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Biosorption of toxic metals from wastewater: A review

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Abstract

Water pollution is one of the most serious problems due to the rapid industrial development that discharges inorganic and organic waste to the aquatic environment in water soluble and insoluble forms. Some of the water soluble wastes contain toxic metals ions which have harmful effect to all forms of life and these enter the food chain through the disposal of waste in water channels. Toxic metals such as Pb²⁺, Hg⁺, Cd²⁺, Cr²⁺ etc are non-biodegradable, accumulate and their concentrations are increased along the food chain. A number of conventional methods viz; chemical precipitation, evaporation, electroplating, ion exchange, membrane processes etc have been employed for the removal of toxic metals ions from liquid water. However all these processes are expensive and have shortcomings such as incomplete

removal of toxic metals, limited tolerance to pH change, moderate or no metal selectivity, production of toxic sludge or other products that also need disposal. The use of sorbents of biological origin may be considered ideal for the purpose of biosorption of toxic metals because of their potentials for toxic metal uptake from wastewater have already been proved. The main advantage of biosorption is that it is a cheap process, with good toxic metal recovery results and ecofriendly. In this article, the biosorption process, biosorbents, preparation and characterization of biosorbent, spectroscopic analysis and biosorption kinetic models have been discussed as an important aspect of toxic metals management strategies.

Keywords: biosorbents, toxic metals, uptake, equilibrium models

Introduction

The continuous increase in the use of toxic metals over the years has inevitably resulted in an increased flux of metallic substances in aquatic environment. Toxic metals are those metallic elements that have a relatively high density and are toxic or poisonous even at low concentration. Toxic metals in general, applies to the group of metals and metalloids with atomic density greater than 4 g/cm³, or 5 times or more, greater than water^[1]. However, chemical properties of toxic metals are the most influencing factors compared to their density. Toxic metals include Pb, Cd, Ni, Co, Fe, Zn, Cr, As, Ag and the Pt group elements. Industrialization and urbanization have increased the anthropogenic contribution of toxic metals in biosphere. Toxic metals have largest availability in soil and aquatic ecosystems and to a relatively smaller proportion in atmosphere as particulate or vapours. Toxic metal toxicity in plants varies with plant species, specific metal, concentration, chemical form and soil composition and pH, as many toxic metals are considered to be essential for plant growth. Some of these toxic metals like Cu and Zn either serve as cofactor and activators of enzyme reactions e.g., in forming enzymes/substrate metal complex^[2] or exert a catalytic property such as prosthetic group in metalloproteins. These essential trace metal nutrients take part in redox reactions, electron transfer and structural functions in nucleic acid metabolism. Some of the toxic metal such as Cd, Hg and As are strongly poisonous to metal-sensitive enzymes, resulting in growth inhibition and death of organisms^[3]. An alternative classification of metals based on their coordination chemistry, categorizes heavy metals as class B metals that come under non-essential trace elements, which are highly toxic elements such as Hg, Ag, Pb, Ni^[4].

Heavy metals can also be classified into four major groups on their health importance:

Essential: Cu, Zn, Co, Cr, Mn and Fe. These metals are called micronutrients and are toxic when taken in excess of requirements.

Non-essential: Ba, Al, Li etc.

Less toxic: Sn and Al.

Highly toxic: Hg, Pb and Cd.

Toxic metals are also called trace elements due to their presence in trace (10 mg/kg) or in ultra-trace (1µg/kg) quantities in the environmental matrices. Toxic metal pollution can originate from natural and anthropogenic sources. Activities such as mining, smelting operation, industrial effluent and agriculture (fertilizer and pesticide), waste, domestic effluents, agricultural

runoff/fungicides, acid rain, solid waste leachates etc have all contributed to some extent to the toxic metal loads in the water bodies [5, 6].

Source of toxic metals contamination in the environment

There are different sources of toxic metals in the environment such as: natural, agricultural [7]. Industrial, Lacerda [8], domestic effluent, atmospheric sources and other sources. Activities such as mining and smelting operations and agriculture have contaminated extensive areas of world such as Japan, Indonesia and China mostly by toxic metals such as Cd, Cu and Zn [9]. Natural sources of toxic metals originate within the Earth's crust; hence their natural occurrence in soil is simply a product of weathering process. The composition and concentration of toxic metals depend on the rock type and environmental conditions, activating the weathering process. The geologic plant materials generally have high concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb. However, class-wise the toxic metal concentrations vary with in the rocks. Soil formation takes place mostly from sedimentary rock, but is only a small source of toxic metals, since it is not generally or easily weathered. However, many igneous rocks such as olivine, augite and hornblende contribute considerable amounts of Mn, Co, Ni, Cu and Zn to the soils. Within the class of sedimentary rocks, shale has highest concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Sn, Hg and Pb followed by limestone and sand stone. Volcanoes have been reported to emit high levels of Al, Zn, Mn, Pb, Ni, Cu and Hg along with toxic and harmful gases [10]. Wind dust, which arises from desert region such as Sahara, has high levels of Fe and lesser amounts of Mn, Zn, Cr, Ni and Pb. Marine aerosols and forest fires also exert a major influence in the transport of some toxic metals in many environments. While the long range transport of dusts, particularly from the Sahara, has received considerable recent attention. Volatile toxic metals such as Hg and Se are part of carbonaceous matter produced during the fire. Natural vegetation emits toxic metals into the soil and atmosphere through leaching from leaves and stems, decomposition and volatilization. Many toxic metals have been detected in inland coastal areas due to sea sprays and aerosols produced in oceanic activities.

Overview of Biosorption

Biosorption can be defined as the ability of biological materials to accumulate toxic metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Biosorption is an eco-friendly and used as a filtering technique for the environmental samples. The first quantitative study was done by L. Hecke on the copper uptake by fungal spores on metal biosorption of *T. tritici* and *U. crameri* in 1902 [11]. Investigations showed that the application of living biomass was used for the removal of metals from aqueous solutions in early 18th and 19th centuries [12, 13]. The use of certain types of living bacterial biomass to clean up the raw sewage and recover nitrogen and phosphorus in an aeration tank was reported by Yan and Vijayraghavan [14]. Before the biosorption processes, many techniques that were being used to remove toxic metal ions from wastewater were; chemical precipitation, ion-exchange, adsorption, membrane filtration, electro-chemical treatment technologies, etc [15].

Chemical precipitation

Chemical precipitation is effective and by far the most widely used process in industry [16] because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with toxic metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

Hydroxide precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control [17]. The solubilities of the various metal hydroxides are minimized in the pH range of 8.0-11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings [18].

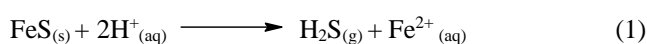
Table 1: Toxic Metal Removal Using Chemical Precipitation.

| Species | Initial metal concentration | Precipitant | Optimum pH | Removal Efficiency(%) | Reference |
|---|-----------------------------|--|-------------|-----------------------|-----------|
| Zn ²⁺ | 32 mg/L | CaO | 9-10 | 99-99.3 | [19] |
| Cu ²⁺ , Pb ²⁺ , Zn ²⁺ , Cr ³⁺ | 100 mg/L | CaO | 7-11 | 99.37-99.6 | [20] |
| Cu ²⁺ , Pb ²⁺ , Zn ²⁺ | 0.018, 1.34, 2.3 mM | H ₂ S | 3.0 | 100>94>92 | [21] |
| Cr ³⁺ | 5363 mg/L | CaO and MgO | 8.0 | >99 | [22] |
| Hg ²⁺ | 65.6, 188 µg.L | 1,3-benzenediamido Ethanethiolate | 4.7 and 6.4 | >99.9 | [23] |
| CuEDTA | 25, 50, 100 mg/L | 1,3,5-hexahydrotriazine dithiocarbamate | 3.0 | 99.0, 99.3, 99.6 | [24] |

Sulfide precipitation

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfides is that the solubilities of the metal sulfide precipitates are dramatically lower than hydroxide precipitates and sulfide precipitates are not amphoteric. And hence, the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulfide sludges also exhibit better thickening and dewatering characteristics

than the corresponding metal hydroxide sludges. Özverdi and Erdem [25] investigated pyrite and synthetic iron sulfide to remove Cu²⁺, Cd²⁺ and Pb²⁺. The mechanism governing the metal removal processes was determined as chemical precipitation at low pH (<3) due to H₂S generation (Equations. (1) and (2) and adsorption at high pH (in the range of 3-6).





Recently, new sulfide precipitation process has been developed based on sulfate-reducing bacteria (SRB). SRB oxidize simple organic compounds under anaerobic conditions and the SRB transform the sulfates into hydrogen sulfide.



Where $CH_3CH(OH)COOH$ stands for simple organic compounds. Hydrogen sulfide reacts with divalent soluble metals to form insoluble metal sulfides (Equation 3). Some attractive findings were reported by Kousi *et al.* [26] who developed an up flow fixed-bed SRB to monitor for the treatment of zinc-bearing wastewater. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

Chemical precipitation combined with other methods

Chemical precipitation has been shown to be successful in combination with other methods. González-Muñoz *et al.* [27] reported sulfide precipitation to reuse and recover heavy metal ions and employed nanofiltration as a second step. Results indicated sulfide precipitation was successful in reducing the metal content and nanofiltration yielded solutions capable to being directly reused in the plant. Ghosh *et al.* [28] used electro-Fenton process and chemical precipitation to treat rayon industry wastewater to reduce its COD (2400 mg/L) and Zn^{2+} (32 mg/L). Results revealed that approximately 88% COD was reduced using electro-Fenton method and zinc removal (99-99.3%) was attained in the range of pH 9-10 using lime precipitation. There are some reports on chemical precipitation in combination with ion-exchange treatments. Papadopoulos *et al.* [29] reported using ion-exchange processes individually and then combining with chemical precipitation in removing nickel from wastewater streams from a rinse bath of aluminum parts. They found that the individual application of ion exchange led to the removal of nickel up to 74.8 %, while using the combination of ion- exchange and precipitation processes, higher removal from 94.2 % to 98.3% was obtained. Besides, treating acid mine water by the precipitation of heavy metals with lime and sulfides, followed by ion exchange was also reported [30].

