

Biosorption of Heavy Metals: A Review

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Abstract-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. Today, 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. The aim of the present study is to review the removal of heavy metals from aqueous solutions using various materials of biological origin such as fungi, algae, yeast and bacterial biomass. This review discuss the significance of heavy metal removal from waste streams and provides 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 are reviewed.

Keywords- Biosorption; Adsorption; Heavy Metals; Wastewater; Fungi; Bacteria; Algae; Yeast

I. INTRODUCTION

Heavy metal pollution is one of the major environmental problems today. Most of heavy metal ions are toxic to living organisms, the sources and toxicity of certain material ions are listed in Table 1. These metal ions are non-degradable and are persistent in the environment. Therefore, the elimination of heavy metal ions from wastewater is important to protect public health. Industrial effluents are a major cause of heavy metal concentration, these effluents are coming from many industries such as corrosion of water pipes, waste of dumping, electroplating, electrolysis, electro-osmosis, mining, surface finishing, energy and fuel producing, fertilizer, pesticide, iron and steel, leather, metal surface treating, photography, aerospace and atomic energy installations etc. [1]. Thus the removal and recovery of heavy metals from effluent streams are essential to the protection of the environment.

TABLE 1 TYPE OF HEAVY METALS AND EFFECTS OF HUMAN BEINGS

Heavy metal	Major source	Toxic effect	References
Lead	Mining, paint, pigments, electroplating, manufacturing of batteries, burning of coal	Anemia, brain damage, anorexia, malaise, loss of appetite, Liver, kidney, gastrointestinal damage, mental retardation in children	[32, 33]
Copper	Plating, copper polishing, paint, printing operations	neurotoxicity, and acute toxicity, dizziness, diarrhea	[34]
Cadmium	Plastic, welding, pesticide, fertilizer, mining, refining	Kidney damage, bronchitis, Gastrointestinal disorder, bone marrow, cancer, lung insufficiency, hypertension, Itai-Itai disease, weight loss	[35, 36]
Zinc	Mining, refineries, brass manufacturing, plumping	Causes short term "metal-fume fever", gastrointestinal distress	[37]
Mercury	Batteries, paper industry, paint industries, mining	Damage to nervous system, protoplasm poisoning, corrosive to skin, eyes, muscles, dermatitis, kidney damage	[38]
Nickel	Porcelain enameling, non-ferrous metal, paint formulation, electroplating	Chronic bronchitis, reduced lung function, lung cancer,	[39]
Arsenic	Smelting, mining, rock sedimentation, pesticides,	Bronchitis, dermatitis, bone marrow depression, hemolysis, hepatomegaly,	[40]
Chromi -um	Textile, dyeing, paints and pigments, steel fabrication	Carcinogenic, mutagenic, teratogenicity, epigastria pain nausea, vomiting, severe diarrhea, producing lung tumors	[41]

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies. Conventional technologies, such as chemical precipitation, lime coagulation, solvent extraction, membrane filtration, reverse osmosis, on exchange and adsorption, are being used for the removal of heavy metal ions from aqueous wastes. Each process has its own merits and limitations in application, so these traditional metal removal methods have certain disadvantage

(incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products). Most of these methods are often ineffective or uneconomical when heavy metal concentration is higher (10-100 mg/L) than permissible concentration less than 1 mg /L), which require a high cost when they used for disposal the heavy metals from aqueous effluents. Increasing environmental awareness and legal constraints being imposed on discharge of effluents are major factors for using cost-effective alternative technologies.

In recent years, microbial biomass has emerged as an option for developing economic and eco-friendly wastewater treatment process., therefore, applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes hot topic in the field of metal pollution control because of its potential application. Alternative process is a biosorption, which utilizes various certain natural materials of biological origin, including bacteria, fungi, yeast, algae, etc. [1].

Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [2]. Biosorption, which is the ability of certain microbial biomaterials to bind and concentrate heavy metals from even the most dilute aqueous solutions, offers a technically feasible and economically attractive alternative [3]. 'Biosorption' has been defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions [4]. Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents [5]. It is consider an ideal alternative method for removing contaminates from effluents

Biosorption is a rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents. It has advantages compared with conventional techniques [6], some of these are listed: (low cost; high efficiency; minimization of chemical and or biological sludge; no additional nutrient requirement; regeneration of biosorbent; and possibility of metal recovery).

The biosorption process involves a solid phase (sorbet 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 [7].

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 [8]. As a result, the idea of the use of biomaterial for the uptake of heavy metals has been extensively studied for the last two decades.

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 [9-16]. 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 [17]. Besides, flexibility to handle the range of physico-chemical parameters in effluents, selectivity to remove only the desired 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. This paper reviews the use of different types of bacteria, algae fungi and yeasts and its wastes as biosorbents to remove heavy metals from wastewaters; these biological biosorbents have a highly effective as well as reliable in the removal of heavy metal ions from wastewater. Hence, this work attempts to summarize recent studies in the removal of heavy metals using biological biosorbents published between 2000 and 2013. Equilibrium studies in biosorption of heavy metals using various kinds of biosorbents are also reviewed.

II. HEAVY METALS

The use of natural materials for heavy metals removal is becoming a concern in all countries. Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern.

Heavy metal ions have great effects on all forms of life. Heavy metal pollution is one of the most important environmental problems today because of their toxicity, bio-accumulation tendency, threat to human life and the environment [18]. Heavy metals are presented in nature and industrial waste water, so the presence of heavy metals in surface and ground water pose a contamination problem. Large number of industries can produce and discharge wastes containing different heavy metals into the environment. The main source of heavy metal pollution are metal plating, mining, smelting, battery manufacturing, tanneries, petroleum refining, pigment manufacture, printing paint manufacture, pesticides, etc.

The term "heavy metal" is entirely applied to a group of metals (and metal-like elements) with density greater than 5 g/cm³ atomic number above 20 and is toxic or poisonous at low concentrations [19].

The main elements that considered as a heavy metals are chromium(Cr), manganese(Mn), cobalt (Co), copper(Cu), zinc(Zn), molybdenum(Mo), mercury(Hg), nickel(Ni), tin(Sn), lead(Pb), cadmium(Cd), antimony(Sb), etc.

Three kinds of heavy metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides such as U, Th, Ra, Am, etc. [1, 20].

Lead, mercury, cadmium and chromium (VI) are at the top on the toxicity list from among various metal ions, the first three, called “the big three”, are in the limelight due to their major impact on the environment [5].

Heavy metals are natural components from the earth’s crust. They cannot be destroyed or degraded. However, most of these heavy metals become toxic at high concentrations due to their ability to accumulate in living tissues.

Removal of heavy metals from industrial wastewater is of primary importance. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters. Table 1 gives the main sources of heavy metal pollutants and its effects on human lives.

A. Copper

Copper, one of the most widely used heavy metal, is mainly employed in, electrical, electroplating industries, and in larger amounts is extremely toxic to living organisms. The presence of copper (II) ions causes serious toxicological concerns, it is usually known to deposit in brain, skin, liver, pancreas and myocardium [21]. Copper usually occurs in nature as oxides and sulphides. Copper is an essential substance to human life. Copper is found in a variety of enzymes and is used for biological electron transport. Like all heavy metals, it is potentially toxic, especially at high concentrations.

Thirty grams of copper sulfate is potentially lethal in humans. In high doses, it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Wilson’s disease, a disease that causes the body to retain copper can lead to brain and liver damage if untreated. Inhalation of copper produces symptoms similar to those of silicosis and allergic contact dermatitis. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. The suggested safe level of copper in drinking water for humans varies depending on the source, but tends to be pegged at 1.3 mg/L according to the US Environmental Protection Agency. Too much copper in water has also been found to damage marine life. The observed effect of these higher concentrations on fish and other creatures is damage to gills, liver, kidneys, and the nervous system. Common oxidation states of copper include the less stable copper (I) state, Cu^+ , and the more stable copper (II) Cu^{2+} [22].

