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Biosorption

Edited by Jan Derco and Branislav Vrana

BIOSORPTION

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Meet the editors

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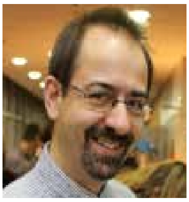

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Contents

Preface

This edited volume is a collection of reviewed and relevant research chapters concerning the developments within the chemical, biochemical, and environmental fields of study. This book includes scholarly contributions by various authors and is edited by experts pertinent to chemical engineering. Each contribution comes as a separate chapter complete in itself but directly related to the book's topics and objectives.

This book contains five chapters. It will be of interest to operators of wastewater treatment plants and sludge treatment and disposal facilities as well as to researchers and university students in the field of environmental engineering.

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Chapter 1

Introductory Chapter: Biosorption

Ján Derco and Branislav Vrana

Additional information is available at the end of the chapter

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1. Introduction

Water quality policy over the world concerning trace pollutants is defined by environmental quality standards expressed in terms of concentrations in water (Canadian Environmental Quality Guidelines (CEQGs); EU [1, 2]), guidelines (CEQGs; (Environment Canada [3])), ambient water quality criteria (United States Environmental Protection Agency (US EPA), n.d. [4]), and peer reviewed literature on thresholds for effects on aquatic biota (e.g., No observable effect concentrations (NOECs); lowest observable adverse effects) is a major driver of continuing interest in these measurements as part of risk/exposure (Lepom et al. [5]) as well as trend assessments (Fliedner et al. [6]).

In Europe, the adoption of the water framework directive (WFD) [7] provides a policy tool that enables sustainable protection of water resources. WFD presents a positive example of complex legislative in water quality protection.

The Decision No 2455/2001/EC of the European Parliament and the Council of November 2001 [8] established the list of 33 priority substances or group of substances, including the priority hazardous substances, presenting a significant risk to water pollution or via the aquatic environment including risks to waters used for the abstraction of drinking water.

The WFD daughter Directive 2013/39/EU [1] extended the list of priority substances to 45, including priority metal species cadmium, lead, mercury, and nickel. It also stresses the need for the development of new water and wastewater treatment technologies to address the problem of pollution by priority and river basin specific pollutants.

Nowadays, micropollutants occurring in the environment are considered to be a serious problem [9]. Aquatic environment is polluted by a broad range of these compounds from various sources including industry, agriculture, and municipal wastewaters. Many of those compounds are present at low concentrations in the environment, but they still pose and

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toxic effects to aquatic organisms, and human health. Their efficient removal from water and reduction of risk presents a new challenge for water managers and development of new water treatment technologies present a challenge for the scientific community [10].

The most problematic micropollutants in waters are heavy metals, pesticides, industrial chemicals and byproducts, personal care products, pharmaceuticals, and other substances that can be toxic to wild animals and humans at low concentrations. Currently, available wastewater treatment technologies are often expensive or ineffective [11]. Research results confirm that large amounts of conventional waste, including egg shells, bones, peat, mushroom, seaweed, yeasts, and carrots [12, 13] show the ability to effectively remove heavy metals from pickled water.

Biosorption refers to a set of processes that involve physical and chemical adsorption, ion exchange, electrostatic interactions, complexation, chelation, and microprecipitation, that occur in the cell wall and precede the anaerobic or aerobic biodegradation processes. It is characterized by high selectivity and efficiency (high performance and low cost). Natural materials, such as marine algae or weeds, or industrial waste, such as excess activated sludge or fermentation wastes, may be used as biosorbents.

Biological sludge wastewater treatment processes utilize biosorption and bioaccumulation as part of organic and inorganic pollutants, priority substances, heavy metals, and organic pollutants/micropollutants removal mechanisms.

The idea of using biomass in technologies to protect the environment originates at the early twentieth century when Arden and Lockett found that some species of living bacteria are capable of removing nitrogen and phosphorus from wastewater during aeration [14–16]. This process is known as activated sludge process. The removal mechanism has been explained in the context of bioaccumulation capacity. This phenomenon as well as the activation process itself has continued to be widely used. The break occurred in the late 1970s of the last century. Knowing the sequestration nature of biologically inactive biomass has led to a shift in research from bioaccumulation to biosorption [17].

The interest in biosorption of organic and inorganic pollutants stems from the fact that these substances are toxic and can destabilize the food chain [18]. The absorption of substances by microbial biomass is generally referred to as biosorption. The mechanism responsible for this accumulation is complex and includes, among other processes, adsorption to the cell surface and/or absorption of the substances into various compartments of the microbial cell. Microbial cells have a disposition to concentrate chemicals from the aquatic environment. Therefore, it is necessary and important to understand the mechanisms and kinetics of biosorption, bioaccumulation and biodegradation processes, and their interactions that govern the fate of hazardous inorganic and organic pollutants in biological treatment of wastewater.

2. Mechanisms and kinetics of biosorption

2.1. Biosorption and bioaccumulation

Biosorption is a physicochemical process that utilizes the mechanisms of absorption, adsorption, ion exchange, surface complexing, and precipitation processes. It is a spontaneous process independent of the metabolism of microorganisms. In biotechnology, it is used to separate inorganic and organic substances from the solution using biosorbents. Biosorption is an important process also in protecting the environment.

Biosorption is defined as the passive adsorption of toxic substances by dead, inactive or biologically derived materials. Biosorption is a consequence of several metabolic processes independent of the cell membrane, the mechanisms responsible for the absorption of the pollutant vary according to the type of applied biomass.

Bioaccumulation is defined as the phenomenon occurring in living organisms. More specifically, bioaccumulation is defined as the absorption of toxic contaminants by living cells or organisms. Compounds are passively or actively transported into cells, accumulated inside them, and they also enter the metabolic cycle through the cell membranes. Bioaccumulation is therefore often dependent on cell metabolisms.

Both bioaccumulation and biosorption have certain advantages and disadvantages. In general, the use of living organisms is not suitable for continuous water purification processes from highly toxic organic/inorganic contaminants. If the concentration of the toxic substance is too high or the process step takes a long-time period, the accumulated substance quantity may reach partition equilibrium, or saturation. Due to the high accumulated pollutant concentration the metabolism of the organism will be disturbed and death may occur. This scenario can be avoided by using inactive, dead biomass. Moreover, if the sorption process is reversible, compounds may be desorbed back to the treated water if the concentration drops. To avoid desorption, a high sorption capacity has to be provided. This is not always feasible in processes applying living cells, because of various restrictions such as requirements of nutrients, aeration, maximum cell density, and so on. This is why we devote more attention to biosorption than bioaccumulation.

2.2. Mechanisms of biosorption

Biosorption of heavy metals and organic compounds occur due to the physicochemical interactions between the metal and the functional groups present at the surface of the biosorbent. The processes involved include physical adsorption, ion exchange, and chemical sorption that are not related to metabolism. The cell walls of microorganisms consist mainly of polysaccharides, proteins and lipids and have carboxyl, sulfate, phosphate and amino groups to form bonds with metals, and their complexes. Such biosorption occurs relatively rapidly and can be reversible [19]. Various mechanisms of removal of heavy-metal by activated sludge microorganisms are discussed in more details e.g. by Pagnanelli et al. [20].

Organic pollutants differ significantly in their structure. As a result, biosorption is affected by molecule size, charge, solubility, hydrophobicity, and reactivity. The biosorbent process can also significantly influence the type of biosorbent and the composition of wastewater [21].

The lipophilic nature of the hydrophobic compounds allows them to pass through cell membranes and absorb into the organic cell matrix. An important component of biosorption of organic pollutants may be absorption in cell membranes or lipid containing cell structures. Other mechanisms are involved in biosorption include surface adsorption, chemisorption, and complexation [22]. For more detailed information we refer the reader to the work Fomina and Gadd [21].

2.3. Modeling of biosorption

The equilibrium distribution of the sorbed pollutant (sorbate) between the sorbent and the aqueous phase is required to determine the maximum sorbent's uptake capacity for a sorbate and to understand the sorption mechanism.

Besides sorbate distribution at equilibrium, the sorption kinetics provides additional important information about the sorption mechanism, especially the rate of pollutant removal. When applied in water treatment technology, information on sorption kinetics is important for setting an optimum residence time of the wastewater at the biosolid phase interface.

2.3.1. Adsorption isotherms

To describe the concentration-dependent equilibrium between the pollutant amount adsorbed on the cells (a) and the pollutant concentration dissolved in aqueous solution (C_e) at equilibrium conditions and constant temperature, which is referred to as the adsorption isotherm. Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, Brunauer-Emmett-Teller (BET), and Radke-Prausnitz models are the most frequently cited literature in the literature [23–26].

When sorption equilibrium is reached, the adsorption capacity can be calculated from mass balance in a batch sorption system consisting of a discrete volume of water and adsorbent:

$$a = \frac{V}{m}(C_0 - C_e) \tag{1}$$

where a is the sorption capacity (kg.kg^{-1}), V is the volume of water/wastewater (m^3) treated in a single sorption step, m is the mass of the adsorbent (kg), C_0 and C_e are the initial and equilibrium aqueous adsorbate concentration (kg.m^{-3}), respectively.

Most often, pollutant distribution is concentration-dependent and in such case non-linear forms of adsorption isotherms are used to describe experimental data resulted from batch adsorption measurements. Langmuir isotherm is defined assuming that adsorption takes place at specific homogeneous sites at the surface of the adsorbent. This means that once the molecule of the adsorbed substance occupies a sorption site, no further adsorption can occur at this site. The Langmuir adsorption isotherm [23] has the form:

$$a = \frac{a_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \tag{2}$$

Where a_{max} (kg.kg^{-1}) is the maximum biosorbent capacity of the adsorbent in the formation of a saturated monomolecular adsorption layer and b (L.kg^{-1}) is Langmuir's empirical constant associated with the free energy of biosorption.

Freundlich's isotherm [24] was postulated for adsorption at heterogeneous surfaces and it takes the form:

$$a = k \ . \ C^{1/n} \tag{3}$$

where k (L.kg^{-1}) is a Freundlich constant referring to biosorbent capacity and n (dimensionless) is a Freundlich constant indicating the intensity of biosorption. Freundlich isotherm does not take into account the saturation of biosorbents.

Tempkin isotherm [25] assumes that biosorption energy decreases linearly with increasing saturation of biosorption sites, rather than decreasing exponentially, as Freundlich isotherma suggests. Tempkin isotherm is given as follows:

$$a = \frac{R \ . \ T}{b_{Te}} \ . \ ln\left(a_{Te} \ . \ C_e\right) \tag{4}$$

where a_{Te} is the Tempkin isotherm constant, b_{Te} is the Tempkin constant referring to the biosorption energy, R is the universal gas constant (8.314 J.mo^{l-1}.K^{-1}), T is the thermodynamic temperature (K), and C_e is the equilibrium pollutant concentration in solution.

BET (Brunauer, Emmett, and Teller) isotherm is described by the following equation [26]:

$$a = \frac{a_{max} \ . \ d \ . \ C}{\left(C_e - C\right) \ . \ \left(1 + (d-1) \ \ . \ C/C_e\right)} \tag{5}$$

where C_e is the equilibrium concentration of adsorbate (kg.m^{-3}), d is the constant expressing the energy of sorbate interaction with the sorbent surface.

2.3.2. Kinetics of adsorption

A pseudo-first order model [27] and the pseudo-second order kinetic model [28] can be applied to fit the experimental data and evaluate the adsorption kinetics.

The Lagergren pseudo-first order model suggests that the rate of sorption is proportional to the number of sites unoccupied by the solutes. The pseudo-first order model can be written in linearized form as follows:

$$a_t = a_e\left(1 - exp\left(-\mathrm{k}_1 \ . \ t\right)\right) \tag{6}$$

where a_e is the amount of pollutant biosorbed at equilibrium (mg.g^{-1}), a_t is the amount of pollutant biosorbed (mg.g^{-1}) at any time t, and k_1 is the first order rate constant (min^{-1}).

The pseudo-second order kinetic model can be written in linearized form as follows:

$$a_t = a_e\left(\left(1 - \frac{1}{1 + a_e . \ k_1 \ . \ t}\right)\right) \tag{7}$$

where k_2 is the second order rate constant (g.mg^{-1}.min^{-1}).

The pseudo-second order model does not identify the diffusion mechanism.

From the majority of biosorption-related work, it follows that the pseudo-first order equation does not describe well-meaning values throughout the contact time. Generally, this equation is only applicable in the initial phase of the adsorption process. This is due to the fact that, using the linearized form of Eq. (6) it is necessary to know the value of the equilibrium adsorption capacity, which can be approximated by the extrapolation of experimental data for infinite time, i.e., the trial and error method. On the other hand, it is not necessary to know this value for the use of the linearized form of the kinetic equation of the pseudo-second-order.

In this context, it should be emphasized that using a non-linear method of determining the values of parameters of non-linear equations in general it is possible to avoid such errors in the modeling of process kinetics.

3. Biosorbents

For several decades, biosorption has been referred to as perspective, low-cost biotechnology applicable in wastewater treatment. However, despite intensive research, significant advances in the knowledge of these complex processes and rich magazines and book publications, the practical application of this process and related technologies are not adequate so far [20].

Previous research has focused on testing the development of more suitable and available biological materials. The biosorbent materials used may be alive or deactivated microorganisms and their components, plant materials, industrial and agricultural wastes, and natural processing residues, e.g. wood, wood bark, and sea algae.

Both live and dead biomass can be used to remove hazardous substances. The inactive (sterilized, dried, and/or otherwise chemically treated) biomass benefits from no need of supplies of substrate, nutrients, eventually oxygen, which would otherwise be needed in order to maintain viable biomass during adsorption. Also, the toxicity of pollutants to be removed by biosorption poses no problem.

Biosorbents for the removal of toxic metals or organic pollutants mainly use biomass of bacteria, yeasts, fibrous fungi, algae, as well as wastes from food and pharmaceutical production, agricultural waste, and other polysaccharide materials. All biomaterials should demonstrate good biosorption capacity and affinity for all types of inorganic ions and organic compounds.

Important biosorbents of the fungus family include the filamentous fungi of the genus *Alternaria, Aspergillus, Rhizopus, Penicillium,* and the yeast *Saccharomyces cerevisiae* and *Saccharomyces carlsbergensis*. These microorganisms are widely used in the food and pharmaceutical industry and end up as waste that is available from individual free or low-cost production. Another important biosorbent to which attention is focused are marine algae, which are also biological resources. The algae include red, green and brown algae, with brown algae being among the excellent biosorbents, for example, *Chlorella vulgaris*.

This is due to the alginate content that is present in the form of gel in the cell walls. The macroscopic structure of the algae provides a conventional basis for the production of biosorbents suitable for the application of sorption processes. It should be noted that algae are not considered waste; in fact, they are the source for the production of agar, alginate and, carrageenan. This means that the choice of algae for biosorption purposes needs to be given the utmost attention.

Scientists work mainly with brown algae using one of the best metal sorbents seaweed, Sargassum seaweed. They focus on the study of sorption properties and biosorption mechanisms. Biosorbents using algae, bacteria, fibrous fungi, and yeasts are also used for analytical techniques, specifically for solid phase extraction to determine metals present in trace amounts in different aqueous matrices [29].

Microbial biomass (bacteria, fungi, and micorrhagia) shows better results of biosorption of dyes than macroscopic materials (seaweed, squirrel crabs, etc.). The reason is the difference in cell wall and functional groups involved in dye binding. Many bacteria, fungi, and microorganisms bind different types of dyes.

The results of the study by Simionato et al. [9] show that the use of chitosan obtained from silkworm chrysalis is a viable alternative for the removal of blue remazol and black remazol five dyes from the wastewater of the textile industry. Potential biosorbents belonging to the class of bacteria include *Bacillus, Geobacillus, Lactobacillus, Pseudomonas, Streptomyces, Staphylococcus, Streptococcus,* and others.

Several studies have recently been carried out to develop cheap sorbents from industrial and agricultural waste. Partial attention was paid in particular to crab shells, activated sludge, rice husks, egg shells, mosses, and lichens. The results showed that, in particular, crab shells have excellent sorption abilities in relation to arsenic, chromium, cobalt, and nickel.

A preferred biosorbent material is activated sludge. There are a large number of binding sites on the cell walls of microorganisms, which are predominantly composed of polysaccharides, proteins, and lipids. This is due to the high biosorption capacity of activated sludge. The amount of excess sludge produced mostly outweighs the possibilities of its use and represents one related problem of wastewater treatment. Thus, this biosorbent is reely available and low-cost.

Authors [30–32] disclose the advantages of using aerobic and anaerobic deactivated sludge to remove dyestuffs and hazardous effluent from wastewater. Qiu et al. [33] presented the results of research into the use of active aerobic and anaerobic sludge for sewage treatment.

The extent of biosorption depends on the type of biomass [34]. In the past, biosorbent phenomena have often been found to bioaccumulate highly hydrophobic organic substances directly depending on the lipid content of biomass. However, non-polar substances have been found to accumulate in organisms according to the distribution equilibrium between the medium and the lipid content of the organism [35]. Other authors found the opposite phenomenon to track DDT [Dichloro-Diphenyl-Trichloroethane or 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)-ethane] adsorption by different soil fractions [36]. Some soil fractions were first extracted with ether and ethanol to remove lipid-like substances. Absence of lipid-like materials did not decrease, on the contrary, increased DDT adsorption with soil, indicating that other substances other than lipids may also play a role in biosorption. A similar finding was obtained by monitoring the adsorption of chlorites with microbial biomass [37]. Bacterial biomass with the highest lipid content among the observed samples had the lowest biosorption capacity. Further, it has been found that in different samples of fibrous fungi biomass, despite the similar lipid content in the cells, the biosorption capacity varied within a wide range. Interestingly, however, it was found that the biosorption capacity of different biomass samples depended directly on the amount of total organic carbon released during the contact of biomass with the pollutant. However, this phenomenon is not elucidated, it can only be assumed that the biosorption capacity increases with the growing proportion of cells destroyed in the medium, which correlates with the total organic carbon content released into the medium. Cell fragments have a larger surface and thus a higher sorption capacity [38]. The authors further found that the biosorption capacity of active and deactivated (inactive/dead) biomass is almost the same for highly biodegradable pollutants.

4. Research and applications of biosorption

4.1. Removal of organic pollutants

Biosorption acquires meaning for the removal of hazardous substances. It can be used as an individual separation process or may be a part of others, biological processes. Aksu, in the review paper [39], deals with the application of biosorption to remove organic pollutants. Among the studied pollutants are pesticides, phenols that are toxic and persistent in the environment.

Various types of pesticides are used in agriculture. Some of them are persistent, have mutagenic and carcinogenic effects, and are generally toxic. Suitable sorbent for removing them appears to be activated carbon. Its disadvantage is the high price. Regeneration of granular activated carbon is also costly.

This has motivated researchers to explore the possibility of using alternative materials that originate in nature or are the waste of other processes, peat, soil, wood, eucalyptus bark, rice husk, chitin, fly ash, or surplus activated sludge. These are relatively inexpensive materials but are usually characterized by low adsorption power values. This disadvantage can be compensated by larger amounts of adsorbent [40, 41]. An alternative for the recovery and/or environmentally acceptable disposal of pollutants could be, passive adsorption of pollutants from aqueous solutions using a renewable non-living microbial mass. The specific surface properties of bacteria, fungi, yeasts, and algae allow the adsorption of various types of pollutants from solutions. More advantageous is the use of inactivated microorganisms. They are not dependent on creating conditions for maintaining metabolic function, including eliminating the effects of toxic substances. They can be stored for a longer period, easily regenerated and reused [39].

The biosorption mechanism on inertial biomass is influenced by the biomass itself, the properties of its surface characteristics, the physical and chemical properties of the adsorbed substances, their mutual affinities, and experimental conditions (pH, temperature, ionic strength, existence of competing organic substances or inorganic ligands in solution).

Conversely, due to the fact that hydrophobic organic pollutants show a high tendency to accumulate on microbial cells or sludge, living biomass can be used to remove very low concentrations of hazardous organic substances from wastewater [42, 43].

Most dyes are of synthetic origin. They are characterized by an aromatic structure, greater stability, and a worse biodegradability. They can affect the processes of photosynthesis in the aquatic environment to toxicise the aquatic ecosystem [44, 45]. Research results [44–46] show that there is a wide range of microorganisms, including bacteria, fungi, and algae, which are capable of biodegradation or bioaccumulation of azo dyestuffs in wastewater by anaerobic/aerobic processes.

For the modeling and optimization of processes using sorption on the activated sludge, the necessary is knowledge about the sorption of organic matter to the sludge. Modin et al. [47] compares primary, anaerobic, and aerobically activated sludge as biosorbent materials. Biosorptive capacity values were determined, process kinetics was studied, and some characteristics of sorbed organic matter were studied. Biosorption of dissolved organic substances occurred almost immediately. This was followed by a slower process that corresponded to first-order kinetics. Biosorption of undissolved particles also corresponded to first order kinetics. However, there was no immediate sorption, but the particles were released during mixing.

Biosorption is used for wastewater treatment since the beginning of the last century, when the activation process was discovered. Controlled withdrawal of excess sludge together with significant participation of biosorption a bioaccumulation processes enable intensification of organic pollutants, nitrogen, and phosphorus removal. Bioaccumulation is usually an active process that is part of the metabolism of microorganisms. Biosorption is a passive process of adsorbing pollutants on the surface of microorganism cell walls. This leads to a decrease in the concentration of these substances in the purified water. However, such contamination remains a part of the activated sludge and its re-release to the environment is dependent on further treatment with the excess sludge produced, especially if the biosorption of these substances is reversible.

An increasingly serious challenge is dangerous (organic) and so-called emerging pollutants, e.g. pesticides, estrogens, personal care products, or pharmaceuticals. These can be removed in the wastewater treatment plant by biotic and abiotic processes, or they can pass through the sewage treatment plant to the recipients without any significant change. In the context of minimizing the production of excess sludge, its disintegration prior to the process of biological stabilization and degradation of biosorbable pollutants on activated sludge, the combined processes of biosorption and chemical oxidation, e.g. using ozone.

The solubility of the pollutant is an important property affecting biosorption. The inverse relationship between water solubility and accumulation of organic molecules with biomass was found [9]. In general, the different types of biomass observed had a greater biosorption capacity for less soluble pollutants. Organic molecules accumulate better in microbial biomass, the higher the biomass-water distribution coefficient (octanol-water model system), but as already mentioned above, there is no direct correlation between biosorbent capacity and lipid content in biomass.

If the contaminant dissociates in the aqueous phase (on a weak acid or a weak base), sorption of the dissociated and non-dissociated forms can take place with different sorption coefficient values for both forms [15]. The effect of the initial concentration of the pollutant on the rate of biosorption was monitored. After 10-fold increase in the initial concentration of the pollutants studied (lindane pesticides and diazinone), the rates of biosorption of these substances on activated sludge were higher for higher concentrations of pollutants.

It can be assumed that in a system containing a mixture of several pollutants of a similar nature, the biosorption capacity of the individual components of the mixture will be affected by the concentration of the other substances in the mixture. A reduction in biosorbent capacity of tetrachloroethane on the *Rhizopus arrhizus* biomass has been shown to be up to 14% in the presence of the same concentration of trichloroethane [13]. Biosorption is usually an exothermic process, so biosorption capacity usually increases with decreasing temperature. However, the change in temperature does not significantly affect the rate of biosorption [8].

Simjonato et al. [9] studied the process of adsorption of blue remazol and black remazol five dyes with chitin and chitosan, which they performed in the column and an aqueous suspension. The results show that better results were obtained in the column with arthritis than in the chitin-packed column. Comparing the results measured in the column and suspension results in better suspension results. A very good description of Langmuir isothermal experimental values was obtained, with the difference between the measured and calculated adsorption capacity values being insignificant.

Biosorption of hazardous pollutants is a suitable technology for removing dyestuffs from municipal and industrial wastewater. Various low-cost biosorbents, such as, for example, biomass of algae, yeast, fungi, vegetable waste, fiber, fruit waste, chitosan, and agricultural waste were studied [48].

4.2. Removal of heavy metals

Biosorption and bioaccumulation can also be applied to remedy environments contaminated with heavy metals as complementary methods to currently used physical and chemical methods. It was found that removal of heavy metals from the environment with biotechnological methods should consider a number of physicochemical factors such as temperature, pH, contact time of biomass, and a solution containing metals, concentration and age of biomass, and toxicity when living microorganisms are applied. Improving the efficiency of removal of metals can be performed through physical and chemical modifications and immobilization of biomass. The most frequently applied reactors include stirred tank reactors, fixed-bed, reactors and fluidized-bed reactors [49].

In the process of biosorption, ions of metals are adsorbed on the surface of a sorbent. Biosorption is a metabolically passive process that uses dead biomass. Biosorption is the first step of bioaccumulation [49].

Environmental pollution of heavy metals is one of the most serious environmental problems. Various biosorbents such as fungi, yeast, bacteria, and algae are used to remove them. These biomaterials are considered to be cost-effective for high-volume and low-heavy wastewater treatment (from 1 to 100 mgl^{-1}). The promising biomaterials for heavy metal removal include *Saccharomyces cerevisiae* fungus. This fungus is commonly used in food and beverage production. Low-cost media is sufficient to cultivate it. It is a by-product/waste from the fermentation industry.

Mustapha and Halimoon [19] examined the microorganisms and mechanisms of heavy metal biosorption in the environment.

Bacterial biosorption is mainly used to remove pollutants from wastewater contaminated by pollutants that are no1t biodegradable, such as metal ions and dyes [19]. Rats are efficient and inexpensive biosorbents, because the requirement for algal nutrition is low. Based on a statistical analysis of algae potential in biosorption, algae were reported to absorb about 15.3–84.6%, which is higher than other microbial biosorbents. All types of brown algae were known to have a high absorption capacity. The metal ion biosorption occurs on the cell surface using the ion exchange method. Brown marine algae have the ability to absorb metals through chemical moieties on their surface such as carboxyl, sulfone, amino, as well as sulfhydryl [19].

The use of fungi as a biological sorbent has been shown to be an effective material, and is also one of the cost-effective and environmentally friendly methods that serve as an alternative to the chemically bonded processing process. The ability of many types of fungi to produce extracellular enzymes to assimilate complex carbohydrates for previous hydrolysis causes the degradation of various degrees of pollutants. Compared to yeast, fibrous fungi are less sensitive to nutrient sweeps, aeration, pH, temperature, and have a lower content of nuclei in biomass [50, 51].

Microbial biomass is one of the cheap and effective biosorbents for removing heavy metals from solutions. The biosorption process has many attractive properties including the removal of metal ions in a relatively wide range of pH and temperature. Many researchers have studied the biosorbent performance of various microbial biosorbents that provide good arguments for introducing biosorption technologies for removing heavy metals from solutions, as well as understanding the mechanism responsible for biosorption [19].

4.3. Removal of micropollutants

The large occurrence and presence of micropollutants (MPs) in the aquatic environment is one of the major challenges worldwide. For example, in 2012, some 143,000 compounds were registered on the European market, many of which at some point in their life cycle would end up in the aquatic environment. Most of them are not removed or transformed into conventional wastewater treatment plants (WWTPs), they can persist in the aquatic environment or create new chemicals by reaction with humic substances and sunlight, and they can be bioactive and can bioaccumulate [52–56].

Although present in almost undetectable (ppb; part per bilion) concentrations, their presence in the aquatic environment is associated with various deleterious effects in organisms such as estrogenicity, mutagenicity, and genotoxicity [57].

There is no legal regulation for removing MPs in WWTPs. However, there are some (EU) regulations that set limit values for certain substances that have specific MP properties, pesticides, lindane, nonylphenol, and synthetic hormones [58] in water.

MP can be divided into several categories such as pharmaceuticals personal care products (PPCP), household chemicals and industrial chemicals. A comprehensive list of 242 chemicals is included in the EU 7PP [59] project of which approximately 70% are pharmaceutical and personal care products, and 30% are industrial products, including perfluorinated compounds, pesticides, herbicides, and food additives.

The vast majority of MP in municipal wastewater belongs to the class of personal hygiene drugs and products PPCP, the fate and processes for removing these compounds are discussed in detail in this text.

About 70% of the wastewater products come from the household, 20% come from livestock, 5% come from hospital wastewater, and the remaining 5% come from outflows from non-specified sources [60].

The removal of micropollutants in wastewater treatment plant depends on their solubility, octanol/water partition coefficient, and Henry's constant. For removing micropollutants in wastewater treatment plants significantly contributes their sorption on suspended particles of primary and secondary sludge. Removal of dissolved organic compounds also involves coagulation, flocculation and biodegradation processes. The majority of conventional wastewater treatment plants do not completely remove these substances. Their removal is influenced significantly by the operational conditions, the biochemical environment (aerobic, anaerobic, anoxic, sludge age (SRT), temperature, pH, and redox potential.

4.4. Biosorption in municipal wastewater treatment

Biosorption and bioaccumulation mechanisms continue to play an important role in newly developed processes and technologies for wastewater treatment.

The fate of the priority substances and micropollutants that are transported by wastewater to wastewater treatment plants (WWTPs) depends on their adsorption on suspended particulates, dissolved humic substances, primary and secondary sludge. Adsorption of insoluble matter in primary and secondary treatment units is an important process of MP removal from wastewater. Adsorption may occur as a result of hydrophobic interactions between aliphatic and aromatic groups of lipid fractions in the primary sludge and the lipophilic cell membrane of the microorganisms in secondary sludge. Interactions also occur between positively charged MP groups and negatively charged microorganisms in secondary sludge.

4.4.1. Integrated and hybrid processes

Both the development of the activated sludge process and the increasing wastewater pollution are also developing biosorption applications. It is, for example, hybrid activated sludge process with activated carbon. Interaction of bio-degradation and adsorption on activated carbon benefits from the higher efficiency and performance of the process due to the concentration of organic matter on activated carbon, consequently higher rates of biological oxidation, as well as better conditions for the degradation of resistant substances, especially for industrial wastewater treatment and groundwater remediation.

In the 1950s of the last century, the activated sludge process with separate sludge regeneration was put into full-scale operation, where the ability to accumulate a substrate was restored. In addition to reducing the volume of aeration tank required and reducing investment costs, this bioreactor configuration is characterized by a high resistance to filamentous sludge bulking. The above mechanisms are also used as part of enhanced biological phosphorus removal processes [14–16].

In a hybrid system, slow and fast biodegradable substances and simultaneous macronutrient removal processes can be carried out by combined activated sludge and immobilized biomass [61]. Higher biomass concentrations and two different solid retention times significantly influence biosorption/bioaccumulation processes and ultimately, their participation in the whole complex of the biological wastewater treatment.

Biosorption and biodegradation also increase the efficiency of anaerobic sludge stabilization. Current research is mainly focused on increasing the efficiency of sludge stabilization. It is also focused on the research of anaerobic decomposition of micro-pollutants. However, there is little information and knowledge about biosorption potential and biosorption mechanisms of these substances. Information on pollutant biosorption on anaerobic sludge is important not only for the removal of pollutants themselves but also for the modeling of biological sludge stabilization systems [33].

Accumulation of dangerous hydrophobic organic pollutants, e.g. in activated sludge biosorption results in their removal from the wastewater stream, but the resulting disposal of contaminated sludge then poses a new environmental problem, especially when pollutants are bound to microbial sludge reversibly [33]. Reduction of sludge mass during stabilization leads to concentration of accumulated compounds, but potentially also to increase of their chemical activity as a result of reduction of sludge sorption capacity in the stabilization processes. This may lead to an increased risk related to compounds sorbed to the stabilized sludge.

However, such contamination remains a part of the activated sludge. Its release to the environment is dependent on further treatment with the excess sludge produced, especially if the biosorption of these substances is reversible.

One of the current trends in the sludge management and the minimization of the release of priority substances and micro-nutrients through the application of the sludge in agriculture is the research of integrated biological and chemical processes to minimize the production of excess sludge and carry out the simultaneous transformation/degradation of micropollutants sorbed on activated sludge [62–63].

5. Conclusions

The past decades brought intensive research leading to an understanding of biosorption processes with the aim of their application in water treatment technology t. Numerous papers were published that significantly contributed to a better characterization of complex phenomena involved in biosorption. Information was gathered on the bioprocess mechanisms and the influence of various factors in the removal of inorganic and organic pollutants by biosorption.

In spite of targeted research on alternative low-cost sorption materials and extensive knowledge and publication results, it was not possible to apply this process practice in great extent, so far.

Further research into the practical use of biosorption to remove specific organic and inorganic pollutants will obviously be geared toward increasing the overall efficiency of the process, not only in terms of cost but also its performance.

The importance of sorption and biosorption processes in wastewater treatment processes and technologies, aerobic and anaerobic sludge stabilization is increasing. New development trends include integrated and hybrid processes aimed at minimizing sludge production and preventing the release of priority substances and micropollutants into the environment through the application of sludge to the soil.

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References

[1] 1EU. Directive 2013/39/EU of the European Parliament and of the council of 12 august 2013 amending directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union. 2013;**L226**:-17

[2] EU. Directive 2008/105/EC of the the European parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy. Official Journal of the European Union. 2008;**L348**:84-96

[3] Environment Canada. 2014. Canadian Environmental Quality Guidelines [WWW Document]. Can. Counc. Minist. Environ. URL https://www.ccme.ca/en/resources/canadian_environmental_quality_guidelines/index.html [Accessed: 3-2-2018]

[4] US EPA. n.d. National Recommended Water Quality Criteria [WWW Document]. URL https://www.epa.gov/wqc/national-recommended-water-quality-criteria [Accessed 3-2-2018]

[5] Fliedner A, Lohmann N, Rüdel H, Teubner D, Wellmitz J, Koschorreck J. Current levels and trends of selected EU water framework directive priority substances in freshwater fish from the German environmental specimen bank. Environmental Pollution. 2016;**216**:866-876. DOI: 10.1016/J.ENVPOL.2016.06.060

[6] Lepom P, Brown B, Hanke G, Loos R, Quevauviller P, Wollgast J. Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European water framework directive. Journal of Chromatography. A. 2009;**1216**:302-315. DOI: 10.1016/j.chroma.2008.06.017

[7] Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for community action in the field of water policy. Official Journal of the European Communities. 2000;**L 327**:1

[8] Decision no. 2455/2001/EC of the European Parliament and of the council establishing the list of priority substances in the field of water policy and amending directive 2000/60/EC. Official Journal of the European Union. 2001;**OJ L 44**:1-5

[9] Ribeiro AR, Nunes OC, Pereira MFR, Silva AMT. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched directive 2013/39/EU. Review. Environment International. 2015;**75**:33-51

[10] Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, Liang S, Wang XC. A review on the occurence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of the Total Environment. 2014;**473-474**:619-641. DOI: 10.1016/j.scitotenv.2013.12.065

[11] Simionato JI, Guerra Villalobos LD, Keller Bulla M, Garcia Coró FA, Garci JC. Application of chitin and chitosan extracted from silkworm chrysalides in the trea tment of textile effluents contaminated with remazol dyes. Acta Scientiarum. Technology Maringá. 2014;**36**(4):693-698. DOI: 10.4025/actascitechnol.v36i4.24428. ISSN printed: 1806-2563, ISSN on-line: 1807-8664

[12] Reza FF, Azimi AA, Nabi Bidhendi GR. Batch kinetics and isotherms for biosorption of cadmium onto biosolids. Desalination and Water Treatment. 2011;**28**(1-3):69-74. DOI: 10.5004/dwt.2011.2203

[13] Ahalya N, Ramachandra TV, Kanamadi RD. Biosorption of heavy metals. Research Journal of Chemistry and Environment. 2003;**7**(4):71-79

[14] Sawyer Clair N. Milestones in the development of the activated sludge process. Water Pollution Control Federation. 1965;**37**(2):151-162. JSTOR 25035231

[15] Alleman James E, Prakasam TBS. Reflections on seven decades of activated sludge history. Water Pollution Control Federation. 1983;**55**(5):436-443. JSTOR 25041901

[16] Jenkins D, Wanner J, editors. Activated Sludge - 100 Years and Counting. IWA Publishing; 2014; ISBN 9781780404943

[17] Lesmana Sisca O, Novie F, Soetaredjo Felycia E, Jaka S, Suryadi I. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. Biochemical Engineering Journal. 2009;**44**(1):19-41. DOI: 10.1016/j.bej.2008.12.009

[18] Velásquez L, Dussan J. Biosorption and bioaccumulation of heavy metals on dead and living biomass of Bacillus sphaericus. Journal of Hazardous Materials. 2009;**167**(1-3): 713-716. DOI: 10.1016/j.jhazmat.2009.01.044. PMID 19201532

[19] Mustapha MU, Halimoon N. Microorganisms and biosorption of heavy metals in the environment: A review paper. Journal of Microbial and Biochemical Technology. 2015;**7**:253-256. http://dx.doi.org/10.4172/1948-5948.1000219

[20] Pagnanelli F, Mainelli S, Bornoroni L, Dionisi D, Toro L. Mechanisms of heavy-metal removal by activated sludge. Chemosphere. 2009;**75**(8):1028-1034. DOI: 10.1016/j.chemosphere.2009.01.043

[21] Fomina M, Gadd GM. Biosorption: Current perspectives on concept, definition and application. Special issue on biosorption. Bioresource Technology. 2014;**160**:3-14. DOI: 10.1016/j.biortech.2013.12.102

[22] Crini G, Badot PM. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Progress in Polymer Science. 2008;**33**:399-447. DOI: 10.1016/j.progpolymsci.2007.11.001

[23] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical Society. 1918;**40**:1361-1403

[24] Freundlich HMF. Over the adsorption in solution. The Journal of Physical Chemistry. 1906;**57**:385-470

[25] Tempkin MI, Pyzhev V. Kinetics of ammonia synthesis on promoted iron catalyst. Acta Phys Chim USSR. 1940;**12**:327-356

[26] Weber WJ Jr. Adsorption. In: Physicochemical Processes for Water Quality Control. New York: Wiley; 1972. pp. 206-211

[27] Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe Kungliga Svenska Vetenskapsakademiens. The Hand. 1898;**24**:1-39

[28] McKay G, Ho YS. Pseudo second order model for sorption processes. Process Biochemistry. 1999;**34**:451-465

[29] Okenicová L, Žemberyová M, Procházková S. Biosorbents for solid-phase extraction of toxic elements in waters. Environmental Chemistry Letters. 2016;**14**:67-77

[30] Otero M, Rozada F, Calvo L, Garcia AI, Moran A. Elimination of organic water pollutants using adsorbents obtained from sewage sludge. Dyes and Pigments. 2003;**57**:55-65. DOI: 10.1016/S0143-7208(03)00005-6

[31] Ju DJ, Byun IG, Park J, Lee CH, Ahn GH, Park TJ. Biosorption of a reactive dye (Rhodamine-B) from an aqueous solution using dried biomass of activated sludge. Bioresource Technology. 2008;**99**:7971-7975

[32] Caner N, Kiran I, Ilhan S, Iscen CF. Isotherm and kinetic studies of Burazol blue ED dye biosorption by dried anaerobic sludge. Journal of Hazardous Materials. 2009;**165**:279-284

[33] Qiu B, Xu X, Dang Y, Wang Q, Sun D, Wei S, Guo Z. Biotransformative removal of cationic red X-GRL by anaerobic activated sludge. RSC Advances. 2015;**5**:25699-25707. DOI: 10.1039/C5RA01331C

[34] Bell JP, Tsezos M. The selectivity of biosorption of hazardous organics by microbial biomass. Water Research. 1988;**22**(10):1245-1251

[35] Lal R, Saxena DM. Accumulation, metabolism, and effects of organochlorine insecticides on microorganisms. Microbiological Reviews. 1982;**46**(1):95-127

[36] Shin YO, Chodan J, Wolcott AR. Adsorption of DDT by soils, soil fractions and biological materials. Journal of Agricultural and Food Chemistry. 1970;**18**:1129-1133

[37] Tsezos M, Seto W. The adsorption of chloroethanes by microbial biomass. Water Research. 1986;**20**(7):851-857

[38] Tsezos M, Bell JP. Comparison of the biosorption and desorption of hazardous organic pollutants by live and dead biomass. Water Research. 1989;**23**(5):561-568

[39] Zümriye A. Application of biosorption for the removal of organic pollutants: A review. Process Biochemistry. 2005;**40**(3-4):997-1026. DOI: 10.1016/j.procbio.2004.04.008

[40] Otero M, Rozada F, Calvo LF, Garcia AI, Moran A. Kinetic and equilibrium modelling of the methylene blue removal from solution by adsorbent materials produced from sewage sludge. Biochemical Engineering Journal. 2003;**15**(1):59-68. DOI: 10.1016/S1369-703X(02)00177-8

[41] Aksu Z, Yener J. A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents. Waste Management. 2001;**21**(8):695-702. DOI: 10.1016/S0956-053X(01)00006-X

[42] O'Mahony T, Guibal E, Tobin JM. Reactive dye biosorption by Rhizopus arrhizus biomass. Enzyme and Microbial Technology. 2002;**31**(4):456-463. DOI: 10.1016/S0141-0229(02)00110-2

[43] Aksu Z, Gönen F. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: Prediction of breakthrough curves. Process Biochemistry. 2004;**39**(5):599-613. DOI: 10.1016/S0032-9592(03)00132-8

[44] Fu Y, Viraraghavan T. Fungal decolourization of wastewaters: A review. Bioresource Technology. 2001;**79**(3):251-262

[45] Robinson T, Mcmullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. Bioresource Technology. 2001;**77**(3):247-255. DOI: 10.1016/S0960-8524(00)00080-8

[46] Manu B, Chaudhari S. Anaerobic decolourization of simulated textile wastewater containing azo dyes. Bioresource Technology. 2001;**82**(3):225-231

[47] Modin O, Saheb Alam S, Persson F, Wilén BM. Sorption and release of organics by primary, anaerobic, and aerobic activated sludge mixed with raw municipal wastewater. PLoS One. 2015;**10**(3):e0119371. DOI: 10.1371/journal.pone.0119371

[48] Han R, Ding D, Xu Y, Zou W, Wang Y, Li Y, Zou L. Use of rice husk for the adsorption. Of Congo red from aqueous solution in column mode. Bioresource Technology. 2008;**99**(8):2938-2946. DOI: 10.1016/j.biortech.2007.06.027

[49] Zabochnicka-Świątek M, Krzywonos M. Potentials of biosorption and bioaccumulation processes for heavy metal removal. Polish Journal of Environmental Studies. 2014;**23**(2):551-561

[50] Leitão AL. Potential of Penicillium species in the bioremediation field. International Journal of Environmental Research and Public Health. 2009;**6**(4):1393-1417. DOI: 10.3390/ijerph6041393

[51] Li X, Li A, Long M, Tian X. Equilibrium and kinetic studies of copper biosorption by dead Ceriporia lacerata biomass isolated from the litter of an invasive plant in China. Journal of Environmental Health Science and Engineering. 2015;**13**:37. DOI: 10.1186/s40201-015-0191-1

[52] Ternes TA. Occurrence of drugs in German sewage treatment plants and rivers. Water Research. 1998;**32**(11):3245-3260. DOI: 10.1016/S0043-1354(98)00099-2

[53] Kreuzinger N, editor. Occurrence of highly discussed pollutants in the stretch of the Austrian Danube related to the Catchment Area. Oral Presentation at SETAC Europe 12th Annual Meeting, Vienna, Austria; 2002

[54] Heberer T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. Toxicology Letters. 2002;**131**(1):5-17

[55] Hollender J, Zimmermann SG, Koepke S, Krauss M, McArdell CS, Ort C, Singer H, Gunten UV, Siegrist H. Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. Environmental Science & Technology. 2009;**43**(20):7862-7869. DOI: 10.1021/es9014629

[56] Fromme H, Küchler T, Otto T, Pilz K, Müller J, Wenzel A. Occurrence of phthalates and bisphenol a and F in the environment. Water Research. 2002;**36**(6):1429-1438

[57] Baronti C, Curini R, D'Ascenzo G, Di Corcia A, Gentili A, Samperi R. Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water. Environmental Science & Technology. 2000;**34**(24):5059-5066. DOI: 10.1021/es001359q

[58] Eggen RI, Hollender J, Joss A. Schã±¥r M, Stamm C. Reducing the discharge of micropollutants in the aquatic environment: The benefits of upgrading wastewatertreatment plants. Environmental Science & Technology. 2014;**48**(14):7683-7689. DOI: 10.1021/es500907n

[59] Schüth PDC. Demonstrating Managed Aquifer Recharge as a Solution to Water Scarcity and Drought: An EU FP7 Project. http://www.marsol.eu/files/marsol_d14-1_list-ofmicropollutants.pdf [Accessed: 31 May 2016]

[60] Hey G. Relevant studies related to the presence of micropollutants in the environment, Published date: May 18, 2016. http://micropollutants.com/About-micropollutants [Accessed: 31 May 2016]

[61] Grandclement C, Seyssiecq I, Piram A, Wong-Wah-Chung P, Vanot G, et al. From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review. Water Research. 2017;**111**:297-317. DOI: 10.1016/j.watres.2017.01.005

[62] Ak S, Muza M, Komesli OT, Gokcay CF. Enhancement of bio-gas production and xenobiotics degradation during anaerobic sludge digestion by ozone treated feed sludge. Chemical Engineering Journal. 2013;**230**:499-505. DOI: 10.1016/j.cej.2013.06.113

[63] Nie YF, Qiang ZM, Zhang HQ, Ben WW. Fate and seasonal variation of endocrine-disrupting chemicals in a sewage treatment plant with A/A/O process. Separation and Purification Technology. 2012;**84**:9-15. DOI: 10.1016/j.seppur.2011.01.030

Chapter 2

Biosorption of Heavy Metals

Saba Shamim

Additional information is available at the end of the chapter

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Abstract

Industrialization has led to introduction of heavy metals in the environment. Heavy metals are known to persist in the environment and become a risk for organisms. Microorganisms are present in industrial effluents. They have adopted different strategies to cope up with the harmful effects of these metals. These strategies can be metabolism dependent or independent. One such strategy is biosorption which is binding of metal ions with metal binding proteins present on the cell wall. Biosorption is exhibited by bacteria, algae, fungi and yeasts. Not only living organisms, but also residuals of dead bodies of microorganisms shows biosorbent properties like agricultural wastes including husk, seeds, peels and stalks of different crops. Different factors affect the rate of biosorption which includes temperature, pH, nature of biosorbents, surface area to volume ratio, concentration of biomass, initial metal ion concentration and metal affinity to biosorbent. Various models including Freundlich model and Langmuir model can be used to describe biosorption. Recovery of biosorbed metals can be done using agents like thiosulfate, mineral acids and organic acids. Choice of desorption agent should be carefully selected to prevent alteration of physical properties of a biosorbent.

Keywords: biosorption, heavy metals, bacteria, algae, fungi, yeasts

1. Introduction

Nature has gifted our earth with four spheres; biosphere, lithosphere, hydrosphere, and atmosphere. Together these spheres are important for maintaining a balanced ecosystem [1]. The industrial revolution in the past five decades is remarkable. Due to anthropogenic activities, increasing population, industrialization and urbanization, all spheres have become polluted [2–7]. There are two main sources of introduction of heavy metals in the environment (1) natural sources which includes volcanic emissions, forest fires, deep-sea vents, and geysers [8] and (2) anthropogenic sources which includes mining and smelting sites, metal-manufacturing plants, painting- and coating-industries and tanneries. These heavy metals are

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released directly into the environment. Metals exhibit health issues [9] if their concentrations exceed allowable limits. Even when the concentration of metals does not exceed these limits, there is still a potential for bioaccumulation and associated chronic toxicity as heavy metals are known to be accumulative within biological systems [10]. These metals include arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc [4, 11]. Industrial effluents are known to contain heavy metals which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, and printing and photographic industries [1, 11–14].

