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Biosoption of metal ions from waste water, factors affecting biosorption and its advantages: A review

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Abstract
Biosorption is a low cost and eco-friendly physico-chemical process, used widely now-a-days to remove metals and dyes from industrial effluents and waste waters. Many living organisms like bacteria, algae, fungi and yeasts and agricultural waters and agro waste materials have been used as biosorpants till date. In the present review an attempt has been made to discuss biosorption, its mechanism, factors affecting biosorption process and advantages of biosorption processes.

Keywords: Metal ions, affecting biosorption, Advantages

Introduction
Biosorption is the most effective and promising method for removing heavy metals from aqueous solution when they are present in extremely low concentrations. Due to its high metal ion removal efficacy, biosorption is a more advantageous technique for the removal of metal ions from aqueous solutions and waste waters than conventional techniques. Its advantages are:

a) Lower operational cost.
b) Minimum formation of sludge.
c) Adsorption i.e. regeneration of the biosorbent.
d) Recovery of metal if it is in enough concentration.
e) No requirement of costly nutrients.
f) No requirement of sterilized conditions.

Biosorption is the use of biological material to remove the substance e.g. heavy metal ions, dyes, pesticides etc., from waste water or water. The two interact with each other resulting in accumulation of sorbate at the interface of biosorbent, which causes reduction in the concentration of sorbate in the solution.
There are two processes which occur in biosorption (Gadd, 2008) [13].

a) Bioaccumulation: It is generally found in living biomass like bacteria, fungi, algae and yeast in which metal ions transport intracellularly.
b) Bioadsorption: In this process metal ions get adsorbed on the surface of the biomass which occur by one or group of mechanisms e.g., ion exchange, complexation, precipitation, and electrostatic attraction etc. Biosorption in a physico-chemical process which involves the mechanisms of adsorption, diffusion, surface complexation etc.

Substance which are to be removed may be of inorganic, organic, insoluble, soluble and gaseous type. In biosorption process both living and dead microorganisms as well as their components may be used as biosorbents to remove heavy metals from aqueous solution. For metal removal, microorganisms such as bacteria, fungi, algae, and microalgae are frequently employed. In simple words it is the property of biomass to remove heavy metals even when it is in very less concentration by binding and concentrating the metal ion from aqueous solution. Biomass has ion exchanger property which is biologically originated. Recently, the biosorption process has emerged as the most promising, environmentally favourable, and cost-effective biotechnology for removing heavy metals from aqueous solutions (ground water, surface water, and waste water) (Nour *et al*., 2015) [34] due to its simplicity and ease of handling.

The term biosorption involve "Bio" which means use of biological material while term "sorption" is of two types (1) Absorption and (2) Adsorption. In absorption one state of substance incorporate with substance which is in different state e.g., solid absorbs liquid and gas, liquid absorb gas e.g., water absorbs gases. While in ease of adsorption one molecule or ion of substance physically adhere onto the other molecules surface e.g., surface of two dimensional molecules. In case of adsorption there are two types of materials i.e. "adsorbate" the material that accumulate at the surface of the solid i.e. interface and "adsorbent" is the solid material at which adsorbate, adsorbed. In case of adsorption "surface complex" form by formation of "molecular phase" which is stable and occur at interface of adsorbent molecule. The surface of most adsorbents involving microorganisms (e.g. bacteria, fungi and algae) contain functional groups e.g., COOH, -OH and-SH etc. (Shamim, 2018; Ayansina and Babalola, 2017) [41, 2, 3]. Uptake capacity of metal ion in biosorption is mainly depends upon the nature of the substrate and involve various mechanisms e.g., adsorption, coordination, complexation, ion exchange and precipitation etc. (Handsa *et al*., 2015) [17]. When living plants are used then uptake capacity in biosorption process includes two stages one is rapid phase and second is the slow phase. There are two types of biosorption mechanisms (Volesky, 1995) [47].

1. **Metabolism Independent:** This includes precipitation, ion exchange, physical or chemical adsorption and complexation (Veglio and Beochini, 1997) [45].
2. **Metabolism Dependent:** In this process, metal ions are transported across the cell membrane, and intercellular precipitation and accumulation occur.

Mechanism of Biosorption

The biosorption mechanism is a complex procedure that depends on a number of variables, including:

1. Biomass/biosorbents such as microorganisms, agricultural wastes, kitchen wastes including other household wastes, pharmaceutical waste, food industry wastes, fruit juices wastes etc.
2. Biomass status i.e. living microorganisms or dead microorganisms.
3. Type of metal ion.
4. Properties of metal and solution chemistry.
5. Environmental or surrounding conditions e.g. pH, temperature of the solution.