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries [23] the other major industries discharging copper in their effluents are paper and pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink [24]. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever [25]. Containing is linked to an increase in lung cancer among exposed workers [26].

B. Chromium

There are two stable oxidation states of chromium found in the environment, Cr (III) and Cr (VI) which have contrasting toxicities, mobility and bioavailability. Chromium compounds of oxidation state Cr^{6+} are powerful oxidants. Chromium hexavalent (VI) compounds are used as pigments for Photography, and in pyrotechnics, dyes, paints, inks, and plastics. They can also be used for stainless steel production, textile dyes, wood preservation, leather tanning, and as anti-corrosion coatings. While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin. Trivalent chromium, Cr (III), is an essential element required for normal carbohydrate and lipid metabolism.

C. Lead

Lead is a heavy metal poison which forms complexes with Oxo-groups in enzymes to affect virtually all steps in the process of hemoglobin synthesis and porphyria metabolism [27]. Toxic levels of lead in human have been associated with encephalopathy, seizures and mental retardation [28].

D. Cadmium

The most severe form of Cd toxicity in humans is “itai-itai”, a disease characterized by excruciating pain in the bone [29, 30]. Other health implications of Cd in humans include kidney dysfunction, hepatic damage and hypertension [31]. However, it has been suggested that overall nutritional status (rather than mere Cd content of food) is a more critical factor in determining Cd exposure. Table 1 shows the sources and toxicity of certain metal ions.

III. BIOSORPTION PROCESS

Biosorption, the process in which a microorganism is used to remove and recover heavy metals from aqueous solutions, has been known for a few decades but has emerged a low cost promising technology in the last decades. In this process, the uptake of heavy metals occurs as a result of physico-chemical interactions of metal ions with cellular compounds of biological species [8].

Biosorption may be simply defined as the removal of substances from solution by biological material. Such substances can be organic or inorganic, and in soluble or insoluble forms [42]. Biosorption is the removal of materials (compounds, metal ions, etc.) by inactive, non-living biomass (materials of biological origin) due to "high attractive forces" present between the two [6]. 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 [42]. 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. On the contrary, bioaccumulation is metabolism-dependent intracellular uptake of metal ions by living microorganisms and is slower process compared to biosorption [43].

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 [44, 45].

Reference [46] suggested the following comparison of characteristic features of heavy metal biosorption and bioaccumulation processes (Table 2).

TABLE 2 COMPARISONS OF CHARACTERISTIC FEATURES OF HEAVY METAL BIOSORPTION AND BIOACCUMULATION PROCESSES

Feature	Biosorption process	Bioaccumulation process
Definition	The passive sorption of the dead microbial cell walls is called as biosorption	The active process of metal removal by living cells is referred to as bioaccumulation
Metal affinity	Higher under favorable conditions	Toxicity affects metal uptake by living cells, but in some instances, there is high metal accumulation
Rate of metal uptake	Generally rapid, a few seconds for outer cell wall accumulation	Normally slower than biosorption
Selectivity	Variety of ligands involved, hence poor	Better than biosorption, but less than some chemical technologies
Temperature	Within a modest range	Inhibited by low temperatures
Versatility	Metal uptake may be affected by anions or other molecules. Extent of metal uptake usually pH dependent	Require an energy source Dependent on plasma membrane ATPase activity

A. Advantages of Biosorption Process

Overall, compared with the conventional heavy metal removal methods, the potential advantages of biosorption process includes [47]:

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

- Greatly improved recovery of bound heavy metals from the biomass;
- Greatly reduced volume of hazardous waste produced.

B. *Factors Effecting on Biosorption of Metals*

Biosorption depends on many factors that can 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 [7, 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) *Characteristics of Biomass:*

The nature of the biomass or derived product may be considered one of the important factors, including the nature of its application such as: freely-suspended cells, immobilized preparations, living biofilms etc. 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, especially evident in some fungal systems because of DE acetylation of chitin to form chitosan-glycan complexes with higher metal affinities [20]. Growth and nutrition on the biomass, and age can also influence biosorption due to changes in cell size, wall composition, extracellular product formation, etc.

3) *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 biomass concentration may also affect biosorption efficiency with a reduction in sorption per unit weight occurring with increasing biomass concentration [50].

4) *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 [51, 52]. 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.

5) *Biomass Concentration:*

Concentration of biomass in solution affects the specific uptake [53]. At a given equilibrium concentration, the biomass adsorbs more metal ions at low cell densities than at high densities [54]. 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 sits [55]. High biomass concentration restricts the access of metal ions to the binding sites [2].

6) *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 [56]. 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.

7) *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 [7].

IV. BIOSORBENTS

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 [1].

Biosorbents for the treatment of water and wastewater containing heavy metals are discussed by many reviews [6, 16, 57-61].

A. Types of Biomass

Biosorbents for the removal of metals mainly come under the following categories:

A large number of biomass types 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 [59, 62, 63]. Sewage sludge and microbial cells such as bacteria, fungi, algae, yeast and Peat moss [64, 65]. Industrial wastes, such as Scerevisiae waste biomass from fermentation and food industry, and other polysaccharide materials, etc. [59]. These biosorbents primarily fall into the following categories as a native biomass.

The development and implementation of cost-effective process for removal/recovery of metals is essential to improve the competitiveness of industrial processing operations. Disadvantages, together with the need for more economical and effective methods for the recovery of metals from wastewaters, have resulted in the development of alternative separation technologies [66].

In recent years, there has been a trend toward the implementation of passive treatment schemes. These take advantage of naturally occurring geochemical and biological processes to improve water quality with minimal operation and maintenance requirements. Biological removal includes the use of microorganisms (fungi, algae, and bacteria), plants (live or dead) and biopolymers and may provide a suitable means for heavy metals treatment from wastewater. In particular, some waste mycelia are available in large quantities for the removal of heavy metals [8, 20].

Microorganisms like, bacteria, fungi, yeast, and algae from their natural habitats are excellent sources of biosorbent [1]. These biosorbents possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution from ppm to ppb level. It can effectively sequester dissolved metal ions out of dilute complex solutions with high efficiency and quickly, therefore it is an ideal candidate for the treatment of high volume and low concentration complex wastewaters [8]. Table 3 shows some examples of types of native biomass that have been used for preparing microorganisms biosorbents.

TABLE 3 TYPES OF NATIVE BIOMASS THAT HAVE BEEN USED FOR PREPARING BIOSORBENTS

Category	Examples
Bacteria	Gram-positive bacteria (Bacillus sp., Corynebacterium sp., etc.). Gram-negative bacteria (Eschrichia sp., Pseudomonas sp., etc.) and Cyanobacteria (Anabaena sp., Synechocystis sp., etc.)
Fungi	Molds (Aspergillus sp., Rhizopus sp., etc.) Mushrooms (Agaricus sp., Trichaptum sp., etc.) and Yeast (Scaccharomyces sp., Candida sp., etc.)
Algae	Micro-algae (clorella sp. Chamydomonas sp., etc.) and Macro-algae (green seaweed (Enteromorpha sp., Codium sp., etc.), brown seaweed (Sargassum sp., Ecklonia sp., etc., and red seaweed (geildium sp., Porphyra sp., etc.))
Industrial wastes	Fermentation wastes, food/beverage wastes, activated sludges, anaerobic sludge, etc.
Agricultural wastes	Fruit/Vegetable wastes, rice straws, wheat bran, soybean halts, etc.
Natural residues	Plant residues, sawdust, tree barks, weeds, etc.
Others	Chitosan-driven materials, cellulose-driven materials, etc.

