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A review on heavy metals biosorption in the environment

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Abstract. Heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb). Little amounts of some heavy metals are needed by living organisms, however excessive levels of these metals can be harmful to the organisms due to their level of toxicity and accumulation behaviour. Different methods such as electrodeposition, electrocoagulation and nanofiltration system have been used to decontaminate the environment from adverse effect of these pollutants yet most of the methods used are ineffective. Biosorption is the removal of organic and inorganic substances from solution by biological material. Cheap biosorbents for the removal of metals are bacteria, fungi, algae, plants, industrial wastes and agricultural wastes. There are many mechanisms involved in biosorption some of which are not fully understood, examples are precipitation, ion exchange, complexation and adsorption. The efficiency of biosorption depends on many factors such as, temperature, characteristics of the biomass, pH, surface area to volume ratio, metal affinity to the biosorbent, concentration and characteristics of the biomass. Compared to other methods biosorption is operated over a wide range of physiochemical conditions and it uses naturally rich renewable biomaterials that can be cheaply produced. However, the potential for biological process improvement (for example through genetic engineering of cells) is restricted because cells are not metabolizing. Biosorption is in its developmental stages and further improvement in both performance and costs can be expected in future.

Keywords: Biosorption; Heavy metals; Precipitation; Ion exchange; Complexation and adsorption.

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Introduction

Heavy metals are natural components of the earth's crust which cannot be degraded or destroyed. The term heavy metals are used describing any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations, they include Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Thallium (Tl) and Lead (Pb). Heavy metal pollution is one the major environmental problems that causes serious health issues (Aktan et al., 2013). Different types of industries use different kinds of heavy metals which is directly or indirectly release into the environment through contaminated wastewater containing these substances (Glombitza and Reichel, 2014). Though heavy metals like copper, iron, zinc are needed by living organism in trace amount, and it becomes harmful to the organisms due to their high level of toxicity and accumulation when given or taken in excess (Zabochnicka-Świątek et al., 2014). Different approaches have been employed to decontaminate the environment from these heavy metal pollutants, of which most of the methods used are not cost effective and far away from their best possible performance (Pandit et al., 2013). A possible way out towards remediating a heavy metal contaminated environment, is by replacing the conventional methods with biological method which is a cheap and efficient method of treating metal-bearing effluents (Czekalski et al., 2014).

Other sources of environmental contamination by heavy can also be as a result of metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground (Tchounwou et al., 2012). The major cause of heavy metal concentration is from industrial wastewater, 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 (Abbas et al. 2014).

Biosorption can be defined as the use of low cost biological materials to remove metal or metalloid species, compounds and particulates from a contaminated evironment (Tchounwou et al., 2012). Ahemad and Malik, (2011), also defined biosorption as the removal of substances from solution by biological material and these substances could either be organic or inorganic, and in soluble or insoluble forms. Biosorption being a physicochemical process and includes mechanisms such as; absorption, adsorption, ion exchange, surface complexation and precipitation. It can also be obtained from living and dead biomass (as well as their excreted and derived products); metabolic processes in living or dead biomass (Ahemad and Malik, 2011). All biological materials can be used as biosorbents for metals sequestration with the exception of mobile alkali metal cations like sodium and potassium ions, and this can be a significant passive process in living and dead organisms (Gadd, 2010). The inexpensive and readily available biosorbents for the removal of metals mainly falls under the following categories; bacteria, fungi, algae, plants, industrial wastes, agricultural wastes and other polysaccharide materials and in addition, generally, all types of biomaterials used for biosorption are found to have good biosorption capacities towards all kinds of metal ions (Kumar et al., 2014).

Mechanism involved in biosorption of heavy metals

Microorganisms are known to be able to withstand unpleasant circumstances and this has been one of their adaptive mechanisms for the past millions of years (Hrynkiewicz and

Baum, 2014). The ability of microorganisms like bacteria, fungi, algae and even plants biomass to remove heavy metal ions and radionuclide or to promote their transformation to less toxic forms has attracted the attention of various environmental scientist, engineers and biotechnologist for many decades (Hrynkiewicz and Baum, 2014).

