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Biosorption of heavy metals from aqueous solutions: an insight and review

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ABSTRACT: Contamination of water bodies by industrial and domestic effluents containing heavy metals is today considered a big threat to man, flora and fauna. Solving this problem resulting from rapid industrialization has been a challenge over time. From different experimental results obtained, biosorption is considered a part of the solution to this problem. Removal of heavy metals from aqueous solutions is an alternative technique that is cost-effective due to availability of large amount of sorption materials and low or no chemical/energy demand. In this article, a review of past and current outcomes of biosorption studies using different biomaterials was carried out. This review also looked into various factors affecting heavy metals biosorption, adsorption isotherm, kinetics and thermodynamics.

Keywords: biosorption, heavy metals, microbial, non microbial, isotherm, kinetics

1. INTRODUCTION

In recent years, rapid industrialization has led to massive generation of wastes. Proper management of industrial, agricultural and domestic wastes is one of the major problems that need to be solved. More challenging is the indiscriminate disposal of these wastes into the environment with the aquatic system acting as sink [1]. This often reduces the primary and/or secondary use of the water body [2]. In the last decades, heavy metal pollution has become one of the major environmental problems facing man. These metals, even in trace amounts are toxic to both flora and fauna. Their toxicity is due to the fact that they are non-biodegradable, toxic at low concentration, persistent in nature and can bioaccumulate [3]. With rapid industrialization in sectors like mining, energy and fuel, metallurgy, electro-osmosis, surface finishing, pesticides, iron and steel, fertilizer, leather, aerospace, atomic energy, photography, electroplating, electrolysis etc heavy metal bearing wastes are being directly and/or indirectly discharged into the environment causing serious environmental pollution that are life threatening [4,5].

Metals are mobilized and transferred into the food web through leaching from waste dumps, polluted water and soils. The metals increase in concentration at every level through the process known as bio-magnification [6] and cause several diseases and health disorders in humans and other living organisms [7]. Hence, there is a need to remove heavy metals from industrial effluent before discharge [1]. Techniques used for heavy metal removal from aqueous solutions can be classified as physical, chemical or biological. Some of the conventional techniques that have been employed to remove heavy metals from wastewater/effluents include lime coagulation, reverse osmosis, ion exchange, solvent extraction, filtration, chemical precipitation, membrane filtration, electrochemical methods and biological techniques. These techniques suffer from at least one economical and/or technical disadvantage such as long processing time, high energy demand, high cost of reagents, high sensitivity to operational conditions, sludge generation, low/no metal recovery and low efficiency at high metal concentration. Hence, the race to search for a low-cost, efficient and eco-friendly technique like adsorption (biosorption).

In recent years, biosorption has emerged as a viable option for developing an eco-friendly wastewater treatment through metabolically induced or physic-chemical pathways of uptake [8]. Biosorption is the ability of biological materials to accumulate ions, atoms or molecules from wastewater or aqueous solutions through physic-chemical pathways of uptake [1]. It is the property of certain biomaterials to bind and concentrate selected ions or other molecules from aqueous solutions [9].

The biosorption process involves a solid phase (sorber or biosorber; adsorber; biological material) and a liquid phase (solvent, normally water) containing a dissolved species (sorbate; adsorbate) to be sorbed (adsorbed; biosorbed). The adsorber has high affinity for the adsorbate, thereby attracting it through a series of mechanisms. The process continues till equilibrium is reached and established between the amount of adsorber-bound adsorbate and its proportion remaining in solution. The adsorber has for the adsorbate determines the amount of adsorbate that will be removed [10].

1.1 Techniques for heavy metal removal

Numerous techniques have been used for the removal of heavy metals from aqueous solutions. Some of these techniques are briefly discussed below.

Chemical precipitation is a very common technique that is widely used in the removal of dissolved (ionic) metals from aqueous solutions and metal bearing effluents. The ionic metals are firstly converted by the aid of a precipitating agent into an insoluble form. This technique is highly dependent on pH. Hydroxide precipitation is the most common precipitation process with sodium and calcium hydroxide being common precipitant. Membrane filtration is capable of removing metal ions, suspended solids and organic components by the use of a filter medium (membrane).

Ion exchange is mostly used for water softening or demineralization as well as to remove other substances from water. It is based on the reversibly exchange of ions between solid and liquid phases. Photocatalytic process can either be photocatalytic reduction or photocatalytic oxidation. It is a reduction or oxidation process induced by photon or UV light and catalyzed by a photocatalyst such as titanium dioxide (TiO₂) and zinc oxide (ZnO). Titanium dioxide act

as a photocatalyst due to its structure characterized by an electron-filled valence band [11]. TiO₂ and ZnO are also widely used because they are insoluble in water, photostable, non-toxic, less expensive with higher photocatalytic efficiency. Photocatalysis is achieved through 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 process is used for the rapid and efficient destruction of environmental pollutants [12].

Solvent extraction is a method used to separate compounds based on their relative solubilities in two different immiscible liquids. This process is also known as partitioning or liquid-liquid extraction. This process has been used for the removal of heavy metals from waste waters of chemical and electronic industries. Common extractants are organic compounds with molecular mass 200-450, almost insoluble in water that selectively extract metals from aqueous solutions.

2. BIOSORBENTS

Biosorbent is a biological material (biomaterial) on which adsorption is taking place [1]. They may be chemically pretreated to improve the metal uptake and/or suitability. Adsorbents of biological origin (biosorbents) are mostly employed for heavy metals removal from wastewater due to the fact that they are low cost, eco-friendly, and have high metal uptake ability [13, 14]. With increase in environmental consciousness and strict government policies, it is imperative to search for new eco-friendly techniques to clean up contaminated water using low cost biosorbents. The rush to discover new biosorbents for removal of heavy metals has led scientists to investigate many adsorbents of biological origin like soil [15], tamarind fruit shell [16], olive stones [17], chitosan [18], hard wood bark [19], bacteria [20], algae [21], fungi [22], yeast [23], keratin [2], seaweed [24] etc.

Biomass used for biosorption may be living or dead. Dead biomass or sorbents derived from them are much easier to use due to their less complex nature. Dead biomasses are also more applicable for large scale use unlike living biomasses in which nutrient supply and complex bioreactor system are required. However, biosorption potentials of living biomass

on an industrial scale still remain fully unexploited and deserve to be studied [25, 26]. Biosorbents for heavy metals removal can be broadly classified as microbial or non-microbial biosorbents.

2.1 Microbial biosorbents

Microbial biosorbents can either be dead or live heterotrophs (fungi, yeast and bacteria) and photo autotrophs (algae and cyanobacteria). They have high potential for heavy metal removal from contaminated water with high metal uptake [27]. These microbial biosorbents are mostly obtained from industrial fermentation, food and activated sludges and have gained popularity over the years [28]. The classification of microbial biosorbents is shown in Figure 1.

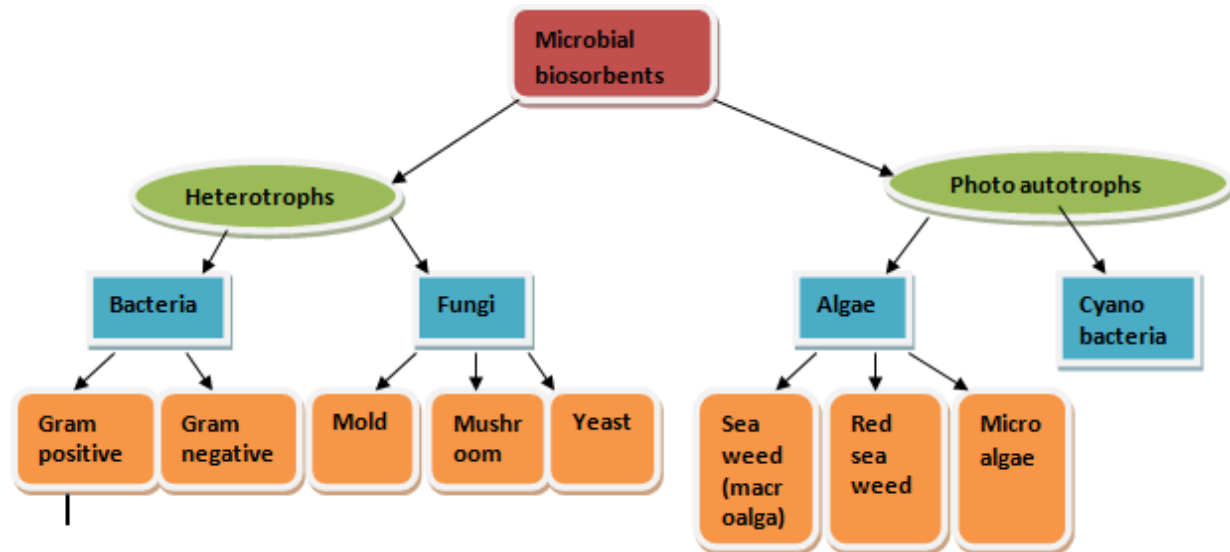


Figure 1 Classification of microbial biosorbents [1]

*It is important to differentiate algae from cyanobacteria that are also aerobic phototrophs and are classified as bacteria [29, 30].

2.1.1 Bacteria

Bacteria are the most copious and versatile microorganisms which constitute a large domain of living biomass. They have a wide variety of shapes and sizes called morphologies. Most bacterial species are either spherical called *cocci* (singular *coccus*) or rod shaped called *bacilli* (singular *bacillus*) [31]. Some can have slightly curved rods or comma-shaped called

vibrio while others can be spiral-shaped called *spirilla* or tightly coiled, called *spirochaetes*. A few others have an unusual shape, such as the star-shaped bacteria [32]. A number of potential bacterial species capable of removing heavy metals from aqueous solutions have been identified from various studies. Majority of these studies carried out with metals and bacteria are related to metabolically mediated bioaccumulation, while the basic principle of biosorption involves the use of dead biomass. This has aroused a lot of controversy. One of the most indepth and significant work carried out on true bacterial biosorption was done by Brierleys [33, 34, 35]. Brierleys carried out the biosorption process using bacteria to the commercial stage [33].