B. Factors Affecting Biomass Choice

When choosing biomass, for large-scale industrial uses, the main factor to be taken into account is its availability and cheapness [5, 6, 67]. Considering these factors, native biomass can come from:

- (i) Industrial wastes, which should be available free of charge;
- (ii) Organisms easily obtainable in large amounts in nature; and
- (iii) Organisms that can be grown quickly or specially cultivated or propagated for biosorption purposes [6, 67].

Adsorptive pollutants like metals can be removed by living microorganisms, but can also be removed by dead biological material [68].

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 heavy metals with no specific activity, while others are specific for certain metals [7].

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 sorption is often unappreciated.

Feasibility studies for large-scale applications using non-living biomass are in fact more applicable than bio accumulative processes that use living microorganisms, since the latter require a nutrient supply and complicated bioreactor system [59]. 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 metals is also limited in living cells since these may be bound intracellularly. For these reasons, attention has been focused on the use of non-living biomass as biosorbents [54, 59].

As mentioned above, 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 [68, 69].

Recent 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.

C. Economic Aspects of Biosorption Technology

The major important economic aspects of biosorption technology are:

- (i) The biomass used must be natural and cheap (low cost and large availability).
- (ii) The selectivity elimination of heavy metal must be under a wide range of pH, temperature and rapid kinetics of adsorption and desorption.
- (iii) The high surface to volume ratio of microorganisms must be found, and
- (iv) Superior capability to detoxify heavy metals [1, 70, 71].

Several important parameters that affect the performance of living biosorbent must be taken into account, these are:

- (i) The physiological state of the organism,
- (ii) The age of the cells, the availability of micronutrients during their growth, and
- (iii) The environmental conditions during the biosorption process (such as pH, temperature and the presence of certain ions).

D. Types of Biological Biosorbents

Generally, the most important biosorbent of microbial origin can be classified into the following categories:

1) Bacteria:

Bacteria are the most abundant and versatile of microorganisms and constitute a significant portion of an entire living terrestrial biomass of about 10^{18} g [72]. Bacteria have simple morphology. The most commonly bacteria present in three basic shapes: spherical or ovoid (coccus), rod (bacillus, with a cylindrical shape), and spiral (spirillum), although there are a great variety of shapes due to differences in genetics and ecology. Bacteria vary in size as much as in shape [1]. There is a great deal of heterogeneity among different bacterial species related to:

- (i) Number of surface binding sites;
- (ii) Binding strength for different ions; and
- (iii) Binding mechanisms.

Bacteria have polysaccharide slime layers and readily provide amino, carboxyl, phosphate and sulphate group for metals biosorption [72]. Bacterial biomass is generally produced as a waste by-product of industrial operations or can be specifically propagated in large scale. The uptake capacities of bacteria generally range between 0.23 to 0.90 mmol/g [73, 74]. Bacteria are used as biosorbents because of their small size, ubiquity, and capability to grow under controlled conditions, and their resistance against a wide range of varying environmental conditions [75-77]. Bacteria species such as Bacillus, Pseudomonas, Streptomyces, Escherichia, Micrococcus, etc., has been tested for uptake metals or organics. Table 4 summarizes some of the important results of metal biosorption using bacterial biomasses, according to some published references [59, 70]. Heavy metal

binding onto the surface of bacterial cell wall is generally, a two-stage process. The first stage involves the interaction between metal ions and reactive groups on cell surface and second stage includes deposition of successive metal species in greater concentrations [78].

TABLE 4 BIOSORPTION DATA OF BIOSORBENT BACTERIA WITH METAL SORBENT AT OPERATING CONDITIONS

Biomass type	Metal studied	pH	T (°C)	C ₀ (mg/L)	W _t (g/L)	N _s (rpm)	Time (h)	q(mg/g) or % removal	References
Staphylococcus saprophyticus	Cr(VI)	2	27	193.6	0.2	150	3	24.1%	[79]
	Pb	4.5		100-150			4	100%	
	Cu	3.5		105			2	14.5%	
Sulphate-reducing bacteria(SRB)	Zn	6.0	30	10-200	1		24	5.6	[80]
Enterobacter cloacae	Pb	5	25	200	0.1	240	2	67.9%	[81]
	Cu	5		150				78.9%	
	Cr(VI)	4		100				55.8%	
	Hg	4		100				43.23%	
	Cd	5		300				58.9%	
			(25-350)						
Bacillus sp. Pseudomonas sp. Micrococcus sp.	Cu	5-9	30	25		100	24	69.34%	[82]
	Cd			25				90.41%	
	Pb			25				84.27%	
			(20-100)						
Pseudomonas sp.	Cr(VI)	5.5	30	1-10 mmol/l	5	200		8.9-238	[83]
	Cu							8.9-238	
	Cd							500	
	Ni							556	
Thiobacillus thiooxidans	Zn	6	30	50	0.25	786	2	95.24	[84]
	Cu	5		25-250				39.84	
Pseudomonas Aeruginosa	Cr(VI)		25	1000				1.07	[85]
	Cu			1000				0.67	
	Zn			1000				1.33	
			(0-1000)						
Bacillus cereus	Cu	5.5	25	(5-100)	1.0		24	50.32	[85]
	Pb							36.71	
Geobacillus thomodentrificans	Cu	5	25	0.5		100	12	57	[86]
	Zn	5		0.5				18	
	Pb	4		2.0				53	
			(0.5-3.0)						
Geobacillus thomocatenulatus	Cu	5	25	1.0		100	12	65	[86]
	Zn	5		1.0				12.3	
	Pb	4		1.0				54	
Bacillus licheniformis	Cr(VI)	3.5	28	1200		120	48	95%	[87]
	Fe	3.5		1500				52%	
	Cu	2.5		1500				32%	
			(200-1500)						
Stenotrophomonas maltophilia	Cu	5.0	25	50	20	140	2	0.57	[88]
	Cd			10				0.12	
	Pb			20				0.41	
			(0-140)						
Actinomycete sp	Cd	6	30	(50-400)	5	150	24	32.63	[88]
	Ni	5						36.55	
Micrococcus sp.	Cr(VI)	5	35	100		120	24	92%	[89]
	Ni			50				90%	

Where:

C₀ is initial concentration of heavy metal in solution, (mg/L)

W_t is the weight of used adsorbent, (g/L)

q is the uptake removal of pollutant, (mg/g)

N_s is the agitation speed of shaker, (rpm)

T is the temperature of the experiment, (°C)

2) *Algae*:

Algae are considered one of the most promising types of biosorbents which are interest in search for and development as a new biosorbent materials [90-93] because of they have high sorption capacity and are readily available in a large quantities in seas and oceans [94, 95]. Algae have low nutrient requirements, being autotrophic, they produce a large biomass, and unlike other biomass and microbes, such as bacteria and fungi. They generally do not produce toxic substances. Three groups of algae are found:

- (i) Micro-algal(green algae or fresh water algae);
- (ii) Macro-algal (brown algae or marine algae);
- (iii) Red algae.

which take more attention in biosorption processes, brown algae distinguished higher uptake capacity compared with red and green algae [96], therefore, the metal uptake capacities exhibited by non-living biomass of micro-algal (green algae) and macro-algal species (brown algae) varies from 0.066 to 1.20 mmol/g and 0.65 to 1.21 mmol/g respectively [5, 97]. Using algae as biosorbent material have been less compared with the other kinds of biomass, especially fungi (15%) and bacteria (85%) [60]. Binding of metal ions on algal surface depends on different conditions [98], these are:

- (i) Ionic charge of metal ion;
- (ii) Algal species; and
- (iii) Chemical composition of the metal ion solution.

Potential metal cation-binding sites of algal cell components include carboxyl, amine, imidazole, phosphate, sulphate, sulfhydryl, hydroxyl and chemical functional groups are contained in cell proteins and sugars [99].

Microalgae can sequester heavy metal ions by the same biosorption mechanisms as other microbial biomass as well as by the formation of phytochelatins which they synthesize in response to toxic heavy metal stress.

