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Assistant Professor, Department of Chemistry, Ram Krishana College, Lalit Narayan Mithila University, Darbhanga, Bihar, India A scientific review on the potential of biosorbents for the removal of toxic heavy metals: A green approach for wastewater treatment

# Dr. Deepa Kumari

#### Abstract

This review paper is helpful to develop Green biosorbents towards the remediation of toxic heavy metal ions from aqueous environment. It will also helpful to find out environmentally benign and economically viable biogenic synthetic routes for synthesis of metal nanoparticles using extract of locally available plant/animal materials. Advantage of this technology is its simplicity, low cost, no chemical used and easy to implement for the people and local community. In future, this review paper will be helpful in finding out locally available and low cost naturally occurring novel adsorbent. Precise monitoring and detection of the toxic metal ions in drinking water, foods and biological fluids are highly essential for the prevention of these undesirable effects of toxic metal ions towards both life and environment and our work may be a promising green alternative in this regard. This green technology based protocol may apply to issues like drinking water purification and wastewater management which establish acceptability of the process in sustainable development and protection of the environment.

**Keywords:** Toxic metals, green adsorbent, adsorption, heavy metal removal, waste water, environmental pollution

#### Introduction

#### A brief introduction to toxic heavy metal

Toxic metal or heavy metal is any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions. They mainly include the transition metals, lanthanides, actinides as well as the metalloids. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr) and lead (Pb), etc. Heavy metals are the natural components of the Earth's crust. They cannot be degraded or destroyed easily. They are kept under the environmental pollutant category due to their toxic effects in plants, human and food. These heavy metals are persistence, accumulate and not metabolized in other intermediate compounds and do not easily breakdown in the environment. Though as trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body or are essential micronutrients for animals, plants and many microorganisms, depending on the route and dose, however, at higher concentrations they can lead to poisoning via metabolic interference and mutagenesis. Therefore, the studies concerning the heavy metal and their harmful effects on living organisms, now a days, have received the highest attention of researchers all over the world.

#### Heavy metal toxicity

Heavy metal toxicity refers to the toxic effects of certain metals in certain forms and doses on living organisms. Some of them are toxic when they form poisonous soluble compounds. The toxicity of heavy metals depends on a number of factors. They are specifically variable according to the type of heavy metal in question, the total dose absorbed, and whether the exposure was acute or chronic. Acute heavy metal intoxications may damage central nervous function, lungs, kidneys, liver, the cardiovascular and gastrointestinal (GI) systems, endocrine glands, and bones. Chronic heavy metal exposure has shown several degenerative diseases of these same systems and may increase the risk of cancers. The age of the person can also influence toxicity. For example, young children are more susceptible to the effects of lead or arsenic exposure because they absorb several times the percent ingested compared with adults and even brief exposures may influence developmental processes.

Corresponding Author: Dr. Deepa Kumari Assistant Professor, Department of Chemistry, Ram Krishana College, Lalit Narayan Mithila University, Darbhanga, Bihar, India The route of exposure is also important. As for instance, though elemental mercury is relatively inert in the gastrointestinal tract and also poorly absorbed through intact skin, yet inhaled or injected elemental mercury may have disastrous effects. Heavy metal toxicity and poisoning could be resulted from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain or any other such sources. This resulted in serious adverse effects on human life. Therefore, extensive studies by international bodies such as the WHO is carried out to observe the effects of these heavy metals on human health.

# Sources of heavy metal pollution

Heavy metal pollution can originate from both natural and anthropogenic sources. They are found naturally in the earth, but rarely at toxic level, and become concentrated as a result of human caused activities. One of the most important anthropogenic sources of heavy metal concentration is the industrial effluents. These effluents are coming from many industries such as corrosion of water pipes, waste of dumping, energy and fuel producing, electroplating, electrolysis, electro-osmosis, iron and steel, leather, metal surface treating, mining, surface finishing, fertilizer, pesticide, photography, aerospace and atomic energy installations, etc.

