Bioremediation of Heavy Metals by Fungus in Aqueous Ecosystem: A Review

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Abstract: Industrial accumulation of heavy metals in aqueous ecosystems menaces both ecosystem and human health, thus embrace the development of potentially cost-effective technology to eliminate toxic heavy metals. Microbial removal of heavy metals from aqueous solution studied extensively and fungi elevate high concentration of heavy metals by investing low cost. pH, metal ions concentration, biomass concentration and time of incubation attribute to heavy metal bioremediation ability from aqueous solution. This review discusses bioremediation technology i.e. biosorption through fungi for potential removal of these metals.
Keywords: Heavy Metals, Fungus, Bioremediation

Introduction:

In twenty first century heavy metals pollution is the major environmental and human health issues as assimilate in food chain via Bioaccumulation. Iron, manganese, mercury, lead, zinc, cadmium, uranium, chromium are the cornerstones of human progress; as a part of materials construction, agriculture, transportation, and in processing of many industrial materials and commercial products they are the pillars of civilization (Spiegel et al., 1985). Conventional methods i.e. reverse osmosis, electro dialysis, ultra filtration, industrial ion exchange process and chemical precipitation remove heavy metals from waste water and prevail upon high costing, high amount of energy, not appropriate for removal of heavy metals at low concentration i.e. up to 50 mg/L, high amount of reagents, causing secondary pollution through the production of chemical sludge and disposal of floc residues making these methods non suitable in long run (Sharma and Singh, 2015; Wei et al., 2016). Use of microbial biomass for removal of heavy metals through biosorption is efficient in removal of heavy metals from aqueous solution without costing much.

Biosorption: Transport against cell membrane, biosorption of cell walls, entrapment in extracellular capsules, precipitation, complexation and oxidation- reduction reaction are methods adopt by microbial biomass for heavy metal bioremediation from aqueous ecosystem (Abbas et al., 2014). Biosorption is the process which is a rapid phenomenon of passive metal concealment by the micro-organisms. **Biosorption** process hence can be defined as ''the process in which micro-organisms are used to remove heavy metals in aqueous solution. It is a physio-chemical intercommunication between heavy metals ions and microbial surfaces''.

Biosorption process comprises of 2 phases

- **Solid phase** – It can be biomass, sorbent, biosorbent biological materials.
- **Liquid phase-** It can be solvent i.e. water, broth in which sorbate or metal ions are dissolved.

Biosorbents: Micro- organisms absorb heavy metals of any concentration on its surface of any concentration on its surface absorb these metals on its surface as a biosorbent and categorized as bacteria (Rajkumar et al., 2009 and Rehman et al, 2008), fungi (Coreno- Alonso et al 2009 and

Khambhaty et al, 2009, algae (Gupta et al, 2010), etc. In recent year focus on the use of biological matters as biosorbent for the removal of heavy metals from the environment (Sharma and Singh, 2019).

Fungi as Biosorbent: Fungi are ubiquitous in natural environment their cell wall and their components have a major role in biosorption process (Sharma and Singh, 2020). The fungal cell wall is comprised of chitin, cellulose, β- Glucan, α- Glucan, chitosans, polyuranides, glycoproteins, lipids, inorganic salts and pigments (Dhankhar and Hooda, 2011). Comparing the usage of fungi as biosorbent is easy grown by simple fermentation techniques with over all low cost (Redha, 2020). White rot fungi are exceedingly specific gatherings of life forms and Basidomycetes, which incorporate all the higher fungi that are portrayed by their sexual fruiting bodies i.e.,*Lentinussajor-cajuis* an outstanding white rot, while a little consideration has been paid to the capacity of its potential for the expulsion of blended pollutants from nature (Yakup and Bayramoglu, 2004).