2. Heavy metals

Heavy metals are usually defined as metals having density more than 5 g/cm^3 [15]. They are classified as essential and non-essential metals. The metals which are need for normal cellular growth are essential metals e.g. zinc, nickel, copper, etc. Such metals are required in low concentrations (nM), but at higher concentrations (μM to mM) all heavy metals have detrimental effects to organisms [16, 17]. If the metals have no known biological function, they are called as non-essential metals e.g. e.g., lead, cadmium, mercury [18]. Such metals are toxic at any concentration [8]. The list of essential and non-essential heavy metals is given (**Table 1**). There are 90 naturally occurring elements in periodic table, 21 are non-metals, 16 are light metals and the remaining 53 (with As included) are heavy metals [19]. In periodic table, transition elements are mostly heavy metals. They have incompletely filled ‘d’ orbitals which allow heavy-metal cations to form complex compounds that may or may not be redox-active. In this way, heavy metals play an important role as ‘trace elements’ (cobalt, copper, nickel, and zinc) in sophisticated biochemical reactions and are important cofactors for metallo-proteins and enzymes [8]. The toxicity of heavy metal ions starts when their concentration becomes higher

Category of heavy metal	Example of heavy metals
Essential	Copper (Cu)
	Nickel (Ni)
	Iron (Fe)
	Zinc (Zn)
	Magnesium (Mg)
Non-essential	Lead (Pb)
	Mercury (Hg)
	Cadmium (Cd)
	Tin (Sn)
	Arsenic (As)

Table 1. Essential and non-essential heavy metals.

in the cells, due to which they form complex compounds [15, 18]. Microorganisms acquire resistance to these toxic metals by lateral gene transfer [20]. The interaction of microorganism with metal ions depends on factors like oxidation state of the metal ion, chemical/physical nature of metals, growth phase of microorganism etc. [21].

3. Methods for removal of heavy metals

Since last many decades, various physical and chemical methods were employed to remove metals from environment. The list is given below [5, 13, 14, 22–24].

Chemicals methods: Chemical precipitation, electrochemical treatment, oxidation/reduction.

Physical methods: Ion exchange, membrane technology, reverse osmosis, and evaporation recovery, filtration.

Biological methods: Microorganisms including bacteria, fungi or algae.

However, these strategies were not the first choice as they are expensive, inefficient, labor-intensive, or the treatment process lacks selectivity [25, 26]. The research on bioremediation or biosorption-based remediation techniques in the past decades has concluded that bioremediation is a natural process and cost effective [4, 27–31].

4. Biosorption

Biosorption is defined as "ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated (by the use of ATP) or spontaneous physico-chemical pathways of uptake (not at the cost of ATP), or as a property of certain types of inactive, non-living microbial biomass which bind and concentrate heavy metals from even very dilute aqueous solutions" [1, 5, 32]. It is a complex process that depends on different-factors like cell physiology, physicochemical factors such as pH, temperature, contact time, ionic strength, and metal concentration, chemistry of the metal ions, cell wall composition of microorganisms [5, 33, 34]. Biosorption of different heavy metals e.g. cadmium, silver, lead, nickel etc. by using microorganisms like fungi, algae or bacteria was studied by different groups [34–42].

4.1. Significance

Bioremediation offer different advantages such as low operating cost, minimum ratio of disposable sludge volume, high efficiency in detoxifying very dilute effluents and even *in situ* remediation [30, 43, 44]. Bacteria detoxify heavy metals in a variety of different ways [45]. Although various types of tolerance mechanisms have been reported in bacteria for heavy metal stress, Cd detoxification has only been restricted to efflux pumps. The plasmid encoded *cad* systems in (*Staphylococcus aureus*) and the *czc* system (*Alcaligenes eutrophus*) are best characterized. These systems actively maintain Cd ions outside the intracellular environment, hence avoiding its toxic effects. Consistently, many researchers reported that sensitive bacteria can accumulate 3–15 times more Cd than resistant strains [46]. The most important aspect of Cd ions is that they covalently bind to sulfhydryl groups. Although this is partially the cause for its high toxicity, this feature is also used by several organisms to render the metal harmless to the cell, through sequestration with metal-detoxifying ligands, the metal becomes less bioavailable.

4.2. Advantages of biosorption

Following are given the advantages of biosorption over conventional metal removal methods [47, 48].

1. Cheaper production of biomass (bacteria or fungi)
2. Use of biomass for removal of heavy metals
3. Multiple heavy metals uptake at a time
4. Treatment of large volumes of wastewater
5. No need for chemical additions as highly selective for uptake and removal of specific metals
6. Functional over wide range of conditions including temperature, pH, presence of other metal ions, etc.
7. Easy and cheaper desorption of metals attached to biomass
8. Reduced volume of waste or toxic materials production

4.3. Disadvantages of biosorption

The disadvantages of biosorption are stated below [49].

1. Saturation of active sites of metal binding ligands
2. Reversible sorption of metals on biomass

5. Biosorption mechanisms

The process of heavy metal ion binding to bacterial cell wall (peptidoglycan) can be metabolism dependent or independent [1].

5.1. Metabolism dependent biosorption

Metabolism dependent biosorption is exhibited by living biological material. It involves various mechanisms like chelation; a specific way in which ions and molecules bind to metal ions and it involves the formation or presence of two or more separate coordinate bonds between a polydentate ligand and a single central atom, physical adsorption; adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. It is a surface phenomenon. Generally the adsorption process is classified as physisorption, characteristic of weak van der Waals forces, or chemisorption, characteristic of covalent bonding. It may also occur due to electrostatic attraction, precipitation; it is the creation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When this reaction occurs in a liquid solution, the solid formed is called the "precipitate" and the chemical that causes the solid to form is called the "precipitant") or complexation (it consists of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are known as ligands or complexing agents. Many metal-containing compounds, especially those of transition metals, are coordination complexes). There may involve a single process or combination of these processes [50, 51]. If the metal binding to cell wall is metabolism dependent then it involves energy from ATP. The ligands present on the cell wall of biological material such as phosphoryl, carboxyl, carbonyl, sulfhydryl and hydroxyl groups immobilizes the metal ion [32] and then uptake occurs [5]. Other factors that effect the metal uptake by living biomass includes nature of heavy metals ions, conditions of the medium, cell wall composition, etc. [5]. The uptake process by living biomass involves adsorption to cell wall and entering into the cytoplasm [29, 31, 52, 53].

5.2. Metabolism independent biosorption

The metabolism independent process mostly occurs in biomass consisting of dead cells [54]. The adsorption process is the main key point behind such physicochemical biosorption mechanism. The adsorption process can be ionic interactions or physiochemical adsorption. Presence of anionic ligands on bacterial cell wall (carboxyl, amine, hydroxyl, phosphate, and sulfhydryl groups) also plays an important role in metal biosorption. Living biological mass is preferred over dead mass, because living cells have ability for continuous metal uptake, and self-replenishment [27, 29, 31]. Previously it is reported that adsorption is a rapid process while accumulation is slow and energy dependent [29, 31 52–53]. The fate of metal inside cell can be accumulation, detoxification and/or efflux depending on the nature of bacteria [31, 55, 56]. In past few decades, many groups worked on heavy metal resistant bacteria that can be used for bioremediation [27, 29, 31, 56–58]. Many workers reported that cells of bacteria of genera *Alcaligenes* and *Pseudomonas* can be used for bioremediation purpose [45].

5.3. Metal accumulation

In order to have the physiological effect on the growth of cells, heavy metals must enter the cell [19, 59, 60]. Metal uptake system in bacteria is grouped in two types; one is fast and unspecific, constitutively expressed and does not require ATP. They are usually driven only by the chemiosmotic gradient across the cytoplasmic membrane of bacteria. The second type of uptake system is highly specific, slow, inducible and dependent on ATP, in addition to the chemiosmotic gradient. They are only induced in times of need, starvation or a special metabolic situation [61].

As cell surface encounter metal ion, formation of a complex takes place, which is a pre-requisite for uptake of metals by the organism [59, 60]. Once surface sorption takes place, the metal is transported into the periplasmic space of Gram-negative cells and transported further into the cytoplasm [60]. When cell encounters high concentration of any heavy metal, the heavy metal ion is transported into the cytoplasm, accumulated inside the cell due to one type of metal uptake which is fast, unspecific, constitutively expressed and does not require ATP [61]. The cations of heavy metals interact with physiological ions Cd^{2+} with Zn^{2+} or Ca^{2+}, Ni^{2+} and Co^{2+} with Fe^{2+}, Zn^{2+} with Mg^{2+} thus inhibit the function of respective physiological cations. This result in oxidative stress in the cell [1].

6. Types of biosorbents

Biosorbents can be classified as living or non- living organic materials. They are discussed below in detail.

6.1. Living organic materials

6.1.1. Bacteria

Among microorganisms, bacteria constitute of being the most abundant, versatile, most diverse creature on this planet earth [48, 62]. They are basically classified on the basis of their morphology as rod, cocci or spirillum [48, 63]. A bacterium has relatively simple morphology consisting of cell wall, cell membrane, capsule, slime layer and internal structures mitochondria, Golgi apparatus, ribosomes, endoplasmic reticulum. Slime layer contains functional groups like carboxyl, amino, phosphate or sulfate for metals chelation [48, 62]. Cell wall in general, is responsible for surface binding sites and binding strength for different metal ions depending on different binding mechanisms. Various bacterial species e.g. *Bacillus*, *Pseudomonas*, *Escherichia* [48] exhibit biosorption property because of their small size and ability to grow in different environmental conditions [64–66].

Gram classification divides bacteria in two broad categories; Gram positive and Gram negative. Gram negative mostly constitute pathogens although pathogens are also reported in Gram positive. Gram positive bacteria are comprised of thick peptidoglycan layer connected by amino acid bridges, also known to contain polyalcohols and teichoic acids. Overall, Gram positive bacterial cell wall comprised of 90% peptidoglycan. Some teichoic acids are linked to lipids of lipid bilayer forming lipoteichoic acid. These lipoteichoic acids are linked to lipids of cytoplasmic membrane. They constitute linkage of peptidoglycan to cytoplasmic membrane. This results in cross linking of peptidoglycan forming a grid like structure. These teichoic acids are responsible for negative charge on cell wall due to presence of phosphodiester bonds between teichoic acid monomers [48]. On the other hand, Gram negative bacterial cell wall contains an additional outer membrane composed of phospholipids and lipopolysaccharides. Gram negative cell wall contains 10–20% peptidoglycan. The negative charge on the Gram negative bacteria is due to lipopolysaccharides, teichoic acids, teichuronic acids. Extracellular polysaccharides also exhibit the property of metal binding. They are not present in all Gram negative bacteria. Moreover, those species that contain them, they can be easily removed by chemical washing or mechanical disruption [49, 67].

6.1.1.1. Bacterial biosorption

Bacterial cell wall encountering the metal ion is the first component of biosorption. The metal ions get attached to the functional groups (amine, carboxyl, hydroxyl, phosphate, sulfate, amine) present on the cell wall [49, 67]. The general metal uptake process involves binding of metal ions to reactive groups present on bacterial cell wall followed by internalization of metal ions inside cell [48]. More metal is uptaken by Gram positive bacteria due to presence of glycoproteins. Less metal uptake by Gram negative bacteria is observed due to phospholipids and LPS [68, 69]. Biosorption of various metals by different bacteria is given in **Table 2**.

Sr. No.	Metals	Bacteria	Temperature (°C)	pH	Agitation	Time	Wt (g/L)	q(mg/g) or % removal	References
1.	Arsenic	*Bacillus* sp. KM02	—	—	—	—	—	—	[108]
		Kocuria sp.	—	—	—	—	—	—	[109]
		Bacillus sp.	—	—	—	—	—	—	[110]
2.	Cadmium	*Pseudomonas putida* mt2	—	—	—	—	—	—	[111–114]
		Cupriavidus metallidurans CH34	—	—	—	—	—	—	[111–114]
		Enterobacter cloacae	25	5	240	2	0.1	58.9%	[115]
		Stenotrophomonas maltophilia	28	5	140	2	20	0.12	[116]
		Actinomycetes sp.	30	6	150	24	5	32.63	[116]
3.	Chromium	*Micrococcus* sp.	35	5	120	24	—	92%	[117]
		Bacillus licheniformis	28	3.5	120	48	—	95%	[116]
		Staphylococcus saprophyticus	27	2	150	3	0.2	24.1	[118]
		Enterobacter cloacae	25	4	240	2	0.1	55.8	[115]
		Pseudomonas aeruginosa	25	—	—	—	—	1.07	[119]
		Micrococcus sp.	35	5	120	24	—	92%	[117]
4.	Cobalt	*Rhodopseudomonas palustris*	—	—	—	—	—	—	[120]
5.	Copper	*Stenotrophomonas maltophilia*	25	5	140	2	20	0.57	[116]
		Bacillus licheniformis	28	2.5	120	48	—	32%	[121]
		Geobacillus thermodenitrificans	25	5	100	12	—	51	[122]
		Bacillus cereus	25	5.5	—	24	1.0	50.32	[119]
		Pseudomonas aeruginosa	25	—	—	—	—	0.67	[119]
		Thiobacillus thiooxidans	30	5	786	2	0.25	39.84	[123]
		Enterobacter cloacae	25	5	240	2	0.1	78.9	[115]
		Staphylococcus saprophyticus	27	3.5	150	2	0.2	14.5	[118]
6.	Gold	*Cupriavidus metallidurans* CH34	—	—	—	—	—	—	[125]

Sr. No.	Metals	Bacteria	Temperature (°C)	pH	Agitation	Time	Wt (g/L)	q(mg/g) or % removal	References
7.	Lead	*Enterobacter cloacae*	25	5	240	2	0.1	67.9	[115]
		Bacillus sp.	30	5–9	100	24	—	69.34	[124]
		Pseudomonas sp.	30	5–9	100	24	—	90.41	[124]
		Micrococcus sp.	30	5–9	100	24	—	84.27%	[124]
		Bacillus cereus	25	5.5	—	24	1.0	36.71	[119]
		Geobacillus thermodenitrificans	25	4	100	12	—	53	[122]
		Stenotrophomonas maltophilia	25	5.0	140	2	20	0.41	[116]
8.	Mercury	*Enterobacter cloacae*	25	4	240	2	0.1	43.23	[115]
9.	Nickel	*Actinomycetes* sp.	30	5	150	24	5	36.55	[116]
		Micrococcus sp.	35	5	120	24	—	90%	[117]
10.	Selenium	*Cupriavidus metallidurans* CH34	—	—	—	—	—	—	[111–114]
11.	Silver	*Cupriavidus metallidurans* CH34	—	—	—	—	—	—	[111–114]
12.	Zinc	*Pseudomonas aeruginosa*	25	—	—	—	—	1.33	[119]
		Geobacillus thermodenitrificans	25	5	100	12	—	18	[122]

Where, Wt = weight of used adsorbent; Q = uptake removal of pollutant (mg/g); Agitation = speed of shaker (rpm); T = Temperature of the experiment (°C).

Table 2. Bacteria and their biosorption features regarding different metals [48, 126, 127].

6.1.2. Algae

Algae are aquatic plants that lack true roots and stems. It can range from micro algae to macroalgae. They are autotrophic. They can grow in big biomass even when less nutrition is provided. They are considered good biosorbent material [48, 70–73] because of their big size, high sorption capacity and no production of toxic substances. Mostly they are classified as microalgae (fresh water or green algae), macroalgae (marine or brown algae) and red algae. Among these three classes, brown alga is reported to have higher metal uptake capacity. The following features are responsible for binding of heavy metal ions to algae surface; algae species, ionic charge of metal and chemical composition of metal ion solution. Metal ion binding sites on algal surface includes sulfhydryl, hydroxyl, phosphate, sulfate, imidazole, amine, carboxyl groups [74]. The metal uptake mechanism of algae is similar to that of bacteria that is bonding of metal ions with the surface followed by internalization. According to Abbas et al., [48], either of two mechanisms in algal biosorption is involved: (1) ion exchange method where ions present on algal surface Ca, Mg, Na, K they are displaced by metal ions, (2) complexation between functional groups and metal ions.

6.1.2.1. Biosorption by algae

According to Abbas et al., [48], algal cell wall is made up of polysaccharides (alginic acid, chitin, xylan, mannan) which provides functional groups (sulfate, hydroxyl, phosphate, imidazole, amino, amine) known to act as metal binding sites [74]. As far as metal binding mechanism is concerned, ionic charge and covalent bonding are hypothesized. Carboxyl and sulfate groups are involved in ionic bonding whereas amino and carboxyl groups are involved in covalent bonding between metal ion and functional group. In response to metal ions, phytochelatins are produced inside the algal body [48]. Biosorption of various metals by different bacteria is given in **Table 3**.

Sr. No.	Metals	Algae	Temperature (°C)	pH	Agitation	Time	Wt (g/L)	q(mg/g) or % removal	References
1.	Arsenic	*Spirogyra hyalina*	25	—	180	2	1	9.8	[128]
2.	Cadmium	*Bifurcaria*	-	4.5	175	3	2.5	95	[129]
		bifurcate	28	7.5	72	60–80	28–51	-	[130]
		Oocystis	25	-	-	9 days	0.17–14	-	[131]
		Pithophora spp.	30	5	150	-	-	22.2	[132]
		(filamentous)	25	6	150	24	4	0.4 mmol/g	[133]
		Sargassum sp.	25	6	-	2	0.25	1.12 mmol/g	[134]
		(brown algae)	25	6	-	2	0.5–1	114.9	[135]
		Sargassum tenerrimum							
		Fucus vesiculosus							
		(brown algae)							
		Ascophyllum nodosum							
3.	Chromium	*Pithophora spp.*	25	-	-	9 days	-	-	[131]
		(filamentous)	30	4	-	6	2–5	68.9	[136]
		Sargassum sp.	30	4	180	3	1–3	265	[132]
		Spirogyra sp.	30	3	150	-	-	20.2	[132]
		(green algae)							
		Sargassum sp.							
		(brown algae)							
4.	Cobalt	*Spirogyra hyalina*	25	—	180	2	2.5	7.856	[128]
5.	Copper	*Calotropis procera*	25	4	150	6	2	14.5	[137]
		Oocystis	28	5.5	60–80	72	4.4–6.0	-	[130]
		Sargassum	25	4.5	175	6	5	-	[138]
		filipendula	30	-	150	-	5	0.66	[139]
		Microalgae	30	4	150	-	-	18.6	[132]
		Sargassum sp.	25	5	-	2	0.25	0.97	[134]
		(brown algae)	25	4	-	2	0.5–1	70.9	[135]
		Fucus vesiculosus							
		(brown algae)							
		Ascophyllum nodosum							
7.	Lead	*Calotropis procera*	25	4	150	6	2	22.8	[137]
		Oocystis	28	5.5	60–80	72	16–80	-	[130]
		Pithophora spp.	25	-	-	9 days	0.12–0.13	-	[131]
		(filamentous)	25	5	-	2	0.25	1.04	[134]
		Fucus vesiculosus							
		(brown algae)							

Sr. No.	Metals	Algae	Temperature (°C)	pH	Agitation	Time	Wt (g/L)	q(mg/g) or % removal	References
8.	Mercury	*Sargassum* sp. (brown algae)	30	4	100	-	-	14.8	[132]
		Cladophora fascicularis	25	-	180	2	1	20	[128]
		Spirogyra hyaline	25	-	180	2	2.5	39.2	[128]
9.	Nickel	*Sargassum* sp. (brown algae)	30	5	150	-	-	26.1	[132]
		Fucus vesiculosus (brown algae)	25	5	-	2	0.25	0.80	[134]
		Ascophyllum nodosum	25	6	-	2	0.5–1	50	[135]
12.	Zinc	Microalgae	30	-	150	-	5	0.72 mmol/g	[139]
		Sargassum sp. (brown algae)	30	3	150	-	-	15.4	[132]
		Ascophyllum nodosum	25	6	-	2	0.5–1	53.2	[135]
13.	Iron	*Sargassum* sp. (brown algae)	30	3	150	—	—	14.6	[132]

Table 3. Algae and their biosorption features regarding different metals [48].

6.1.3. Fungi

Fungi are eukaryotic living organism which includes yeasts, mushrooms, molds, etc. The cell wall structure of fungi offers good metal binding properties. Fungi in living and dead both forms can be used as biosorbent material [48, 75]. Metal uptake by fungi involves two processes (i) active uptake or bioaccumulation or intracellular uptake, it is dependent on cell metabolism and (ii) biosorption or passive uptake which involves binding of metal ions to surface of cell wall and it is independent of cell metabolism. The energy independent metal uptake mechanism can be affected by temperature, metabolic inhibitors, etc. Metal uptake by fungi was reported both active and passive. Active uptake occurred only with living cells. In this case, the interaction of metal ions with cell surface functional groups may involves ion-exchange, complexation or just physical adsorption.

6.1.3.1. Biosorption by fungi

According to Das et al., [69] fungal cell wall exhibit excellent metal biding properties due to its components. The cell wall of fungus is composed mainly of chitins, mannans, glucans, in addition to lipids, polysaccharides, pigments e.g. melanin [48, 76–78]. Fungal cell wall is reported to be made up of 90% polysaccharides. The functional groups which are involved in metal binding includes carboxyl, phosphate, uranic acids, proteins, nitrogen containing ligands, chitin or chitosan [48, 79]. Biosorption ability of fungal cells can be manipulated by physical of chemical treatments including autoclaving, heat processes or dimethyl sulfoxide, laundry detergent, orthophosphoric acid, formaldehyde, gluteraldehyde, NaOH, respectively [69]. Macrofungi also called as mushrooms, grow wild in all types of environments ranging from forests to polluted soils and water bodies. They uptake the metals in their fruiting bodies, mycelia and sporocarps [48]. Biosorption of various metals by different fungi and mushrooms is given in **Tables 4** and **5** respectively.

6.1.4. Yeasts

Yeasts are famous organisms while studying biosorption. *Saccharomyces cerevisiae* is well known yeast which is considered a model system to study biosorption. They are easy to grow, non-pathogenic and give high biomass yield using simple growth medium [80]. The availability of complete genome information makes its genetic engineering an easy job [75, 81]. They are also considered ideal experimental organism in molecular biology experimentation [75, 82–84]. The property of biosorption by yeast cells is affected by various factors including properties of metal ions (valency, radius), cell age of *S. cerevisiae* cells, conditions of culture (composition of growth medium, carbon source), biosorption conditions (initial concentration of metals and biomass, availability of metal ions, temperature, pH, other ions in growth medium) [75]. Moreover, the large size of yeast makes them promising candidates for metal bioremediation. *Saccharomyces cerevisiae* is a widely studied yeast strain. Its different forms are already studied for its biosorption properties including immobilized versus fess cell, living versus dead cells, engineered versus non engineered cells, cultural versus waste cells, etc. [69, 85–89].

Sr. No.	Metals	Bacteria	Temperature (°C)	pH	Agitation	Time	Wt (g/L)	q(mg/g) or % removal	References
1.	Arsenic	*Penicillium chrysogenum*	25	3–4	190	—	1	24.5	[140]
2.	Cadmium	*Aspergillus cristatus*	25	6	120	2	0.4	23.2	[142]
		Aspergillus niger	25	4.75	125	6	0.7	13	[143]
		Hydrilla verticillata	25	5	150	0.33	3–9	15	[141]
3.	Chromium	*Aspergillus niger*	28	4.5	150	1	10	16.39	[144, 145]
		Pleurotus ostreatus	25	4.5	150	3	2	1.97	[146]
		Trichoderma viride	-	6	150	0.75	3.75	4.66	[147]
		Mucor	35	5.5	-	-	-	-	[148]
		Penicillium canescens	20	6	100	4	2	34.8	[149]
4.	Copper	*Pleurotus ostreatus*	25	4.5	150	3	2	4.0	[150]
		Fomes fasciatus	25	5.5	200	1	1	32.2	[151]
		Aspergillus lentulus	35	6	180	0.41	4	-	[152]
5.	Lead	*Rhizopus nigricans*	25	5.5	225	-	25	80.8	[153]
		Trichoderma	25	7	-	0.33	-	71	[154]
		longibrachiatum	25	5.5	-	3	2	4.84	[155]
		Pleurotus ostreatus							
6.	Mercury	*Aspergillus flavus*	30	5.5	100	8	10	95.3%	[156]
		Aspergillus fumigatus	30	5.5	100	8	10	95.3%	[140]
7.	Nickel	*Aspergillus niger*	25	4.5	150	3	1	7.69	[157]

Table 4. Fungi and their biosorption features regarding different metals [48].

Sr. No.	Mushrooms	Metals	References
1.	Volvariella volvacea (edible Mushroom) – mycelia, sporocarps	Cadmium, lead, Copper, Chromium	[158]
2.	Ganoderma lucidum	Chromium	[69, 159]
3.	Coriolopsis strumosa	Copper	[160]
4.	Daedalea tenuis	Copper	[160]
5.	Lentinus strigosus	Copper	[160]
6.	Lenzites malaccensis	Copper	[160]
7.	Phellinus xeranticus	Copper	[160]
8.	Rigidoporus lineatus	Copper	[160]
9.	Rigidoporus microporus	Copper	[160]
10.	Trametes lactinea	Copper	[160]
11.	Ganoderma lucidum	Copper	[159, 160]
12.	Agaricus macrospores	Cadmium, mercury, copper	[161]

Table 5. Mushrooms and biosorption of different metals [48].

6.1.4.1. Biosorption by yeast

The free form of yeast cells is not considered good candidates for biosorption [86]. Free cells face the problem of separation of solid liquid phase. This problem seems to be less effective in flocculating cell [90]. Pretreatment of yeast cells can result in increased surface to volume ration for binding of metal with the metal binding sites. It is reported that pH above 5 optimizes the metal biosorption in yeast cells [91]. According to Abbas et al., [48] in yeasts, higher concentration of heavy metals can be accumulated by bioaccumulation process than biosorption. However, general biosorption is responsible for the major uptake of heavy metals for many filamentous fungi. Biosorption of various metals by different yeasts is given in **Table 6**.

Sr. No.	Metals	Yeasts	Temperature (°C)	pH	Agitation	Time	Wt (g/L)	q(mg/g) or % removal	References
1.	Cadmium	*Saccharomyces cerevisiae*	25	7	100	2	2	12.3	[69]
2.	Chromium	*Saccharomyces cerevisiae*	25	5.2	150	1	80	55.3%	[162]
		Candida utilis	25	5.5	160	1	1.0	28	[162]
3.	Cobalt	*Saccharomyces cerevisiae*	25	7	100	2	2	8.2	[162, 163]
4.	Copper	*Saccharomyces cerevisiae*	25	7	100	2	2	29.9	[162]
		Candida pelliculosa	30	6	120	120	13.3	95.04%	[164]
		Schizosaccharomyces pombe	25	4	-	96	-	74.85	[165]
5.	Lead	*Mucor rouxii*	25	5.0	125	15	—	17.13	[166]
6.	Mercury	*Saccharomyces cerevisiae*	25	7	100	2	2	76.2	[162]
7.	Nickel	*Saccharomyces cerevisiae*	25	7	100	2	2	14.1	[162]
8.	Zinc	*Saccharomyces cerevisiae*	25	7	100	2	2	11.8	[162]

Table 6. Yeasts and their biosorption features regarding different metals [48].

6.2. Non-living organic materials

6.2.1. Wastes of agricultural or food industry

The wastes of agriculture or food industry includes agricultural byproducts as corn cobs, soya bean hulls, cotton seeds hulls [92] or fruit peels. They contain cellulosic material in their cell wall which is known to contain functional groups like phenolics or carboxylic. On the basis of cation exchange between functional groups and metal ions, the binding of metal ion with functional group results in biosorption and thus removal of metal ion from medium [49].

7. Factors affecting biosorption

Biosorption process is affected by following factors.

Temperature: For efficient removal of metal ions from environment, the optimum temperature needed to be investigated. It is generally assumed that biosorption is carried out between 20 and 35°C. High temperatures above 45°C may results in damage to proteins which in turn affects metal uptake process [48, 93–95].

pH: It is a very important parameter. It affects solubility of metal ions and binding sites of biomass. At lower pH, the biosorption of metals is affected [96, 97]. General range of pH for metal uptake is between 2.5–6. Above this limit, metal uptake ability of biosorbent gets compromised [48].

Nature of biosorbents: Metal uptake is reported in different forms like biofilms, freely suspended microbial cells or immobilization of microbial cells. It can be altered by physical or chemical treatments. Physical treatments include autoclaving, drying, boiling, sonication, etc. Chemical treatment as the name indicates involves chemicals like acid or alkali to improve biosorption capacity. According to Wang and Chen, [75], the fungal cells are deacetylated which affects the structure of chitin resulting in the formation of chitosan-glycan complexes which have results high metal affinities. Abbas et al., [48] also report about effect of age, growth medium components on biosorption as they might result in cell wall composition, cell size and EPS formation.

Surface area to volume ratio: This property plays an important role in efficient removal of heavy metal from medium. The surface area property plays a significant role in case of biofilms [48]. The binding of metal ions with microbial cell wall is previously reported [98]. Although intracellular metal adsorption is energy-consuming process but still microorganisms prefer it over wall adsorption.

Concentration of biomass: The concentration of biomass is directly proportional to the metal uptake [48, 98, 99]. It is reported that electrostatic interaction between the cells plays an important role in metal uptake. At a given equilibrium, the biomass adsorbs more metal ions at low cell densities than at high densities [100]. Metal uptake depends on biding sites. More biomass concentration or more metal ions restricts the access of metal ions to binding sites [48, 101].

Initial metal ion concentration: The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases [102]. 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. Thus, at a given concentration of biomass, the metal uptake increases with increase in initial concentration [48].

Metal affinity to biosorbent: Physical/chemical pretreatment 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 [48, 94].

8. Kinetics of biosorption

Before going in the details of studying kinetics of biosorption, one should understand the quality of a biosorbent. For observing the quality of a biosorbent, two factors should be considered (i) how much metal ion is attracted by the biosorbent, (ii) to which extent metal ions are retained on biosorbent in an immobilized form. The metal uptake by the biosorbent can be calculated by checking the difference in initial quantities of metal ions in medium to that remained in the medium after biosorption takes place. This is studied by the following Eq. 1 [48, 49, 94]:

$$q = \frac{V(Ci - Ce)}{M} \tag{1}$$

q = amount of metal biosorbed by biomass (mg/g); V = Volume of metal solution (L); Ci = Initial concentration of metal (mg/L); Ce = Concentration of metal (mg/L) at equilibrium; M = Mass of adsorbent.

Units = milligrams of solute sorbed per gram of dry biosorbent material (when engineering process – mass balance calculations are to be considered) or mmol/g (when the mechanism or stoichiometry are to be considered).

According to Abdi and Kazemi [49], in order to observe biosorption kinetics of any heavy metal, sorption performance of a biosorbent must be taken into consideration. For it, a biosorption isotherm should be studied. A biosorption isotherm is the plot of uptake of metal (q) versus equilibrium solute concentration in the solution (Cf). For studying the isotherm plots, parameters including temperature, pH and ionic strength are kept constant whereas metal concentration is varied. Literature showed that confusion prevails regarding pH because it is common believe that pH of a medium changes during whole process of biosorption. Biosorption isotherms are typically described by two models (i) Freundlich and (ii) Langmuir. These models are two - parameters models which are vastly used to describe the equilibrium state for adsorption of metal ions experimental work [48].

Freundlich model: Freundlich and Kuster in (1907) published first mathematical equation to describe the isotherm. It is a non-liner sorption model. It involves monolayer sorption of metal with active sites and is described by continuous interactions between adsorbed molecules [49, 103]. It is given by Eq. 2:

$$qe = K\,Ce_{n}^{1} \tag{2}$$

K = mg/g or l/mg; 1/n or n = Freundlich constant related to adsorption capacity; n = Freundlich constant related to adsorption intensity.

Langmuir model: Langmuir in 1918 published a model for describing gas or liquid adsorbed on solid material. It describes the monolayer sorption of metal with active sites and do not involve interactions between adsorbed molecules [48, 49]. It is given by Eq. 3:

$$qe = \frac{qmaxbCe}{1+bCe} \tag{3}$$

qe = Amount of metal ion removed (mg/g); Ce = Equilibrium concentration (mg/L); b = Langmuir constant related to affinity; qmax = maximum metal uptake (mg/g) under the given conditions.

k, n = Freundlich and Langmuir constants (n value greater than 1.0 shows that sorption is favorable physical process) [49, 104].

9. Desorption and recovery of metals

After biosorption of heavy metal from environment, its recovery is another crucial step which involves desorption of metal from biosorbent. According to previous literatures [105–107], various agents were used for this purpose which includes complexing agents (thiosulfate, EDTA), mineral acids (HNO_3, H_2SO_4, HCl), organic acids (acetic acid, citric acid). Before choosing the recovery agents, it should be kept in mind that chosen recovery agent should given least harm to physical properties of a biosorbent so that its efficiency of metal binding must remain in its original state to ensure its maximum efficiency for metal binding [94, 106, 107].

10. Conclusions

Biosorption is eco-friendly and cheap method of removing metals from the environment. Previous researches conducted during last five decades provided vast amount of information about different types of biosorbents and their mechanism of metal uptake. More research is needed to explore new biosorbents from environment. A deep insight is required not only on method of metal removal, but also its efficient recovery so that it can be obtained in usable form.

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References

[1] Shamim S. Comparative analysis of metal resistance, accumulation and antioxidant enzymes in *Cupriavidus metallidruans* CH34 and *Pseudomonas putida* mt2 during cadmium stress. Ph. D. thesis. Department of Microbiology and Molecular Genetics, University of the Punjab: Pakistan; 2016

[2] Fulekar MH, Singh A, Bhaduri AM. Genetic engineering strategies for enhancing phytoremediation of heavy metals. African Journal of Biotechnology. 2009;**8**(4):529-535

[3] Shokrzadeh M, Saravi SSS. The study of heavy metals (zinc, lead, cadmium, and chromium) in water sampled from Gorgan coast (Iran). Toxicology and Environmental Chemistry. 2009;**91**(3):405-407. DOI: 10.1080/02772240902830755

[4] Tálos K, Páger C, Tonk S, Majdik C, Kocsis B, Kilár F, Pernyeszi T. Cadmium biosorption on native *Saccharomyces cerevisiae* cells in aqueous suspension. Agriculture and Environment. 2009;**1**:20-30

[5] Joo JH, Hassan SHA, Oh SE. Comparative study of biosorption of Zn^{2+} by *Pseudomonas aeruginosa* and *Bacillus cereus*. International Biodeterioration and Biodegradation. 2010;**64**:734-741. DOI: 10.1016/j.ibiod.2010.08.007

[6] Kermani AJN, Ghasemi MF, Khosravan A, Farahmand A, Shakibaie MR. Cadmium bioremediation by metal-resistant mutated bacteria isolated from active sludge of industrial effluent. Iranian Journal of Environmental Health Science and Engineering. 2010;**7**(4):279-286

[7] Singh JS, Abhilash PC, Singh HB, Singh RP, Singh DP. Genetically engineered bacteria: An emerging tool for environmental remediation and future research perspectives. Gene. 2011;**480**:1-9. DOI: 10.1016/j.gene.2011.03.001

[8] Janssen PJ, Houdt RV, Moors H, Monsieurs P, Morin N, Michaux A, Benotmane MA, Leys N, Vallaeys T, Lapidus A, Monchy S, Médigue C, Taghavi S, McCorkle S, Dunn J, van der Lelie D, Mergeay M. The complete genome sequence of *Cupriavidus metallidurans* strain CH34, a master survivalist in harsh and anthropogenic environments. PLoS One. 2010;**5**(5):1-33. DOI: 10.1371/journal.pone.0010433

[9] Kang SH, Singh S, Kim JY, Lee W, Mulchandani A, Chen W. Bacteria metabolically engineered for enhanced phytochelatin production and cadmium accumulation. Applied and Environmental Microbiology. 2007;**73**(19):6317-6320. DOI: 10.1128/AEM.01237-07

[10] El-Sherif IY, Ashmawy A, Badr S. Biosorption of cadmium and nickel by Nile water algae. Journal of Applied Sciences Research. 2008;**4**(4):391-396

[11] Zhang H, Dang Z, Zheng LC, Yi XY. Remediation of soil co-contaminated with pyrene and cadmium by growing maize (*Zea mays* L.). International Journal of Environmental Science and Technology. 2009;**6**(2):249-258

[12] Ike A, Sriprang R, Ono H, Murooka Y, Yamashita M. Bioremediation of cadmium contaminated soil using symbiosis between leguminous plant and recombinant rhizobia with the MTL4 and the PCS genes. Chemosphere. 2007;**66**:1670-1676. DOI: 10.1016/j.chemosphere.2006.07.058

[13] Siñeriz ML, Kothe E, Abatel CM. Cadmium biosorption by Streptomyces sp. F4 isolated from former uranium mine. Journal of Basic Microbiology. 2009;**49**:55-62. DOI: 10.1002/jobm.200700376

[14] Pagnanelli F, Viggi CC, Toro L. Isolation and quantification of cadmium removal mechanisms in batch reactors inoculated by sulphate reducing bacteria: Biosorption versus bioprecipitation. Bioresource Technology. 2010;**101**:2981-2987. DOI: 10.1016/j.biortech.2009.12.009

[15] Nies DH. Microbial heavy-metal resistance. Applied Microbiology and Biotechnology. 1999;**51**:730-750

[16] Grosse C, Anton A, Hoffmann T, Franke S, Schleuder G, Nies DH. Identification of a regulatory pathway that controls the heavy-metal resistance system Czc via promoter czcNp in *Ralstonia metallidurans*. Archives of Microbiology. 2004;**182**(2-3):109-118. DOI: 10.1007/s00203-004-0670-8

[17] Nies DH. The elements: Essential and toxic effects on microorganisms. In: Anke K, Ihnat M, Stoeppler M, editors. Metals and their Compounds in the Environment, Part II. Weinheim: John Wiley; 2004

[18] Rehman A. Survey of protozoan fauna surviving in stress conditions in industrial wastes and their role in bioremediation - Ph. D. thesis. Department of Zoology, University of the Punjab, Lahore; 2006

[19] Weast RC. CRC Handbook of Chemistry and Physics. 64th ed. Boca Raton: CRC; 1984

[20] Zhang Y, Zhang H, Li X, Su Z, Zhang C. The cadA gene in cadmium-resistant bacteria from cadmium-polluted soil in the Zhangshi area of northeast China. Current Microbiology. 2008;**56**(3):236-239. DOI: 10.1007/s00284-007-9064-x

[21] Kalantari N. Evaluation of toxicity of iron, chromium and cadmium on *Bacillus cereus* growth. Iranian Journal of Basic Medical Sciences. 2008;**10**(4):222-228

[22] Norton L, Baskaran K, McKenzie T. Biosorption of zinc from aqueous solutions using biosolids. Advances in Environmental Research. 2004;**8**:629-635

[23] Crini G. Non-conventional low-cost adsorbents for dye removal: A review. Bioresource Technology. 2006;**97**:1061-1085. DOI: 10.1016/j.biortech.2005.05.001

[24] Costa MC, Martins M, Jesus C, Duarte JC. Treatment of acid mine drainage by sulphate-reducing bacteria using low cost matrices. Water, Air, and Soil Pollution. 2008;**189**: 149-162

[25] Chen G, Zeng G, Tang L, Du C, Jiang X, Huang G, Liu H, Shen G. Cadmium removal from simulated wastewater to biomass byproduct of *Lentinus edodes*. Bioresource Technology. 2008;**99**(15):7034-7040. DOI: 10.1016/j.biortech.2008.01.020

[26] Tang L, Zeng GM, Shen GL, Li YP, Zhang Y, Huang DL. Rapid detection of picloram in agricultural field samples using a disposable immunomembrane based electrochemical sensor. Environmental Science and Technology. 2008;**42**:1207-1212

[27] Malik A. Metal bioremediation through growing cells. Environment International. 2004;**30**:261-278. DOI: 10.1016/j.envint.2003.08.001

[28] Tabak H, Lens P, Hullebusch EV, Dejonghe W. Developments in bioremediation of soils and sediments polluted with metals and radionuclides-1. Microbial processes and mechanisms affecting bioremediation of metal contamination and influencing metal toxicity and transport. Reviews in Environmental Science and Bio/Technology. 2005; **4**:115-156

[29] Gadd GM. Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment. Journal of Chemical Technology and Biotechnology. 2009;**84**:13-28

[30] Choudhary S, Sar P. Characterization of a metal resistant Pseudomonas sp. isolated from uranium mine for its potential in heavy metal (Ni^{2+}, Co^{2+}, Cu^{2+}, and Cd^{2+}) sequestration. Bioresource Technology. 2009;**100**:2482-2492. DOI: 10.1016/j.biortech.2008.12.015

[31] Hajdu R, Pinheiro JPR, Galceran J, Slaveykova VI. Modeling of Cd uptake and efflux kinetics in metal-resistant bacterium *Cupriavidus metallidurans*. Environmental Science and Technology. 2010;**44**:4597-4602. DOI: 10.1021/es100687h

[32] Volesky B. Biosorption process simulation tools. Hydrometallurgy. 2003;**71**:179-190

[33] Gabr RM, Hassan SHA, Shoreit AAM. Biosorption of lead and nickel by living and non-living cells of *Pseudomonas aeruginosa* ASU 6a. International Biodeterioration and Biodegradation. 2008;**62**:195-203

[34] Hassan SHA, Kim SJ, Jung AY, Joo JH, SE O, Yang JE. Biosorptive capacity of Cd(II) and Cu(II) by lyophilized cells of *Pseudomonas stutzeri*. Journal of General and Applied Microbiology. 2009;**55**:27-34

[35] Vasudevan P, Padmavathy V, Dhingra SC. Kinetics of biosorption of cadmium on Baker's yeast. Bioresource Technology. 2003;**89**:281-287

[36] Cruz C, Costa A, Hemriques CA, Luna AS. Kinetic modeling and equilibrium studies during cadmium adsorption by dead Sargassum sp. biomass. Bioresource Technology. 2004;**91**:249-257

[37] Dostalek P, Patzak M, Matejka P. Influence of specific growth limitation on biosorption of heavy metals by *Saccharomyces cerevisiae*. International Biodeterioration and Biodegradation. 2004;**54**:203-207

[38] Göksungur Y, Üren S, Güvenç U. Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. Bioresource Technology. 2005;**96**:103-109. DOI: 10.1016/j.biortech.2003.04.002

[39] Ledrich ML, Stemmler S, Laval-Gilly P, Foucaud L, Falla J. Precipitation of silver-thiosulfate complex and immobilization of silver by *Cupriavidus metallidurans* CH34. Biometals. 2005;**18**:643-650. DOI: 10.1007/s10534-005-3858-8

[40] Wang J, Chen C. Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review. Biotechnology Advances. 2006;**24**:427-451. DOI: 10.1016/j.biotechadv.2006.03.001

[41] Ghorbani F, Younesi H, Ghasempouri SM, Zinatizadeh AA, Amini M, Daneshi A. Appli cation of response surface methodology for optimization of cadmium biosorption in an aqueous solution by *Saccharomyces cerevisiae*. Chemical Engineering Journal. 2008;**145**:267-275

[42] Fereidouni M, Daneshi A, Younesi H. Biosorption equilibria of binary Cd(II) and Ni(II) systems onto *Saccharomyces cerevisisae* and *Ralstonia eutropha* cells: Application of response surface methodology. Journal of Hazardous Materials. 2009;**2**(3):1437-1448. DOI: 10.1016/j.jhazmat.2009.03.041

[43] Volesky B, Schiewer S. Biosorption, metals. In: Flickinger MC, Drew SW, editors. Encyclopedia of Bioprocess Technology: Processes Fermentation Biocatyalysis and Biosorption. New York: John Wiley and Sons; 2000. pp. 433-453

[44] Valls M, de Lorenzo V. Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. FEMS Microbiology Reviews. 2002;**26**: 327-338

[45] Sinha S, Mukherjee SK. Pseudomonas aeruginosa KUCD1, a possible candidate for cadmium bioremediation. Brazilian Journal of Microbiology. 2009;**40**:655-662. DOI: 10.1590/S1517-838220090003000030

[46] Lima AIG, Corticeiro SC, Figueira EMAP. Glutathione-mediated cadmium sequestration in *Rhizobium leguminosarum*. Enzyme and Microbial Technology. 2006;**39**(4):763-769

[47] Aksu Z, Sag Y, Kutsal T. The biosorption of copper by *C. vulgaris* and *Z. ramigera*. Environmental Technology. 1992;**13**:579-586

[48] Abbas SH, Ismail IM, Mostafa TM, Sulaymon AH. Biosorption of heavy metals: A review. Journal of Chemical Science and Technology. 2014;**3**(4):74-102

[49] Abdi O, Kazemi MA. Review study of biosorption of heavy metals and comparison between different biosorbents. Journal of Materials and Environmental Science. 2015;**6**(5):1386-1399

[50] Chen XC, Wang YP, Lin Q, Shi JY, WX W, Chen YX. Biosorption of copper(II) and zinc(II) from aqueous solution by *Pseudomonas putida* CZ1. Colloids and Surfaces B: Biointerfaces. 2005;**46**(2):101-107. DOI: 10.1016/j.colsurfb.2005.10.003

[51] Akhtar N, Iqbal M, Zafar SI, Iqbal J. Biosorption characteristics of unicellular green alga *Chlorella sorokiniana* immobilized in loofa sponge for removal of Cr(III). Journal of Environmental Sciences. 2008;**20**:231-239

[52] Galceran J, van Leeuwen HP. Dynamics of biouptake processes: The role of transport, adsorption and internalisation. In: van Leeuwen HP, Köster W, editors. Physicochemical Kinetics and Transport at Biointerfaces. Chichester: John Wiley and Sons; 2004. pp. 147-203. DOI: 10.1002/0470094044.ch4

[53] Wilkinson KJ, Buffle J. Critical evaluation of physicochemical parameters and processes for modelling the biological uptake of trace metals in environmental (aquatic) systems. In: Van Leeuwen HP, Koester W, editors. Physicochemical Kinetics and Transport at Biointerfaces. Chichester: John Wiley and Sons; 2004. pp. 447-533

[54] Volesky B. Advances in biosorption of metals: Selection of biomass types. FEMS Microbiology Reviews. 1994;**14**:291-302

[55] Bruins MR, Kapil S, Oehme FW. Microbial resistance to metals in the environment. Ecotoxicology and Environmental Safety. 2000;**45**:198-207. DOI: 10.1006/eesa.1999.1860

[56] Nies DH. Efflux-mediated heavy metal resistance in prokaryotes. FEMS Microbiology Reviews. 2003;**27**:313-339

[57] Diels L, Spaans P, Van Roy S, Hooyberghs L, Ryngaert A, Wouters H, Walter E, Winters J, Macaskie L, Finlay J, Pernfuss B, Woebking H, Pumpel T, Tsezos M. Heavy metals removal by sand filters inoculated with metal sorbing and precipitating bacteria. Hydrometallurgy. 2003;**71**:235-241

[58] Shamim S, Rehman A. Cadmium resistance and accumulation potential of Klebsiella Pneumoniae strain CBL-1 isolated from industrial wastewater. Pakistan Journal of Zoology. 2012;**44**(1):203-208

[59] Campbell PGC, Errecalde O, Fortin C, Hiriart-Baer VP, Vigneault B. Metal bioavailability to phytoplankton-applicability of the biotic ligand model. Comparative Biochemistry and Physiology Part C: Toxicology and Pharmacology. 2002;**133**:189-206