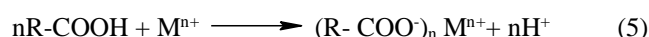
Heavy metal chelating precipitation

Conventional chemical precipitation processes have many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation processes to treat the heavy metal wastewaters especially containing coordinated agents. As an alternative, many companies use chelating precipitants to precipitate heavy metals from aqueous systems. Matlock *et al.* [31] reviewed and examined the effectiveness of three widely used commercial heavy metal precipitants, trimercaptotriazine, potassium/sodiumthiocar-bonate and sodiumdimethyldithiocarbamate. Since commercial heavy metal precipitants today either lack the necessary binding sites or pose too many environmental risks to be safely utilized, there is a definite need for new and more effective precipitants to be synthesized to meet the discharged requirements. Matlock *et al.* [31] designed and synthesized a

new thiol-based compound, 1,3-benzenediamidoethanethiol ($BDET^{2-}$) dianion. $BDET^{2-}$ can effectively precipitate mercury in the leachate solution and heavy metals from acid mine drainage. Fu *et al.* [32] employed dithiocarbamate-typesupra molecular heavy metal precipitants, N,N-bis-(dithiocarboxy)piperazine (BDP) and 1,3,5-hexahydrotriazinedithiocarbamate (HTDC) in treating complex heavy metal wastewater. Results indicated that both BDP and HTDC could effectively reduce heavy metal ions in wastewater to much lower than 0.5 mg/L. The xanthate process has also been shown to be an effective method for heavy metal removal from contaminated water. Potassium ethyl xanthate was employed to remove copper ions from wastewater [33] and results showed that ethyl xanthate was suitable for the treatment of copper-containing wastewater over a wide copper concentration range (50, 100, 500 and 1000 mg/L) to the level that meets the Taiwan EPA's effluent regulations (3 mg/L).

Ion exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [34]. Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution [35]. The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process:



The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time [36]. Ionic charge also plays an important role in ion-exchange process. The influence of ionic charge on the removal of Ce^{4+} , Fe^{3+} and Pb^{2+} from aqueous systems by cation-exchange resin purolite C100 was tested by Abo-Farha *et al.* [37]. They found that the metal ions adsorption sequence can be given as $Ce^{4+} > Fe^{3+} > Pb^{2+}$. Similar results for Co^{2+} , Ni^{2+} and Cr^{3+} on an Amberlite IRN-77 cation- exchange resin were previously obtained by Kang *et al.* [38]. Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions [39, 40, 41]. Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. Some researchers have reported that the surface of clinoptilolite loaded with amorphous Fe-oxide species would significantly improve the exchange capacity of clinoptilolite

[42]. Doula [43] employed clinoptilolite Fe system to simultaneously remove Cu, Mn and Zn from drinking water. He found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use. Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are limited at present compared with the synthetic resins. And the application of zeolites is on the laboratory experiments scale. More work is needed for the application of zeolites at an industrial scale.

Biosorption process

Biosorption is a physico-chemical process and includes such mechanisms as absorption, adsorption, ion exchange, surface complexation and precipitation. It is a property of living and dead biomass (as well as excreted and derived products); metabolic processes in living organisms may affect physico-chemical biosorption mechanisms, as well as pollutant bioavailability, chemical speciation and accumulation or transformation by metabolism-dependent properties [44]. Biosorption are passive, metabolism independent physico-chemical interactions between heavy metal ions and microbial surfaces.

It could be interpreted that biosorption process consists of two phases: One phase is a solid phase (biomass/sorbent/biosorbent/biological material) and another is a liquid phase (solvent, usually water) containing a dissolved species to be sorbed (sorbate/metal ion) principally, process, which is metabolism-independent accumulation of metals, is often rapid. Generally, biosorption is a property of certain types of inactive, dead, microbial biomaterials to bind and concentrate heavy metals from even very dilute aqueous solutions. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria, which was found responsible for this phenomenon. Living as well as dead (metabolically inactive) biological materials have been sought to remove metal ions. It was found that various functional groups present on their cell wall offer certain forces of attractions for the metal ions and provide a high efficiency for their removal [45]. According to Marin et al. [46] the polar groups of proteins, amino acids, lipids and structural polysaccharides (chitin, chitosan, glucans) may be involved in the process of biosorption.

Advantages of biosorption process

Overall, compared with the conventional toxic metal removal methods, the potential advantages of biosorption process:

1. Use of naturally abundant renewable biomaterials that can be cheaply produced;
2. Ability to treat large volumes of wastewater due to rapid kinetics;
3. High selectivity in terms of removal and recovery of specific heavy metals;
4. Ability to handle multiple toxic metals and mixed wastes;
5. High affinity, reducing residual metals to below 1 ppb in many cases;
6. Less need for additional expensive reagents which typically cause disposal and space problems;
7. Operation over a wide range of physiochemical conditions including temperature, pH, and presence of other ions (including Ca(II) and Mg(II));

8. Relatively low capital investment and low operational cost;
9. Greatly improved recovery of bound heavy metals from the biomass;
10. Greatly reduced volume of hazardous waste produced.

Disadvantages of biosorption processes

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 metal valency state. For example less soluble forms or even for degradation of organometallic complexes [47].

Factors Affecting biosorption of metals

Biosorption depends on many factors that can have effect on it. Some of these factors are related to the biomass and metal and the others are related to environmental conditions. The major factors that affect the biosorption process are:

1. Temperature

In contrast to bioaccumulation process, biosorption efficiency remains unaffected within the range 20-35 °C, although high temperatures, e.g. 50 °C, may increase biosorption in some cases, but these high temperatures may cause permanent damage to microbial living cells and then decreasing metal uptake [48]. Adsorption reactions are generally exothermic and the extent of adsorption increases with decreasing temperature. The maximum biosorption capacity for Ni and Pb by *S. cerevisiae* was obtained at 25 °C and found to decrease as the temperature was increased to 40 °C [49].

2. Acidity

pH seems to be the most important parameter in the biosorption processes. Biosorption is similar to an ion-exchange process, i.e. biomass can be considered as natural ion-exchange materials which mainly contain weakly acidic and basic groups. Therefore, pH of solution influences the nature of biomass binding sites and metal solubility; it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions. Metal biosorption has frequently been shown to be strongly pH dependent in almost all systems examined, including bacteria, cyanobacteria, algae, and fungi. Competition between cations and protons for binding sites means that biosorption of metals like Cu, Cd, Ni, Co and Zn is often reduced at low pH values [47]. Generally, the heavy metal uptake for most of the biomass types decline significantly when pH of the metal solutions is decreased from pH 6.0 to 2.5. At pH less than 2, there are minimum or negligible removal metal ions from solutions. The metal uptake increases when pH increases from 3.0 to 5.0. Optimum value of pH is very important to get a highest metal sorption, and this capacity will decrease with further increase in pH value.

Biomass concentration

Concentration of biomass in solution affects the specific uptake. At a given equilibrium concentration, the biomass adsorbs more metal ions at low cell densities than at high densities. So electrostatics interaction between the cells plays an important role in metal uptake. At lower biomass concentration, the specific uptake of metals is increased because an increase in biosorbent concentration leads to interference between the bindings sites ^[50].

3. Initial metal ion concentration.

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases. Increasing amount of metal adsorbed by the biomass will be increased with initial concentration of metals. Optimum percentage of metal removal can be taken at low initial metal concentration. Thus, at a given concentration of biomass, the metal uptake increases with increase in initial concentration ^[51].

4. Effect of pH on mechanisms of biosorption process.

The acidity (pH) is an important parameter for adsorption/biosorption of toxic metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorption/biosorption (i.e. the surface charge of adsorption/biosorption) and the degree of ionization of the adsorbate during reaction. Since, it influences not only the solution chemistry of the adsorbate but also the activity of the functional groups in the adsorbent/biosorbent and the competition of adsorbate/sorbate ions. The variation of pH affects the effectiveness as hydrogen ion itself is a tough competing adsorbate ^[52]. At higher solution pH, the solubility of metal decreases sufficiently allowing precipitation, which may complicate the sorption process. The activity of binding sites can also be changed by adjustment of the pH value, for example, during the biosorption of toxic metal ions by bacterial biomass, pH 3 to 6 has been found favorable for biosorption ^[53]. A protonated bacterial biomass releases H⁺ ions during the biosorption of metals, which in turn decreases the solution pH. These changes in pH are rapid during the initial period, as most of the reaction tends to occur during the initial stage, followed by slow attainment of equilibrium. The pH value should be controlled over the entire contact period until equilibrium is reached ^[54]. The biosorption of heavy metals onto *Pseudomonas aeruginosa* was influenced by pH value during the uptake of cations on the surface of biomass. Moreover, it has been shown that the industrial biomass *Pseudomonas aeruginosa* is efficient for the removal of heavy metals at pH between 3 and 5 ^[55]. Adsorption of Pb²⁺, Cd²⁺, Cu²⁺ and Zn²⁺ ions onto treated *Azolla filiculoides* by H₂O₂/MgCl₂, in a batch biosorption experiments was investigated. Results showed that the decreasing of biosorption levels by lowering the pH can be explained due to competition between protons and metal ions for capturing the same sites ^[56]. The removal of cadmium by dead biomass of mycelialin batch experiments at different pH values ranging from 3-8 was studied. The adsorption of metal ions depends on pH value, which influences the electrostatic binding of ions to corresponding functional groups. The result indicated that maximum adsorption of different metal species occurs at pH values of 4. The formation of metal hydroxide and other metal complexes significantly reduce the amount of toxic metal ions adsorbed at high pH value.