A study on the recovery of heavy metals from aqueous solution using bacteria was carried out by Seki et al [36]. Purple non-sulphur bacteria, *Rhodabacter sphaeroides*, hydrogen bacteria and *Alcaligenes eutrophus* H16 were applied for the biosorption of Cd and Pb ions by Ilhan et al [37].

Bacteria make excellent biosorbents due to their small size, capability to grow under controlled conditions, high content of potentially active chemisorption sites, ubiquity and their resistance to against a wide range of varying environmental conditions [38, 39, 40, 41].

2.1.2 Fungi

Fungi are a large and widely diversified class of organisms that are eukaryotic. They can be classified as microscopic and macroscopic with the former possessing more biotechnological importance.

Three classes of fungi have been identified with practical importance: yeasts, molds and mushroom, with yeasts and filamentous fungi being used to remove heavy metals in waste water treatment. Fungi as a biomass have been reported to be efficient and economical for heavy metals removal from aqueous solutions by biosorption due to their high percentage cell wall material (which shows excellent metal binding properties) [42], eco friendly nature, ease of modification (chemically and genetically) and availability in large quantities from food and antibiotic industries. Unique features like chitin, polyphosphate, lipids and proteins among different species of fungi makes it cell wall to show exceptional binding capabilities

[43] due to high amount of polysaccharides and glycoproteins which contain different metal binding groups like phosphates, amines, hydroxyls and carboxyls. The details are in Table 1.

Table 1 Summary of some results obtained from using bacteria to biosorbed heavy metals according to some published references

Bacteria species	Metals	pH	T (°C)	Co (mg/L)	Wt (g)	q _e (mg/g)	Ref.
<i>Lyngbyaputealis</i>	Cr(VI)	2	25			18	41
<i>Bacillus pumilus</i>	Pb(II)	6	25			28.06	42
<i>Streptomyces</i>	Zn(II)	7.5	20			30	43
<i>Aeromonas caviae</i>						155.3	44
<i>Entorobacter cloacae</i>	Pb	5	25	200	0.1	67.90%	45
	Hg	4		100		43.23%	
	Cd	5		300		59.90%	
<i>Bacillus thioaparans</i> U3	Pb(II)	4	35			90.1	46
<i>Pseudomonas aeruginosa</i>	Cr(VI)		25			1.07	47
	Cu					0.67	
	Zn					1.33	
<i>Staphylococcus saprophyticus</i>	Cr(VI)	2	27	193.6	0.2	24.1%	48
	Pb	4.5		150		100%	
	Cu	3.5		105		14.5%	
Sulphate reducing bacteria (SRB)	Zn	6	30			5.6	49
<i>Pseudomonas</i> sp.	Cu	5.5	30			8.9-238	50
	Cd					500	
	Ni					556	

Yeast is another promising biosorbent under this class that is receiving increasing attention over the past years due to its unusual nature. Yeasts have been proven to be capable of removing heavy metals from aqueous solutions according to numerous literatures [44]. *Saccharomyces* is the most commonly used yeasts in biotechnology. *S. cerevisiae* has been used for biosorption in different forms which include living cell/dead cell [45] wild type/mutant type, flocculant/non flocculant cell [46], immobilized cell/free cell [47], engineered and non engineered cell, laboratory culture/waste cells from different industries [48].

Mold is a fungus that grows in the form of multicellular filaments called hyphae. A large number of molds have been used in heavy metal biosorption. *Aspergillus niger* had been found to be efficient in lead, copper and cadmium removal [49]. Kogej and Pavko carried out biosorption of lead in a batch stirred tank reactor and a continuous packed bed column using

self immobilized *Rhizopus nigricans* [50]. Niu and Volesky [51] examined the fungus *Penicillium chrysogenum* for the biosorption of gold from cyanide solution and reported higher uptake at lower pH values.

Biosorption of heavy metals by macro fungi or mushroom is still in its early stage. Till now, only a relatively little work has been reported. Table 2 gives the summary of some results using fungi as adsorbent.

Table 2 Summary of some results obtained from using fungi to biosorb heavy metals obtained from different literatures

Fungi species	Metals	pH	T (°C)	Co (mg/L)	Wt (g)	q _e (mg/g)	Ref.
Penicillium canescens	Hg(II) Cd(II) Pb(II)					54.8 102.7 213.2	61
Rhizopus nigricans	Pb	5.5	25	300	25	80.8	62
Saccharomyces cerevisiae (immobilized cells in a sol-gel matrix)	Pb					41.9	63
Candida spp	Cd Pb Cu Fe	5	28		0.2	2.05 1.03 28.08 25.68	64
Aspergillus niger	Cr(IV)	2	22.3	50	10	2.2	65
Spent yeast	Cu	4	35	20-80	63.3	0.014-0.037	66
Waste tea fungal	As	6-8	22	1	1	0.004 mmol/g	67
Saccharomyces cerevisiae	Ni Zn Co Fe	7	25	25-200	2	14.1 11.8 8.2 5	68
Aspergillus niger	Pb					172.25	69
Mucor rouxii	Pb Cd Ni Zn	5	25	10		17.13 10.07 6.07 6.28	70

2.1.3 Algae

Algae are photo autotrophs that belong to a wide and diverse eukaryotic organism. The use of algal biomass as biosorbent is gaining popularity as an attractive alternative as they are eco friendly, low cost, have high efficiency in dilute effluents, high surface area to volume, have regeneration and metal recovery potential [52]. Algae have some advantages over bacteria and fungi as biosorbent because algae generally do not produce toxic substances and have low nutrient requirements, being autotrophic they produce a large a biomass. Sorption of metals by algae generally depends on ionic charge of the metal ion, algal species and chemical composition of the metal ion in solution [53, 54,55].

Algae can be single cellular organisms as well as from large thallus (large aggregate of single cells). Most algae are microorganisms but microscopic species occur as sea weeds [56, 57]. Algae can generally be classified into three: macro algal (brown algae or marine algae or sea weed), red sea weeds (red algae). The use of algae as biosorbent is not as popular when compared with fungi (15 %) and bacteria (85 %) [58].

Phosphate, sulphate, imidazole, carboxyl, amine, sulfhydryl and hydroxyl are some of the metal binding sites of algal cell components [59]. The use of several algae in biosorption has been investigated. Dried biomass of a green alga, *Chlorella vulgaris* was used in the biosorption of Pb in a single staged batch reactor in the concentration range of 25 – 200 mg/L [60]. De Carvalho et al [61] investigated the multi metal sorption with brown marine alga, *Ascophyllum nodosum*. They found out that each metal inhibited the uptake of the other using two systems of either (Cu+Zn), (Cu+Cd) or (Zn+Cd). Table 3 is a list of several types of algae used for biosorption and references.

Table 3 Summary of some results obtained from using algae to biosorbed heavy metals according to some published references

Algae species	Metals	pH	T (°C)	Co (mg/L)	Wt (g)	q _e (mg/g)	Ref.
Sargassum filipendula	Cu Ni	4.5	25	250	5		81
Ecklonia radiata	Pb Cu	4.5				2.6 2.2 (meq/g)	82
Microalgae	Cu Zn		30	50-250	5	0.66 0.72 (mmol/g)	83
Ascophyllum nodosum	Cd Ni Zn Cu Pb	6 6 6 5 5	25	10-150	0.5, 1	114.9 50 53.2 70.9 204.1	84
Green algae (spirogyra spp)	Cr(VI)	4	30	1-25	1	265	85
V.dichotoma	Pb Cd Ni Zn			0.4 0.1 0.1 0.1		0.7 0.28 0.37 0.42 (mmol/g)	86
Cladophora fascicularis	Cd Hg Pb		25	20-80	1	20 20 20	87
Sargassum vulgare	Cd Cu	4.5				87 59	88
Lyngbya putealis (HH-15)	Cr(VI)	3		50		94.8	89
Bifurcaria bifurcate	Cd	4.5		10-350	2.5	95	90

2.2 Non microbial biosorbents

Non microbial biosorbents for heavy metal recovery can be classified as: agricultural wastes, keratinous materials, aquatic wastes, industrial wastes, plant residue/shells, chitin/chitosan, cellulose based materials etc.

2.2.1 Agricultural wastes

Agricultural wastes are potential source of low cost biosorbents. Their main constituents are lignin, cellulose and may also contain polar functional groups of lignin which include alcohols, ketones, phenolic groups, aldehydes, carboxylic and ether groups [62]. These functional groups can donate electron pair and bind heavy metals to form complexes with the metal ion in solution [63].

Agricultural wastes like wood, peat, pine bark, banana pith, soybean hulls, cotton hulls, rice bran, sawdust, wool, orange peel have all been employed for heavy metal removal from aqueous solutions. Ajmal et al [64] studied the uptake of Zn(II), Cd(II), Cr(II) and Ni(II) onto untreated and phosphate treated rice husk. The phosphate treated rice husk was found to adsorb more Ni(II) and Cd(II) with the sorption of Cd(II) dependent on time of contact, temperature, adsorbent dose, pH and concentration. Munagapati et al [65] employed the bark powder of *Acacia leucocephala* as an biosorbent for Cu(II), Pb(II) and Cd(II) removal with maximum uptake of 147.1, 185.2 and 167.7 mg/g respectively. Langmuir model was found to best describe the biosorption process and biosorption mechanism involved was physico-chemical adsorption with hydroxyl, carboxyl and amine groups present on the biosorbent. Table 4 provides a summary of different biosorbent and their performances.

2.2.2 Keratinous materials

Keratin is a group of animal proteins which is characterized chemically by its high sulphur and low solubility in water, weak acids and alkalis, organic solvents and is insensitive to the attack of common proteolytic enzymes such as trypsin or pepsin. They are classified as heterogenous proteins due to their amino acid structure and composition.

Keratins are divided into two major classes which are epithelial keratins (soft keratins) and trichocytes keratins (hard keratins). The soft keratins stabilize the cells in the epithelia and are found in the stratum corneum of the skin. The hard keratins help as structural scaffolding and are found in a range of fibrous biomaterials like feathers, human hair, sheep's wool, fur, nails and horns of mammals. Keratins have high relative molecular mass and are

formed by condensation reaction between L-amino acids forming polypeptide chains. The chemical formula of amino acid condensation reaction is shown in Figure 2.