[60] Pabst MW, Miller CD, Dimkpa CO, Anderson AJ, McLean JE. Defining the surface adsorption and internalization of copper and cadmium in a soil bacterium, *Pseudomonas putida*. Chemosphere. 2010;**81**:904-910. DOI: 10.1016/j.chemosphere.2010.07.069

[61] Nies DH, Silver S. Ion efflux systems involved in bacterial metal resistances. Journal of Industrial Microbiology. 1995;**14**:186-199

[62] Norberg A, Persson H. Accumulation of heavy metal ions by Zoogloea ramigera. Biotechnology and Bioengineering. 1984;**26**:239-245. DOI: 10.1002/bit.260260307

[63] Wang JL, Chen C. Biosorbents for heavy metals removal and their future - a review. Biotechnology Advances. 2009;**27**:195-226. DOI: 10.1016/j.biotechadv.2008.11.002

[64] Urrutia MM. General bacterial sorption processes. In: Wase J, Forster C, editors. Biosorbents for metal ions, CRC Press. UK: London; 1997. pp. 39-66

[65] Vasudevan P, Padmavathy V, Tewari N, Dhingra SC. Biosorption of heavy metal ions. Journal of Scientific and Industrial Research. 2001;**60**:112-120

[66] Kinoshita H, Sohma Y, Ohtake F, Ishida M, Kawai Y, Kitazawa H, Saito T, Kimura K. Biosorption of heavy metals by lactic acid bacteria and identification of mercury binding protein. Research in Microbiology. 2013;**164**(7):701-709. DOI: 10.1016/j.resmic.2013.04.004

[67] Vijayaraghavan K, Yun KS. Bacterial biosorbents and biosorption. Biotechnology Advances. 2008;**26**(3):266-291. DOI: 10.1016/j.biotechadv.2008.02.002

[68] Gourdon R, Bhende S, Rus E, Sofer SS. Comparison of cadmium biosorption by gram-positive and gram-negative bacteria from activated sludge. Biotechnology Letters. 1990;**12**(11):839-842

[69] Das N, Vimala R, Karthika P. Biosorption of heavy metals – An overview. Indian Journal of Biotechnology. 2008;**7**:159-169

[70] Kuyicak N, Volesky B. Biosorption by fungal biomass. In: Volesky B, editor. Biosorption of Heavy Metals. Florida: CRC press; 1990. pp. 173-198

[71] Khani MH. Uranium biosorption by Padina sp. algae biomass: Kinetics and thermodynamics. Environmental Science and Pollution Research International. 2011;**18**:1593-1605

[72] Flouty R, Estephane G. Bioaccumulation and biosorption of copper and lead by a unicellular algae *Chlamydomonas reinhardtii* in single and binary metal systems: A comparative study. Journal of Environmental Management. 2012;**111**:106-114

[73] Trinelli MA, Areco MM, Mdos SA. Co-biosorption of copper and glyphosate by *Ulva lactuca*. Colloids and Surfaces B: Biointerfaces. 2013;**105**:251-258

[74] Oyedepo TA. Biosorption of lead (II) and copper (II) metal ions on *Calotropis procera* (Ait.). Science Journal of Pure and Applied Chemistry. 2011;**1**:1-7

[75] Wang J, Chen C. Biosorption of heavy metals by saccharomyces cerevsiae: A review. Biotechnology Advances. 2006;**24**:427-451. DOI: 10.1016/j.biotechadv.2006.03.001

[76] Gadd GM, Griffiths AJ. Effect of copper on morphology of *Aureobasidium pullulans*. Transactions of the British Mycological Society. 1980;**74**:387-392

[77] Gadd GM, Mowll JL. Copper uptake by yeast-like cells, hyphae and chlamydospores of *Aureobasidium pullulans*. Experimental Mycology. 1985;**9**:230-240

[78] Remacle J. The cell wall and metal binding. In: Volesky B, editor. Biosorption of Heavy Metals. Boca Raton, Florida, USA: CRC Press; 1990. pp. 83-92

[79] Huang C, Huang CP. Application of *Aspergillus oryzae* and *Rhizopus oryzae* for Cu (II) removal. Water Research. 1996;**30**:1985-1990

[80] Kapoor A, Viraraghavan T. Fungi as biosorbent. In: DAJ W, Forster CF, editors. Biosorbents for Metal Ions. London, UK: Taylor and Francis; 1997. pp. 67-85

[81] Peregol P, Howell SB. Molecular mechanisms controlling sensitivity to toxic metal ions in yeast. Toxicology and Applied Pharmacology. 1997;**147**:312-318. DOI: 10.1006/taap.1997.8271

[82] Eide D. Molecular biology of iron and zinc uptakes in eukaryotes. Current Opinion in Cell Biology. 1997;**9**:573-577

[83] Eide DJ. The molecular biology of metal ion transport in *Saccharomyces cerevisiae*. Annual Review of Nutrition. 1998;**18**:441-469. DOI: 10.1146/annurev.nutr.18.1.441

[84] Zhou. Microbiology. 2nd ed. Beijing: Higher Education Press; 2002. (in Chinese)

[85] Horikoshi T, Nakajima A, Sakaguchi R. Studies on the accumulation of heavy metal elements in biological systems: Accumulation of uranium by microorganisms. European Journal of Applied Microbiology and Biotechnology. 1981;**12**:90-96

[86] Veglio F, Beolchini F. Removal of metals by biosorption: A review. Hydrometallurgy. 1997;**44**:301-316

[87] Marques PA, Pinheiro HM, Teixeria JA, Rosa MF. Removal efficiency of Cu^{2+}, Cd^{2+} and Pb^{2+} by waste brewery biomass: pH and cation association effects. Desalination. 1999; **124**:137-144

[88] Park JK, Lee JW, Jung JY. Cadmium uptake capacity of two strains of *Saccharomyces cerevisiae* cells. Enzyme and Microbial Technology. 2003;**33**:371-378

[89] Bakkaloglu I, Butter TJ, Evison LM, Holland FS, Hancock IC. Screening of various types of biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption, sedmimentation and desorption. Water Science and Technology. 1998;**38**:269-277

[90] Soares EV, Coninck GD, Duarte F, Soares HMVM. Use of saccharomyces cerevisaie for Cu2+ removal from solution: The advantages of using a flocculent strain. Biotechnology Letters. 2002;**24**:663-666

[91] Mapolelo M, Torto N. Trace enrichment of metal ions in aquatic environments by *Saccharomyces cerevisiae*. Talanta. 2004;**64**:39-47. DOI: 10.1016/j.talanta.2003.10.058

[92] Kelly-Vargas K, Cerro-Lopez M, Reyna-Tellez S, Bandala ER, Sanchez-Salas JL. Biosorption of heavy metals in polluted water, using different waste fruit cortex. Physics and Chemistry of the Earth. 2012;**37-39**:26-29. DOI: 10.1016/j.pce.2011.03.006

[93] White C, Sayer JA, Gadd GM. Microbial solubilization and immobilization of toxic metals: Key biogeochemical processes for treatment of contamination. FEMS Microbiology Reviews. 1997;**20**(3-7):503-516

[94] Ahalya N, Ramachandra TV, Kanamadi RD. Biosorption of heavy metals. Research Journal of Chemistry and Environment. 2003;**7**:71-79

[95] Goyal N, Jain SC, Banerjee UC. Comparative studies on the microbial adsorption of heavy metals. Advances in Environmental Research. 2003;**7**:311-319

[96] Greene B, Darnall DW. Microbial oxygenic photoautotrophs (cyanobacteria and algae) for metal-ion binding. In: Ehrlich HL, Brierley CL, editors. Microbial Mineral Recovery. New York: McGraw-Hill; 1990. pp. 227-302

[97] Deng X, Wang P. Isolation of marine bacteria highly resistant to mercury and their bioaccumulation process. Bioresource Technology. 2012;**121**:342-347

[98] Gadd GM, White C. Copper uptake by Penicillium ochro-chloron: Influence of pH on toxicity and demonstration of energydependent copper influx using protoplasts. Journal of General Microbiology. 1985;**131**:1875-1879

[99] Modak JM, Natarajan KA. Biosorption of metals using nonliving biomass-a review. Minerals and Metallurgical Processing. 1995;**12**:189-196

[100] Gourdon R, Bhande S, Rus E, Sofer SS. Comparison of cadmium biosorption by gram-positive and gram-negative bacteria from activated sludge. Biotechnology Letters. 1990;**12**(11):839-842

[101] Nuhoglu Y, Malkoc E. Investigations of nickel (II) removal from aqueous solutions using tea factory waste. Journal of Hazardous Materials. 2005;**127**:120. DOI: 10.1016/j.jhazmat.2005.06.030

[102] Zouboulis AL, Matis KA, Hancock IC. Biosorption of metals from dilute aqueous solutions. Separation and Purification Methods. 1997;**26**:255-295. DOI: 10.1080/03602549708014160

[103] Jalali-Rad R, Ghafourian H, Asef Y, Dalir ST, Sahafipour MH, Gharanjik BM. Biosorption of cesium by native and chemically modified biomass of marine algae: Introduce the new biosorbents for biotechnology applications. Journal of Hazardous Materials. 2004;**116**(1-2):125-134. DOI: 10.1016/j.jhazmat.2004.08.022

[104] El-Sikaily A, El-Nemr A, Khaled A. Copper sorption onto dried red alga *Pterocladia capillacea* and its activated carbon. Chemical Engineering Journal. 2011;**168**(2):707-714. DOI: 10.1016/j.cej.2011.01.064

[105] Kiran I, Akar T, Tunali S. Biosorption of Pb (II) and Cu (II) from aqueous solution by pretreated biomass of *Neurospora crassa*. Process Biochemistry. 2005;**40**(11):3550-3558. DOI: 10.1016/j.procbio.2005.03.051

[106] Alluri HK, Ronda SR, Settalluri VS, Bondili JS, Suryanarayana V, Venkateshwar P. Biosorption: An eco-friendly alternative for heavy metal removal. African Journal of Biotechnology. 2007;**6**:2924-2931

[107] Ahemad M, Kibret M. Recent trends in microbial biosorption of heavy metals: A review. Biochemistry and Molecular Biology. 2013;**1**(1):19-26

[108] Dey U, Chatterjee S, Mondal NK. Isolation and characterization of arsenic-resistant bacteria and possible application in bioremediation. Biotechnology Reports. 2016;**10**:1-7. DOI: 10.1016/j.btre.2016.02.002

[109] Banerjee S, Datta S, Chattyopadhyay S, Sarkar P. Arsenic accumulation and transforming bacteria from contaminated soil for potential use in bioremediation. Journal of Environmental Science and Health. Part A. Toxic/Hazardous Substances and Environmental Engineering. 2011;**46**(14):1736-1747. DOI: 10.1080/10934529.2011.623995

[110] Majumder A, Ghosh S, Saha N, Kole SC, Sarkar S. Arsenic accumulating bacteria isolated from soil for possible application in bioremediation. Journal of Environmental Biology. 2013;**34**(5):841-846

[111] Shamim S, Rehman A. Physicochemical surface properties of *Cupriavidus metallidurans* CH34 and *Pseudomonas putida* mt2 under cadmium stress. Journal of Basic Microbiology. 2013;**54**(4):306-314. DOI: 10.1002/jobm.201200434

[112] Shamim S, Rehman A, Qazi MH. Swimming, swarming, twitching and chemotactic response of *Cupriavidus metallidurans* CH34 and *Pseudomonas putida* mt2 in the presence of cadmium. Archives of Environmental Contamination and Toxicology. 2013;**66**(3):407-414. DOI: 10.1007/s00244-013-9966-5

[113] Shamim S, Rehman A, Qazi MH. Cadmium resistance mechanism of *Cupriavidus metallidurans* CH34 and *Pseudomonas putida* mt2. Archives of Environmental Contamination and Toxicology. 2013;**67**(2):149-157. DOI: 10.1007/s00244-014-0009-7

[114] Shamim S, Rehman A. Antioxidative enzyme profiling and biosorption ability of *Cupriavidus metallidurans* CH34 and *Pseudomonas putida* mt2 under cadmium stress. Special issue, microbes in bioremediation. Journal of Basic Microbiology. 2015;**55**(3):374-381. DOI: 10.1002/jobm.201300038

[115] Rani MJ, Hemambika B, Hemapriya J, Kannan VR. Comparative assessment of heavy metal removal by immobilized and dead bacterial cells: A biosorption approach. African Journal of Environmental Science and Technology. 2010;**4**(2):077-083

[116] Congeevaram S, Dhanarani S, Park J, Dexilin M, Thamaraiselvi K. Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. Journal of Hazardous Materials. 2007;**146**:270-277. DOI: 10.1016/j.jhazmat.2006.12.017

[117] Sulaymon AH, Mohammed AA, Al-Musawi TJ. Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae. Environmental Science and Pollution Research International. 2012;**20**:3011-3023. DOI: 10.1007/s11356-012-1208-2

[118] Jencarova J, Luptakova A. The elimination of heavy metal ions from waters by biogenic iron sulphides. Chemical Engineering Transactions. 2012;**28**:205-210

[119] Babak L, Šupinova P, Zichova M, Burdychova R, Vitova E. Biosorption of Cu, Zn and Pb by thermophilic bacteria – Effect of biomass concentration on biosorption capacity. Acta Universitatis Agriculturae Et Silviculturae Mendelianae Brunesis. 2012;**60**:9-18

[120] Gao R, Wang Y, Zhang Y, Dai W. Cobalt (II) bioaccumulation and distribution in *Rhodopsseudomonas palustris*. Biotechnology and Biotechnological Equipment. 2017;**31**(3): 527-537. DOI: 10.1080/13102818.2017. 1292 148

[121] Karakagh RM, Chorom M, Motamedi H, Kalkhajeh YKY, Oustan S. Biosorption of Cd and Ni by inactivated bacteria isolated from agricultural soil treated with sewage sludge. Ecohydrology and Hydrobiology. 2012;**12**(3):191-198. DOI: 10.1016/S1642-3593(12) 70203-3

[122] Samarth DP, Chandekar CJ, Bhadekar RK. Biosorption of heavy metals from aqueous solution using *Bacillus licheniformis*. International Journal of Pure and Applied Sciences and Technology. 2012;**10**(2):12-19

[123] Nagashetti V, Mahadevaraju GK, Muralidhar TS, Javed A, Trivedi D, Bhusal KP. Biosorption of heavy metals from soil by *Pseudomonas aeruginosa*. International Journal of Innovative Technology and Exploring Engineering (IJITEE). 2013;**2**(6):9-17

[124] Hussein H, Ibrahim SF, Kandeel K, Moawad H. Biosorption of heavy metals from waste water using Pseudomonas sp. Electronic Journal of Biotechnology. 2004;**7**(1):1-2. DOI: 10.2225/vol7-issue1-fulltext-2

[125] Monsieurs P, Hobman J, Vandenbussche, Mergeay M, Houdt RV. Response of *Cupriavidus metallidurans* CH34 to metals. In: Mergeay M, Houdt RV, editors. Metal Response in Cupriavidus Metallidurans; Volume I: From Habitats from Genes and Proteins. Springer Briefs in Molecular Science, Biometals. pp. 45-89

[126] Hemambika B, Rani MJ, Kannan VR. Biosorption of heavy metals by immobilized and dead fungal cells: A comparative assessment. Journal of Ecology and the Natural Environment. 2011;**3**(5):168-175

[127] Romera E, Gonzalez F, Ballester A, Blazquez ML, Munoz JA. Biosorption with algae: A statistical review. Critical Reviews in Biotechnology. 2006;**26**:223-235. DOI: 10.1080/07388550600972153

[128] Viraraghavan T, Srinivasan A. Fungal biosorption and biosorbents. In: Kotrba P, Mackova M, Macek T, editors. Microbial Biosorption of Metals. Dordrecht: Springer; 2011. pp. 143-158. DOI: 10.1007/978-94-007-0443-5-6

[129] Gina KY, Tanga YZ, Aziz MA. Derivation and application of a new model for heavy metal biosorption by algae. Water Research. 2002;**36**:1313-1323

[130] Sheikha D, Ashour I, Abu Al-Rub FA. Biosorption of zinc on immobilized green algae: Equilibrium and dynamics studies. The Journal of Engineering Research. 2008;**5**(1):20-29

[131] Ramsenthil R, Meyyappan R. Single and multi-component biosorption of copper and zinc ions using microalgal resin. International Journal of Environmental Science and Development. 2010;**1**(4):298-301

[132] Subhashini S, Kaliappan S, Velan M. Removal of heavy metal from aqueous solution using *Schizosaccharomyces pombe* in free and alginate immobilized cells. In: 2nd International Conference on Environmental Science and Technology IPCBEE. Vol. 6. Singapore: IACSIT Press; 2011. pp. V2107-V2111

[133] Hajar M. Biosorption of cadmium from aqueous solution using dead biomass of brown alga Sargassum sp. Chemical Engineering Transactions. 2009;**17**:1173-1178. DOI: 10.3303/CET0917196

[134] Brinza L, Dring MJ, Gavrilescu M. Marine micro and macro algal species as biosorbents for heavy metals. Environmental Engineering and Management Journal. 2007;**6**:237-251

[135] Kumar JI, Oommen C. Removal of heavy metals by biosorption using freshwater alga *Spirogyra hyaline*. Journal of Environmental Biology. 2012;**33**(1):27-31

[136] Yavuz H, Denizli A, Güngünes H, Safarikova M, Safarik I. Biosorption of mercury on magnetically modified yeast cells. Separation and Purification Technology. 2006;**52**:253-260. DOI: 10.1016/j.seppur.2006.05.001

[137] Lodeiro P, Cordero B, Barriada JL, Herrero R, de Vicente MES. Biosorption of cadmium by biomass of brown marine macroalgae. Bioresource Technology. 2002;**96**(16):1796-1803. DOI: 10.1016/j.biortech.2005.01.002

[138] Brahmbhatt, Rinku NH, Patel V, Jasrai RT. Removal of cadmium, chromium and lead from filamentous alga of Pithophora sp. of industrial wastewater. International Journal of Environmental Sciences. 2012;**3**(1):408-411. DOI: 10.6088/ijes.2012030131039

[139] Saravanan, Brindha V, Krishnan S. Studies on the structural changes of the biomass Sargassum sp. Journal of Advanced Bioinformatics Applications and Research. 2011; **2**(3):193-196

[140] Mamisahebei S, Khaniki GRJ, Torabian A, Nasseri S, Naddafi K. Removal of arsenic from an aqueous solution by pretreated waste tea fungal biomass. Journal of Environmental Health Science and Engineering. 2007;**4**(2):85-92

[141] Rodríguez IA, Martínez-Juárez VM, Cárdenas-González JF, Moctezume-Zárate. Biosorption of arsenic (III) from aqueous solutions by modified fungal biomass of Paecilomyces sp. Bioiorganic Chemistry and Applications. 2013;**2013**:1-5. DOI: 10.1155/2013/376780

[142] Martínez-Júarez VM, Cárdenas-González JF, Torre-Bouscoulet ME, Acosta-Rodríguez I. Biosorption of mercury (II) from aqueous solutions onto fungal biomass. Bioinorganic Chemistry and Applications. 2012;**2012**:1-5. DOI: 10.1155/2012/156190

[143] Bunluesin S, Kruatrachue M, Pokethitiyook P, Upathan S, Lanza GR. Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass. Journal of Bioscience and Bioengineering. 2007;**103**(6):509-513. DOI: 10.1263/jbb.103.509

[144] Kujan P, Prell A, Safar H, Sobotka M, Rezanka T, Holler P. Use of the industrial yeast *Candida utilis* for cadmium sorption. Folia Microbiology (Praha). 2006;**54**(4):257-260

[145] Javaid A, Bajwa R. Biosorption of Cr (III) ions from tannery wastewater by *Pleurotus ostreatus*. Mycopathologia. 2007;**5**:71-79

[146] Park D, Yun Y-S, Park JM. Use of dead fungal biomass for the detoxification of hexavalent chromium: Screen and kinetics. Process Biochemistry. 2005;**40**:2559-2565

[147] Cossich ES, Tavares CRG, Ravagnani TMK. Biosorption of chromium (III) by Sargassum sp. biomass. Electronic Journal of Biotechnology. 2002;**5**(2):133-140

[148] El-Kassas HY, El-Taher EM. Optimization of batch process parameters by response surface methodology for mycoremediation of chrome-VI by a chromium resistant strain of marine *Trichoderma viride*. American-Eurasian Journal of Agriculture and Environmental Science. 2009;**5**(5):676-681

[149] Sethi BK, Kanungo S, Rout JR, Nanda PK, Sahoo SL. Effect of chromium on Mucor species and optimization of growth conditions. Nature and Science. 2010;**8**(4):29-32

[150] Jha S, Dikshit SN, Pandey G. Comparative study of growing/immobilized biomass verses resting biomass of *A. lentulus* for the effect of pH on Cu^{2+} metal removal. Research Journal of Pharmaceutical, Biological and Chemical Sciences. 2012;**3**(3):421-427

[151] Parungao MM, Tacata PS, Tanayan CRG, Trinidad LC. Biosorption of copper, cadmium and lead by copper-resistant bacteria isolated from Mogpog River, Marinduque. The Philippine Journal of Science. 2007;**136**(2):155-165

[152] Sutherland C, Venkobachar C. A diffusion-chemisorption kinetic model for simulating biosorption using forest macro-fungus, fomes fasciatus. International Research Journal of Plant Science. 2010;**1**(4):107-117

[153] Hassan SW, El-Kassas HY. Biosorption of cadmium from aqueous solutions using a local fungus *Aspergillus cristatus* (Glaucus group). African Journal of Biotechnology. 2012;**11**(9):2276-2286. DOI: 10.5897/AJB11.3140

[154] Osman MS, Bandyopadhyay M. Biosorption of lead (II) ions from wastewater by using a fungus *P. ostreatus*. Journal of Civil Engineering. 1999;**27**(2):193-196

[155] Barros LM Jr, Macedo GR, Duarte MML, Silva EP, Lobato AKCL. Biosorption of cadmium using the fungus *Aspergillus niger*. Brazilian Journal of Chemical Engineering. 2003;**20**(3):229-239. DOI: 10.1590/S0104-66322003000300003

[156] Murugesan GS, Sathishkumar M, Swaminathan K. Arsenic removal from groundwater by pretreated waste tea fungal biomass. Bioresource Technology. 2006;**97**(3):483-487. DOI: 10.1016/j.biortech.2005.03.008

[157] Tay C-C, Liew H-H, Yong S-K, Surif S, Redzwan G, Abdul-Talib S. Cu (II) removal onto fungal derived biosorbents: Biosorption performance and the half saturation constant concentration approach. International Journal of Research in Chemistry and Environment. 2012;**2**(3):138-143

[158] Purkayastha RP, Mitra AK. Metal uptake by mycelia during submerged growth and by sporocarps of an edible fungus *Volvariella volvacea*. Indian Journal of Experimental Biology. 1992;**30**:1184-1187

[159] Muraleedharan TR, Venobachar C. Mechanism of biosorption of copper (II) by Ganoderma lucidium. Biotechnology and Bioengineering. 1990;**35**:320-325

[160] Muraleedharan TR, Iyengar L, Venkobachar C. Screening of tropical wood rotting mushrooms for copper biosorption. Applied and Environmental Microbiology. 1995;**61**: 3507-3508

[161] García MA, Alonso J, Melgar MJ. Agaricus macrosporus as a potential bioremediation agent for substrates contaminated with heavy metals. Journal of Chemical Technology and Biotechnology. 2005;**80**:325-330. DOI: 10.1002/jctb.1203

[162] Anaemene IA. The use of Candida sp. in the biosorption of heavy metals from industrial effluent. European Journal of Experimental Biology. 2012;**2**(3):484-488

[163] Arakaki AH, Vandenberghe LPS, Soccol VT, Musakai R, Filho EFD, Gregório A, Soccol CR. Optimization of biomass production with copper bioaccumulation by yeasts in submerged fermentation. Brazilian Archives of Biology and Technology. 2011;**54**(5):1027-1034. DOI: 10.1590/S1516-89132011000500021

[164] Apinthanapong M, Phensaijai M. Biosorption of copper by spent yeast immobilized in sodium alginate beads. Kasetsart Journal (Natural Science). 2009;**43**:326-332

[165] Prakash BS, Kumar SV. Batch removal of heavy metals by biosorption onto marine algae-equilibrium and kinetic studies. International Journal of Chemical Technology Research. 2013;**5**(3):1254-1262

[166] Muraleedharan TR, Iyengar L, Venkobachar C. Biosorption: An attractive alternative for metal removal and recovery. Current Science. 1991;**61**(6):379-385

Biosorption of Multicomponent Solutions: A State of the Art of the Understudy Case

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Additional information is available at the end of the chapter

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Abstract

Although there has been an intense study and exploitation of research regarding biosorption processes, the lack of coherent and similar methodologies, essential to the elaboration of any consequential and universal conclusion, associated with the lack of biosorption studies conducted at a pilot and industrial scale, with multicomponent solutions or real effluents, as well as the lack of information regarding the pollutant interactions makes the implementation and commercialization of biosorption technology very complicated. This chapter summarizes the existing knowledge and the experimental work conducted at a pilot scale or industrial scale with multicomponent solutions and critically reviews aspects related to biosorption research regarding the advantages, the disadvantages, the rationale, the scope and scientific value of biosorption processes and the obstacles to commercial success.

Keywords: biosorption, bioremoval, metals, organic pollutants, pilot and industrial scale

1. Introduction

Although the contamination of water resources is a widely recognized fact and a critical universal issue, it is still a common occurrence [1, 2]. The major sources of aquatic as well as terrestrial and atmospheric systems contamination are effluent outfalls and gas emissions from industries, agricultural activities and refinery contaminants [2] that end up entering water bodies via rain water, soil and groundwater systems. The contaminants comprise (i) inorganic chemicals such as metals, extensively used in a wide variety of industries, including metal plating, mining, batteries, electroplating, ceramic, chemical manufacturing of paint and coating, health-care products, extractive metallurgy, petrochemical and fine chemistry [3] and (ii) organic chemicals such as industrial solvents, volatile organic compounds (VOCs), pharmaceuticals, insecticides, pesticides, dyes [1] and food processing wastes [2].

The non-natural redistribution of these chemicals has culminated first in their increasing discharge and accumulation into the different environmental matrices and second in the development of environmental and health problems (**Figure 1**) [3, 4]. Therefore, there is a constant search for economical, efficient, effective and eco-friendly processes able to not only decontaminate wastewaters but also ensure that the presence of the pollutants discharged into the aquatic systems is below the permissible limits.

In the past decades, great attention and concern have been given to the continuous and increasing discharge of metals such as chromium, mercury, lead [2], cadmium and nickel into the environment. This increasing concern is due to metals' inherent properties, (i) persistence in nature, (ii) tremendous toxicity even at low concentrations and (iii) tendency for bioaccumulation via food chain in living tissues, which may culminate in the triggering of several serious diseases and health disorders [3].

Chromium compounds, for instance, are carcinogenic and nephrotoxic in nature. Exposure to mercury and lead may provoke allergic skin reaction, eventual negative reproductive effects as well as damage to brain function and disruption of the nervous system [2]. Cadmium exposure may cause severe damage in different organs including the testis, lungs, liver and kidneys and even lead to infertility [5, 6]. It also affects the action of enzymes and induces genomic instability through complex and multifactorial mechanisms, such as proteinuria, and an increase in the frequency of kidney stone formation, eventually causing certain types of cancer (group B1) [3]. Besides being listed in the carcinogenic group B2, nickel has been implicated as a teratogen nephrotoxin and an embryotoxin element. Acute and chronic nickel exposure can cause several disorders such as cyanosis, chest pain, tightness, pulmonary fibrosis, skin dermatitis, lungs and kidney damage and renal oedema [7].

The capacities of metals to disrupt the function of fundamental biological molecules, such as DNA, proteins and enzymes, and to displace certain metals essential for the cell viability by

Figure 1. Sources of pollution by organic and inorganic chemicals, their transport, transformation, fate and impact into the different environmental matrices.

similar metals are the two major causes of their toxicity. For instance, lead can replace calcium in the bone and other tissues where it is required, whereas cadmium can replace zinc in some proteins that require it for their structure as well as function [2].

More recently, the discharge of organic chemicals such as pharmaceutical products [8], volatile organic compounds, aromatic hydrocarbons [9] and dyes [10] has also caught the world attention, due not only to their persistence, toxicity and mobility in the environment but also to their widespread use and discharge as well as their impact on all forms of life.

Despite the fact that every single aspect connected to pharmaceutical efficiency and patient security to be under scrutiny [8], the complete extent and consequences of the presence of emerging pollutants in the environment matrices and on the wellbeing of all forms of life are not yet sufficiently studied in terms of toxicity, degradability and occurrence, allowing it to remain unregulated.

Pharmaceutical compounds have been detected at trace concentrations (ng/L levels) in a wide variety of environmental water samples including sewage flows, rivers, lakes, groundwater aquifers and drinking water [11]. Although the concentrations of these pharmaceutical products have been detected at trace concentrations in a broad variety of aquatic environments, their continuous input may compose a potential threat for living organisms. Furthermore, pharmaceutical products are often synthesized in order to remain unchanged during their passage through the human body, which makes them and their metabolites persistent pollutants in environmental matrices [8].

The increased use of organic compounds in almost, if not all, industrial sectors as well as in household activities and consequent discharge and accumulation into the environment has increased in an extremely significant way in the past years [2, 12–14]. Most of these compounds are extremely toxic to humans due to (i) their general carcinogenic and mutagenic properties, (ii) their capacity to form intermediates with the same or even the higher level of toxicity [15] and (iii) their persistence and mobility into the different environmental matrices [7].

More than 1×10^5 dyes are currently marketed with an annual production exceeding 7×10^5 tons per year, of which about 2% are discharged directly to effluents from manufacturing operations, whereas 10% are discharged from textile and related industries [16]. The dye lost through the practices of textile industry poses a serious problem for wastewater management and treatment, since it can reach loss values as high as 50%. About 2×10^5 tons of dyes are discharged annually into the environment, especially into water bodies [17].

Although chemical precipitation, reverse osmosis, complexation, solvent extraction, ion exchange, adsorption on granular activated carbon, condensation, thermal degradation, oxidation and incineration comprise the conventional abiotic methods usually employed to remove different types of pollutants from effluents [7], biotic methods such as water purification treatments and standard sewage as well as auxiliary reed bed and wetlands approaches [18] have been used for many years. The outstanding ability of microorganisms to detoxify organic and inorganic pollutants [15, 18] and to the downside of the abiotic methods which can be summarized (i) as expensive, (ii) not environmentally friendly and (iii) usually dependent on the concentration of the waste [7] makes them an attractive alternative to decontaminate contaminated solutions.

2. Biosorption: a general overview

Microorganisms, in particular bacteria and fungi, have been receiving particular attention in the area of environmental microbiology and biotechnology due to their ability not only to decompose a wide range of organic compounds, from natural and anthropogenic origin, but also to accomplish changes in the speciation and mobility of metals and radionuclides as well as other inorganic elements by oxidation-reduction and other changes, most of which are a direct consequence of metabolic properties of living organisms and microorganism [18].

Although the term *biosorption* presents a multidimensional character, its definition is rather difficult and has been evolving over the past few decades, due to the diversity of the mechanisms that contribute to the overall process, depending on the sorbate and the biosorbent, on the environmental conditions and on the metabolic processes in the case of living organisms [18, 19].

Some publications [18, 20, 21] indicate that most researchers define biosorption as a passive and metabolically independent process that can be performed either by dead biomass or fragments of cells and tissues or by living cells as an active and metabolic-dependent process. It is important to highlight that both mechanisms can overlap adding additional confusion in the use of the terminology.

It is also important to highlight that (i) biosorption is a crucial part of many processes taking place in nature, including, for example, antigen-antibody immune reactions and adsorption to host cells, as the first stage in virus replication or sorption in soil and that (ii) numerous methodological approaches used in medicine, life sciences and biotechnology are, in fact, based on biosorption processes, for instance, the staining of microbial cells for electron microscopy and targeted therapies in cancer treatment. It is therefore possible to affirm that many life phenomena are in some way related to interactions between a sorbate and biological surfaces [18]. Basically, biosorption is a reversible and rapid process of binding of ions or neutral molecules from aqueous solutions onto functional groups that are present on the surface of biomass, independent on cellular metabolism, efficient and selective [21].

Presently, it is accepted that biosorption is a physico-chemical process, simply defined as the removal of substances from solution by biological material, and includes mechanisms such as absorption, adsorption, surface complexation ion exchange and precipitation [18]. The addition of the prefix *bio* to the term *sorption* denotes the involvement of a biological entity (living or death biomass, as well as their metabolites or synthesized products). Although the majority of biosorption research has been focused on metals and/or metalloid species, the substances to be sorbed can be from either organic or inorganic origin and presented in soluble or insoluble forms. Therefore, considering the diversity of sorbates and sorbents that can be used in all domains of life, it is plausible to use the term biosorption to describe any system where a sorbate (e.g. an atom, molecule, a molecular ion) interacts with a biosorbent (a solid surface of a biological matrix) resulting in an accumulation at the sorbate-biosorbent interface and therefore a reduction in the solution sorbate concentration.

The mesmerizing features of biosorption processes over traditional treatment methods comprise (i) economical operating costs; (ii) inexpensive biological materials, usually obtained from agriculture or from industrial wastes; (iii) high efficiency; (iv) no additional nutrient requirement; (v) minimization of biological or chemical sludge; (vi) biosorbent regeneration; and (vii) the possibility of metal recovery. In addition to all this captivating features, biosorption processes can be accomplished in an extensive range of pH values (from pH 3 to pH 9) and temperature values ranging from 4 to 90°C.

The first paper on biosorption was published in 1951, and since then, enormous efforts have been made to accomplish efficient, effective and economic biosorbents to be employed in wastewater treatment. Fundamental progresses have been accomplished over the past decades in order to understand the complex biosorption mechanisms, the methods for its quantification (equilibrium and kinetics) and the factors that influence efficiency and the rate of the process (**Figure 2**) [20].

Although the majority of the biosorption research conducted till now has been performed on microbial systems, mainly bacteria, microalgae and/or fungi, with metals and related substances (**Table 1**), the term is now being applied to all types of organic compounds and to particulates.

The massive research concerning biosorption of metals is an unsurprising fact, taking into account not only the toxicity effect and increased discharge of these contaminants into the environment but also the nature of adsorption and ion exchange mechanisms. Nevertheless, it is also crucial to highlight that regardless the continuous increase in published research related to the biosorption of hazardous substances and/or elements, there has been little or no exploitation in a pilot and industrial scale and/or context [18] and on the decontamination of multicomponent solutions [3, 4, 7, 22, 23]. In fact, despite the biosorption process that has been discussed in literature for 60 years with over 13,000 scientific papers in peer-reviewed journals [19], so far most of this research was performed in a laboratory scale, using batch tank reactors or packed mini-column, and has not been extensively implemented in an industrial scale and in multicomponent solutions. The team of Professor Bohumil Volesky from McGill University, Canada, and his company BV Sorbex comprise the few researchers that have contributed to

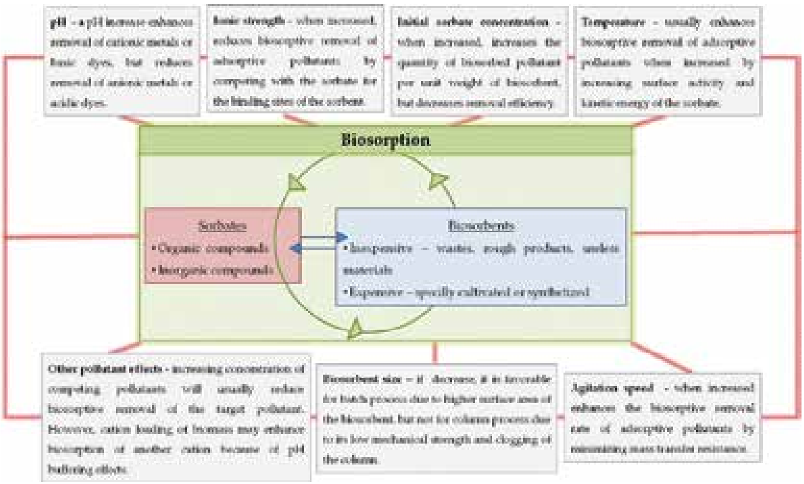

Figure 2. Biosorption process: a global overview (adapted from Refs. [2, 19]).

Position	Paper	Times cited
1	Review of second-order models for adsorption systems *Journal of Hazardous Materials* 136 (3): 681–689	1402
2	Biosorption of heavy metals *Biotechnology Progress* 11 (3): 235–250	1323
3	A review of the biochemistry of heavy metal biosorption by brown algae *Water Research* 37 (18): 4311–4330	1133
4	Application of biosorption for the removal of organic pollutants: A review *Process Biochemistry* 40 (3–4): 997–1026	1002
5	Biosorbents for heavy metals removal and their future *Biotechnology Advances* 27 (2): 195–226	903
6	Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature *Progress in Polymer Science* 33 (4): 399–447	832
7	Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste *Dyes and Pigments* 54 (1): 47–58	759
8	Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water *Journal of Hazardous Materials* 137 (2): 762–811	757
9	Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies *Environmental Science & Technology* 36 (9): 2067–2073	749
10	Interactions of fungi with toxic metals *New Phytologist* 124 (1): 25–60	740

Table 1. The top 10 publications in the ISI Web of Science database (Web of Science Core Collection) for 'all years' (1970–2016) with 'biosorption' in the topic.

the scale-up of sorption process field, from a laboratory scale to a pilot or industrial scale [21]. The team of the Centre of Biological Engineering from the University of Minho, Portugal, has also been contributing to the study and understanding of (i) the scale-up of biosorption processes from a laboratory scale to a pilot scale and (ii) the increase of solution complexity to be decontaminated, evolving from single-component solutions to multicomponent solutions, mixing organic and inorganic compounds [3, 4, 7, 9, 15, 24], the main subject of this chapter.

3. Biosorption in multicomponent solutions

Although most of industrial and household effluents and wastewater are composed by a cocktail of contaminants made of metal residues and organic compounds, few studies regarding the simultaneous removal of multicomponent solutions have been conducted and optimized, studies that would better simulate the behaviour of the pollutants present in real effluents. The effect that different types of contaminants (inorganic versus inorganic and inorganic versus organic) have on each other and the effect that different initial concentrations of metal exert on the bioremoval (biodegradation and biosorption among other biological processes) of the organic contaminant have also been poorly investigated. For these reasons, the authors opted to review the state of the art of biosorption from multicomponent solutions, from a laboratory scale to a pilot and/or industrial scale.

Costa and Tavares [3] studied the ability of two fungi and one bacteria (*Penicillium* sp., *Alternaria* sp. and *Streptococcus equisimilis*) to simultaneously treat tertiary solutions containing diethylketone, Cd(II) and Ni(II), and they determined the influence of the initial concentration of metal on (a) the microbial growth, (b) the biosorption capacity of these pollutants and (c) the biological activity after exposure. The results obtained regarding the tertiary solutions allowed to infer that *S. equisimilis* presented the best performance in terms of uptake, for all the conditions tested and that an increase in the initial concentration of metal promoted an increase in the uptake. For the same experimental conditions, the biosorption data obtained for the three microorganisms showed (i) a higher affinity of the biosorbents towards Ni(II) and (ii) a strong and detrimental effect of the metals either in the biosorption process or in the microbial growth. These results may be explained by the fact that not only Ni(II) can be used by the cells as a cofactor, competing actively and passively with Cd(III) but is also less toxic than Cd(II).

More complex systems were further evaluated [4] with a suspended bacterial culture of *Streptococcus equisimilis* with different initial concentrations of Ni(II) (5–450 mg/L) and Cd(II) (5–100 mg/L) in single-component solutions compared to vermiculite to decontaminate single-component solutions composed either by diethylketone, Cd(II) or Ni(II) and binary-component solutions composed either by diethylketone and Cd(II) or diethylketone and Ni(II). A *S. equisimilis* biofilm supported on vermiculite to decontaminate binary solutions composed either by diethylketone and Cd(II) or diethylketone and Ni(II) was also evaluated. The principal aim of this research was the characterization of the interactions between the different concentrations of sorbates and the biosorbents used, when employed in single or binary solutions. For the first set of experiments (*S. equisimilis* and different concentrations of Ni(II) or Cd(II), it was observed that the uptake and percentage of influent Ni(II) sorbed depended on the initial concentration of the sorbate. No significant pH changes had occurred, and the uptake suffered a 30-fold increase with the increase of the initial concentration between 5 and 80 mg/L. Nevertheless, there were no significant changes (<10%) in terms of biosorption percentage for the same initial concentration. The biosorption of Cd(II) was also found to depend on the initial concentration, suffering fluctuations lower than 18%. In these assays, there was an increase in terms of pH (from 6.05 to 6.98). This increase resulted in an increase in the hydroxyl and other anionic functional groups, which made the bacterial surface more negative increasing the number of electrostatic interactions. For the second set of experiments, it was observed that the presence of Cd(II) decreases significantly the sorption percentage of diethylketone, but the presence of this organic compound increased Cd(II) sorption percentage. The presence of Ni(II) has a synergetic effect on diethylketone biosorption. For the third set of experiments, it was established that the presence of the biofilm is an advantage, obtaining promising results, specially taking into account not only the concentrations employed but also the toxicity of the metals. In these experiments, a common increase in terms of sorption efficiency was observed, and this may be explained by the functional groups present on the biofilm that can implement the substrate molecule adsorption and eventually promote the biodegradation of diethylketone and by the increase of the available sites for sorption.

Attempting to mimetize the complexity of real effluents and wastewaters, biosorption experiments of multicomponent solutions (Al(III), Ni(II), Cd (II) and Mn(II)) by a *S. equisimilis* biofilm supported into vermiculite were performed first at a laboratory scale in batch system (4 g/L of diethylketone and 5–100 mg/L of each metal) and second at a pilot scale in open systems (7.5 g/L of diethylketone and 100 mg/L of each metal) [7]. Diethylketone was periodically added to the bioreactor and was used as the only carbon source. At laboratory scale, the authors observed that diethylketone and removal percentages higher than 95% were achieved in less than 4 hours for all the initial concentrations of metal tested and that the increase of the initial concentration of metals accelerates the complete bioremoval (by biodegradation and/or biosorption processes, for instance) of diethylketone. Regarding the results obtained for the four metals (5–80 mg/L), it is was found that they follow the sequence Al(III) > Cd(II) ≥ Ni(II) ≥ Mn(II), whereas for the experiment conducted with an initial concentration of 100 mg/L, the bioremoval efficiency followed a different sequence Al(III) > Ni(II) > Cd(II) > Mn(II). This difference may be explained by the increase in the initial concentration of metal, which will influence the ionic strength of the elements in solutions, and also by the fact that many divalent metal cations are structurally similar, allowing the substitution of essential metals, such as Ni(II) and Mn(II) for non-essential metals such as Cd(II). The uptake of all metals increased with the increase of the initial concentration of each metal.

At a pilot scale, it was observed that the biosorption percentage of all the sorbates (organic and inorganic) tended to increase through time and followed the sequence diethylketone > Al(III) > Cd(II) ≈ Ni(II) ≥ Mn(II), and this is explained by the bioavailability and structural similarity between Ni(II) and Cd(II) that promote the uptake of Cd(II) by the cell enzymes instead of Ni(II) and by the combination of the reduced size of the ionic radius of Mn(II) associated with its reduced electronegativity and the small porosity of the support. The complete bioremoval of diethylketone and its metabolites was achieved, even after the addition of diethylketone to the bioreactor and the sorption percentage of each metal increased through time.

The effect of different initial concentrations of Cd(II), Cu(II), Zn(II), Pb(II) and As(II) (10 mg/L or 100 mg/L) on the bioremoval of fluorene (10 mg/L) by *Sphingobacterium* sp. KM-02 was also assessed [25]. The presence of those metals at 10 mg/L decreased fluorine bioremoval, and the microbial growth and the inhibition effect followed the trend Cd(II) ≈ Cu(II) > Zn(II) > Pb (II) > As(II). Cd(II) and Cu(II) strongly inhibited fluorene bioremoval and microbial growth, whereas Zn(II) and Pb(II) exert a modest inhibitory effect. As(II), on the other hand, has no negative effect on microbial growth and fluorene bioremoval.

3.1. Correlation between metal concentration and microbiological processes

Metals including cadmium, chromium (III and VI), copper, lead, mercury, nickel and zinc are reported to inhibit microbiological processes such as acidogenesis, methanogenesis, nitrogen transformation, biomass production and enzymatic activity [22]. *S. equisimilis* exposure (in the form of biofilm supported into vermiculite or in suspension) to solutions containing either Cd(II) or Ni(II) (5–100 mg/L) led to microbial growth inhibition [3, 4]. Nevertheless, it is important to mention that the addition of metals may also have the opposite effect and enhance and/or stimulate microbiological processes. The growth of a suspend culture of *Alternaria* sp. and *Penicillium* sp. when exposed to Ni(II) concentration ranging from 5 to 100 mg/L was enhanced [3], and when this metal was mixed with diethylketone, the entrapment metabolic pathway selected by those microorganisms was different, since no metabolite was formed during the experimental period, as opposite to what occurred when exposed only to diethylketone.

Although studies concerning the influence of metals on organic contaminant bioremoval are scarce, it has been demonstrated that those elements are able to inhibit organic contaminant bioremoval, under both aerobic and anaerobic conditions.

Cadmium, chromium (II), copper, mercury and zinc were found to inhibit the biodegradation of 2,4-DME in lake water samples inoculated with either a sediment or an aufwuch (floating algal mat) sample [26]. In the aufwuch samples, mercury revealed to be the most toxic metal, with a microbial inhibitory concentration (MIC) of 2×10^{-3} mg total mercury/L, whereas in the sediment samples, zinc was the most toxic metal with a MIC of 6×10^{-3} mg total zinc/L. Naphthalene (NAPH)-degrading *Burkholderia* sp. was used in a pure culture and reported a MIC of 1 mg solution-phase cadmium/ L [27]. Comparable values of MIC were reported for cadmium (0.629 mg total cadmium/L for aufwuch samples and 0.1 mg total cadmium/L for sediment samples) [26].

Not all studies were focused on the effect of single metals on bioremoval of a single, pure organic pollutant. Benka-Coker and Ekundayo [28] investigated the impact of copper, manganese, lead and zinc on crude oil biodegradation by *Pseudomonas* sp. and *Micrococcus* sp. These authors inferred that the crude oil was mostly reduced by zinc and slightly by manganese. Interestingly, combinations of these metals presented a lesser toxic profile than some single metals. For instance, toxicity of 0.5 mg total zinc/L was mitigated by the addition of 0.5 mg total copper, lead and manganese/L.

3.2. Correlation between metal concentration and bioremoval inhibition

It is acknowledged that the bioremoval of an organic pollutant decreases as the concentration of bioavailable metal increases in co-contaminated systems (**Figure 3**). However, this pattern is not always observed. Two other additional patterns describing the effect of metals on the bioremoval of organic pollutants have been shown.

Low metal concentration enhances bioremoval of organic pollutant; high metal concentrations inhibit it—additional pattern 1: diverse studies showed a pattern of metal toxicity in which low metal concentrations enhance bioremoval activity, till the maximum level of stimulation is reached. After this point, an increase in metal concentration will lead to an increase in metal toxicity (**Figure 3**, Line 2). Sustaining this pattern is the result obtained by Capone et al. [29] showing that methanogenesis was enhanced by the addition of some metals.