There are two principal mechanisms which involved in biosorption by microalgae appear: (i) ion exchange wherein ions such as Na, Mg, and Ca become displaced by heavy metal ions, and (ii) complexation between metal ions and various functional groups such as carboxyl, amino, thiol, hydroxy, phosphate, and hydroxy-carboxyl, that can interact in coordinated way with heavy metal ions.

In general, the mechanism of biosorption is based on a number of metal-binding processes taking place with components of the algae cell wall. The algae cell walls can reversibly biosorb metals, and thus function in a similar way to an ion-exchange resin. Thus, the biosorption mechanism can be considered as being dependent on the composition of the algal cell wall. Algal cell walls can be made up with further polysaccharides: mannan, xylan, alginic acid, chitin, etc. these components, along with the proteins present, can provided acid binding sites such as amino, amine, hydroxyl, imidazole, phosphate and sulphate groups [99]. The biosorption mechanism has been described as not involving van der Waals' forces at the cellulose network of the cell walls, thus both ionic charge and covalent bonding are involved in the metal biosorption process. It is thought that the proteins and polysaccharides are the major components responsible for the biosorption. Covalent bonding could be expected with amino and carboxyl groups and ionic charge bonding with carboxyl and sulphate groups associated with these components. Studies with the micro algal (*Scenedesmus obliquus*) indicated that the cell wall behaved like a weak acidic cation exchanger containing various cell wall ligands with different exchange capacities [3]. Table 5 listed several types of algae used as a biosorbent including the main effective parameters used as operating conditions.

TABLE 5 BIOSORPTION DATA OF BIOSORBENT ALGAE WITH METAL SORBENT AT OPERATING CONDITIONS

Biomass type	Metal studied	pH	T (°C)	C ₀ (mg/L)	W _t (g/L)	N _s (rpm)	Time (h)	q(mg/g)	References
Calotropis procera(Ait)	Pb	4	25	25-100	2	150	6	22.8	[100]
	Cu	5						14.5	
Bifurcaria bifurcata,	Cd	4.5		10-350	2.5	175	3	95	[101]
Oocystis	Cd	7.5	28	0.5-35	28,51	60-80	72		[102]
	Cu	5.5		0.5-25	4.4,60				
	Pb	5.5		10-30	16-80				
	Zn	5.5		2-12	0.5-157.5				
Green algae	Zn	5	25	20-350	3		1	7.62	[103]
Sargassum filipendula	Cu	4.5	25	250	5	175	6		[104]
	Ni								
Filamentous alga of pithpphora spswas	Cd		25	2-30	0.17-14		9 days		[105]
	Cr(VI)			2-30	0.13-4.9				
	Pb			2-30	0.12-10.3				

Sargassum sp.	Cr(III)	4.0	30	92,162	2-5		6	68.9	[131]
Microalgae	Cu Zn		30	50-250	5	150		0.66 0.72mmol/g	[106]
Green algae(Spirogyra spp)	Cr(VI)	4.0	30	1-25	1,2,3	180	3	265	[107]
Brown algae(Sargassum sp.)	Cr Zn Ni Cu Cd Hg Fe	3 3 5 4 5 4 3	30 30 30 30 30 30 30			150 150 150 150 150 100 150		20.2 15.4 26.1 18.6 22.2 14.8 14.6	[107]
Schizosaccharomyces pombe	Cu	4	25	100-400 100	300 beads		96	70%	[108]
Sargassum tenerrimum	Cd	6	25	100 20-500	4.0 0.05-8	150	24	0.4 mmol/g	[109]
Brown algae(Fucus vesiculosus)	Cu Pb Ni Cd	5 5 5 6	25	10-150	0.25		2	0.97 1.04 0.80 1.12 mmol/g	[95]
Brown marine macro algae	Cd Zn Pb	5	25	75-100	2.0		1	24-40 19-32 32-50	[95]
Sargassum glaucescens	Cd	5	25	0-150	2.5	150	2	84.7	[110]
Ascophyllum nodosum	Cd Ni Zn Cu Pb	6 6 6 5 5	25	10-150	0.5,1		2	114.9 50 53.2 70.9 204.1	[111]
Fucus vesiculosus	Cu	5.5	20	.01-.4 mmol/L	0.08			1.85 mmol/g	[111]
Cladophora fascicularis	Cd Hg Pb		25	20-80	1	180	2	20 20 20	[112]
Spirogyra hyalina	Cd Hg Pb AS Co		25	40 40 80 40 80	2.5	180	2	9.832 39.212 15.471 8.719 7.856	[112]
Sargassum Sp.	Cd	5	25	150	2.5	150	2	84.7	[112]
Sargassum Sp. Wightii(Greville)	Cr	4	25	50 50-400	8		12	85.3	[112]

3) Fungi:

Fungi are one of the industrial fermentation waste biomass which is really excellent metal sorbets. So, fungi including yeasts have received increased attention. Fungi gives good efficient and economical for sequestering heavy toxic metals from dilute aqueous solutions by biosorption because:

- (i) It offers the advantage of having a high percentage of cell wall materials;
- (ii) It shows excellent metal binding properties;
- (iii) It is available in large quantities from the antibiotic and food industries;
- (iv) It provides an eco-friendly environment.

Three groups of fungi have a major practical importance: the molds, yeasts and mushrooms. Filamentous fungi and yeasts have been used in many wastewater treatments to bind metallic elements.

Fungi are found entirely in natural environments and important in industrial processes. The structure of fungi has a wide range of morphologies from unicellular yeasts to polymorphic and filamentous fungi; many of them have complex macroscopic fruiting bodies.

In the field of biosorption, both living and dead fungal cells possess a remarkable ability for taking up toxic and precious metals [1]. Two different modes are found for removing metal ions by living and dead cells:

The first mode of metal uptake 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 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.

The active mode can contribute significantly to metal removal for yeast, but at high metal concentrations active mode may not contribute significantly to metal uptake, especially for filamentous fungi. The mechanism of intracellular uptake is complex and not fully understood. The biosorptive capacity of dead fungal cells has been studied extensively in comparison to living cells. The biosorptive capacity of dead cells may be greater, equivalent to or less than that of living cells. Use of dead biomass in industrial applications offers certain advantages over living cells. The dead biomass can be procured from industrial sources as a waste product from established fermentation processes [113].

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

Fungal cell walls are complex macromolecular structures mainly consisting of chitins, glucans, mannans and proteins, but also containing other polysaccharides, lipids and pigments, e.g. melanin [114-116].

The sequestering of heavy metal ions by fungal biomass has mainly been traced to the cell wall. Many types of polysaccharides are the main (up to 90%) constituents of the fungal cell wall.

In the fungal cell wall, several types of ionizable sites affect the metal uptake capacity: phosphate groups, carboxyl groups on uranic acids and proteins, and nitrogen- containing ligands on protein as well as on chitin or chitosan [117].

In yeasts, higher concentration of heavy metals can be accumulated by bioaccumulation process than biosorption. However, general biosorption is responsible for the major uptake of heavy metals for many filamentous fungi.

A wide range of biosorption capacities from 0.012 to 1.979mmol/g for fungi has been reported [118].

Biosorption of heavy metals by macro fungi or mushroom is a known phenomenon later but till now a little work has been done, because of mushrooms grow under natural habitats, the pollutants of heavy metals found in the soil or in the natural substrates are removal by the fruiting bodies of mushrooms and the result, that the metals are accumulated in the mycelia and sporocarps [119]. Tables 6 and 7 give real examples for using several types of fungi and yeast with its operating conditions.

