



## **A review study of biosorption of heavy metals and comparison between different biosorbents**

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### **Abstract**

With rapid industrial development, problems related to pollution are becoming severe. Water pollution is one of the most serious problems because inorganic and organic wastes are discharged to the aquatic environment either in water soluble or insoluble forms. Heavy metal ions have lethal effects on all forms of life and these enter the food chain through the disposal of wastes in water channels. From among various metal ions, lead, mercury, cadmium and chromium(VI) are at the top on the toxicity list. Due to non-biodegradability, metal ions accumulate and their amounts are increased along the food chain. Hence, their toxic effects are more pronounced in the animals at higher trophic levels. Various techniques have been employed for the treatment of dye/metal bearing industrial effluents, however those processes are often inefficient and economically unviable. A variety of biological materials have been used as sorbents for the uptake of metal ions from aqueous solutions. The main advantage of biosorption is that it is a cheap process with good metal recovery results and eco-friendly. Natural biomasses can be used as biosorbents, either ones that are abundant locally or residual byproducts from industrial plants, mainly agricultural wastes. The biosorption mechanism and important effective factors on batch biosorption process were studied.

Keywords: biosorption, heavy metals, removal, algae, bacteria

### **1. Introduction**

Although this fact is widely recognized, pollution of water resources is a common occurrence. In particular, potable water has become greatly affected, and in many instances has lost its original purpose. There are many sources of water pollution, but two main general categories exist: direct and indirect contaminant sources. Direct sources include effluent outfalls from industries, refineries contaminants that enter to water supply from soils/ground water systems and from the atmosphere via rain water. Some organic water pollutants include industrial solvents, volatile organic compounds, insecticides, pesticides and food processing wastes, etc. Inorganic water pollutants include metals, fertilizers and acidity caused by industrial discharges, etc. A major group of contaminants of concern, are metals. Metals are extensively used in several industries, including mining, metallurgical, electronic, electroplating and metal finishing. The presence of metal ions in final industrial effluents is extremely undesirable, as they are toxic to both lower and higher organisms. Under certain environmental conditions, metals may accumulate to toxic levels and cause ecological damage. Of the important metals, mercury, lead, cadmium and chromium(VI) are regarded as toxic; whereas, others, such as copper, nickel, cobalt and zinc are not as toxic, but their extensive usage and increasing levels in the environment are of serious concerns. Radionuclides, such as uranium, possess high toxicity and radioactivity, and exhibit a serious threat, even at small concentrations. In most developed and developing countries, stricter environmental regulations, with regard to contaminants discharged from industrial operations, are being introduced [1,2].

Metallic species mobilized and released into the environment by the technological activities of humans tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, thus posing a serious threat to the environment, animals, and humans. It is essential to realize that the metal is only removed the procedure of metal removal from aqueous solutions often leads to effective metal concentration. Apart from their slow natural process of metal mineralization, the ultimate removal is attained only when the metal become

concentrated to the point that it can be either returned to the process or resold. This aspect of the operation deals with the potential recovery of the metal, which ideally should go hand in hand with the removal aspect. Various techniques have been employed for the treatment of dye/metal bearing industrial effluents, which usually come under two broad divisions: abiotic and biotic methods. Abiotic methods include precipitation, adsorption, ion exchange, membrane and electrochemical technologies, this method is expensive, not environment friendly and usually dependent on the concentration of the waste. Therefore, the search for efficient, eco-friendly and cost effective remedies for wastewater treatment has been initiated. In recent years, research attention has been focused on biological methods for the treatment of effluents [1,3].

Sorption and/ or complexation of dissolved metals based on the chemical activity of microbial biomass, known as biosorption, provides the foundation for the new biosorption technology for metal removal and recovery, which offers promise as an alternative for potentially economically attractive treatment particularly suited for a wide variety of industrial metal-bearing point-source effluent discharges[4].

## 2. Heavy metals

### 2.1. Sources of discharge of metals

Effluents from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large-scale sector, contains considerable amounts of toxic metal ions. Mine tailing and effluents from non-ferrous metals industry are the major sources of heavy metals in the environment. Lead present in petrol-based materials and many other industrial facilities Chromium industrial operations including plating, petroleum refining, leather, tanning, wood preserving, textile manufacturing and pulp processing. It exists in both hexavalent and trivalent forms. Iron and steel units, electroplating industries and galvanizing units Major applications for Zinc in paint, rubber, dye, wood preservatives, and ointments and electroplating industries. Nickel galvanized, paint and powder batteries processing units[6]. Cu is mainly employed in electric goods industry and brass production. Cadmium use is increasing in industrial applications such as electroplating, and making pigments and batteries.