Bioremoval inhibition of organic pollutants is due to low metal concentration; lower bioremoval inhibition of organic pollutants is due to high metal concentration—additional pattern 2: several studies suggested that low concentrations of metal strongly inhibit bioremoval activity, until a maximum of inhibition is achieved (**Figure 3**, Line 3). After this point, an

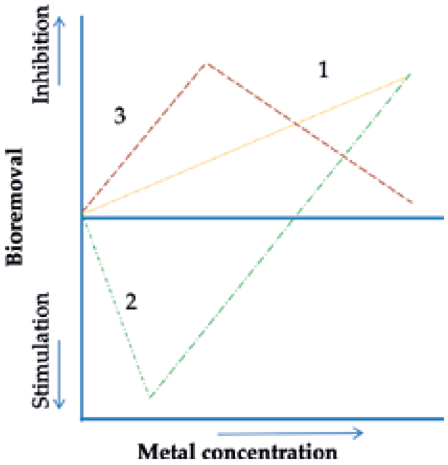

Figure 3. Metal concentration impact on bioremoval inhibition pattern of organic pollutants, assuming (1) a direct or linear relationship, (2) additional pattern 1 and (3) additional pattern 2.

increase in metal concentration will lead to a decrease of metal toxicity. An example is the work conducted by Said and Lewis [26] where an increase in metal concentration was responsible for a decrease in 2,4-DME bioremoval.

Briefly, the existence of different patterns of responses of organic pollutants towards metals is possible to assume and that this variety of responses makes the understanding and prediction of metal toxicity in the environment more difficult, since these elements may influence both the ecology and physiology of the pollutant-degrading microorganisms.

Unless the models used to predict the influence of metals on the bioremoval of organic pollutants incorporate both the ecologic and physiologic effects of metals towards the pollutant-degrading microorganisms, they may fail their main purpose.

3.3. Biosorption in multi-metal solutions

As previously mentioned, despite the research concerning biosorption processes has been well documented in the literature, biosorption of different metal ions by different types of biological materials has been mainly conducted in single-metal solutions [21]. Information concerning biosorption studies in binary- [30–34], tertiary- [31–35] and quaternary-component solutions [36] is very scarce. Moreover, the use of different evaluation methodologies makes any attempt to draw any meaningful and universal conclusion very difficult and, on the other hand [37], the influence that anions may exert on the biosorption process of metal cations has been somehow neglected.

Nostoc muscorum, a cyanobacterium indigenous from coal mining sites, was employed as biosorbent to decontaminate aqueous solutions containing Cd(II), Cu(II), Pb(II) and Zn(II) (5 or 10 mg/L) [38]. The results obtained in these experiments showed a maximum bioremoval of both Pb(II) (96.3%) and Cu(II) (96.4%) followed by Cd(II) (80.0%) and Zn(II) (71.3%) after 60 h of culture period. The bioremoval of Cd(II), Cu(II) and Pb(II) was maximum at 5 mg/L, whereas Zn(II) bioremoval has a maximum when all the four heavy metals were set at 5 mg/L. These results suggest a dependence of metal bioremoval by *N. muscorum* on the metals and their concentration combination in the multi-metal solution. It was also observable that the metals' uptake depended upon their concentration combination in solution and the bioremoval order observed was Pb(II) > Cu(II) > Cd(II) > Zn(II). In this study, Pb(II) showed not only a better bioremoval efficiency compared with the other three metals but also that its bioremoval was unaffected by the presence of the three other metals. However, the presence of Pb(II) exerted a strong negative effect on the bioremoval of all other metals. These results may be explained by taking into consideration the Pb(II) strong interaction with the functional groups present on the biomass and because Pb(II) presents the smallest radius among the four metals tested in these assays (the smaller the hydrated radius, the higher is the affinity of its binding).

3.3.1. *Effect of anions*

Three aspects related to the influence of anions on the biosorption processes are usually considered in the available literature: (i) the influence that the anion has on the maximum biosorption capacity of the sorbent, in single-metal solutions [39]; (ii) the influence of anion concentration on the biosorption of several metal ions, in multi-metal solutions [37–41]; and (iii) the nature of the biosorbent that can influence significantly the effect of the anion on the biosorption capacity [21].

The biosorption of four metals—Cr(VI), Co(II), Ni(II) and Zn(II)—by the *Aspergillus niger* fungus [40] revealed that the presence of anions such as NO_3^- and SO_4^{2-} did not significantly affect the biosorption performance of the four metals, whereas the presence of Cl^- did negatively affect the biosorption performance of the four metals in multi-metal solutions.

Kuyuca and Volesky [42] studied the biosorption of Co(II) ions in the presence of SO_4^{2-} and PO_4^{3-} by the brown macroalga *Ascophyllum nodosum* and concluded that the presence of these anions did not reveal any influence on the biosorption performance, as opposite to the presence of NO_3^- anions, that strongly inhibited the biosorption process. The opposite situation was observed in the biosorption of Zn(II) by the cyanobacterium *Oscillatoria angustissima* [41], and it was stated that the presence of SO_4^{2-}, NO_3^- and Cl^- had the following biosorption inhibition order $SO_4^{2-} > Cl^- > NO_3^-$.

The degree of inhibition for the biosorption of La(III), Cd(II), Pb(II) and Ag(I) cations, by the *Rhizopus arrhizus* fungus [43], usually followed the order EDTA > SO_4^{2-} > Cl^- > PO_4^{3-} > glutamate > CO_3^{2-}.

As referred previously, the influence of the anion on the biosorption capacity will vary depending on the metal ion oxidation state, as it was observed for the biosorption of Cr(III) and CR(VI) ions [44], with the following inhibitory orders $SO_4^{2-} > Cl^- \approx NO_3^-$ and $NO_3^- > SO_4^{2-}$.

3.3.2. *Effect of the ionic concentration*

Considering the limited number of active sites present on the biosorbent surface, it is accepted that the biosorption capacity of the biosorbent towards a specific pollutant (metal or not) in a multicomponent solution is inferior to the one in single-component solutions; therefore, the contaminants will compete for the active sites, available for sorption [44].

This is the case of the amount of Cr(VI) biosorbed per unit weight of *Rhizopus arrhizus* that decreased with the increase of Fe(III) concentration as an antagonistic effect [45, 46].

Fagundes-Klen et al. [47] observed that the amount of Zn(II) biosorbed by *S. filipendula* in the presence of high concentrations of Cd(II) decreased significantly (56.8 %) when comparing the biosorption results achieved in single-metal solution. These results are easily explained by the reduced number of coordination, the ionic radius and the higher ionization potential of Zn(II).

It is therefore worth noting that as the ionic concentrations become higher, there is a growing force able to overcome the mass resistance transfer of metal ions through the biosorption process. The published data [48] showed that even though lead ions (Pb^{2+}) have higher affinity than copper (Cu^{2+}) to be biosorbed by an algae belonging to the genera *Gelidium* uptake, Cu^{2+} uptake was higher than Pb^{2+} uptakes due to the higher initial concentration of Cu^{2+}. Similar results described the biosorption of Pb^{2+} and Cu^{2+} by pine cone shells [49]. When binary solutions were tested, the uptake of both metals was significantly inhibited, revealing an antagonistic effect.

3.3.3. Effect of electronegativity and atomic weigh of metals

In multi-metal solution, the electronegativity and atomic weight of metals can also have an important role in the biosorption process and efficiency. Biosorption experiments showed that when mixed, Ni(II) and Zn(II) sorption by wheat straw presented different performances, revealing a competition between both metals for the actives sites present on the biosorbent surface and a higher preference for Zn(II) rather than Ni(II) [50]. These results are easily justified taking into consideration the more appealing physical characteristics of Zn(II): lower electronegativity and higher atomic weight of Zn(II). The oxygen-containing group present on the wheat straw (negative sites) repels Ni(II) more than Zn(II), making it more difficult to be sorbed.

3.3.4. Effect of temperature

As previously mentioned (see Section 2, **Figure 2**), temperature also plays an important role on the biosorption processes, as well as on all biological and physico-chemical processes. The biosorption of Cr(III), Cu(II) and Zn(II) by wine-processing waste sludge (WPWS) in a ternary system was found to be significantly affected by temperature. At normal conditions, the biosorption of these three metals in a mixture by WPWS followed the trend Cr(III) > Cu(II) > Zn(II). However, when the temperature decreases to 10°C, the biosorption of Cr(III) was inferior than Cu(II) [50].

4. Critical assessment concerning the biosorption research on multicomponent solutions

As previously mentioned, in the past few decades, there has been an intense study and research concerning biosorption processes to treat contaminated environmental matrices and wastewaters. However, it is doubtful whether such a remarkable rise in published output has significantly enhanced the knowledge about biosorption process, or aided any industrial exploitation, which so often is the primary underlying principle for such investment and work [18, 19, 21]. Despite the incontestable progress made over decades of research, most of the biosorption studies are still conducted at a laboratory scale and involve (i) the characterization of a selected sorbent, which will sorb a given contaminant from solution, (ii) the study of the effect of physico-chemical parameters may have on biosorption and (iii) the use of metals. Considering that the majority of elements present in the periodic table are classified as metals, the potential number of 'original' research is most likely beyond comprehension, especially if coupled with the gigantic number of microbial species, strains and metabolites/derived substances. It is therefore expected that the output of publications related to biosorption shows no sign of decreasing and will be increased due to the continuing number of new journals, including those that are web based [18, 19].

It is also logical to infer that several technical and scientific issues should be solved in order to meet the industrial demands and bring the biosorption technology into commercialization. Based on this, several future perspectives can be made:

- Although a large number of biological materials are available, it is still essential to find and/or prepare more economic, efficient and selective sorbents.
- It is necessary to elaborate, improve and/or simplify the mathematical models used to describe the multicomponent systems.
- To achieve the best biosorption performance, it is crucial to identify the biosorption mechanism underlying relatively to the class of biosorbents used.
- To obtain the best biosorption performance, it is essential to identify the biosorption mechanism in relation to the general group of the selected biosorbent.
- Biosorption studies should also be conducted at a pilot or industrial scale and with multicomponent solutions or, if possible, real effluents and wastewaters. This will allow to understand the interactions between all the sorbents and the sorbate and thus optimize the biosorption process, promoting its future commercialization.
- Although there is a significant number of patents and publications available, the biosorption process has been so far mainly performed at a laboratory scale. Up-scale of the biosorption processes should be enhanced.
- In order to apply the biosorption technology at an industrial scale, economic analyses are necessary to estimate the overall cost of the sorbent and biosorption process.
- Additional attention should be paid to the application of biosorption technology in product separation, recovery and purification.
- The use of similar and universal evaluation methodologies allows to draw meaningful and universal conclusions [21].
- Eradicate the poor and misleading communications, and the use of loose terminology, which is associated with the great complexity of biosorption phenomena, has intricated the process of prioritizing fundamental scientific and commercial tasks and of creating clear information for the industry.

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References

[1] Anastopoulos I, Kyzas GZ. Composts as biosorbents for decontamination of various pollutants: A review. Water, Air, and Soil Pollution. 2015;**226**:61-76. DOI: 10.1007/s11270-015-2345-2

[2] Abdi O, Kazemi M. A review study of biosorption of heavy metals and comparison between different biosorbents. J Mater Environ Sci. 2015;**6**(5):1386-1399 ISSN: 2028-2508

[3] Costa F, Tavares T. Bioremoval of Ni and Cd in the presence of diethylketone by fungi and by bacteria: A comparative study. International Biodeterioration & Biodegradation. 2017; **120**:115-123. DOI: 10.1016/j.ibiod.2017.02.018

[4] Costa F, Tavares T. Biosorption of nickel and cadmium in the presence of diethylketone by a *Streptococcus equisimilis* biofilm supported on vermiculite. International Biodeterioration & Biodegradation. 2016;**115**:119-132. DOI: 10.1016/j.ibiod.2016.08.004

[5] Ahmed S, Chughtai S, Keane MA. The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolites. Sep Purif Technol. 1998;**13**:57-64. DOI: 10.1016/S1383-5866(97)00063-4

[6] Chaudhuri D, Majumder A, Misra AK, Bandyopadhyay K. Cadmium removal by *Lemna minor* and *Spirodela polyrhiza*. International Journal of Phytoremediation. 2014;**16**:1119-1132. DOI: 10.1080/15226514.2013.821446

[7] Costa F, Tavares T. Sorption studies of diethylketone in the presence of Al^{3+}, Cd^{2+}, Ni^{2+} and Mn^{2+}, from lab-scale to pilot scale. Environmental Technology. 2017:1-13. DOI: 10.1080/09593330.2016.1278462

[8] Silva B, Costa F, Neves IC, Tavares T. Psychiatric Pharmaceuticals as Emerging Contaminants in Wastewater. 1st ed. Springer Cham Heidelberg New York Dordrecht London: Springer International Publishing; 2015. DOI: 10.1007/978-3-319-20493-2

[9] Costa F, Quintelas C, Tavares T. Kinetics of biodegradation of diethylketone by *Arthrobacter viscosus*. Biodegradation. 2012;**23**(1):81-92. DOI: 10.1007/s10532-011-9488-7

[10] Khan A, Singh VV, Dumar D. Removal of some basic dyes from artificial textile wastewater by adsorption on Akansh Kinari coal tabrez. J Sci Ind Res India. 2004;**63**(4):335-364 0975-1084 (online); 0022-4456 (print)

[11] Santos LH, Araújo AN, Fachini A, Pena A, Delerue-Matos C, Montenegro MC. Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. Journal of Hazardous Materials. 2010;**175**(1-3):45-95. DOI: 10.1016/j.jhazmat.2009.10.100

[12] Mak VWY, Chatzis I, Hudgins RR, Fayed ME. Removal of VOCs by sorption in fixed beds of popcorn. Canadian Journal of Chemical Engineering. 2004;**82**(1):194-197. DOI: 10.1002/cjce.5450820125

[13] Fan J, Sun Y, Li X, Zhao C, Tian D, Shao L, Wang J. Pollution of organic compounds and heavy metals in a coal gangue dump of the Gequan Coal Mine, China. Chinese Journal of Geochemistry. 2013;**32**:241-247. DOI: 10.1007/s11631-013-0628-0

[14] Costa F, Quintelas C, Tavares T. An approach to the metabolic degradation of diethylketone (DEK) by *Streptococcus equisimilis*: Effect of DEK on the growth, biodegradation kinetics and efficiency. Ecological Engineering. 2014;**70**:183-188. DOI: 10.1016/j.ecoleng.2014.05.009

[15] Costa F, Neto M, Nicolau A, Tavares T. Biodegradation of diethylketone by *Penicillium* sp. and *Alternaria* sp.—A comparative study biodegradation of diethylketone by fungi. Current Biochemical Engineering. 2015;**2**:81-89. DOI: 10.2174/2212711901666140812225947

[16] Seow TW, Lim CH. Removal of dye by adsorption: A review. International Journal of Applied Engineering Research. 2016;**11**(4):2675-2679 0973-4562

[17] The Environmental, Health and Economic Impacts of Textile Azo Dyes. Available from: https://www.researchgate.net/file.PostFileLoader.html?id=593cf7e2cbd5c26bf031fcab&assetKey=AS%3A503972613505026%401497167842679 [Accessed: 2017-08-03]

[18] Gadd GM. Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment. Journal of Chemical Technology & Biotechnology. 2009;**84**:13-28. DOI: 10.1002/jctb.1999

[19] Fomina M, Gadd GM. Biosorption: Current perspectives on concept, definition and application. Bioresource Technology. 2014;**160**:3-14. DOI: 10.1016/j.biortech.2013.12.102

[20] Volesky B, Biosorption of Heavy Metals. 1990. CRC Press, Boca Raton, FL. ISBN 978084 9349171

[21] Michalak I, Chojnacka K, Witek-Krowiak A. State of the art for the biosorption process—A review. Applied Biochemistry and Biotechnology. 2013;**170**:1389-1416. DOI: 10.1007/s12010-013-0269-0

[22] Sandrin TR, Maier RM. Impact of metals on the biodegradation of organic pollutants. Environmental Health Perspectives. 2003;**111**(8):1091-1101. DOI: 10.0000/www.ncbi.nlm.nih.gov/generic-8F48966398F4

[23] Abdulaziz M, Musayev S. Multicomponent biosorption of heavy metals from aqueous solutions: A review. Polish Journal of Environmental Studies. 2017;**26**(4):1433-1441. DOI: 10.15244/pjoes/67975

[24] Quintelas C, Costa F, Tavares T. Bioremoval of diethylketone by the synergistic combination of microorganisms and clays: Uptake, removal and kinetic studies. Environmental Science and Pollution Research. 2012;**20**(3):1374-1383. DOI: 10.1007/s11356-012-1055-1

[25] Nam I-H, Kim Y, Cho D, Kim J-G, Song H, Chul-M C. Effects of heavy metals on biodegradation of fluorene by a *Sphingobacterium* sp. strain (KM-02) isolated from polycyclic aromatic hydrocarbon-contaminated mine soil. Environmental Engineering Science. 2015;**32**(10):1-8. DOI: 10.1089/ees.2015.0037

[26] Said WA, Lewis DL. Quantitative assessment of the effects of metals on microbial degradation of organic chemicals. Applied and Environmental Microbiology. 1991;**57**:1498-1503

[27] Sandrin TR. Naphthalene Biodegradation in a Cadmium Cocontaminated System: Effects of Rhamnolipid, pH, and Divalent Cations [PhD Thesis]. Tucson, AZ: University of Arizona; 2000

[28] Benka-Coker MO, Ekundayo JA. Effects of heavy metals on growth of species of *Micrococcus* and *Pseudomonas* in a crude oil/mineral salts medium. Bioresource Technology. 1998;**66**:241-245. DOI: 10.1016/S0960-8524(98)00057-1

[29] Capone DG, Reese DD, Kiene RP. Effects of metals on methanogenesis, sulfate reduction, carbon dioxide evolution, and microbial biomass in anoxic salt marsh sediments. Applied and Environmental Microbiology. 1983;**45**:1586-1591

[30] Xie P, Hao X, Mohamad OA, Liang J, Wei G. Comparative study of chromium biosorption by *Mesorhizobium amorphae* strain CCNWGS0123 in single and binary mixtures. Applied Biochemistry and Biotechnology. 2013;**169**:570-587. DOI: 10.1007/s12010-012-9976-1

[31] Abu Al-Rub FA, El-Naas MH, Ashour I, Al-Marzouqi M. Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions. Process Biochemistry. 2006;**41**:457-464. DOI: 10.1016/j.procbio.2005.07.018

[32] Pagnanelli F, Trifoni M, Beolchini F, Esposito A, Toro L, Vegliò F. Equilibrium biosorption studies in single and multi-metal systems. Process Biochemistry. 2001;**37**:115-124. DOI: 10.1016/S0032-9592(01)00180-7

[33] Aksu Z, Dönmez G. Binary biosorption of cadmium(II) and nickel(II) onto dried *Chlorella vulgaris*: Co-ion effect on mono-component isotherm parameters. Process Biochemistry. 2006;**41**:860-868. DOI: 10.1016/j.procbio.2005.10.025

[34] Mohapatra H, Gupta R. Concurrent sorption of Zn(II), Cu(II) and Co(II) by *Oscillatoria angustissima* as a function of pH in binary and ternary metal solutions. Bioresource Technology. 2005;**96**:1387-1398. DOI: 10.1016/j.biortech.2004.11.004

[35] Pradhan S, Rai LC. Biotechnological potential of *Microcystis* sp. in Cu, Zn and Cd biosorption from single and multimetallic systems. Biometals. 2001;**14**:67-74. DOI: 10.1023/A:1016607729691

[36] Chong KH, Volesky B. Metal biosorption equilibria in a ternary system. Biotechnology and Bioengineering. 1996;**49**:629-638. DOI: 10.1002/(SICI)1097-0290(19960320)49:6<629:AID-BIT4>3.0.CO;2-Q

[37] Michalak I, Chojnacka K. The application of macroalga *Pithophora varia* Wille enriched with microelements by biosorption as biological feed supplement for livestock. Journal of Science and Food Agriculture. 2008;**88**:1178-1186. DOI: 10.1002/jsfa.3195

[38] Roy AS, Kazarika J, Manikandan NA, Pakshirajan K, Syiem MB. Heavy metal removal from multicomponent system by the cyanobacterium *Nostoc muscorum*: Kinetics and interaction study. Applied Biochemistry and Biotechnology. 2015;**175**:3863-3874. DOI: 10.1007/s12010-015-1553-y

[39] Han X, Wong YS, Wong MH, Tam NFY. Effects of anions species and concentration on the removal of Cr(VI) by a microalgal isolate, *Chlorella miniata*. Journal of Hazardous Materials. 2008;**158**:615-620. DOI: 10.1016/j.jhazmat.2008.02.024

[40] Pulsawat W, Leksawasdi N, Rogers PL, Foster LJR. Anions effects on biosorption of Mn(II) by extracellular polymeric substance (EPS) from *Rhizobium etli*. Biotechnology Letters. 2003;**25**:1267-1270 ISSN: 0141-5492

[41] Filipović-Kovačević Ž, Sipos L, Briški F. Biosorption of chromium, copper, nickel and zinc ions onto fungal pellets of *Aspergillus niger* 405 from aqueous solutions. Food Technology and Biotechnology. 2000;**38**:211-216 ISSN: 1330-9862

[42] Ahuja P, Gupta R, Sabena RK. Zn^{2+} biosorption by *Oscillatoria anguistissima*. Process Biochemistry. 1999;**34**:77-85. DOI: 10.1016/S0032-9592(98)00072-7

[43] Kuyuca N, Volesky B. Accumulation of cobalt my marine alga. Biotechnology and Bioengineering. 1989;**33**:809-814. DOI: 10.1002/bit.260330703

[44] Tobin JM, Cooper DG, Neufeld RJ. Influence of anions on metal adsorption by *Rhizopus arrhizus* biomass. Biotechnology and Bioengineering. 1987;**30**(7):882-886. DOI: 10.1002/bit.260300711

[45] Vijayaraghavan K, Balasubramanian R. Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions. Journal of Environmental Management. 2015;**160**:283-296. DOI: 10.1016/j.jenvman.2015.06.030

[46] Sag Y, YAlcuk A, Kutsal T. Use of a mathematical model for prediction of the performance of the simultaneous biosorption of Cr(VI) and Fe(III) on *Rhizopus arrhizus* in a semi-batch reactor. Hydrometallurgy. 2001;**59**:77-87. DOI: 10.1016/S0304-386X(00)00143-2

[47] Fagundes-Klen MR, Ferri P, Martins TD, Tavares CRG, Silva EA. Equilibrium study of the binary mixture of cadmium–zinc ions biosorption by the *Sargassum filipendula* species using adsorption isotherms models and neural network. Biochemical Engineering Journal. 2007;**34**:136-146. DOI: 10.1016/j.bej.2006.11.023

[48] Vilar VJP, Loureiro JM, Botelho CMS, Boaventura RAR. Continuous biosorption of Pb/Cu and Pb/Cd in fixed-bed column using algae *Gelidium* and granulated agar extraction algal waste. Journal of Hazardous Materials. 2008;**154**:1173-1182. DOI: 10.1016/j.jhazmat.2007.11.060

[49] Martín-Lara MA, Blázquez G, Calero M, Almendros AI, Ronda A. Binary biosorption of copper and lead onto pine cone shell in batch reactors and in fixed bed columns. International Journal of Mineral Processing. 2016;**148**:72-82. DOI: 10.1016/j.minpro.2016.01.017

[50] Liu C-C, Wang M-K, Chiou C-S, Li Y-S, Yang C-Y, Lin YA. Biosorption of chromium, copper and zinc by wine-processing waste sludge: Single and multi-component system study. Journal of Hazardous Materials. 2009;**171**:386-392. DOI: 10.1016/j.jhazmat.2009.06.012

Chapter 4

Application of Biosorption for Removal of Heavy Metals from Wastewater

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Additional information is available at the end of the chapter

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Abstract

Fresh water accounts for 3% of water resources on the Earth. Human and industrial activities produce and discharge wastes containing heavy metals into the water resources making them unavailable and threatening human health and the ecosystem. Conventional methods for the removal of metal ions such as chemical precipitation and membrane filtration are extremely expensive when treating large amounts of water, inefficient at low concentrations of metal (incomplete metal removal) and generate large quantities of sludge and other toxic products that require careful disposal. Biosorption and bioaccumulation are ecofriendly alternatives. These alternative methods have advantages over conventional methods. Abundant natural materials like microbial biomass, agro-wastes, and industrial byproducts have been suggested as potential biosorbents for heavy metal removal due to the presence of metal-binding functional groups. Biosorption is influenced by various process parameters such as pH, temperature, initial concentration of the metal ions, biosorbent dose, and speed of agitation. Also, the biomass can be modified by physical and chemical treatment before use. The process can be made economical by regenerating and reusing the biosorbent after removing the heavy metals. Various bioreactors can be used in biosorption for the removal of metal ions from large volumes of water or effluents. The recent developments and the future scope for biosorption as a wastewater treatment option are discussed.

Keywords: biosorption, heavy metal, isotherm, water, waste, pollution

1. Introduction

Water plays an important role in the world economy. Majority (71%) of the Earth's surface is covered by water, but fresh water constitutes a miniscule fraction (3%) of the total. Water fit for human consumption is obtained from the fresh water bodies. Approximately, 70% of the fresh water goes to agriculture. This natural resource is becoming scarce at many places and its unavailability is a major social and economic concern [1]. Though access to safe drinking water has improved over the last few decades, it is estimated that five million deaths per year are caused due to consumption of polluted drinking water or drought. In many developing countries, 90% of all wastewater still goes untreated into the fresh water bodies making it unfit for human consumption, which either leads to scarcity or affects the human population [2]. The concern to protect fresh water bodies for a healthy population is a challenge in recent times.

Industrialization to a larger degree is responsible for the contamination of environment especially water where lakes and rivers are overwhelmed with a large number of toxic substances. Heavy metals are reaching hazardous levels when compared with the other toxic substances [3]. Heavy metals are a unique group of naturally occurring compounds. Their continuous release leads to overconsumption and accumulation. As a result, people around the globe are exposed to adverse consequences of these heavy metals. Many industries (fertilizers, metallurgy, leather, aerospace, photography, mining, electroplating, pesticide, surface finishing, iron and steel, energy and fuel production, electrolysis, metal surface treating, electro-osmosis, and appliance manufacturing) discharge waste containing heavy metals either directly or indirectly into the water resources [4]. Toxic heavy metals, which are of concern, are chromium (Cr), lead (Pb), zinc (Zn), arsenic (As), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd), mercury (Hg), and so on. As these metals are not biodegradable, they tend to accumulate in the living organisms and lead to various diseases and disorders which ultimately threaten human life. They can cause ill health, even when present in the range of parts per billion (ppb) [5]. Biosorption has emerged as an attractive option over conventional methods for the removal of heavy metal ions from effluents discharged from various industries which ultimately reach and pollute fresh water bodies. This chapter reports the toxicity of heavy metals, the advantages of biosorption, various biosorbents used for the removal of metal ions, effect of immobilization and modifications of biosorbents, various factors affecting the process of biosorption, different bioreactors used in biosorption, and the application of biosorption for the removal of metal ions from various wastewaters like industrial effluents and contaminated water resources. The recent advances, current status, and future of the process are discussed.

2. Toxicity of heavy metals

The pathway of exposure for heavy metals is mainly through inhalation, dermal contact, and ingestion. The individual metal exhibits its own specific signs of toxicity [6]. The severity of health effects is dependent on time and dose, the type of heavy metal, and its chemical form. The nature of effect may be toxic, mutagenic, neurotoxic, teratogenic, or carcinogenic [6]. Many studies reported that heavy metals affect cell organelles and interact with cell components causing cell damage and apoptosis. Even at a low level of exposure, they induce multiple organ damage.

Intoxication of heavy metals also leads to damage to the major systems in the body and may lead to an increased risk in developing cancers [7]. Metal ion pollution is highly persistent, and most of them are nonbiodegradable. The presence of various heavy metals such as chromium (Cr), lead (Pb), zinc (Zn), arsenic (As), copper (Cu), nickel (Ni), cobalt (Co), cadmium (Cd), and mercury (Hg) causes disturbances in circulatory, gastrointestinal, and nervous systems. They also affect various organs and lead to blindness, deafness, brain damage, loss of fertility, cancer, and many other severe health problems that ultimately cause death of the individual [7–9].

3. Conventional methods for heavy metal removal

Heavy metals like nickel, copper, zinc, cadmium, chromium, lead, and mercury are major pollutants that affect the fresh water reservoirs due to the discharge of large amounts of metal-contaminated wastewater from industries. Because of their persistent, non-biodegradable, and toxic nature, they accumulate in the environment such as in the food chain and cause serious health disorders. Over the last few decades, many conventional treatment methods have been used for the removal of heavy metals from contaminated wastewaters. The commonly used methods include chemical precipitation, ultra-filtration, ion exchange, reverse osmosis, electro winning, and phytoremediation, and they are introduced briefly [10–14].

Chemical precipitation is the most widely used method for heavy metal removal from inorganic effluents. The conceptual mechanism involved is that the dissolved metal ions get precipitated by chemical reagents (precipitants) and result in the formation of metal hydroxides, sulfides, carbonates, and phosphates (insoluble solid particles) that can be simply separated by sedimentation or filtration.

Ion exchange is based on the reversible exchange of ions between solid and liquid phases. An ion exchanger is a solid resin capable of exchanging both cations and anions from an electrolytic solution and releases counter-ions of similar charge in a chemically equivalent amount.

Membrane filtration is capable of removing not only metal ions but also suspended solid and organic components. A membrane is a selective layer used to make contact between two homogenous phases with a porous or non-porous structure for the removal of pollutants of varied size.

Ultrafiltration (UF) is a permeable membrane separation process with pore sizes in the range of 0.1–0.001 micron which permeates water and low molecular weight solutes, while retaining the macromolecules, particles, and colloids that are larger in size. The removal of Cu (II), Zn (II), Ni (II), and Mn (II) from aqueous solutions was achieved by using ultrafiltration assisted with a copolymer of malic acid and acrylic acid attaining a removal efficiency of 98.8% by forming macromolecular structures with the polymers which are rejected by the membrane [15].

Microfiltration (MF) works with the same principle as ultrafiltration. The major difference between the two processes is that the solutes which are removed by MF are larger than those rejected by UF. Cross-flow microfiltration (CFMF) in yeast-based bioaccumulation process was used for the removal of metal ions from tap water artificially contaminated with Cu (II), Cd (II), Pb (II), and Cr (III). The method was efficient for the removal of metal ions with an efficiency of 31, 7, 63, and 71%, respectively [16].

Nanofiltration (NF) is used for the separation of large molecules possible by small pores when they are within the molecular weight range from 300 to 500 Da with a pore diameter of 0.5–2 nm. A commercially available nanofiltration membrane NF270 was used for the removal of Cd (II), Mn (II), and Pb (II) with an efficiency of 99, 89, and 74%, respectively [17].

Reverse osmosis (RO) is a pressure-driven membrane separation process that forces the solution to pass through a semi-permeable membrane for the removal of heavy metals from various industries. Reverse osmosis was used for the removal of Cu (II), Ni (II), and Zn (II) by using a polyamide thin-film composite membrane TW30-1812-50 [18].

Electrodialysis (ED) is a novel liquid hybrid membrane separation process used for the separation of ionized species in the solution that passes through an ion exchange membrane when electric potential is applied or due to concentration gradient. The removal of heavy metal ions in groundwater in Korea was achieved by an ED system for the removal of arsenic, lead, manganese, and nitrate nitrogen with 73.9, 89.9, 98.9, and 95.1%, respectively [19].

Photocatalysis is used for the rapid and efficient destruction of environmental pollutants by using semiconductors which are non-toxic. This method is achieved by a five-step process: transfer, adsorption to the surface of the semiconductor, photocatalytic reactions at the surface, and finally decomposition and removal of the pollutants at the interface region. The heavy metals present in the pharmaceutical waste were photocatalytically degraded and removed by using selenium-doped ZnO nanocomposite semiconductor and the removal capacity was found to be 0.421 (Cu), 0.211 (Cr), 0.147 (Pb), and 0.097 (Cd) per 0.5 g of ZnO/Se nanocomposite [20].

Besides these conventional methods, techniques like coagulation/flocculation [21], electro-coagulation [22], electro-floatation [23], and electro-deposition [24] have been used for the removal of heavy metals from contaminated water resources. However, all the above-mentioned technologies are associated with various disadvantages like incomplete metal removal, generation of sludge, high reagent and energy requirements, and aggregation of metal precipitates and fouling of the membranes.

4. Bioaccumulation and biosorption

In view of the disadvantages associated with conventional methods for metal removal, there is a need for alternative, cost-effective technologies. In recent years, biosorption/bioaccumulation processes have been considered as novel, economic, efficient, and eco-friendly alternative treatment technologies for the removal of heavy metals from contaminated wastewaters generated from various industries.

4.1. Bioaccumulation

Bioaccumulation is a metabolism-mediated active process in which the metal ions accumulate the biosorbent intracellularly in the living cells. The process occurs in two steps: the first step is the adsorption of metal ions onto cells, which is quick and identical to biosorption, and the later step is slower which includes the transport of metal species inside the cells by active transport [25]. Unlike biosorption, it is an irreversible, complex process which depends on the metabolism of the cells. The process of bioaccumulation occurs by cultivating the biomass of a microorganism in the vicinity of the metal to be accumulated. Since the solution contains the growth medium, the organism begins its metabolic processes and activates the intracellular transport systems for the accumulation of the sorbate. However, the major limitation of the process is that the nutritive medium for growth of the microorganism contains organic carbon sources [26, 27]. Bioaccumulation is an active process which requires a living biosorbent and is mediated by the metabolism of the microorganism used. The process operates by cultivating the microbe in the presence of a metal ion which has to be removed. Part of the biosorbate accumulates inside the cell which enables the biomass to increase and bind greater amounts of metal ions. The organisms which are capable of resisting high loads of metal ions are best suited for accumulating metal species. They do not possess any mechanisms for hindering the accumulation of metal ions in large quantities [28]. They may possess special mechanisms for synthesizing special intracellular binding regions rich in thiol groups as a response to metal ions in their surviving environment. It was found that morphology and physiology of the cell changes upon increase in concentration of the metal ion to be accumulated [29]. Efficient bioaccumulation can be achieved by selecting the microbes that are screened from polluted environments [30]. *Pichia stipitis* yeast was capable of bio-accumulating Cu (II) and Cr (III) with the maximum uptake capacity of 15.85 and 9.10 mg/g, respectively, from aqueous solutions with an initial concentration of 100 ppm at pH 4.5 [31]. *Aspergillus niger* was capable of removing Cu (II) and Pb (II) with the maximum uptake capacity of 15.6 and 34.4 mg/g, respectively [32]. **Table 1** summarizes some more examples of biosorbents used for metal bioaccumulation.

Biosorbent type	**Metal ion**	**Uptake capacity[a] (mg/g)**	**Reference**
Pichia guilliermondii	Cu (II)	20	[29]
Aspergillus niger	Pb (II)	172.25	[33]
Aspergillus flavus	Cu (II)	93.65	
Bacillus circulans	Cr (VI)	34.5	[34]
Bacillus megaterium		32	
Saccharomyces cerevisiae	Cr (III) & (VI)	11.3, 3.3	[35]
Drepanomonas revolute	Zn (II), Cd (II), Cu (II)	22.1, 0.75, 0.2	[36]
Uronema nigricans	Zn (II), Cd (II), Cu (II)	24.3, 0.37, 0.95	
Euplotes sp.	Zn (II), Cd (II), Cu (II)	71.5, 0.83, 0.25	

[a] Since the process of bioaccumulation is achieved with the living organisms, the uptake capacity was determined with the wet weight of the biosorbent.

Table 1. Use of microorganisms for bioaccumulation of metal ions.

4.2. Biosorption

Biosorption can be defined as a simple metabolically passive physicochemical process involved in the binding of metals ions (biosorbate) to the surface of the biosorbent which is of biological origin [25]. Biological removal includes the use of microorganisms, plant-derived materials, agriculture or industrial wastes, biopolymers, and so on. It is a reversible rapid process involved in binding of ions onto the functional groups present on the surface of the biosorbent in aqueous solutions by means of various interactions rather than oxidation through aerobic or anaerobic metabolism [37]. The advantages of this process include are simple operation, no additional nutrient requirement, low quantity of sludge generation, low operational cost, high efficiency, regeneration of biosorbent, and no increase in the chemical oxygen demand (COD) of water, which are otherwise the major limitations for most of the conventional techniques [27]. Biosorption can remove contaminants even in dilute concentrations and has special relevance with respect to heavy metal removal owing to toxicity at ppb levels. Microorganisms (live and dead) and other industrial and agriculture byproducts can be used as biosorbents for the process of biosorption.

The first stage in biosorption is that biosorbent should be suspended in the solution containing the biosorbate (metal ions). After incubation for a particular time interval, equilibrium is attained. At this stage, the metal-enriched biosorbent would be separated [27]. The process of biosorption is advantageous because it is reversible, does not require nutrients, a single-stage process, of quick range, has no danger of toxic effects and cellular growth, allows intermediate equilibrium concentration of metal ions, and is not controlled by metabolism [26].

Biosorption capacity (mg/g) of the biosorbent can be defined as the amount of biosorbate (metal ions) biosorbed per unit weight of the biosorbent and can be expressed by using the following mass balance equation:

$$qe = \frac{(Ci - Ce)\,V}{m} \tag{1}$$

The percent biosorption (R%) known as biosorption efficiency for the metal was evaluated from the following equation:

$$R\,\% = \frac{Ci - Ce}{Ci} \times 100 \tag{2}$$

where q_e is the amount of adsorbed metal ions of the adsorbent (mg g^{-1}), C_i is the initial concentration of metal ion in the solution (mg L^{-1}), C_e is the equilibrium concentration of metal ion in the solution (mg L^{-1}), V is the volume of the medium (L), and m is the amount of the biomass used in the adsorption process (g).

5. Mechanism of biosorption

The mechanism of biosorption is a complex process which involves the binding of sorbate onto the biosorbent. Many natural materials can be used as biosorbents which involve the binding of metal ions by physical (electrostatic interaction or van der Waals forces) or chemical (displacement of either bound metal cations (ion exchange) or protons) binding, chelation, reduction, precipitation, and complexation (refer **Figure 1**). Biosorbents contain chemical/functional groups like amine, amide, imidazole, thioether, sulfonate, carbonyl, sulfhydryl, carboxyl, phosphodiester, phenolic, imine, and phosphate groups that can attract and sequester metal ions. The key factors controlling and characterizing these mechanisms are [38, 39]:

- the chemical, stereochemical, and coordination characteristics of metal ions like molecular weight, ionic radius, and oxidation state of the targeted metal species;
- properties of the biosorbent, that is, the structure and nature (in case of microorganism—living/non-living);
- type of the binding site (biological ligand)
- the process parameters like pH, temperature, concentration of sorbate and sorbent, and other competing metal ions; and
- availability of the binding sites.

The combined effects of the above parameters influence the metal speciation (the formation of new forms of metal as a result of biosorption).

5.1. Complexation

It is defined as the formation of a complex by the association of two or more species. Mononuclear (monodentate) complexes are formed between the metal ion and the ligands in which the metal atom occupies the central position. Polynuclear (multidenate) complex is formed by more than one metal ion in the center and the metal atom may carry a positive,

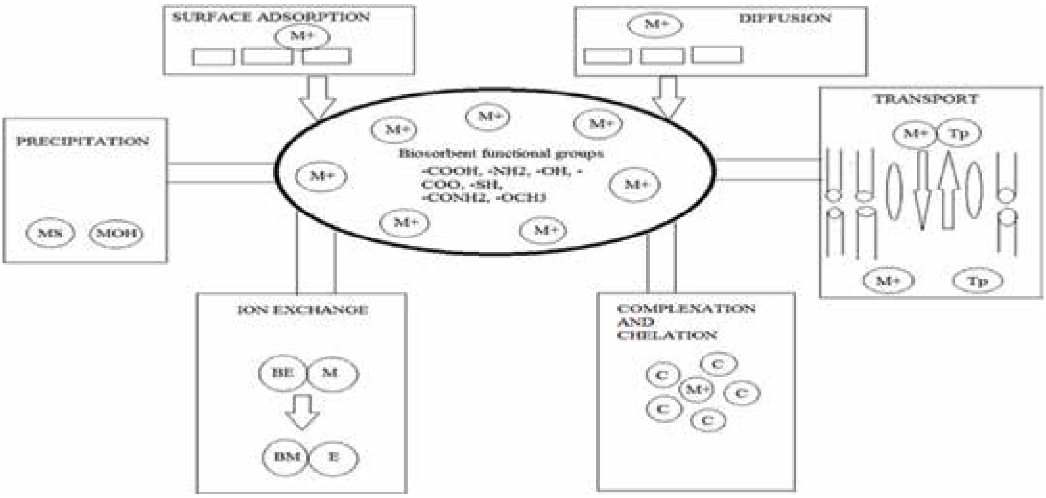

Figure 1. Hypothesis of different mechanisms of biosorption. M+: heavy metal ions, C: chelating agents, BE: molecules with exchangeable ions, BM: molecules with metal ions, Tp: transport protein.

negative, or neutral charge depending on the number of binding ligands involved. The complex formation to the monodentate ligand is more preferable than multidentate because the latter contains multiple ligands which may lead to multiple species binding. The metal ion interacts with the ligands by covalent bonds. The attenuated total reflection infrared spectral (ATR-IR) analysis of *Cyanobacterium microcystis* after the biosorption of antimony (III) suggested the involvement of carboxyl, hydroxyl, and amine groups through surface complexation [40]. A similar mechanism of biosorption was reported by other studies by using *Acidiphilium*, *Termitomyces clypeatus,* and alkali-modified sewage sludge for the removal of Cd (II), Cr (VI), and Cd (II), respectively [41–43].

5.2. Chelation

It refers to the process in which a chelating agent binds to the metal ion at more than one place at a time in order to form a ring structure and the complex is known as chelate. Mostly polydentate ligands participate in the reaction to form stable structures by multiple bonding. An increase in binding sites of the ligand increases the stability of the structure. Chelates are more stable than complexes because of multiple binding with the metal ion in more than one place. Rice straw was used as a potential biosorbent for the removal of Cd (II) from the effluent. The biosorbed Cd (II) chelates with the functional groups such as C=C, C–O, and O–H and carboxylic acids which are present on the surface of the biosorbent [44]. A similar mechanism of biosorption was reported in the removal of Cr (III) and Cu (II) by carboxyl and hydroxyl groups present on the surface of soybean meal waste [45].

5.3. Coordination

The metal atom in the complex is bound to its immediate neighbors by a coordinate covalent bond by accepting a lone pair of electrons from the non-metal atom. The non-metal atom is known as the donor (coordinating atom) and the metal atom which accepts the electron pair is known as the acceptor. Compounds having such types of bonds in their structure are known as coordinate compounds. Some examples of coordinating groups are =O, $–NH_{2,}$ –NH, –N=, –OH, –S–, –O–R, and =NOH.

5.4. Ion exchange

Ion exchange is an important concept in biosorption which involves the exchange of binary metal ions during biosorption with the counter-ions present on the surface of the biosorbent. Most of the purification process works on the mechanism of ion exchange. Ion exchange can take place either by cation or anion exchange. Carboxyl groups can be a good example of cation exchangers while amino/imidazole groups represent anion exchangers. The process of biosorption of Cr (III), Cd (II), and Cu (II) by *Spirulina* was studied. Three functional groups capable of cation exchange were identified on the surface: phosphate, carboxyl, and hydroxyl groups [46]. Ion exchange mechanism of biosorption was reported in other studies using rice straw for the removal of cadmium by exchange with K^+, Na^+, Mg^+, and Ca^+ and for the removal of Cu (II), Zn (II), and Pb (II) using watermelon rind [44, 47].

5.5. Precipitation

The metal ions form precipitates with the functional groups present on the surface of the microbial cells and remain intact or penetrate into the microbial cell. Most cases involve the formation of insoluble inorganic metal precipitates. Organic metal precipitates may be formed when microbial cells are used. Most of the extracellular polymeric substances excreted by the microbes are involved in the formation of organic precipitates. Precipitation of Cu (II) onto *Mesorhizobium amorphae* causes deformation, aggregation, and damage to the cell surface as shown by scanning electron microscope-energy dispersive X-ray (SEM-EDX) analysis [48]. This mechanism of precipitation for biosorption of metal ions was reported by other studies using soybean meal, watermelon rind, and green tomato husk (*Physalis Philadelphia lam*) for the removal of Cr (III) and Cu (II); Cu (II), Zn (II), and Pb (II); and Fe and Mn, respectively [45, 47, 49].

5.6. Reduction

In this process, the metal interacts with the functional groups like carboxyl, gets reduced, and leads to the growth of crystals. Elements like gold and palladium have been obtained by the process of reduction. The metal gets reduced once it binds to the biosorbent at discrete places. Removal of toxic hexavalent chromium can be done by the process of reduction. Many organisms remove Cr (VI) by reduction to Cr (III) by biosorption from the aqueous solution [50–52].

The mechanism of biosorption can be studied using different techniques. The acidic and basic properties of the functional groups that are present on the material surface and ion exchange properties can be determined by Boehm method or potentiometric titration [53]. Fourier transform infrared spectrometry (FTIR) offers important information about the functional groups that are present on the surface of biosorbents like carboxyl, amino, amide, hydroxyl, sulfate, carbonyl, ether, ester, and the nature of the bond that are involved in biosorption [54]. Scanning electron microscope (SEM) is a powerful technique for qualitative evaluation of the structure and morphological changes of the biosorbent before and after metal biosorption. Energy dispersive X-ray (EDX) technique provides valuable information about the availability of various elements on the surface of the biosorbent. X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique for analyzing the surface chemistry of the biosorbent, that is, electronic state and empirical formula of the elements present and oxidative state of the biosorbed metal ion [55].

6. Types of biosorbents

Identification of biosorbents for the process of biosorption is a major challenge. It is desirable to develop/obtain biosorbents with the capacity to bind/uptake metal ions with greater affinities [56]. A wide variety of materials available in nature can be used as biosorbents for the removal of metals from contaminated water resources. Any kind of plant, animal, and microbial biomass and their derivatives; plant, industrial and agriculture wastes; and byproducts discharged from various industries can be employed as biosorbents. It is important to select a biosorbent from the large spectrum of available materials. The desired characteristics of an ideal biosorbent are [56]:

- high affinity for metals (biosorption capacity)
- low economic values (low cost)
- availability in large quantities
- easy desorption of the adsorbed metal ions and possible multiple reuse of the biosorbent

The use of different materials as biosorbents is explained in detail:

6.1. Industrial byproducts

Low-cost materials from different industries have been used for the treatment of wastewater. Many industries, especially food industries, dispose large quantities of waste and byproducts. The cost for disposal is sometimes challenging. Using these zero-cost industrial wastes as effective biosorbents for treating wastewater effluents can solve the dual problem (waste disposal and effluent treatment) [57]. Waste byproducts produced from different industries, that is, steel, aluminum, paper, fertilizer, food, mining, and pharmaceuticals, can be used as biosorbents. It is estimated that the use of biosorbents from industrial waste will grow at an annual rate of 5% [58]. **Table 2** summarizes the type and source of the biosorbent, type of biosorbate targeted, and maximum biosorption capacity/biosorption efficiency of various industrial biosorbents.