# Heavy metal pollution and its effect on different ecosystems

Heavy metal pollution is affecting different types of ecosystems - be it natural or man-made. Our natural waters, particularly the estuaries and freshwater systems, currently are not only being polluted to varying degrees, but are also condemned to fairly long-term pollution due to metals deposited in sediments from past human activities, from as long ago as the Middle Ages. Also, the landfills are contributing to the higher concentration of heavy metal in ground water bodies by leaching process and the surface water bodies by the runoff from the land filled areas. Road dust is another such reason which is responsible for the increase in the heavy metal concentration in the aquatic, terrestrial and atmospheric systems. Soil ecosystem is mostly polluted by irrigation with discharge of industrial effluent and domestic sewage directly on earth surface.

#### Effects of metal on living organisms

Metal pollution is one of the major environmental problems today. Many of the metal ions are toxic to living organisms. They are non-degradable and are persistent in the environment. The severity and health outcomes of toxic metal exposure depend on several factors, including the type and form of the element, route of exposure (oral/inhalation/topical/ocular), duration of exposure (acute vs. chronic), and a person's individual susceptibility (CDC 2012). Metals can be classified into the following four major groups on the basis of their health importance. The metals like Cu, Zn, CO, Cr, Mn and Fe is called Essential element which also known by micronutrients. Theses metal can be toxic when taken in excess of requirements. The metal like Ba, Al, Li and Zr is considered as Non-essential element based on their environment persistence. Similarly Sn and Al considered as less toxic where as Hg, As, and Cd represent highly toxic due to their toxicity, bioaccumulation capacity and persistence capacity. Some of the important metals with their major sources and toxic effects are shown in the table below:

Table 1: Some important metals with their major sources and toxic effects

Metal	Major source	Toxic effect
As	Mining, pesticides, rock sedimentation, smelting	Bronchitis, bone marrow, dermatitis depression, hemolysis, hepatomegaly
Cd	Fertilize, mining, plastic, pesticide, refining, welding	Kidney damage, bronchitis, Gastrointestinal disorder, cancer, lung insufficiency, Itai–Itai
Cr	Textile, dyeing, paints and pigments, steel fabrication	Carcinogenic, mutagenic, nausea, teratogenicity, vomiting, severe diarrhea, producing lung tumors
Cu	Plating, copper polishing, paint, printing operations	Neurotoxicity, and acute toxicity, dizziness, diarrhea
Pb	Mining, paint, electroplating, pigments, batteries coal,	Anemia, brain damage, anorexia, malaise, loss of appetite, liver, kidney, mental retardation
Hg	Batteries, paper industry, paint industries, mining	Damage nervous system, protoplasm poisoning, corrosive to skin and kidney damage
Ni	Non-ferrous metal, paint enameling, electroplating	Chronic bronchitis, reduced lung function, lung cancer
Zn	Mining, refineries, brass manufacturing, plumping	Causes short term "metal-fume fever", gastrointestinal distress

#### Conventional methods for treatment of water

A variety of conventional treatment technologies, based on the principle of precipitation, ion exchange, electrolysis, solvent extraction, reverse osmosis, membrane and biosorption process have been proposed and is tested for removal efficiency of different pollutants from potable water as well as industrial effluent (McNeill and Edwards, 1997: Baciocchi et al., 2005; Kumari et al., 2006; Balasubramanian et al., 2009; Moussavi and Barikbin, 2010) [27, 9, 21, 10, 30]. Each technique provides a different and unique approach and perhaps provides certain advantages over others for a particular situation. But these process are not very popular because one or more disadvantage. However, when large volumes of water containing toxic elements are to be treated, it would, be of great advantage if the method would provide reliable results without involving much cost and working efforts

# Advantages and limitations of phytoremediation techniques

Environmentally friendly, cost-effective, and aesthetically pleasing. Metals absorbed by the plants may be extracted from harvested plant biomass. May reduce the entry of contaminants into the environment by preventing their leakage into the groundwater systems. It is potentially the least harmful method because it uses naturally occurring organisms and preserves the environment in a more natural state.