Various concepts for bio-removal of heavy metals from waste streams and bioremediations of contaminated environment are being anticipated, some of which are brought to industrial level (Singh et al., 2008; Yu et al., 2013). There are many mechanisms employed in biosorption of which some of these mechanisms are not fully understood (Neethu et al., 2015). Biosorption mechanism may be classified according to dependence on the cell's metabolism which is called metabolism dependent or according to the location where the metal removed from solution is found which is called non -metabolism dependent or metabolism independent; this is based on physical adsorption, ion exchange and chemical sorption, which is not dependent on the cells' metabolism. (Davis et al., 2003). During metabolism independent, physicochemical interaction between the metal and the functional groups like polysaccharides, proteins and lipids have abundant metal binding groups such as carboxyl, sulphate, phosphate and amino group present on the microbial cell surface is used for metal uptake. This type of biosorption, i.e., non-metabolism dependent is relatively rapid and can be reversible (Sardrood et al., 2013). The two classifications of biosorption mechanism is illustrated in Figure 1.

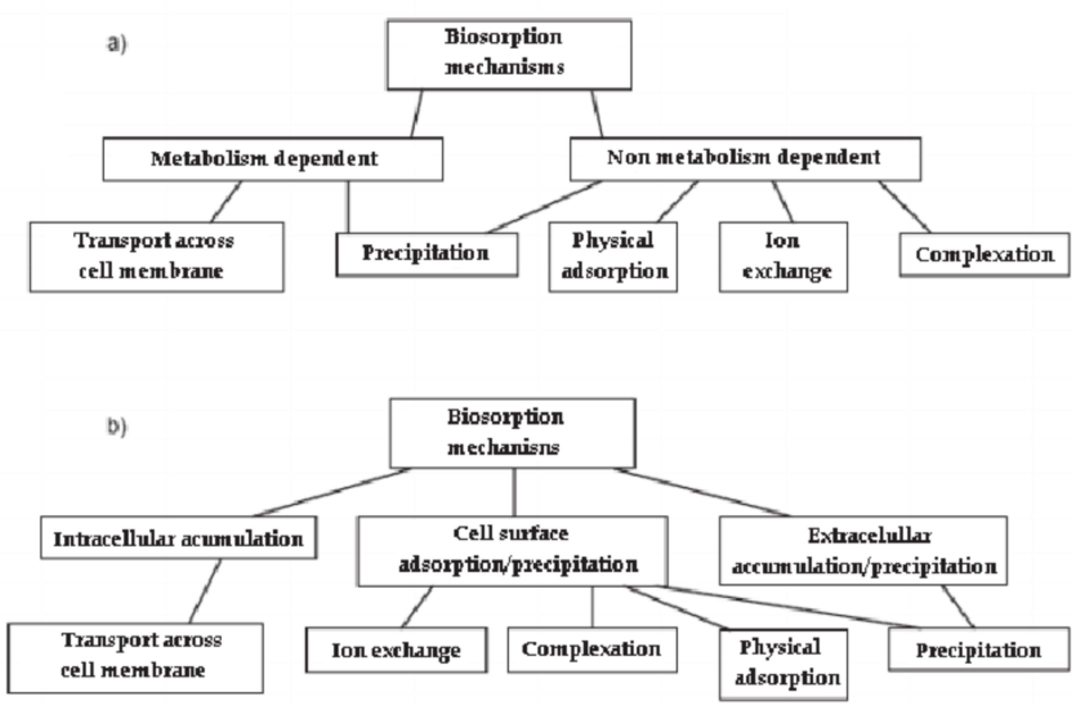

Figure 1. Diagram showing both dependent and non-dependent biosorption mechanism (Volesky et al., 1993).