5. Effect of pH on sorption.

One of the mechanisms involved in the sorption of positively charged metal species is ion-exchange. Vegetal biomaterials (constituted principally by lignin and cellulose as major constituents and by a non negligible portion of fatty acid, bearing functional groups such as alcohol, ketone and carboxylic groups that can be involved in complexation reactions with metallic cations) can be viewed as natural ion-exchange materials. These materials primarily contain weak acid and basic groups on the surface, whose ionization degree strongly depends on the pH of the solution. Several authors have performed potentiometric titrations to investigate acid-base properties on the surface of biosorbents and to determine the number of active sites for metal ion sorption. The strong pH dependence of the sorption parameters can depend on several factors, which can be simplified as follows:

1. Behaviour and speciation of metal ions;
2. Dependence of the acid-base characteristics of the Adsorbing material on the pH;
3. Dependence of the interaction metal ion-sorbent on the pH.

Soluble hydrolysis products are important when cation concentrations are very low and can profoundly affect the chemical behaviour of the metals; the formulas and charges of the hydrolysis products formed in such systems can control such important aspects of chemical behaviour as:

1. Sorption of the dissolved metals in mineral and soil particles;
2. Tendency of metal species to coagulate colloidal particles;
3. Solubility of the hydroxide (or oxide) of the metals;
4. Extent to which the metals can be complexed in solution or extracted from solution by natural agents;
5. Oxydizability or reducibility of the metals to another valence state.

Based on these considerations, they demonstrated the influence of pH on sorption taking as an example the behaviour of one of the most important toxic metal ion, lead, in presence of different coordinating groups. Firstly they took into account the hydrolysis of this metal ion at two different concentrations, 100 mg/L and 0.05 mg/L, i.e. at concentration in strong polluted water and at concentration equal to EU recommended value for drinking water. At 100 mg L⁻¹, the species Pb(OH)⁺ (pH > 6) and the polynuclear species Pb₃(OH)₄²⁺ and Pb₆(OH)₈⁴⁺ (pH > 7) are formed before hydroxide precipitation occurs at pH~9.5; at 50 µg L⁻¹, Pb²⁺ do not form precipitates and only the mononuclear species are formed instead of the polynuclear ones observed at 100 mg L⁻¹. Metal ion hydrolysis equilibria, as well as hydroxide precipitation, can help explain the dependence of metal ion sorption on the pH. In most cases, the observed pH dependence lies in a range in which the metal ion is completely insensitive to the acidity of the medium. In metal ion sorption, pH effects are commonly accounted for by charge variations on the sorbent surface: protonation of basic sites or dissociation of acidic groups. According to the majority of authors a negative charge favours metal ion sorption by an ionic exchange mechanism or by electrostatic interactions, i.e. the sorption is completely determined by the acid-base behaviour of the functional groups on the surface of the adsorbing material. The real behaviour is certainly far more complex and can be rationalised in terms of metal ion

coordination by surface binding groups. The presence of phenolic, carboxylic, catecholic, amino, and mercapto groups on the surface is well known. As a working hypothesis they imagined that the different binding groups on the solid particles, dispersed in the metal ion solution, behave as different ligands. With this simplifying assumption, they considered their system as set of solution equilibria. In this assumption they treated their system as solution equilibria between various ligands competing for a metal ion or for various metal ions. For example, a carboxylic group near a phenolic group on the surface can be assumed to behave as a salicylate ligand, limited to form only 1:1 chelates being anchored to a solid surface.

Biosorbents

Biosorbents are materials of biological origin that have the ability to remove some heavy metals from waste water. The first major challenge for the biosorption field was to choose the most promising types of biomass/biosorbent from enormously available and inexpensive biomaterials. Even though several materials of biological origin bind heavy metals, biomaterials with sufficiently high metal-binding capacity and selectivity for heavy metals are appropriate for full-scale biosorption process^[57]. Metal biosorption by biomass depends on the various components of the cell especially through cell surface and the structure of the cell wall. The various chemical components of the bacterial cell surface that proves to be important for metal biosorption are peptidoglycan, teichoic acids and lipoteichoic acids. Various polysaccharides and proteins also proved to be involved in metal binding in certain kinds of biomass. The polysaccharides include, chitin, glycan, cellulose etc, which exist in fungi or algae cell walls.

The most common source of biosorbents can be the waste material from the industries as in comparison with the application of biomass from large scale fermentation processes, e.g. Yeast by-products from beer production or the use of *Streptomyces* and filamentous fungi from pharmaceutical production^[58]. The major criteria to be taken into consideration while selecting the biomass is its origin. As stated earlier, biomass can be obtained from activated sludge or fermentation waste from industries from those of food, dairy and starch. Microorganisms categorized as e.g. bacteria, yeast and fungi that are retrieved from their natural habitats are good source of biomass. Fast growing organisms like crab shells, sea weeds, tamarind seeds, fibrous plant wastes are specifically cultivated for biosorption process^[59]. Other than microorganisms as a source of agricultural products, such as rice straw, coconut husks, peat moss, wool, are put in use for the biosorption process^[60]. Other abundantly available low cost adsorbents used are, waste tea, wheat bran, hard wood, saw dust, pea pod, cotton and mustard seed cakes^[61]. Biosorption can also be performed using cheap and abundantly available materials such as citrus peels which can prove to be a cost effective method for removing heavy metals from wastewater. Non living biomass is most commonly used in comparison to the use of the living

microorganism because of its advantages. Non living things can be obtained with much lower cost, it is not subject to metal toxicity, the nutrient supply is not necessary, greater binding capacities to toxic metals has been reported as in the case of the removal of cadmium^[62]. Pine bark was one of the biosorbents which was cost effective and environment friendly and adsorbed two ions, Cu (II) and Zn (II) from its aqueous solutions. The optimum sorption pH for both the ions Cu (II) and Zn (II) were found to be in the range of 4.5-5. The study indicates that the sorption behaviour of both Cu (II) and Zn (II) on the pine bark was found to satisfy both Langmuir assumption and also Freundlich's assumption^[63].

A much more cost effective method is the use of citrus peels for biosorption purpose which makes the process cheap and much more efficient. Pectin present in the citrus peels has an efficient metal binding capacity and its role was further investigated by using citrus peels, native orange peels, protonated peels, depectinated peels and extracted pectic acid. The binding capacity was found to be significantly higher for pectic acid. Protonated peels and native peels showed moderate metal binding capacity whereas depectinated peels showed the least metal binding capacity^[64].

For efficient performance of the biosorbents, the ionic state of the biomass plays an important role, hence, biosorbents can be obtained with different ionic forms such as protonated (H^+ form) or saturated cations, such as, Na^+ , Ca^{2+} , Mg^{2+} , etc. This is done by pretreating the biomass with mineral acids, bases/salts. Treatment process varies for different types of biomass and metal ions which are to be biosorbed. In order to develop an effective biosorbent and for its subsequent reuse (desorption process) the study of mechanism of metal binding is very important. Adsorption process contained a lot of activated carbon which was the most commonly used adsorbent, in comparison with biological waste water treatment, proved to be more efficient because it contained Extracellular polymeric substances (EPS). EPS being a biopolymer compound contained many functional groups. EPS was found to adsorb various substances like, colour, metals, organic compounds and other compounds. Due to these positive effects EPS was extracted from activated sludge process and used as biosorbents^[65].

Types of biosorbents

Biosorbents for the removal of toxic metals mainly come under the following categories which have been tested for their metal binding capacity under various conditions, these includes agricultural products, such as rice straw, coconut husks, waste coffee powder, dried plant leaves, wool, cotton seed hulls, waste tea, cork biomass^[66]. Sewage sludge and microbial cells such as bacteria, fungi, algae, yeast and Peat moss^[67]. Industrial wastes, such as *Scerevisiae* waste biosorbent from fermentation and food industry, and other polysaccharide materials, etc^[68]. These biosorbents primarily fall into the following categories as a native biomass. Generally, the most important biosorbent of microbial origin can be classified into the following categories (Table 2).