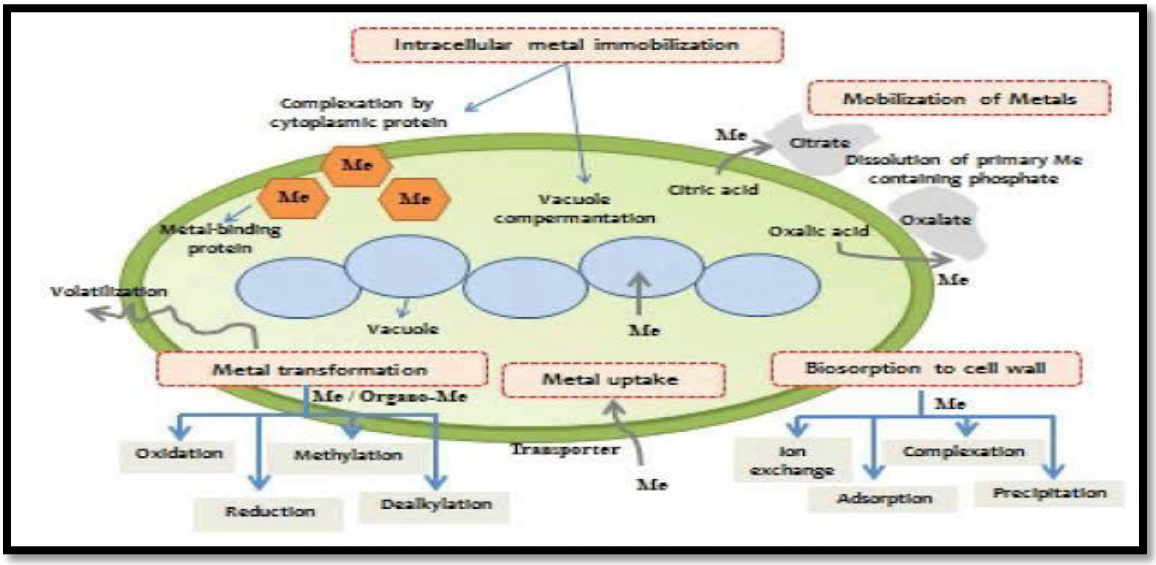

Fig: Schematic of Fungi and metal interaction

Biosorption of cadmium (Cd): Cadmium is major heavy metals found in polluted aquatic environments and it can be controlled through biosorption process various microorganism plays an important role in the biosorption of heavy metals which were been studied from time to time. Gami et al., 2009 isolated 19 fungal species and out of 19 isolates they workwith the living as well as dried biomass of *Aspergillus fumigatus* on biosorption of cadmium. Fazil et al., 2015 determined the cadmium tolerant and bioremediation ability of seven fungal isolates that includes *Aspergillus versicolor*, *Aspergillus fumigatus, Paecilomyces*sp. 9, *Pacecilomyces*sp. G, *Trichoderma* sp., *Microsporum* sp. and *Cladosporium* sp.

Biosorption of chromium (Cr): Chromium is non biodegradable, toxic pollutant that persistent in nature. Therefore biosorption is one of the most appropriate methods for the removal of Chromium from the environment and it was reported several time as follows, Marandi, 2011 they work on the dead biomass of *Phanerochaetecrysosporium* as a new biosorbent for the removal of chromium. Narasimhulu and Setty, 2012 they studied the biosorption of chromium ions from wastewater using biomass of *Aspergillus niger* species. Smily et al, 2017 studied Chromium biosorption ability of *Trichoderma* sp. BSCR02 when it is untreated or alkali treated.

Mechanism of biosorption – The illustration of the component of biosorption is important to empower the innovation to be created. Such components are entangled and not completely comprehended. Ion exchange, complexation, transport across the cell membrane, physical adsorption and precipitation are the mechanism involve in biosorption. Many groups of cell constituents like structural polysaccharides, acetamido group of chitins, carboxyl and sulphahydral group of protein, phosphate, phosphodiester, hydroxyl in polysaccharides participate in biosorption.

- **Ion exchange:** Microbial cell wall have polysaccharides and bivalent metal ions such as K^+, Na^+, Ca^+ and Mg^+ these ions result in biosorption of heavy metals (Ahalya et al., 2003).
- **Complexation:** Organic acids are also produced by the microorganisms such as oxalic acid, citric acid, malic acid, gluconic acid, lactic acid and fumaric acid, these acids have a capacity to chelate toxic heavy metals which may lead to the formation of metallo-organic molecules.
- **Transport across cell membrane:** The same mechanism which used to convey metabolically important ions such as Sodium, Potassium and Magnesium involved in biosorption of heavy metals.
- **Physical adsorption:** Van der Waal's forces helps in the physical adsorption of heavy metals (Kuyucak and Volesky, 1989). Biosorption by dead biomass of microorganisms takes place through electrostatic interactions and cell walls of microbial cells.
- **Precipitation:** Removal of the metals from solution may be associated with active defense system of the microorganisms. Microorganisms react in the presence of toxic metals producing compounds that favors the process of precipitation, precipitation process does not dependent on the cellular metabolism where as it involve the metals and cell surface interaction.