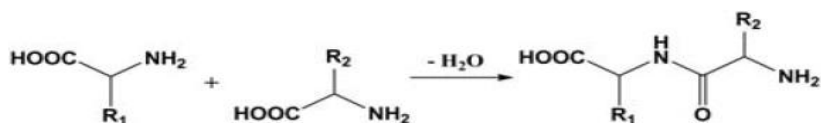


Figure 2 Condensation reaction of amino acids [66]

Peptide bonds link the amino acids and are formed after the condensation reaction. Polypeptide chain is formed from a number of these condensation reactions. R1 and R2 are the side chains of the amino acid residue.

Keratinous materials have been used to remove heavy metals from aqueous solutions in their native, pretreated and modified forms with significant metal uptake. El-Sayed et al worked on the sorption of low-class nature wool or wool waste for the removal of Cr(VI), Zn(II), Co(II), Ni(II) and Cu(II). They reported sorption efficiency in the order: Cu(II) > Co(II) \approx Ni(II) > Zn(II) > Cr(VI). The effect of modification of wool for Cu(II) sorption was also studied [67]. The effects of parameters like contact time, pH and temperature on the sorption of Cu(II) by wool was also studied by Sheffield and Doyle [68]. It was found that higher temperature and longer heating times improved the removal of Cu(II).

Chicken feathers make up 4 – 6 % of the total weight of matured chickens [2] with an estimated 15 million tons available globally yearly as a waste product from chicken slaughter points [69]. Results obtained from heavy metal sorption from aqueous solutions using chicken feathers have been largely encouraging [70]. These feathers are usually processed to produce a low-grade animal feed, burnt or disposed at dumpsites. Feathers are composed of 91 % keratin, 1.3 % fat and 7.9 % water making them good biosorbent for heavy metals removal.

Salaudeen and co workers investigated the ability of chicken feather to biosorb Pb(II) and Cu(II) from aqueous solutions. From their results, maximum uptake of Pb(II) and Cu(II) were 79.36 and 61.92 mg/g respectively with negative standard Gibb's free energy (ΔG) indicating a spontaneous adsorption [3]. Cu(II) and Zn(II) removal efficiency was studied by Al-Asheh [71]. A comparison between the removal efficiency of both metal ions by untreated

native chicken feathers and alkali treated feathers was done. The treated feather was found to performed better.

Much work has not been done on the use of hair for heavy metal biosorption. Ferguson et al investigated the removal of Zn(II), Cu(II), Mn(II) and As(III) from aqueous solutions using human hair [72]. The hair samples performed better for Zn and Cu removal compared to Mn and As. The authors concluded that the higher removal of Cu(II) was probably due to higher binding capacity and stability especially of Cu-S interaction and due to higher electrostatic interactions between Cu(II) and hair. Perm-lotion-treated human hair was showed to be capable of removing Pb(II) and Cu(II) from aqueous solutions by Jung et al with over 90 % removal at pH of 4.2 [73].

In conclusion, carboxyl, hydroxyl, amino and sulphur-containing groups are present on the surface of keratin biomaterials. These functional groups have high affinity for heavy metals. Table 4 gives the summary of previous research on biosorption of heavy metals using some biomaterials carried out by different researchers.

2.3 Factors affecting choice of biomass

The choice of biomass for large scale industrial use depends majorly on availability and cheapness. Therefore for a biomass to be accepted as an industrial adsorbent, several factors need to be considered:

- Availability in large quantity at one location
- Ease of recovery of adsorbed metals
- Low economic value
- High adsorption capacity

Table 4 Summary of different biosorbent and their performances according to some published references

Biosorbents	Metals	pH	T (°C)	Co (mg/L)	Wt (g)	q _e (mg/g)	Ref.
Chitin	Zn		25		0.6	5.86	103
Wool powder	Co(II)					53.78 (mmol/g)	104
Chitosan	Fe(II) Pb(II) Cu(II)	4	25	1mM		54.8% 50% 48%	105
Wool nano fibre	Cu(II)					0.173 (mmol/g)	106
Chicken feather	Pb(II) Cu(II)	4	25		0.0 5	79.36 61.92	3
Natural chicken feather	Cu(II) Zn(II)					0.186 0.098 (mmol/g)	107
<i>Gmelina arborea</i> leaves	Pb(II) Cd(II)	5	30	10- 100	0.5	26.88 20.88	108
Saw dust	Pb(II) Cu(II) Zn(II)		21	10- 500		26 22.5 19.75	109
Treated chicken feather	Pb(II)					0.047 (mmol/g)	110
Walnut shell	Pb Ni Cr Cd	5 5.1 5.1 5.3		49.4 48.6 49.2 48.6	0.5	91.1% 35.3% 60.3% 65.4%	111
Egg shell	Pb Ni Cr Cd					98.6% 14.4% 99.5% 41.9%	111
Natural hair	Cu(II) Zn(II)					0.087 0.131	107
Treated hair	Pb(II) Cu(II)					0.11 0.141 (mmol/g)	102
Tilapia fish shell	Zn Pb Fe	6 5.5 4.5		10 0.3 300 (ppb)	0.0 2 0.0 01 0.8	92.3% 89.3% 64.2%	112
Coconut shell powder	Cu(II)		27			7.463	113

3. HEAVY METALS

Heavy metals are metals with specific gravity greater than 5.0 g/cm³. This includes transition metals and higher atomic metals from group III to IV of the periodic table [74]. These metals are toxic or poisonous at low concentration. Lead, copper, cadmium, nickel, cobalt, chromium, manganese, antimony, arsenic, mercury, zinc, molybdenum, etc are some metals considered as heavy metals. These metals can be classified into three broad classes as given in Table 5.

Table 5 Metal classification

Precious metals	Radionuclides	Toxic metals
Gold, Silver, Platinum, Palladium, Ruthenium, Rhodium, Iridium, Osmium	Uranium, Radium, Thorium, Plutonium, Radon	Mercury, Copper, Lead, Cadmium, Nickel, Cobalt, Tin, Zinc, Chromium

The toxicity of these metals occurs even at low concentration, hence, heavy metals can also be classified based on their toxicity. Classification of heavy metals based on toxicity is shown in Table 6.

Table 6 Classification of heavy metals based on toxicity [75]

Toxicity	Heavy metals
Low toxicity	Iron, molybdenum, manganese
Average toxicity	Zinc, copper, vanadium, nickel, tungsten, chromium
High toxicity	Mercury, arsenic, lead, cadmium, antimony, uranium

Metals like nickel, copper, zinc, iron, cobalt, manganese, chromium, molybdenum and selenium are essential metals required for various physiological or biochemical functions. Deficient supply of these metals (micro-nutrients) can result in poor state of health [76]. In biological systems, heavy metals can affect cellular organelles and components like cell membrane, endoplasmic reticulum, mitochondrial, lysosome, nuclei and some metabolic,

detoxification and damage repair enzymes [77]. Some of these heavy metals are briefly discussed below.

3.1 Arsenic

Arsenic is a ubiquitous element that occurs at low concentration in virtually all environmental matrices. It occurs as inorganic trivalent arsenite and pentavalent arsenate and organic methylated metabolites-monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide. Common sources of arsenic include pesticides, herbicides, smelting, semiconductors and rock sedimentation [1]. Arsenic concentration in water is usually less than 10 µg/L.

3.2 Cadmium

Cadmium is a soft, silvery-white metal that is chemically similar to zinc and mercury. It has considerable toxicity with destructive impact on most organs. The major industrial uses of cadmium include ceramics, fertilizers, fungicides, mining and plastics [1]. Inhalation, ingestion and cigarette smoke are the major routes of exposure to cadmium. It is a severe pulmonary and gastrointestinal irritant that is fatal if ingested or inhaled. Health effects include hypertension, weight loss, Itai-Itai etc. It is also known to be carcinogenic, mutagenic and teratogenic [1].

3.3 Chromium

Oxidation states of chromium ranges from Cr(II) to Cr(VI) having two stable oxidation states of Cr(III) and Cr(VI) with contrasting toxicities, bioavailability and mobility. Compounds of chromium are stable in Cr(III) state and occur in nature in this form. Cr(VI) is the second most stable state while elemental chromium, Cr(0) does not exist. Chromium is an integral part of many industrial processes like leather tanning, steel production, textile industries, electroplating etc.

3.4 Lead

Lead is a naturally occurring bluish-gray metal with a crustal abundance of 14 ppm making it the 38th most abundant element in the crust [78]. It has many applications

domestically and industrially in pipes, paints, mining fossil fuel, canned foods, batteries etc. in adult humans, drinking water account for about 35-50 % of lead while in children, it is about 50 %. The highest amount is taken into the kidney, followed by liver, heart, brain and other soft tissues. However, skeleton contain the highest body fraction of lead [79]. Mental retardation, brain damage, encephalopathy, seizures, loss of appetite [1] are some common effects of lead poisoning with the nervous system being the most vulnerable target of lead poisoning.

3.5 Mercury

Mercury is commonly known as quicksilver. It is extremely rare with a crustal abundance of 0.08 ppm. It exists in nature in three forms: inorganic, organic and elemental forms. Each of these has its associated toxicity. People are exposed to inorganic mercury through their occupation and organic mercury (e.g methylmercury) through their diet. The peripheral and central nervous systems are the main target of methylmercury and elemental mercury. Inhalation of mercury vapour is harmful to the nervous, immune and digestive systems, kidneys, lungs and may result in fatality. Salts of inorganic mercury are corrosive to the eyes, gastrointestinal tract, skin and become toxic to the kidney if ingested. Mercury is a component of many products like batteries, thermometers, barometers, electric switches, dental fillings (dental amalgam), skin-lightening creams, pharmaceuticals and lamps.

3.6 Copper

Copper is malleable, ductile and soft metal with very high electrical and thermal conductivity. It is used in electroplating and in electrical industries. At high concentrations, it becomes toxic to living organisms. Its presence can cause serious toxicological issues because it is known to deposit in the pancreas, skin, myocardium and liver [80]. An adult human is made up of about 1.4 to 2.1 mg of copper per kilogram of body weight [81]. Short term exposure to copper can lead to gastrointestinal distress while long term exposure can lead to liver or kidney damage. High concentration of copper in water can destroy marine life damaging the liver, gills, kidney and nervous system in fish and other creatures. Leather processing, pesticides, fungicides and mining industries are some industrial sources of

copper. Table 7 is a summary of heavy metals, their sources, health effects and World Health Organization guidelines for drinking water.