TABLE 6 BIOSORPTION DATA OF BIOSORBENT FUNGI WITH METAL SORBENT AT OPERATING CONDITIONS

Biomass type	Metal studied	pH	T (°C)	C ₀ (mg/L)	W _t (g/L)	N _s (rpm)	Time (h)	q(mg/g)	References
<i>Rhizopus nigricans</i>	Pb	5.5	25	300 (10-300)	25 25-200	225		80.8	[120]
<i>Trichoderma longibrachiatum</i>	Pb	7.0	25	100 (25-100)			0.33	71.0	[177]
<i>Pleurotus ostreatus</i>	Pb	5.5	25	1-25	2		3	4.84	[178]
<i>Aspergillus cristatus</i>	Cd	6.0	25	100	0.4	120	2	23.2 6	[121]
<i>Aspergillus niger</i>	Cd	4.75	25	5-10	0.7	125	6	13	[179]
<i>Hydrilla verticillata</i>	Cd	5.0	25	1-100	3-9	150	0.33	15	[180]
<i>Aspergillus flavus I-V, Aspergillus fumigatus I-II</i>	Hg	5.5	30	100 100-500	10	100	8	95.3 %	[122]
<i>p. chrysogenum</i>	As	3-4	25	1-300	1	190		24.5 2	[181]
Waste tea fungal	As(III) As(V)		30	1.3 0.9	20	160	1.5		[123]
Waste tea fungal	As	6-8	22	1	1	160	1.5	0.004 mmol /g	[182]
<i>Aspergillus niger</i>	Ni	4.5	25	25-100	1	150	3	7.69	[124]
Waste activate sludge	Ni	4	25	25-75	1	150-250	2	11.4 4	[124]
<i>Pleurotus ostreatus fungal</i>	Cu	5	25	50	2	125	0.16	4.0	[125]

A.lentulus	Cu	6	35	100	4	180	0.41		[126]
Fomes fasciatus	Cu	5.5	25	100	1.0	200	1	32.2	[127]
Waste mycelium of Aspergillus awamori	Cu	5	20	50 25-100	1	150	3	28.7 5	[183]
Penicillium canrscens	Cr(VI)	6	20	100 10-750	2	100	4	34.8	[184]
Living mycelium of phanerochaete chrysosporium	Cr(VI) Cu		27	100 20-500		100	2	48.6 90.6	[128]
Mucor	Cr(VI)	5.5	35	50 50-400	0.0165				[129]
Trichoderma viride	Cr(VI)	6		175	3.75	150	0.75	4.66	[130]
Aspergillus niger	Cr(VI)	4.5	28	300	10	150	1	16.3 9	[185]
Pleurotus ostreatus	Cr(III)	4.5	25	14.35 4-20	2	150	3	1.97	[186]
Aspergillus niger	Cr(VI)	2	22-28	50 25-200	10	200	158	2.2	[187]

TABLE 7 BIOSORPTION DATA OF BIOSORBENT YEAST WITH METAL SORBENT AT OPERATING CONDITIONS

Biomass type	Metal studies	pH	Biomass type T (°C)	Metal studied		q (mg/g) or % removal	N _s rpm	Time (h)	References
				Co(mg/L)	W _t (g/L)				
Saccharomyces cervisiae	Hg Cu Ni Zn Cd Co Cr Fe Al	7	25	25-200	2	76.2 29.9 14.1 11.8 12.3 8.2 6.2 5 4.1	100	2	[132]
Candida spp	Hg Zn Cd Pb Fe Cu Cr	5	28	0.008 0.091 0.006 0.003 0.075 0.82 0.027	0.2	2.74 31.16 2.05 1.03 25.68 28.08 9.28	150	2	[133]
Thiobacillus thiooxidans	Zn Cu	6 5	30 30	25-150 25-150	0.25 0.25	95.24 32.36	786	2	[84]
Saccharomyces cervisiae	Cd Cr(III) Cr(VI) Cu Pb Zn	5.8 5.2 5-6 6.5 5.2 5.8	25	5.0mm/L 10-60	80	65.3% 55.3% 49.0% 50.7% 50.2% 47.6%	150	1	[134]
Saccharomyces cervisiae	Cr(III)	5.5 5.5	35 35	200 200	2.0 2.0	Static =35 Aerobic =86.3	120	6	[135]
Candida utilis	Cd	5.5	25	50 5-100	1.0	Dried =28 cell=8.7 Native=5.5	160	1	[188]
Candida pelliculosa	Cu	6.0	30	100 100-1000	13.397	95.04%	120	120	[189]
Schizosaccharomyces pombe	Cu	4.0	25	100 100-400		74.85		96	[108]
Spent yeast	Cu	4.0	35	20-80	63.33	0.014-0.037	200	8	[190]
Yeast biomass	Cr(VI)	4.0	30	120 10-250	40	86.95		0.75	[136]

							180		
Saccharomyces cerevisiae	Cu Cd Pb Ni	5.0	28	50 50-500	0.005	0.64 0.66 0.60 0.68	150	48	[137]
Agarose gel polymers	Pb	2.0	35	50 25-200	1% (w/v)	115	150	4	[191]
Saccharomyces cerevisiae	Cr Sn	6.5	25	-----	0.4	29% 33% removal	110	1	[138]
Saccharomyces cerevisiae	Cu Ni Zn	6.0	25	5 -50 5-200 5-50 (5 , 100)	4.0	91 mmol/g 64 mmol/g 110 mmol/g	150	1	[139]
Mycelial biomass of Pleurotus floida	Cd	5.0	25	10	1.0	9.76	125	2	[140]
Saccharomyces cerevisiae	Cd	5.0	25	37.5	0.1	25			[192]
Strain of Saccharomyces cerevisiae	Cr Cu Ni Zn	6.0	25	34mmol/l	12		150	0.5	[193]
Mucor rouxii	Pb Cd Ni Zn	5.0	25	10.0		17.13 10.07 6.07 6.28	125	15	[141]
Saccharomyces cerevisiae	Cu	4.0	30	25 10-250	1.0	120.7	200	3	[193]
Saccharomyces cerevisiae	Cd	6	28	250 50-350	3	55"dead cell" 36 "live cell"	120	24	[194]
Saccharomyces cerevisiae	U(VI)	5	27	100 25-300	10	7.89		1.25	[195]

V. MECHANISMS

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 [42, 142, 143]. 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 metal ions considered a complicated process. Several factors are found to influence on the mechanism of metal biosorption:

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

The unclear definition of sorption may be gives 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:

- Based on cell metabolism: in this criteria, biosorption mechanisms are classified as metabolism dependent and non-metabolism dependent;
- 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 [144].

In the biosorption process, two types of biological cells (living and dead cells) as well as chemical pretreated biomass can be used. The 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 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:

- (i) There is no need of growing;
- (ii) 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:

- (i) Absence of toxicity limitations, absence of nutrient requirements in the feed solution and reuse of regenerated biomass;
- (ii) 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.

Figs. 1 and 2 represent biosorption mechanisms according to the dependence on the metabolism of cells and biosorption mechanisms according to location where the metal removed is found.