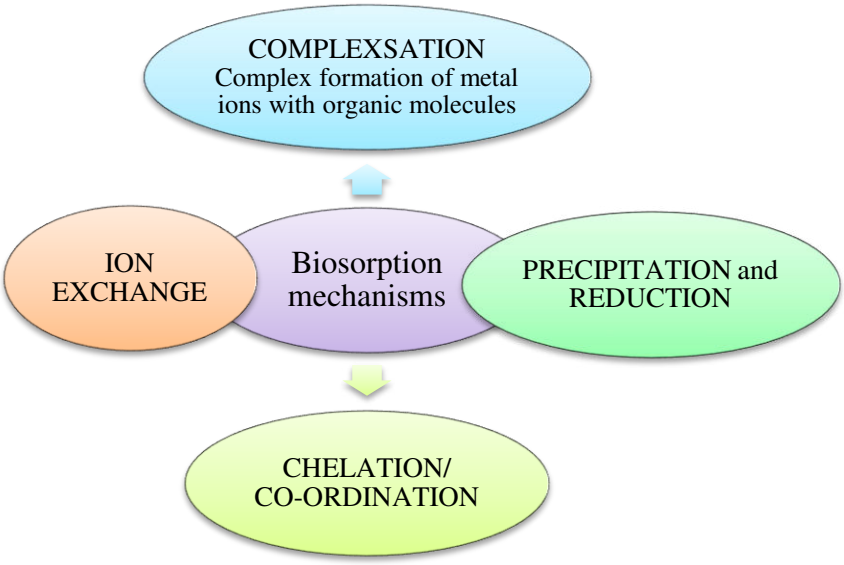

Fig: Different mechanisms involved in biosorption process

Factor affecting biosorption assay: There are several factors that influence the mechanism of biosorption such as

- **State of biomass i.e. it is living or non- living:** Biosorption can be carried out by 2 ways i.e. metabolically independent biosorption non- living bacterial and fungal biomass can be used as there are many functional groups such as amine, methyl, carbonyl, etc that were present on their surface and they have an ability to bind the heavy metal ions from aqueous solution. While in case of metabolically dependent process the live biomass of micro-organisms was used in which the heavy metals were taken up by the micro-organisms as nutrient through cell membrane and get binds to cytoplasmic compounds, so both the forms can be used for biosorption process. The removal of heavy metals by dead and live micro-organisms were investigated by many investigators such as Liu et al., 2004, Gabra et al., 2008, Joo et al., 2010 and Duda- Chodak et al., 2013 etc. and they found that heavy metals binding capacity of dead biomass is higher than live biomass.
- **Physical Condition:** There are many physical conditions that effect biosorption process such as pH, Temperature, Biomass dose, Time of contact between biosorbate and heavy metal ions as follows:

- **pH:** The one of the most critical factor that has effect on the biosorption was pH as the pH decide the chemical nature of solution, the most prominent pH value for the biosorption process was found to be 3 to 7 by various studies such as Sethuraman and Balasubramanian, 2010, karmeem et al., 2014 this is because if the pH is too low than the available site of the biosorbate was occupied by the H^- ions of the solution on the other side if the pH is too high than the number of OH^- ions increases in the solution which further hinders the binding of the metal ions to the biosorbate sites (Marandi, 2011).
- **Time of contact:** Biosorption process was a continuous process and this process comprises 2 phases, the rapid phase in which maximum amount of biosorption occurred this was followed by slow phase in which biosorption occur but at very low speed this effect was investigated by various investigators such as Gani et al., 2009, Giri, 2012, Garcia et al., 2016 and Gonzalez et al., 2017.
- **Biomass dose:** This is a factor that has strong influence on the process of biosorption as the increase in the biomass dose the biosorption of heavy metals on the biomass also increases (Vijavaraghavan and Yun, 2008), but with the increase in biomass dose biosorption per unit of biosorbate decreases because the number of binding sites increases, the similar pattern was observed by several investigators during their studies such as Rathinam et al., 2010.
- **Temperature:** It was found that the temperature may have certain crucial effect on those factors that affect the rate of biosorption and it was observed by several studies such as by Murthy et al., 2012, Ahmed and Kibert, 2013, Verma, 2017 that with increase in temperature above 35^0Cdecreases the biosorption rate concluding that biosorption rate concluding that biosorption is a exothermic reaction.