Table 7 Sources, health effects and WHO guidelines for drinking water, 2008 [1]

Metal	Major source	Health effect	WHO permissible limit for drinking water (mg/l)
As	Pesticides, herbicides, smelting, semiconductors, rock sedimentation	Skin damage, circulatory system problems, increased risk of cancer, bone marrow depression	0.01
Cd	Ceramics, fertilizers, fungicides, mining, plastics	Hypertension, carcinogenic, teratogenic, mutagenic, liver and kidney damage, Itai-Itai disease, weight loss	0.003
Cr	Leather, tanning, steel production, textile industries, electroplating	Bleeding of the gastrointestinal tract, ulcers of the skin and mucus membrane	0.05
Cu	Leather processing, pesticides, fungicides, volcanic eruption	Gastrointestinal distress, liver or kidney damage, Wilson's disease, dizziness, diarrhea	2.0
Hg	Batteries, mining, dental fillings, vaccines, fish, paints	Mental disturbances, gingivitis, haematological changes, insomnia, chest pain, dyspnoea, haemoptysis, impairment of pulmonary function, abortion and foetal malnutrition, Minamata disease, corrosive to skin, eyes, muscles	0.001
Ni	Diesel exhaust, batteries, electroplating, pigments	Carcinogenic, affects reproductive health, chronic bronchitis, reduced lung function, lung cancer	0.02
Pb	Pipes, paints, mining, burning of fossil fuels, canned foods, batteries	Inhibition of haem synthesis, irritation, mental retardation, brain damage, tumour producing, encephalopathy, seizures, loss of appetite	0.01

4. BIOSORPTION AND BIOACCUMULATION

There is confusion regarding the use of the terms biosorption and bioaccumulation. The difference between the two terms is majorly based on the state of the biomass. In this regard,

bioaccumulation is defined as an active biosorption process in which living cells are employed as biomass. Living organisms have the ability to adsorb and retain heavy metals from their surroundings. In bioaccumulation, heavy metals are transferred in the cells and gather intracellularly [82]. Bioaccumulation occurs in two steps: the first step is a rapid process that involves the adsorption of metal ions onto cells and is a much slower step which includes the transport of metal species across the cell membrane into the cells.

Biosorption on the other hand is a passive process which involves rapid metal uptake by dead biomass. Table 8 gives the differences between bioaccumulation and biosorption processes.

Table 8 Differences between bioaccumulation and biosorption [83,84]

	Biosorption	Bioaccumulation
Definition	simple metabolically passive physicochemical process of metal ion uptake	Metabolism mediated active process in which metal ions uptake on biosorbent is intracellularly in living cells
Selectivity	Poor due to variety of ligands but can be increased through modification	Better than biosorption but less than some chemical technologies
Ph	pH of solution strongly affects sorption capacity of heavy metals though the process can take place over wide range of pH	Significant pH can seriously affect living cells.
Cost	Usually low. Biomass can be gotten from wastes	Usually high since process involves living cells that need to be supported
Rate of uptake	Generally fast, few seconds for outer cell wall accumulation	Slower compared to biosorption. Intercellular uptake takes a long time
Energy demand	Low	Energy is required for cell growth
Regeneration and reuse	High possibility of biosorbent regeneration and reuse	Reuse is limited due to intercellular accumulation
Metal recovery	Metal recovery is very possible with an adequate eluent	Biomass cannot be reuse even if it is possible
Temperature	Within a modest range	Inhibited by low temperature

Metal affinity	Higher under favourable conditions	Toxic metal affects uptake by living cells but in some cases high metal uptake is possible
Versatility	Anions and some molecules affect metal uptake	Energy source is required. Dependent on plasma membrane ATPase activity

4.1 Advantages of biosorption

Biosorption have some advantages over other conventional techniques which are listed below:

- (1) Availability of vast amount of cheap biomaterials
- (2) There is little or sludge generation
- (3) With biosorption, there is little consumption of expensive chemicals and energy
- (4) Possibility of metal ions removal in the presence of other ions
- (5) High recovery and suitable for all metals
- (6) Biosorbents can be regenerated and reuse
- (7) Relatively high efficiency at low and high metal concentration
- (8) Fast kinetics that ensure short processing time for large volume of waste.

4.2 Disadvantages of biosorption

- (1) For some biosorbents, there is possibility of early saturation (due to complete occupation of sorption sites), desorption is therefore required before reuse.
- (2) Changing metal valency state through biological means is almost not possible as in for less soluble forms.

4.3 Factors affecting biosorption

There are several variables that affect biosorption, some are related to adsorbate (metal ion) and biosorbent while others are related to the environment. Some of these factors are discussed below.

4.3.1 pH

pH is perhaps the most important of these factors. The metal solution pH influences the metal solubility, concentration of counter ions on functional groups of the biosorbent, degree of ionization, metal speciation and biosorbent binding sites [85]. pH of solution affects the competition ability between hydrogen ions and metal ions for the biosorbent active sites [86]. The sorption of metal cations like Co, Mn, Ni, Cd, Cu, Zn, Pb tend to increase with increase in pH [87] while metals like Ag, Hg or Au which form negatively charged complexes or have strong 'b' character (i.e tendency to form strong covalent bonds) may show decrease uptake or no significant change in uptake with increase pH [88].

Biosorption of heavy metals is affected by pH in three ways: firstly, pH affect the active sites i.e at low pH, the active sites becomes protonated, hence, a competition is set up between protons and metal ions for the active sites on the sorbent [89]. At very low pH, all the active sites become protonated and desorption of already sorbed metal can now occur [90]. This is why acid solutions are effective in metal elution and regeneration of the biosorbent. A 2 unit decrease in pH can result in $\approx 90\%$ decrease in metal uptake in some cases [87].

Secondly, very low pH values such as those used in desorption (regeneration) can damage the biosorbent [91]. Thirdly, sorption is highly dependent on solubility, therefore, increasing pH leads to decrease in solubility of metal complexes in solution.

Salaudeen et al observed a rapid increase in the sorption of Pb, Cu, Cr and Cd using termite feather biomass in pH range of 3-4 and minimum sorption at pH of 1 [85]. Mungasavalli and co workers reported pH of 3 as the optimum pH for Cr biosorption using *Aspergillus niger* [92]. Biosorption Cd by *Rhizopus cohnii* was found to increase by increasing pH from 2.0 to 4.5 and reached a peak in the pH range of 4.5 to 4.6 as reported by Luo and Xiao [93].

Finally, if the objective of the experiment is to remove metal ions from aqueous solution solely by biosorption, it is best to carry out the sorption experiment at pH values where precipitation does not occur. Table 9 gives the pH for metal hydroxide precipitation.

Table 9 pH for metal hydroxide precipitation ^[50]

Metals	pH value of precipitation
Aluminium	5.2
Cadmium	9.7
Chromium	6.5 – 7.3
Copper	7.1 – 7.3
Iron	4.3
Lead	6.3
Nickel	9.2 – 9.4
Tin	1.0 – 4.5
Zinc	8.3 – 8.5

4.3.2 Temperature

Temperature determines the thermodynamic parameters of sorption process and affects kinetic energy of the metal ions. Unlike bioaccumulation, within the range of 20 – 35 °C, biosorption efficiency remains largely unaffected although, high temperature (e.g 50 °C) may improve biosorption but physical structure of biosorbent may become damaged at higher temperature.

According to Wasewar ^[94] improvement in metal uptake with increase in temperature may be attributed to increase in number of adsorption active sites of due to decrease in the thickness of boundary layer of the adsorbent. Kuyucak and Volesky reported 50 – 70 % increase in Co uptake by brown alga *Ascophyllum nodosum* when temperature was increased from 4 – 23 °C ^[91].

Farhan and Khadom reported a decrease in sorption of Pb, Co, Zn, Cd and Cu onto *Saccharomyces cerevisiae* with increasing temperature with a maximum equilibrium uptake at 27 °C ^[95].

4.3.3 Biomass type/nature of biomass

A large number of biomaterials have been employed for the biosorption of metal ions. It has been reported that dead biomass are more efficient for metal ion sorption compared to living biomass. Chemical pretreatment of biomass e.g alkali treatment is known to improve biosorption efficiency as well as physical treatment such as boiling, crushing, ashing, drying and mechanical disruption are known to affect biosorption.

4.3.4 Biosorbent dose

Biosorbent dosage has a strong influence on biosorption of heavy metals because the biosorbent provides the sorption site for metal ions. Mostly, higher biosorbent dose at a given initial metal concentration increases percentage biosorption (%) due to larger surface area (which in turn increases the number of available sorption sites) but decreases the metal uptake per unit mass of biosorbent. Therefore, comparing sorbent using percentage biosorption is crude and inaccurate. It can only serve the purpose of quick and approximate screening of biosorbents. The better approach is to use metal uptake per unit mass of adsorbent.

Venugopal and Mohanty reported an increase in percentage biosorption of Cr using *Parthenium hysterophorus* from 61.28 to 80.81 % with an increase in biosorbent dosage from 0.1 to 1 g due to availability of more sorption sites but decrease in metal uptake from 9.43 to 0.37 mg/g because of increases biosorbent to metal ratio [96].

4.3.5 Contact time

Contact time with aqueous solution is another key parameter for successful biosorption process. Biosorption of metal ions consist of two steps: an initial step where the rate of uptake is rapid and high (usually within an hour with about 90 % uptake) and a second slower step where equilibrium is attained. Metal uptake is rapid and fast in the first step due to availability of vacant active sites for metal sorption. As time increases, rate of biosorption decreases due to saturation of active sites. The fast and rapid primary sorption is as a result of extracellular binding and slow sorption due to intracellular binding [97].