Microorganisms Involved In Biosorption

There are many types of biosorbents derived from various forms of raw biomass, which includes bacteria, fungi, yeasts, and algae (Kaushik, 2009). The complex structure of raw biomass shows that there are many means employed by these biosorbents in removing various pollutants, but many of these means are yet to be understood for now. Pollutants can be trapped by many chemical and functional groups such as; amide, amine, carbonyl, carboxyl, hydroxyl, imine, imidazole, sulfonate, sulfhydryl, thioether, phenolic, phosphate, and phosphodiester groups, but it depends on the type of biosorbent to be used however, the presence of some functional groups restricts the biosorption of pollutants for example steric (Park et al., 2010). The importance of any given group for biosorption of a certain pollutant by a certain biomass is determined by some factors, like; the number of reactive sites in the biosorbent, accessibility of the sites, chemical state of the sites and affinity between the sites and the particular pollutant of interest which is the binding strength (Mustapha and Halimoon, 2015).

Bacteria as biosorbents of heavy metals

Bacteria have evolved a number of efficient systems for detoxifying metals ions they develop these resistance mechanisms mostly for their survival bacterial biosorption is mainly used for the removal of pollutants that are not biodegradable such as metals ions and dyes from effluents contaminated, however, the large scale isolation, screening and harvesting of bacterial may be complicated but still remain one of the efficient way of remediating pollutants and different bacterial strains has been used for the removal of different metal ions (Hrynkiewicz et al., 2014).

Algae as biosorbents of heavy metals

Algae are efficient and cheap biosorbents as the requirement of nutrient by algae is little and biosorption of metal ions occurs on the cell surface by means of ion exchange method. Based on statistical analysis on algae potentiality in biosorption, it has been reported that algae absorb about 15.3%-84.6% which is higher as compared to other microbial biosorbents and brown marine algae is known to have high absorption capacity for metals like Cd, Ni, Pb through chemical groups on their surface such as carboxyl, Sulfonate, amino, as well as sulfhydryl (Mustapha and Halimoon, 2015).

Fungi as biosorbents of heavy metals

One of the most efficient and ecofriendly method which serves as an alternative to the use of chemicals during treatment process is the use of fungi as biosorbents material. Many types of fungi possess the capability to produce extracellular enzymes for the assimilation of complex carbohydrates for former hydrolysis and makes it capable for the degradation of various degrees of pollutants (Czekalski et al., 2014). Most important roles of fungi are as decomposers of organic material, with concomitant nutrient cycling as pathogens, they also have the benefit of being relatively uncomplicated to grow in fermenters, therefore being appropriate for large scale production. Another benefit is the easy separation of fungal biomass by filtration because of its filamentous structure. In comparison to yeasts, filamentous fungi are less sensitive to variations in nutrients, aeration, pH, temperature and have a lower nucleic content in the biomass (Leitão et al., 2009). The interaction between fungi and metal during biosorption of these toxic metals is shown in Figure 2.

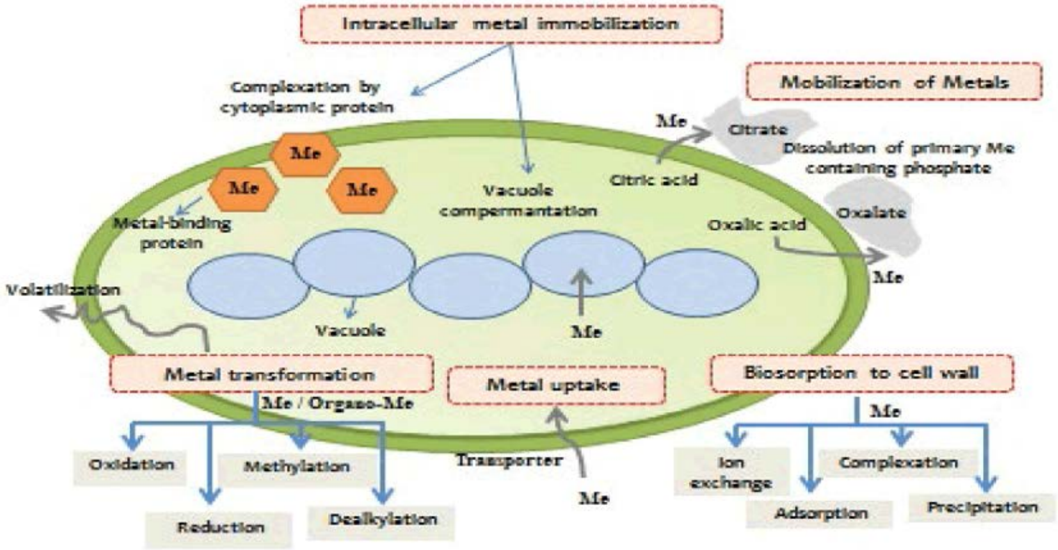

Figure 2. Ways fungi absorb toxic metals into its cell wall (Chaney et al., 2007).