Table 2: Different Types of Naturally Available Material used for the Biosorption Process

| Category | Examples |
|---------------------|--|
| Bacteria | Gram Positive bacteria like (<i>Bacillus</i> sp., <i>Corenybacterium</i> sp., etc), Gram Negative bacteria like (<i>Escherichia</i> sp., <i>Pseudomonas</i> sp., etc), Cyanobacteria like (<i>Anabaena</i> sp., <i>Synechocystis</i> sp., etc.) |
| Fungi | Molds like (<i>Aspergillus</i> sp., <i>Rhizopus</i> sp., etc.), Mushrooms like (<i>Agaricus</i> sp., <i>Trichaptum</i> sp., etc) Yeast like (<i>Saccharomyces</i> sp., <i>Candida</i> sp., etc.) |
| Algae | Micro-algae like (<i>Chlorellasp.</i> , <i>Chlamydomonas</i> sp., etc.) Macro-algae like (green seaweed (<i>Enteromorpha</i> sp., <i>Codium</i> sp., etc.), brown seaweed (<i>Sargassum</i> sp., <i>Eckloniasp.</i> , etc) and red seaweed (<i>Geildium</i> sp., <i>Porphyra</i> sp., etc. |
| Industrial wastes | Wastes from fermentation industry, food and beverage industry, activated, anaerobic sludges, etc. |
| Agricultural wastes | Wastes from fruit and vegetables like, Orange peels, wastes from fibrous plants, wheat bran, rice husk, soybean hulls, etc. |
| Natural residues | Plant residues, sawdust, tree barks, seaweeds, etc. |
| Others | Chitosan and cellulose driven materials etc. |

Source: Park *et al* ^[70]

Metal Affinity to the Biosorbent

Physical/chemical pretreatment affects permeability and surface charges of the biomass and makes metal binding groups accessible for binding. It can be manipulated by pretreating the biomass with alkalis, acids detergents and heat, which may increase the amount of metal uptake ^[55]. Toxic metal affinity to biosorbents have been studied by various researchers such as; Mechanisms of biosorption. The realization of mechanisms by which biosorbents uptake pollutants is essential and very important for the development of biosorption processes for the concentration, removal and recovery of pollutants from aqueous solutions ^[50]. Fundamentally, many types of biosorbents are 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, therefore, the mechanism of uptake toxic metal ions considered a complicated process. Several factors are found to influence on the mechanism of toxic metal biosorption:

1. The state of biomass (living or non-living);
2. Types of biomaterials;
3. Properties of metal solution chemistry; and
4. Environmental conditions such as pH, temperature, etc.

The unclear definition of sorption may be given a clue that the mechanisms involved in biosorption are often difficult to characterize, except perhaps in the simplest laboratory systems. Biological material is complex and a variety of mechanisms may be operative under given conditions but are not fully understood. Biosorption mechanisms may be classified according to following criteria:

1. Based on cell metabolism: in this criteria, biosorption mechanisms classified as metabolism dependent and non-metabolism dependent;
2. Based on location where biosorption occurs: in these

criteria, biosorption mechanisms are classified as extra cellular accumulation/precipitation, cell surface sorption/precipitation and intra cellular accumulation.

Biosorption of metals occurs mainly through several interactions such as physical adsorption, ion exchange, complexation, precipitation and entrapment in inner space ^[71]. In the biosorption process, two types of biological cells (living and dead cells) as well as chemical pretreated biomass can be used. The toxic metal ion uptake by living and dead cells can consist of two different modes. The mechanisms of uptake by living materials (bioaccumulation) and removal by dead ones (biosorption) are entirely different.

The first uptake mode is independent of cell metabolic activity and involves surface binding of metal ions to cell walls and extracellular material. This is referred to biosorption or passive uptake. The second mode of toxic metal uptake into the cell across the cell membrane is dependent on the cell metabolism, and is referred to intracellular uptake, active uptake or bioaccumulation. Intracellular uptake of the metal ions occur by the cells metabolism using only living cells, while cell surface sorption allows interaction between toxic metal ions and functional groups such as carboxylate, hydroxyl, sulfate, phosphate and amino groups present on the cell surface.

(a) Metal biosorption process using living cells.

Two steps are found for metal biosorption process using living cells: First, the metal ions are adsorbed to the surface of the cells by interaction between metal and functional groups found on the surface of the wall. Second, due to active biosorption, metal ions penetrate the cell membrane and enter into the cells. Active mode is metabolism dependent and related to metal transport and deposition.

(b) Metal biosorption using dead cells.

Metal removal by non-living cells is mainly in passive mode which is metabolism independent and proceeds rapidly by any one or a combination metal binding mechanisms such as complexation, ion exchange, physical adsorption etc. It is a dynamic equilibrium of reversible adsorption-desorption. It is independent of energy.

The use of dead materials has several advantages because:

1. There is no need of growing;
2. Growth media is not required; and

These materials are available as wastes or by-products.

These interactions occur through ion-exchange, complexation and physical adsorption.

The use of dead biomass seems to be preferred due to

1. Absence of toxicity limitations, absence of nutrient requirements in the feed solution and reuse of regenerated biomass;
2. Live and dead cells of fungi and yeast are capable of removing heavy metals from waste streams; the toxicity of heavy metals on the growth of fungi is well known.

Effect of Pretreatment on Biosorption

Since the biosorption process involves mainly cell surface sequestration, the modification of cell wall can greatly enhance metal binding. Various methods have been employed to modify the cell wall of the microbes in order to help metal binding capacity of the biomass. Biosorbents are

prepared by pretreating the biomass by different methods. Effective biosorption of certain metals by a certain biomass depends on various factors such as, a number of sites in the biosorbent material, easy accessibility of the site, the chemical nature of the site and the binding site between site and metal [72]. These modifications can be introduced, either during the growth of the micro organism or in the pre grown biomass. The cell surface phenomenon is greatly affected by the condition in which the micro organism grows. Biomass can be pre-treated directly, but if it is larger in size (sea weeds) they are sized into fine particles or granules.

The physical treatments involved in the modification of the cell walls include, heating/boiling, freezing/thawing, drying and lyophilisation. The various chemical treatments used for the modification of biomass include, washing the biomass with detergents, cross linking with organic solvent, alkali or acid treatments. These pre- treatments could modify the characteristic of cell surface, either by removing or masking the groups or by exposing more metal binding sites [56]. Luef *et al.* [60] reported that *Aspergillus niger* biomass grown in potassium hexacyanoferate obtained in large amount form citric acid fermentation plant showed very high biosorption due to change in the cell wall composition. As the cell wall plays an important role in the biosorption by the non viable cells biosorption can be enhanced by heat or chemical sterilization or by crushing. Thus the degraded cells offer a larger available surface area and expose intra cellular components and more surface binding sites because of the destruction of the cell membranes [61].

Desorption and metal recovery

The total biosorption process includes, sorption followed by desorption required to concentrate the solute. The efficiency of the biosorption process used for the removal of heavy metals depends upon the regeneration of the biosorbent after metal desorption. The regeneration of the biosorbent is crucially important to maintain a cost effective process and in recovering the metals extracted from the liquid phase. For this purpose it is desirable to desorb the sorbed metals and to regenerate the biosorbent materials to use for successive cycles of applications. Non destructive recovery by mild and cheap desorbing agents is appropriate for the regeneration of biomass. Appropriate eluants used for the desorption process depends on the type of the biosorbents and the mechanism of biosorption. Acidic and alkaline conditions were used for desorption. The eluants such as CaCl_2 with HCl, NaOH, and HCl with EDTA were reported [62]. Dilute mineral acids (HCl, H_2SO_4 , HNO_3) have been used for the removal of biomass [63]. The desorption data showed that nearly 99% of Cr was adsorbed on *Mucorhiemalisx* could be desorbed using 0.1N NaOH [64]. Desorption with nitric acid showed the high elution efficiency and biosorptive property preservation for heavy metals like Chromium, cadmium, copper by blue green algae *Spirulina spp.* [65]. Immobilization is a key aspect for the purpose of biosorption application as is it important to decrease the cost of immobilization and consequent distribution, regeneration and reuse of biosorbents. The efficiency of the desorbing agent or the eluant is often expressed taking into consideration S/L ratio i.e. the solid to liquid ratio. To make the process more economical, high values of S/L are desirable for complete elution [66]. This technology has certain economic heavy metals such as, silver, tellurium, cadmium etc. From waste cadmium, tellurium, photovoltaic cells, if disposed into landfill sites may pose

severe environmental and health hazards. The technology can also be used to remove heavy metals like, mercury, arsenic, lead etc. Sequestered in food and food products caused due to metal biomagnification/accumulation.

Mushrooms as a Biosorbent

Biosorption is the ability of certain biomaterials to bind and concentrate toxic metals from even the most dilute aqueous solutions, offers a technically feasible and economically attractive alternative [67]. In general, biosorption has been defined as the property of certain biomolecules (or types of biosorbent) to bind and concentrate selected ions or other molecules from aqueous solutions. Algae, bacteria, fungi and yeasts have proved to be potential metal biosorbents. It is consider an ideal alternative method for removing contaminates from effluents [68, 67].

Biosorption is a rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents. It has advantages compared with conventional techniques, some of these are: (low cost; high efficiency; minimization of chemical and or biological sludge; no additional nutrient requirement; regeneration of biosorbent; and possibility of toxic metal recovery). The biosorption process involves a solid phase (sorbent or biosorbent; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbet (adsorbate, metal). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases [48].

Biosorption process, in which microorganisms are used to remove and recover heavy metals from aqueous solutions, have been known for few decades but have emerged as a low cost promising technology in the last decades. In this process, the uptake of heavy metals and radioactive compounds occurs as a result of physico-chemical interactions of metal ions with the cellular compounds of biological species. As a result, the idea of the use of mushroom material for the uptake of toxic metals has been extensively studied for the last two decades [77]. Shweta *et al.* [78] reviewed the role of mushroom as a product and their role in mycoremediation. Mushroom has been used for consumption for a long time due to their flavor and richness in protein. Mushrooms are also known as mycoremediation tool because of their use in remediation of different types of pollutants. Mycoremediation relies on the efficient enzymes, produced by mushroom, for the degradation of various types of substrate and pollutants. Besides waste degradation, mushroom produced a vendible product for consumption. However, sometimes they absorb the pollutant in their mycelium (biosorption process) and cannot be consumed due to absorbed toxicants.