4.3.6 Initial metal concentration

The initial metal ion concentration provides an important driving force to overcome all mass transfer resistance between the solid and aqueous [98]. The metal uptake (mass of sorbed metal per unit mass of adsorbent) of the biosorbent increases initially with increase in metal ion concentration before reaching a point of saturation. However, high metal ion concentration results to decrease in removal efficiency (%) due to low interaction of the ions with the available sorption sites. The work of Salaudeen and coworkers corroborated this fact of increase in initial metal ion concentration translating to increase in uptake (mg of metal removed per g of adsorbent). When initial metal ion concentration was increased from 20-120 mg/L, the uptake of Cr, Cu and Pb by termite feather increased significantly and slightly for Cd [85].

4.3.7 Presence of cations

The presence of other sorbable cations coexisting with the metal of interest leads to competition for active binding sites or formation of complex with it. The presence of these cations will inhibit/reduce the biosorptive removal of the metal ion of interest. The level of inhibition/reduction is dependent on the binding strength of all the cations involved. Magnesium and sodium are known to compete with zinc for binding sites of algae with about 90 % reduction in zinc biosorption at 200 mM NaCl or $Mg(NO_3)_2$. However, their level of interference with the biosorption of lead or copper is much lower with less than 50 % reduction of lead or copper sorbed at 200 mM NaCl or $Mg(NO_3)_2$ [99]. The inhibition in the biosorption of heavy metals by alkali metals (K, Na) onto microbial biomass is not as significant as the inhibition of biosorption of uranium and radium by heavy metals (Fe, Cu, Zn) [100].

According to different literatures, alkaline and alkaline earth metals (light metals) bind less strongly compared to heavy metals or radioactive elements. Hence, the light metals interfere less strongly with the sorption of heavy metals [101].

4.3.8 Agitation speed

Increase in agitation speed increases biosorption rate of sorbate by reducing its mass transfer resistance. Although too high a speed may damage the structure of fragile sorbent [102]. A moderate speed ensures the best homogeneity. Low agitation speed results in low contact between sorbate and sorbent, moderate speed results in best homogeneity, while high speeds result in the occurrence of vortex phenomenon which leads to loss of homogeneity. Too high speed leads to excessive turbulence which may reduce the time of contact between the biosorbent and metal ion, hence reducing the biosorption performance [103].

Liu et al reported 120 rpm as the optimum speed for cadmium and zinc biosorption using *Aspergillus niger* [103]. From the work of Yeddou-Mezenner, biosorption efficiency increased from 32.4 to 65 % when the agitation speed was increased from 0 to 80 rpm [104].

Other factors that affect biosorption are presence of anions (ligands), surface area to volume ratio, surface area of biosorbent etc.

4.4 Mechanism of biosorption

The biosorption of heavy metals by sorbent takes place through several mechanisms, with different mechanisms given in different literatures based on the type of biosorbent and classification criteria. The mechanisms of biosorption can also be classified based on:

- Cell metabolism: here, mechanisms of biosorption are classed as metabolism dependent and non-metabolism dependent;
- Location where biosorption takes place within the cell: here, mechanisms of biosorption are classified as extracellular accumulation/precipitation, cell surface sorption/precipitation and intracellular accumulation.

Generally, biosorption of heavy metals occurs via: physical adsorption, ion exchange, complexation/coordination, precipitation and transport across cell membrane.

4.4.1 Physical adsorption

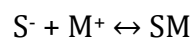
Physical adsorption takes place on the surface of biosorbent through weak electrostatic force of attraction such as van der waal's forces. This can be affected by surface area of the biosorbent and sometimes by pH of solution [105]. From the work of Chojnacka, it was learnt that the biosorption of Cr(III) ions by grass and wheat straw was through physical adsorption mechanism following Langmuir model monolayer form.

4.4.2 Ion exchange

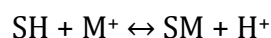
Ion exchange is the replacement of an ion on a solid phase with another exchangeable ion in solution. It involves the exchange of binary metal ions with counter-ions from the sorbent surface during biosorption. Ion exchange can take place through cation or anion exchange. Carboxyl groups are examples of cation exchangers while amino/imidazole groups are examples of anion exchangers. Biosorption of Cd(II), Ni(II), Zn(II), Pb(II) and Cu(II) by dead macrophytes was found to be through ion exchange [106]. Perpetuo et al reported that biosorption of copper ions by *Gandoderma lucidium* was through ion exchange mechanism which was possible in microorganisms due to the composition of their cell walls that contain polysaccharides that can undergo ion exchange with their counter ions [107].

4.4.3 Difference between ion exchange and sorption

Sorption refers to the uptake of metal cation by a active free site of the sorbent that has not been previously occupied by another cation. According to the Langmuir adsorption model, sorbent sorption sites are free with uniform energy throughout. Hence, adsorption reaction can be given as;



While the ion exchange equation takes the form



Where S^- is the free sorption site, M^+ is the metal ion and SH is a sorption site already occupied by a proton (H) that takes part in ion exchange with the metal cation (M).

4.4.4 Complexation/cooordination

This is the formation of a complex as a result of interaction between metal ions and functional groups. The metal ions can bond with monodentate or polydentate ligands (chelation). The attraction between the metal ion and functional group is significant and is based on the Hard and Soft Acids and Bases (HSAB) theory which classify elements as hard or soft acids (mostly metals) and hard or soft bases (mostly non metals) [108]. The theory is that “in a competitive situation, hard acids tend to form complexes with hard bases and soft acids tend to form complexes with soft bases” [109]. According to HSAB theory, the adsorption of hard metals is mainly through electrostatic interactions with small ligands containing oxygen such as carboxyl groups, while the adsorption of soft metals is mainly through interactions with sulphur-containing ligands such as sulphate [110]. Table 10 shows Classification of metals and ligands according to the HSAB theory.

Table 10 Classification of metals and ligands according to the HSAB theory [109]

Classification of metals		
Hard	Soft	Intermediate
H ⁺ , Na ⁺ , Ca ²⁺ , Ni ⁺ , Zn ²⁺ , Fe ³⁺ , U ⁴⁺ , Si ⁴⁺ , K ⁺	Cu ²⁺ , Hg ⁺ , Pt ²⁺ , Hg ²⁺ , Ag ⁺	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Pb ²⁺
Classification of ligands		
Hard	Soft	Intermediate
H ₂ O, OH ⁻ , F ⁻ , CH ₃ CO ₂ ⁻ , PO ₄ ³⁻ , CO ₃ ²⁻ , ROH, RO ⁻ , RNH ₂	CO, C ₆ H ₆ , CN ⁻ , I ⁻ , R ₂ S, RS ⁻ , S ²⁻	Br ⁻ , NO ₂ ⁻ , C ₆ H ₅ NH ₂ ⁻ , C ₅ H ₅ N

Cu(II) being a soft acid, would favour binding covalently to biosorbent containing soft bases such as nitrogen or sulphur containing ligands; Fe(II), Co(II), Ni(II) and Pb(II) which are intermediate acids will bind favourably with intermediate ligands.

Aksu et al hypothesized that the biosorption of copper by *C. vulgaris* and *Z. raigera* occurs through adsorption and complex formation between the copper ion and functional groups present on the cell wall [111]. Han and coworkers also reported that Cr(III) sorption by

green microalgal *Chlorella miniate* was through complex formation between phosphate, carboxyl, and amine ligands and the Cr(III) [112].

4.4.5 Precipitation

Precipitation is the formation of insoluble metal as a result of chemical interaction between the metal and functional groups on the cell surface to form precipitate. It is one of the few mechanisms involved in the metabolism dependent biosorption, although metabolism independent biosorption can as well occur by precipitation. Precipitation metabolism dependent biosorption takes place as a result of the microorganism's active defence system response in the presence of toxic metal ions. In metabolism independent biosorption, precipitation occurs due to the chemical reaction between metal ions and functional groups present on the surface of the microbial cells, the reaction may as well be a redox reaction [113].

Witek-Krowiack and Reddy; Liu et al; Garcia-Mendiata et al all reported precipitation mechanism for the sorption of Cr(III), Cu(II); Cu(II), Zn(II) and Pb(II); Fe and Mn using soyabean meal [114], watermelon rind [115] and tomato husk [116] respectively.

4.4.6 Reduction

In this process, there is formation of crystals after reduction of the metal due to the interaction of the metal with functional groups like carboxyl group. The metal gets reduced once it binds to the biosorbent. Gold and palladium have been obtained by this process as well as removal of toxic Cr(VI). Cr(VI) is reduced to Cr(III) by biosorption from aqueous solution by many organisms.

4.5 Processes involved in biosorption

The following are the summary of the processes involved in biosorption.

- Bulk diffusion: it involves migration of sorbate from the bulk solution towards the liquid film surrounding the sorbent.

- Film diffusion: the sorbate passes through the thin liquid film onto the surface of the sorbent. This process is also known as external diffusion.
- Pores diffusion: the sorbate passes through the pores on the sorbent into the internal active binding sites. Also known as intraparticle diffusion.
- Adsorption (reaction): if the uptake or attraction of the sorbate onto the sorbent is through electrical attraction, the process is known as ion exchange; if through Van der Waal's force of attraction, it is physisorption and if through chemical interaction then it is chemisorptions.