Detoxifying mechanisms of bacteria

The detoxifying mechanisms of bacteria can be categories into; intracellular sequestration, export keeping the toxic ion out of cell by altering a membrane transport system involved in initial cellular accumulation and extracellular sequestration by specific mineral-ion binding (Figure 3).

Intracellular sequestration

Intracellular process of heavy metals adsorption is a complex process and it proceeds through intracellular assembly of sugar nucleotide precursors after and then transported outside the cell. Different enzymes and regulatory molecules are involved in several metabolic pathways that participates in intracellular heavy metal sequestration. The substrate which is any form of sugar enters into bacterium either actively or passively, which is catabolized by periplasmic oxidation or intracellular phosphorylation while some of the precursors which do not take part in the central metabolic pathways act as a raw material. The synthesis of biomolecule cannot continue through simple sugar molecules instead the intracellular machinery requires charged and energy rich precursor monosaccharide in the form of nucleotide diphosphate or monophosphate sugar, and this crucial step is governed by an independent pathway, where phosphorylated sugar, often in the form of sugar-11P and rarely in form of sugar-2P or sugar- 6P, serves as an activated primary residue (Ozer et al., 2003).

Export keeping the toxic ion out of cell by altering a membrane transport system

Plants have a range of potential mechanisms at the cellular level that might be involved in the detoxification and thus tolerance to heavy metal stress and these all appear to be involved primarily in avoiding the build-up of toxic concentrations at sensitive sites within the cell.

Heavy metals such as Cu and Zn are essential for normal plant growth and development since they are constituents of many enzymes and other proteins but high concentrations of both essential and non-essential heavy metals in the soil can lead to toxicity symptoms and stunted growth of most plants. The toxicity symptoms experience in the presence of high concentrations of heavy metals may be due to a range of interactions at the cellular or molecular level and may result from the binding of metals to sulphydryl groups in proteins, leading to an inhibition of activity or disruption of structure, or from the displacing of an essential element resulting in deficiency effects, furthermore, high level of heavy metal may stimulate the formation of free radicals and reactive oxygen species, perhaps resulting in oxidative stress (Ziagova et al., 2007). Some plant species, however, have evolved and developed adaptive features or strategies to thrive on such metalliferous soils, maybe by adapting mechanisms that may also be involved in the general homeostasis and constitutive tolerance to, essential metal ions as found in all plants. Figure 4 shows how toxic ions are being kept out of cell by altering a membrane transport system (Ziagova et al., 2007).