Biotechnological approaches can succeed in those areas and are designed to cover such niches. Microorganisms have evolved various measures to respond to heavy-metal stress via processes such as transport across the cell membrane, biosorption to cell walls and entrapment in extracellular capsules, precipitation, complexation and oxidation-reduction reactions. They have proven capability to take up heavy metals from aqueous solutions, especially when the metal concentrations in the effluent range from less than 1 to about 20 mg/L. Besides, flexibility to handle the range of

physico-chemical parameters in effluents, selectivity to remove only the desired toxic metals and the cost-effectiveness are some added advantages of biological metal cleanup techniques. These factors have promoted extensive research on the biological methods of metal removal.

Factors affecting biosorbent choice

The choice of biomass for toxic metal removal is depending on its availability and cheapness. Considering these factors, native biosorbent can come from:

1. Industrial wastes, which should be available free of charge;
2. Organisms easily obtainable in large amounts in nature; and
3. Organisms that can be grown quickly or specially cultivated or propagated for biosorption purposes.

Adsorptive pollutants like toxic metals can be removed by living microorganisms, but can also be removed by dead biological material. Strong biosorbent behavior of certain micro-organisms towards metallic ions is a function of the chemical make-up of microbial cells. This type of biosorbent consists of dead and metabolically inactive cells. Some types of biosorbents would be broad range, binding and collecting the majority of toxic metals with no specific activity, while others are specific for certain metals [79].

Biomass used for biosorption may be living or dead. While the use of dead biomass or derived products may be easier by reducing complexity, the influence of metabolic processes on biosorption is often unappreciated. Feasibility studies for large-scale applications using non-living biosorbent are in fact more applicable than bio accumulative processes that use living microorganisms, since the latter require a nutrient supply and complicated bioreactor system. In addition, maintenance of a healthy microbial population is difficult due to toxicity of the pollutants being extracted and other unsuitable environmental factors like temperature and pH of the solution being treated. Recovery of valuable toxic metals is also limited in living cells since these may be bound intracellular. For these reasons, attention has been focused on the use of non-living biomass as biosorbents [53].

Dead biomass has advantages over living microorganisms. However, many attributes of living microorganisms remain unexploited in an industrial context and are all worthy of further attention since they may be of use for specific applications [61]. The biosorption experiments have focused attention on waste materials, which are by products or the waste materials from large-scale industrial operations. For e.g. the waste mycelia available from fermentation processes, olive solid residues activated sludge from sewage treatment plants bio solids, aquatic macrophytes [80].

Economic aspects of biosorption technology

The major important economic aspects of biosorption technology are:

1. The biosorbent used must be natural and cheap (low cost and large availability).
2. The selectivity elimination of heavy metal must be under a wide range of pH, temperature and rapid kinetics of adsorption and desorption.
3. The high surface to volume ratio of microorganisms must be found and
4. Superior capability to detoxify heavy metals [81].

Preparation and characterization of modified Biosorbent

Physical treatments such as boiling, drying, autoclaving and mechanical disruption will all affect binding properties while chemical treatments such as alkali treatment often improve biosorption capacity growth and nutrition on the biosorbent, and age can also influence biosorption due to changes in cell size, wall composition, extracellular product formation, etc [74].

The surface area to volume ratio

It may be important for individual cells or particles, as well as the available surface area of immobilized biofilms. In addition, the biosorbent dosage may also affect biosorption efficiency with a reduction in sorption per unit weight occurring with increasing biosorbent dosage.

Identification of functional groups on the surface of biosorbents and their role in metal sorption

The sorption of metal ions by biomass occurs via functional groups on its surface by one or more mechanisms. All the sorbents derived from different by-products of agriculture share a common network of lignin and cellulose, and differ for the presence of functional groups which characterize each single biomass. Identification of the functional groups is crucial for understanding the mechanism that governs the sorption process. Indeed, each functional group presents its own coordinating abilities toward the different metal ions. These coordinating abilities can be rationalized in term of the hard/soft character both of the binding group and of the metal ion. In order to highlight the importance of each different binding group in the mechanism of metal ion adsorption [82]. Table 4, the representative functional groups and classes of organic compounds in biomass.

Table 4: Representative Functional Groups and Classes of Organic Compounds in Biomass.

| Formula of the functional group | Name | Classes of compounds |
|--|------------------------|--------------------------------------|
| $R - \text{O} - \text{H}$ | Hydroxyl | Alcohols, carbohydrates |
| $R - \text{C} \begin{array}{l} \text{=O} \\ \text{OH} \end{array}$ | Carboxyl | Fatty acids, proteins, organic acids |
| $R - \text{C} \begin{array}{l} \text{H} \\ \\ \text{NH}_2 \\ \\ \text{H} \end{array}$ | Amino | Proteins, nucleic acids |
| $R - \text{C} \begin{array}{l} \text{=O} \\ \text{O} - \text{R} \end{array}$ | Ester | Lipids |
| $R - \text{C} \begin{array}{l} \text{H} \\ \\ \text{SH} \\ \\ \text{H} \end{array}$ | Sulphydryl | Cystine (amino acids) proteins |
| $R - \text{C} \begin{array}{l} \text{=O} \\ \text{H} \end{array}$ | Carbonyl, terminal end | Aldehyde, polysaccharide |
| $R - \text{C} \begin{array}{l} \text{O} \\ \\ \text{C} - \text{C} \\ \quad \end{array}$ | Carbonyl, internal | Ketones, polysaccharides |
| $R - \text{O} - \text{P} \begin{array}{l} \text{O} \\ \\ \text{OH} \\ \\ \text{OH} \end{array}$ | Phosphate | DNA, RNA, ATP |

Source: [83]

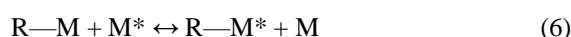
Chemical treatments of the sorbent, alkaline and alkaline-earth metal ion release and spectroscopic techniques are the procedures widely followed to reveal the binding groups.

Chemical treatment of sorbent surface

The contribution of each functional group can be evaluated by chemical treatment. It consists in carrying out chemical reactions that selectively block different functional groups on the sorbent surface. The most common chemical modifications are esterification of carboxylic and phosphate groups, methylation of amines, and modification of mercapto groups. Carboxylic groups can be alkylated by reaction with methanol or ethanol in acidic media, while amines by reaction with formaldehyde and formic acid. Alkylation of both functional groups prevents their participation in metal biosorption, thus reducing the biosorption efficiency. Chemical treatments were also used to selectively extract different compounds, such as fats or polyphenols, in order to improve metal sorption^[84].

Alkaline and alkaline-earth metal ion release

Vegetal biomaterial can be viewed as a natural ion-exchange material that primarily contains weak acidic and basic groups on its surface. One of the common procedures to investigate whether ion-exchange is the mechanism responsible for metal sorption is to determine the concentration of alkaline and alkaline-earth metal ions or protons (when the sorbent is pretreated with acid) released from the sorbent to the solution after metal uptake. The determination of the concentration of ions released into the solution (M: Na⁺, K⁺, Ca²⁺, Mg²⁺, H⁺) allows the balance of the concentration of the absorbed toxic metal ion (M*), through a charge balance, not explicitly reported in equation (6).



On the solid material the appearance of the sorbed metals, associated with the disappearance of alkaline and alkaline-earth metal ions, can be followed by Scanning Electron Microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX). This technique greatly contributes to indicate that ion exchange takes place between alkaline and alkaline-earth metal ions on the sorbent and the toxic metal ions in the solution.

Spectroscopic Analysis of Biosorbents

Useful information on the role of functional groups on metal sorption can be reached by non-destructive spectroscopic methods, observing the modifications induced by the metal on the spectra of the pure adsorbent.

Fourier transform infrared spectroscopy (FTIR)

FTIR is one of the most used techniques. Infrared Spectroscopy belongs to the group of molecular vibrational spectroscopies which are molecule-specific, and give direct information about the functional groups, their kind, interactions and orientations. Its sampling requirements allow the gain of information from solids, and in particular from solid surfaces. Even if historically IR has been mostly used for qualitative analysis, to obtain structural information, nowadays instrumental evolution makes non-destructive and quantitative analysis possible, with significant accuracy and precision. The shift of the bands and the changes in signal intensity allow the identification of the functional groups

involved in metal sorption. Using this technique, carbonyl, carboxylic, aromatic, amine, and hydroxyl groups has been found to be involved in metal uptake by different biosorbents.

Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)

DRIFTS occurs when light strikes on the surface of a material and is partially reflected and transmitted. The light that penetrates the material may be absorbed or reflected out again. The diffuse reflectance (radiation reflected from an absorbing material) is thus composed of surface-reflected and bulk re-emitted components, and contains information relative to the structure and composition of the sample. Even if DRIFTS has been not of large use, it has found interesting applications on verifying the enhancement of cadmium sorption capacity by juniper wood when carbonyl groups were substituted by sulfonic groups and on determining that Cr³⁺, Cu²⁺ and Zn²⁺ were sorbed onto the organic polymeric fraction of olive mill wastewater by ion exchange between alkaline and alkaline-earth metal ions and protons bound to carboxylic groups.

