marketing in different fields.

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Conflict of interest

The authors declare that there are no conflicts of interest.

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