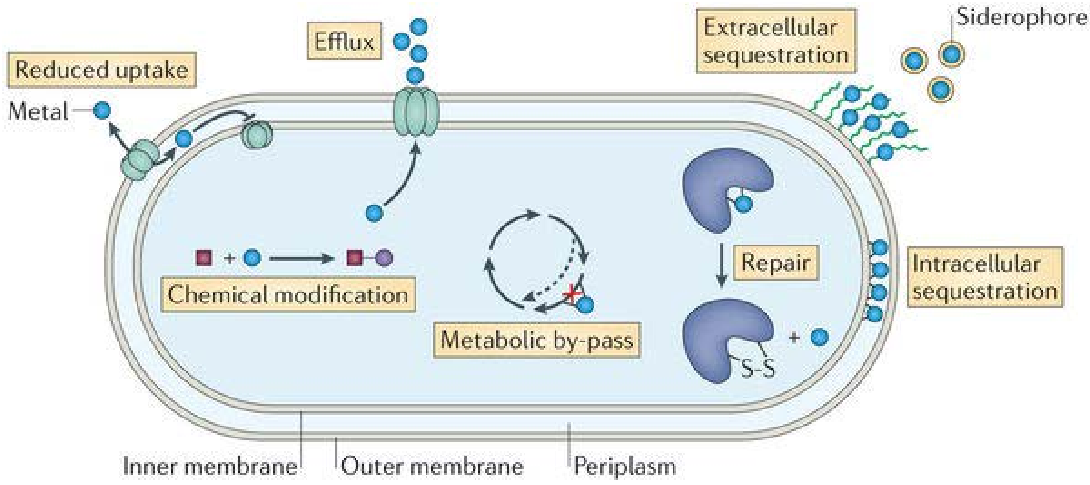

Figure 3. Intracellular and Extracellular sequestration (Ozer et al., 2003).

Extracellular sequestration by specific mineral-ion binding

There numerous strategies for avoiding heavy metal build up extracellularly, they include roles for mycorrhizas and for cell wall and extracellular exudates. Tolerance could also involve the plasma membrane, either by reducing the uptake of heavy metals or by stimulating the efflux pumping of metals that have entered the cytosol. Within the protoplast a variety of potential mechanisms exist, for example, for the repair of stress-damaged proteins involving heat shock proteins or metallothioneins, and for the chelation of metals by organic acids, amino acids or peptides, or their compartmentation away from metabolic processes by transport into the vacuole. The specific mineral-ion binding through extracellular sequestration is also shown in Figure 4.

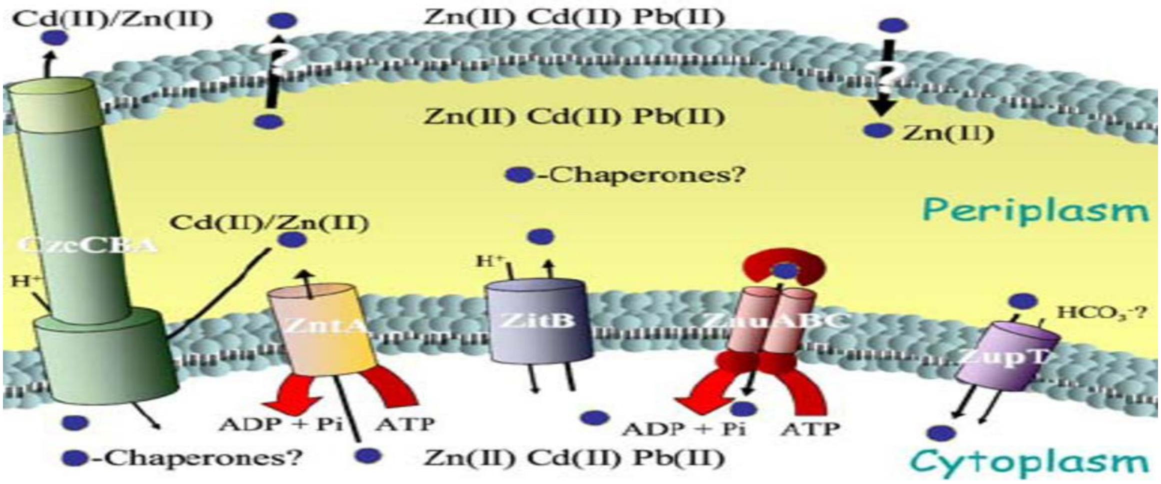

Figure 4. Export keeping certain toxic metal ion out of cell (Ziagova et al., 2007).

Factors affecting biosorption of metals

The success of biosorption depends on many factors, some of which are related to the biomass and metal and the others are related to environmental conditions (Ghosh et al., 2016). The major factors that affect the biosorption process are.

Temperature

The optimum temperature for biosorption efficiency is within the range 20-35 °C (Aksu and Dönmez, 2001), although high temperatures like; 50 °C, may increase biosorption in some cases, of which may cause permanent damage to microbial living cells thus decreasing metal uptake (Ahalya et al., 2015). Absorption reactions generally are exothermic and the extent of adsorption increases with decreasing temperature. The maximum biosorption capacity for Ni and Pb by Sacharomyces cerevisiae was obtained at 25 °C and found to decrease as the temperature was increased to 40 °C (Tchounwou et al., 2012).