Type of biosorbent	Source of biosorbent	Biosorbate	Biosorption capacity/ efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
Tea industry waste	Local tea factory	Cr (VI)	54.65 mg/g^{a*}	Langmuir	-OH, -SO_3, C-O, -CN		[59]
Sugar industry waste (bagasse)	Food canning processes	Cd (II), Fe (II)	96.4%, 93.8%^{a*}				[60]
Peach and apricot stones	Juice and jam industry	Pb (II)	97.64%, 93%^{a*}	Langmuir			[61]
Antibiotic waste	Antibiotic production complex	Cationic dye (Basic blue 41)	111 mg/g^{a*}	Freundlich		Ion exchange or complexation	[62]
Sludge	Paper mill	Ni (II), Cu (II), Pb (II), Cd (II)	13.7, 13.9, 14.1, 14.8 mg/g^{a*}	Freundlich		Ion exchange and physic-chemical adsorption	[63]
Waste green sands	Iron foundry industry	Zn (II)	10.0 mg/g^{a*}	Freundlich			[64]
Fly ash	Cement industry	Pb	22 mg/g^{a*}			Precipitation	[65]

^{a}Indicates the dry weight of the biosorbent, *Indicates batch biosorption experiments at laboratory scale.

Table 2. Use of industrial byproducts for biosorption of metal ions.

6.2. Agricultural waste materials

A great deal of interest in the removal of pollutants from wastewaters has focused on the use of agricultural waste/byproducts as biosorbents. Agricultural wastes especially those with high percentage of cellulose and lignin contains polar functional groups like amino, carbonyl, alcoholic, phenolic, and ether groups having high potential for metal binding [66]. These groups donate a lone pair of electrons and form complexes with metal ions in the solution [67]. Due to their unique chemical composition (the presence of hemicellulose, lipids, lignin, water hydrocarbons, simple sugars, and starch having a variety of functional groups) and availability, the use of agro-wastes seems to be a viable option for heavy metal remediation. Grapefruit peel was reported to biosorb cadmium and nickel with a biosorption capacity of 42.09 and 46.13 mg/g from aqueous solutions. Equilibrium data showed the better fit with the Freundlich isotherm model with the ion exchange mechanism. FTIR analysis showed that the carboxyl and hydroxyl groups are mainly involved in the biosorption of metal ions [68]. The bark powder of *Acacia leucocephala* was used as a low-cost biosorbent for the removal of Cu (II), Cd (II), and Pb (II) with the biosorption capacity of 147.1, 167.7, 185.2 mg/g, respectively, from the aqueous solution. The biosorption mechanism involved is physico-chemical adsorption involving carboxyl, hydroxyl, and amine groups present on the surface of the biosorbent for biosorption. The Langmuir model shows the best fit than the Freundlich model [69]. **Table 3** summarizes the type of the biosorbent, biosorbate, and maximum biosorption capacity of the different agriculture wastes as biosorbents.

6.3. Microbial biosorbents

Microorganisms capable of tolerating unfavorable conditions evolved their use as biosorbents in the removal of metal ions from wastewaters. They include bacteria, yeast, algae, and fungi. Experiments focused on the use of dead and or living microorganisms offer options for the type of remediation to perform [82]. However, the use of dead microbial biomass for the binding of metal ions has been preferred over living biomass because of the absence of the requirement of nutrients and monitoring BOD and COD in effluents. Hence, the use of dead biomass is economical [83]. These biosorbents can effectively sequester metal ions in the solution and decrease the concentration from the ppm to ppb level efficiently; therefore, they are considered as ideal candidates for the treatment of complex wastewaters with high volume and low concentration of metal ions [84]. A large quantity of materials of microbial origin has been investigated as biosorbents for the removal of metal ions extensively [85]. Reports do not include the use biomass of any pathogens for water treatment. Most of the microbial groups are composed of a large number of functional groups which indicate their potential as biosorbents. Some studies which identified the functional groups involved in the biosorption of metal ions are given in **Table 4**.

6.3.1. Algae as biosorbents

The use of algae as a biosorbent has received focus due to the scarce requirement of nutrients, high sorption capacity, plentiful availability, high surface area to volume ratio, less volume of sludge to be disposed, and the potential for metal regeneration and recovery. They are considered as both economic and ecofriendly solutions for wastewater treatment [92]. Different groups of algae differ in the composition of the cell wall. The cell wall of brown algae mainly contains three components: cellulose (structural support), alginic acid (a polymer of mannuronic and

Type of biosorbent	Biosorbate	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
Rice husk	Ni (II)	51.8%^{a*}	Langmuir and Freundlich	–OH, C=O, C–H		[70]
Cabbage, cauliflower waste	Pb (II)	60.57, 47.63 mg/g^{a*}	Langmuir	-OH, C=O	chemisorption	[71]
Sugarcane bagasse	Ni (II)	2 mg/g^{a*}	Langmuir		Ion exchange	[72]
Papaya wood	Cd (II), Cu (II), Zn (II)	97.8%, 94.9%, 66.8%^{a*}	Langmuir			[73]
Green coconut shell (powder)	Cr (III), Cr (VI), Cd (II),	90%, 86%, 99%^{a*}	Freundlich		Ion exchange	[74]
Wheat shell	Cu	99%^{a*}	Langmuir			[75]
Peanut hull	Cu	12 mg/g^{a*}	Langmuir		Ion exchange	[76]
Barley straws	Cu, Pb	4.64, 23.20 mg/g^{a*}	Langmuir		Chemisorption and ion exchange	[77]
Neem bark	Pb	86.7%^{a*}	Freundlich	O–H, C–O, N–H, C–N, C–O, S–O	Ion exchange	[78]
Iris peat	Cu (II), Ni (II)	17.6, 14.5 mg/g^{a*}	Langmuir			[79]
Date pit	Cu (II),Cd (II)	35.9, 39.5 mg/g^{a*}	Freundlich	–C=C, –C=N	Hydrogen bonding and electrostatic attraction	[80]
Cassava peelings	Cu (II), Cd (II)	127.3, 119.6 mg/g^{a*}	Langmuir		Ion exchange	[81]

^{a}Indicates the dry weight of the biosorbent, *Indicates batch biosorption experiments at laboratory scale.

Table 3. Use of agricultural wastes for biosorption of metal ions.

guluronic acid with its corresponding salts), and sulfated polysaccharide with high contents of carboxyl groups that are involved in the process of the biosorption of metals. Red algae have received attention for biosorption due to the presence of sulfated polysaccharide made of galactans (having high contents of hydroxyl and carboxyl groups). Green algae contain cellulose with a high percentage of protein bound to polysaccharides which contain many functional groups like amino, sulfate, hydroxyl, and carboxyl [93]. Hence several authors focused on the removal of metal ions using algal biomass from contaminated water resources. It has been reported that algae can biosorb about 15.3–84.6% which is higher compared to the other microbial biosorbents [94]. The biosorption capacity of green algal species, *Spirogyra* sp. and *Cladophora* sp. for the removal of Pb (II) and Cu (II) from aqueous solutions, was studied. The capacity of *Spirogyra* was 87.2 and 38.2 mg/g and for that of *Cladophora* was 45.4 and 13.7 mg/g

Biosorbent	Biosorbate	Functional groups	Reference
Mucor rouxii	Cu (II)	Amino, carboxyl, phosphate	[86]
Streptomyces rimosus	Pb (II)	–COO, –C–O, –NH, –C=O, –OH	[87]
Maugeotia genuflexa	As (III)	Carboxyl, hydroxyl, amide	[88]
Rhizopus cohnii	Cd (II)	Carboxyl, amino, hydroxyl	[89]
Oedogonium hatei	Ni (II)	Carboxyl, phosphate, amide, hydroxide, thiol	[90]
Bacillus subtilis	Au (III)	Amino, carboxyl, hydroxyl	[91]

Table 4. Functional groups of microbial biomass involved in biosorption of metals.

Biosorbent type	Metal ion	Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
Stoechospermum marginatum	Cr (VI)	32.63 mg/g^{a*}	Freundlich		Ion exchange	[97]
Ulva lactuca sp.	Cd (II)	35.72 mg/g^{a*}	Langmuir	Amido, hydroxyl, C=O, C–O	chemisorption	[98]
Spirulina platensis	Cu (II)	90.6%^{a*}				[99]
Oedogonium hatei	Ni	40.9 mg/g^{a*}	Langmuir and Freundlich	–OH, –CH, C=O, –CN, =C–N		[90]
Maugeotia genuflexa	Ar (III)	57.48 mg/g^{a*}	Langmuir	Carboxyl, hydroxyl, amide	Ion exchange	[88]
Spirulina platensis	Cu	67.93 mg/g^{a*}				[100]
Palmaria palmate	Cr (VI)	33.8 mg/g^{a*}	Langmuir	–NH, C=O, C–O, –S=O	Ion exchange and complexation	[101]
Fucusvesiculosus		42.6 mg/g^{a*}				
Enterobacter sp.	Pb (II), Cu (II), Cd (II)	50, 32.5, 46.2 mg/g^{a*}	Freundlich			[102]
Cladophora spp	Pb (II), Cu (II)	46.51, 14.71 mg/g^{a*}	Langmuir		Physical adsorption or ion exchange	[95]
Laminaria japonica	Zn (II)	91.5 mg/g*				[37]
Spirogyra sp	Pb (II)	140 mg/g^{a*}	Langmuir	Carboxyl, amino, amide, hydroxyl		[103]
Ecklonia sp	Cr (VI)	60%^{a*}		Amino and carboxyl	Chemisorption and Ion exchange	[51]

^{a}Indicates the dry weight of the biosorbent, *Indicates batch biosorption experiments at laboratory scale.

Table 5. Algal biomass used for biosorption of metals.

for Pb (II) and Cu (II), respectively. The biosorption process showed the better fit with the Langmuir model, and the mechanism involved for biosorption is physical or ion exchange [95]. A marine algae *Sargassum filipendula* was used as a biosorbent for Cu (II) and Ni (II) ions with biosorption capacity of 1.324 and 1.070 mmol/g. An ion exchange mechanism was involved in biosorption with the Langmuir isotherm model showing the better fit [96]. **Table 5** summarizes some more examples of algae as biosorbents.

6.3.2. Bacteria as biosorbents

THE cell surface structure plays a vital role in biosorption. The cell wall of bacteria is primarily made up of peptidoglycan. Different species of bacteria can be classified based on cell wall composition. Two major types of bacteria are present. Gram-positive bacteria contain thick peptidoglycans bridged by amino acids. The teichoic acids present in the cell wall are linked with the lipids of the cytoplasmic membrane by forming lipoteichioc acids which are responsible for strong bonding with the membrane. The presence of phospodiester bonds between the teichoic acid monomers gives an overall negative charge and hence are involved in the biosorption of divalent cations (metal ions). Gram-negative bacteria have a thin cell wall containing a less amount of peptidoglycan. However, the presence of an additional outer layer composed of phospholipids and lipopolysaccharides confers an overall negative charge facilitating metal binding [104]. Most bacteria develop many resistance mechanisms and efficient systems for the removal of metal ions for their survival. Some bacteria produce slime or a capsule-like layer on the surface of cell wall. These are mostly composed of polysaccharides which are charged and help to detoxify metal ions from wastewaters [105]. Because of their high surface to volume ratio and high content of potential active sorption sites, bacteria make excellent biosorbents for sequestering metal ions form industrial effluents. *Enterococcus faecium*, a lactic acid bacterium, was able to biosorb Cu (II) ions from aqueous solutions with the maximum biosorption capacity of 106.4 mg per gram of dry biomass and showed better fit with the Freundlich isotherm model [106]. The dead cells of *Bacillus subtilis* biosorb Cu (II), Fe (II), and Zn (II) from its solutions by 25.86, 21.30, and 26.83%, respectively [107]. **Table 6** summarizes some more examples of bacteria as biosorbents.

6.3.3. Fungi as biosorbents

Fungi are also considered as economic and ecofriendly biosorbents because of characteristic features, that is, easy to grow, high yield of biomass, and ease of modification (chemically and genetically) [120]. The cell wall of fungi shows excellent binding properties because of distinguishing features like chitin, lipids, polyphosphates, and proteins among different species of fungi [121]. The cell wall of fungi is rich in polysaccharides and glycoproteins which contain various metal-binding groups like amines, phosphates, carboxyls, and hydroxyls. The fungal organisms are used in a wide variety of fermentation processes. Hence, they can be easily produced at the industrial level for biosorption of metal ions from a large volume of contaminated water resources. Besides, the biomass can be easily and cheaply obtained from inexpensive growth media or even as byproducts from many fermentation industries. Further, fungi are less sensitive to the variations in nutrients and other process parameters like pH, temperature, and aeration [122]. Because of their filamentous nature, they are easy to separate by means of simple techniques like filtration.

Biosorbent type	**Metal ion**	**Biosorption capacity/efficiency (mg/g or %)**	**Isotherm model**	**Functional groups involved**	**Mechanism**	**Reference**
Bacillus cereus	Zn (II)	66.6 mg/g[a*]	Langmuir and Freundlich	Amino, carboxyl, hydroxyl, carbonyl	Physic-chemical adsorption and ion exchange	[108]
Bacillus pumilus	Pb (II)	28.06 mg/g[a*]	Langmuir			[109]
Trametes versicolor	Cu (II)	140.9 mg/g[a*]	Langmuir	–NH_2, –OH, –C=O	chemisorption	[110]
Lactobacillus delbruckii bulgaricus, streptococcus thermophilus	Fe (II), Zn (II)	100%, 90%[a*]		Carboxyl and hydroxyl		[111]
Bacillus coagulans	Cr (II)	39.9 mg/g[*]				[112]
Bacillus thuringiensis	Ni (II)	15.7%[a*]	Langmuir			[113]
Bacillus thioparans	Cu (II), Pb (II)	27.3, 210.1 mg/g[*]	Langmuir			[114]
E. coli	Ni (II)	6.9 mg/g[b*]	Redlich-Peterson	C–H	Ion exchange	[115]
Pseudomonas putida	Zn	17.7 mg/g[a*]				[116]
Arthrobacter sp	Cu (II)	32.64 mg/g[a*]	Langmuir			[117]
Bacillus licheniformis	Cr (VI), Fe (II), Cu (II)	95%, 52%, 32%[b*]				[118]
Rhizobium spp	Cd (II), Co (II)	135.3, 167.5 mg/g[a*]	Langmuir			[119]

[a]Indicates the dry weight of the biosorbent; [b]Indicates the wet weight of the biosorbent; [*]Indicates batch biosorption experiments at laboratory scale.

Table 6. Bacterial biomass used for biosorption of metals.

Yeasts are unicellular. Most of the yeast biomass either biosorb a wide range of metals or strictly are specific to a single metal ion. *Saccharomyces cerevisiae* biomass has been widely studied as a yeast biosorbent, with high biosorption capacity [123, 124]. Yeast is also reported to have high bioaccumulation capacity and hence can be used as a suitable biosorbent for the removal of metal ions by growing them in metal-laden solutions. Many works reported that ion exchange was the key mechanism for fungi metal biosorption experiments. When *Saccharomyces cerevisiae* is grown in the media containing zinc in the concentration of 1.4372 g/L, the maximum amount of zinc found in the yeast cell was 1699 g/g of the biomass [125]. The filamentous industrial fungus *Rhizopus cohnii* was used as a biosorbent for the removal of cadmium from wastewater with the maximum biosorption capacity of 40.5 mg/g and the functional groups

Biosorbent type	Metal ion	Biosorption capacity Biosorption capacity/efficiency (mg/g or %)	Isotherm model	Functional groups involved	Mechanism	Reference
Penicillium canescens	As (III), Hg (II), Cd (II), Pb (II)	26.4, 54.8, 102.7, 213.2 mg/g[a*]				[126]
Penicillium chrysogenum	Ni	82.5 mg/g[a*]				[127]
Aspergillus niger	Cu (II)	9.53 mg/g[b*]				[128]
Pencillium purpurogenum	As (III), Hg (II), Cd (II), Pb (II)	35.6, 70.4, 110.4, 252.8 mg/g[a*]	Langmuir			[129]
Pencillium simpliccium	Cd (II), Zn (II), Pb (II)	52.50, 65.60, 76.90 mg/g[a*]	Redlich-peterson and Langmuir		Chemical ion exchange	[130]
Saccharomyces cerevisiae	Pb (II), Ni (II), Cr (VI)	270.3, 46.3, 32.6 mg/g[a*]	Langmuir		Physical adsorption	[131]
Lentinus sajor	Cr (VI)	18.9 mg/g[a*]	Langmuir	C–O, N–H, C–H	Physic-chemical adsorption	[132]
Pleurotus ostreatus	Cr (VI)	20.71%[b*]		–COOH, $-NH_2$		[133]
Aspergillus terreus	Cu (II)	180 mg/g[a*]	Freundlich			[134]
Phanerochaete chrysosporium	Ni (II), Pb (II)	55.9, 53.6 mg/g[b*]			Ion exchange	[135]
Pleurotus ostreatus	Cu (II), Ni (II), Zn (II), Cr (VI)	8.06, 20.4, 3.22, 10.75 mg/g[a*]	Langmuir	–COOH, $-NH_2$	Ion exchange, surface complexation and electrostatic interaction	[121]
Trametes versicolor	Ni (II)	212.5 mg/g[a*]	Langmuir	Carboxyl, hydroxyl, amine	Physico-chemical interaction	[136]

[a]Indicates the dry weight of the biosorbent; [b]Indicates the wet weight of the biosorbent; [*]Indicates batch biosorption experiments at laboratory scale.

Table 7. Fungal biomass used for biosorption of metals.

involved in biosorption was carboxyl, amino, and hydroxyl groups. The Langmuir isotherm model showed the better fit with an ion exchange mechanism for biosorption [89]. **Table 7** summarizes some more examples of fungi as biosorbents.

7. Effect of pretreatment on biosorption

Since the process of biosorption relies on the number and availability of functional groups on the surface of the biosorbent, modification by changing the surface characteristics can greatly influence the capacity of biosorbent used for the removal of metal ions [137]. Microbial-derived biosorbents are amenable for modification in order to increase the available binding sites and enhance the biosorption capacity leaving low residual metal concentration. A number of methods have been employed for surface modification of microbial biomass. The physical methods of pretreatment include heating, autoclaving, freeze drying, thawing, and lyophilization. Various chemical methods used for the pretreatment include acid or alkali treatment, washing with detergents, treatment with organic chemicals such as formaldehyde, sodium hydroxide, dimethyl sulfoxide, and cross-linking with organic solvents [3]. Physical- or chemical-treated microbial biomass show altered properties of metal biosorption compared to the original biomass. If the biomass is large in size, they are grounded into fine granules and are treated further for efficient biosorption [8]. The characteristic feature of pretreatment is to modify the surface groups either by removing or masking or by exposing the greater number of binding sites [3]. It is also observed that the longer duration of pretreatment can

Type of biosorbent	**Type of treatment**	**Metal ions**	**Biosorption capacity/ efficiency (mg/g or %)**	**Isotherm model**	**Functional groups involved**	**Mechanism**	**Reference**
Saccharomyces cerevisiae	Ethanol	Cd (II), Pb (II)	15.63 and 17.5 mg/g[a*]	Langmuir			[140]
Bacillus subtilis	Supercritical CO2, autoclaving	Ni (II)	98.54%, 99.2%[a*]		Carboxyl, phosphate amino, hydroxyl		[141]
Penicillium lanosa coeruleum	Heat, NaOH, detergent Gulteraldehyde	Pb (II), Cu (II) Ni	127%, 106%, 95%, 162% 72%[a*]				[142]
Mucor rouxii	0.5 N NaOH	Pb (II). Cd (II), Ni (II), Zn (II)	66%, 76%, 189%, 120%[a*]				[143]
Termitomyces clypeatus	Acid and alkali	Cr	100%[a*]	Langmuir and Freundlich	Amino, carboxyl, phosphate, hydroxyl, carbonyl	Physical adsorption, ion exchange, complexation, electrostatic attraction	[144]
Aspergillus niger	0.5 N NaOH	Pb (II), Ni (II)	80%, 60%[a*]				[145]
Aspergillus versicolor	DMSO	Pb (II)	30.6 mg/g[a*]	Redlich-Peterson	N–H, C–H, C=O, COO–	Ion exchange	[146]
Pencillium chrysogenum	Alkali	Cr (III), Ni (II), Zn (II)	27.2, 19.2, 24.5 mg/g[a*]		Amino, carboxyl, hydroxyl		[147]
Anabaena variabilis	Acetic acid	Cr, Ni	84.60%, 83.10%[a*]				[148]

[a]Indicates the dry weight of the biosorbent, [*]Indicates batch biosorption experiments at laboratory scale.

Table 8. Use of chemically modified (treated) biosorbents for the biosorption of metals.

further enhance the biosorption capacity. *Saccharomyces cerevisiae* treated with glutaldehyde increased the biosorption of Cu (II) ions [138]. The autoclaving of cells increases the surface area caused by cell rupture resulting in higher binding capacity compared to the normal cells. The treatment of autoclaved *Aspergillus niger* biomass treated with various chemicals increased the biosorption capacity for chromium from 2.16 to 86.88% when compared with the untreated biomass [139]. Hence, different pretreatments modify the surface functional groups (by masking or exposing) that influence biosorption capacity. The masking of carboxylic and amine groups present on the surface of *Saccharomyces cerevisiae* biomass by esterification and methylation decreased the biosorption capacity for Cu (II) ions which indicates that those functional groups are involved in the biosorption of metal ions and the study showed the better fit with the Freundlich isotherm model [138]. Various studies reported the use of treated biomasses for the removal of metal ions with high absorption rates was given in **Table 8**.

8. Immobilization of biosorbent

A major consideration for any biosorption is the separation of solid and liquid phases. Centrifugation and filtration are the routinely used techniques but not recommended at the industrial level. A continuous system with the biosorbent attached to a suitable bed is advantageous [149]. The use of free microbial cells as a biosorbent in continuous system is associated with many disadvantages such as the difficulty in separation of biomass, loss of biosorbent after regeneration, low strength, and little rigidity [150]. Microbial biomass can be immobilized by using a biopolymeric or polymeric matrix. The technique of immobilization is a key element that improves the performance of the biosorbent by increasing the capacity, improving mechanical strength and resistance to chemicals, and facilitating easy separation of biomass from a solution containing pollutants [151]. The process of immobilization is well suited for non-destructive recovery. Immobilization of the biosorbent into suitable particles can be done by using techniques like entrapment (in a strong but permeable matrix) or encapsulation (within a membrane-like structure) [152]. A number of matrices have been employed for immobilization including sodium or calcium alginate, polyacrylamide, silica, polysulfone, and polyurethane. It is very important to use a suitable immobilization matrix since it determines the mechanical strength and chemical resistance of the biosorbent particle targeted for biosorption while the matrix should be cheap and feasible to operate [153]. The use of an immobilized biosorbent is also associated with some disadvantages like increase in the cost of the biosorbent and an adverse effect on the mass transfer kinetics. This is because immobilization reduces the number of binding sites that are accessible to metal ions as majority of the sites are embedded within the bead [154]. The live and heat-inactivated *Trametes versicolor* immobilized within carboxyl methylcellulose (CMC) beads were efficient in the removal of Cu (II), Pb (II), and Zn (II) from the aqueous solution. The biosorption capacity were found to be 1.51 and 1.84 mmol, 0.85 and 1.11 mmol, and 1.33 and 1.67 mmol for Cu, Pb and Zn of both live and heat-inactivated biosorbents, respectively. The study shows the best fit with the Langmuir isotherm model [155]. **Table 9** gives the examples of various immobilization matrices used for the biosorption of metal ions.

Immobilized matrix	Type of biosorbent	Metal biosorbed	Isotherm model	Functional groups involved	Mechanism	Reference
Silica	*Aspergillus niger*	Cr, Cu, Zn, Cd				[156]
	Phaseous vulgaris	Ni (II)	Langmuir	C–O, –C–S		[157]
Polyurethane	*Phanerochaete chrysosporium*	Pb (II), Cu (II), Cd(II)				[158]
	Corynebacterium glutamicum	Reactive yellow 2	Redlich-peterson		Chemisorption	[159]
Polyacrylamide	*Pseudomonas sp*	U	Freundlich			[160]
	pseudomonas maltophilia	Au	Langmuir			[161]
Calcium alginate	*Bacillus cereus*	Pb (II)	Freundlich			[162]
	Trametes versicolor	Cd (II)	Langmuir and Freundlich			[163]
Sepiolite	*Aspergillus niger*	Fe (II, III)				[164]

Table 9. Various immobilization matrixes used with biomass for biosorption of metals.

9. Desorption and the regeneration of biosorbents

In order to keep the process costs down and for recovery of valuable metal ions after the biosorption, it is crucial for regeneration of the biosorbent [152]. The primary objective of desorption is to retain the adsorption capacity of the biosorbent. The process of desorption should be such that the metal can be recovered in the concentrated form (in case of metals of economic value), and the biosorbent needs be restored to the original state with undiminished biosorption capacity for reuse [8]. Hence an appropriate eluent for desorption should meet the following requirements [112]

- low cost;
- environment friendly;
- non-damaging to the biomass; and
- ensure intact metal-binding capacity.

The possible eluents are dilute mineral acids (HCl, H_2SO_4 and HNO_3), organic acids (citric, acetic and lactic acids), and complexing agents (EDTA, thiosulphate, etc.) for the recovery of the biosorbent and metal recovery. Desorption efficiency can be determined by the S/L ratio, that is, solid to liquid ratio. The solid represents the biosorbent and liquid represents the eluent (volume) applied. For complete elution and to make the process economical, high S/L values are desirable [3]. Although, desorption is considered advantageous, in some instances,

Type of biosorbent	Type of eluent	Metal ion	% of desorption	Isotherm model	Functional groups involved	Mechanism	Number of cycles	Reference
Spirulina sp	0.1 M HNO3	Cr, Cd, Cu	98	Langmuir	Carboxyl, phosphate, hydroxyl, amine	Ion exchange		[46]
Aspergillus niger	0.1 N NaOH	Cr	90%	Freundlich	Carboxyl, amide, phosphate, hydroxide	Chemisorption		[166]
Aspergillus flavus	0.1 N HNO3, 0.1 N NaOH	Cu (II)	80%					[167]
Raw wheat bran	0.01 mol/L HCl, HNO3	Cd (II), Pb (II)	100%, 57%	Langmuir			Four	[168]
Scenedesmus sp	0.1 M H2SO4	Zn	99%	Freundlich			Five	[169]
Aspergillus niger	0.5 N H2SO4	Cr				Redox reaction		[50]
Montmorillonite	0.1 M HCl	Ni (II), Mn (II)	92.8%, 90%	Freundlich		Physical adsorption	Three	[170]
Rhizopus nigricans	HNO3	Pb (II), Cd (II), Ni (II), Zn (II)	90%				Five	[171]

Table 10. Use of different eluents for desorption of metal ions.

a loss in the capacity of the biosorbent to retain the desired metal ion has been reported. The metal Cr (VI) was desorbed almost completely from the *Mucor hiemalis* biomass by using 0.1 N of NaOH. The biomass retained its activity of biosorption and desorption up to five cycles. Experimental data fit well with the Langmuir isotherm model, and FTIR analysis showed that the amino groups are involved in biosorption [165]. **Table 10** summarizes the use of different eluents for the desorption of metal ions from different biosorbents.

10. Factors affecting biosorption

Various factors influence the biosorption process namely, biomass concentration, initial metal concentration, and operational factors like pH, temperature, concentration of the initial metal ion, and concentration of the biosorbent.

10.1. Effect of pH

The pH of the solution is an important factor since it influences the metal chemical speciation, solubility, and the total charge of the biosorbent [82]. At low pH (acidic pH), the hydronium ions are closely associated with the active ligands of the biosorbent and therefore, there exists a competition between the protons and metal ions for the binding sites [172]. At higher pH, there exists lower number of H+ ions, and the number of active sites of the functional groups is free and exposed (negative charge) which results in increased biosorption by attracting positive charged metal ions. At higher pH, the metal might begin to precipitate and form hydroxides and as a consequence hinder the biosorption process [108]. The increase in pH from 1 to 4 increased the biosorption of Cr (VI) from wastewaters by *Saccharomyces cerevisiae* biomass [173]. For biosorption of Cr by pretreated *Aspergillus niger* the optimum pH was found to be 3 [166]. An increase in pH from 2.0 to 4.5 increased the biosorption of cadmium by *Rhizopus cohnii* biomass and thereafter it reached a plateau in the pH range from 4.5 to 6.5 [89].

10.2. Effect of temperature

Temperature deals with the thermodynamics of the process and kinetic energy of the metal ions [82]. The temperature can have a positive or negative effect on biosorption at certain intervals. An increase or decrease in temperature causes a change in the biosorption capacity of the biosorbent. High/increasing temperature enhances the biosorptive removal of biosorbates but it is associated with the limitation of structural damage to the biosorbent [38]. Hence, optimum temperature for efficient biosorption has to be chosen for the maximum binding of metal ions. In this context, a maximum biosorption of 86% for cadmium ions was achieved with *Saccharomyces cerevisiae* at 40°C [173]. A rise in incubation temperature from 25 to 40°C sharply increased the biosorption rates of Cr (VI) by *Streptococcus equisimilis* [174].

10.3. Effect of initial metal concentration

The mass transfer resistance between the liquid and solid phases can be overcome by the initial concentration of metal ion [175]. The biosorption capacity (quantity of biosorbed metal ions per unit weight of the biosorbent) of the biosorbent increases initially with the increase in metal ion concentration and then reaches a saturation value. However, the biosorption efficiency of the biosorbent decreases with increase in metal ion concentration. The higher biosorption efficiency at low metal concentration is due to the complete interaction of ions with the available binding which sites results in higher rates of efficiency. At higher concentrations, the number of metal ions remaining unbound in the solution is high due to the saturation of available binding sites [176]. The effect of different initial concentration (25–500 mg/L) of Cd ions on the biosorption of *Hypnea valentiae* was studied. It was found that highest biosorption efficiency (86.8%) was observed with a Cd concentration of 25 mg/L from simulated wastewaters [177]. The biosorption efficiency of the cashew nut shell decreased from 86.03 to 76.17% with the increase in copper ion concentration from 10 to 50 mg/L [178].

10.4. Effect of biosorbent dose

Biosorbents provide the binding sites for metal biosorption, and hence its dosage strongly affects the biosorption process [179]. The increase of the biosorbent dose at a given initial metal concentration increases the biosorption of metal ions due to greater surface area which in turn increases the number of available binding sites [179]. At lower concentrations of the biosorbent, the amount of metal biosorbed per unit weight of the biosorbent is high. Conversely, at high concentration of the biosorbent, the quantity of metal ion biosorbed per unit weight decreases.

This is because of lower adsorbate to binding site ratio due to the insufficient amount of solute present for complete distribution onto the available binding sites and possible interaction between binding sites. The biosorption of Cd and Pb ions by *Anabaena sphaerica* was increased with an increase in the biosorbent dose from 0.025 to 0.25 g/100 ml but stabilized at higher biomass dosages because of the formation of aggregates which reduce the effective surface area for biosorption [180]. The biosorption efficiency of *Parthenium hysterophorus* for Cr biosorption increased from 61.28 to 80.81% with an increase in biomass concentration from 0.1 to 1 g because of the availability of more binding sites but the biosorption capacity decreased from 9.43 to 0.37 mg/g due to decreased metal to biosorbent ratio [181]. A similar trend was observed in many other studies in respect of the effect of biomass concentration.

10.5. Effect of contact time

The time required to attain maximum biosorption depends on the type of biosorbent, metal ion, and their combination. The rate of biosorption is rapid initially (within an hour) with almost 90% of the metal binding because all the active sites are vacant and available for metal ion biosorption. But with increase in time the rate of biosorption decreases due to increase in percentage saturation by metal ions remaining in the solution [182]. Most of the Cd and Zn ions are biosorbed onto *Aspergillus niger* biomass within the first 6 h and there is no further biosorption after 24 h [183]. *Bacillus cereus* and *Pseudomonas aeruginosa* biosorb Zn ions with an equilibrium contact time of 30 min [108].

10.6. Effect of agitation speed

The increase in agitation speed increases the biosorption capacity of the biosorbent by minimizing its mass transfer resistance. While the added turbulence enhances the sorption of the metal ions [184], it may also lead to the destruction of the physical nature of the biosorbent. A moderate speed ensures the best homogeneity for the suspension with a high capacity of biosorption. High agitation speeds result in the occurrence of vortex phenomenon which results in the loss of the homogenous nature of the suspension. Excessive turbulence may also reduce the time of interaction between the biosorbate and biosorbent, thus decreasing the extent of biosorption [183]. The optimum speed of agitation for the biosorption of Cd and Zn by *Aspergillus niger* was found to be 120 rpm [183]. With an increase in agitation speed from 0 to 80 rpm, the biosorption efficiency also increased from 32.4 to 65% [62].

11. Biosorption equilibrium isotherms

Sorption isotherms explain the equilibrium relationships between biosorbent and biosorbate and the mass of the biosorbed component per unit mass of biosorbent and the concentration of biosorbate in the medium under a given set of conditions (temperature and concentration). It also determines the equilibrium distribution of metal ions and how selective retention takes place when two or more biosorbent components are present [185]. The term "isotherm" can be defined as a curve explaining the retention of a substance on a solid at various concentrations

[82]. The determination of equilibrium parameters is the basic requirement for designing a good biosorption system. For determination of the best-fitting sorption isotherm, linear regression is frequently used. In order to predict the isotherm parameters, the method of least squares is applied.

The biosorption capacities of different biosorbents for different pollutants can be best explained by biosorption equilibrium isotherms. Several isotherm models are available to describe the mechanism of the biosorption process and the equilibrium biosorption distribution. Some of the isotherms used in biosorption studies are Langmuir, Freundlich, and Temkin isotherms. However, the biosortion process may show better fit with a specific isotherm.

Biosorption isotherm data of Pb (II) and Cu (II) ions onto green algal species, *Spirogyra* and *Cladophora,* were in good agreement with the Langmuir isotherm demonstrating the formation of the monolayer coverage of metal ions on the outer surface of the biosorbent [95]. The Langmuir model fitted well with the biosorption of Pb (II), Zn (II), and Ni (II) ions onto *Bacillus subtilis* [186]. Freundlich isotherm showed the best fit for the biosorption of Cu (II) ions onto lactic acid bacterium, *Enterococcus faecium* [106]. Biosorption of Cr (VI) ions onto *Bacillus thuringiensis* also shows the better fit with Freundlich isotherm [187].

12. Bioreactors used for biosorption

Various types of bioreactors have been investigated for application at the industrial level. A bioreactor is a system used for the production of microorganisms or desired metabolites employing defined and controllable factors. The typical categories of bioreactors used for the biosorption are stirred tank bioreactors (STRs), air lift bioreactors (ALRs), fluidized bed bioreactors (FBRs), and fixed bed bioreactors (FXRs). These reactors can be operated either in batches or in continuous modes or both (fixed bed and stirred tank bioreactors). Factors (pH, temperature, mixing and agitation, and nutrient availability) affecting the process of biosorption in the bioreactor have to be optimized and controlled by using cooling jackets (temperature), baffles/agitators (mixing), feed lines (supplies nutrients), and acid/base addition (pH) [188].

12.1. Fixed bed bioreactors

It is designed with the biosorbent fixed onto a bed and a container having the bed within. During biosorption, the water contaminated with heavy metals is passed through the column. The biosorbents biosorb the metal ions until the maximal capacity is reached. The biosorbent is then regenerated for the release of heavy metals. In order to ensure continuous working conditions, the presence of two columns is employed. Biosorption is performed on one column while the regeneration of spent biosorbent on the other by rinsing with a suitable chemical reagent. Most of the biosorption processes have used fixed bed bioreactors. Its advantages include simplicity in construction and operation and possibility to carry out process in a countercurrent flow (a current flowing in opposite direction) [189]. However, it is necessary to examine the pressure drop and the effect of column dimensions when operated in a continuous mode [190].

Type of reactor	Biosorbent	Metal species	Biosorption efficiency	Reference
FBRs	*Pseudomonas aeruginosa*	Cd (II), Cr (VI)	67.17%, 49.25%[a*]	[191]
	Sand grains	Cu (II), Pb (II), Ni (II)	96%, 93%, 98%[a*]	[193]
ALRs	*Trichoderma viridae*	Cr (VI)	94.3%[b*]	[194]
	Scenedesmus incrassatulus	Cr (VI)	43.5%[a#]	[195]
STRs	*Rhizopus arrhizus*	Cr (VI)	70.5%[a#]	[196]
	Trichoderma viridae	Cr (VI)	60%[b*]	[194]
PBCs	*Aspergillus niger*	Cu (II)	83.96%[a#]	[197]
	Ulva reticulate	Cu (II), Co (II), Ni (II)	56.3%, 46.1%, 46.5%[a#]	[198]
	Sewage sludge	Cr (VI), Ni (II)	90%[a#]	[199]
	Microcystis aeruginosa	Pb (II), Cd, (II), Hg (II)	80%, 90%, 90%[a#]	[200]

[a]Indicates the dry weight of the biosorbent; [b]Indicates the wet weight of the biosorbent; [*]Indicates batch biosorption experiments at laboratory scale; and [#]Indicates continuous biosorption experiments.

Table 11. Use of different bioreactors for biosorption of metal ions.

12.2. Fluidized bed and air lift bioreactors

These two reactors almost work on the same principle of separation and can be operated in the batch mode. The reactor contains liquid, gaseous, and solid phases. The solid phase is a biosorbent on solid particles used for the retention of metals. The reactor operates with the idea that the gas allows the liquid containing the metal species to be removed to rise. The liquid then flows upward through the middle of the reactor and comes back down through the edges resembling a fountain [191]. In this the liquid is in continuous movement and moves the entire volume of the column. The metal species then adhere to the biosorbent. Once the biosorbent is harvested, the target molecule is separated. Since the particles are in continuous movement, it is preferred and also reduces the clogging effect of the biosorbent. Fluidized reactors are associated with the low mass transfer [38].

12.3. Stirred tank bioreactors

Liquid phase can be separated from the solid phase by a membrane system. Though the process is simple, the cost of operation is high due to high energy requirements [192].

The efficiency in the removal of metal ions largely depends on the type of bioreactor, type of biosorbent, and operating conditions. Recent studies evaluated the efficiency of different biosorbents in the removal of metal ions by using various types of bioreactors (**Table 11**).

13. Application of the biosorption process at pilot scale

Many researchers have attempted pilot-scale studies to make the technology of biosorption available at the industrial scale. A small pilot plant with a three-zone contact settling was developed in a single vessel using anaerobically digested sludge as the biosorbent for the removal of Cu (II) ions. The efficient metal removal (similar to the batch experiments) of 90 mg/g of the biosorbent was observed [201]. Flotation is a separation process that can effectively separate the metal-loaded biosorbent suspended in the aqueous solution. The technique of biosorptive flotation was applied for the removal of nickel, copper, and zinc ions from the aqueous solutions using grape stalks as the sorbent. Two feed solutions containing different metal concentrations were prepared. The dilute metal solution was applied followed by the concentrated metal solution in the counter-current mode in order to improve the performance of the biosorbent. The experiments were conducted in 10 L columns and satisfactory metal removal was observed (Cu—95%; Zn—98%; Ni—70%; Ca—82%). The biosorbent after regeneration by using an aqueous mixture of sodium sulfate and sodium citrate can be used for the second cycle [202]. A two-step operation for biosorption and sedimentation was operated in a 200 L pilot plant for the removal of pollutants using biomass of *Cunninghamella elegans* and the obtained results proved that the biosorption process is effective in treating wastewaters efficiently [203].

14. Biotechnological intervention: genetically engineered microorganisms (GEM)

Most biosorbents sequester metal ions by using cell-surface moieties. However, they lack the property of specificity and affinity for metals. By using the available genetic engineering technologies specific tailoring can be done to the microbial biosorbents with required selectivity and affinity for metal ions [204]. Genetic engineering technology involves altering the genetic material of the organism in order to develop an efficient strain for the removal of metal ions against the wide range of contaminants present in the wastewater [205]. One such emerging strategy which has received increased attention in recent times is the use of metal-binding proteins such as metallothioneins and phytochelatins. For example, *E. coli* was modified to express phytochelatin 20 on its surface enhancing the accumulation of Hg by 25 times over that by wild-type strains [204]. The technology also offers the advantage of developing microbial strains that can withstand complex environmental conditions and stressful situations. A major obstacle associated with the molecular approach is that it has been applied to only limited bacterial strains like *Escherichia coli*. Hence, other microorganisms need to be explored using this molecular intervention. **Table 12** shows the list of selected genetically engineered bacteria used for the removal of metal ions.

Metal ion	Initial concentration (ppm)	Biosorption efficiency %	Genetically engineered bacteria	Expressed gene of interest	Reference
Hg	7.4	96	*E. coli*	Hg^{2+} transporter	[206]
As	0.05	100	*E. coli*	Metalloregulatory protein ArsR	[207]
Ni	10 uM	15 μmol	*E. coli*	nixA gene	[208]
Cr	10	48–93.8%	*Alcaligenes eutrophus*	pEBZ141(Cr resistance genes)	[209]
Hg		77.58 mg/g	*Rhodopseudomonas palustris*	pSUTP+pGPMT	[210]

Table 12. Use of genetically engineered microorganisms for biosorption of metal ions.

15. Application of biosorption for real wastewaters/effluents

Efforts have been devoted to apply the process of biosorption as a waste treatment method. Instead of aqueous metal solutions, the experiments involved the effluents collected from various polluted sources. Various studies have reported high removal efficiencies.

The electroplating waste containing Cu (II), (6 mg/L) along with other ions (Zn, Cr (VI), Na, Ca, K), was treated with different agro-waste/natural biosorbents at the optimum conditions (pH −6.0, determined by batch experiments). Removal efficiency for Cu ranged from 77 to 95%. Other metals in the effluents were also removed to various extents [211].

Industrial effluent samples were collected from El-Fayoum for chemical production company outfalls in Egypt to decontaminate Co (II), Cd (II), Cr (III), and Pb (II) by using four red seaweeds namely *Corallina mediterranea, Galaxaura oblongata, Jania rubens* and *Pterocladia capillacea*. The biosorption efficiencies of the four biomasses were within the range from 57 to 94% and the highest efficiency was observed with *Galaxaura oblongata* biomass followed by *Corallina mediterranea, Pterocladia capillacea* and *Jania rubens* with mean biosorption efficiencies of 84, 80, 76, and 72%, respectively. The study demonstrates that the four seaweeds can be promising, cheap, efficient, and biodegradable biosorbents for lowering of metal ion pollution from the environment [212].

In related study, the efficacy of sugarcane bagasse (the immobilized and native form) for the removal of chromium from wastewater collected from the local tanning plant (Kasur, Pakistan) was evaluated. At a biosorbent dose of 0.1 g and pH of 2.0, the biosorption efficiency was found to be 411 mg/g of biomass which is equivalent to 73% of total chromium present in the wastewater. This highest efficiency was observed with the immobilized form of the biomass when compared with the other forms (native and chemically treated). At the batch level, the maximum uptake was 80.6 and 41.5% in batch mode for Cr (VI) and Cr (III) [213].

The removal efficiency with real effluents can be affected due to the presence of other components like other metals, organic matter, anions, and so on which can compete for the binding sites. The fungal biosorbent *Pleurotus ostreatus* was used for the treatment of wastewater collected from the main drain of the local electroplating industrial units situated at Shahdra, Lahore, Pakistan. A slight wane in the biosorption efficiency when the biomass was used for real wastewater treatment was observed. In case of a real effluent, the metal removal efficiencies for Cu (II), Ni (II), Zn (II), and Cr (VI) were 46.01, 59.22, 9.1, and 9.4%, respectively, while for the single synthetic metal solution, it was 52, 63.52, 10.9, and 11.8%, respectively. This moderate to slight decrease in the removal efficiency of biosorbent might be due to the competition of various contaminants for binding sites as reported in many other studies. Another compounding factor is high COD which also causes reduction in biosorption [121].

The potential of seaweed (*Sargassum)* biomass was used to decontaminate heavy metal ions from urban real storm water runoff. The biosorbent was able to remove metal ions but the efficiency was slightly lesser (90, 65, 50, and 40%) than the single synthetic solute system (80, 50, 15, and 10%) of Pb, Cu, Zn, and Mn, respectively, under similar conditions. The other contaminants like anions, organics, and other trace metals present in the runoff may compete with the existing binding sites of the biosorbent resulting in a decrease in the efficiency of biosorption [214].

However, the removal efficiency attained with real effluents may be comparable with single or simulated synthetic metal solutions.

Gooseberry fruit (*Emblica officinalis*) waste was used as the biosorbent for the removal of Cu from the real electroplating wastewater (50 ml), containing various metals including Cu, from the local electroplating plant in Aligarh city. The wastewater (pH 3.0) was freed of suspended matter, diluted 10 times to the final concentration of Cu (II) of 38 mg and the pH was then adjusted to pH 4.2 before biosorption. The efficiency of metal removal was 98.07% in the column process (1 ml/min) and 65% in batch experiments. The removal efficiency (as calculated from the data given) for mono-metallic solution batch experiments was comparable [215].

In another study, wastewater having heavy metals and textile dyes was collected from the local metal, and the textile processing industry in Turkey was treated with *Punica granatum* L. peels. Under optimum experimental conditions the removal of Pb (II) was 98.07%. Simulated water containing interfering ions also showed a removal efficiency of 98.18%. This was compared well with removal efficiencies (94% as calculated from the data) with mono-metal solutions under optimal conditions. Thus, other components of wastewater such as different metallic salts and dyes did not interfere with removal [216].

The effluent discharged from the battery industries located in the Northern region of Kolkata was treated by *Aspergillus versicolor* biomass to remove Pb (II) ions. It was observed that the efficiency for the removal of Pb (II) ions was found to be 86% which was almost similar to the value obtained by the mono-metallic synthetic system. Hence the study suggests that the presence of additional cations or anions present in the effluent does not affect the biosorption efficiency of the biomass used in the experiment [217].

Modification to the process conditions with real wastewaters may be necessary to achieve removal efficiencies comparable to those obtained with mono-metal solutions.

A *Spirogyra* granule packed column was employed for treating various industrial effluents which was done by passing wastewaters (1 L, 0.6 ml/min) from different industries namely the carpet industry, paper mill industry, and electroplating industry near Varanasi, India. The packed column achieved removal efficiency of >90% for Cu, Cd, Zn, Ni, Pb, and Cr from the three industrial wastewaters. However, this required the reduction of pH from 7.8 to 4.5 (for metals other than Cr) and 2 (for Cr) although the optimum pH of 5.0 was used with metal solutions [218].

Neem sawdust was employed as the biosorbent in a column bioreactor for the removal of Cr (VI) at 94 mg/L from 1.5 L of raw tannery wastewater collected from a common effluent treatment plant in India. The results revealed that the biosorbent of 20 g was sufficient for the removal of chromium with the removal efficiency of 99%. Batch experiments were conducted at 2 g/L dosage at initial concentrations of 150 mg/L in 100 ml shake flasks [219].

16. Commercialization and adoption of biosorption as waste treatment technology

In spite of the advantages over other conventional techniques, there is a glaring lack of adoption of biosorption as a waste treatment technology. Few commercial ventures offering

Biosorbent	**Source**
AlgaSORB	*Algal biomass*
B.V.SORBEX	Biomass from various sources
AMT-Bioclaim	*Bacillus* sp.
Bio-Fix	Different biomass
Rahco	Different biomass
MetaGeneR	Different biomass
AquaSorb	Activated carbons
P.O.L. Sorb	Sphagnum Peat Moss
MSR	*Rhizopus arrhizus*
Azolla Biofilter	*Azolla filiculoides*

Table 13. Commercial biosorbents.

biosorption as a treatment have emerged. A few commercial biosorbents are available, as shown in **Table 13**. There is a dearth of field trials for a seemingly promising decade-old technology.

Volesky and Naja reported that the lack of commercialization was due to non-technical reasons—due to lack of partners. Computer models based on pilot tests can reduce the scope of field tests. Data and cases of application can attract investors, consultants, distributors, and clients [220].