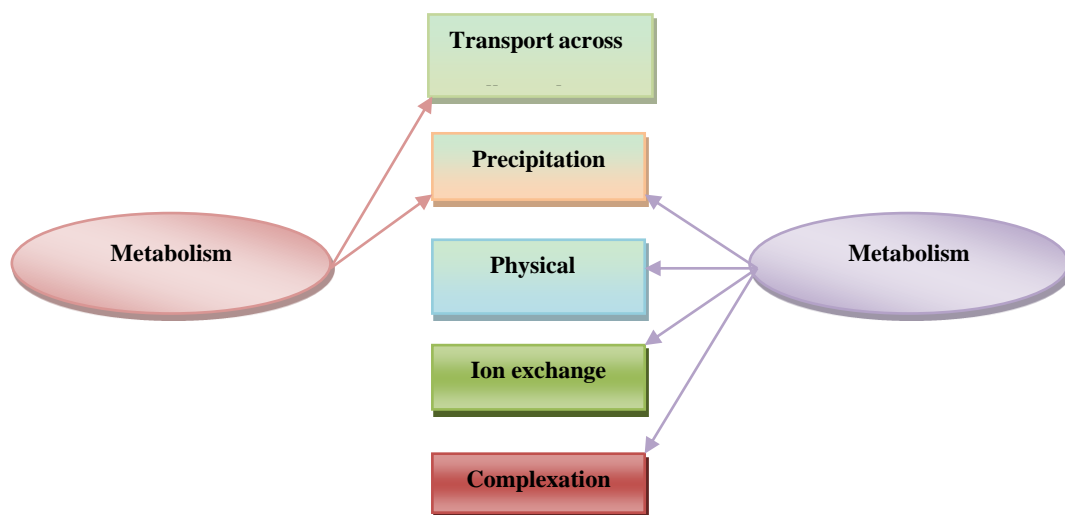


Fig. 1 Biosorption mechanisms according to the dependence on the metabolism of cells [145]

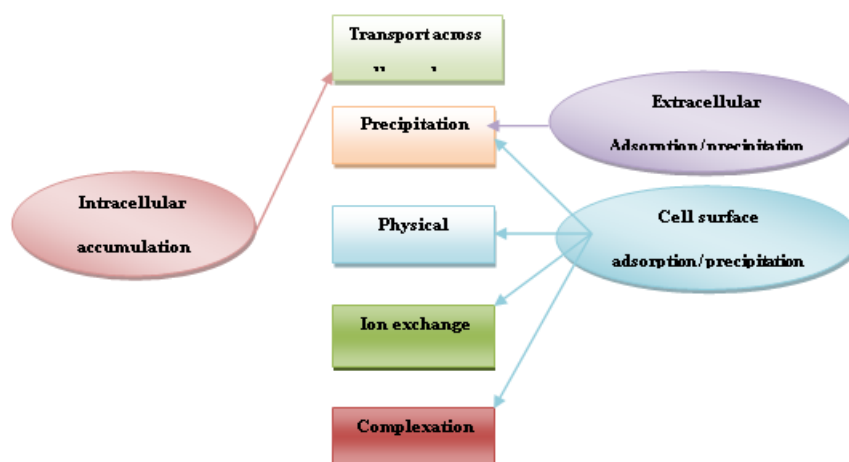
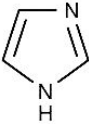


Fig. 2 Biosorption mechanisms according to location where the metal removed are found [145]

A. Effect of pH on Mechanisms of Biosorption Process:

The acidity (pH) is an important parameter for adsorption/biosorption of 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 [196]. Table 8 shows the functional groups present in biosorbents responsible for the binding of sorbent and their acidity constants. The surface charge is predominantly negative over the pH range of 3.0–10.0. Below a pH of 3.0, the overall surface charge on microorganism's cells becomes positive.

TABLE 8 MAJOR BINDING GROUPS FOR BIOSORPTION [4]

Binding group	Structural Formula	pKa	Ligand atom	Occurrence in selected biomolecules
Hydroxyl	—OH	9.5 – 13.0	O	PS, UA, SPS, AA
Carbonyl (ketone)	C=O	-	O	Peptide bond
Carboxyl	—COOH	1.7 - 4.7	O	UA, AA
Sulfhydryl (thiol)	—SH	8.3 - 10.8	S	AA
Sulfonate	—SO ₃	1.3	O	SPS
Thioether	-S	-	S	AA
Amine	—NH ₂	8.0 - 11.0	N	Cto, AA
Secondary amine	-NH	13.0	N	Cti, PG, AA
Amide	$\begin{array}{c} \text{—C=O} \\ \\ \text{NH} \end{array}$	-	N	AA
Imine	=NH	11.6 – 2.6	N	AA
Imidazole		6.0	N	AA
Phosphonate	$\begin{array}{c} \text{OH} \\ \\ \text{—P=O} \\ \\ \text{OH} \end{array}$	0.9 – 2.1 6.1 – 6.8	O	PL
Phosphodiester	$\begin{array}{c} \text{P=O} \\ \\ \text{OH} \end{array}$	1.5	O	TA, LPS

PS: polysaccharides, UA: uronic acids, SPS: sulfated PS, AA: amino acids, Cto: chitosan, Cti: chitin, PG: peptidoglycan, PL: phospholipids, TA: teichoic acid, LPS: lipo, PS.

At higher solution pH, the solubility of metal decreases sufficiently allowing precipitation, which may complicate the sorption process [197]. The activity of binding sites can also be changed by adjustment of the pH value, for example, during the biosorption of metal ions by bacterial biomass, pH 3 to 6 has been found favorable for biosorption [59]. 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 [198].

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 [199].

Adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} ions onto treated *Azolla filiculoides* by $H_2O_2/MgCl_2$, 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 [200].

The removal of cadmium by dead biomass of *mycelial* in 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 metal ions adsorbed at high pH value. Table 9 shows the pH values for metal hydroxide precipitation [119].

TABLE 9 METAL HYDROXIDE PRECIPITATIONS [201]

Metal	pH value
Lead	6.3
Chromium	6.5-7.3
Cadmium	9.7
Copper	7.1-7.3
Nickel	9.2-9.4
Zinc	8.3-8.5
Iron	4.3
Aluminum	5.2
Tin	1.0-4.5

VI. EQUILIBRIUM AND KINETIC STUDIES

A. Biosorption Isotherms

Biosorption is usually described through isotherm. Adsorption isotherm is relatively simple method for determining the feasibility of using a certain adsorbent material for a particular application. It is represented the equilibrium relationship between the adsorbate concentration in the fluid phase and the adsorbate concentration in the adsorbent particles at a given temperature. It is a plot of the amount of adsorbate per unit weight of adsorbent q_e against the equilibrium concentration of the adsorbate remaining in solution C_e . The quantity described is nearly always normalized by the mass of adsorbent to allow comparison of different materials [146].

By knowing the adsorption isotherm, the affinity of the adsorbate for an adsorbent is quantified. For most applications in wastewater treatment, the amount of adsorbate adsorbed is usually a function of the aqueous-phase concentration [147]. Some typical isotherm shapes are shown as arithmetic graphs as shown in Fig. 3 [148].

From the above curves, it will be noted that the adsorption is specific property related to the nature of the adsorbate-adsorbent system [149].

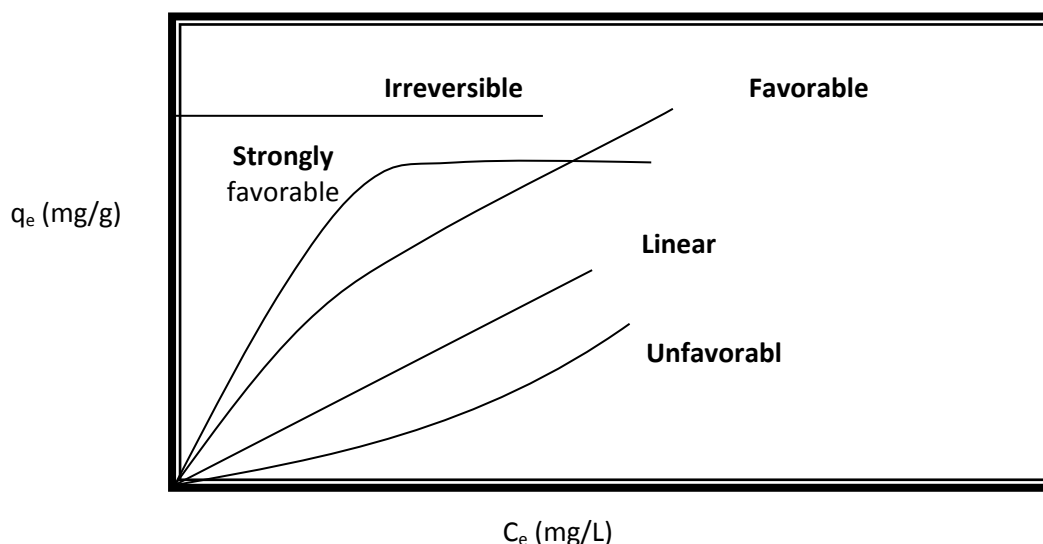


Fig. 3 Types of adsorption equilibrium isotherm relations [148]

B. Biosorption Isotherm Models

1) Single Isotherm Models

Isotherm curves (Fig. 3) can be evaluated by varying the initial solute concentrations, while fixing the environmental parameters, such as pH, temperature and ionic strength. In general, the uptake increases with increasing the concentration, and will reach saturation at higher concentrations [150].