### 2.2. Impact of Metals on the Environment

Depending on the angle of interest and the environmental impacts, metals can be divided into four major categories: (1) Toxic heavy metals, (2) strategic metals, (3) precious metals, and (4) radionuclides (51). In terms of environmental threat it is mainly categories 1 and 4 that are of interest for removal from the environment. The toxic metals ions are not only potential human health hazards but also to another life forms. Toxic metal ions cause physical discomfort and sometimes life-threatening illness including irreversible damage to vital body system. From the eco-toxicological point of view, the most dangerous metals are mercury, lead, cadmium and chromium(VI). In many instances the effect of heavy metals on human is not well understood. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. Therefore, their toxic effect is more pronounced in animals at higher trophic levels. Among commonly used heavy metals, Cr(III), Cu, Zn, Ni and are comparatively less toxic than Fe and Al. Chromium compounds are nephrotoxic and carcinogenic in nature. In humans, lead is extremely toxic and can damage the nervous system, kidneys, and reproductive system, particularly in children while chronic exposure to elevated levels of cadmium is known to cause renal dysfunction, bone degeneration, liver damage, and blood damage. The Environmental Protection Agency (EPA) requires lead and cadmium in drinking water not to exceed 0.015 and 0.005 mg L<sup>-1</sup>, respectively. Cadmium has a half-life of 10–30 years, and its accumulation in human body affects kidney, bone and also causes cancer. Exposure to mercury may cause allergic skin reactions, possible negative reproductive effects as well as disruption of the nervous system and damage to brain function [7]. Metals and their "free radicals" are highly reactive attacking other cellular structures. The ability of metals to disrupt the function of essential biological molecules, such as protein, enzyme and DNA is major cause of their toxicity. Displacement of certain metals essential for cell by a similar metal is another cause of toxicity. For example cadmium can substitute for the essential metal zinc in certain protein that require zinc for their structure and function. The alteration in protein can lead to toxic consequences. In the same way, lead can substitute for calcium in bone and in other sites where calcium is required [8]. Target hazard quotients (THQ) were developed by the Environmental Protection Agency (EPA) in the US for the estimation of potential health risks associated with long term exposure to chemical

pollutants. The THQ is a ratio between the measured concentration and the oral reference dose, weighted by the length and frequency of exposure, amount ingested and body weight. The THQ value is a dimensionless index of risk associated with long term exposure to chemicals based upon reference upper safe limits. A limited number of THQ investigations have been reported in foodstuffs with the focus being on estimating health risks associated with exposure to heavy metals found in sea foods, and in one case breast milk. Calculations of THQ values for seafoods are apposite as many species accumulate heavy metals and other pollutants in their tissues. Many of the reported THQ values calculated from metal contaminants in seafood range from a safe level (<1) to a level of concern (typically THQ >1 to <5) with a small number being above 10. It should be noted that THQ values are additive, not multiplicative, thus a THQ value of 20 is larger but not ten-fold greater than a THQ = 2. In addition to their roles in health and disease, dietary metal ions have been the focus of discussions on the mechanism of ageing. Redox active metal ions such as Cu (I)/(II) and Fe(II)/(III) are especially implicated in the free radical theory of ageing as they are credited with enhancing oxidative stress. However, beyond radicals, metal ions can disrupt normal cell and tissue function through multiple pathways including interactions with proteins and other biomolecules and disruption of membrane potentials. As far as mode of exposure of element is concerned, more than one exposure route are involved in the phenomenon of elemental intake [9].

### **3. Conventional methods for heavy metal removal from industrial effluents**

1. Precipitation is the most common method for removing toxic heavy metals up to parts per million (ppm) levels from water. Since some metal salts are insoluble in water and which get precipitated when correct anion is added. Although the process is cost effective its efficiency is affected by low pH and the presence of other salts (ions). The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. Precipitation with lime, bisulphide or ion exchange lacks the specificity and is ineffective in removal of the metal ions at low concentration. Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluents. Though it is relatively expensive as compared to the other methods, it has the ability to achieve ppb levels of clean up while handling a relatively large volume. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to pH of the solution.

2. Electro-winning is widely used in the mining and metallurgical industrial operations for cheap leaching and acid mine drainage. It is also used in the metal transformation and electronics and electrical industries for removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes.

3. Electro-coagulation is an electrochemical approach, which uses an electrical current to remove metals from solution. Electro-coagulation system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants presents in wastewater are maintained in solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.

4. Cementation is a type of another precipitation method implying an electrochemical mechanism in which a metal having a higher oxidation potential passes into solution e.g. oxidation of metallic iron, Fe(0) to ferrous iron(II) to replace a metal having a lower oxidation potential. Copper is most frequently separated by cementation along with noble metals such as Ag, Au and Pb as well as As, Cd, Ga, Pb, Sb and Sn can be recovered in this manner.

5. Reverse osmosis and electro-dialysis involves the use of semi-permeable membranes for the recovery of metal ions from dilute wastewater. In electro-dialysis, selective membranes (alternation of cation and anion membranes)

are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated ion migrates, allowing the recovery of metals [5].

## 4. Biosorption

### 4.1. The Initial History of Biosorption

Although the ability of living microorganisms to take up metals from aqueous solution was investigated as early as 18th and 19th centuries [10], it is only during the last 3 decades that living or non-living microorganisms have been used as adsorbents for removal and recovery of materials from aqueous solutions. The earliest technological applications of biosorption techniques involved sewage and waste treatment [11]. It was also investigated for use in renovating wastewater generated by the chemical industry [12]. The first patent for a biosorption apparatus used for biological treatment of wastewater was registered by the Ames Crosta Mills & Company Ltd. In 1973 [13]. Scientists in life sciences primarily focused on the toxicological effects and accumulation of heavy metals in microorganisms, while environmental scientists and engineers used this capability of microorganisms as a means of monitoring heavy metal pollution, as well as, for removal/recovery of metals from metal-bearing wastewaters [13]. Some review papers have reported that the first quantitative study on metal biosorption was done by L. Hecke, who reported on the copper uptake by fungal spores of *tritici* and *crameri* in 1902 [14]. Similar studies were also reported by F. Pichler and A. Wobler in 1922, in which uptake of Ag, Cu, Ce, and Hg by corn smut were evaluated [13].