Isotherms models: Biosorption is mainly described through isotherms. It basically represents equilibrium state between the concentration of absorbate in liquid phase and the concentration of absorbate in the absorbent particles at given physical conditions (Abbas et al., 2014). It is a plot of the amount of absorbate per unit weight of absorbent q_e against the equilibrium concentration of absorbate remaining in solution C_e. Some of typical isotherm shapes are as follows.

Biosorption isotherm models: They are mathematical relationship which can be characterized by a number of parameters which are an adjustable and provide a behavior of an experiment over a wide range of environment conditions.

Freundlich model: It was published by the Freundlich and Kuster in 1907, and was expressed as

$$q_e = KC_e^{1/n}$$

Here, K(mg/g) $(1/\text{mg})^{1/n}$ and n are Freundlich constants, which are adsorption capacity and adsorption intensity respectively.

Langmuir model: It was provided by Irving Langmuir in 1918, it was based on a assumption that maximum adsorption occur in a condition when the saturated monolayer of solute is present on a assumption that maximum adsorption occur in a condition when the saturated monolayer of solute is present on the surface of adsorbate and energy of adsorption is constant and no further migration of adsorbate occur (Kumar et al., 2008). Langmuir model was expressed as

$$q_e = \frac{Q_0 b C_e}{1 + bC_e}$$

Here q_e is the uptake of metal per unit weight of adsorbent (mg/g), Q_0 is moles of solute sorbed per unit weight of adsorbent (mg/g), b is aconstant that is related to the affinity between biosorbents and biosorbate (l/mg) and C_e is the equilibrium concentration of ions (mg/L).

Biosorption kinetics study:

In biosorption process the study of kinetic models were important as they help in testing the experimental values obtained during biosorption process. Mainly two kinetic models were studied i.e.

- **Pseudo- First order kinetic model:** It is also known as Lagergen rate equation, it was one of the first models that were used for calculating absorption rate in a liquid and solid system. It was given as

$$\frac{dq}{dt} = K_l(q_{eq} - q_t)$$

If the conditions were adjusted t=0 to t=t and $q_t = 0$ to $q_t = q_t$ then the above equation can be given as:

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

Where

q_{eq} =amount of metal ions adsorbed at equilibrium

q_t = amount of metal ions adsorbed at time t

K_L = Equilibrium rate constant

- **Pseudo- Second order kinetic model:** The Pseudo second kinetic model was represented as follows

$\frac{d_{qt}}{dt} = K_s(q_{eq} - q_t)^2$

Where

K_s = Rate constant of adsorption

q_{eq}= Amount of metal ions adsorbed at equilibrium

q_t = Amount of adsorbate on adsorbent at time t

It may be represented as

$$\frac{t}{q_t} = \frac{1}{K_s q^2 eq} + \frac{t}{q_{eq}}$$

It was suggested that the process was found to be fitted in that particular kinetic model in which the value of r^2 is close to 1. If the absorption process fits in Pseudo- First order kinetic model then it was found that the process was **physisorption** i.e. the intermolecular forces were involved in the absorption process such as Van der waals forces, while if the process fits in Pseudo- Second order kinetics model then the process was **chemisorption** i.e. biosorbate and biosorbent binds to one another through chemical reactions.

Conclusion: Biosorption techniques can be an option in contrast to the regular modern strategies for evacuation of heavy metals due to being harmless to the ecosystem and maintainable for use. A few sorts of biosorbent materials can be utilized, for example microorganisms (fungi). Biosorption process can be take place by several mechanisms including physical adsorption, ion- exchange, complexation, precipitation and

transport across the cells. The biosorption limit of biosorbents can be influenced by the pH of the climate, temperature, contact time, biomass dose, beginning metal focus and different components. A major limitation of the researches conducted in this area, studying the biosorption capacity of different biomass, is they did not encounter for the complexity of real- life contaminated water.

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