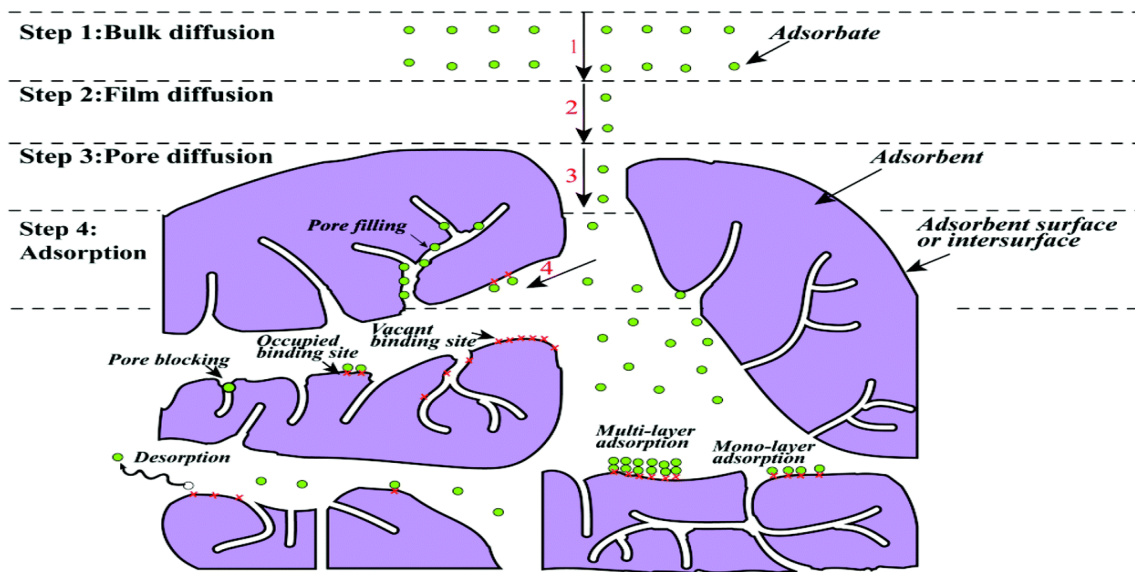


Figure 3 Adsorption processes [117]

5. BIOSORPTION ISOTHERM

Biosorption isotherm is a relatively simple technique for determining the feasibility of a certain biosorbent for a particular application obtained by plotting the amount of metal ion biosorbed per mass of adsorbent against concentration of metal ion left in solution after sorption. The least squares method is normally used in determining the isotherm parameters while the linear regression is used to best fit sorption isotherm. The sorption process can be favourable, irreversible, linear or unfavourable. Figure 4 shows Adsorption isotherms as follows.

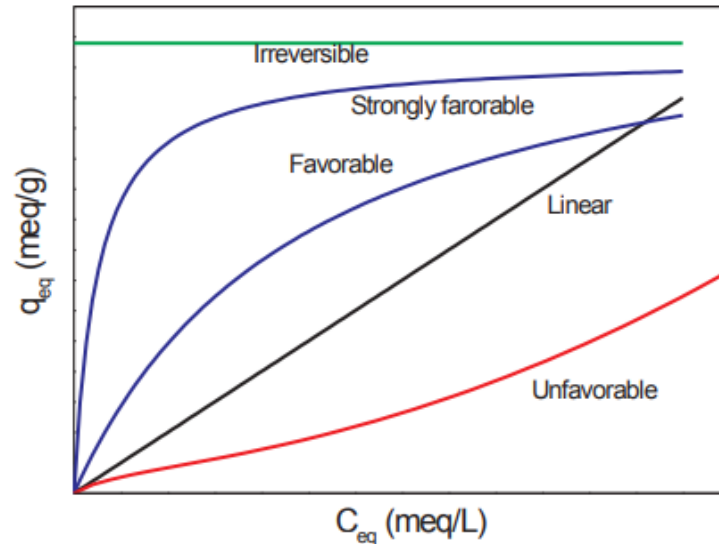


Figure 4 Adsorption isotherms ^[118]

Some of the isotherm models that have been reported are classed as

- Single isotherm model: Langmuir, Freundlich, Temkin, Dubin-Radushkevich, BET, Redlich-Peterson, Harkins-Henderson, Toth, Radke-Praunsitz, Khan, etc.
- Multi component isotherm models: extended Langmuir, competitive Redlich-Peterson, extended Freundlich, Sheindorf-Rebuhn-Sheintuch, extended Sips isotherm etc.

Langmuir, Freundlich, Temkin and Dubin-Radushkevich models will be discussed.

5.1 Langmuir isotherm model

Irving Langmuir published a model in 1918 ^[118] based on the adsorption of gas or liquid on solid where he considered adsorption as a chemical phenomenon. Some of the assumptions of this model are:

- The sorbent surface has a fixed number of sorption sites which are uniform energetically.
- There is interaction among adsorbed species because the amount of sorbate adsorbed has no effect on adsorption rate.

- After saturation of the sorbent surface, only a monolayer is formed (one sorbate per sorption site).
- There is no transmigration of adsorbed species.

The non-linear Langmuir equation is given below

$$q_e = \frac{Q_{max}bC_e}{1 + bC_e}$$

Its linear forms are given below

- Type I (Hanes-Woolf linearization)

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max}}\right)C_e + \frac{1}{Q_{max}b}$$

- Type II (Lineweaver-Burk linearization)

$$\frac{1}{q_e} = \left(\frac{1}{Q_{max}b}\right)\frac{1}{C_e} + \frac{1}{Q_{max}}$$

- Type III (Eadie-Hoffsie linearization)

$$q_e = \left(\frac{-1}{b}\right)\frac{q_e}{C_e} + Q_{max}$$

- Type IV (Scratchard linearization)

$$\frac{q_e}{C_e} = -bq_e + Q_{max}b$$

Where Q_{max} is saturated amount of adsorbed adsorbate (mg/g), C_e is equilibrium concentration of adsorbate in solution (mg/L), b is Langmuir adsorption constant (L/mg) and q_e is uptake at equilibrium (mg/g). An important feature of Langmuir isotherm equation is the equilibrium parameter or separation factor, R_L which is a dimensionless constant.

$$R_L = \frac{1}{1 + bC_0}$$

Where C_0 is initial concentration (mg/L) .

Adsorption is unfavourable if $R_L > 1$, linear if $R_L = 1$, irreversible if $R_L = 0$ and favourable for $0 < R_L < 1$.

Langmuir Constants are shown in Table 11.

Table 11 Langmuir constants obtained from different literatures

Biosorbent	Metal	Qmax (mg/g)	b (L/mg)	R _L	R ²	Ref.
Teff straw (<i>Eragrostis tef</i>)	Cu	34	0.173		0.998	165
	Cd	27.2	1.908		0.940	
	Pb	17.5	0.114		0.945	
<i>Sargassum tenerrimum</i> at pH of 4.0	Cu	158.73	0.0014		0.984	166
Chicken feather	Pb	79.36	0.0625	0.195	0.991	3
	Cu	61.92	0.0781	0.018	0.874	
Anaerobic biomass	Pb	286	0.0063		0.92	167
	Cd	64	0.0134		0.95	
	Cu	60	0.024		0.95	
	Ni	25	0.03		0.97	
Melina tree leaves	Pb	26.88	0.07		0.909	108
	Cd	20.88	0.045		0.955	
Phosphoric acid modified rice husk	Zn	101.1	0.065	0.133	0.99	168
Almond shell	Cu	6.64	0.08		0.98	169
Water hyacinth	Cu	11.54	0.217		0.9933	170
	Zn	17.67	0.143		0.9948	
Coffee powder	Fe(III)	85.47	0.14	0.13	0.9993	171
Tea powder	Fe(III)	285.71	0.02	0.5	0.9999	171
Dried activated sludge	Fe	6.04	0.53		0.9945	172
Non living cells of <i>Chlorella vulgaris</i>	Cd	45.045	0.491	0.039	0.929	173
	Cu	57.143	0.658	0.030	0.960	
	Pb	62.50	2.254	0.009	0.994	
Acid activated carbon of <i>Juniperus procera</i> leaves	Pb(II)	30.3	0.08		0.997	175
	Cr(VI)	23.0	0.01		0.991	
Saw dust	Pb(II)	30.48	0.0137		0.999	175
	Cu(II)	30.90	0.0073		0.986	
	Zn(II)	26.74	0.0071		0.999	

5.2 Freundlich isotherm model

Freundlich isotherm model is an empirical equation which is used to describe adsorption on heterogenous surface [119]. The Freundlich model unlike the Langmuir model can neither describe the arithmetic linearity range at very low concentrations nor sorbent saturation at very high concentrations. This makes it impossible for Freundlich model to describe the saturation point of an adsorbent [120]. The non linear Freundlich equation is given as

$$q_e = k_f C_e^{1/n}$$

While the linearized form is

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

where k_f is Freundlich constant (mg/g)(1/mg)^{1/n}, n is Freundlich intensity parameter. Values n is an indication of degree of non-linearity between solution concentration and adsorption with $n = 1$ indicating that the adsorption is linear, $n < 1$ indicating a chemical process while $n > 1$ indicate a physical process [121]. Freundlich Constants are shown in Table 12.

Table 12 Freundlich constants obtained from different literatures

Biosorbent	Metal	n	1/n	K _f (mg/g)	R ²	Ref.
Teff straw (<i>Eragrostis tef</i>)	Cu	1.53		2.01	0.967	165
	Cd	2.11		3.52	0.977	
	Pb	1.51		1.82	0.957	
<i>Sargassum tenerrimum</i> at pH of 4.0	Cu	1.291		0.215 (L/g)	0.958	166
Chicken feather	Pb	2.309	0.433	4.674	0.675	3
	Cu	2.532	0.395	4.145	0.711	
Melina tree leaves	Pb	12.79	0.078	4.079	0.973	108
	Cd	11.79	0.085	2.302	0.945	
Phosphoric acid modified rice husk	Zn	1.6	0.625	7.61	0.89	168
Almond shell	Cu	2.23		0.91	0.97	169
Water hyacinth	Cu	2.7198		2.9154	0.9801	170
	Zn	2.2530		3.7740	0.9949	
Coffee powder	Fe(III)	1.50		11.12	0.9849	171
Tea powder	Fe(III)	1.09		5.88	0.9997	171
Dried activated sludge	Fe	1.4454		1.946	0.999	172
Non living cells of <i>Chlorella vulgaris</i>	Cd	4.141	0.241	19.355	0.996	173
	Cu	4.261	0.235	26.002	0.901	
	Pb	5.491	0.182	36.216	0.910	
Acid activated carbon of <i>Juniperus procera</i> leaves	Pb(II)	0.50		21.23	0.965	174
	Cr(VI)	0.20		24.45	0.920	
Saw dust	Pb(II)		0.382	2.67	0.982	175
	Cu(II)		0.495	1.19	0.973	
	Zn(II)		0.500	1.00	0.999	

5.3 Temkin isotherm model

Temkin model [122] assumes that there is an equal distribution of binding energies over a number of exchange sites on the surface. The model contains a factor that considers adsorbent-adsorbate interactions explicitly. The non linear form is expressed as

$$q_e = \frac{RT}{b} \ln(A_T C_e)$$

While the linearized form is given as

$$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T} \right) \ln C_e$$

$$B = \frac{RT}{b_T}$$

Hence, the equation can be given as

$$q_e = B \ln A_T + B \ln C_e$$

Where A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R is absolute temperature in Kelvin and B is a constant related to heat of sorption (J/mol). Temkin Constants are shown in Table 13.