Ruchloft first reported that activated sludge efficiently removed even radioactive metals like plutonium-239 from contaminated domestic wastewater in 1949 [14], and the first patent on the use of biosorption technology for removing uranium or thorium ions from aqueous suspension/solution was granted to Volesky and Tsezos in 1982 [15].

Goodman and Roberts (1971) reported the practical use of biosorption technology for monitoring trace heavy metals in the environment [16]. Neufeld and Hermann (1975) studied the kinetics of biosorption by activated sludge and reported rapid uptakes of Cd, Hg, and Zn in the first few min, followed by a slow uptake over the next 3 h [17]. Friedmann and Dugan (1968) used a pure culture of *Zoogloea* for a metal-binding study [18]. Extensive screening of microorganisms for metal uptake had been carried out by Nakajima and his coworkers (1978), who reported that the ability of microorganisms to accumulate uranium ions was in the order of: actinomycetes > bacteria > yeast > fungi [19,20].

Gould and Genetelli (1984) examined the competition between metal ions for binding sites of anaerobic sludge, and reported a binding affinity order of: Cu > Cd > Zn > Ni [20]. Chiu and his coworkers (1976) analyzed biological sorption of uranium on mycelia of *Penicillium C-1* [21], while Tsezos and Volesky (1981) focused on biosorptive removal of uranium and thorium by dead fungal biomass of *Rhizopus arrhizus* [22].

Steen and Karickhoff (1981) reported uptake of hydrophobic organic pollutants by mixed microbial populations [23].

At this point, it should be noted that there was some confusion prevalent in the literature regarding the use of terms 'bioaccumulation' and 'biosorption', based on the state of the biomass used in this research at the time. The early studies prior to 1980 have been reviewed in detail by Muraleedharan et al. [24]. As pioneers in this area, Volesky and Tsezos also provide their viewpoints on the initial history of biosorption research in their special review papers [25].

### 4.2. Definition and properties

Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution. This implies that the removal mechanism is not metabolically controlled. In contrast, the term bioaccumulation describes an active process whereby removal of metals requires the metabolic activity of a living organism. In recent years research on the mechanisms of biosorption has intensified since biomass can be employed to sequester heavy metals from industrial effluents (e.g. from the mining or electroplating industry) or to recover precious metals from processing solutions [26]. There are three principle advantages of biological technologies for the removal of pollutants; first, biological processes can be carried out in situ at the contaminated site; Second, bioprocess technologies are usually environmentally benign (no secondary pollution) and third, they

are cost effective. Of the different biological methods, bioaccumulation and biosorption have been demonstrated to possess good potential to replace conventional methods for the removal of dyes/metals. Herein, therefore, bioaccumulation is defined as the phenomenon of living cells; whereas, biosorption mechanisms are based on the use of dead biomass. To be precise, bioaccumulation can be defined as the uptake of toxicants by living cells. The toxicant can transport into the cell, accumulate intracellularly, across the cell membrane and through the cell metabolic cycle. Conversely, biosorption can be defined as the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources. Biosorption is due to a number of metabolism-independent processes that essentially take place in the cell wall, where the mechanisms responsible for the pollutant uptake will differ according to the biomass type. Biosorption possesses certain inherent advantages over bioaccumulation processes. Thus, owing to its favorable characteristics, biosorption has, not surprisingly, received much attention in recent years [1].

#### 4.3. Advantages

- 1) Growth-independent, non-living biomass is not subject to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions. Therefore, the problems of disposal of surplus nutrients or metabolic products are not present.
- 2) Biomass can be procured from the existing fermentation industries, which is essentially a waste after fermentation.
- 3) The process is not governed by the physiological constraint of living microbial cells.
- 4) Because of non-living biomass behave as an ion exchanger; the process is very rapid and takes place between few minutes to few hours. Metal loading on biomass is often very high, leading to very efficient metal uptake.
- 5) Because cells are non-living, processing conditions are not restricted to those conducive for the growth of cells. In other words, a wider range of operating conditions such as pH, temperature and metal concentration is possible. No aseptic conditions are required for this process. Metal can be desorbed readily and then recovered if the value and amount of metal recovered are significant and if the biomass is plentiful, metal-loaded biomass can be incinerated, thereby eliminating further treatment.

#### 4.4. Disadvantages

- 1) Early saturation can be problem i.e. when metal interactive sites are occupied, metal desorption is necessary prior to further use, irrespective of the metal value.
- 2) The potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing. Because production of the adsorptive agent occurs during pre-growth, there is no biological control over characteristic of biosorbent. This will be particularly true if waste biomass from a fermentation unit is being utilized.
- 3) There is no potential for biologically altering the metalvalency state. For example less soluble forms or even for degradation of organometallic complexes [5].