The BV Biosorbex Inc. is a Canadian company, started by Professor Bohumil Volesky of McGill University, Montreal, Canada, involved in commercializing biosorption. Its services include the biosorption-based removal of heavy metals from industry waters using reactors carrying novel biosorbents as granules offered at the 1/10th the cost of ion exchange resins. The biosorbents may be made from industrial waste, algal biomass, and specialized biomass. The biosorbents are reported to function between pH 4–10 and 5–75°C with efficiencies of >99.9% at 10–50 ppb concentrations of heavy metal and organic matter (<5000 mg/L). The company can conduct lab-scale studies, consultancy, design process, and operate waste treatment plants. Pilot biosorption systems may involve column, fluidized bed, or mixed tank reactors. The company plans to capture 15% of market of ion exchange resin (http://www.bvsorbex.net/invest.htm).

AlgaSorb by Biorecovery Inc. has algal biomass immobilized in silica gel. In a pilot study two columns in series with different biosorbents of algae were used to remove mercury from groundwater. Algasorb 624 with high Hg retention but high leakage was used followed by AlgaSorb 620 having the opposite characteristics. Sodium thiosulphate (0.1 M) followed by deionized water (10 bed volumes) was used for regeneration. The study was successful for varying levels of mercury and in the presence of Ca, Mg, and organic matter [221]. Immobilization protects algae against decomposition by microbes. Also, a hard material suitable for packing into columns is obtained. A portable effluent treatment equipment has two columns operating in series or parallel at flow rates of 1 gallon/min and has 0.25ft^3 of

AlgaSorb in each column. Equipment for operating at higher flow rates has been designed. Both metal cations and oxyanions can be bound while Ca, Mg, Na, and K ions do not interfere to a significant extent [222].

Bioclaim by Vistatech Partnership Pvt. Ltd. developed *B. subtilis* biomass obtained by treating with NaOH and immobilizing in binders like polyetheimine and glutaraldehyde. The biosorbent is stable and used for removing metals including gold from gold cyanide.

US Bureau of Mines devised bio-fix beads by immobilizing biomass in porous polysulfone beads. Immobilized *Sphagnum* biomass has 4-5-5.0 meq cations per gram capacity comparable to ion exchange resin, with an operational pH range of 3.0–8.0, and metal affinity in the order of Al > Cd > Cu > Zn > Fe > Mn > Ca > Mg. Majority of equilibrium sorption occurred in 20 min. Bio-fix was used for four onsite field trials. The regeneration by sulfuric acid and subsequent neutralization is done by Na_2CO_3. The beads were stable to physical and environmental deterioration and displayed over 95% removal over 250 cycles of regeneration. The source of wastewater and the presence of organic matter below 50 mg/L did not inhibit metal removal. Such promising results encouraged field trials.

A three column-circuit (lead, scavenger and elution) was used to remove metals from wastewater from taconite operation. Several metals (Ni, Co, Cu, Zn) were removed (98%) with 20 min residence time and 40–50BV of solution at low temperatures of water (1–3°C) or air (<=0°C). The metals were precipitated by treating the elute with MgO and evaporating to obtain residue.

Employing a similar setup, 90–95% of removal was obtained for Zn, Fe, and Mn. However, the presence of suspended solids interfered with the operational efficiency.

In a low maintenance circuit, beads filled in bags made of Polymax B material were placed in troughs or in buckets in the flow of wastewater discharge. Over a 11-month period, Fe concentration of wastewater from an abandoned silver mine was reduced to below 1 ppm level from 20 to 60 ppm levels. This involved 2300 L of beads placed in troughs. Both bucket and trough circuits were used to treat discharge for abandoned mine containing Cd, Cu, Fe, Pb, and Zn. Drinking water standards were (85–89% removal) met with either system at flow rates of 0.3–0.5 L/min with weekly replacement of 50% of beads. Operating cost with bio-fix beads compared well with lime precipitation treatment for similar wastewaters [223].

BIOS process by the Noranda technology center utilized a bed of sawdust, algae and sphagnum moss near seepage. The metal-saturated biomass is later disposed of (as tailings or sent to smelter) or washed for recovery of metals. The bed contained bark (20 years old), wood pulp, and sawdust. Total void volume was 7 L. A Plexiglas reactor was used in 30 L capacity to treat acid mine drainage (AMD). Over a 7-day residence time at room temperature, pH was not effected but Cu (100%) and Zn (65%) were removed.Better metal removal (95–100% for Al, Cu, Zn, Fe) was achieved for a 14-day residence time. The pH did not increase and stabilized at 3 over 12 bed volumes. At lower temperature of 10^0C (as compared to 20^0C), the removal of metal (except for Cu) ions was reduced. The process compared well with lime organic mixture (LOM) and the anoxic lime stone drain (ALD) methods and was better compared to the Biotrench method in terms of metal removal [224].

Later, different combinations of treatments (LOM/BIOS/ALD, BIOS/ALD and LOM/ALD) were executed to treat AMD. The volume of the initial reactor was 30 L except in the case of LOM/ALD (20 L). The downstream reactors were of 4 L. With LOM/BIOS/ALD, As, Cd and Cu were removed beyond detection. Fe and Zn were also reduced by 93 and 50%, respectively. The pH was increased to 6.3. With the BIOS/ALD system, pH increased to 6.3 and As, Cd, and Cu were removed beyond detection. Metal Al was reduced to 0.7 ppm while Fe and Zn were removed at 99 and 38% efficiency. BOD and COD were negligible. There was no influence of low temperature. The LOM/ALD was referred as the best treatment, achieving the removal of all metals including Zn (99%) and Mn (68%), not attained with other combinations, along with negligible BOD and COD [225].

AquaSorb is a granular, powdered, and extruded activated carbon used primarily for the treatment of water, waste liquid streams and the recovery and recirculation of process liquors. The source of carbon which is activated for water treatment is from coconut shell, coal, and wood raw material by chemical or steam activation. Specially designed AquaSorb for the use in liquid phase adsorption systems in the range of granular, ground, and extruded (pelletized) form can be supplied by Jacobi Carbons. It can be applied as home water filters for the dechlorination of water, in order to reduce chloramines and produce water with good taste, more pure and palatable than the normal municipal water (https://www.wateronline.com/doc/aquasorb-activated-carbon-0001).

The highest grade of Sphagnum Peat Moss is used for the development of P.O.L. Sorb which acts as a superb adsorbent for solutions due to the inherent capillary action of the activated peat which provides powerful wicking action that encapsulates oils, solvents, heavy metals, pesticides, herbicides, and so on which are in contact. It is manufactured by The ARK Enterprises, Inc. The raw material of POL Sorb is leafy, stem free, and least an abundant part of the peat in its natural or partial biodegraded state (http://www.arkent.com/POL%20Sorb%20Flyer.pdf).

MSR is a biosorbent produced by immobilizing the inactivated cells of *Rhizopus arrhizus* with the desirable particle size of 0.5–1.2 mm. The characteristic features of the biosorbent are that it is resistant to chemicals, compression and abrasion, high porosity, and is with good wetting ability. These proprietary immobilized particles (MSRs) were used for the recovery of uranium from lore leaching operations [226].

17. Conclusions

One advantage of biosorption is the removal of residual or minute concentrations of contaminants. Conventional water treatments may not completely remove contaminants. Hence, biosorption may be integrated downstream of other conventional water treatments. This is especially relevant in the case of pollutants like heavy metals whose effects are felt even at ppb levels.

The efficiency for the removal of specific metals is hindered by the presence of other contaminants. This may be important during the recovery of specific metals of economic value. In this regard, biosorption may be applied to wastes and effluents before it enters the sewage or natural discharge streams like rivers, seas and so on.

However, with the aim of treating effluent/remediating water resources of all/most contaminants, it may be an advantage to have all pollutants (metal or contaminants) removed simultaneously using a non-specific/non-selective biosorbent and reducing the number of operations/steps. Multiple biosorbents of different specificities/selectivities can also be used.

The strains or biomass used as the biosorbent should be of safe origin especially for water treated for human or animal consumption. Hence, pathogens and toxin-producing organisms need to be avoided. In this regard biomass from food-grade microorganisms like lactic acid bacteria and (wine/beer yeast) and agro-waste is of significance.

Regeneration and immobilization of biomass in order to reduce the cost of biomass involve the use of hazardous solvents which can lead to pollution. Hence, the use of harmless chemicals may be explored.

The existing waste can be classified as solid (degradable and non-degradable) and liquid in nature. A lot of solid non-biodegradable wastes (plastic) can be recycled to form chemically and mechanically robust and inert matrices to hold the biosorbent. Degradable wastes or biomass (agricultural/domestic/industrial) can be employed as biosorbents. A compatible biosorbent-matrix combination can then be employed to treat liquid discharge/effluents. This can make the waste treatment economical and sustainable while addressing the problems of solid and liquid effluents simultaneously.

Nature provides a diversity of biomass varying in binding specificity, efficiency, and ruggedness. This diversity can be tailored to site-specific waste treatment needs by applying the advanced techniques of recombinant DNA technology, synthetic biology and so on. Strains can be modified to express single/multiple metal-binding proteins on the cell surface. Chimeric proteins with multiple metal-binding domains having suitable binding and regeneration conditions can be engineered and expressed. Binding and regeneration conditions for the biosorbents can also be manipulated. Strains tolerant to harsh waste environments, and/or able to accumulate the toxic metals can be developed. However, laws regulating the dispersal or release/containment of genetically modified organisms will need to be considered. Techniques like genome shuffling are considered natural and can be employed for the modification of microorganisms. Confusion exists on the Crispr–Cas9 technology if it can be considered a genetic modification. Also, biosorption processes involving dead biomass may be a convincing argument against such regulations.

Nanotechnology is a cutting-edge technology involving the development of novel materials through the manipulation at nanoscale. The use of biomass has been explored to produce nanometal particles of silver, Cu, gold and so on. This novel use of biosorption linking the wastewater treatment to synthesis/the recovery of metals/nanometals from wastewater makes economic sense for capital investment.

The development of novel efficient biosorbents (nanocellulose, nanocomposites like pectin/ TiO_2, nano Fe_3O_4/*Sphaerotilus natans*, ostrich bone waste-zero valent iron, polyaniline-modified nanocellulose) has also been obtained by varied treatments including solvents, heat, and so on. This may be the answer to optimizing and economizing biosortion-based waste treatment by improving stable efficient biosorbents.

Biosorbents carrying metals can be included into feeds or fertilizers as metals bound to organic ligands have greater bioavailability. Also, they can enhance the shelf life of the feed involved.

However, biomass may also bind hazardous chemicals (like dyes) when used with industrial effluents. The use of such biomass into feeds is not recommended.

Biosorption is beneficial over conventional techniques. The potential has been demonstrated at laboratory and pilot scales even with actual effluent/discharges. But there is a dearth of examples in the real scenario at organized levels like municipalities/cities/pollution treatment centers/industries. Few commercial ventures have been made. This might be because of the diversity of pollutants and their chemical and biological waste background. A set of promising biosorbents/processes may need to be optimized or standardized for specific effluent types. The cost and feasibility in terms of large-scale applications may be evaluated.

Routine adoption at municipal and industrial levels requires success stories at field studies. Better metal removal efficiencies at lower costs and labor when compared to other conventional treatments can convince the industry/state to adopt biosorption. However, there is a lack of field experiments. Executing field studies needs great coordination, capital, manpower, and infrastructure.

State intervention is needed to assist the scientific community to not only fund and coordinate such large studies in terms of manpower/infrastructure but to also access the industry(s) concerned. The general indifference of the industry toward waste treatment may be an issue.

The state can act as bridge for informing and facilitating the availability of biomass from different sources to different polluting units. Such efforts will create a mutually sustainable waste treatment scenario. For example, the disposal of agro-waste from the rural setup to polluting units in order to treat effluents is a win-win for both parties.

An environment encouraging start-ups based on biosorption technology needs to be created.

Stringent norms and scrutiny against effluent discharge can convince the industry to view waste treatment as a necessary investment rather than an avoidable overhead cost. Under this scenario start-ups like Biosorbex, investing in eco-friendly waste treatment technologies, can flourish.

Efforts may be devoted to also apply biosorption at domestic (household) or community levels rather than awaiting the installation of large centralized water treatment setups.

Techniques like response surface methodology, artificial neural networking, boosted regression tree, and genetic algorithm may be used for process optimization. Modeling should be done in solutions with multiple metals and organic matter simulating the real wastewater conditions. Pilot and field studies should be conducted comparing biosorption with the conventional techniques. The use of computer-based simulations or modeling can reduce the number of field trials.

The challenges encountering biosorption are similar to those faced by membrane filtration technology before achieving relevance and popularity as today. This includes the cost and stability of the biosorbent (membrane), the decrease in binding sites (fouling), and poor understanding and general reluctance to adopt new technologies etc. Hence, given its eco-friendly nature and other merits, it will find its place as a routine water treatment process.

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References

[1] Baroni L, Cenci L, Tettamanti M, Berati M. Evaluating the environmental impact of various dietary patterns combined with different food production systems. European Journal of Clinical Nutrition. 2007;**61**:279

[2] UIET SH. Environmentally sound technologies for wastewater and stormwater management: An international source book. International Water Association: Osaka. 2002; **15**:1-617

[3] Vieira RH, Volesky B. Biosorption: A solution to pollution? International Microbiology. 2000;**3**:17-24

[4] Das N, Vimala R, Karthika P. Biosorption of heavy metals—An overview. Indian Journal of Biotechnology. 2008;**7**:159-169

[5] Monachese M, Burton JP, Reid G. Bioremediation and tolerance of humans to heavy metals through microbial processes: A potential role for probiotics? Applied and Environmental Microbiology. 2012;**78**:6397-6404

[6] Verma R, Dwivedi P. Heavy metal water pollution—A case study. Recent Research in Science and Technology. 2013;**5**:98-99

[7] Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy metal toxicity and the environment. In: Molecular, Clinical and Environmental Toxicology. Vol. 101. Basel: Springer; 2012. p. 133-164

[8] Alluri HK, Ronda SR, Settalluri VS, Bondili JS, Suryanarayana V, Venkateshwar P. Biosorption: An eco-friendly alternative for heavy metal removal. African Journal of Biotechnology. 2007;**6**:2924-2931

[9] Wuana RA, Okieimen FE. Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology. 2011;**2011**:1-20

[10] Joshi NC. Heavy metals, conventional methods for heavy metal removal, biosorption and the development of low cost adsorbent. European Journal of Pharmacy and Medical Research. 2017;**4**:388-393

[11] Lakherwal D. Adsorption of heavy metals: A review. International Journal of Environmental Research and Development. 2014;**4**:41-48

[12] Gunatilake S. Methods of removing heavy metals from industrial wastewater. Journal of Multidisciplinary Engineering Science Studies. 2015;**1**:12-18

[13] Barakat M. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry. 2011;**4**:361-377

[14] Azimi A, Azari A, Rezakazemi M, Ansarpour M. Removal of heavy metals from industrial wastewaters: A review. Chemical and Biochemical Engineering Reviews. 2016;**4**:37-59

[15] Qiu Y-R, Mao L-J. Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid. Desalination. 2013;**329**:78-85

[16] Brady D, Rose P, Duncan J. The use of hollow fiber cross-flow microfiltration in bioaccumulation and continuous removal of heavy metals from solution by saccharomyces cerevisiae. Biotechnology and Bioengineering. 1994;**44**:1362-1366

[17] Al-Rashdi B, Johnson D, Hilal N. Removal of heavy metal ions by nanofiltration. Desalination. 2013;**315**:2-17

[18] Bakalár T, Búgel M, Gajdošová L. Heavy metal removal using reverse osmosis. Acta Montanistica Slovaca. 2009;**14**:250

[19] Choi SY, Keun-Young P, Hee JK, Kweon JH. Removal of heavy metal and nitrate nitrogen in polluted groundwater by electrodialysis process. Journal of Water Resource and Hydraulic Engineering. 2015;**4**:412

[20] Shyni LS, Jagadish K, Srikantaswamy S, Abhilash M. Photocatalytic degradation and removal of heavy metals in pharmaceutical waste by selenium doped ZnO nano composite semiconductor. Journal for Research. 2016;**2**:47-54

[21] Johnson PD, Girinathannair P, Ohlinger KN, Ritchie S, Teuber L, Kirby J. Enhanced removal of heavy metals in primary treatment using coagulation and flocculation. Water Environment Research. 2008;**80**:472-479

[22] Un UT, Ocal SE. Removal of heavy metals (Cd, Cu, Ni) by electrocoagulation. International Journal of Environmental Science and Development. 2015;**6**:425

[23] Merzouk B, Gourich B, Sekki A, Madani K, Chibane M. Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique: A case study. Journal of Hazardous Materials. 2009;**164**:215-222

[24] Addi Y, Duverneuil P, Khouider A. Electrodeposition of heavy metals (Cu; Ni; Zn and Cd) from industrial effluents. ECS Transactions. 2009;**19**:63-67

[25] Mrvčić J, Stanzer D, Šolić E, Stehlik-Tomas V. Interaction of lactic acid bacteria with metal ions: Opportunities for improving food safety and quality. World Journal of Microbiology and Biotechnology. 2012;**28**:2771-2782

[26] Chojnacka K. Biosorption and Bioaccumulation in Practice. UK: Nova Science Publishers; 2009. p. 137

[27] Chojnacka K. Biosorption and bioaccumulation–the prospects for practical applications. Environment International. 2010;**36**:299-307

[28] Deng X, Wilson D. Bioaccumulation of mercury from wastewater by genetically engineered *Escherichia coli*. Applied Microbiology and Biotechnology. 2001;**56**:276-279

[29] de Silóniz Ma-I, Balsalobre L, Alba C, Valderrama Ma-J, Peinado JM. Feasibility of copper uptake by the yeast *Pichia guilliermondii* isolated from sewage sludge. Research in Microbiology. 2002;**153**:173-180

[30] Koçberber N, Dönmez G. Chromium (VI) bioaccumulation capacities of adapted mixed cultures isolated from industrial saline wastewaters. Bioresource Technology. 2007;**98**:2178-2183

[31] Yilmazer P, Saracoglu N. Bioaccumulation and biosorption of copper (II) and chromium (III) from aqueous solutions by *Pichia stipitis* yeast. Journal of Chemical Technology and Biotechnology. 2009;**84**:604-610

[32] Dursun A, Uslu G, Cuci Y, Aksu Z. Bioaccumulation of copper (II), lead (II) and chromium (VI) by growing *Aspergillus niger*. Process Biochemistry. 2003;**38**:1647-1651

[33] Iram S, Shabbir R, Zafar H, Javaid M. Biosorption and bioaccumulation of copper and lead by heavy metal-resistant fungal isolates. Arabian Journal for Science and Engineering. 2015;**40**:1867-1873

[34] Srinath T, Verma T, Ramteke P, Garg S. Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere. 2002;**48**:427-435

[35] Ksheminska H, Fedorovych D, Babyak L, Yanovych D, Kaszycki P, Koloczek H. Chromium (III) and (VI) tolerance and bioaccumulation in yeast: A survey of cellular chromium content in selected strains of representative genera. Process Biochemistry. 2005;**40**:1565-1572

[36] Martín-González A, Díaz S, Borniquel S, Gallego A, Gutiérrez JC. Cytotoxicity and bioaccumulation of heavy metals by ciliated protozoa isolated from urban wastewater treatment plants. Research in Microbiology. 2006;**157**:108-118

[37] Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. Water Research. 2003;**37**:4311-4330

[38] Park D, Yun Y-S, Park JM. The past, present, and future trends of biosorption. Biotechnology and Bioprocess Engineering. 2010;**15**:86-102

[39] Tsezos M, Remoundaki E, Hatzikioseyian A. Biosorption-principles and applications for metal immobilization from waste-water streams. In: Proceedings of EU-Asia Workshop on Clean Production and Nanotechnologies; Seoul; 2006. pp. 23-33

[40] Wu F, Sun F, Wu S, Yan Y, Xing B. Removal of antimony (III) from aqueous solution by freshwater *Cyanobacteria microcystis* biomass. Chemical Engineering Journal. 2012;**183**:172-179

[41] Chakravarty R, Banerjee PC. Mechanism of cadmium binding on the cell wall of an acidophilic bacterium. Bioresource Technology. 2012;**108**:176-183

[42] Ramrakhiani L, Majumder R, Khowala S. Removal of hexavalent chromium by heat inactivated fungal biomass of *Termitomyces clypeatus*: Surface characterization and mechanism of biosorption. Chemical Engineering Journal. 2011;**171**:1060-1068

[43] Hu J-L, He X-W, Wang C-R, Li J-W, Zhang C-H. Cadmium adsorption characteristic of alkali modified sewage sludge. Bioresource Technology. 2012;**121**:25-30

[44] Ding Y, Jing D, Gong H, Zhou L, Yang X. Biosorption of aquatic cadmium (II) by unmodified rice straw. Bioresource Technology. 2012;**114**:20-25

[45] Witek-Krowiak A, Reddy DHK. Removal of microelemental Cr (III) and Cu (II) by using soybean meal waste–unusual isotherms and insights of binding mechanism. Bioresource Technology. 2013;**127**:350-357

[46] Chojnacka K, Chojnacki A, Gorecka H. Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue–green algae *Spirulina* sp.: Kinetics, equilibrium and the mechanism of the process. Chemosphere. 2005;**59**:75-84

[47] Liu C, Ngo HH, Guo W. Watermelon rind: Agro-waste or superior biosorbent? Applied Biochemistry and Biotechnology. 2012;**167**:1699-1715

[48] Mohamad OA, Hao X, Xie P, Hatab S, Lin Y, Wei G. Biosorption of copper (II) from aqueous solution using non-living *Mesorhizobium amorphae* strain ccnwgs0123. Microbes and Environments. 2012;**27**:234-241

[49] García-Mendieta A, Olguín MT, Solache-Ríos M. Biosorption properties of green tomato husk (*Physalis philadelphica lam*) for iron, manganese and iron–manganese from aqueous systems. Desalination. 2012;**284**:167-174

[50] Park D, Yun Y-S, Jo JH, Park JM. Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*. Water Research. 2005;**39**:533-540

[51] Park D, Yun Y-S, Park JM. Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp. Chemosphere. 2005;**60**:1356-1364

[52] Park D, Yun Y-S, Park JM. Use of dead fungal biomass for the detoxification of hexavalent chromium: Screening and kinetics. Process Biochemistry. 2005;**40**:2559-2565

[53] Michalak I, Chojnacka K. Interactions of metal cations with anionic groups on the cell wall of the macroalga *Vaucheria* sp. Engineering in Life Sciences. 2010;**10**:209-217

[54] Pistorius A, DeGrip WJ, Egorova-Zachernyuk TA. Monitoring of biomass composition from microbiological sources by means of FT-IR spectroscopy. Biotechnology and Bioengineering. 2009;**103**:123-129

[55] Michalak I, Chojnacka K, Witek-Krowiak A. State of the art for the biosorption process—A review. Applied Biochemistry and Biotechnology. 2013;**170**:1389-1416

[56] Macek T, Mackova M. Potential of biosorption technology. In: Microbial Biosorption of Metals. Netherlands: Springer; 2011. p. 7-17

[57] De Gisi S, Lofrano G, Grassi M, Notarnicola M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustainable Materials and Technologies. 2016;**9**:10-40

[58] Federici F, Fava F, Kalogerakis N, Mantzavinos D. Valorisation of agro-industrial by-products, effluents and waste: Concept, opportunities and the case of olive mill wastewaters. Journal of Chemical Technology and Biotechnology. 2009;**84**:895-900

[59] Malkoc E, Nuhoglu Y. Potential of tea factory waste for chromium (VI) removal from aqueous solutions: thermodynamic and kinetic studies. Separation and Purification Technology. 2007;**54**:291-298

[60] Kumar A, Sahu O. Sugar industry waste as removal of toxic metals from waste water. World Journal of Chemical Education. 2013;**1**:17-20

[61] Rashed M. Fruit stones from industrial waste for the removal of lead ions from polluted water. Environmental Monitoring and Assessment. 2006;**119**:31-41

[62] Yeddou-Mezenner N. Kinetics and mechanism of dye biosorption onto an untreated antibiotic waste. Desalination. 2010;**262**:251-259

[63] Suryan S, Ahluwalia S. Biosorption of heavy metals by paper mill waste from aqueous solution. International Journal of Environmental Sciences. 2012;**2**:1331

[64] Lee T, Park J-W, Lee J-H. Waste green sands as reactive media for the removal of zinc from water. Chemosphere. 2004;**56**:571-581

[65] Alinnor I. Adsorption of heavy metal ions from aqueous solution by fly ash. Fuel. 2007;**86**:853-857

[66] Hossain M, Ngo H, Guo W, Setiadi T. Adsorption and desorption of copper (II) ions onto garden grass. Bioresource Technology. 2012;**121**:386-395

[67] Demirbas A. Heavy metal adsorption onto agro-based waste materials: A review. Journal of Hazardous Materials. 2008;**157**:220-229

[68] Torab-Mostaedi M, Asadollahzadeh M, Hemmati A, Khosravi A. Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel. Journal of the Taiwan Institute of Chemical Engineers. 2013;**44**:295-302

[69] Munagapati VS, Yarramuthi V, Nadavala SK, Alla SR, Abburi K. Biosorption of Cu (II), Cd (II) and Pb (II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics. Chemical Engineering Journal. 2010;**157**:357-365

[70] Bansal M, Singh D, Garg V, Rose P. Use of agricultural waste for the removal of nickel ions from aqueous solutions: Equilibrium and kinetics studies. International Journal of Civil and Environmental Engineering. 2009;**418**:763-776

[71] Hossain M, Ngo H, Guo W, Nguyen T, Vigneswaran S. Performance of cabbage and cauliflower wastes for heavy metals removal. Desalination and Water Treatment. 2014; **52**:844-860

[72] Alomá I, Martín-Lara M, Rodríguez I, Blázquez G, Calero M. Removal of nickel (ii) ions from aqueous solutions by biosorption on sugarcane bagasse. Journal of the Taiwan Institute of Chemical Engineers. 2012;**43**:275-281

[73] Saeed A, Akhter MW, Iqbal M. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Separation and Purification Technology. 2005;**45**:25-31

[74] Pino G, de Mesquita LS, Torem M, Pinto G. Biosorption of heavy metals by powder of green coconut shell. Separation Science and Technology. 2006;**41**:3141-3153

[75] Basci N, Kocadagistan E, Kocadagistan B. Biosorption of copper (II) from aqueous solutions by wheat shell. Desalination. 2004;**164**:135-140

[76] Johnson P, Watson M, Brown J, Jefcoat I. Peanut hull pellets as a single use sorbent for the capture of Cu (II) from wastewater. Waste Management. 2002;**22**:471-480

[77] Pehlivan E, Altun T, Parlayıcı S. Utilization of barley straws as biosorbents for Cu^{2+} and Pb^{2+} ions. Journal of Hazardous Materials. 2009;**164**:982-986

[78] Naiya T, Bhattacharya A, Das S. Adsorption of Pb (II) by sawdust and neem bark from aqueous solutions. Environmental Progress & Sustainable Energy. 2008;**27**:313-328

[79] Gupta BS, Curran M, Hasan S, Ghosh T. Adsorption characteristics of Cu and Ni on Irish peat moss. Journal of Environmental Management. 2009;**90**:954-960

[80] Al-Ghouti MA, Li J, Salamh Y, Al-Laqtah N, Walker G, Ahmad MN. Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. Journal of Hazardous Materials. 2010;**176**:510-520

[81] Horsfall MJ, Spiff AI, Abia A. Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (*Manihot sculenta cranz*) waste biomass on the adsorption of Cu^{2+} and Cd^{2+} from aqueous solution. Bulletin of the Korean Chemical Society. 2004;**25**:969-976

[82] Hlihor RM, Bulgariu L, Sobariu DL, Diaconu M, Tavares T, Gavrilescu M. Recent advances in biosorption of heavy metals: Support tools for biosorption equilibrium, kine-tics and mechanism. Revue Roumaine de Chimie. 2014;**59**:527-538

[83] Rezaei H. Biosorption of chromium by using *Spirulina sp*. Arabian Journal of Chemistry. 2016;**9**:846-853

[84] Chen C, Wang J. Cation (K^+, Mg^{2+}, Na^+, Ca^{2+}) release in Zn (II) biosorption by *Saccharomyces cerevisiae*. Huan Jing Ke Xue. 2006;**27**:2261-2267

[85] Tapia J, Muñoz J, González F, Blázquez M, Ballester A. Mechanism of adsorption of ferric iron by extracellular polymeric substances (EPS) from a bacterium *Acidiphilium* sp. Water Science and Technology. 2011;**64**:1716-1722

[86] Majumdar SS, Das SK, Saha T, Panda GC, Bandyopadhyoy T, Guha AK. Adsorption behavior of copper ions on *Mucor rouxii* biomass through microscopic and FTIR analysis. Colloids and Surfaces. B, Biointerfaces. 2008;**63**:138-145

[87] Selatnia A, Boukazoula A, Kechid N, Bakhti M, Chergui A, Kerchich Y. Biosorption of lead (II) from aqueous solution by a bacterial dead *Streptomyces rimosus* biomass. Biochemical Engineering Journal. 2004;**19**:127-135

[88] Sarı A, Uluozlü ÖD, Tüzen M. Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solution by algae (*Maugeotia genuflexa*) biomass. Chemical Engineering Journal. 2011;**167**:155-161

[89] Luo J-M, Xiao X. Biosorption of cadmium (II) from aqueous solutions by industrial fungus *Rhizopus cohnii*. Transactions of Nonferrous Metals Society of China. 2010;**20**:1104-1111

[90] Gupta VK, Rastogi A, Nayak A. Biosorption of nickel onto treated alga (*Oedogonium hatei*): Application of isotherm and kinetic models. Journal of Colloid and Interface Science. 2010;**342**:533-539

[91] Ji Y, Gao H, Sun J, Cai F. Experimental probation on the binding kinetics and thermodynamics of Au (III) onto *Bacillus subtilis*. Chemical Engineering Journal. 2011;**172**:122-128

[92] Pahlavanzadeh H, Keshtkar A, Safdari J, Abadi Z. Biosorption of nickel (II) from aqueous solution by brown algae: Equilibrium, dynamic and thermodynamic studies. Journal of Hazardous Materials. 2010;**175**:304-310

[93] Romera E, González F, Ballester A, Blázquez M, Munoz J. Comparative study of biosorption of heavy metals using different types of algae. Bioresource Technology. 2007;**98**:3344-3353

[94] Mustapha MU, Halimoon N. Microorganisms and biosorption of heavy metals in the environment: A review paper. Journal of Microbial Biochemical Technology. 2015; **7**:253-256

[95] Lee Y-C, Chang S-P. The biosorption of heavy metals from aqueous solution by *Spirogyra* and *Cladophora* filamentous macroalgae. Bioresource Technology. 2011;**102**:5297-5304

[96] Da Kleinübing S, Da Silva E, Silva M, Guibal E. Equilibrium of Cu (II) and Ni (II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: Competitiveness and selectivity. Bioresource Technology. 2011;**102**:4610-4617

[97] Koutahzadeh N, Daneshvar E, Kousha M, Sohrabi M, Bhatnagar A. Biosorption of hexavalent chromium from aqueous solution by six brown macroalgae. Desalination and Water Treatment. 2013;**51**:6021-6030

[98] Lupea M, Bulgariu L, Macoveanu M. Biosorption of Cd (II) from aqueous solution on marine green algae biomass. Environmental Engineering & Management Journal (EEMJ). 2012;**11**:607-615

[99] Al-Homaidan AA, Al-Houri HJ, Al-Hazzani AA, Elgaaly G, Moubayed NM. Biosorption of copper ions from aqueous solutions by *Spirulina platensis* biomass. Arabian Journal of Chemistry. 2014;**7**:57-62

[100] Celekli A, Yavuzatmaca M, Bozkurt H. An eco-friendly process: Predictive modelling of copper adsorption from aqueous solution on *Spirulina platensis*. Journal of Hazardous Materials. 2010;**173**:123-129

[101] Murphy V, Hughes H, McLoughlin P. Comparative study of chromium biosorption by red, green and brown seaweed biomass. Chemosphere. 2008;**70**:1128-1134

[102] Lu W-B, Shi J-J, Wang C-H, Chang J-S. Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 possessing high heavy-metal resistance. Journal of Hazardous Materials. 2006;**134**:80-86

[103] Gupta V, Rastogi A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. Journal of Hazardous Materials. 2008;**152**:407-414

[104] Paknikar K, Pethkar A, Puranik P. Bioremediation of metalliferous wastes and products using inactivated microbial biomass. Indian Journal of Biotechnology. 2003;**2**:426-443

[105] Moat AG, Foster JW, Spector MP. Microbial Physiology. 4th ed. New York: John Wiley & Sons; 2003. p. 734

[106] Yilmaz M, Tay T, Kivanc M, Turk H. Removal of copper (II) ions from aqueous solution by a lactic acid bacterium. Brazilian Journal of Chemical Engineering. 2010;**27**:309-314

[107] Sabae S, Hazaa M, Hallim S, Awny N, Daboor S. Bioremediation of Zn, Cu and Fe using *Bacillus subtilis* d215 and *Pseudomonas putida biovar* ad 225. Bioscience Research. 2006;**3**:189-204

[108] Joo J-H, Hassan SH, Oh S-E. Comparative study of biosorption of Zn^{2+} by *Pseudomonas aeruginosa* and *Bacillus cereus*. International Biodeterioration and Biodegradation. 2010; **64**:734-741

[109] Çolak F, Atar N, Yazıcıoğlu D, Olgun A. Biosorption of lead from aqueous solutions by *Bacillus* strains possessing heavy-metal resistance. Chemical Engineering Journal. 2011;**173**:422-428

[110] Subbaiah MV, Vijaya Y, Reddy AS, Yuvaraja G, Krishnaiah A. Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu (II) onto *Trametes versicolor* biomass. Desalination. 2011;**276**:310-316

[111] Sofu A, Sayilgan E, Guney G. Experimental design for removal of Fe (II) and Zn (II) ions by different lactic acid bacteria biomasses. International Journal of Environmental Research. 2015;**9**:93-100

[112] Vijayaraghavan K, Yun Y-S. Bacterial biosorbents and biosorption. Biotechnology Advances. 2008;**26**:266-291

[113] Öztürk A. Removal of nickel from aqueous solution by the bacterium *Bacillus thuringiensis*. Journal of Hazardous Materials. 2007;**147**:518-523

[114] Rodríguez-Tirado V, Green-Ruiz C, Gómez-Gil B. Cu and Pb biosorption on *Bacillus thioparans* strain u3 in aqueous solution: Kinetic and equilibrium studies. Chemical Engineering Journal. 2012;**181**:352-359

[115] Quintelas C, Rocha Z, Silva B, Fonseca B, Figueiredo H, Tavares T. Removal of Cd (II), Cr (VI), Fe (III) and Ni (II) from aqueous solutions by an *E. Coli* biofilm supported on kaolin. Chemical Engineering Journal. 2009;**149**:319-324

[116] Green-Ruiz C, Rodriguez-Tirado V, Gomez-Gil B. Cadmium and zinc removal from aqueous solutions by *Bacillus jeotgali*: Ph, salinity and temperature effects. Bioresource Technology. 2008;**99**:3864-3870

[117] Hasan SH, Srivastava P. Batch and continuous biosorption of Cu^{2+} by immobilized biomass of *Arthrobacter* sp. Journal of Environmental Management. 2009;**90**:3313-3321

[118] Samarth DP, Chandekar CJ, Bhadekar R. Biosorption of heavy metals from aqueous solution using *Bacillus licheniformis*. International Journal of Pure and Applied Science and Technology. 2012;**10**:12-19

[119] Abd-Alla MH, Morsy FM, El-Enany A-WE, Ohyama T. Isolation and characterization of a heavy-metal-resistant isolate of *Rhizobium leguminosarum bv. Viciae* potentially applicable for biosorption of Cd^{2+} and Co^{2+}. International Biodeterioration and Biodegradation. 2012;**67**:48-55

[120] Mulligan C, Yong R, Gibbs B. Remediation alternative treatment option for heavy metal bearing wastewaters: A review. Bioresource Technology. 2001;**53**:195-206

[121] Javaid A, Bajwa R, Shafique U, Anwar J. Removal of heavy metals by adsorption on *Pleurotus ostreatus*. Biomass and Bioenergy. 2011;**35**:1675-1682

[122] Leitão AL. Potential of *Penicillium* species in the bioremediation field. International Journal of Environmental Research and Public Health. 2009;**6**:1393-1417

[123] Gaensly F, Picheth G, Brand D, Bonfim T. The uptake of different iron salts by the yeast *Saccharomyces cerevisiae*. Brazilian Journal of Microbiology. 2014;**45**:491-494

[124] Ponce de León C, Bayón MM, Paquin C, Caruso J. Selenium incorporation into *Saccharomyces cerevisiae* cells: A study of different incorporation methods. Journal of Applied Microbiology. 2002;**92**:602-610

[125] Shet AR, Patil LR, Hombalimath VS, Yaraguppi DA, Udapudi BB. Enrichment of *Saccharomyces cerevisiae* with zinc and their impact on cell growth. Biotechnology, Bioinformatics and Bioengineering. 2011;**1**:523-527

[126] Say R, Yilmaz N, Denizli A. Removal of heavy metal ions using the fungus *Penicillium canescens*. Adsorption Science and Technology. 2003;**21**:643-650

[127] Haijia S, Ying Z, Jia L, Tianwei T. Biosorption of Ni^{2+} by the surface molecular imprinting adsorbent. Process Biochemistry. 2006;**41**:1422-1426

[128] Dursun A, Uslu G, Tepe O, Cuci Y, Ekiz H. A comparative investigation on the bioaccumulation of heavy metal ions by growing *Rhizopus arrhizus* and *Aspergillus niger*. Biochemical Engineering Journal. 2003;**15**:87-92

[129] Say R, Yılmaz N, Denizli A. Biosorption of cadmium, lead, mercury, and arsenic ions by the fungus *Penicillium purpurogenum*. Separation Science and Technology. 2003; **38**:2039-2053

[130] Fan T, Liu Y, Feng B, Zeng G, Yang C, Zhou M, Zhou H, Tan Z, Wang X. Biosorption of cadmium (II), zinc (II) and lead (II) by *Penicillium simplicissimum*: Isotherms, kinetics and thermodynamics. Journal of Hazardous Materials. 2008;**160**:655-661

[131] Özer A, Özer D. Comparative study of the biosorption of Pb (II), Ni (II) and Cr (VI) ions onto *S. cerevisiae*: Determination of biosorption heats. Journal of Hazardous Materials. 2003;**100**:219-229

[132] Arıca MY, Bayramoğlu G. Cr (VI) biosorption from aqueous solutions using free and immobilized biomass of *Lentinus sajor*-caju: Preparation and kinetic characterization. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2005;**253**:203-211

[133] Arbanah M, Miradatul Najwa M, Ku Halim K. Utilization of *Pleurotus ostreatus* in the removal of Cr (VI) from chemical laboratory waste. International Refreed Journal of Engineering Science. 2013;**2**:29-39

[134] Gulati R, Saxena R, Gupta R. Fermentation waste of *Aspergillus terreus*: A potential copper biosorbent. World Journal of Microbiology and Biotechnology. 2002;**18**:397-401

[135] Çeribasi IH, Yetis U. Biosorption of Ni (II) and Pb (II) by *Phanerochaete chrysosporium* from a binary metal system–kinetics. Water SA. 2001;**27**:15-20

[136] Subbaiah MV, Yun YS. Biosorption of nickel (II) from aqueous solution by the fungal mat of *Trametes versicolor* (rainbow) biomass: Equilibrium, kinetics, and thermodynamic studies. Biotechnology and Bioprocess Engineering. 2013;**18**:280-288

[137] Gupta R, Saxena R, Mohapatra H, Ahuja P. Microbial variables for bioremediation of heavy metals from industrial effluents. In: Singh VP, Stapleton RD, editors. Progress in Industrial Microbiology, Vol. 36. Elsevier; 2002. P. 189-229

[138] Jianlong W. Biosorption of copper (ii) by chemically modified biomass of *Saccharomyces cerevisiae*. Process Biochemistry. 2002;**37**:847-850

[139] Narvekar S, Vaidya VK. Removal of chromium (VI) from aqueous solution by chemically modified biomass of *Aspergillus niger*. Journal of Industrial Pollution Control. 2008;**24**:153-159

[140] Göksungur Y, Üren S, Güvenç U. Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. Bioresource Technology. 2005;**96**:103-109

[141] Al-Gheethi A, Mohamed R, Noman E, Ismail N, Kadir OA. Removal of heavy metal ions from aqueous solutions using *Bacillus subtilis* biomass pre-treated by supercritical carbon dioxide. CLEAN–Soil, Air, Water. 2017;**45**:22

[142] Ilhan S, Cabuk A, Filik C, Caliskan F. Effect of pretreatment on biosorption of heavy metals by fungal biomass. Trakya University Journal of Science. 2004;**5**:11-17

[143] Yan G, Viraraghavan T. Effect of pretreatment on the bioadsorption of heavy metals on *Mucor rouxii*. Water SA-Pretoria. 2000;**26**:119-124

[144] Khowala LRS. Effect of pretreatment on hexavalent chromium biosorption and multi-metal biosorption efficiency of *Termitomyces clypeatus* biomass. International Journal of Integrative Sciences, Innovation and Technology. 2012;**1**:7-15

[145] Rao PR, Bhargavi C. Studies on biosorption of heavy metals using pretreated biomass of fungal species. International Journal of Chemistry and Chemical Engineering. 2013; **3**:171-180

[146] Çabuk A, Ilhan S, Filik C, ÇALIŞKAN F. Pb^{2+} biosorption by pretreated fungal biomass. Turkish Journal of Biology. 2005;**29**:23-28

[147] Tan T, Cheng P. Biosorption of metal ions with *Penicillium chrysogenum*. Applied Biochemistry and Biotechnology. 2003;**104**:119-128

[148] Parameswari E, Lakshmanan A, Thilagavathi T. Effect of pretreatment of blue green algal biomass on bioadsorption of chromium and nickel. Journal of Algal Biomass Utilisation. 2009;**1**:9-17

[149] Aksu Z. Application of biosorption for the removal of organic pollutants: A review. Process Biochemistry. 2005;**40**:997-1026

[150] HAO Z-L, LIU Y-M. Bioleaching of heavy metals from sewage sludge. Journal of Shijiazhuang Vocational Technology Institute. 2009;**2**:005

[151] Ahmady-Asbchin S, Bahrami AM. Nickel biosorption by immobilized biomass of *Bacillus* sp. from aqueous solution. Advances in Environmental Biology. 2011;**5**: 1656-1663

[152] Volesky B. Detoxification of metal-bearing effluents: Biosorption for the next century. Hydrometallurgy. 2001;**59**:203-216

[153] Bai RS, Abraham TE. Studies on chromium (VI) adsorption–desorption using immobilized fungal biomass. Bioresource Technology. 2003;**87**:17-26

[154] Aksu Z, Gönen F. Biosorption of phenol by immobilized activated sludge in a continuous packed bed: Prediction of breakthrough curves. Process Biochemistry. 2004;**39**:599-613

[155] Bayramoğlu G, Bektaş S, Arıca MY. Biosorption of heavy metal ions on immobilized white-rot fungus *Trametes versicolor*. Journal of Hazardous Materials. 2003;**101**:285-300

[156] Baytak S, Türker AR, Çevrimli BS. Application of silica gel 60 loaded with *Aspergillus niger* as a solid phase extractor for the separation/preconcentration of chromium (III), copper (II), zinc (II), and cadmium (II). Journal of Separation Science. 2005;**28**:2482-2488

[157] Akar T, Kaynak Z, Ulusoy S, Yuvaci D, Ozsari G, Akar ST. Enhanced biosorption of nickel (II) ions by silica-gel-immobilized waste biomass: Biosorption characteristics in batch and dynamic flow mode. Journal of Hazardous Materials. 2009;**163**:1134-1141

[158] Pakshirajan K, Swaminathan T. Continuous biosorption of Pb, Cu, and Cd by *Phanerochaete chrysosporium* in a packed column reactor. Soil and Sediment Contamination. 2006;**15**:187-197

[159] Won SW, Mao J, Sankar G, Lee H-C, Yun Y-S. Adsorptive characteristics of the polyurethane-immobilized *Corynebacterium glutamicum* biosorbent for removal of reactive yellow 2 from aqueous solution. Korean Journal of Chemical Engineering. 2016;**33**:945-951

[160] D'SOUZA S, Sar P, Kazy SK, Kubal B. Uranium sorption by *Pseudomonas* biomass immobilized in radiation polymerized polyacrylamide bio-beads. Journal of Environmental Science and Health, Part A. 2006;**41**:487-500

[161] Tsuruta T. Biosorption and recycling of gold using various microorganisms. The Journal of General and Applied Microbiology. 2004;**50**:221-228

[162] Paul S, Bera D, Chattopadhyay P, Ray L. Biosorption of Pb (II) by *Bacillus cereus* immobilized in calcium alginate gel. Journal of Hazardous Substance Research. 2006;**5**:1-13

[163] Arıca MY, Kacar Y, Genç Ö. Entrapment of white-rot fungus *Trametes versicolor* in Ca-alginate beads: Preparation and biosorption kinetic analysis for cadmium removal from an aqueous solution. Bioresource Technology. 2001;**80**:121-129

[164] Bag H, Türker AR, Tunceli A, Lale M. Determination of Fe (ii) and Fe (III) in water by flame atomic absorption spectrophotometry after their separation with *Aspergillus niger* immobilized on sepiolite. Analytical Sciences. 2001;**17**:901-904

[165] Tewari N, Vasudevan P, Guha B. Study on biosorption of Cr (VI) by *Mucor hiemalis*. Biochemical Engineering Journal. 2005;**23**:185-192

[166] Mungasavalli DP, Viraraghavan T, Jin Y-C. Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*: Batch and column studies. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2007;**301**:214-223

[167] Jayaraman M, Arumugam R. Biosorption of copper (II) by *Aspergillus flavus* (ed4). International Journal of Science Research. 2014;**3**:335-340

[168] Ogata F, Kangawa M, Iwata Y, Ueda A, Tanaka Y, Kawasaki N. A study on the adsorption of heavy metals by using raw wheat bran bioadsorbent in aqueous solution phase. Chemical & Pharmaceutical Bulletin. 2014;**62**:247-253

[169] Sarwa P, Verma SK. Recovery and recycling of Zn (II) from wastewater by *Scenedesmus* sp. Mcc 26 isolated from a heavy metal contaminated site. CLEAN–Soil, Air, Water. 2014;**42**:1298-1303

[170] Akpomie KG, Dawodu FA, Adebowale KO. Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential. Alexandria Engineering Journal. 2015;**54**:757-767

[171] Joshi J, Sahu O. Adsorption of heavy metals by biomass. Journal of Applied Environmental. Microbiology. 2014;**2**:23-27

[172] Feng N, Guo X, Liang S, Zhu Y, Liu J. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. Journal of Hazardous Materials. 2011;**185**:49-54

[173] Hlihor R, Diaconu M, Fertu D, Chelaru C, Sandu I, Tavares T. Bioremediation of Cr (VI) polluted wastewaters by sorption on heat inactivated *Saccharomyces cerevisiae* biomass. International Journal of Environmental Research. 2013;**7**:581-594

[174] Goyal N, Jain S, Banerjee U. Comparative studies on the microbial adsorption of heavy metals. Advances in Environmental Research. 2003;**7**:311-319

[175] Dang V, Doan H, Dang-Vu T, Lohi A. Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw. Bioresource Technology. 2009;**100**:211-219