#### Methods for the removal of toxic metals

Various efficient methods have been developed for heavy metal removal. The conventional methods for the removal of heavy metals include the chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation, etc. These processes are generally efficient in removing the bulk of metals from solution at high or moderate concentrations but are not effective when the heavy metal concentration in water sources is present at low concentrations. However, these chemical processes also produce a large amount of metallic sludge which ultimately leads to metal recovery difficult. The sludge also needs further disposal. In addition, effluent after such treatment usually has unacceptably high total dissolved solids and therefore, these methods are not commonly used. For all these reasons, adsorption technology has gained a wider application particularly due to its inherent low cost, simplicity, versatility and easily availability. Along with using commercial activated carbon, researchers are also working on inexpensive materials, such as chitosan, zeolites, and other adsorbents, which have high adsorption capacity and are locally available for heavy metal removal purpose (Lakherwal, 2014)<sup>[24]</sup>. Biosorption process is also one of the important adsorption method used for the same purpose. Various other non-conventional biosorbents like saw dust, rice husk ash, activated coconut shell powder controlled burnt wood charcoal, fly ash, peat, wood, jute fibers, clay minerals, etc. have been used for heavy metal removal.

## Process of concern Adsorption

Adsorption is a mass transfer process in which a substance is transferred from a liquid phase to the surface of a solid and becomes bound by physical and or chemical interactions (Babel, S., 2003)<sup>[8]</sup>. Usage of activated carbon is the most common and effective method for removal of heavy metals, but this is not attractive due to the high regeneration cost. Therefore, the research thirst over the years is leading to find improved and tailor-made materials, which will meet several requirements such as regeneration capability, easy availability, cost effectiveness, and etc. Consequently, low-cost adsorbents have drawn the attention to many researchers and characteristics as well as application of many such adsorbents are reported.

### Biosorption

The method of biosorption for the removal of heavy metals from any water sources is now one of the most widely used adsorption method. Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure. Algae, fungi, bacteria and yeast have proved to be potential metal adsorbents due to metal sequestering properties and can decrease the heavy metal ion concentration in the solutions (Volesky and Schiewer, 1999)<sup>[46]</sup>. But chief biosorbents like plant products which are also very easily available are mainly used for this purpose. Biosorption process uses biomass, either living or dead microorganisms, to remove heavy ions from polluted water sources. Dead biosorbents are more favorable as they are not affected by the heavy metals, cost less, can be regenerated and reused and are easier to operate and maintain. The removal of heavy metals from aqueous solution using biomass is based on metal sorption. Basically, the process of biosorption requires a solid phase (the sorbent) and a liquid phase (the solvent, water) containing a dissolved metal ions to be sorbed (sorbate). The metal ions are attracted and bonded to the sorbent due to the high affinity of the sorbent for the ions through a complex process that depends on various mechanisms involving ion exchange, chemisorption, complexation, adsorption on the surface and pores, chelation and adsorption by physical forces which is a result of concentration gradient and diffusion through cell wall and membrane (Sud *et al.*, 2008) <sup>[41]</sup>. The advantages of this technique over other conventional methods are that it is low cost technique, have high efficiency, minimization of chemical and biological sludge, regeneration of biosorbent and possibility of metal recovery. Therefore, this technique is gaining much importance in the research regarding the heavy metal removal.

# A brief overview of the removal from different water sources

Limited accessibility to clean water is a global human health concern of today's world with the increasing population. Water contamination by toxic organic chemicals and heavy metals from the miscellaneous industrial wastewater discharges has become a worldwide environmental concern. Thus, heavy metal pollution is considered as a major problem of increasing magnitude. Heavy metals are persistent, and therefore, very difficult to eliminate naturally from the environment, even at a presence of trace amounts. Because of their high solubility in the aquatic environment, heavy metals can be adsorbed by living organisms. Once entered into the food chain, these heavy metals start accumulating in higher concentration in the body of the higher living organism, particularly in the human body. If they are ingested beyond the permitted concentration, they can cause serious health disorders. Therefore, many methods such as precipitation followed by coagulation or filtration by membrane, adsorption, etc., have been used for removal of metal from water. Among several methods, the adsorption process is one of the most efficient methods for the removal of heavy metals from water solution. But in recent years, there have been an explosive growth in biosorption research for the heavy metal removal work. With the help of low cost biosorbent, we can easily carry out removal of heavy metals which is also environment friendly as there is no issue regarding the end of use option of biosorbent.