#### 4.5. Mechanisms of Pollutants Removal by Biosorbents

There are many types of biosorbents derived from various forms of raw biomass, including bacteria, fungi, yeasts, and algae. The complex structure of raw biomass implies that there are many ways, by which these biosorbents remove various pollutants, but these are not yet fully understood. For example, the structure and functional aspects of extracellular polymeric substances (EPS) of microorganisms are related with their roles in metal biosorption. Thus, there are many chemical/functional groups that can attract and sequester pollutants, depending on the choice of biosorbent. These can consist of amide, amine, carbonyl, carboxyl, hydroxyl, imine, imidazole, sulfonate, sulfhydryl, thioether, phenolic, phosphate, and phosphodiester groups [25]. However, the presence of some functional groups does not guarantee successful biosorption of pollutants, as steric, conformational, or other barriers may also be present. The importance of any given group for biosorption of a certain pollutant by a certain biomass depends on various factors, including the number of reactive sites in the biosorbent, accessibility of the sites, chemical state of the sites (i.e. availability), and affinity between the sites and the particular pollutant of interest (i.e. binding strength) biosorption of metals or dyes occurs mainly through interactions such as ion exchange, complexation, adsorption by physical forces, precipitation and entrapment in inner spaces [25].

#### 4.5.1. Ion-exchange

Ion-exchange is an important concept in biosorption, because it explains many of the observations made during heavy metal uptake experiments. Furthermore, it is a natural extension to the premise that alginate plays a key role in biosorption by brown algae, since it has been shown that ion-exchange takes place between metals when binding to alginate. Kuyucak and Volesky, reported an enhanced release of ions ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ) from the alga *Ascophyllum nodosum* when reacted with a cobalt bearing aqueous solution rather than cobalt-free solution. Furthermore, when the alga was pre-treated with  $\text{CaCl}_2$  and  $\text{HCl}$ , a 2:3 stoichiometric relationship was observed between  $\text{Ca}^{2+}$  release and  $\text{Co}^{2+}$  uptake. Schiewer and Volesky [2] point out, however, that a ratio closer to one would have been achieved if protons were included in the charge balance. It was concluded that ion-exchange was the dominant mechanism. Untreated biomass generally contains light metal ions such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . These are originally bound to the acid functional groups of the alga and were acquired from seawater [26].

#### 4.5.2. Definition of biosorption

This definition are based on the text by Stumm and Morgan [43]. Any combination of cations with molecules or anions containing free electron pairs (bases) is termed coordination, also known as complex formation. Coordination or complex formation, in turn, may be either electrostatic (i.e. Coulombic) or covalent in character. The heavy metal cation that is bound is often designated as the central atom, and is distinguished from the anions or molecules with which it forms a coordination compound, the ligand(s). When the ligand is composed of several atoms, the atom responsible for the basic or nucleophilic nature of the ligand is termed the ligand atom. A base containing more than one ligand atom, a multidentate complex, may occupy more than one coordination position in the complex. Complex formation with multidentate ligands is termed chelation; complexes are chelates. Furthermore, the coordination number refers to the number of ligand atoms surrounding the central atom, where most metal cations engage in coordinations of 2, 4, 6, and 8, with 4 and 6 being the most common. In the case of polymers these values may be lower due to steric effects. A proton complex has a coordination number of one, as opposed to the higher coordination numbers found in metal complexes [26].

Although this terminology is typically employed for aqueous complexation with small ligands, the terms are often applied in the literature when dealing with more complex molecules, thus this outline is intended to serve as a basis for its usage.

The terms inner-sphere and outer-sphere complex are used to distinguish between binding which is, respectively, largely covalent in character or chiefly electrostatic in nature. In the first case, the interacting ligand is immediately adjacent to the metal cation. In the second case, ions of opposite charge are attracted and approach each other within a critical distance and effectively form what is termed an ion pair. In outer-sphere complexes, the metal ion or the ligand or both generally retain their coordinated water when the complex is formed. In other words, the metal ion and the ligand are most often separated by one or more water molecules [26].

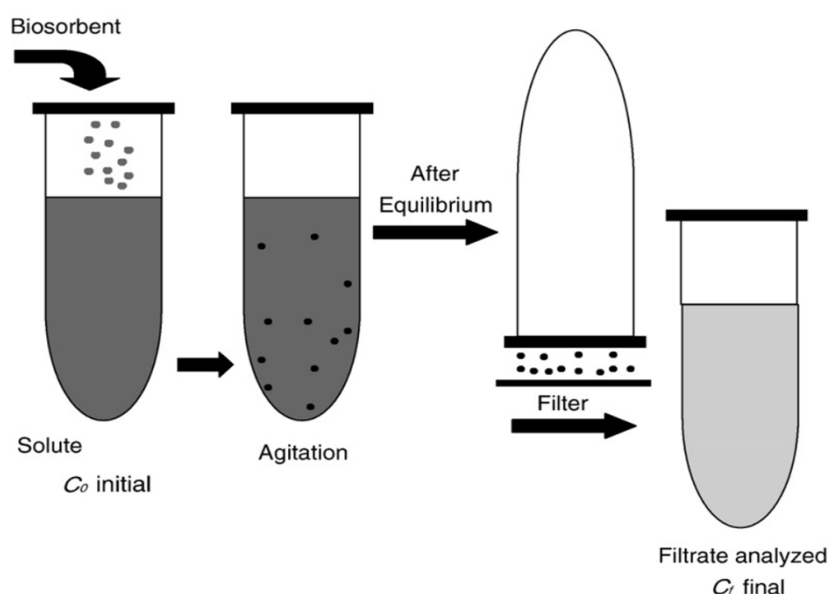
#### 4.5.3. Complexation

Metal-ion binding to alginic acid extracted from *Laminaria digitata*, reported that the amount of protons released into solution decreased in the order  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$ . He explained these results in terms of the relative ability of the binding metal to compete with protons for organic binding sites. The affinity sequence for metal-ion binding to alginate extracted from *L. digitata* followed a similar trend:  $\text{Cu}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Co}^{2+}$ . The binding strength of alkaline earth metals to both polymannuronate and polyguluronate was found to decrease in the order  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ .

Haug and Smidsrod interpreted the preferential binding of heavier ions to stereochemical effects, since larger ions might better fit a binding site with two distant functional groups [26].

#### 4.6. Batch experimental

A biosorption process can be performed via several modes; of which, batch and continuous modes of operation are frequently employed to conduct laboratory scale biosorption processes. Although most industrial applications prefer a continuous mode of operation, batch experiments have to be used to evaluate the required fundamental information, such as biosorbent efficiency, optimum experimental conditions, biosorption rate and possibility of biomass regeneration, batch system shown in Fig. 1.



**Figure 1:** batch experiment system

#### 4.7. Factors influencing batch biosorption

The important factors include: solution pH, temperature, ionic strength, biosorbent dosage, biosorbent size, initial solute concentration, agitation rate. Of these, the solution pH usually plays a major role in biosorption, and seems to affect the solution chemistry of metals/ dyes and the activity of the functional groups of the biomass [1].

##### 4.7.1. Effect of pH

It has been shown that the affinity of cationic species for the functional groups presents on the cellular surface is strongly dependent on the pH of the solution. The biosorptive capacity low at low pH values and increases with pH until reaching an optimum pH, However at pH higher than metals begins to precipitate due to formation of  $M(OH)$ . At low pH values, cell wall ligands are closely associated with hydronium ions and restrict the biosorption of  $m^{n+}$  as a result of competition between  $H_3O^+$  and  $m^{n+}$  with the bacterial biosorbent cell wall ligands. As the pH increases, more ligands, such as carboxyl, phosphate, imidazole, and amino groups, would be exposed and carry negative charges which attract  $m^{n+}$  and biosorb it onto the cell surface [27].

##### 4.7.2. Effect of temperature

If temperature increasing, it usually enhances biosorptive removal of adsorptive pollutant by increasing surface activity and kinetic energy of the adsorbate, but may damage physical structure of biosorbent [25].

##### 4.7.3. Effect of Ionic strength

If ionic strength increasing, it reduces biosorption removal of adsorptive pollutant by competing with the adsorbate for binding sites of biosorbent.

##### 4.7.4. Effect of initial pollutant concentration

If initial pollutant concentration increasing, it increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases its removal efficiency [25].

##### 4.7.5. Effect of biosorbent dosage

The dosage of a biosorbent strongly influences the extent of biosorption. In many instances, lower biosorbent dosages yield higher uptakes. An increasing the biomass concentration generally increases the amount of solute biosorbed, due to the increased surface area of the biosorbent, which in turn increases the number of binding sites

conversely, the quantity of biosorbed solute per unit weight of biosorbent decrease with increasing biosorbent dosage, which may be due to the complex interaction of several factors. An important factor at high sorbent dosages is that the available solute is insufficient to completely cover the available exchangeable sites on the biosorbent, usually resulting in low solute uptake . Also, as suggested by, the interference between binding sites due to increased biosorbent dosages cannot be over ruled, as this will result in a low specific uptake [28].

#### 4.7.6. Effect of biosorbent size

If biosorbent size decrease, it is favorable for batch process due to higher surface area of the biosorbent, but not for column process due to its low mechanical strength and clogging of the column [25].

#### 4.7.7. Effect of agitation speed

If agitation speed increasing, it enhances biosorptive removal rate of adsorptive pollutant by minimizing its mass transfer resistance, but may damage physical structure of biosorbent [25].

#### 4.7.8. Effect of Other pollutant concentration

If coexisting pollutant competes with a target pollutant for binding sites or forms any complex with it, higher concentration of other pollutant will reduce biosorptive removal of the target pollutant [25].

#### 4.8. Batch experimental data modeling

Models have an important role in technology transfer from a laboratory- to industrial-scale. Appropriate models can help in understanding process mechanisms, analyze experimental data, predict answers to operational conditions and optimize processes. As an effective quantitative means to compare binding strengths and design biosorption processes, employing mathematical models for the prediction of binding capacities can be useful [1].

#### 4.9. Biosorption isotherms

The quality of a biosorbent is judged by how much sorbate it can attract and retain in an immobilized form. The solute uptake by a biosorbent can be calculated from the differences between the initial quantities of solute added to that contained in the supernatant, which is achieved using the following equation:

$$q = \frac{V(C_i - C_e)}{M} \quad (1)$$

Where  $q$  is the amount of metal biosorbed by biomass (mg/g);  $C_i$  is the initial concentration of metal (mg/L);  $C_e$  is the concentration of metal (mg/L) at equilibrium;  $V$  is the volume of the metal solution(L); and  $M$  is the mass of adsorbent (g) [29].The sorption uptake can be expressed in different units depending on the purpose of the exercise: for example, milligrams of solute sorbed per gram of the(dry) biosorbent material (the basis for engineering process–mass balance calculations), or mmol/g (when the stoichiometry and/or mechanism are to be considered). A biosorption isotherm, the plot of uptake ( $q$ ) versus the equilibrium solute concentration in the solution ( $C_f$ ), is often used to evaluate the sorption performance. Isotherm curves can be evaluated by varying the initial solute concentrations, while fixing the environmental parameters, such as pH, temperature and ionic strength. In general, the uptake increases with increase in concentration, and will reach saturation at higher concentrations. In most biosorption studies, pH seems to be an important parameter for the evaluation of an isotherm. However, confusion prevails in reporting isotherms based on the pH. In the literature pertaining to biosorption, isotherms have been reported on the basis of the initial, final or controlled, pH conditions. This is because; during biosorption, the pH of the reaction mixture tends to change due to the chemical interaction between the biomass and sorbent. The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) models (two-parameter models) have been used to describe biosorption isotherm. Langmuir and Freundlich isotherm equations were used to described the equilibrium state for metal ions adsorption experiments. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules [30]. The general form of this model is:



$$q_e = k_f \cdot c_e^{1/n} \quad (2)$$

where  $K_F$  (mg/g) and  $n$  the Freundlich constants. The logarithmic form of Eq. (2) is:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3)$$

where, intercept  $\log(K_F)$ , and the slope  $1/n$ . The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate [31]. The general Langmuir equation is commonly presented as:

$$q_e = \frac{q_{\max} b c_e}{1 + b c_e} \quad (4)$$

and the equation may be linearized as follow:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} b} + \frac{c_e}{q_{\max}} \quad (5)$$

where  $q_e$  is the amount of metal ion removed (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $b$  the Langmuir constant related to affinity, and  $q_{\max}$  (mg/g) is the maximum metal uptake under the given conditions, the Freundlich and Langmuir constants, along with the regression coefficients have been calculated from the corresponding plots.  $k$  and  $n$ , the Freundlich constants, are related to the sorption capacity and the sorption intensity, respectively [30].  $n$  value greater than 1.0 shows that the sorption is favourable physical process [32].

Some other two-parameter models widely used for describing biosorption isotherms include,

Temkin (Temkin, 1934):

$$Q = \frac{RT}{b_{Te}} \ln(a_{Te} C_f) \quad (6)$$

Dubnin–Radushkevich (Dubinin, 1960):

$$Q = Q_D \exp \left( -B_D \left( RT \ln \left( 1 + \frac{1}{C_f} \right) \right)^2 \right) \quad (7)$$

Where  $b_{Te}$  is the Temkin constant related to the heat of sorption;  $a_{Te}$  the Temkin isotherm constant;  $R$  the gas constant (8.314 J/mol K);  $T$  the absolute temperature;  $Q_D$  the Dubinin–Radushkevich model uptake capacity and  $B_D$  the Dubinin–Radushkevich model constant. Despite the simplicity of these two-parameter models, some three-parameter models have also been widely used by investigators, including: Redlich–Peterson and Sips. Radke–Prausnitz [1].

## 5. A comparison between different biosorbents

### a) Algae:

New biosorbent materials has focused especially on algae, due to its high sorption capacity and its availability in almost unlimited amounts. They are divided into several evolutionary pathways completely independent: a red pathway with red algae (Rhodophyta), a brown pathway with brown algae (inter alia, Chromophyta) and a green pathway that includes green algae (Chlorophyta). Differences between these types of algae are mainly in the cell wall, where sorption takes place. Research in the field of biosorption has mostly concerned itself with brown algae, the cell walls of brown algae generally contain three components: cellulose, the structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium and calcium; and sulphated polysaccharides. As a consequence, carboxyl and sulphate are the predominant active groups in this kind of algae [33]. The carboxylic groups are generally the most abundant acidic functional group in the brown algae. They constitute the highest percentage of titrate blesites (typically greater than 70%) in dried brown algal biomass. The adsorption capacity of the algae is directly related to the presence of these sites on the

alginate polymer, which itself comprises a significant component (up to 40% of the dry weight, of the dried seaweed biomass) [34].

The role of carboxylic groups in the adsorption process has been clearly demonstrated by a reduction in cadmium and lead uptake by dried *Sargassum* biomass following partial or complete esterification of the carboxylic sites [34]. The second most abundant acidic functional group in brown algae is the sulfonic acid of fucoidan. Sulfonic acid groups typically play a secondary role, except when metal binding takes place at low pH. Hydroxyl groups are also present in all polysaccharides but they are less abundant and only become negatively charged at pH>10, thereby, also playing a secondary role in metal binding at low pH [35].

#### *b) Bacteria:*

Bacteria are a major group of unicellular living organisms belonging to the prokaryotes, which are ubiquitous in soil and water, and as symbionts of other organisms. Bacteria can be found in a wide variety of shapes, which include cocci (such as *Streptococcus*), rods (such as *Bacillus*), spiral (such as *Rhodospirillum*) and filamentous (such as *Sphaerotilus*). Eubacteria have a relatively simple cell structure, which lack cell nuclei, but possess cell walls. The bacterial cell wall provides structural integrity to the cell, but differs from that of all other organisms due to the presence of peptidoglycan (poly- N-acetylglucosamine and N-acetylmuramic acid), which is located immediately outside of the cytoplasmic membrane. Peptidoglycan is responsible for the rigidity of the bacterial cell wall, and determines the cell shape.

It is also relatively porous and considered as an impermeability barrier to small substrates. The cell walls of all bacteria are not identical. In fact, the cell wall composition is one of the most important factors in the analysis and differentiation of bacterial species. Accordingly, two general types of bacteria exist, of which Gram-positive bacteria (Fig. 1) are comprised of a thick peptidoglycan layer connected by amino acid bridges. Imbedded in the Gram-positive cell wall are polyalcohols, known as teichoic acids, some of which are lipid linked to form lipoteichoic acids. Because lipoteichoic acids are covalently linked to lipids within the cytoplasmic membrane, they are responsible for linking peptidoglycan to the cytoplasmic membrane.