[176] Naiya TK, Bhattacharya AK, Mandal S, Das SK. The sorption of lead (II) ions on rice husk ash. Journal of Hazardous Materials. 2009;**163**:1254-1264

[177] Rathinam A, Maharshi B, Janardhanan SK, Jonnalagadda RR, Nair BU. Biosorption of cadmium metal ion from simulated wastewaters using *Hypnea valentiae* biomass: A kinetic and thermodynamic study. Bioresource Technology. 2010;**101**:1466-1470

[178] SenthilKumar P, Ramalingam S, Sathyaselvabala V, Kirupha SD, Sivanesan S. Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. Desalination. 2011;**266**:63-71

[179] Kumar D, Gaur J. Metal biosorption by two cyanobacterial mats in relation to ph, biomass concentration, pretreatment and reuse. Bioresource Technology. 2011;**102**:2529-2535

[180] Abdel-Aty AM, Ammar NS, Ghafar HHA, Ali RK. Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena sphaerica* biomass. Journal of Advanced Research. 2013;**4**:367-374

[181] Venugopal V, Mohanty K. Biosorptive uptake of Cr (VI) from aqueous solutions by P*arthenium hysterophorus* weed: Equilibrium, kinetics and thermodynamic studies. Chemical Engineering Journal. 2011;**174**:151-158

[182] Abdel-Ghani N, Hegazy A, El-Chaghaby G. *Typha domingensis* leaf powder for decontamination of aluminium, iron, zinc and lead: Biosorption kinetics and equilibrium modeling. International Journal of Environmental Science and Technology. 2009;**6**:243-248

[183] Liu Y-G, Ting F, Zeng G-M, Xin L, Qing T, Fei Y, Ming Z, Xu W-h, Huang Y-e. Removal of cadmium and zinc ions from aqueous solution by living *Aspergillus niger*. Transactions of Nonferrous Metals Society of China. 2006;**16**:681-686

[184] Chong H, Chia P, Ahmad M. The adsorption of heavy metal by bornean oil palm shell and its potential application as constructed wetland media. Bioresource Technology. 2013;**130**:181-186

[185] Igwe J, Abia A. A bioseparation process for removing heavy metals from waste water using biosorbents. African Journal of Biotechnology. 2006;**5**:1167-1179

[186] Wierzba S. Biosorption of lead (II), zinc (II) and nickel (II) from industrial wastewater by *Stenotrophomonas maltophilia* and *Bacillus subtilis*. Polish Journal of Chemical Technology. 2015;**17**:79-87

[187] Şahin Y, Öztürk A. Biosorption of chromium (VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*. Process Biochemistry. 2005;**40**:1895-1901

[188] Andersson EL. Analysis of Various Bioreactor Configurations for Heavy Metal Removal Using the Fungus *Penicillium ochro-chloron* [Thesis]. Worcester: Worcester Polytechnic Institute; 1999. p. 96

[189] Chatterjee A, Schiewer S. Biosorption of cadmium (II) ions by citrus peels in a packed bed column: Effect of process parameters and comparison of different breakthrough curve models. CLEAN–Soil, Air, Water. 2011;**39**:874-881

[190] Djafer A, Moustefai SK, Idou A, Douani M. Batch and continuous packed column studies biosorption by yeast supported onto granular pozzolana. International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering. 2013; **7**:665-671

[191] Ilamathi R, Nirmala G, Muruganandam L. Heavy metals biosorption in liquid solid fluidized bed by immobilized consortia in alginate beads. International Journal of ChemTech Research. 2014;**6**:652-662

[192] Alok S, Immanuel G. Effect of different impellers and baffles on aerobic stirred tank fermenter using computational fluid dynamics. Journal of Bioprocessing & Biotechniques. 2014;**4**:1

[193] Lee C, Yang W. Heavy metal removal from aqueous solution in sequential fluidized-bed reactors. Environmental Technology. 2005;**26**:1345-1354

[194] Morales-Barrera L, Cristiani-Urbina E. Removal of hexavalent chromium by *Trichoderma viride* in an airlift bioreactor. Enzyme and Microbial Technology. 2006;**40**:107-113

[195] Jácome-Pilco CR, Cristiani-Urbina E, Flores-Cotera LB, Velasco-García R, Ponce-Noyola T, Cañizares-Villanueva RO. Continuous Cr (vi) removal by *Scenedesmus incrassatulus* in an airlift photobioreactor. Bioresource Technology. 2009;**100**:2388-2391

[196] Prakasham R, Merrie JS, Sheela R, Saswathi N, Ramakrishna S. Biosorption of chromium VI by free and immobilized *Rhizopus arrhizus*. Environmental Pollution. 1999; **104**:421-427

[197] Mukhopadhyay M, Noronha S, Suraishkumar G. Copper biosorption in a column of pretreated *Aspergillus niger* biomass. Chemical Engineering Journal. 2008;**144**:386-390

[198] Vijayaraghavan K, Jegan J, Palanivelu K, Velan M. Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column. Chemosphere. 2005; **60**:419-426

[199] Barros A, Prasad S, Leite VD, Souza AG. The process of biosorption of heavy metals in bioreactors loaded with sanitary sewage sludge. Brazilian Journal of Chemical Engineering. 2006;**23**:153-162

[200] Chen J-Z, Tao X-C, Xu J, Zhang T, Liu Z-L. Biosorption of lead, cadmium and mercury by immobilized *Microcystis aeruginosa* in a column. Process Biochemistry. 2005; **40**:3675-3679

[201] Artola A, Martin MJ, Balaguer M, Rigola M. Pilot plant biosorption in an integrated contact–settling system: Application to Cu (II) removal by anaerobically digested sludge. Journal of Chemical Technology and Biotechnology. 2001;**76**:1141-1146

[202] Zouboulis AI, Lazaridis NK, Matis KA. Removal of toxic metal ions from aqueous systems by biosorptive flotation. Journal of Chemical Technology and Biotechnology. 2002;**77**:958-964

[203] Tigini V, Prigione V, Anastasi A, Vaglio M, Varese G. In scale-up of biosorption process for the textile wastewaters treatment using a selected fungal biomass. In: 22nd IFATCC International Congress, AICTC; 2010. p. A09

[204] Bae W, Mehra RK, Mulchandani A, Chen W. Genetic engineering of *Escherichia coli* for enhanced uptake and bioaccumulation of mercury. Applied and Environmental Microbiology. 2001;**67**:5335-5338

[205] Sayler GS, Ripp S. Field applications of genetically engineered microorganisms for bioremediation processes. Current Opinion in Biotechnology. 2000;**11**:286-289

[206] Zhao X, Zhou M, Li Q, Lu Y, He N, Sun D, Deng X. Simultaneous mercury bioaccumulation and cell propagation by genetically engineered *Escherichia coli*. Process Biochemistry. 2005;**40**:1611-1616

[207] Kostal J, Yang R, Wu CH, Mulchandani A, Chen W. Enhanced arsenic accumulation in engineered bacterial cells expressing arsr. Applied and Environmental Microbiology. 2004; **70**:4582-4587

[208] Krishnaswamy R, Wilson DB. Construction and characterization of an *Escherichia coli* strain genetically engineered for Ni (II) bioaccumulation. Applied and Environmental Microbiology. 2000;**66**:5383-5386

[209] Srivastava N, Jha M, Mall I, Singh D. Application of genetic engineering for chromium removal from industrial wastewater. International Journal of Chemical and Biological Engineering. 2010;**4**:633-638

[210] Deng X, Jia P. Construction and characterization of a photosynthetic bacterium genetically engineered for Hg^{2+} uptake. Bioresource Technology. 2011;**102**:3083-3088

[211] Singha B, Das SK. Adsorptive removal of Cu (II) from aqueous solution and industrial effluent using natural/agricultural wastes. Colloids and Surfaces. B, Biointerfaces. 2013;**107**:97-106

[212] Ibrahim WM. Biosorption of heavy metal ions from aqueous solution by red macroalgae. Journal of Hazardous Materials. 2011;**192**:1827-1835

[213] Ullah I, Nadeem R, Iqbal M, Manzoor Q. Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass. Ecological Engineering. 2013;**60**:99-107

[214] Vijayaraghavan K, Teo TT, Balasubramanian R, Joshi UM. Application of sargassum biomass to remove heavy metal ions from synthetic multi-metal solutions and urban storm water runoff. Journal of Hazardous Materials. 2009;**164**:1019-1023

[215] Rao RAK, Ikram S. Sorption studies of Cu (II) on gooseberry fruit (*Emblica officinalis*) and its removal from electroplating wastewater. Desalination. 2011;**277**:390-398

[216] Ay ÇÖ, Özcan AS, Erdoğan Y, Özcan A. Characterization of *Punica granatum* l. peels and quantitatively determination of its biosorption behavior towards lead (II) ions and acid blue 40. Colloids and Surfaces. B, Biointerfaces. 2012;**100**:197-204

[217] Bairagi H, Khan MMR, Ray L, Guha AK. Adsorption profile of lead on *Aspergillus versicolor*: A mechanistic probing. Journal of Hazardous Materials. 2011;**186**:756-764

[218] Singh A, Kumar D, Gaur J. Continuous metal removal from solution and industrial effluents using *Spirogyra* biomass-packed column reactor. Water Research. 2012;**46**:779-788

[219] Vinodhini V, Das N. Relevant approach to assess the performance of sawdust as adsorbent of chromium (VI) ions from aqueous solutions. International Journal of Environmental Science and Technology. 2010;**7**:85-92

[220] Volesky B, Naja G. Biosorption: Application strategies. In: 16th International Biohydrometallurgy Symposium; 2005. pp. 25-29

[221] Barkley NP. Extraction of mercury from groundwater using immobilized algae. Journal of the Air & Waste Management Association. 1991;**41**:1387-1393

[222] Bates E, Herrmann J, Sanning D. The us environmental protection agency's site emerging technology program. JAPCA. 1989;**39**:927-935

[223] Jeffers TH, Bennett PG, Corwin RR. Biosorption of metal contaminants using immobilized biomass field studies. US Bureau of Mines, Report of investigations. 1993; **9461**:1-10

[224] Kuyucak N, St-Germain P. Passive Treatment Methods for Acid Mine Drainage. In: Hager JP, editor. EPD Congress 1993. Warrendale: TMS publisher; 1993. p. 319-331

[225] Kuyucak N, St-Germain P. In possible options for in-situ treatment of acid mine drainage seepages. In: International Land Reclamation and Mine Drainage Conference and 3rd International Conference on Abatement of Acid Drainage; 1994. pp. 26-29

[226] Tsezos M, Noh S, Baird M. A batch reactor mass transfer kinetic model for immobilized biomass biosorption. Biotechnology and Bioengineering. 1988;**32**:545-553

Chapter 5

Microbial-Based Bioremediation of Selenium and Tellurium Compounds

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Abstract

The chalcogens selenium (Se) and tellurium (Te) are rare earth elements, which are mainly present in the environment as toxic oxyanions, due to the anthropogenic activities. Thus, the increased presence of these chalcogen-species in the environment and the contamination of wastewaters nearby processing facilities led to the necessity in developing remediation strategies aimed to detoxify waters, soils and sediments. Among the different decontamination approaches, those based on the ability of microorganisms to bioaccumulate, biomethylate or bioconvert Se- and/or Te-oxyanions are considered the leading strategy for achieving a safe and eco-friendly bioremediation of polluted sites. Recently, several technologies based on the use of bacterial pure cultures, bacterial biofilms or microbial consortia grown in reactors with different configurations have been explored for Se- and Te-decontamination purposes. Further, the majority of microorganisms able to process chalcogen-oxyanions have been described to generate valuable Se- and/or Te-nanomaterials as end-products of their bioconversion, whose potential applications in biomedicine, optoelectronics and environmental engineering are still under investigation. Here, the occurrence, the use and the toxicity of Se- and Te-compounds will be briefly overviewed, while the microbial mechanisms of chalcogen-oxyanions bioprocessing, as well as the microbial-based strategies used for bioremediation approaches will be extensively described.

Keywords: selenium, tellurium, bioremediation, microbial consortia, biological reactors

1. Introduction

The chalcogens tellurium (Te) and selenium (Se) are naturally occurring rare elements of the Earth crust belonging to the group 16 of the periodic table that are defined as metalloids, due to their intermediate chemical–physical properties between metal and non-metals [1]. Te estimated average amount in the environment is around 0.027 ppm [2], while Se is unevenly distributed on the Earth's surface with a concentration ranging from 0.01 to 1200 ppm [3, 4]. These elements can be found in natural rocks and ores, soils, sediments or in association with rare minerals (e.g., calaverite $AuTe_2$, sylvanite $AgAuTe_4$, crooksite CuTlSe, calusthalite PbSe) [4–6]. Moreover, Se is an essential micronutrient for living systems, being part of the structure of several important enzymes, (i.e., glutathione peroxidases and thioredoxin reductases), as the 21st amino acid seleno-cysteine, in at least 25 human selenoproteins [7], while, to date, any biological function has been ascribed to Te [8]. Both these chalcogens exist in four different valence states in the environment (i.e., +VI, +IV, 0 and –II), and among them the oxyanion forms of Selenate (SeO_4^{2-}), Tellurate (TeO_4^{2-}), Selenite (SeO_3^{2-}) and Tellurite (TeO_3^{2-}) are the most abundant in soils and waters [9, 10].

The wide spread use of Se- and Te-compounds by anthropogenic activities related to oil refining, phosphate and metal ore mining, electronics and industrial glasses, have led to an increase in the presence of these chemicals in the environment [6, 11]. In this regard, although Se is an essential micronutrient, it is toxic at concentrations higher than the human dietary requirement (25–30 $\mu g\ day^{-1}$) [10], while the toxicity exerted by Te is even more dramatic, negatively affecting both prokaryotes and eukaryotes at concentration as low as 1 $\mu g\ mL^{-1}$ [6]. Particularly, Se- and Te- oxyanions are recognized as harsh toxicants of public health and environmental concern due to their association with oxygen, which makes them highly bioavailable, enabling the mobilization of Se- and Te-compounds through water and soil [12, 13]. On the contrary, Se and Te organic forms (e.g., dimethyl selenide, trimethyl selenonium, selenomethionine, selenocysteine, Se-methilselenocysteine, dimethyl telluride), as well as their zero-valence states (Se^0 and Te^0) showed lower toxicity levels [2, 12, 14]. Considering the shared physical–chemical features of Se and Te, the suggested mechanism of toxicity exerted by the chalcogen-oxyanions is based on their interaction with glutathione molecules (GSHs) and related molecules, which are likely responsible for their reduction [8, 13, 15]. This bioconversion mechanism leads to the generation of reactive oxygen species (ROS), such as hydrogen peroxide (H_2O_2) [16] or superoxide ions (O^{2-}) [17], therefore causing cell death [18–20]. An additional target of TeO_3^{2-} is the impairment of the heme metabolism in *E. coli* K-12 cells, by which this oxyanion is responsible for the accumulation of the heme precursor protoporphyrin IX, causing iron depletion and, subsequently, cell death [21].

Despite the toxic effects of Se- and Te-oxyanions, in the last 20 years several microorganisms able to sequester, bioconvert or biomethylate these chalcogen-ions have been isolated from extreme environments, such as ocean hydrothermal vents and the highly alkaline water Monolake (California), to name a few [22]. Mainly anaerobic or facultative-anaerobic bacteria capable of growing phototrophycally or chemotrophycally under oxic and anoxic conditions have been described for their metabolic potential in bioconverting these species, while much less is known about strictly aerobic microorganisms [23]. In this regard, anaerobic microorganisms have been described for their use of chalcogen-oxyanions as terminal electron acceptors to sustain their growth [19, 22, 24–29]. Although the exact biochemical mechanisms behind Se and Te metabolism and bioconversion in these microorganisms have not been fully elucidated, there is a strong movement toward eco-friendly approaches for bioremediation of chalcogen-contaminated areas of interest. Moreover, among bacterial strains able to bioconvert Se- and Te-oxyanions in their less toxic and less bioavailable elemental form (i.e., Se^0 and Te^0), some of them were characterized for the generation of either intra- or extracellular precipitates and/or nanomaterials, for example, nanoparticles (NPs) and nanorods (NRs) [8, 19].

Here, we will overview the microbial-based strategies that, to date, are applied as tools for bioremediation purposes of chalcogens polluted environments, and briefly will be described the valuable role of bacteria for the recovery of metalloids in their zero-valence state in the form of nanomaterials.

1.1. Environmental toxicity of selenium and tellurium compounds

Annually, the total average amount of either Se or Te produced worldwide is 2500–2800 or 220 tons, respectively, with USA, Japan, Russia, Canada, Germany, Belgium and Sweden as main manufacturers [7, 30]. The accumulation of Se- or Te-compounds in the environment mainly relies on their anthropogenic use in several application fields, causing therefore their emission in the atmosphere [31, 32]. Se-accumulation derives from metallurgic industries, glass manufactures, pigments production, electronics and agriculture applications [33], while Te-containing compounds are used in copper refining [19], tarnishing metals [34], vulcanization of rubber [8], production of color glass or ceramics [19], photovoltaic cells and solar panels [8], as well as catalysis of several reactions [19]. Recently, the possibility to develop new Te-based nanomaterials such as fluorescent quantum dots (QDs) has been extensively investigated to create new high-tech probes in biological detection [8, 35], exasperating the already dramatic waste disposal circumstances.

Among the different Se-species present in the environment, the inorganic forms of Se^{2-}, SeO_4^{2-}, or SeO_3^{2-} are generally found in surface and ground waters as pollutants [36], while the organic and volatile ones (i.e., methylselenides, trimethylselenonium ions and selenoamino acids) occur in air and soils [37]. Similarly, Te-compounds result to be highly concentrated either in soils [38, 39] or waters [34] mainly in the form of TeO_4^{2-} and TeO_3^{2-}, being the latter highly soluble and toxic [35, 40, 41].

The presence of Se- and Te-compounds in water reservoirs has become a problem for both human health and ecological wildlife [42–45], which led to the development of several strategies aimed to protect aquatic and human life [46], as Se-poisoning events have occurred in the last few years worldwide, such as in the Kesterson Wildlife reservoir (California) [47], the uranium mine in Saskatchewan (Canada), and the Lake Sutton (USA) [48], causing physical deformities and mutations [46]. The major areas of the world affected by water contamination due to the presence of SeO_4^{2-} and SeO_3^{2-} are North America, Australia and New Zealand [23], while higher level of Te-oxyanions has been detected in the surface waters of Te-contaminated basins in Angola and Panama as compared to the deep ones, indicating a difference in behavior between Te and Se, which, as nutrient, is usually highly concentrated in the deep ocean [49]. Finally, Te-compounds emission in the atmosphere is now investigating, even if the implication related to the presence of Te-species in the air has not been established yet [19].

2. Bioremediation of chalcogen-contaminated environments

The exploitation of microorganisms for the decontamination of Se- and/or Te-polluted environments is based on the capability of several bacterial strains to sequester, bioconvert or biomethylate chalcogen-oxyanions [19]. Se- or Te-species sequestration is achieved by microorganisms through either their uptake in the bacterial cell or the interaction with charged surface biomolecules [19], while the bioconversion of these oxyanions in bacteria leads to their reduction to Se^0 and Te^0 in the form of metalloid precipitates [19]. Further, some microorganisms can biomethylate Se or Te-oxyanions, producing volatile methyl derivatives, which can react in the atmosphere with NO_3 radicals, ozone and atmospheric particles, increasing their residence times [19, 50].

2.1. Bioremediation of Se-polluted environments using bacterial pure cultures as planktonic cells

In the last 30 years, Se-oxyanions sequestration by microorganisms has been investigated as a potential strategy for the decontamination of Se-polluted environments. Indeed, several bacterial strains have been described for their ability to uptake SeO_4^{2-} and/or SeO_3^{2-} using several processes, such as the sulfate transporter in *E. coli* [51], the sulfate permease in *Salmonella typhimurium* [52], the sulfite uptake system in *Clostridium pasteurianum* [53], the polyol ABC transporter in *R. sphaeroides* [54]. Thus, once inside the bacterial cell, the sequestered Se-oxyanions are usually incorporated into Se-amino acids (i.e., seleno-cysteine and -methionine) to biosynthesize selenoproteins [55].

An alternative Se-bioremediation approach is based on the bacteria's ability to biomethylate Se-oxyanions, resulting in the production of Se-methyl derivates (i.e., dimethyl selenide, dimethyl selenyl sulfide, dimethyl diselenide), as in the case of *Aeromonas* sp. VS6, *Citrobacter freundii* KS8 and *P. fluorescens* K27 [56], *Clostridium collagenovorans*, *Desulfovibrio gigas* and *Desulfovibrio vulgaris* [57], *Enterobacter cloacae* SLS1a-1 [58], *R. sphaeroides* and *R. rubrum* S1 [59]. Se-oxyanions biomethylation is achieved in microorganisms through the Challenger mechanism [56], which consists of several reduction-methylation steps that change Se-redox state from either VI or IV to II [60].

Recently, the exploitation of microorganisms able to bioconvert Se-oxyanions to Se^0 has emer ged as a cost-effective *green* alternative strategy for the decontamination of Se-polluted environments, with a particular focus on surface waters and wastewaters. To date, Se-bioremediation approaches exploit bacterial strains capable of reducing SeO_4^{2-} and SeO_3^{2-} [23] either to conserve energy [61–63] or to detoxify their environmental niches [23]. Since Se-oxyanions bio-reduction under anoxic conditions is more characterized as compared to the aerobic mode, mainly anaerobic bacterial strains have been used for Se-decontamination purposes [23]. However, studies evaluating either SeO_4^{2-} or SeO_3^{2-} bioconversion by aerobic or microaerophilic microorganisms have also been conducted [61, 64–67], highlighting some disadvantages of these experimental conditions: a competition between the dissolved oxygen and the Se-oxyanion as terminal electron acceptor [68, 69], and the additional energetic cost to aerate a bioreactor [23].

Regardless, aerobic bacterial strains have been explored as pure cultures at laboratory scale for Se-bioremediation purposes, yet little work about the use of these microorganisms for large-scale applications have been conducted [23].

Among the microorganisms described for their tolerance toward Se-oxyanions, bacterial strains belonging to *Pseudomonas, Desulfovibrio, Thauera, Enterobacter, Wolinella* and *Bacillus* genera have been characterized for their capability to bioconvert SeO_4^{2-} to SeO_3^{2-} mainly under anoxic growth conditions [61, 70, 71]. Moreover, several anaerobic microorganisms have been characterized for their use of SeO_4^{2-} as terminal electron acceptor to support their growth [26, 70–73], coupling the bioconversion of this Se-oxyanion to the oxidation of different carbon sources, such as aliphatic (pyruvate, lactate, acetate) as well as aromatic compounds (i.e., benzoate, 3-hydroxybenzoate, 4-hydroxybenzoate) [61, 74, 75]. Nevertheless, facultative anaerobes, such as *Pseudomonas stutzeri,* showed their proficiency of bioreducing SeO_4^{2-} solely for detoxification purposes [70].

Unlike SeO_4^{2-}, both aerobic and anaerobic microorganisms can bioconvert the highly soluble and reactive SeO_3^{2-} [76] into Se^0 through either detoxification strategies or anaerobic respiration [77–79]. SeO_3^{2-} detoxification occurs through several mechanisms based on Painter-type reactions [17, 80–82], where glutaredoxin/thioredoxin reductase systems [19, 83] and siderophores mediate the oxyanion reduction [19, 65]. SeO_3^{2-} detoxification is mostly achieved by thiol molecules present in the cytoplasm of bacterial cells, such as GSHs, mycothiols (MSHs), and glutaredoxins [17, 84]. Moreover, GSHs can be exported into the periplasm of Gram-negative bacteria, leading to the bioreduction of SeO_3^{2-} in the periplasm or at their cell membrane [85]. Secondary SeO_3^{2-}-detoxification strategies exploited by microorganisms involved the interaction between SeO_3^{2-} and reactive biogenic sulfide, [86, 87], as well as the exploitation of iron siderophores [19, 88]. On the other hand, SeO_3^{2-} bioconversion during anaerobic respiration is mostly mediated by the presence of terminal nitrite, sulfite or fumarate reductases [19, 24, 61, 66, 67, 72, 89, 90], as described for *T. selenatis* AX, *Rhizobium sullae* HCNT1 and *C. pasteurianum,* to name a few [91–93]. Further, *Geobacter sulfurreducens* [94], *Shewanella oneidensis* MR-1 [90] and *Veillonella atypica* [94] showed high proficiency in bioreducing SeO_3^{2-} to Se^0 through dissimilatory reduction in anoxic conditions, while among the bacterial strains able to anaerobically bioconvert SeO_4^{2-} into SeO_3^{2-}, a high yield of Se^0 production by further reducing SeO_3^{2-} has been observed for *Bacillus beveridgei* [22], *D. indicum* [75], *Desulfovibrio desulfuricans* [95], *E. cloacae* SLD1a-1 [96] and *Sulfospirillum barnesii* SES-3 [25, 96]. Nevertheless, fewer bacterial species (i.e., *Bacillus selenitireducens* and *Aquificales* sp.) have been described for their ability to use SeO_3^{2-} as terminal electron acceptor as compared to those using SeO_4^{2-} [26, 27].

2.2. Bioremediation of Te-polluted environments using bacterial pure cultures as planktonic cells

Although Te does not have an essential biological role for living organisms [8], bacterial cells are able to uptake Te-oxyanions and to biomethylate and/or bioconvert them either as a decontamination strategy or during the anaerobic respiration [8, 19]. Particularly, TeO_3^{2-} uptake within bacterial cells has been ascribed to the phosphate transporter in *E. coli* [97], *Lactococcus lactis* [98] and *R. capsulatus* [99, 100], considering that this Te-species is a strong competitive inhibitor of the phosphate group [19]. However, other carriers can be used to assist TeO_3^{2-} uptake in microorganisms, such as the ActP monocarboxylate transporter of *R. capsulatus* [101], as well as an ATP-dependent efflux pump responsible for the arsenite/arsenate/antimonite resistance in *E. coli* [102]. Since Te shares several chemical properties with Se, microorganisms tolerant and/or resistant toward Te-oxyanions process them exploiting similar mechanisms to those described above for Se-species. In this regard, the biomethylation of Te-oxyanions to produce dimethyl telluride and dimethyl ditelluride [56] has been observed in several bacteria able to biomethylate Se-oxyanions as well, such as *R. rubrum* G9, *R. capsulatus* [59], *P. fluorescens* K27 [103] and *D. gigas* [57]. Moreover, *P. aeruginosa* ML4262 [104], *G. stearothermophilus* V [105] and *Mycobacterium tuberculosis* [106] showed their capability of biomethylating only Te-oxyanions.

Despite of TeO_3^{2-} presence in lower amount in the environment compared to TeO_4^{2-} [39], tellurite showed toxicity 10 times higher than tellurate [40, 41], leading the experimental research to focus on the study of TeO_3^{2-}-tolerant/resistant microorganisms as ideal candidate for bioremediation purposes. Nevertheless, *B. beveridgei* [22], *B. selenitireducens*, *S. barnesii* [29] and *Shewanella frigidimarina* ER-Te-48 [28, 107] showed their ability under anaerobic growth conditions to use both TeO_4^{2-} and TeO_3^{2-} oxyanions as terminal electron acceptors in the respiratory chain to sustain their growth [8]. To date, the proposed mechanisms of Te-oxyanions bioconversion in microorganisms are similar to those described for Se-species [13, 56, 88, 104, 108]. Further, TeO_3^{2-} processing in microorganisms have been ascribed to enzymatic reductions by periplasmic or cytoplasmic oxidoreductases [107, 109], such as nitrate reductases [109, 110], catalases [111] and thiol:disulfide oxidoreductase [112]. However, the function of all these enzymes for bioconverting Te-oxyanions appears to be not specific, leading to a low resistance level toward Te-species in these microorganisms. To date, only one specific TeO_3^{2-} reductase has been identified as responsible for the anaerobic respiration of this Te-oxyanion in *Bacillus* sp. GT-83 [113].

2.3. Bioremediation of chalcogen-polluted environments based on bacterial biofilms

The majority of the investigations regarding the bioremediation of Se- and Te-contaminated environments have been focused on the exploitation of bacterial species grown as free planktonic cells [8]. However, in natural settings microorganisms are most often found in close association with surfaces and interfaces as complex communities, which are indicated as biofilms [114–116]. In bacterial biofilms, the cells are embedded and protected from the surrounding environments by the presence of a matrix defined as Extracellular Polymeric Substance, containing a high amount of water, polysaccharides, proteins, extracellular-DNA (e-DNA) and lipids [117, 118]. The communal life of bacterial cells in the form of biofilm offers them several advantages [114, 117, 119], resulting in their innate ability to populate a vast array of environments [119], including those contaminated by chalcogen-oxyanions. Thus, peculiar features of bacterial biofilms (i.e., quorum sensing signaling process, different cellular physiology, presence of the EPS and colony morphology variants) [120–124] confer them tolerance and/or resistance toward either Se- or Te-oxyanions without having specific Se- and Te- genetic resistant determinants [19]. In this regard, sulfate-reducing bacteria (SRB) within a biofilm produce sulfide (S_2), which can abiotically bioconvert SeO_4^{2-} and/or SeO_3^{2-}, leading to the precipitation of Se^0 in the EPS [86]. Unlike SRB, *S. oneidensis* biofilms grown under anaerobic conditions can reduce TeO_3^{2-} and SeO_3^{2-}, accumulating Te^0 and Se^0 in both the cells and the EPS, respectively [125].

Since microorganisms grown as biofilms showed to play an important role in metal and chalcogen geochemistry [126], several biofilm-based reactors have been used to support the biosorption and the bioconversion of Se- and Te-oxyanions as detoxification strategy [8]. Indeed, *Burkholderia cepacia* biofilm grown on alumina surface [127], as well as a mixed species biofilm composed of *Dechloromonas* sp. and *Thauera* sp. [128] have been explored for Se-oxyanions bioremediation, resulting in the uptake and bioconversion of SeO_4^{2-} to Se^0 by the bacterial cells. Similarly, biofilms-containing denitrifying and sulfate-reducing microorganisms grown on a hallow-membrane biofilm reactor have been successfully used to remove SeO_4^{2-} from wastewater [129, 130], while the pre-grown biofilm of the SRB *Desulfomicrobium norvegicum* resulted able to abiotically reduce SeO_3^{2-} extracellularly through its production of S-Se granules within the EPS [86]. Further, biofilm formed by TeO_3^{2-}-resistant isolates of non-sulfur marine photosynthetic bacteria showed their proficiency in bioconverting this Te-oxyanion through intracellular reduction [131].

3. Microbial consortia for the treatment of selenium and tellurium contaminated wastewaters

3.1. Microbial consortia

In the environment, microorganisms usually thrive as communities composed by multiple species, generally referred as microbial consortia [132]. The employment of these microbial consortia in the treatment of environmental matrices contaminated with different inorganic or organic pollutants is currently a field of great interest for researchers [133]. There are significant advantages for the utilization of microbial consortia over pure cultures, such as the larger volumes of wastewaters treatable, the ability of microbial communities to adapt to diverse conditions, the presence of synergic interactions among members within the consortium and the possibility to work in non-aseptic conditions [23]. This last aspect is particularly significant, since it facilitates process control and it reduces both maintenance and operational costs [134].

In the following section, the different biological systems based on processes of biosorption and bioconversion of Se- and Te-oxyanions from contaminated matrices by using microbial consortia will be discussed.

3.2. Microbial consortia for Se-removal from contaminated environments

In recent years, the utilization of biological treatments based on the exploitation of microbial consortia has become the leading approach for the removal of toxic Se-species from environmental matrices, particularly from wastewaters (i.e., mine runoff, agricultural drainage, and flue gas desulfurization wastewater from plants) [23]. This decontamination strategy has several advantages over chemical–physical remediation technologies, being: the cost-effectiveness of microbial-based remediation approach, the avoidance in employing hazardous chemicals, and the possibility to recover Se^0 in a recyclable form either as precipitates or as nanostructures, which are technologically and economically more valuable [23, 135]. Since using microbial consortia under aerobic conditions has a lower efficiency of the whole system compared to the anaerobic processes, microbial communities used in these systems are mostly capable of anaerobically bioconverting Se-oxyanions to their elemental state [136]. In this regard, the dissimilatory reduction of SeO_4^{2-} under anaerobic conditions by a microbial community was firstly reported for sediment slurries by Oremland and coworkers [89], while an anaerobic co-culture isolated from agricultural drainage water in the San Joaquin Valley in California of a not-identified Gram-positive rod-shaped bacterium and a *Pseudomonas* sp. was capable of bioconverting both SeO_4^{2-} and SeO_3^{2-} to Se^0 [72]. Further, several anaerobic microbial consortia able to process Se-species have been found in biological wastewaters, such as activated, denitrifying, sulfate-reducing and methanogenic sludges [135]. Among them, methanogenic anaerobic granular sludges were the most effective to remove high SeO_4^{2-} concentrations using different electron donors (e.g., methanol, ethanol, acetate, lactate, glucose) [137].

Considering the large amount of Se-oxyanions present in laden wastewaters, different technologies and reactor configurations have been developed in order to treat these environmental samples (**Figure 1**), such as the ABMet® biofilter system, the electro-biochemical reactors (EBR), the biofilm reactors (BSeR), the membrane biofilm reactors (MBfR), the upflow anaerobic sludge blanket reactors (UASB) and the sequencing batch reactors (SBR) [23]. In the following sub-sections, examples of bioreactor configurations used to bioremediate Se-contaminated waters and their operating procedures are briefly discussed.

3.2.1. The ABMet® reactor system

The ABMet® reactor is both a biological and a filtration system, in which microbial consortia are grown on porous granular activated carbon (GAC) beds, creating anoxic conditions for optimal SeO_4^{2-} and SeO_3^{2-} reduction [23]. The system consists of biofilter tanks where Se-oxyanions are bioconverted to their elemental state, followed by the removal of Se^0 from the biofilter through a backwash cycle [138, 139]. This reactor uses a nutrient dosage tank generally containing a molasses-based solution, which acts as an electron donor sink for the microbial consortia, allowing the bioconversion of Se-oxyanions [139]. Thus, in this reactor configuration, the microbial communities require only a small amount of supplemented nutrient, decreasing the maintenance costs of the entire system [23]. Further, the GAC beds are used as substratum to sustain the bacterial growth, allowing the formation of a biofilm, which is morphologically more robust as compared to planktonic cells, resisting to the washing steps of the reactor [23]. Recently, Se-oxyanions bioconversion using anaerobic microbial communities inoculated in a ABMet® biofilter system has been observed within 16 h of empty bed contact time (EBCT) (i.e., the residence time of the water in the reactor) with a removal efficiency of 99.3% at the Duke Energy and Progress Energy in North Carolina [138]. Moreover, co-contaminants present in these wastewaters, such as NO_3^- and heavy metals, along with Se-oxyanions resulted to be removed with a high efficacy by the microbial consortium grown on the ABMet® biofilter system [23].

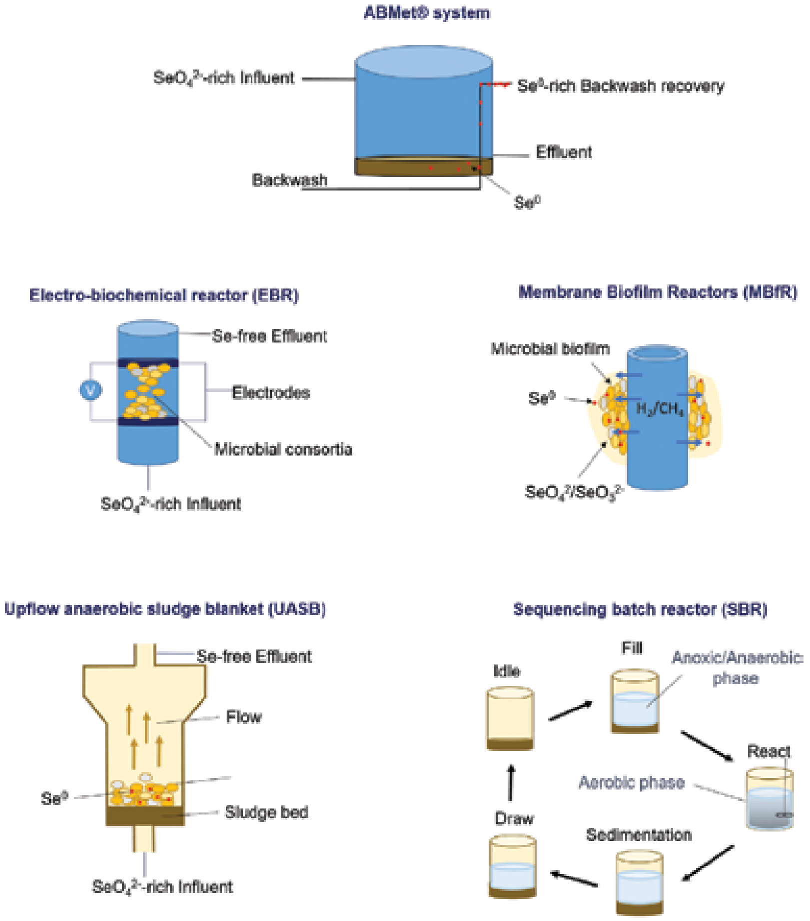

Figure 1. Schematic illustration of bioreactor configurations used for bioremediation of chalcogen-contaminated matrices.

3.2.2. The EBR system

Se-wastewater treatment is also achieved by using the electro-biochemical reactor (EBR), which utilizes the ability of certain microbial consortia to accept electrons from graphite electrodes reducing inorganic compounds (e.g., SeO_4^{2-} and SeO_3^{2-}) through direct interspecies electron transfer [140]. In this process, electrons obtained from the oxidation of electron donors (i.e., graphite electrodes) are transferred to the outer surface of a bacterial cell to reduce the extracellular terminal electron acceptor (i.e., Se-oxyanions) [140]. The efficiency of this system is strictly dependent on the retention times of the microbial consortia, with optimal performances between 6 to 18 h [141]. In this regard, on-site pilot scale study using an EBR system in British Columbia (Canada) for the decontamination of coal mine wastewaters from Se-oxyanions reported a decrease of their concentration from over 500–5 μg L^{-1} (below US discharge limits), showing its high effectiveness even with influent streams at temperature as low as 1°C [141].

3.2.3. The BSeR and MBfR systems

Reactors containing multispecies biofilms (BSeR) represent another promising approach for the treatment of Se-contaminated wastewaters. Indeed, microbial biofilms play a dominant role in the biogeochemical natural cycle of different inorganic compounds. In a recent study, a multispecies biofilm composed of strains (i.e., *Rhodococcus* sp., *Pseudomonas* sp., *Bacillus* sp. and *Arthrobacter* sp.) adapted to high concentration of SeO_3^{2-} has been investigated for its potential in converting these oxyanions to their elemental form (Se^0) [142]. Moreover, it has been highlighted the presence of specific biofilm regions where Se^0 was deposited as sub-micrometer-sized particles, associated with the microbial biomass [142]. In the BSeR methodology, bacterial biofilms are grown on granular activated carbon in anaerobic fixed-film reactors showing a high bioprocess proficiency toward both SeO_4^{2-} and SeO_3^{2-} [143], which resulted in the recovery of ca. 97% of Se^0 from agriculture drainage wastewater (Garfield Wetlands-Kessler Springs, Utah, USA) [144].

Another configuration of reactor based on microbial biofilms is the membrane biofilm reactor (MBfR) [129, 130, 145, 146]. MBfR in its standard configuration consists of a bundle of bubble-less gas transfer to a membrane delivering H_2 directly to the grown biofilm consisting of autohydrogenotrophic bacteria (e.g., *Cupriavidus metallidurans*) on the outer surface of the membrane [146], resulting in a higher efficiency of Se-oxyanions bioconversion as compared to other systems [143]. Although the membrane of the MBfR system can be made of either organic or inorganic materials, mostly hollow-fiber membranes are used at high gas pressures, providing a high surface-to-volume ratio [23]. Moreover, hydrophobic membranes are generally used in these systems, allowing to maintain the pores dry to achieve a fast diffusion of gas molecules [23]. In the MBfR system, the reduction of Se-oxyanions is coupled with the oxidation of H_2, acting as electron donor, which supports the growth of the autotrophic microbial consortia [129]. SeO_4^{2-} removal in this system has been improved to 94% by changing H_2 pressure, with Se^0 retained inside the microbial biofilm [129] in the form of crystalloid aggregates [147]. Similarly to the ABMet® system, the MBfR reactor resulted able to remove several oxidized toxic contaminants, such as chromium and arsenic, along with Se-oxyanions [23]. The microbial composition of a MBfR system exposed to different concentrations of SeO_4^{2-} was characterized by Ontiveros-Valencia and coworkers through 16S rRNA pyrosequencing [147]. Results showed that biofilms exposed to a high load of SeO_4^{2-} were composed principally by denitrifying bacteria belonging to the genera of *Denitratisoma* and *Dechloromonas*, which were previously reported as capable of reducing SeO_4^{2-} [147]. Recently, Lay and coworkers developed an MBfR system in which methane gas (CH_4) acted as electron donor instead of H_2, exploiting the microbial consortium capability to oxidize CH_4 coupled with SeO_4^{2-} reduction [148]. Particularly, the utilization of methane over H_2 has the advantages of lower cost and high availability from anaerobic digestion. Once again, the final product of the process are Se^0-nanospheres, accumulated in the microbial biomass [148]. A characterization of the microbial consortium by 16S rRNA sequencing revealed the presence of a specific methanotrophic genus (*Methylomonas*) that is able to simultaneously oxidize CH_4 and reduce SeO_4^{2-}, along with methanotrophic bacteria, which, upon methane utilization, are capable of generating organic metabolites suitable as electron donors for SeO_4^{2-}-reducing microorganisms present in the biofilm [148]. Although the MBfR system resulted to be a promising technology to efficiently remove Se-oxyanions from contaminated environments, its implementation at industrial scale has not been investigated yet, likely due to the high cost of electron donors needed to the working-system, which is still prohibitive for large-scale applications [143].

3.2.4. The UASB system

Sludge-based reactors have also been employed for the treatment of Se-contaminated wastewaters [68]. Indeed, the most implemented process for anaerobic treatment of industrial effluents is the upflow anaerobic sludge blanket (UASB) reactor, because of the accumulation of microbial biomass and suspended solid, and a dense sludge bed at the bottom of the reactor, in which Se-oxyanions bioconversion occurs [68]. In this regard, the natural aggregation of some bacteria forming flocculates or granules leads to a high retention of active anaerobic sludge even at great organic load rates [149]. Additionally, the wastewater is kept in good contact with the bacterial biomass through both the turbulence of the upflow influent flow and the biogas produced by the anaerobic microorganisms [68]. UASB reactors have been pilot-tested for Se-removal at the Adams Avenue Agricultural Drainage Research Center in San Joaquin Valley (California) [150]. The influent had a total Se content of 500 $\mu g\ L^{-1}$ and the removal efficiency ranged from 58 to 90% [150]. The efficiency of UASB reactors for the removal of Se-oxyanions was tested by Lenz and coworkers in a series of studies evaluating SeO_4^{2-} removal from synthetic wastewater by microbial consortia under methanogenic, sulfate-reducing and denitrifying conditions [151–153]. Using lactate as electron donor, a SeO_4^{2-} removal efficiency of 99% was obtained in both methanogenic and sulfate-reducing conditions, demonstrating that UASB reactors can be effectively applied to remove SeO_4^{2-} from contaminated wastewaters, with the involvement of sulfate-reducing bacteria (sulfate-reducing conditions) and a selenium-respiring sub-population (methanogenic conditions) [151]. Since the use of UASB reactors under methanogenic conditions leads to the recovery of decontaminated water, Se^0 and energy, methanogenic sludges are promising for Se-oxyanions bioconversion [143]. Further, Dessì and coworkers evaluate SeO_4^{2-} removal in UASB reactors as function of the temperature, observing that the maximum efficiency of removal was obtained at thermophilic conditions (55°C) [154]. Another advantage of working at this temperature is the better retention of reduced Se in the microbial biomass. Additionally, they performed a characterization of the microbial consortia through DGGE analysis, correlating the high SeO_4^{2-} removal efficiency to the presence of SeO_4^{2-}-respiring microorganisms, such as *Sulfurospirillum barnesii* and *D. indicum* [154]. UASB reactors are very promising for removing Se-oxyanions from contaminated wastewaters, however they require constant control, since any change in operation conditions may lead to an increase of the effluent Se-concentration through either biomethylation or bioconversion of Se-species [23].

3.2.5. The SBR system

Se-wastewater can be processed using a sequencing batch reactor (SBR), in which the biodegradation and solid separation take place in the same reactor [23]. In this configuration, the treatment is carried out in consecutive stages in the same tank: filling, reaction, sedimentation, draw, purging and inactivity [155]. The selection and enrichment of the desired microbial consortia is achieved by the alternation of anaerobic and aerobic phases, which results in the complete integration of both oxic and anoxic conditions in the same reactor [69, 155]. The SRB systems have been mostly used in the treatment of textile wastewater, thanks to their efficiency in removing dyes [69]. Further, this system has been employed for Se-laden wastewater treatment by Rege and coworkers, which used a denitrifying bacterial consortium for the reduction of both SeO_3^{2-} and SeO_4^{2-} with acetate as electron donor, observing a lag phase of 150 h and a SeO_3^{2-} reduction rate higher than SeO_4^{2-} [156]. In other studies, SBR reactors have been used for the remediation of SeO_4^{2-} specifically inoculating the bacterial strains *Thauera selenatis* [157] and *Bacillus* sp. SF-1 [158]. However, SeO_3^{2-} accumulation in the reactor over the time exerted to a toxic effect toward the bacteria present in the system [158]. More recently, Mal and coworkers studied the potential of SeO_4^{2-} removal in the presence of NH_4^+ in an SBR inoculated with an activated sludge collected from a wastewater treatment plant [159]. In this study, the microbial consortium removed up to 100% of SeO_4^{2-} and 95% of ammonium through partial nitrification as well as nitrification/denitrification, with alternating between anaerobic and aerobic phases [159]. The efficiency of the system was improved by prolonging the anaerobic phase from 3 to 4.5 h. Interestingly, the effluent presented low concentrations of both volatile and elemental Se, suggesting that most part of biogenic Se^0 formed by the microbial consortium was retained in the activated sludge [159].

Even if the performances of the bioreactor configurations described above are promising, there are still challenges for the utilization of these approaches to remediate Se-laden wastewater, such as the presence of co-contaminations with different types of metals, the discharge limits for the effluent, and the disposal of the concentrated selenium solids [23, 143]. The bioremediation of Se-contaminated soils has been less explored than wastewater treatment. In this regard, a study by Prakash and coworkers, analyzing the capability of a microbial consortium, composed by aerobic rhizo-bacteria belonging to *Bacillus* genus, to remove SeO_4^{2-} and SeO_3^{2-} contamination from soils amended with different concentrations of these oxyanions [160]. The study revealed higher rate of removal for SeO_3^{2-} as compared to SeO_4^{2-}, due to the greater bioavailability in the soils of SeO_3^{2-} [160]. Moreover, microbial consortia can play a major role in assisting hyperaccumulator plants in phytoremediation approaches by enhancing both plant growth and Se-accumulation (**Figure 2**) [161, 162].

3.3. Microbial consortia for Te-removal from contaminated environments

Since Te-biogeochemistry is still poorly understood [34], to date few examples of microbial consortia employed for the bioconversion of Te-oxyanions into their elemental state (Te^0) are available in the literature [8]. Further, although Te-species are toxic for living organisms at very low concentrations [6], evaluating the actual amount of Te-contaminants present in environmental samples is challenging, due to their low general availability on Earth [34]. Indeed, even if TeO_4^{2-}- and/or TeO_3^{2-}- reducing bacteria are frequently isolated from natural microbial communities adapted to the stress exerted by Te-oxyanions [28, 107], the application of microbial consortia for their removal from contaminated matrices is still in its infancy.