# Laboratory based removal of heavy metal vs. its field applicability

### Conventional processes for metal removal from water

Many researches are going on, now a day, to find a suitable technique for the efficient removal of the heavy metals from water sources. Some of the processes that are commonly used in this regards are:

### (I) Chemical precipitation

Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The concept mechanism of heavy metal removal by this process is presented in the following equation (Wang *et al.*, 2006) <sup>[49]</sup>:

M2++2 (OH)  $\longrightarrow$  M (OH) 2

Where, M2+ and OH- represent the dissolved metal ions and the precipitant respectively, while M(OH)2 is the insoluble meta hydroxide. Adjustment of the pH to the basic conditions (pH 9-11) is the major parameter that significantly improves metal removal by this technique. Lime and limestone are the most commonly used precipitant agents due to availability and low cost in most countries (Mirbagherp and Hosseini, International Journal of Chemical Studies

2005) <sup>[28]</sup>. But the main disadvantage associated with this technique is that it requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks include its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and long-term environmental impacts of sludge disposal (Aziz *et al.*, 2008) <sup>[7]</sup>.

## (II) Ion exchange

Ion exchange is another method used successfully in the industries for the removal of heavy metals from water. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets fouled by organics and other solids in the waste water. Moreover, the ion exchange is non-selective and is highly sensitive to the pH of the solution. Other than that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Kurniawan *et al.*, 2005) <sup>[22]</sup>.

## (III) Electrolytic recovery

Electrolytic recovery or electro-winning is one of the many techniques used to remove metals from water. This process uses electricity to pass a current through an aqueous metalbearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. The major disadvantage of this technique is that corrosion can become a significant limit, where electrodes would frequently have to be replaced (Kurniawan *et al.*, 2005) <sup>[22]</sup>.

# (IV) Activated carbon

Activated carbon has been the most popular used materials for the removal of heavy metals and other species (Netzer et al., 1974) <sup>[33]</sup>. It is the most widely used adsorbent. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It can remove a wide variety of toxic metals. Any carbon material can be used to make activated carbon; however, commercial activated carbon is manufactured from only a few carbon sources; wood, peat, coal, oil products, nut shells and pits. The activating chemical corrodes the carbon to form the pore structure and they are usually strong acids, bases or corrosives (Lokeshwari and Joshi, 2009)<sup>[25]</sup>. The disadvantage mainly associated with this technique is that commercial activated carbon also requires complex agents to improve its removal performance for heavy metals. Along with that high cost of this material makes its application less economically attractive in some low cost applications for industrial scale (Ayoub et al., 2013)<sup>[6]</sup>.

# (V) Activated alumina

Activated alumina is aluminum oxide, the same chemical substance as sapphire and rubies, but without the impurities that give the germs their colour. Activated alumina has a very high surface- area-to-weight ratio, with lots of turnel-like pores that run all through it. This means there is a lot of surface area against which the water interacts, thereby removing metals from water. Activated alumina removes a variety of contaminants that often co-exist with fluoride such as excessive arsenic and selenium (Ghorai *et al.*, 2013) <sup>[15]</sup>.

The main disadvantage of activated alumina is that the adsorption efficiency is highest only at low pH and contaminants like arsenates must be peroxided to arsenates before adsorption.

**(VI)** Adsorption: Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness (Kwon *et al.*, 2010) <sup>[23]</sup>. Adsorption is commonly used technique for the removal of metal ions from various industrial effluents (Gottipati and Mishra, 2012) <sup>[17]</sup>. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials (Wang *et al.*, 2015) <sup>[47]</sup>.

Methods such as precipitation followed by coagulation or filtration by membranes have been used for removal of metals from water. These processes become unfeasible since they produce slug, low metal removal rates, and high costs (Ahmaruzzaman, 2011)<sup>[4]</sup>. Among several methods, the adsorption process is one of the most efficient methods for removal of heavy metals from water solution (Singh *et al.*, 2011)<sup>[40]</sup>.