Table 13 Temkin constants obtained from different literatures

Biosorbent	Metal	A_T (L/mg)	b_T	B (J/mol)	R^2	Ref.
Chicken feather	Pb	6.418	117.60	21.07	0.775	3
	Cu	1.153	118.20	20.96	0.843	
Phosphoric acid modified rice husk	Zn	1.075	97.79	25.34	0.616	168
Almond shell	Cu	1.01 (L/g)	820.77		0.95	169
Water hyacinth	Cu	2.8016	1.1200		0.9886	170
	Zn	6.3063 (L/g)	0.7220		0.9870	
Coffee powder	Fe(III)	1.64	62.61	39.57	0.9794	171
Tea powder	Fe(III)	1.33	47.08	52.62	0.9437	171
Dried activated sludge	Fe	8.816	2431.6		0.9545	172
Acid activated carbon of <i>Juniperus procera</i> leaves	Pb(II)	0.89	387	6.45	0.992	175
	Cr(VI)	0.23 (L/g)	753 (J/mol)	3.29	0.935	

5.4 Dubinin-Radushkevich (DR) isotherm model

DR isotherm model is an empirical model developed to account for the effect of porous structure of the sorbent [123] and sorption is assumed to follow a pore filling mechanism. It is

generally applied to homogenous and heterogenous surface adsorption. The non-linear DR isotherm model is given as

$$q_e = (q_s)\exp(-K_{DR}\varepsilon^2)$$

While the linearized form is given as

$$\ln q_e = \ln(q_s) - (K_{DR}\varepsilon^2)$$

K_{DR} and q_s can be obtained from the plot of $\ln q_s$ versus ε^2

$$\varepsilon = RT\ln(1 + 1/C_e)$$

the parameters are defined as follow: K_{DR} is Dubinin-Radushkevich constant related to mean free energy of adsorption (mol^2/kJ^2), q_s is the theoretical adsorption capacity (mg/g), T is the absolute temperature (K), R is the universal gas constant and ε is the Polanyi potential. The physical or chemical nature of adsorption can be determined using the mean free energy of adsorption 'E' which can be obtained from the equation

$$E = \frac{1}{\sqrt{2K_{DR}}}$$

$E < 8$ kJ/mol indicates a physical adsorption, while $8 < E < 16$ kJ/mol is an indication of chemical adsorption. This is helpful in understanding the mechanism of biosorption [124]. Dubinin Radushkevick constants are shown in Table 14.

Table 14 Dubinin Radushkevick constants obtained from different literatures

Biosorbent	Metal	Qs (mg/g)	K _D (mol ² /kJ ²)	E (kJ/mol)	R ²	Ref.
Chicken feather	Pb	91.286	3 x 10 ⁻⁷	1.291	0.948	3
	Cu		5 x 10 ⁻⁵	0.102	0.906	
Phosphoric acid modified rice husk	Zn	70.60	1 x 10 ⁻⁶	0.707	0.792	168
Almond shell	Cu	3.17 x 10 ⁻⁴ (mol/g)	4 x 10 ⁻⁹	11.18		169
Water hyacinth	Cu	8.6	0.9429		0.8397	170
	Zn	11.5	0.4602		0.8041	
Coffee powder	Fe(III)	40.06	3 x 10 ⁻⁶		0.9398	171
Tea powder	Fe(III)	45.96	9 x 10 ⁻⁶		0.9536	171
Dried activated sludge	Fe	3.15	2.54 x 10 ⁻⁴		0.9275	172
Acid activated carbon of <i>Juniperus procera</i> leaves	Pb(II)	20.1	2 x 10 ⁻⁶		0.851	175
	Cr(VI)	13.5	8 x 10 ⁻⁵		0.712	

6. BIOSORPTION KINETICS

Kinetic studies are important in practical application of sorption, process design and operation control [126]. It is required in order to identify the mechanism of adsorption and its potential rate controlling steps like mass transport and chemical reaction processes. Sorbate uptake rate that controls residence time in solid-solution interface is expressed in terms of adsorption kinetics [127]. Biosorption (adsorption) process consists of four consecutive simple steps [128] which have been discussed earlier in this paper under the subheading 'processes involved in biosorption'.

Several kinetic models have been applied in the study of biosorption. Examples include pseudo-first order, pseudo second order, Weber-Morris intraparticle diffusion, Elovich model, Adam-Bohart-Thomas relation, first-order reversible reaction model, external mass transfer model, first order equation of Bhattacharya, Bangham equation and Ritchie's equation [129]. The first three of these models will be discussed.

6.1 Pseudo first order kinetic model

The Lagergren rate equation which is one of the most widely used sorption rate equation is based on solid capacity. The model assumes that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites.

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

After integration within the boundary conditions $t=0$ to $t=t$, the linear form is obtained

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$

Where q_e is the amount of sorbate sorbed at equilibrium (mg/g), q_t is the amount of sorbate at any time t in mg/g, K_1 is the pseudo first order rate constant (min^{-1}). A plot of $\log(q_e - q_t)$ versus t will give the pseudo first order kinetic plot.

6.2 Pseudo second order kinetic model

Pseudo second order kinetic model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. It is given as

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

Integrating between the limits $t=0$ to $t=t$ and $q_0=0$ to $q_t=q_t$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} - K_2 t$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Where q_e is the amount of sorbate sorbed at equilibrium (mg/g), q_t is the amount of sorbate at any time t in mg/g, t is time in minutes and K_2 is pseudo second order rate constant (g/mg.min). a plot of t/q_t against t will give a straight line of pseudo second order kinetic plot. Unlike pseudo first order kinetic model that mostly does not fit well over the entire range of contact time and which is generally applicable over initial time (usually first 30minutes) of the sorption process, pseudo second order kinetic model can be applicable over the whole state of equilibrium.

6.3 Weber-Moris intraparticle diffusion model

The pseudo first and second order kinetic equation cannot identify the diffusion mechanism during sorption process hence, Weber and Moris introduced this kinetic model to help in describing the intraparticle diffusion rate constant (K_{id}), boundary resistance (C) and to examine the contribution of surface and pore diffusion to the overall process. The model assumes that sorbate uptake varies almost proportionally to the half power of time $t^{1/2}$ and not time t

$$q_t = K_{id}t^{1/2} + C$$

a plot of q_t versus $t^{1/2}$ will give the Weber-Moris intraparticle diffusion plot. C is an indication of the boundary layer thickness. The larger the intercept of the plot, the greater the boundary layer effect [130]. K_{id} is the intraparticle diffusion rate constant. A linear plot passing through the origin is an indication of sorption process controlled by intraparticle diffusion while a multi-linear plot with two or more steps with non passing through the origin indicates that intraparticle diffusion was not the rate limiting step of the sorption process [131]. Pseudo first and second order kinetic constants obtained from different literatures are shown in Table 15.

Table 15 Pseudo first and second order kinetic constants obtained from different literatures

Sorbent	Metal	Co (mg/ L)	q _{e,exp} (mg/ L)	Pseudo first order			Pseudo second order			Ref.
				q _e (mg/ L)	K ₁ (Min ⁻¹)	R ²	q _e (mg/L)	K ₂ (g/mg.min)	R ²	
Dried activated sludge	Cd(II)	20	9.50				9.8	0.0157	0.995	183
	Pb(II)	20	14.10				13.8	0.0113	0.994	
Cystine modified biomass	Cd(II)	5	4.98				41.99	51.47	0.998	184
	Pb(II)	80	43.48				43.86	123.46	0.999	
Green algae spirogyra	Pb(II)	100	52	43	0.0297	0.927	51.17	0.0005	0.997	185
Protonated rice bran	Ni(II)	100	25.04	3.38	0.0092	0.971	25.20	0.0088	1.000	186
Surfactant modified coconut Coir	Cr(VI)	60	45.50	21.03	0.044	0.963	46.08	0.0050	0.999	187
Coffee powder		25		2.49	0.021	0.9745	10.25	0.04	0.999	171
Tea powder		25		2.59	0.014	0.7548	12.06	0.03	0.999	171
Dried activated sludge	Fe	10		1.034	1.996	0.9875	0.0394	0.332	0.996	172
Non living cells of <i>Chlorella vulgaris</i>	Cd			23.89	-0.021	0.809	23.75	0.0094	0.995	173
	Cu			24.42	-0.330	0.792	24.39	0.1664	0.999	
	Pb			24.86	-0.375 (L/min)	0.753	25.06	0.2307	0.999	

7. BIOSORPTION THERMODYNAMICS

Adsorption thermodynamics studies are important in interpreting adsorption behaviour especially with respect to equilibrium of the process [24]. Nature and behaviour of adsorption can be obtained from thermodynamic parameters like Gibb's free energy (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) associated with the uptake process using the equations below:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -RT\ln K_c$$

From the two equations above, the van't Hoff equation can be obtained

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Where K_c is the equilibrium constant i.e the ratio of the equilibrium concentration of the sorbate on the adsorbent to the equilibrium concentration of the sorbate in solution, R is the universal gas constant (J/molK) and T is absolute temperature (K). a plot of $\ln K_c$ versus $1/T$ gives the van't Hoff plot from which ΔH° and ΔS° can be obtained from the slope and intercept of the plot. ΔG° values between -20 kJ/mol to -40 kJ/mol is indicative of electrostatic interaction that exist between sorption sites and sorbate (physiosorption). While values above -40 kJ/mol correspond with charge sharing and transfer to the sorbate from the sorbent surface in order to create a coordinate bond (chemisorption) [132].

Negative enthalpy values indicate an exothermic process while positive values correspond to endothermic process. Positive values of entropy change indicate increase randomness at the solid-liquid boundary during sorption due to dehydration of sorbate before reaching adsorption sites [133]. Negative values of Gibb's free energy reflect the degree of spontaneity of the adsorption process, with more negative values indicating an adsorption process that is energetically favourable.