Mechanism of Biosorption Process using Non-Living Biomass: Biosorption using non-living biomass are usually occurred in passive mode (Veglio and Beochini, 1997; Madrid and Camara, 1997; Wang *et al*., 2000) [45, 27, 48] e.g. agricultural waste biomass, fruit waste, Pharmaceutical industry waste etc. According to Goyal *et al*. (2003) [14] metal removal by non-living process includes two step processes:

a) Passive removal: It occurs promptly, with the first step consisting of passive removal, which may be ion exchange or physical adsorption at the cell surface. This process takes 30- 40 minutes to attain equilibrium. It is a metabolically independent mechanism, meaning it does not require energy and depends primarily on functional groups present on the cell surface.

b) Active removal: In this case metal transport and deposition occurs and it is metabolism dependent process.

Factors affecting biosorption process

Process of biosorption i.e. both performance efficiency and behaviour is not only affected by operating conditions of the process but also physicochemical properties of the adsorbent and adsorbate. The important characteristics of adsorbent and adsorbate are composition, types of charge on the functional groups, structure, and size of particle and pH of aqueous solution. The cell wall composition of biomass or adsorbents also affects uptake capacity and percent removal (Goyal *et al*. 2003) [14]. To understand the complete process and efficiency of biosorption it is necessary and important to analyze all the factors which influence the process which are as follows:

Effect of pH on biosorption process

As protons can be adsorbed on the biomass surface, the pH of the adsorbate solution has the greatest impact on the biosorption process (Pandey *et al*., 2007, Fomina and Gadd, 2014; Romera *et al*., 2018; Hilhor *et al*., 2017) [37, 12, 40, 18]. In general, it has been reported that at extremely low pH=2, almost no metal ion is removed from aqueous solution. Increasing the pH of an aqueous solution to a threshold that differs for metal ions and biomass results in metal ion removal. So it is necessary to know upper limit of pH for particular biomass and metal ion for efficient biosorption process. Due to the high mobility and concentration of H^+ ions, which compete with metal ions for binding sites and are preferentially adsorbed on the surface of the biomass, biosorption is minimal in highly acidic media (Lu and Xia, 2011; Malkoc *et al*., 2006 and Budinova *et al*., 2011) [26, 29, 6]. At higher pH, functional groups deprotonate and become negatively charged, attracting positively charged metal ions, which are then adsorbed on the surface of biomass (Feng *et al*., 2011) [10]. Therefore, at different pH, speciation of metal ions and the charges on functional groups on the biomass are important for efficient performance of biosorption.

The overall surface charge on biomass becomes positive when pH of solution is lowered, this will result in inhibition of attraction of metal cations which are also positively charged (Gupta *et al*., 2019) [15]. The pH of point zero charge (pHpzc) can also be used to examine the effect of pH on the biosorption process. At pHpzc, surface of biomass is neutral and when pH of the solution is <pHpzc, biomass becomes positively charged certain functional groups becomes protonated. Deprotonation of functional groups on the biomass occurs and becomes negatively charged when pH increases above pHpzc. On the other hand, at higher pH (highly alkaline condition) there is increase in amount of hydroxyl ions (OH^-) in the solution. There is reaction between metal ions and OH^- which initiates precipitation by forming the metal hydroxides resulting the negligible amount of biosorption process. Precipitation occurs at high pH which depend on metal hydroxides "solubility product constant" i.e. K *sp*. (Farroq *et al*., 2010) [9]. According to Hilithor *et al*. (2013) [19] when pH of solution Cr (VI) increased from 1 to 4 creates negative charge on functional groups on surface of dead biomass of *Sacchaomyces cerevisiae*. This occurs due to deprotonation of functional groups on biomass surface resulting in attraction of Cr (III) which were obtained by reduction of Cr (IV) ions. When pH

decreased from 4 to 1, then Cr (VI) reduction to Cr (III) increased. The concentration of total Cr decreased as the pH rose from 1 to 4.5 (Hilhor *et al*., 2013) [19].

Effect of biomass particle size on biosorption process

In the case of surface reactions, the smaller the particle size, the greater the surface area for the attachment of metal ions to the surface of biomass (Yeddou-Mezenner, 2010; Stasinakis *et al*., 2008) [49, 43]. Another reason is that when particle size decreases then decrease in the diffusion of intraparticles occurs which results in increased rate of diffusion and biosorption (Fernando *et al*., 2009) [11].

Effect of initial concentration of metal ions:

It is an important parameter in the biosorption process because it plays a crucial role in overcoming "mass transfer resistance" that occurred between biomass (solid phase) and aqueous solution containing metal ion and increasing the uptake capacity (mg/g) (Dang *et al*., 2009; Oyelude and Appiah – Takyi, 2012; Velkova *et al*., 2012) [7, 36, 35, 46]. On the other hand, removal efficiency decreases by increasing the initial concentration of metal ion. When initial concentration of metal ions increases, there is an initial increase in removal efficacy because at lower initial concentrations of metal ions in the solution, nearly all metal ions interact with binding sites or active sites, resulting in nearly one hundred percent biosorption or metal removal. On the other hand at higher metal ion concentration, there is presence of unabsorbed ions in aqueous solution because binding sites or active sites saturated and no active sites left empty for further adsorption process (Naiya *et al*., 2009) [33].

