Biosorption and Bioaccumulation: the Novel Metal Recovery Techniques

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Abstract
Biosorption and its more specific form, bioaccumulation, are the newly developed procedures for recovery of metals from aqueous environments which have considerable advantages in comparison with the classical separation methods. The affordable cost, biocompatibility, non-toxicity, high selectivity, large capacity and separation rate, high potential of recovery and reuse of biosorbent, the possibility to recover the adsorbed compounds as well as low sludge production rate are the main benefits of biosorption. In the current study, different perspectives of biosorbents classification are presented. The most common biosorbents are introduced and the main mechanisms involved in both biosorption and bioaccumulation processes are explained.

Keywords: Biosorption, Bioaccumulation, Biomass, Metal Recovery, Wastewater Treatment, Mechanism

Introduction
‘Sorption’ as a general word can be classified into two specified concepts: absorption and adsorption. Biosorption using various (micro)organisms and biomaterials is a newly developed subset of adsorption which can be utilized for selective uptake of ions or molecules [1]. Elimination of trace concentrations of toxic and radioactive metals such as cadmium, nickel and uranium from polluted waters and recovery of precious metals, sometimes in very low concentrations (ppb) are among the most important applications of this technique. Moreover, biosorption process is able to sorb both organic and inorganic materials from aqueous solutions [1]. Selectivity, adequate sorption capacity, recoverability, accessibility, strength and cost effectiveness are some of the most important advantages of using biomass as sorbents [2]. Besides biosorption, other biological processes like bio-oxidation, bio-reduction, bio-sedimentation, bio-leaching, bio-coagulation, bio-floatation and bio-accumulation are introduced and applied [3].

It is found that bacterial cells, various types of algae, fungi and yeasts, biological components such as crabshells, chitosan, plant fibers, different parts of living creatures’ bodies such as human hair and humic acid are biomasses which have been used as sorbent for elimination of a variety of metals. Regarding the high diversity of biosorbents in nature, more studies on the
type and structure of biosorbents are necessary to have a deeper understanding of biosorption mechanisms. The present work investigates and compares the different biosorbents and various mechanisms involved in this process.

**Biosorbents Classification**

In a general classification, biosorbents can be divided into two groups: dead and alive. The dead ones have the capability of long-term usage in biosorption and desorption cycles. They follow simpler mechanisms in the process with no environmental limitation for their growing. However, most dead biomasses have a relatively low mechanical strength and a powdery form with a very fine particle size which lead to a considerable loss of biosorbent mass during the recovery, and make it difficult to separate the biosorbent from treated solution [1]. In spite of such constraints, application of dead biomass in metal recovery/elimination is reported to be more successful as compared with alive ones [4].

From other perspective, all biosorbents can be basically categorized into two groups: cheap and expensive (Fig. 1). Almost all living biomaterials such as fungi, bacteria and also biosorbents directly obtained from environment and wastes, without applying any modification or combination methods, are placed in the low-cost group. However, using certain culture media and applying specific modification procedures in order to resolve shortcomings of primary biomasses increase the final cost of the biosorbent products. On the other hand, some biosorbents such as biopolymers and viruses may belong to both high-cost and low-cost groups depending on the type and specific conditions of production/growth.

![Fig. 1. Classification of biosorbents based on the final cost.](image)

Regardless of being dead or alive, or the cost, known and available biosorbents also can be classified into different groups, including bacteria, fungi, algae, plants, viruses and (micro)organisms byproducts which are explained in the following sections. Three types of the most common biomasses (Bacteria, Fungi and Algae) are explained in more details as follows:
-**Bacteria**

Some of the most crucial properties of bacteria as biosorbents are their small size, ability to grow under controlled conditions, stability over a wide range of environmental conditions and acceptable sorption capacity. However, their relatively low selectivity and lack of recoverability are considered as weaknesses [5].

-**Fungi**

Fungi can be classified into three main groups: molds, mushrooms and yeasts. From another perspective, fungi can be classified into two groups: micro (unrecognizable with naked eye) and macro. Ecofriendly, accessibility, bonding ability with metals (*via* various mechanisms) and selectivity are the most remarkable advantages of fungi [6]. Moreover, the enhanced sorption capacity resulted from the presence of different functional groups, simple and inexpensive culturing in a short period of time with high growth rate, non-pathogenic nature for most well-known fungal sorbents, and availability of various fungi (such as *Aspergillus niger*, *Saccharomyces cerevisiae* etc.) in industrial, food and fermentation wastewaters are the other advantages of this group of biosorbents.

-**Algae**

On the contrary of fungi that grow in dark places, algal cultures need to have special conditions for their well growth and propagation, e.g., sufficient light. Accessibility, high sorption capacity, no toxin production during photosynthesis and no need for large amounts of nutrients are among advantages of algal biosorbents. Another important feature of algae is their biocompatibility and producing environmentally useful compounds and byproducts during the biosorption processes. However, weak selectivity and difficult separation of sorbed metals from metal-laden cells are some of the weaknesses [7, 8].

Figure 2 shows the number of studies carried out in the field of biosorption of precious metals over the period of 2010 to 2018 by bacterial, fungal and algal biosorbents. According to the figure, the total number of studies (yellow curve) has raised up in the recent years.