Empirical models are simple mathematical relationships, characterized by a limited number of adjustable parameters, which give a good description of the experimental behavior over a large range of operating conditions. The model used to describe the results should be capable of predicting heavy metal binding at both low and high concentrations [151].

a) Freundlich Model:

The first mathematical equation fits to an isotherm was published by Freundlich and Kuster in 1907. Freundlich showed that adsorption from solution could be expressed by empirical formula:

$$q_e = KC_e^{1/n} \quad (1)$$

Where K (mg/g) (l/mg)^{1/n} and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

b) Langmuir Model:

In 1918, Irving Langmuir published a new model isotherm for gas or liquid adsorbed on solid, which retained his name. The Langmuir adsorption model is valid for single-layer adsorption. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [152, 153].

The Langmuir isotherm equation is:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2)$$

The Langmuir isotherm is used most frequently to describe the adsorption isotherm which is limited by the assumptions of uniform energies of adsorption on the surface of adsorbent. It is based on four assumptions [154].

- The surface of the adsorbents is uniform, that is, all the adsorption sites are equivalent.
- There is no interaction between molecules adsorbed on neighboring sites.
- All adsorption occurs through the same mechanism.
- Molecules are adsorbed at the define sites on the adsorbent surface.

The important characteristics of a Langmuir isotherm equation can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, ' R_s ' which is defined by the following equation [155]:

$$R_s = \frac{1}{1 + bC_o} \quad (3)$$

The separation factor as described above was calculated using the Langmuir model constants. This separation factor yields the type of isotherm as shown in Table 10:

TABLE 10 VALUES OF SEPARATION FACTOR AND TYPE OF ISOTHERM [155]

Values of R_s	Type of isotherm
$R_s > 1$	Unfavorable
$R_s = 0$	Linear
$0 < R_s < 1$	Favorable
$R_s < 0$	Irreversible

c) *Temkin Model:*

Temkin isotherm takes into account the adsorbing species- adsorbent interaction, and the adsorption isotherm expressed as:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (4)$$

The linearized form of the above equation is:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5)$$

Where $B_1 = RT/b$; R is the universal constant (8.314 KJ/mol.K) and T is the absolute temperature (K).

In the previous equations K_T (l/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant B_1 (KJ/mole) is related to the heat of adsorption.

d) *BET Model:*

Often molecules do form multilayer, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid. In 1938 Stephan Brunaur, Paul Emmett and Edward Teller developed a model isotherm that takes this possibility into account, their model is called BET isotherm model. This model extends the Langmuir model from a monolayer to several molecular layers. Above the monolayer, each additional layer of adsorbate molecules is assumed to equilibrate with the layer below it and layers of different thickness are allowed to coexist [156], it takes the following form:

$$q_e = \frac{BQC_e}{(C_s - C_e)[1 + (B - 1)(C_e/C_s)]} \quad (6)$$

e) *Harkins-Henderson Model:*

This model explains multilayer adsorption and also for the existence of heterogeneous pores distribution in the adsorbent and expressed as:

$$q_e = \frac{K_h^{1/n_h}}{C_e^{1/n_h}} \quad (7)$$

Where, K_h (mg/g)(mg/L) $^{1/n_h}$ and n_h are the model parameters related to adsorption capacity and adsorption intensity respectively [157].

f) *Redlich-Peterson Model:*

The Redlich-Peterson model expressed by the following equation:

$$q_e = \frac{A_R C_e}{1 + B_R C_e^{m_R}} \quad (8)$$

Where, A_R (L/mg), B_R (L/mg) m_R and m_R are the model parameters. This model expresses the adsorption process when dealing with a certain pollutants at high concentration.

g) *Toth Model:*

This model is derived from potential theory, is used in heterogeneous system. It assumes a quasi-gaussian energy distribution. Most sites have adsorption energy lower than the peak of maximum adsorption energy, the model is expressed as:

$$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}} \quad (9)$$

Where, K_t (mg/g), a_t and t represents the Toth isotherm constants.

h) Radke-Praunsitz Model:

The Radke–Praunsitz model expressed empirically by the following equation:

$$q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}} \quad (10)$$

The K_{RP} (L/mg), F_{RP} and N_{RP} are the model parameters, which are obtained by a non-linear statistical fit of the equation to the experimental data.

The Radke–Praunsitz equation has several important properties making it suitable for use in many adsorption processes. At low concentration it reduces to a linear isotherm. At high concentration it becomes Freundlich isotherm and for the special case of $N_{RP} = 0$ it becomes Langmuir isotherm.

For the adsorption of lead at low concentration (below 0.07 mg/l), it was found that the obtained experimental data fit well with Radke–Praunsitz model [158].

i) Combination of Langmuir-Freundlich Model:

This model is referred as (Sips model) is widely used for a single component adsorption. When a single component adsorption process obeys Langmuir isotherm in some condition and turned to obey Freundlich isotherm or vice-versa. This variation in the behavior is found clearly in the adsorption of a single heavy metal component onto peat, and maize husk especially for zinc removal [159]. The Sips model can be expressed as:

$$q_e = \frac{b q_m C_e^{1/n}}{1 + b C_e^{1/n}} \quad (11)$$

j) Khan Model:

This model is derived by [160] to represent the adsorption isotherm of phenol onto activated carbon. This model is expressed by the following equation:

$$q_e = \frac{q_{\max} b_k C_e}{(1 + b_k C_e)^{a_k}} \quad (12)$$

Where, q_{\max} (mg/g), b_k (L/mg) and a_k represent the model parameters.

2) Multi-component Isotherm Models:

The experimental measurement of multi-component adsorption/biosorption isotherm is time consuming because of large number of variables involved. Thus, the problem of predicting multi-component adsorption isotherm from single component adsorption data has attracted a lot of attention. Several isotherms have been proposed to describe the competitive adsorption. Most of these isotherms are based on single component isotherm parameters and correction factors extracted from the experimental competitive data [161]. Some of these models are:

a) Extended Langmuir Model:

The Langmuir isotherm can be extended for multi-component system to give the following form [161]:

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}}{1 + \sum_{k=1}^N b_k C_{e,k}} \quad (13)$$

Where $C_{e,i}$ is the equilibrium concentration of the component i in the multi-component solution, $q_{e,i}$ is the equilibrium uptake of the component i , $q_{m,i}$ and b_i are the single component Langmuir parameters for component i .

This model is applicable when each single component obeys the Langmuir model in a single component system [161].

b) Combination of Langmuir-Freundlich Model:

The competitive Langmuir-Freundlich model related to the individual isotherm parameters is expressed in the following equation [162]:

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1 + \sum_{i=1}^N b_i C_{e,i}^{1/n_i}} \quad (14)$$

c) *Redlich-Peterson Model:*

The competitive Redlich-Peterson model related to the individual isotherm parameters is given by the following equation [162]:

$$q_{e,i} = \frac{K_{Ri} (b_{Ri}) C_{e,i}}{1 + \sum_{k=1}^N b_{R,k} (C_{e,k})^{m_{R,k}}} \quad (15)$$

Where K_{Ri} (L/mg), b_{Ri} (l/mg) m_{R} and $m_{R,i}$ are the Redlich-Peterson single component parameter for component i .

d) *Extended Freundlich Model:*

The empirical extended form of the Freundlich model restricted to binary mixtures can be given by following equation [163]

$$q_{e,i} = \frac{K_i C_{e,i}^{ni+1}}{C_{e,i}^{n1} + \sum_{j=1}^N K_j C_{e,j}^{nj}} \quad (16)$$

Where K_i (mg/g)(L/mg) $1/n$ and ni are derived from the corresponding individual Freundlich isotherm equation for the component i .