Effect of amount of adsorbent

"Potential of any adsorbent to remove heavy metal ions from aqueous solution" is the amount of adsorbent (Rathinam *et al*., 2010) [39]. Since adsorbent provides active sites for the removal of metal ions from aqueous solution, the quantity of adsorbent has a significant impact on the efficiency of metal ion removal. When metal ion conc. keeps constant and conc. of biomass increased, then there is increase in uptake capacity of metal ions due to availability of higher number of active sites for biosorption process (Duran *et al*., 2011; Kumar and Gaur, 2011; Jaikumar and Ramamurthi, 2009) [8, 25, 21]. When low biomass dose is used then concentration of metal ion adsorbed/unit biomass weight is high. When dose of biomass increases then it results in reduction of adsorption capacity. This occurs due to the reason that there is higher number of empty binding sites on biomass than the number of metal ions in the aqueous solution. However, another aspect is that at higher adsorbent dose adsorption of the metal ions are higher because more empty active sites are available for metal ion binding.

Effect of temperature

It is an important parameter in case of treatment of waste water because due to processing they are discharged at high temperature. Uptake capacity and removal increases with increase in temperature for endothermic reactions. The reason behind this is that activity of biomass surface increases and hence more empty binding sites are available for metal ion binding (Moussous *et al*., 2012; Majdik *et al*., 2010; Baccar *et al*.; 2010) [32, 4] and vice-versa for exothermic reactions (Krishni and Hameed, 2013; Johari *et al*., 2013) [24, 23].

Effect of contact time

Optimisation of contact time is the most important metric to evaluate the biosorption of metal ions. In batch experimental studies for removal of highest concentration of metal ions from adsorbate solution, it is important to determine the optimized contact time. While selecting the treatment system for waste water, it is important to know the "equilibrium time" of the study (Abdel-Ghani *et al*., 2007) [1]. It is reported from previous studies that in the beginning of the experiment removal of the metal ion is rapid, but there is decrease in the adsorption process gradually with time until the equilibrium state is achieved. Initially, there is a greater percentage of metal ion removal due to the availability of a greater number of vacant binding sites, which results in a larger surface area for metal ion removal. As competition between metal ions for adsorption on active sites decreases the availability of binding sites, the adsorption process declines in comparison to the beginning (Abdel-Ghani *et al*., 2009) [2].

Effect of agitation speed

Optimization of agitation speed is an important factor in biosorption process. Increasing the speed of agitation decreases the "mass transfer resistance" resulting in increase in percent removal only up to certain speed. Due to the fragmentation of biomass (Parvathi *et al*., 2007; Martinez - Garcial *et al*., 2006) [38, 30], subsequent increases in speed have no effect on removal efficacy (Mishra *et al*., 2003) [31].

Type of operation

Type of operation (batch mode and continuous mode) has much influence on the biosorption process (uptake capacity and removal efficiency). Both batch and continuous mode has different dynamics.

Advantages of Biosorption Process; (Banat *et al*. 2007; Igwe and Abia 2006; Singh and Kausal, 2013) [5, 20, 42]

- Bioadsorption is a growth-independent process; non-living biomass not only removes pollutants, but also does not require expensive nutrients for cell growth in feed solution. Therefore, the disposal of metabolite products and nutrients is unnecessary.
- There are various sources of biomass which are easily available throughout the year e.g. agricultural wastes, pharmaceutical industry wastes, fermentation industry waste, food industry waste and house hold wastes. Biomass is low cost or zero cost because they are obtained from waste material.
- Biomass can be chemically pretreated to improve the metal ion removal efficacy.
- Both living as well as dead microbial biomass (Bacteria, algae, fungi and yeast) can be used for biosorption process.
- Due to the fact that nonliving detritus functions as an ion exchanger, biosorption is very rapid and takes only a few minutes to complete. Metal loading on empty binding sites are very rapid resulting in efficient metal removal.
- Different biomass have different metal removal capacity which depend on biomass type, preparation

type, pretreatment (physical or chemical) and type of metal ion in solution.

- No sludge production i.e. on problem of sludge disposal and secondary contamination of environment as occur in many techniques e.g. precipitation.
- Aseptic/sterile conditions are not necessary for biosorption. Several operating parameters, including pH, temperature, adsorbent dose, metal ion concentration, agitation speed, and contact time, are required.
- The desorption process can recover both metal and biomass if the metal ion concentration has a significant economic value. If enough detritus is present, it can be incinerated while carrying metal ions.
- Desorbed biomass can be used for number of cycles for biosorption.

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