# Biosorption: Environmentally sound process for heavy metal removal

Biosorption is a physicochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure (Volesky et al., 1999)<sup>[46]</sup>. It is a passive, non-energy dependent, fast and reversible mechanism that takes place in both living and nonliving plants. The major advantages of this technology over conventional ones are its low cost, high efficiency, the minimization of chemical sludge, regeneration of biosorbent, and the possibility of metal recovery (Kim et al., 2005)<sup>[19]</sup>. Biosorbents primarily fall into the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes, natural residues and other biomaterials. In general, all types of biomaterial have shown good biosorption capacities towards all types of metal ions (Mahamadi and Chapeyama, 2011)<sup>[26]</sup>. Potent metal biosorbents under the class of bacteria include genre of Bacillus (Nakajima and Tsuruta, 2004) [32], Pseudomonas (Uslu and Tanyol, 2006)<sup>[44]</sup> and Streptomyces (Selatnia et al., 2004) [39]. Important fungul biosorbent includes Aspergillus, Rhizopus and Penicillum, etc. (Mahamadi and Chapeyama, 2011)<sup>[26]</sup>.

Another important biosorbent, which has gained momentum in recent years, is seaweed. Marine algae, popularly known as seaweeds having a division of red, green, and brown seaweed; of which brown seaweeds are found to be excellent biosorbent. Their microscopic structure offers a convenient basis for the production of biosorbent particles that are suitable for sorption process application (Volesky *et al.*, 1999) <sup>[46]</sup>. Similarly, microalgae are known to exhibit a number of heavy metal uptake processes involving different metabolisms (Rai *et al.*, 2015) <sup>[34]</sup>. Monteriro *et al.*, 2012 <sup>[29]</sup> emphasize that accumulation of heavy metals by microalgae typically comprises a two-stage process: an initial rapid (passive) removal of metals by the cell, occurring at the cell surface, and a much slower one that occurs inside the cell. Other such effective biosorbent used in this regard are terrestrial plants, fresh water plants, lofa etc. aquatic weeds (Hubbe et al., 2011)<sup>[18]</sup>. Agricultural wastes have been well studied by many researchers due to its low cost and availability in nature (Sud et al., 2008) [41]. They have showed the high potential of agricultural biowastes as biosorbent for the removal of toxic heavy metals. Forest biowastes are also potent candidates for biosorbent having low cost, high efficiency and it's easily availability. Various forest biowastes, such as bark, chestnut bur, sawdust, pinecone, pine needle and pine-nut cone, were examined as biosorbents for removal of cationic metals, i.e. Cd (II) and Pb (II). Metal nanoparticles have received considerable attention in recent years as a heavy metal removal tool from polluted water systems. Among all metal nanoparticles, iron oxide, silver nanoparticles has been successfully applied in the removal of metals namely arsenic, cadmium, zinc, lead, copper, etc.

#### **Current researches on biosorption**

Many research works have been carried out worldwide in the field of heavy metal removal using the biosorption method. Mane et al., in 2011 has used pretreated algal biomass to remove selenium. They used algae isolates i.e., Spirogyrasp and Nostoc commune for this experiment. They treated the biomass using chemical treatment and used it for selenium removal and to compare the results they used live algae for the same purpose. They observed that the Spirogyra sp and Nostoc commune, when treated biomass with NaOH showed increase on biosorption of selenium in comparison with living biomass physically or chemically is able to remove selenium to considerable extent. Wang and Chen in 2009 [48] have carried out survey of the biosorbents used for heavy metal removal. Their study emphasizes the potential of biomass in wastewater treatment application, especially heavy metal removal. They also found during the review that the biomass can be modified chemically or physically to increase the adsorption capacity.

Moustafa and Idris in 2003<sup>[31]</sup> have done an investigation on the ability of algae to eliminate a number of various heavy metals, particularly lead and cadmium in one metal solution system. They also tried to identify the limiting parameters for the metal removal process. They used the strain Chlorella vulgaris for its high tendency to remove heavy metals. This was done in two successive steps; the first is the adsorption on its surface followed by fixation. They observed that the algae were able to remove 60 percent lead and 65 percent cadmium. Similarly, Sweetly et al., 2014 <sup>[42]</sup> have done an experiment to observe the biosorption of heavy metal lead from aqueous solution by non-living biomass of Sargassum myriocystum. It was found that 2g of algae biomass was optimum to remove 89.75% of lead with contact time of 60 minutes. It was also found that this alga exhibits maximum adsorption efficiencies of the lead uptake at pH 5 and temperature at 25 °C. Therefore, it indicates that this alga is considered as a potential adsorbent, ecofriendly and cost-effective approach for effluent treatment.