The cross-linked peptidoglycan molecules form a network, which covers the cell like a grid. teichoic acids give the Gram-positive cell wall an overall negative charge, due to the presence of phosphodiester bonds between the teichoic acid monomers. In general, 90% of the Gram-positive cell wall is comprised of peptidoglycan. On the contrary, the cell wall of Gram-negative bacteria is much thinner, and composed of only 10–20% peptidoglycan. In addition, the cell wall contains an additional outer membrane composed of phospholipids and lipopolysaccharides.

The highly charged nature of lipopolysaccharides confers an overall negative charge on the Gram-negative cell wall. Showed that the anionic functional groups present in the peptidoglycan, teichoic acids and teichuronic acids of Gram-positive bacteria, and the peptidoglycan, phospholipids, and lipopolysaccharides of Gram-negative bacteria were the components primarily responsible for the anionic character and metal-binding capability of the cell wall. Extracellular polysaccharides are also capable of binding metals (McLean) However, their availability depends on the bacterial species and growth conditions; and they can easily be removed by simple mechanical disruption or chemical washing [1].

#### *Mechanism of bacterial biosorption:*

The bacterial cell wall is the first component that comes into contact with metal ions/dyes, where the solutes can be deposited on the surface or within the cell wall structure. Since the mode of solute uptake by dead/inactive cells is extracellular, the chemical functional groups of the cell wall play vital roles in biosorption. Due to the nature of the cellular components, several functional groups are present on the bacterial cell wall, including carboxyl, phosphonate, amine and hydroxyl groups[1].

#### *c) fungi*

Fungal cell walls and their components have a major role in biosorption and also take up suspended metal particulates and colloids. Fungi are ubiquitous in natural environments and important industrial processes. Their most important roles are as decomposers of organic material, with concomitant nutrient cycling as pathogens and

symbiotic with animals and plants, and as spoilage organisms of natural and synthetic materials [11]. White rot fungi are highly specialized groups of organisms. They are Basidiomycetes, which include all the higher fungi that are characterized by their sexual fruiting bodies [16]. *Lentinussajor-cajuis* a wellknown white rot, fungus whereas a little attention has been paid to the ability of its potential for the removal of mixed pollutants from environment [36].

d) cultural waste

cultural waste and other agricultural by-products such as sugarcane bagasse, soya bean hulls, walnut hulls , cotton seed hulls and corn cobs.[37].carrot residues , used for biosorption because there are readily available, for example carrot residues was used as a biosorbent for the removal of heavy metals. The cation exchange properties of these residues can be attributed to the presence of carboxylic and phenolic functional groups, which exist in either the cellulosic matrix or in the materials associated with cellulose, such as hemicellulose and lignin [38].

table 1,2 and 3 Comparison of biosorption maximum capacity(q) forCr(VI), Pb(II), Zn(II), by different biosorbents.Tables shows that algae have good adsorption capacity for removal of heavy metals with respect to other biosorbentns.

**Table1:** Comparison of biosorption maximum capacity of Cr(VI) on different biosorbents

Biosorbent	pH	T(°C)	q <sub>max</sub>	reference
<i>Lentinussajor-caju (fungi)</i>	2	25	18.0	[36]
<i>Lyngbyaputealis (bacteria)</i>	2	25	113.6	[39]
<i>Bacillus coagulans(bacteria)</i>	2.5	28±3	39.9	[1]
<i>Bacillus megaterium(bacteria)</i>	2.5	28±3	30.7	[1]
<i>Aeromonascaviae (bacteria)</i>	2.5	20	284.4	[1]
<i>Bacillus thuringiensis(bacteria)</i>	2	25	83.3	[1]
<i>Cupressus Female Cone(cultural waste)</i>	3	20	119.0	[1]
<i>durian shell (cultural waste)</i>	2.5	60	117.0	[40]
<i>Oedogoniumhatei (raw alga)</i>	2	45	31.0	[41]
<i>Oedogoniumhatei (acid treated)</i>	2	45	35.2	[41]
<i>Palmaria palmate(red alga)</i>	2	25	33.8	[39]
<i>Polysiphonialanosa(red alga)</i>	2	25	45.7	[39]
<i>Ulvalactuca(green alga)</i>	2	25	27.6	[39]
<i>Ulvaspp (green alga)</i>	2	25	30.2	[39]
<i>Sargassumsiliquosum (brown alga)</i>	2.5	25	66.4	[42]
<i>Sargassummuticum (brown alga)</i>	2.5	25	196.1	[42]
<i>Fucusvesiculosus (brown alga)</i>	2	25	42.6	[39]
<i>Sargassum sp. (brown alga)</i>	5	25	53.3	[43]

**Table.2:** Comparison of biosorption maximum capacity of Pb(II) on different biosorbent

biosorbent	pH	T(°C)	q <sub>max</sub> (mg/g)	Reference
<i>Mucorrouxii(fungi)</i>	6	25	25.22	[44]
<i>Cunninghamellaechinulata (fungi)</i>	5	25	45	[44]
<i>Chondracanthuschamissoi(alga)</i>	4	25	283	[45]
<i>Enterobacter sp. J1(alga)</i>	6	25	50	[46]
<i>Cladophora spp. (alga)</i>	5	25	46.51	[29]
<i>tobacco (dustcultural waste)</i>	7	25	39.6	[47]
<i>cork wastes(dustcultural waste)</i>	5	25	13.46	[48]
<i>Bacillus cereus(bacteria)</i>	6	25	22.1	[49]
<i>Bacillus pumilus(bacteria)</i>	6	25	28.06	[49]
<i>Bacillus thioparans U3 (bacteria)</i>	4	35	90.1	[50]