X-ray biosorption spectroscopy (XAS)

XAS specifically examines the local structure of elements in a sample. The structure of a material is deduced on theoretical basis, but usually the interpretation of XAS spectra is founded on databases of known structures. This technique is useful in the case of heterogeneous samples and a wide variety of solid materials can be examined directly and non-destructively. Also the structure of amorphous phases can be easily achieved, as the local structure does not depend on long-range crystalline order. The application of XAS varies from the trace element concentration up to that of major elements. So it is useful to speciate trace elements adsorbed on the surface of biomass. X-ray absorption spectroscopy consists in the absorption of high energy X-rays by an atom in a sample. This absorption takes place at the energy corresponding to the binding energy of the electron in the sample. The interaction of ejected electrons with the surrounding atoms produces the observed spectrum. (XAS) and extended X-ray absorption fine structure (EXAFS) were used to ascertain the ligands involved in metal binding and the coordination environment for Cr³⁺ bound to alfalfa shoot biomass by Tiemann *et al.*^[85].

X-ray photoelectron spectroscopy (XPS)

XPS was introduced by the Nobel Prize winner Siegbahn in 1949, is the main technique used for qualitative and quantitative elemental analysis of surfaces. It provides significant information on the chemical bonding of atoms. The absorption of high-energy electromagnetic radiation (X-ray or UV) by surfaces leads to the emission of photoelectrons; those generated in the outermost layers emerge from the surface into the vacuum and can be detected. The measure of the kinetic energy of the emitted photoelectrons allows the determination of the binding energies of electrons and the intensity function (number of photoelectrons vs. kinetic energy), and quantitative results were obtained from the knowledge of the number of atoms involved in the emission process. Ashkenazy *et al.*^[86] using X-Ray photoelectron spectroscopy (XPS) pointed out the involvement of nitrogen in lead sorption and the lead-oxygen interaction at the carboxyl group on the basis of the decrease in nitrogen concentration and of the shift of oxygen peak. The

same technique confirmed that chromium was sorbed onto grape stalks in both its trivalent and hexavalent forms, and allowed the ascertainment of the oxidation state of chromium bound on pine needles. Furthermore it was used to explain the increase of cadmium and lead sorption onto baker's yeast after modification of sorbent surface by cross linking cysteine.

Scanning-electron microscopy (SEM)

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope, which provides images of the sample surface by scanning it with a high-energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface. The samples must be electrically conductive, at least on their surface, for conventional SEM imaging. Nonconductive samples are coated with an ultra-thin layer of electrically- conducting material; this coating prevents the accumulation of static electric charges on the sample surface during electron irradiation. Magnification of the imaging can be controlled over a range of up to 6 orders of magnitude from about x25 to 250,000 times. When coupled with energy dispersive X-ray analysis (EDAX), the atom concentrations on the sorbent surface can be determined. This enables the confirmation of a mechanism of ion exchange, generally investigated by determining the concentration of alkaline and alkaline-earth metal ions released from the sorbent after metal sorption.

Point of zero charge

The point of zero charge is the pH at which the surface of biosorbent is generally neutral, i.e., contains as much positively charged as negatively charged surface functions. Below this value, the surface is positively charged; beyond this value, it is negatively charged. So normally, it is always easier to adsorb a cation on a negatively charged surface, and an anion on a positively charged surface. However, other interactions may be stronger than purely electrostatic forces, making the effect of surface charge not so important. Additionally, a cation is often complexed with ligands, some of them being possibly negatively charged. Therefore, in such a case, the cation is in fact a negative complex, which may adsorb very well on a positively charged surface. Point of zero charge determination of biosorbent is important in elucidating biosorption mechanism. The surface chemistry of any material (adsorbent) is determined by the acidic or basic character of their surface. The acidic means a positive surface charge and basic means negative surface charge. Therefore, it is very important to know the surface charge of the material in the aqueous media, especially in biosorption studies because if high surface area of the material is produced but the surface charge of the material is opposing the biosorption due to the fact of being same charge as the adsorbate, then there is the need to modify and find the pH conditions that shows the best biosorption. It is necessary to find out the pH at which the surface charge of the material is zero in the aqueous media or in other words the pH_{pzc} (pH point of zero charge) of the biosorbent material. Biosorption of cations is favour at $pH > pH_{pzc}$, while anion biosorption is favoured at $pH < pH_{pzc}$. The specific biosorption of cations shifts pH_{pzc} towards lower values whereas the specific biosorption of anions shifts pH_{pzc} towards higher values. The plot of change

in solution pH (ΔpH) versus initial pH (pH_i) showed that with increasing initial solution pH. It is clear that there is an observed relationship between cation biosorption and the magnitude of negative charge on the surface of the biosorbent, which is related to the surface functional groups. Ionization of the polar functional groups on the biosorbent surface is brought about by the change in solution pH. For pH values greater than the pK_a of most functional groups on biosorbent surfaces, the sites will be mainly in the dissociated form and can exchange H^+ with cations in solution [87].

Biosorption Kinetics Models

Predicting the rate at which biosorption takes place for a given system is probably the most important factor in biosorption system design, with adsorbate residence time and the reactor dimensions controlled by the system's kinetics. A number of adsorption processes for pollutants have been studied in an attempt to find a suitable explanation for the mechanisms and kinetics for sorting out environment solutions. In order to investigate the mechanisms of adsorption, various kinetic models have been suggested. In order to investigate the biosorption processes of onto *pleurotus pulmonarius* biosorbent four kinetic models were used.

The rate and mechanism of the biosorption process can be elucidated based on kinetic studies. Toxic metal ions biosorption on solid surface may be explained by two distinct mechanisms

1. An initial rapid binding of metal ions molecules on the biosorbent surface.
2. Relatively slow intra-particle diffusion.

To analyze the biosorption kinetics of the toxic metal ions, the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were applied [88]. Each of these models, their non-linear and Linear form equations presented in Table 5.

Table 5: Pseudo-First and Second-Order Models and their non-Linear and Linear equations.

| Model | Nonlinear Form | Linear Form |
|---------------------|---------------------------|-----------------------------------|
| Pseudo-first-order | $dq/dt = k_1(q_e - qt)$ | $\ln(q_e - qt) = \ln q_e - k_1 t$ |
| Pseudo-second-order | $dq/dt = k_2(q_e - qt)^2$ | $t/qt = 1/k_2 q_e^2 + (1/q_e)t$ |

where, q_e and q_t refer to the amount of metal ions adsorbed (mg/g) at equilibrium and at any time t (min), respectively and k_1 (1/min), k_2 (g/mg min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively.

Pseudo-first order model is a simple kinetic model, which was proposed by Lagergren [89] and is used for estimation of the surface biosorption reaction rate. The values of $\ln(q_e - qt)$ were linearly correlated with t . The plot of $\ln(q_e - qt)$ Vs t should give a linear relationship from which the values of k_1 were determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of contact time and is generally applicable over the initial stage of the biosorption processes [90].

In the pseudo-second order model the slope and intercept of the t/qt Vs t plot were used to calculate the second-order rate constant, k_2 . The values of equilibrium rate constant (k_2). Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of metal ions into the biosorbent pores [91].

The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t/dt = \alpha \exp(\beta q_t) \quad (8)$$

where, α is the initial biosorption rate (mg/g/min) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation Chien and Clayton^[92] assumed $\alpha\beta t \gg t$ and by applying boundary conditions

$$q_t = 0 \text{ at } t = 0 \text{ and } q_t = q_t \text{ at } t = t \text{ Eq. (8) becomes}$$

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (9)$$

Since, metal ions biosorption fits with the Elovich model, a plot of q_t Vs $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The experimental data such as the initial biosorption rate (α) biosorption constant (β) and the correlation co-efficient (γ) are calculated. The model parameters indicate that the initial biosorption (α) increases with temperature similar to that of initial biosorption rate (h) in pseudo-second-order kinetics models. This may be due to increase in the pore or active site on the biosorbents.

Intra-Particle diffusion model

The kinetic results were analyzed by the Weber and Morris [93] Intra-particle diffusion model to elucidate the diffusion mechanism. The model is expressed as

$$q_t = K_{id} t^{1/2} + I \quad (10)$$

where, I is the intercept and K_{id} is the intra-particle diffusion rate constant. The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. The K_{id} value was higher at the higher concentrations. Intra-particle diffusion is the sole rate-limiting step if the regression of q_t Vs $t^{1/2}$ is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that Intra-particle diffusion was not the only the rate limiting step.

Biosorption Isotherms

The capacity of biosorption isotherm provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently a biosorbent will adsorb and allows an estimate of the economic viability of the biosorbents commercial applications for the specified solute. Biosorption isotherms usually describe the equilibrium relation between sorbent and sorbate. They give the equilibrium relationship between the quantity of metal sorbed and that remaining in aqueous solution at a fixed temperature. By plotting solid phase concentration against liquid phase concentration, it is possible to predict the equilibrium isotherm. The isotherm thus yields certain constants whose values express the surface properties and affinity of the sorbent.

The Langmuir model

The Langmuir biosorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form can be represented as

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (11)$$

where, q_e is the amount of toxic metal ions biosorbed at equilibrium (mg/g), C_e is the concentration of toxic metal ions in the aqueous phase at equilibrium (mg/L), q_m is the maximum toxic metal ions uptake (mg/g) and K_L is the Langmuir constant related to biosorption capacity and the energy of biosorption (g/mg).

A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L . The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high biosorption affinity. Weber and Chakraborti.^[94] expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) defined in the following equation:

$$R_L = 1/1 + K_L C_0 \quad (12)$$

where, C_0 is the initial metal ions or dyes concentration (mg/L). Four scenarios can be distinguished: The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, the isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for toxic metal ions removal were calculated at different concentrations and temperatures.