Rao *et al.*, 2010 <sup>[35]</sup> carried out an investigation to found out the Cd (II) adsorption from aqueous solution using Terminalia catappa Linn leaf powder. It was observed that the adsorption is more dependent on parameters such as contact time, initial concentration of the biosorbet, pH and adsorbent dosage. For its fast kinetics and high adsorption capacity Terminalia catappa Linn leaf powder can be regarded as a potential biosorbent for Cd (II) removal from aqueous solutions. Another study was carried out by Kim *et al.*, 2005 <sup>[19]</sup> on new efficient forest biowaste as biosorbent for removal of cationic heavy metals. They found that the biosorption shown by forest biowaste i.e., the chestnut bar was much higher than those of agricultural biomass which have been considered as good biosorbents by many researchers. Therefore, abundant and cheap chestnut bur must also be one of potent candidates that can be used to manufacture commercial biosorbent having low cost and high efficiency.

#### Factors affecting the adsorption of heavy metals

For evaluating the potential of biosorbent for metal removal, it is very important to investigate the removal efficiency of a given biosorbent for the target metal. Metal uptake can involve different types of biosorption processes that are affected by various physical and chemical factors, and these factors determine the overall biosorption performance of a given biosorbent.

#### (I) **pH** of the solution

For the target metal, and the quality of target removed, solution pH has been known to be the most important regulator of the biosorption process. The pH affects the solution chemistry of metal itself, the activity of functional groups on the biosorbent, and the competition with coexisting ions in solution (Vijayaraghavan and Yup, 2008)<sup>[45]</sup>. The extent of removal of metal ions is minimum at lower pH values which are attributed to the competition between hydrogen and metal ions for retention in the available sites of the adsorbent. pH is an environmental factor that does not affect only site dissociation, but also the solution chemistry of the heavy metal ions: hydrolysis, complexation, by organic or inorganic ligand, redox reactions, precipitation are strongly influenced by pH and on the other side strongly influences the speciation and biosorption availability of the metal ions in solution (Abbas et al., 2014)<sup>[1]</sup>.

# (II) Initial concentration of the solution

Studies have reported a decrease in the percentage of removal of metal ions with the increase in initial metal concentration in solution. Goswami *et al.*, 2011 <sup>[16]</sup>, reported that there was a decrease in the percentage of removal of arsenic corresponding to an increased initial arsenic concentration. Taty-Costodes *et al.* 2003 <sup>[43]</sup> found that the initial ion concentration exhibits quite an interesting effect on the equilibrium sorption capacity of the Pinus sylvestris for Cd(II) and Pb(II). At a fixed biosorbent dose, pH and temperature, the equilibrium sorption capacity improved with higher initial ion concentration.

#### (III) Dose of adsorbent

With the increase in dose of adsorbent, percentage of removal of metals increases as the metals in solution gets more number of adsorption sites for removal. The decrease in arsenic concentration or increase in arsenic removal efficiency can be achieved by increasing the dose of the adsorbent due to more availability of the surface-adsorbent sites (Goswami *et al.*, 2011)<sup>[16]</sup>.

#### (IV) Contact time

Heavy metal adsorption increases with the increase in contact time of the solution with the adsorbent and it will increase until the process attains equilibrium. For this reason, solution of metal is taken for heavy metal analysis with specific time intervals.

#### Mechanism of adsorption

The adsorption study can be studied using the following models:

### (I) Adsorption kinetics

The rate and mechanism of the adsorption process can be elucidated based on kinetics studies. In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, and to correlate solute uptake, which is important in predicting the reactor volume, pseudo-first order and pseudo-second order kinetic models are generally used (Rao *et al.*, 2010) <sup>[35]</sup>.

### (II) Adsorption isotherms

Adsorption isotherms are useful in finding out the adsorption capacity of the adsorbent, the solute-solution interaction, and the degree of accumulation of adsorbate on the surface of the adsorbent (Rao *et al.*, 2010) <sup>[35]</sup>. The applicability of the isotherm equations is compared through interpreting the correlation coefficient R2. The experimental data are analyzed using the Freundlich, Langmuir, Tempkin, and DR isothermal models.

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