Extended Langmuir, extended Freundlich and Redlich-Peterson models were applied to describe the competitive adsorption of phenol and nickel onto dried activated sludge. It was found that, the experimental data fitted very well to the Redlich-Peterson model [164].

Five models (extended Langmuir, combination of Langmuir-Freundlich, modified Temkin, Harkins-Jura and Halsey-Henderson) were used in competitive adsorption of Pb^{2+} , Cd^{2+} and Hg^{2+} onto GAC. Extended Langmuir model was found to be the best fit to the experimental data [165].

C. Kinetic Modeling of Adsorption/Biosorption in a Batch System

For any practical applications, the process design, operation control and adsorption kinetics are very important [166]. The adsorption kinetics in a wastewater treatment is significant, as it provides valuable insights into the reaction pathways and the mechanism of an adsorption reaction [167]. Also, the kinetics describes the solute uptake, which in turn controls the residence time of adsorbate at the solid-solution interface [168].

Adsorption/biosorption is a multi-step process, comprising of four consecutive elementary steps [169].

1. Transfer of solute from the bulk of solution to the liquid film surrounding the particles;
2. Transport of the solute from the boundary liquid film to the surface of the particles (external diffusion);
3. Transfer of solute from the surface to the internal active binding sites (intra-particle diffusion); and
4. Interaction of the solute with the active binding sites.

Over 25 models have been reported in the literature, all of which have attempted to quantitatively describe the kinetic behavior during the adsorption process. Each adsorption/biosorption kinetic model has its own limitations, which are derived according to specific experimental and theoretical assumptions. Even though they violate the fundamental assumptions, many adsorption models have been used to successfully test experimental data [170]. Of these, the following models have often been used to describe adsorption/biosorption kinetic process.

1) *Pseudo-First Order Kinetic Model:*

The Lagergren rate equation [171] was the first rate equation for the adsorption of liquid/solid system based on solid capacity. The Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption of a solute from a liquid solution. It may be represented as:

$$\frac{dq}{dt} = k_L(q_{eq} - q_t) \quad (17)$$

Integrating Eq. (17) for the boundary conditions; $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\log\left(\frac{q_{eq}}{q_{eq} - q_t}\right) = \frac{k_L t}{2.303} \quad (18)$$

which is the integrated rate law for a pseudo-first order reaction, where q_{eq} is the amount of pollutant adsorbed at equilibrium (mg/g); q_t is the amount of pollutant adsorbed at time t (mg/g); and k_L is the equilibrium rate constant of pseudo-first sorption (l/s). Eq. (18) can be rearranged to obtain a linear form:

$$\log(q_{eq} - q_t) = \log q_{eq} - \left(\frac{k_L t}{2.303}\right) \quad (19)$$

In order to fit Eq. (19) to experimental data, the equilibrium adsorption capacity, q_{eq} , must be known.

2) Pseudo-Second Order Kinetic Model:

There are certain assumptions in description of this kinetic model [167].

1. There is a monolayer of adsorbate on the surface of adsorbent.
2. The energy of adsorption for each adsorbent is the same and independent of surface coverage.
3. The adsorption occurs only on localized sites and involves no interactions between adsorbed pollutants.
4. The rate of adsorption is almost negligible in comparison with the initial rate of adsorption.

The kinetic rate equation can be written as follows:

$$\frac{dq_t}{dt} = k_s(q_{eq} - q_t)^2 \quad (20)$$

Where k_s is the rate constant of adsorption, (g/mg.s), q_{eq} is the amount of pollutant adsorbed at equilibrium, (mg/g), q_t is amount of adsorbate on the surface of the adsorbent at any time, t , (mg/g).

Separating the variables in Eq. (20) gives:

$$\frac{dq_t}{(q_{eq} - q_t)^2} = k_s dt \quad (21)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; the integrated form of Eq. (21) becomes:

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + k_s t \quad (22)$$

Which is the integrated rate law for a pseudo-second order reaction? Eq. (22) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{k_s q_{eq}^2} + \frac{t}{q_{eq}}} \quad (23)$$

This has a linear form of:

$$\frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{t}{q_{eq}} \quad (24)$$

3) Weber and Morris Intra-particle Diffusion Model:

Weber and Morris proposed intra-particle diffusion model, which can be written as [172, 173]

$$q_t = k_{id}t^{1/2} + C \quad (25)$$

Where q_t (mg/g) is the amount adsorbed at time t (s), K_{id} (mg/g s^{1/2}) is the rate constant of intra-particle diffusion, C is the value of intercept which gives an idea about the boundary layer thickness, i.e. the larger intercept; the greater is the boundary layer effect. The linear plots of qt versus $t^{1/2}$ with zero intercept indicates that intra-particle alone determines the overall rate of adsorption. In this case intra-particle diffusion is not the only determining mechanisms; in addition other mechanisms such as electrostatic interaction, ion exchange may be operating to different extents.

4) Elovich Kinetic Model:

A widely used equation to describe the kinetics of chemisorption is the Elovich equation:

$$\frac{dq}{dt} = a \exp(-bq_t) \quad (26)$$

Where a (mg/g.s) and b (g/mg) are parameters of the equation. The parameter (a) is regarded as the initial rate because $dq/dt \rightarrow a$ as $q \rightarrow 0$ and parameter b is related to the extent of surface coverage and activation energy for chemisorption. Given that $q = 0$ at $t = 0$, the integrated form of Eq. (26) becomes:

$$q_t = \frac{1}{b} \ln(t + t_o) - \frac{1}{b} \ln t_o \quad (27)$$

Where $t_o = 1/ab$. If $t \gg t_o$, Eq. (27) is simplified as:

$$q_t = \frac{1}{b} \ln ab + \frac{1}{b} \ln t \quad (28)$$

The application of the Elovich equation in liquid phase adsorption is gaining in popularity [174].

Pseudo-second order kinetic model was applied on biosorption of lead onto dried activated sludge with correlation coefficient of 0.994 [20].

It was found that pseudo-second order model could be represent the adsorption of lead onto GAC better than Elovich model with correlation coefficient of 0.994,0.726 respectively [175].

Some researchers applied first and second-order-pseudo models in GAC adsorption of phenol. Pseudo-second order model fit the data with 0.998 correlation coefficient for the concentration of 1000 mg/L, and pseudo-first order model fit the data with 0.900 correlation coefficient for 100 mg/l concentration [176].

VII. CONCLUSIONS

In the present study, the sources of heavy metal ions as a toxic materials as well as the reason why they need to be removed from our environment have reviewed. Conventional methods of removal are expensive; hence the search of using low cost, friendly ecosystem material must be needed. From the above literature study, it is observed that biosorption is the most economical and eco-friendly method for removal of heavy metal from domestic as well as industrial wastewater. It is being an alternative to conventional methods for the removal of toxic heavy metals from industrial effluents. It offers several advantages including cost effectiveness, high efficiency, minimization of chemical/biological sludge, and regeneration of biosorbent with possibility of metal recovery. The process of biosorption has many attractive features including removal of metals over quit broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost. Biological biomass can be regenerated relatively easily and used again. Most significantly, the metal removal capacity of biological biomass is a good or better than other conventional adsorbents. The new biological – based technologies need not necessarily replace conventional treatment approaches but may complement them. So, the biosorption technology becomes more beneficial and attractive than currently used technologies.

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