Characteristics of the biomass

The nature of the biomass or derived product may be considered as one of the important factors, including the nature of its application such as: freely-suspended cells, immobilized preparations, and living biofilms. The biding properties are affected by physical treatments such as boiling, drying, autoclaving and mechanical disruption while chemical treatments such as alkali treatment often improve biosorption capacity, especially evident in some fungal systems because of acetylation of chitin to form chitosan-glycan complexes with higher metal affinities (Wang and Chen, 2009).

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 (Ahalya et al., 2015).

Acidity

pH is the most important parameter in the biosorption processes because the pH of a solution influences the nature of biomass binding sites and metal solubility and also affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Deng and Wang, 2012).

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 (Deng and Wang, 2012). At pH less than 2, there are minimum or negligible removal metal ions from solutions. The metal uptake increases when pH increases from 3.0 to 5.0. Optimum value of pH is very important to get a highest metal sorption, and this capacity will decrease with further increase in pH value.

Biomass concentration

Biomass concentration in solution seems to have great influence on the specific uptake; for lower values of biomass concentrations there is an increase in the specific uptake The increase in biomass concentration leads to interference between the binding sites. Gadd, (2010) invalidated this hypothesis attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution. Hence this factor needs to be taken into consideration in any application of microbial biomass as biosorbent. High biomass concentration restricts the access of metal ions to the binding sites (Gadd, 2010).

Initial metal ion concentration

The mass transfer resistance of metal between the aqueous and solid phases is influenced by the initial concentration. 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, so at a given concentration of biomass, the metal uptake increases with increase in initial concentration (Zouboulis and Martis, 1997).

Metal affinity to the biosorbent

Physical and chemical pre-treatment 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.

Advantages of biosorption process

The adoption of biosorption process as a means of removing heavy metals in the environment is of greater advantage when compared with other conventional heavy metal removal methods. Some of vital advantages are as follows.

Biosorption is operated over a wide range of physiochemical conditions including temperature, pH, and presence of other ions, it also have the ability to treat large side of wastewater due to rapid kinetics. More so, biosorption uses naturally rich renewable biomaterials that can be cheaply produced, it also involves less need for additional expensive reagent, which typically cause disposal and space problems, biosorption also have high selectivity when it comes to the removal and recovery of certain heavy metals. Furthermore, biosorption deals with low capital investment and low operational cost, it has the ability to handle multiple heavy metals and mixed wastes (Aktan et al., 2013). Lastly, biosorption has improved in the recovery of bound heavy metals from the biomass and also reduced the level of hazardous waste produced (Aksu and Dönmez, 2001).

Limitations of biosorption process

One of the major drawbacks of biosorption is early saturation, which occurs when metal interactive sites are occupied, metal desorption is necessary due to further use, irrespective of the metal value. Furthermore, the potential for biological process improvement for instance, through genetic engineering of cell, these cells are restricted because cells are not metabolizing (Tabaraki et al., 2013). Production of the adsorptive agent occurs during pre-growth, there is no biological control over characteristic of biosorbent. This will be particularly true if waste biomass from a fermentation unit is being utilized, and lastly, there is no potential for biologically altering the metal valency state, For example less soluble forms or even for degradation of organometallic complexes (Colak et al., 2011).

Conclusion

Microbial biomass is one of the cheapest and most convenient way of removing heavy metals from solutions in the environment. Biosorption also deal with the ability to handle multiple heavy metals and mixed waste and have high selectivity when it comes to the removal and recovery of certain heavy metals in the environment. The biosorption of these heavy metals is demonstrated as a useful alternative for the removal of toxic metals from industrial effluents. Biosorption is more advantageous than conventional treatment methods in terms of cost, efficiency, regeneration of biosorbent and the extent of reduction of chemicals. Biosorption is in its developmental stages and further improvement in both performance and costs can be expected in future than currently used of chemical for heavy metal removal.

Conflict of interests

The authors declare that there are no conflicts of interest.

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