The Freundlich model

The Freundlich biosorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the biosorption sites are distributed exponentially with respect to heat of biosorption. The biosorption isotherm is expressed by the following equation

$$q_e = k_F C_e^{1/n} \quad (13)$$

Linearized Freundlich equation

$$\ln q_e = \ln K_F + 1/n_F \ln C_e \quad (14)$$

where q_e is the amount of metal ions biosorbed at equilibrium (mg/g) and C_e is the concentration of metal ions in the aqueous phase at equilibrium (mg/L). K_F (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively. The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot. The Freundlich exponent, n_F , should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favourable biosorption^[95].

Temkin isotherm

The Temkin adsorption isotherm assumes that the heat of biosorption decreases linearly with the sorption coverage due to biosorbent-adsorbate interactions. The Temkin isotherm equation is given as

$$q_e = RT/\ln(K_T C_e) \quad (15)$$

The linearized form of the above equation is:

$$q_e = B_1 + \ln K_T B_1 \ln C_e \quad (16)$$

where $B_1 = RT/b$; R is the universal constant (8.314 KJ/mol.K) and T is the absolute temperature (K). A plot of q_e Vs $\ln C_e$ enables the determination of isotherm constants KT and bT from the slope and intercept.

The biosorption energy in the Temkin model, bT , is positive for toxic metal ions biosorption from the aqueous solution, which indicates a favorable biosorption. The experimental equilibrium curve is close to that predicted by Temkin model.

Jovanovic biosorption isotherm

A biosorption surface assumption, considered in Jovanovic isotherm model corresponds to another approximation for monolayer localized biosorption without lateral interactions. This model is similar to that of Langmuir model, except that the allowance is made in the former for the surface binding vibrations of a biosorbed species.

The Jovanovich model leads to the following relationship [96].

The Jovanovic model leads to the following relationship:

$$q_e = q_{max}(1 - e^{-K_j C_e}) \quad (17)$$

The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln q_{max} - K_j C_e \quad (18)$$

where K_j (L/g) is a parameter, q_{max} (mg/g) is the maximum toxic metals uptake. The q_{max} is obtained from a plot of $\ln q_e$ and C_e .

Redlich-Peterson Model

The three empirical parameters Redlich-Peterson isotherm consists of both Langmuir and Freundlich isotherms [97]. To provide a wide concentration range, the model has a linear dependence on concentration in the numerator and an exponential function in the denominator and the mechanism of biosorption is a hybrid and does not follow ideal monolayer biosorption. It can be applied either in homogeneous or heterogeneous systems due to its adaptability

The competitive Redlich-Peterson model related to the individual isotherm parameters is given by the following equation:

$$q_e = K_R C_e / (1 + a R C_e^g) \quad (19)$$

The linear form of the isotherm can be expressed as follows:

$$\ln C_e / q_e = g \ln C_e - \ln K_R \quad (20)$$

where K_R (L/g) and aR (L/mg) are the Redlich-Peterson isotherm constants, and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for $g = 1$ and Henry's law for $g = 0$.

A plot of $\ln C_e / q_e$ Vs $\ln C_e$ enables the determination of isotherm constants g and KR from the slope and intercept. The value of g lies between 0 and 1, indicating favourable biosorption.

Halsay biosorption isotherm

The Halsay biosorption isotherm [98] can be given as:

$$q_e = \exp(\ln K_{Ha} - \ln C_e / n_{Ha}) \quad (21)$$

The linear form of the isotherm can be expressed as follows:

$$\ln C_e = \ln K_{Ha} / n_{Ha} - \ln C_e / n_{Ha} \quad (22)$$

where K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants. A plot of $\ln q_e$ Vs $\ln C_e$, enables the determination of n_{Ha} and K_{Ha} from the slope and intercept. This equation is suitable for multilayer biosorption and the fitting of the experimental data to this equation attest to the heteroporous nature of biosorbent. The model predictions based on the non-linear form of the Halsey models.

Dubinin-Radushkevich biosorption isotherm

The Dubinin-Radushkevich biosorption isotherm [99] is assumed that the characteristic of the sorption curve is related to the porosity of the biosorbent. The linear form of the isotherm can be expressed as follows

$$\ln q = \ln Q_D - B_D [RT \ln(1 + 1/C_e)]^2 \quad (23)$$

where Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol²/kJ²). A plot of $\ln q_e$ Vs $RT \ln(1 + 1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

Hurkins-Jura biosorption isotherm

The Hurkins-Jura biosorption isotherm can be expressed as:

$$q_e = \sqrt{A_H / B_H} + \log C_e \quad (26)$$

which can rearranged as follows:

$$1/q_e^2 = B_H / A_H - 1/A_H (\log C_e) \quad (24)$$

where A_H (g²/L) and B_H (mg²/L) are two parameters characterizing the sorption equilibrium. The isotherm equation accounts for multilayer biosorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins-Jura isotherm parameters are obtained from the plots of $1/q_e^2$ Vs $\log C_e$ enables the determination of model parameters A_H and B_H from the slope and intercept [12].

Thermodynamic Studies

In order to study the feasibility of the biosorption process, the thermodynamic parameters such as changes in standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy change, (ΔS°) using the equations (25-26)

$$\Delta G^\circ = -RT \ln K_{ad} \quad (25)$$

$$K_c = C_{Ad} / C_e \quad (26)$$

$$\Delta G^{\circ} = -\Delta S^{\circ}(T) + \Delta H^{\circ} \quad (27)$$

where, C_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on the sorbent in mg/L and K_c is the equilibrium constant. The Gibbs free energy (ΔG°) for the biosorption of toxic metal ions onto *Pleurotus pulmonarius* biosorbent at all temperatures was obtained from Equation 36. The values of ΔH° and ΔS° were calculated from the slope and intercept of the plot $\log K_c$ against $1/T$, where R is the universal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the absolute temperature (K).

Review of some investigation on biosorption of some toxic metals from wastewater

The literature review of some researchers on the area of biosorption of some toxic metals from waste water and physico-chemical properties of leachate are summarized thus: Boldizar *et al.* [51] investigated the biosorption characteristics of Cd^{2+} and Zn^{2+} ions from monocomponent aqueous solutions by *Agaricus bisporus macrofungus*. The initial metal ion concentrations, contact time, initial pH and temperature were parameters that influence the biosorption. Maximum removal efficiencies up to 76.10 % and 70.09 % (318 K) for Cd^{2+} and Zn^{2+} , respectively and adsorption capacities up to 3.49 and 2.39 mg/g for Cd^{2+} and Zn^{2+} , respectively at the highest concentration. The experimental data were analyzed using pseudo-first- and pseudo-second-order kinetic models, various isotherm models in linear and nonlinear (CMA-ES optimization algorithm) regression and thermodynamic parameters were calculated. The results showed that the biosorption process of both studied metal ions, followed pseudo second-order kinetics, while equilibrium is best described by Sips isotherm. The changes in morphological structure after heavy metal-biomass interactions were evaluated by SEM analysis. Their results confirmed that macrofungus *A. bisporus* could be used as a cost effective, efficient biosorbent for the removal of Cd^{2+} and Zn^{2+} from aqueous synthetic solutions. Suseem and Mary [100] studied the sorption capacity of mushroom *Pleurotus eous* which they evaluated on the biosorption of heavy metals such as lead, chromium and nickel from aqueous solutions. The optimum sorption conditions were studied for each metal separately. The desired pH of the aqueous solution was found to be 5.0, 3.0 and 7.0 for the removal of lead (Pb), chromium (Cr) and nickel (Ni) respectively. The percentage removal of all the heavy metals was found to be biosorbent dependent and found to increase with the increase in biosorbent dosage and agitation speed. The contact time was optimized to be 9 hours for all the three metals. Comparative studies on biosorption of three heavy metals Pb, Cr, Ni by the mushroom *P.eous* shows high metal uptake with respect to lead rather than chromium and nickel. Hence the present data demonstrates the suitability of fruiting bodies of *P.eous* as an efficient biosorbent for the removal of toxic heavy metals and further the studies confirms that the biosorption varies with metals. Hany *et al.* [101] carried out a study on biosorption for Cr(VI), Cu(II), Cd(II) and Ni(II). These heavy metals were investigated in their study using nonliving biomass of different *Pseudomonas* species. The applicability of the Langmuir and Freundlich models for the different biosorbent was tested. The coefficient of determination (R^2) of both models were mostly greater than 0.9. In case of Ni(II) and Cu(II), their coefficients were found to be close to one. This indicates that both models adequately describe the