8. DESORPTION, REGENERATION AND REUSE STUDIES

Desorption, regeneration and reuse studies of adsorbents are important features for in knowing their potential for commercial purpose. Desorption of loaded sorbent enables it reuse. Uptake of heavy metals from aqueous solution takes place until all the active sorption sites are filled. After getting filled, it is important to recover the metal ions which involves desorption of ions from the sorbent. From literature, several agents have been employed for this purpose which includes:

- Mineral acids: HCl, H₂SO₄, HNO₃
- Complexing agents: thiosulphate, EDTA
- Organic acids: citric acid, acetic acid

It is very important that the agent used for desorption does not significantly degrade or damage the sorbent [134]. Therefore, a good eluent for desorption should be environmentally friendly, low cost, have high capacity, efficient and non-damaging to the sorbent [83]. Desorption process is possible due to the fact that adsorption is sometimes reversible making it possible to regenerate the adsorbent using suitable eluent [135].

Desorption percentage is calculated using.

$$\% \text{ desorption} = \frac{\text{amount of sorbate desorbed}}{\text{amount of sorbate adsorbed}} \times 100$$

Salaudeen and coworkers used 0.1M EDTA and 0.1M HNO₃ for the elution of adsorbed Pb(II) from termite feathers with 67 and 69% desorption obtained [85]. Salaudeen and Olayinka also investigated the desorption of Pb(II) and Cu(II) sorped onto chicken feather. 0.1M HNO₃ was found to perform well but not as good as 0.1M EDTA solution at same concentration [136]. Sar et al [137] studied the desorption of bound uranium and thorium. From their work, mineral acids were effective (>70% recovery) with maximum amount of U and Th recovered with carbonates of sodium (98%) and calcium (93%) [137].

Massacci et al from their work titled regeneration of biomass after sorption of heavy metals reported that after 15 minutes contact with sorbate (pH 5-7), the sorbent eluted about 70% of the initial Hg concentration. After a contact time of only 5mins (washing at pH of 2

with HCl) more than 50% of sorbed Hg was recovered. The regeneration procedure was concluded to be effective and the sorbent could be reuse for new cycles of sorption.

Finally, Salaudeen reported in his Ph.D research work that the sorption capacity of Pb onto sheep fur in the first cycle (using virgin sorbent) was 82.22% which decreased to 38.98% in the second cycle after desorption and regeneration with 0.1M EDTA [138].

9. INSTRUMENTAL TECHNIQUES

Various instrumental techniques are usually employed in biosorption studies. Some of these techniques are quantitative while others are qualitative. A few of such instrumental techniques are discussed below. Analytical techniques in biosorption studies is shown in Figure 5.

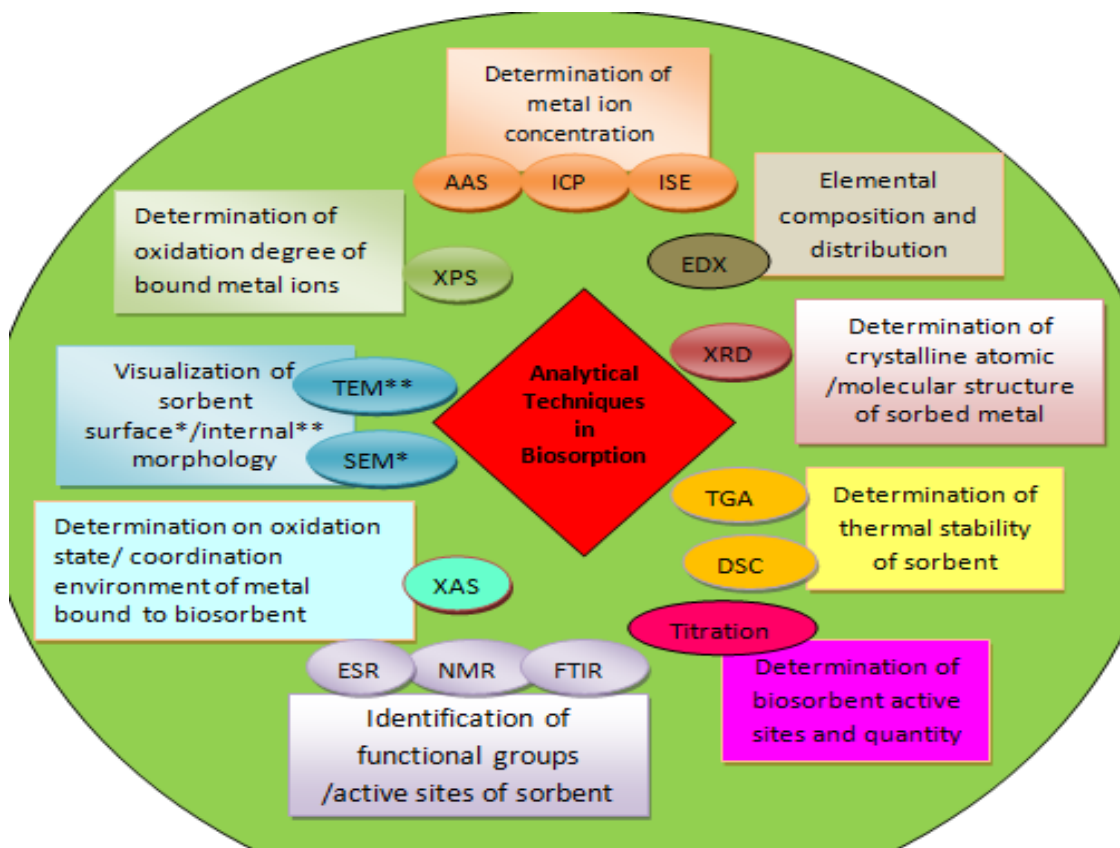


Figure 5 Analytical techniques in biosorption studies

9.1 Atomic Absorption Spectroscopy (AAS)

This is a spectral based analytical technique for the quantitative determination of metals. AAS is capable of determining over 70 elements in solution or directly in solid samples. AAS is mostly used to quantify the residual metal concentration in solution after biosorption.

9.2 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

This is an analytical technique that is employed in the determination of different elements especially heavy ions. It is a very sensitive technique for trace elements with detection limits around 0.01-1 µg/L (ppb) in solution. Typical sample preparation consists of diluting the sample in 2% nitric acid.

9.3 Fourier Transform Infra Red spectroscopy (FTIR)

FTIR spectroscopy is usually applied in order to examine the surface morphology of the sorbent/structural changes in the sorbent and to elucidate the functional groups probably responsible for metal uptake. Salaudeen et al recorded the full scan spectra of virgin and metal loaded chicken feather within the range of 4000 – 400cm⁻¹ with 45 scans and a resolution of 4 cm⁻¹ using Shimadzu FTIR-8400S. Both spectra were similar indicating that the main functional groups on the chicken feather did not change significantly [3, 24].

An investigation about the involvement of amino, carboxylic and phosphate groups in the biosorption of Pb(II) by fish scales was carried out by Nadeem et al. from their work, the surface functional groups were affected in different ways by different methods of treatment employed [139].

9.4 Scanning Electron Microscopy (SEM)

This is an electron microscope that scans the surface of a sample using a focused beam of electrons to produce images (surface topography) of the sample. It is employed to analyze the morphological structure of the biosorbent. SEM has the ability to achieve a maximum magnification of up to 1-2 million times with little or no sample preparation. SEM creates

images by detecting knocked-off or reflected electrons thereby providing information on the sample's surface and its composition.

In his Ph.D research work, Salaudeen observed no significant difference in the surface morphology of the biosorbents before and after use which is an indication of possibility of re-use of the biosorbents. He also observed smoother surfaces after metal biosorption indicating closure of the superficial layers on the sorbents due to acidic nature of the aqueous solution [138]. There was a significant difference in the surface morphology of coffee husks before and after biosorption as reported by Oliveria et al [140]. The coffee husks surface became smoother after Cu(II) sorption, with the authors concluding that it was due to differences in ionic states and sorption mechanisms. Sar et al use SEM to elucidate a desirable highly porous nature of biobeads entrapping bacterial cells over the porous walls [137].

9.5 Transmission Electron Microscopy (TEM)

TEM is a microscopy technique which makes use of electron beam transmitted through a sample to form an image. TEM provides important information about the inner structure of the sample such as morphology, crystal structure and stress state information. TEM can provide magnification as high as 50 million times but with lower optimal spatial resolution of <50pm compared to SEM's $\approx 0.5\text{nm}$. The information type in TEM is 2D compared to SEM's 3D.

Sar et al used TEM on uranium and thorium loaded cells to reveal a dark electron opaque region throughout the cytoplasm. They concluded that this dark region is an indication of intracellular sequestration of biosorbed metals [137]. From the work of Suh et al on the biosorption of Pb(II) using *S. cerevisiae*, TEM studies revealed that after varying exposure intervals of the sorbent to the sorbate solution, the first step is a rapid accumulation to the cell wall and a passive transportation of the sorbate into the cytoplasm through the cell wall [140].

9.6 Nuclear Magnetic Resonance (NMR)

NMR is a spectroscopic technique with application in quality control and for the determination of molecular structure, content and purity of a sample. Tarley and Arruda used ^{13}C NMR spectroscopy in the characterization of rice milling byproduct. The structure of lignin cellulose was revealed from the spectrum. Repeating units of hemicelluloses, cellulose and lignin were concluded to be the reason for the resonance lines [141].

Other instrumental techniques are

- Electron Paramagnetic Resonance (EPR) Spectroscopy
- Energy Dispersive X-ray (EDX) spectroscopy
- X-ray Diffraction (XRD) spectroscopy
- X-ray Photoelectron Spectroscopy (XPS)
- Thermal Gravimetric Analysis (TGA)
- Differential Scanning Calorimetry (DSC)
- Electron Spin Resonance (ESR) spectroscopy
- Particle-Induced X-ray emission (PIXE)
- Ion Selective Electrode (ISE)
- X-ray Absorption Spectroscopy (XAS)

CONCLUSION

There has been better understanding of the concept of biosorption of heavy metals due to increasing number of research carried out in this field. One of the major motivation for researchers is the advantages this technique possess over other conventional techniques like ion exchange, precipitation, electroplating, membrane filtration, solvent extraction etc. biosorption is known to be cost-effective with little or sludge generation. From this review, it could be concluded that the most eco-friendly and low-cost technique for heavy metal removal from aqueous solutions is biosorption due to it numerous advantages already stated in this work.

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