**Table.3:** Comparison of biosorption maximum capacity of Zn(II) on different biosorbent

biosorbent	pH	T(°C)	q <sub>max</sub> (mg/g)	Reference
<i>tobaccodust(cultural waste)</i>	7	25	25.1	[47]
<i>Chlorella vulgaris (fungi)</i>	5	20	17	[44]
<i>Cunninghamellaechinulata(fungi)</i>	6	25	18.8	[44]
<i>Mucorrouxii (fungi)</i>	5	25	16.6	[44]
<i>Geobacillustoebiisub.sp. decanicus(bacteria)</i>	5	80	21.1	[1]
<i>Acenitobacterlwoffii(bacteria)</i>	6	25	36	[51]
<i>Streptomyces rimosus(bacteria)</i>	7.5	20	30	[52]
<i>Delftiastruhatensis (bacteria)</i>	6	25	14	[53]
<i>Azollafiliculoides(Algae)</i>	5	25	34	[44]
<i>Fucusvesiculosos (Algae)</i>	4.5	25	52.3	[26]
<i>Laminaria japonica (Algae)</i>	4.5	25	91.5	[26]

## 6. Instrumentation for Biosorption Research

Information on the active sites involved in the binding of pollutants can be obtained through use of a number of sophisticated analytical tools, including Atomic absorption spectroscopy (AAS) and Inductively coupled plasma (ICP) for determine metal concentration in aqueous phase, UV-Vis spectrophotometer for determine metal or dye concentration in aqueous phase by measuring its color intensity, infrared absorption spectroscopy or Fourier transformed infrared spectroscopy (IR or FTIR), for determine active sites of the biosorbent, scanning electron microscopy (SEM), for visual confirmation of surface morphology of the biosorbent, transmission electron microscopy (TEM), for visual confirmation of inner morphology of biomass, especially cells, energy dispersive Xray spectroscopy (EDS), for element analysis and chemical characterization of metal bound on the biosorben, X-ray diffraction (XRD) analysis, for crystallographic structure and chemical composition of metal bound on the biosorbent nuclear magnetic resonance (NMR), for determine active sites of the biosorbent, X-ray photoelectron spectroscopy (XPS), determine oxidation state of metal bound on the biosorbent and its ligand effects [54,55].

## 7. Conclusion and propose for future

Biosorption is in its developmental stages and further improvement in both performance and costs can be expected in future. We must continue fundamental research to better understand the mechanisms of biosorption and on what drives the selectivity of biosorptive and bioaccumulatory processes [56]. Various high techniques like XAS, SEM will be helpful in this area. More comprehensive or specific models for equilibria or kinetic studies should be developed that can simulate more complex biosorption systems, such as hybrid biosorption system [55]. Unlike laboratory solutions, industrial effluents contain various pollutants including those of interest. Thus, there is a need to investigate the simultaneous removal of many coexisting pollutants. It is desirable to develop general-purpose biosorbents that can remove a variety of pollutants. One such possibility would be the use of 'combo' biosorbents consisting more than one type of biomass [10]. Although 'combo' biosorbents would tend to further complicate characterization of these biosorption systems, it may represent a more realistic approach to the design of biosorbent systems [57]. A more concern to biosorption of dye.

Further study is therefore required to drop the overall cost for pretreatments or to develop new methods (pretreatments) that are both cheap and effective. more attention needs to immobilized biomass, rather than native biomass, Immobilization techniques increase the overall cost of biosorbents, and decrease their biosorptive rates and capacities. more work needs to be done to understand the effect of various immobilization techniques on the rate and equilibrium uptake of pollutant by immobilized biomass.

However, precious metal resources are getting paid attention because of their price increases and limited deposits. For the recovery of precious metals such as gold, platinum, palladium, ruthenium, etc the recovery efficiency and purity of finally recovered products would be additional criteria for evaluating biosorbents and related processes.

Biosorbents can be also used for the purification of ionic pharmaceuticals like proteins, antibodies, and peptides. For this, column chromatography would be more effective for the high-purity products than fixed or moving bed adsorption. Heat resistance of biosorbents and release of impurity during autoclave and purification must be considered for pharmaceutical applications. The difficulties that exist for biosorption application should be pushing researchers to consider applying hybrid technologies, which involve combining various processes for large-scale treatment of real wastewater [58,55].

When living cell systems are used to treat metal-containing wastewaters, the metal tolerances of the living cell is very important in its application in a real case. Genetic engineering may further enhance the potential of robust environmental strains [59]. However, the issue of living genetically modified organisms (LMO) should be addressed prior to field applications. The application of modern molecular biotechnology to microorganisms may greatly enhance the specificity of biosorbents particularly if applied to synthesis of metal-specific peptides or cell wall polymer composition [55,57]. Protein engineering may also conceivably lead to enhanced metal specificity, stability, and other useful properties of peptides or other biopolymers [60].

Although biosorption is one of the main components of environmental biotechnology, to the best of our knowledge, Needless to say, a weak relationship between researchers slows down development of biosorption technology and delays its commercialization .

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