experimental data of the biosorption of these metals. The maximum adsorption capacity was found to be the highest for Ni followed by Cd(II), Cu(II) and Cr(VI). Whereas the Freundlich constant k in case of Cd(II) was found to be greater than the other metals. Maximum Cr(VI) removal reached around 38 % and its removal increased with the increase of Cr(VI) influent. Cu(II) removal was at its maximum value in presence of Cr(VI) as a binary metal, which reached 93% of its influent concentration. Concerning to Cd(II) and Ni(II) similar removal ratios were obtained, since it was ranged between 35 to 88 % and their maximum removal were obtained in the case of individual Cd(II) and Ni(II). Padma and Dhara [102] investigated the biosorption of the hexavalent chromium ion (Cr^{+6}) onto the cell surface of different sized fungal species in aerobic condition. Batch experiments were conducted with various initial concentrations of chromium ions to obtain the sorption capacity and isotherms. The results obtained at pH 5.5 of chromium solution were 97.39 % reduction by *Trichoderma* and 100 % reduction by *Agaricus*. They found that the sorption isotherms of fungus for Chromium (VI) appeared to fit Freundlich and Langmuir's models. The results of FT-IR analysis suggested that the chromium binding sites on the fungal cell surface were most likely carboxyl and amine groups. The fungal surfaces showed efficient biosorption for Chromium in Cr^{+6} oxidation state. Biosorption isotherm curves, derived from equilibrium batch sorption experiments, were used in the evaluation of metal uptake by these fungal biosorbents. Jiuzhou *et al.* [103] studied the biosorption of Pb^{+2} ions in both simulated and real wastewater by spent mushroom *Tricholoma lobayense*. The results show a biomass with a high potential for removing lead ions from wastewater. The optimum pH for the adsorption is 4, and the adsorption process is fast. The best sorbent mass of the biomaterial is 5 g/L with an initial lead (II) concentration of 1 mmol/L. The process follows the Langmuir isotherm model, and the biosorption capacity of lead ions reaches to 210 mg/g, which is higher than many biosorbents previously studied. The mechanism of biosorption may be mainly attributed to ion exchange. The FTIR study identifies the functional groups responsible for this process. A scanning electron microscope showed a significant change of the sorbent surface after the biosorption process. The energy dispersive elemental analysis also confirmed the adsorption of Pb^{+2} ions. Devlina *et al.* [104] conducted a study using dried biomass of macrofungi viz. oyster mushroom (*Pleurotus platypus*), milky mushroom (*Calocybe indica*) and paddy straw mushroom (*Volvariella volvacea*) for the removal of Ag^{+} and Zn^{2+} ions from aqueous medium. The influence of various factors viz. pH, biomass dosage, initial metal concentration, contact time and temperature on removal of Ag^{+} and Zn^{2+} ions were investigated under batch mode. Under optimized condition, maximum removal of Ag^{+} and Zn^{2+} was noted by *Pleurotus platypus* followed by *Calocybe indica* and *Volvariella volvacea*. Among the three macrofungi, maximum uptake of Ag^{+} and Zn^{2+} were noted onto *P.platypus* which were found to be 46.7 mg/g and 135.1 mg/g respectively under optimized conditions. They concluded that, *Pleurotus platypus* can serve as a potential biosorbent for the removal of Ag^{+} and Zn^{2+} ions from industrial waste water. Mahmooda *et al.* [76] studied the bioremediation of xenobiotics of textile industry effluent was carried out by biosorption using dead fungus biomass of *Aspergillus flavus*. The dead biomass of fungus *Aspergillus*

flavus shows maximum biosorption for three toxic components of textile industry effluent under different parameters. Methyl orange biosorption was found to be 53.62 % at room temperature, at pH 5.5, with biomass concentration of 2 g/L having contact time of 40 min and the dye concentration was 1ppm. Chromium biosorption was 72.18 %, at pH 6, at room temperature with biomass concentration of 2g/L having contact time of 10 min and solution concentration 200ppm. Lead biosorption was found to be 76.12 %, at pH 7, at room temperature with biomass concentration 2 g/L having contact time of 40 min and solution concentration 1ppm. Desorption studies were also performed and was found that dead fungal biomass can be reused further. Korrapati and Parcha [105] carried out biosorption experiments for Chromium (Cr (VI)), Copper (Cu(II)), Cadmium (Cd(II)) and Nickel(Ni (II)) were investigated in their study using nonliving biomass of different *Pseudomonas* species. The Langmuir and Freundlich models for the different biosorbent were applied and tested. Maximum Cr(VI) removal reached around 40 % and its removal increased with the increase of Cr(VI) influent. Cu (II) removal was at its maximum value in presence of Cr(VI) as a binary metal, which reached 95% of its influent concentration. Concerning to Cd(II) and Ni(II) similar removal ratios were obtained, since it was ranged between 36-90 % and their maximum removal were obtained in the case of individual Cd(II) and Ni(II). Lamroom and Ralegankar [106] conducted a study of the biosorption of Cd, Cu, Zn, Fe, Pb and Ni on a non-treated biomass of some edible mushroom. Non – treated biomass of *Agaricus bitorquis*, *Pleurotus florida*, *Volvariella volvacea*, *Volvariella diplasia* and *Pleurotus sajor-caju* were used for adsorption of different metal ions a pH 6. All tested mushrooms had more or less similar adsorption for all elements in the range of 98.97 %-84.40 %. On the basis of percent adsorption, the affinity ranking of biomass towards the metal ion was established as Cd > Zn > Ni > Pb > Cu > Fe. The efficiency of biosorption (E), per gram adsorption (Q), fraction of ion adsorbed (Xa), biosorption rate (P) and distribution coefficient of the heavy metal (D) values were in a range 84.52- 98.97 %, 79.23-283.21 (mM/g), 84.40-98.97 %, 84-52, 98.97 % and 0.11-1.35 respectively. *Agaricus bitorquis* showed maximum biosorption for for Cd (98.97 %), Ni (97.22 %) and Fe (88.81 %). *Volvariella volvacea* had a more sorption for Cu (93.59 %) and Pb (98.69%) where as *Volvariella diplasia* for Zn (98.04%). Both *Pleurotus sajor-caju* and *Pleurotus florida* showed comparatively moderate sorption for Cd (98.94 % and 98.93 %), Ni (both 97.22 %) and Fe (88.24 % and 84.84 %) respectively. Arbanah *et al* [80] conducted a study on biosorption of Cr(III), Fe(II), Cu(II), Zn(II) ions from liquid laboratory chemical waste by *pleurotus ostreatus*. In the first batch treatment study, synthetic heavy metal solution was introduced prior to the treatment of liquid laboratory chemical waste. The highest biosorption efficiency for Fe(II) and Cu(II) was found to be at pH 6 while Cr(III) at pH 5 while Zn(II) at pH 4. About 80.52 % of Fe(II) and 45.20 % of Cu(II) was removed at pH 6. The biosorption efficiency of Cr(III) at pH 5 is 12.47 % while only 5.04 % for Zn(II). The results show that agitation speed of 150 rpm and temperature of 25°C is the best condition for biosorption of heavy metals. Throughout their research, the percentage 'heavy metal removal was found to increase with the increasing contact time between *Pleurotus ostreatus* (*P.ostreatus*) and liquid

laboratory chemical waste. The contact time can rise up to 10 hours. Almost 17.02 % of Cr(III), 55.35 % of Fe(II), 36.80 % of Pb(II), 15.34 % of Cu(II) and 13.34 % of Zn(II) were removed from chemical waste under suitable treatment conditions. This validates that *P.ostreatus* is a good biosorbent agent for laboratory chemical waste treatment. Salman *et al* [79] reviewed the biosorption of heavy metals. They reported that, industrial effluents containing heavy metals may consider a major source of contamination causes serious environmental problems. Decontamination of heavy metals from wastewater has been a challenged for a long time. A number of methods have been developed for removal of toxic metal ions from wastewaters such as precipitation, evaporation, electroplating, ion exchange, membrane processes, etc. However, these conventional technologies are providing expensive due to non- regenerable materials used, high cost and generation of toxic sludge. Biosorption is a process which represents a biotechnological innovation as well as a cost effective excellent tool for removing heavy metals from aqueous solutions. It represents a typical technique for using economical alternate biological materials for the purpose. They suggested that, biosorption is one of the main components of environmental and bioresource technology. Application of microorganisms (specifically bacteria, algae, yeasts and fungi) as biosorbents for heavy metal removal have received growing interest due to high surface to volume ratio; large availability, rapid kinetics of adsorption and desorption and low cost. They reviewed the removal of heavy metals from aqueous solutions using various materials of biological origin such as fungi, algae, yeast and bacterial biomass. Their review discussed the significance of heavy metal removal from waste streams and provided brief overview of potential of biosorbents and biosorption technology, highlights the undelaying features of biosorption and the operation conditions such as pH, dose required, initial concentration, temperature, and treatment performance. Also sorption isotherms, sorption kinetics as well as models used to characterize biosorbent sorption.

Conclusion

Biosorption can be used as an alternative to conventional systems for the removal of toxic metal ions from wastewater. Further investigation in a view of modelling and regeneration of biosorbent material, testing of immobilised raw biomass with industrial effluents are required for enhancing biosorption process. Also, biosorption studies rarely deals with multiple toxic metal uptake systems which can be further investigated. There is a necessity to have more knowledge involved in the basic mechanism of biosorption in order to develop better and effective biosorbents. For the better application of biosorption in the future is to use hybrid technology for the removal of pollutants with the help of living cells and to develop excellent commercial biosorbents in the form of an ion-exchange resin. The use of biosorption isotherms can be employed to describe the equilibrium relation between sorbent and sorbate. Various biotechnology based processes such as biosorption, bioreduction, bio precipitation bioprocesses and non-biotechnology based processes, for example chemical precipitation, floatation, electrochemical process, membrane technology will also prove useful for treating large scale effluents. The future development of the biosorption process requires a thorough investigation in the direction of modelling, of regeneration and immobilization of biosorbents and of treating industrial

effluents. Various commercial microbial biosorbents are available for example alga sorb, AMT- Bioclaim and Bio-fix. Biosorption is regarded as a potential cost effective biotechnology process for the treatment of high volume low concentration complex waste waters containing toxic metals.

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