![Fig. 2. The number of papers published in the field of precious metal biosorption from 2010 to 2018 (based on scholar.google.com).](image_url)

The other types of biomasses are plants, agricultural/food/industrial wastes, biopolymers such as chitin and chitosan, as well as viruses. Modified/hybrid biosorbents are also the more
advanced forms of biosorbents with enhanced characteristics (such as higher sorption capacity and selectivity) compared with the virgin ones. However, the modified ones usually impose higher costs on system. Some of the most successful and promising modification methods include physical and chemical modification, cell immobilization on inert support materials, trapping cell inside a polymer network (via chemical cross linking agents), magnetic modification, and cell modification during the growth (i.e., optimization of growth conditions and genetic engineering) [9, 10].

**Biological Sorption Mechanisms**

Generally, there are three main mechanisms for biological sorption of metals from aqueous systems including biosorption, intracellular sorption of metal ions, and chemical transformation of metal ions by microorganisms. Biosorption shows the highest elimination rate for metal ions uptake as compared with the other mechanisms.

Cells as the smallest part of alive/dead organisms play an important role in biological uptake processes. Cells structure is very complex and the shapes and types of cells affect the sorption process [11]. As it was explained previously, biosorbents are categorized into “dead” and “alive” ones, which can be classified further into “passive” and “active” types, based on sorption dependence on cellular metabolism. Sorption into “passive uptake” occurs on the cell walls via bonding with functional groups available on the surface or outside the cell. This type known as “biosorption” is not much dependent on cell metabolism and occurs in both dead and alive cells. Electronegativity of functional groups plays a more important role in biosorption than the cellular metabolism. It is established that the capacity of metal biosorption could be increased by an increase in the surface electronegativity. The known mechanisms for biosorption so far are as follows:

- Ion exchange
- Physisorption
- Precipitation (at micro-scale)
- Complexation (chelation)

Moreover, the mechanisms mentioned can take place both on the surface and outside the cell. In contrast, for metal sorption inside living cells, there would be a dependency on intracellular metabolic activities and diffusion energy of metals. This type of metal uptake occurs after saturation of cell surface; the whole process is called as “active uptake” or “bioaccumulation”. Therefore, bioaccumulation includes intracellular interactions in addition to all mechanisms that take place in passive uptake. In other words, bioaccumulation is a two-step process; the first one is irrelevant to cellular metabolism followed by a cellular metabolism-dependent step. Certainly, active uptake only occurs in alive cells with participating all internal parts of cell, outer membrane and cell wall in metal uptake [11, 12]. It can be claimed that in bioaccumulation, metal ions first get close to the surface of living cells and then are sorbed by functional groups available on the outer membrane or cell wall (passive uptake). After the whole cell surface is covered, a fraction of accumulated metals transfers into the cell via “membrane transport mechanism” (active uptake). Finally, under favorable growth conditions, the available surface area of the biomass would increase, and therefore, the amount of sorption would be raised. Because of complexity of mechanisms involved and dependence on multiple factors, the exact mechanisms of sorption are not possible to be explained clearly in many cases. Since viruses do not have any cell wall, no internal sorption occurs. Therefore, despite some similarities, their sorption mechanisms are very different from other biosorbents.
All mechanisms involved in biosorption and bioaccumulation along with where they occur are shown in Fig. 3.

**Fig. 3.** All mechanisms involved in biosorption and bioaccumulation including: step 1: metal ions in the solution bulk (mass) keep in contact with biosorbents (dead or alive). Based on the system (biosorbent/metal ion), biosorption might occur via precipitation outside the cell. Step 2: metal ions diffuse into the liquid film and sorbed to the sorbent through one of the biosorption mechanisms, i.e., microprecipitation, physisorption, ion exchange and complexation. Step 3: for living cells, uptake can be followed by bioaccumulation and transport across cell membrane. However, the occurrence of this phenomenon also depends on temperature, pressure changes and metabolic inhibitors as well.

Transport across cell membrane is a mechanism leads to bioaccumulation inside the living cells and usually occurs in three successive steps: metal ions first get close to the outer membrane of the cell, then attach to the inner membrane and finally transport into the cell or cytoplasm. Due to the significant role of intracellular metabolism besides the cell membrane, this mechanism is more complex than the other aforementioned mechanisms [11]. Based on the definition for “active uptake”, transport across the cell membrane (or entrapment in the inner space) can only take place in living/growing cells. To our knowledge, two ways have been suggested for the entrance of metal ions into the cell: direct transport (energy-dependent) and indirect transport (via ligands). Therefore, energy is a necessary factor for direct transport across cell membrane. Precious metal transport across cell membrane is probably similar to the transportation of essential cellular metabolic ions (such as sodium, potassium and magnesium). Metabolic ion transport is carried out via some pumps (sodium and potassium) in cell membrane that provide the energy required for transportation [13]. This route is not well-known due to scarce information; however, the undeniable role of proteins is established. On the other side, for indirect transport, transfer of metallic ions into the cell is carried out via ligands such as phosphate, peptides and amino acids. After passing the metal ions across the membrane and transport into the cytoplasm, based on the type of metal ions, microorganisms
interact differently. Some of the known reactions are accumulation, precipitation, efflux, redox, repair and metabolic by-pass.

Conclusions
The present study introduced biosorption and bioaccumulation as two novel and different metal recovery methods from wastewaters. Dead and alive cells can participate in biological sorption lead to different types of sorption: passive and active uptake. Biosorption occurs on the cell walls via bonding with functional groups available on the surface or outside the cell (passive uptake). Bioaccumulation is a two-step process with the first one irrelevant to cellular metabolism (passive) followed by a cellular metabolism-dependent step (active). The main mechanisms in each type of sorption are introduced. Different classifications of biomasses used for biological sorption are studied and explained.

References