One of the first studies regarding bioremediation of Te-contaminated environments was carried out by Baesman and coworkers, which isolated sediment slurries resistant to TeO_3^{2-} at Mono

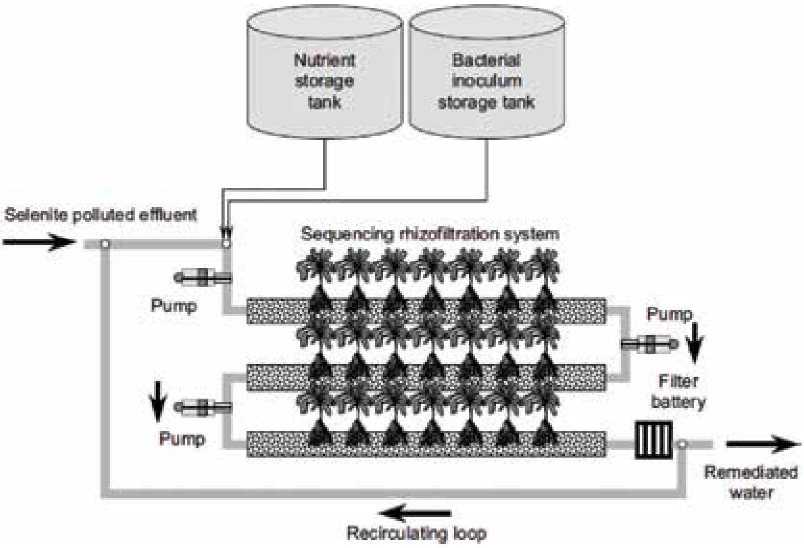

Figure 2. Schematic illustration of a phytoremediation system for the treatment of Se-wastewater through a synergistic cooperation of a Se-hyperaccumulator plant and selenite/selenate bioconverting bacteria of the rhizosphere [162].

Lake (California) [22]. Thus, the identified slurries were exposed under anaerobic conditions of growth to different concentrations of TeO_3^{2-} with either lactate or H_2 as electron donors, and they were incubated at 28°C for 30 days [22]. During the timeframe of microbial consortium's growth, a progressively blackening of the cultures has been observed, which indicated both Te-oxyanions bioreduction and the simultaneous accumulation of Te^0 precipitates, as proven by electron microscopy observations of the solid phase of the slurries [22].

More recently, Ramos-Ruiz and coworkers analyzed an anaerobic mixed microbial culture in a methanogenic granular sludge obtained from a wastewater treatment plant at Mahou's (beer brewery in Spain) [163]. In this regard, the granular sludge was chosen over planktonic cells considering that the latter one should be exposed more directly to the toxic Te-species [163]. As a result, the anaerobic sludge was able to catalyze the reduction of both TeO_4^{2-} and TeO_3^{2-} added to the system at a concentration of 20 mg L^{-1}, showing a rate of TeO_3^{2-} reduction seven-fold higher than TeO_4^{2-} one in all conditions tested [163]. As a consequence of Te-oxyanions bioconversion by the anaerobic sludge, the formation of intra and extracellular Te-nanoprecipitates has been detected through electron microscopy [163]. Interestingly, the microbial consortium did not show any lag phase when exposed to Te-oxyanions even in the case of a sludge originated from wastewater not contaminated with Te-species [163]. In order to avoid the possibility of an abiotic bioreduction of TeO_4^{2-} and/or TeO_3^{2-} by biogenic S^{2-} produced by SRB microorganisms generally present in microbial consortia, all the experiments have been performed in a (S)-free medium. Furthermore, the authors observed an increase of both TeO_4^{2-} and TeO_3^{2-} reduction rates after the amendment of different redox mediators, with riboflavin and lawsone causing the highest effect [163]. Finally, the addition of these redox mediators increased the percentage of extracellular Te-nanoprecipitates, determining a change in the shape of the nanomaterials produced [163].

A following study by the same research group evaluated the feasibility to use UASB reactors for the bioconversion of TeO_3^{2-} to Te-nanoprecipitates using a methanogenic microbial consortium in granular sludge, and the subsequent separation of the nanomaterials from the water effluent [164]. In this study, ethanol was added to the system as exogenous source of electron-donating substrate, while riboflavin was supplied as redox mediator during the biological process [164]. UASB reactors were operated with hydraulic retention time of 14 h at 28°C and supplemented with up to 20 mg L^{-1} of TeO_3^{2-} [164]. Similarly to the above-mentioned study [164], the presence of riboflavin as redox mediator enhanced the efficiency of TeO_3^{2-} bioconversion, lowering the toxicity of this oxyanion toward the microbial consortium. Moreover, a continuous removal of TeO_3^{2-} by the anaerobic microbial consortium was observed in the UASB reactor, showing a bioreduction efficiency ranging from 83%, when riboflavin was absent, to 99.5%, when riboflavin was added to the system [164].

TeO_3^{2-} removal from wastewater using a UASB bioreactor was also recently investigated by Mal and coworkers, which inoculated a UASB reactor with anaerobic granular sludge fed with lactate as carbon source, with a hydraulic retention time of 12 h at 30°C [165]. In the UASB reactor, firstly a concentration of 10 mg L^{-1} of TeO_3^{2-} was added, which was subsequently increased after 42 days to 20 mg L^{-1}. Te-oxyanion removal started immediately after the initial TeO_3^{2-} addition [165]. Particularly, after the first 3–4 weeks of sludge incubation in the reactor, a significant improvement of TeO_3^{2-} removal efficiency was observed, suggesting an adaptation of the microbial consortium to the presence of this oxyanion [165]. Furthermore, TeO_3^{2-} was almost completely bioconverted to its elemental state in the form of Te-nanostructures associated with the loosely bound EPS fraction surrounding the sludge, suggesting a pivotal role played by EPS and its functional groups in the biogenesis of Te-nanoprecipitates. In this regard, the possibility to easily recover Te-nanostructures associated with the EPS fraction opens new possibility to combine oxyanion removal with the recovery of Te^0 [165].

4. Microbial generation of Se- and Te-nanostructures

It is nowadays recognized the key role played by bacteria not only as tool for bioremediation purposes of highly contaminated Se- and Te-matrices, but also as a mean by which the less toxic and bioavailable elemental form of these chalcogens (i.e., Se^0 and Te^0) are generated and recovered. Indeed, yet Se and Te are elements featured by unique chemical-physical (i.e., semiconductive, photoconductive and catalytic) properties [166–169], which result to be emphasized in the nanosized material containing Se^0 and Te^0 as building blocks, forming nanoparticles (NPs) and/or nanorods (NRs). Se and Te as nanoscale structures are characterized by a large surface-to-volume ratio and a large surface energy as compared to their bulk counterparts [8], which make them suitable for biotechnological applications, such as: biomedicine, electronics, environmental engineering and agricultural industries [168, 170], to name a few. Since bacteria are considered inexpensive catalysts, their use for the production of Se- and Te-based nanostructures is an attractive choice over the chemical synthesis processes [79]. Thus, microorganisms capable of generating biogenic nanomaterials are seen as *green* and cost-effective exploitable methods to synthesize high-quality nanostructures [10], whose process occurs at standard conditions (i.e., near neutral pH, controlled temperature and pressure), and, more importantly, avoiding the use of harsh reducing agents as well as the production of toxic wastes deriving from the chemical synthesis approaches [171].

Considering the peculiar photoconductive, semiconductive and optical properties of Se, the use of Se-based nanomaterials has been investigated in a wide range of applications, such as in the production of new optical devices, photovoltaic solar cells, photographic exposure meters and rectifiers and photo-assisted fuel cells [172–175]. Moreover, Se-nanostructures resulted to act as good catalyst for both the chelation of mercury ions (Hg^{2+}) present as contaminants in different polluted environments [176], and the degradation of several toxic chemical compounds (e.g., trypan blue dye) [177], as well as an efficient bio-sensor for H_2O_2 in different matrices [178]. Similarly, Te is a narrow band-gap *p*-type semiconductor, which is featured by high photoconductivity, piezoelectricity and thermoelectricity [168, 169]. These versatile properties led to the exploitation of Te-nanomaterials as optoelectronic, piezoelectric and thermoelectric devices, infrared detectors and gas sensors [179, 180], to name a few. Further, since these chalcogen-nanostructures showed great adsorptive ability, biological reactivity and antioxidant functions, their use in biomedicine have been recently explored [8, 170, 181]. Both Se- and Te-nanomaterials resulted efficient tools in protecting living organisms from DNA oxidation [181], as well as promising antimicrobial and anticancer agents [182–187]. In this regard, several Se-nanostructures produced by different microorganisms have been tested for their antimicrobial efficacy, highlighting their ability to prevent the growth of pathogenic bacteria (i.e., *E. coli*, *P. aeruginosa*, *S. aureus*) either in the form of planktonic cells or as biofilms [182, 183, 186, 187]. Particularly, biogenic Se-nanomaterials resulted to be more efficient as compared to those synthesized by mean of chemical processes, showing a strong inhibitory effect of pathogenic bacterial growth at lower concentrations [183]. Moreover, studies carried out to evaluate the cytotoxicity of biogenic Se-nanostructures toward human cell lines (i.e., fibroblasts and dendritic cells) revealed their high biocompatibility [187], which is a fundamental feature for their possible biomedical applications. Although Te-nanostructures produced by microorganisms are less studied for biomedical applications than those containing Se, recently the potential of such nanomaterials as antimicrobials has been assessed [186], showing their good efficacy in inhibiting pathogens growth. Further, a promising technological application of biogenic Te-based nanostructures regards the production of quantum dots (QDs), which are semiconductors nanocrystals featured by unique electronic and optical properties, due to quantum confinement effects [188].

5. Summary

Bioremediation strategies of Se- and Te-polluted environments based on the ability of microorganisms to bioprocess these toxic oxyanion species is an environmental-sustainable choice to reclaim contaminated soils, groundwater, surface water bodies and sediments. The primary microbial process after biosorption is the bioreduction of chalcogen-oxyanions into their less toxic and bioavailable elemental forms (i.e., Se^0 and Te^0) generating, as end-products nanoscale materials, which can be recovered from the biomasses and used for technological purposes.

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References

[1] Haynes WM. Section 4: Properties of the elements and inorganic compounds. In: Haynes WM, Lide DR, Bruno TJ, editors. CRC Handbook of Chemistry and Physics. 95th ed. Boca Raton: CRC Press/Taylor and Francis; 2014. pp. 115-120. ISBN: 13:978-1-4822-0867-2

[2] Ba LA, Doring M, Jamier V, Jacob C. Tellurium: An element with great biological potency and potential. Organic & Biomolecular Chemistry. 2010;**8**(19):4203-4216. DOI: 10.1039/c0Ob00086h

[3] Vriens B, Lenz M, Charlet L, Berg M, Winkel LHE. Natural wetland emissions of methylated trace elements. Nature Communications. 2014;**5**:3035. DOI: 10.1038/ncomms4035

[4] Reilly C. Chapter 1: Introduction. In: Reilly C, editor. Selenium in Food and Health. 2nd ed. New York: Springer Science + Business Media; 2006. pp. 1-18. ISBN: 978-0-387-33243-7

[5] Chasteen TG, Fuentes DE, Tantalean JC, Vasquez CC. Tellurite: History, oxidative stress, and molecular mechanisms of resistance. FEMS Microbiology Reviews. 2009;**33**(4):820-832. DOI: 10.1111/j.1574-6976.2009.00177.x

[6] Taylor DE. Bacterial tellurite resistance. Trends in Microbiology. 1999;**7**(3):111-115. DOI: 10.1016/S0966-842X(99)01454-7

[7] Mehdi Y, Hornick J, Istasse L, Dufrasne I. Selenium in the environment, metabolism and involvement in body functions. Molecules. 2013;**18**:3292-3311. DOI: 10.3390/molecules 18033292

[8] Turner RJ, Borghese R, Zannoni D. Microbial processing of tellurium as a tool in biotechnology. Biotechnology Advances. 2012;**30**:954-963. DOI: 10.1016/j.biotechadv.2011.08.018

[9] Cooper WC. Tellurium. New York: Van Nostrand Renhod Co; 1971. p. 437

[10] Lampis S, Zonaro E, Bertolini C, Bernardi P, Butler CS, Vallini G. Delayed formation of zero-valent selenium nanoparticles by *Bacillus mycoides* SelTE01 as a consequence of selenite reduction under aerobic conditions. Microbial Cell Factories. 2014;**13**:35. DOI: 10.1186/1475-2859-13-35

[11] Whitten KW, Davis RE, Peck ML. Chapter 6: Chemical periodicity. In: Whitten KW, Davis RE, Peck ML, editors. General Chemistry. 6th ed. Orlando: Saunders College Publishing; 2000. pp. 927-930. DOI: 10.1021/ed079p637

[12] Barceloux DG. Selenium. Journal of Toxicology. Clinical Toxicology. 1999;**37**(2):145-172. DOI: 10.1081/CLT- 100102417

[13] Turner RJ. Tellurite toxicity and resistance in gram-negative bacteria. Recent Research Developments in Microbiology. 2001;**5**:69-77. ISBN: 81-7736-055-8

[14] Martens DA, Suarez DL. Selenium speciation of soil/sediment determinated with sequential extractions and hydride generation atomic absorption spectrophotometry. Environmental Science & Technology. 1996;**31**:133-139. DOI: 10.1021/es960214+

[15] Spallholz JE. On the nature of selenium toxicity and carcinostatic activity. Free Radical Biology & Medicine. 1994;**17**:45-64. DOI: 10.1016/0891-5849(94)90007-8

[16] Bebien M, Lagniel G, Garin J, Touati D, Vermeglio A, Labarre J. Involvement of superoxide dismutases in the response of *Escherichia coli* to selenium oxides. Journal of Bacteriology. 2002;**184**:1156-1164. DOI: 10.1128/JB.184.6.15561564.2002

[17] Kessi J, Hanselmann KW. Similarities between the abiotic reduction of selenite with glutathione and the dissimilatory reaction mediated by *Rhodospirillum rubrum* and *Escherichia coli*. The Journal of Biological Chemistry. 2004;**279**:50662-50669. DOI: 10.1074/jbc.M405887200

[18] Perez MJ, Calderon IL, Arenas FA, Fuentes DE, Pradenas GA, Fuentes LE, Sandoval JM, Castro ME, Elias AO, Vasquez CC. Bacterial toxicity of potassium tellurite: Unveiling an ancient enigma. PLoS One. 2007;**2**:e211. DOI: 10.1371/journal.pone.0000211

[19] Zannoni D, Borsetti F, Harrison JJ, Turner RJ. The bacterial response to the chalcogen metalloids Se and Te. Advances in Microbial Physiology. 2008;**53**:1-71. DOI: 10.1016/S00 65-2911(07)53001-8

[20] Holmgren A. Thioredoxin and glutaredoxin systems. The Journal of Biological Chemistry. 1989;**264**:13963-13966

[21] Morales EH, Pinto CA, Luraschi R, Munoz-Villagran CM, Cornejo FA, Simpins SW, Nelson J, Arenas FA, Piotrowski JS, Myers CL, Mori H, Vasquez CC. Accumulation of heme biosynthetic intermediates contributes to the antimicrobial action of the metalloid tellurite. Nature Communications. 2017;**8**:15320. DOI: 10.1038/ncomms15320

[22] Baesman SM, Stolz JF, Kulp TR, Oremland RS. Enrichment and isolation of *Bacillus beveridgei* sp. nov., a facultative anaerobic haloalkaliphile from Mono Lake, California, that respires oxyanions of tellurium, selenium, and arsenic. Extremophiles. 2009;**13**:695-705. DOI: 10.1007/s00792-009-0257-z

[23] Tan LC, Nanchariah YV, van Hullebusch ED, Lens PNL. Selenium: Environmental significance, pollution, and biological treatment technologies. Biotechnology Advances. 2016;**34**:886-907. DOI: 10.1016/j.biotechadv.2016.05.005

[24] Schroder I, Rech S, Krafft T, May JM. Purification and characterization of the selenate reductase from *Thauera selenatis*. The Journal of Biological Chemistry. 1997;**272**:23765-23768. DOI: 10.1074/jbc.272.38.23765

[25] Stolz JF, Oremland RS. Bacterial respiration of arsenic and selenium. FEMS Microbiology Reviews. 1999;**23**:615-627. DOI: 10.1111/j.1574-6976.1999.tb00416.x

[26] Switzer-Blum J, Bindi AB, Buzzelli J, Stolz JF, Oremland RS. *Bacillus arsenoselenatis* sp. nov. and *Bacillus selenitireducens* sp. nov.: Two haloalkaliphiles from Mono Lake, California, which respire oxyanions of selenium and arsenic. Archives of Microbiology. 1998;**171**:19-30. DOI: 10.1007/s002030050673

[27] Takai K, Hirayama H, Sakihama Y, Inagaki F, Yamato Y, Horikoshi K. Isolation and metabolic characteristic of previously uncultured members of the order *Aquificales* in subsurface gold mine. Applied and Environmental Microbiology. 2002;**68**:3046-3054. DOI: 10.1128/AEM.68.6.3046.3054.2002

[28] Csotonyi JT, Stackebrandt E, Yurkov V. Anaerobic respiration on tellurate and other metalloids in bacteria from hydrothermal vent fields in the eastern Pacific Ocean. Applied and Environmental Microbiology. 2006;**72**:4950-4956. DOI: 10.1128/AEM.00223-06

[29] Baesman SM, Bullen TD, Dewald J, Zhang DH, Curran S, Islam FS, Beveridge TJ, Oremland RS. Formation of tellurium nanocrystals during anaerobic growth of bacteria that use Te oxyanions as respiratory electron acceptors. Applied and Environmental Microbiology. 2007;**73**:2135-2143. DOI: 10.1128/aem.02558-06

[30] Brown TJ, Wrighton CE, Raycraft ER, Shaw RA, Deady EA, Rippingale J, Bide T, Idoine N. World Mineral Production 2009-2013. Nottingham: British Geological Survey; 2015. p. 88. ISBN: 978-0-85272-857-4

[31] Winkel LH, Vriens B, Jones J, Schneider L, Pilon-Smits E, Banuelos G. Selenium cycling across soil-plant-atmosphere interfaces: A critical review. Nutrients. 2015;**7**:4199-4239. DOI: 10.3390/nu7064199

[32] Wen H, Carignan J. Reviews on atmospheric selenium: Emissions, speciation and fate. Atmospheric Environment. 2007;**41**:7151-7165. DOI: 10.1016/j.atmosenv.2007.07.035

[33] USGS. Mineral commodity summaries. Geological Survey. 2015;**196**. DOI: 10.3133/70140094

[34] Belzile N, Chen YW. Tellurium in the environment: A critical review focused on natural waters, soils, sediments and airborne particles. Applied Geochemistry. 2015;**63**:83-92. DOI: 10.1016/j.apgeochem.2015.07.002

[35] Deng ZT, Zhang Y, Yue JG, Tang FQ, Wei Q. Green and orange CdTe quantum dots as effective pH-sensitive fluorescent probes for dual simultaneous and independent detection of viruses. The Journal of Physical Chemistry. B. 2007;**111**:12024-12031. DOI: 10.1021/jp074609z

[36] Vesper DJ, Roy M, Rhoads CJ. Selenium distribution and mode of occurrence in the Kanawha formation, southern West Virginia U.S. International Journal of Coal Geology. 2008;**73**:237-249. DOI: 10.1016/j.coal.2007.06.003

[37] Pyrzynska K. Determination of selenium species in environmental samples. Microchimica Acta. 2002;**140**:55-62. DOI: 10.1007/s00604-001-0899-8

[38] Dolor MK, Helz GR, McDonough VF. Sediment profiles of less commonly determined elements measured by laser ablation ICP-MS. Marine Pollution Bulletin. 2009;**59**:182-191. DOI: 10.1016/j.marpolbul.2009.03.027

[39] Perkins WT. Extreme selenium and tellurium contamination in soils - an eighty year-old industrial legacy surrounding a Ni refinery in the Swansea Valley. Science of the Total Environment. 2011;**412**:162-169. DOI: 10.1016/j.scitotenv.2011.09.056

[40] Dopp E, Hartmann LM, Florea AM, Rettenmeier AW, Hirner AV. Environmental distribution, analysis, and toxicity of organo-metal(loid) compounds. Critical Reviews in Toxicology. 2004;**34**:301-333. DOI: 10.1080/10408440490270160

[41] Kobayashi A, Ogra Y. Metabolism of tellurium, antimony and germanium simultaneously administered to rats. The Journal of Toxicological Sciences. 2009;**34**:295-303. DOI: 10.2131/jts.34.295

[42] Luoma SN, Presser TS. Emerging opportunities in management of selenium contamination. Environmental Science & Technology. 2009;**43**:8483-8487. DOI: 10.1021/es900828h

[43] Yoon BM, Shim SC, Pyun HC, Lee DS. Hydride generation atomic absorption determination of tellurium species in environmental samples with in situ concentration in a graphite furnace. Analytical Sciences. 1990;**6**:561-566. DOI: 10.2116/analsci.6.561

[44] Fujino O, Hara K, Ikejima S, Goda S. Determination of tellurium in lake water by ICP-MS. Bunseki Kagaru. 1997;**46**:857-862. DOI: 10.2116/bunsekikagaru.46.857

[45] Najafi NM, Tavakoli H, Alizadeh R, Seidi S. Speciation and determination of ultra trace amounts of inorganic tellurium in environmental water samples by dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry. Analytica Chimica Acta. 2010;**670**:18-23. DOI: 10.1016/j.aca.2010.04.059

[46] Canton SP, van Derveer WD. Selenium toxicity to aquatic life: An argument for sediment-based water quality criteria. Environmental Toxicology and Chemistry. 1997;**16**:1255-1259. DOI: 10.1002/etc.5620160622

[47] Ellis AS, Johnson TM, Herbel MJ, Bullen TD. Stable isotope fractionation of selenium by natural microbial consortia. Chemical Geology. 2003;**195**:119-129. DOI: 10.1016/S0009-2541(02)00391-1

[48] Lemly AD. Teratogenic effects and monetary cost of selenium poisoning of fish in Lake Sutton, North Carolina. Ecotoxicology and Environmental Safety. 2014;**104**:160-167. DOI: 10.1016/j.ecoenv.2014.02.022

[49] Cutter GA, Cutter LS. Sources and cycling of selenium in the western and equatorial Atlantic Ocean. Deep-Sea Research Part II. 2001;**48**:2917-2931. DOI: 10.1016/S0967-0645(01)00024-8

[50] Atkinson R, Aschmann SM, Hasegawa D, Thompson-Eagle ET, Frankenberger WT Jr. Kinetics of the atmospherically important reactions of dimethyl selenide. Environmental Science & Technology. 1990;**24**:1326-1332. DOI: 10.1021/es00079a005

[51] Springer SE, Huber RE. Sulfate and selenate uptake and transport in wild and in two selenate-tolerant strains of *Escherichia coli* K12. Archives of Biochemistry and Biophysics. 1973;**156**:595-603. DOI: 10.1016/0003-9861(73)90310-X

[52] Brown TA, Shrift A. Assimilation of selenate and selenite by *Salmonella thyphimurium*. Canadian Journal of Microbiology. 1980;**26**:671-675. DOI: 10.1139/m82-045

[53] Bryant RD, Laishley EJ. Evidence for proton motive force dependent transport of selenite by *Clostridium paesteurianum*. Canadian Journal of Microbiology. 1989;**35**:481-486. DOI: 10.1139/m89-074

[54] Bebien M, Chauvin JP, Adriano JM, Grosse S, Vermeglio A. Effect of selenite on growth and protein synthesis in the phototrophic bacterium *Rhodobacter sphaeroides*. Applied and Environmental Microbiology. 2001;**67**:4440-4447. DOI: 10.1128/AEM.67.10.4440-4447.2001

[55] Fisher JC, Hollibaugh JT. Selenate-dependent anaerobic arsenite oxidation by a bacterium from Mono Lake, California. Applied and Environmental Microbiology. 2008;**74**:2588-2594. DOI: 10.1128/AEM.01995-07

[56] Chasteen TG, Bentley R. Biomethylation of selenium and tellurium: Microorganisms and plants. Chemical Reviews. 2003;**103**:1-25. DOI: 10.1021/cr010210+

[57] Michalke K, Wickenheiser B, Mehring M, Hirner AV, Hensel R. Production of volatile derivatives of metal(loid)s by microflora involved in anaerobic digestion of sewage sludge. Applied and Environmental Microbiology. 2000;**67**:2791-2796. DOI: 10.1128/AEM.66.7.2791-2796.2000

[58] Dungan RS, Frankenberg WT. Biotransformation of selenium by *Enterobacter cloacae* SLD1a-1: Formation of dimethylselenide. Biogeochemistry. 2001;**55**:73-86. DOI: 10.1023/A:1010640307328

[59] Van Fleet-Stalder V, Chasteen TG. Using fluorine-induced chemiluminescence to detect organi-metalloids in the headspace of phototrophic bacterial cultures amended with selenium and tellurium. Photochemistry and Photobiology B: Biology. 1998;**43**:193-203. DOI: 10.1016/S1011-1344(98)00108-8

[60] Challenger F. Biological methylation. Chemical Reviews. 1945;**36**:315-361. DOI: 10.1002/9780470122570.ch8

[61] Nancharaiah YV, Lens PNL. Ecology and biotechnology of selenium-respiring bacteria. Microbiology and Molecular Biology Reviews. 2015;**79**:61-80. DOI: 10.1128/MMBR.00037-14

[62] Staicu LC, van Hullebusch ED, Lens PN, Pilon-Simts EA, Oturan MA. Electrocoagulation of colloidal biogenic selenium. Environmental Science and Pollution Research International. 2015;**22**:3127-3137. DOI: 10.1007/s11356-014-3592-2

[63] Mal J, Veneman WJ, Nancharaiah YV, van Hullebusch ED, Peijnenburg WJGM, Vijver MG, Lens PNL. A comparison of fate and toxicity of selenite, biogenically and chemically synthesized selenium nanoparticles to the zebrafish (*Danio rerio*) embryogenesis. Nanotoxicology. 2017;**11**:87-97. DOI: 10.1080/17435390.2016.1275866

[64] Kuroda M, Notaguchi E, Sato A, Yoshioka M, Hasegawa A, Kagami T, Narita T, Yamashita M, Sei K, Soda S, Ike M. Characterization of *Pseudomonas stutzeri* NT-I capable of removing soluble selenium from the aqueous phase under aerobic conditions. Journal of Bioscience and Bioengineering. 2011;**112**:259-264. DOI: 10.1016/j.jbiosc.2011.05.012

[65] Kagami T, Narita T, Kuroda M, Notaguchi E, Yamashita M, Sei K, Soda S, Ike M. Effective selenium volatilization under aerobic conditions and recovery from the aqueous phase by *Pseuodomonas stutzeri* NT-I. Water Research. 2013;**47**:1361-1368. DOI: 10.1016/j.watres.2012.12.001

[66] Stolz JF, Basu P, Santini JM, Oremland RS. Arsenic and selenium in microbial metabolism. Annual Review of Microbiology. 2006;**60**:107-130. DOI: 10.1146/annurev.micro.60.080805.142053

[67] Williams KH, Wilkins MJ, N'Guessan AL, Arey B, Dodova E, Dohnalkova A, Holmes D, Lovley DR, Long PE. Field evidence of selenium bioreduction in a uranium-contaminated aquifer. Environmental Microbiology Reports. 2013;**5**:444-452. DOI: 10.1111/1758-2229.12032

[68] Seghezzo L, Zeeman G, van Lier JB, Hamelers HVM, Lettinga G. A review: The anaerobic treatment of sewage in UASB and EGSB reactors. Bioresource Technology. 1998;**65**:175-190. DOI: 10.1016/S0960-8524(98)00046-7

[69] Chan YJ, Chong MF, Law CL, Hassel DG. A review on anaerobic-aerobic treatment of industrial and municipal wastewater. Chemical Engineering Journal. 2009;**155**:1-18. DOI: 10.1016/j.cej.2009.06.041

[70] Oremland RS, Blum JS, Culbertson CW, Visscher PT, Miller LG, Dowdle P, Stromaier FE. Isolation, growth, and metabolism of an obligately anaerobic, selenate-respiring bacterium, strain SES-3. Applied and Environmental Microbiology. 1994;**60**:3011-3019

[71] Fujita M, Ike M, Nishimoto S, Takahashi K, Kashiwa M. Isolation and characterization of a novel selenate-reducing bacterium, *Bacillus* sp. SF-1. Biotechnology and Bioengineering. 1997;**80**:755-761. DOI: 10.1016/S0922-338X(97)81130-0

[72] Macy JM, Michel TA, Kirsch DG. Selenate reduction by a *Pseudomonas* species: A new mode of anaerobic respiration. FEMS Microbiology Letters. 1989;**61**:195-198. DOI: 10.1111/j.1574-6968.1989.tb03577.x

[73] Switzer Blum J, Stolz JF, Ohren A, Oremland RS. *Selenihalanaerobacter shriftii* gen. Nov. sp. nov., a halophilic anaerobe from Dead Sea sediments that respires selenate. Archives of Microbiology. 2001;**175**:208-219. DOI: 10.1007/s002030100257

[74] Narasingarao P, Haggblom MM. Identification of anaerobic selenate-respiring bacteria from aquatic sediments. Applied and Environmental Microbiology. 2007;**73**:3519-3527. DOI: 10.1128/AEM.02737-06

[75] Rauschenbach I, Narasingarao P, Haggblom MM. *Desulfurispirillum indicum* sp. nov., a selenate- and selenite-respiring bacterium isolated from an estuarine canal. International Journal of Systematic and Evolutionary Microbiology. 2011;**61**:654-548. DOI: 10.1099/ijs.0.022392-0

[76] Ziemkiewicz PF, O'Neal M, Lovett RJ. Selenium leaching kinetics and in situ control. Mine Water and the Environment. 2011;**30**:141-150. DOI: 10.1007/s10230-011-0154-4

[77] Me L, Frankeberger WT. Reduction of selenium oxyanions by *Enterobacter cloacae* SLD1a-1: Isolation and growth of the bacterium and its expulsion of selenium nanoparticles. Applied and Environmental Microbiology. 1997;**63**:3079-3084

[78] Viamajala S, Bereded-Samuel Y, Apel WA, Petersen JN. Selenite reduction by a denitrifying culture: Batch- and packed-bed reactor studies. Applied Microbiology and Biotechnology. 2006;**71**:953-962. DOI: 10.1007/s00253-005-0276-3

[79] Nancharaiah YV, Lens PNL. Selenium biomineralization for biotechnological applications. Trends in Biotechnology. 2015;**33**:323-330. DOI: 10.1016/j.tibtech.2015.03.004

[80] Kessi J, Ramuz M, Wehrli E, Spycher M, Bachofen R. Reduction of selenite and detoxification of elemental selenium by the phototrophic bacterium *Rhodospirillum rubrum*. Applied and Environmental Microbiology. 1999;**65**:4734-4740

[81] Painter EP. The chemistry and toxicity of selenium compounds with special reference to the selenium problem. Chemical Reviews. 1941;**28**:179-213. DOI: 10.1021/cr60090a001

[82] Kessi J. Enxymatic systems proposed to be involved in the dissimilatory reduction of selenite in the purple non-sulfur bacteria *Rhodospirillum rubrum* and *Rhodobacter capsulatus*. Microbiology. 2006;**152**:731-743. DOI: 10.1099/mic.0.28240-0

[83] Nogueira CW, Rocha JB. Toxicology and pharmacology of selenium: Emphasis on synthetic organoselenium compounds. Archives of Toxicology. 2011;**85**:1313-1359. DOI: 10.1007/s00204-011-0720-3

[84] Turner RJ, Weiner JH, Taylor DE. Selenium metabolism in *Escherichia coli*. Biometals. 1998;**11**:223-237. DOI: 10.1023/A:1009290213301

[85] Pittman MS, Robinson HC, Poole RK. A bacterial glutathione transporter (*Escherichia coli* CydDC) exports reductant in the periplasm. Journal of Biophysical Chemistry. 2005;**280**:32254-32261. DOI: 10.1074/jbc.M503075200

[86] Hockin SL, Gadd L. Linked redox precipitation of sulfur and selenium under anaerobic conditions by sulfate-reducing bacterial biofilms. Applied and Environmental Microbiology. 2003;**69**:7063-7072. DOI: 10.1128/AEM.69.12.7063-7072.2003

[87] Pettine M, Gennan F, Campanella L, Casentini B, Marani D. The reduction of selenium (IV) by hydrogen sulfide in aqueous solutions. Geochimica et Cosmochimica Acta. 2012;**83**:37-47. DOI: 10.1016/j.gca.2011.12.024

[88] Zawadzka AM, Crawford RL, Paszczynki AJ. Pyridine-2,6-bis(thiocarboxylic acid) produced by *Pseudomonas stutzeri* KC reduces and precipitates selenium and tellurium oxyanions. Applied and Environmental Microbiology. 2006;**72**:3119-3129. DOI: 10.1128/AEM.72.5.3119-3129.2006

[89] Oremland RS, Maest A, Presser TS, Miller LG. Selenate reduction to elemental selenium by anaerobic bacteria in sediments and culture: Biogeochemical significance of a novel, sulfate-independent respiration. Applied and Environmental Microbiology. 1989;**55**: 2333-2343

[90] Li DB, Cheng YY, Wu C, Li WW, Li N, Yang ZC, Tong ZH, Yu HQ. Selenite reduction by *Shewanella oneidensis* MR-1 is mediated by fumarate reductase in periplasm. Scientific Reports. 2014;**4**:3755. DOI: 10.1038/srep03735

[91] Basaglia M, Toffanin A, Baldan E, Bottegal M, Shapleigh JP, Casella S. Selenate-reducing capacity of the copper-containing nitrite reductase of *Rhizobium sullae*. FEMS Microbiology Letters. 2007;**269**:124-130. DOI: 10.1111/j.1574-6968.2006.00617.x

[92] Harrison G, Curie C, Laishley EJ. Purification and characterization of an inducible dissimilatory type sulphite reductase from *Clostridium pasteurianium*. Archives of Microbiology. 1984;**138**:72-78. DOI: 10.1007/BF00425411

[93] DeMoll-Decker H, Macy JM. The periplasmic nitrite reductase of *Thauera selenatis* may catalyze the reduction of selenite to elemental selenium. Archives of Microbiology. 1993;**160**:241-247. DOI: 10.1007/BF00249131

[94] Pearce CI, Pattrick RAD, Law N, Charnock JM, Coker VS, Fellowes JV, Oremland RS, Lloyd JR. Investigating different mechanisms for biogenic selenite transformations: *Geobacter sulfurreducens*, *Shewanella oneidensis* and *Veillonella atypica*. Environmental Technology. 2009;**30**:1313-1326. DOI: 10.1080/09593330902984751

[95] Oremland RS, Zehr JP. Formation of methane and carbon dioxide from dimethylselenide in anoxic sediments and by a methanogenic bacterium. Applied and Environmental Microbiology. 1986;**52**:1031-1036

[96] Oremland RS, Herbel MJ, Blum JS, Langley S, Beveridge TJ, Ajayan PM, Sutto T, Ellis AV, Curran S. Structural and spectral features of selenium nanospheres produced by Se-respiring bacteria. Applied and Environmental Microbiology. 2004;**70**:52-60. DOI: 10.1128/AEM.70.1.52-60.2004

[97] Tomas JM, Kay WW. Tellurite susceptibility and non-plasmid mediated resistance in *Escherichia coli*. Antimicrobial Agents and Chemotherapy. 1986;**30**:127-131. DOI: 10.1128/AAC.30.1.127

[98] Turner MS, Tan YP, Giffard PM. Inactivation of an iron transporter in *Lactococcus lactis* results in resistance to tellurite and oxidative stress. Applied and Environmental Microbiology. 2007;**73**:6144-6149. DOI: 10.1128/AEM.00413-07

[99] van Veen HW. Phosphate transporter in prokaryotes: Molecules, mediators and mechanisms. Antoine van Leeuwenhoek. 1997;**72**:299-315. DOI: 10.1023/A:1000530927928

[100] Harris RM, Webb DC, Howitt SM, Cox GB. Characterization of PitA and PitB from *Escherichia coli*. Journal of Bacteriology. 2001;**183**:5008-5014

[101] Borghese R, Zannoni D. Acetate permease (ActP) is responsible for tellurite (TeO_3^{2-}) uptake and resistance in cells of the facultative phototroph *Rhodobacter capsulatus*. Applied and Environmental Microbiology. 2010;**76**:942-944. DOI: 10.1128/AEM.02765-09

[102] Turner RJ, Hou Y, Weiner JH, Taylor DE. The arsenical ATPase efflux pump mediates tellurite resistance. Journal of Bacteriology. 1992;**174**:3092-3094. DOI: 10.1128/jb.174.9.3092-3094.1992

[103] Basnayake RST, Bisu HJ, Akpolat OM, Chasteen TG. Production of dimethyl telluride and elemental tellurium by bacteria amended with tellurite or tellurate. Applied Organometallic Chemistry. 2001;**15**:499-510. DOI: 10.1002/aoc.186

[104] Trutko SM, Akimenko VK, Suzina NE, Anisimova LA, Shlyapnikov MG, Baskunov BP, Duda VI, Boronin AM. Involvement of the respiratory chain of gram-negative bacteria in the reduction of tellurite. Archives of Microbiology. 2000;**173**:178-186. DOI: 10.1007/s002039900123

[105] Moscoso H, Saavedra C, Loyola C, Pichuantes S, Vasquez C. Biochemical characterization of tellurite-reducing activities of Bacillus Stearothermophilus V. Research in Microbiology. 1998;**149**:389-397

[106] King WE, Davis L. Potassium tellurite as an indicator of microbial life. American Journal of Public Health (NY). 1914;**4**:917-932

[107] Maltman C, Donald LJ, Yurkov V. Two distinct periplasmic enzymes are responsible for tellurite/tellurate and selenite reduction by strain ER-Te-48 associated with the deep sea hydrothermal vent tube worms at the Juan de Fuca ridge black smokers. Archives of Microbiology. 2017;**199**:1113-1120. DOI: 10.1007/s00203-017-1382-1

[108] Turner RJ, Weiner JH, Taylor DE. Tellurite-mediate thiol oxidation in *Escherichia coli*. Microbiologica. 1999;**145**:2549-2557. DOI: 10.1099/00221287-145-9-2549

[109] Avazeri C, Turner RJ, Pommier J, Weiner JH, Giordano G, Vermeglio A. Tellurite and selenate reductase activity of nitrate reductases from *Escherichia coli*: Correlation with tellurite resistance. Microbiologica. 1997;**143**:1181-1189. DOI: 10.1099/00221287-143-4-1181

[110] Sabaty M, Avazeri C, Pignol D, Vermeglio A. Characterization of the reduction of selenate and tellurite by nitrate reductases. Applied and Environmental Microbiology. 2001;**67**:5122-5126. DOI: 10.1128/AEM.67.11.5122-5126.2001

[111] Calderon I, Arenas FA, Perez JM, Fuentes DE, Araya MA, Saavedra CP, Tantalean JC, Pichuantes SE, Youderian PA, Vasquez CC. Catalases are NAD(P)H-dependent tellurite reductases. PLoS One. 2006;**1**:e70. DOI: 10.1371/journal.pone.0000070

[112] Borsetti F, Francia F, Turner RJ, Zannoni D. The disulfide binding protein DsbB allows the transfer of oxidizing equivalents from the toxic metalloid tellurite (TeO_3^{2-}) to the plasma membrane electron transport system of *Rhodobacter capsulatus*. Journal of Bacteriology. 2007;**189**:851-859. DOI: 10.1128/JB.01080-06

[113] Etezad SM, Khajeh K, Soudi M, Ghazvini PTM, Dabirmanesh B. Evidence on the presence of two distinct enzymes responsible for the reduction of selenate and tellurite in *Bacillus* sp. STG-83. Enzyme and Microbial Technology. 2009;**45**:1-6. DOI: 10.1016/j.enzmictec.2009.04.004

[114] Costerton JW, Geesey GG, Cheng KJ. How bacteria stick. Scientific American. 1978; **238**:86-95

[115] Branda SS, Vik A, Friedman L, Kolter R. Biofilms: The matrix revisited. Trends in Microbiology. 2005;**13**:20-26. DOI: 10.1016/j.tim.2004.11.006

[116] Kolter R, Greenberg EP. The superficial life of microbes. Nature. 2006;**441**:300-302. DOI: 10.1038/441300a

[117] Harrison JJ, Turner RJ, Marques LLR, Ceri H. Biofilms: A new understanding of these microbial communities is driving a revolution that may transform the science of microbiology. American Scientist. 2005;**93**:508-515

[118] Flemming HC, Wingender J. The biofilm matrix. Nature Reviews. Microbiology. 2010; **8**:623-633. DOI: 10.1038/nrmicro2415

[119] Harrison JJ, Ceri H, Stremick C, Turner RJ. Biofilm susceptibility to metal toxicity. Environmental Microbiology. 2004;**6**:1220-1227. DOI: 10.1111/j.1462-2920.2004.00656.x

[120] Harrison JJ, Ceri H, Turner RJ. Multimetal resistance and tolerance in microbial biofilms. Nature Reviews. Microbiology. 2007;**5**:928-938. DOI: 10.1038/nrmicro1774

[121] Harrison JJ, Ceri H, Roper NJ, Badry EA, Sproule KM, Turner RJ. Persister cells mediate tolerance to metal oxyanions in biofilm and planktonic *Escherichia coli*. Microbiologica. 2005;**151**:3181-3195. DOI: 10.1099/mic.0.27794-0

[122] Harrison JJ, Turner RJ, Ceri H. High-throughput metal susceptibility testing of microbial biofilms. BMC Microbiology. 2005;**5**:53. DOI: 10.1186/1471-2180-5-53

[123] Stewart PS. Diffusion in biofilms. Journal of Bacteriology. 2003;**185**:1485-1491. DOI: 10.1128/JB.185.5.1485-1491.2003

[124] Workentine ML, Harrison JJ, Welije AM, Tran VA, Stenroos PU, Tremaroli V, Vogel HJ, Ceri H, Turner RJ. Phenotypic and metabolic profiling of colony morphology variants

evolved from *Pseudomonas fluorescence* biofilms. Environmental Microbiology. 2010;**12**: 1565-1577. DOI: 10.1111/j.1462-2920-2010.02185.x

[125] Klonowska A, Heulin T, Vermeglio A. Selenite and tellurite reduction by *Shewanella oneidensis*. Applied and Environmental Microbiology. 2005;**71**:5607-5609. DOI: 10.1128/AEM.71.9.5607-5609.2005

[126] Warren LA. Biofilms and metal geochemistry: The relevance of micro-organism-induced geochemical transformations. In: Gadd GM, Semple KT, Lappin-Scott HM, editors. Microorganisms and Earth Systems- Advances in Geomicrobiology 65. Cambridge: University Press; 2005. pp. 11, ISBN: 0521862221-34

[127] Templeton AS, Trainor TP, Spromann AM, Brown FE Jr. Selenium speciation and partitioning within *Brukolderia cepacia* biofilms formed on a-Al_2O_3 surfaces. Geochimica et Cosmochimica Acta. 2003;**67**:3547-3557. DOI: 10.1016/S0016-7037(03)00212-6

[128] Lenz M, Lens PNL. The essential toxic: The changing perception of selenium in environmental sciences. Science of the Total Environment. 2009;**407**:3620-3633. DOI: 10.1016/j.scitotenv.2008.07.056

[129] Chung J, Nerenberg R, Rittmann BE. Bioreduction of selenate using a hydrogen-based membrane biofilm reactor. Environmental Science & Technology. 2006;**40**:1664-1671. DOI: 10.1021/es051251g

[130] Chung J, Rittmann BE, Wrhigth WF, Bowman RH. Simultaneous bio-reduction of nitrate, perchlorate, selenate, chromate, arsenate and dibromochloropropane using a hydrogen-based membrane biofilm reactor. Biodegradation. 2007;**18**:199. DOI: 10.1007/s10 532-006-9055-9

[131] Yamada L, Miyagishima N, Matsunaga T. Tellurite removal by a marine photosynthetic bacteria. Journal of Marine Biotechnology. 1997;**5**:46-49

[132] Navarrete-Bolanos JL, Serrato-Joya O, Botello-Alvarez E, Jimenez-Islas H, Cardenas-Manriquez M, Conde-Barajas E, Rico-Martinez R. Analyzing microbial consortia for biotechnological process design. In: Mendez-Villas A, editor. Communicating Current Research and Educational Topics and Trends in Applied Microbiology. Vol. vol. 1. Badajoz: Formatex; 2007. pp. 437-449. ISBN: 9788461194223

[133] Edwards SJ, Kjellerup BV. Applications of biofilms in bioremediation and biotransformation of persistent organic pollutants, pharmaceutical/personal care products, and heavy metals. Applied Microbiology and Biotechnology. 2013;**97**:9909-9921. DOI: 10.1007/s00253-013-5216-z

[134] Rashamuse KJ, Witheley CG. Bioreduction of Pt (IV) from aqueous solution using sulphate-reducing bacteria. Applied Microbiology and Biotechnology. 2007;**75**:1429-1435. DOI: 10.1007/s00253-007-0963-3

[135] Soda S, Kashiwa M, Kagami T, Kuroda M, Yamashita M, Ike M. Laboratory-scale bioreactors for soluble selenium removal from selenium refinery wastewater using anaerobic sludge. Desalination. 2011;**279**:433-438. DOI: 10.1016/j.desal.2011.06.031

[136] Gao D, Liu L, Liang H, Wu WM. Aerobic granular sludge: Characterization, mechanism of granulation and application to wastewater treatment. Critical Reviews in Biotechnology. 2011;**31**:137-152. DOI: 10.3109/07388551.2010.497961

[137] Astratinei V, van Hullebusch E, Lens PNL. Bioconversion of selenate in methanogenic anerobic granular sludge. Journal of Environmental Quality. 2006;**35**:1873-1883. DOI: 10.2134/jeq2005.0443

[138] Sonstegard J, Pickett T, Harwood J, Johnson D. Full scale operation of GE ABMet® biological technology for the removal of selenium from FGD wastewaters. In: 69th Annual International Water Conference; Orlando, USA; 2007. p. 580

[139] Sonstegard J, Harwood J, Pickett T. ABMet®: setting the standard for selenium removal. In: Proceedings of 71st International Water Conference; Texas, USA. 2010. p. 216

[140] Lovley DR. Extracellular electron transfer: Wires, capacitors, iron lungs, and more. Geobiology. 2008;**6**:225-231. DOI: 10.1111/j.1472-4669.2008.00148.x

[141] Opara A, Peoples MJ, Adams JD, Martin AS. Electro-Biochemical Reactor (EBR) Technology for Selenium Removal from British Columbia's Coal-Mining Wastewaters. Available from: http://www.inotec.us/uploads/5/1/2/8/5128573/selenium_removal_coal_mine_water_inotec-sme2014.pdf

[142] Yang SE, George GN, Lawrence JR, Kaminskyj SGW, Dynes JJ, Lai B, Pickering IJ. Multispecies biofilms transform selenium oxyanions into elemental selenium particles: Studies using combined synchrotron X-ray fluorescence imaging and scanning transmission X-ray microscopy. Environmental Science & Technology. 2016;**50**:10343-103450. DOI: 10.1021/acs.est.5b04529

[143] Bjornstedt M, Kumar S, Holmgren A. Selenodiglutathione is a highly efficient oxidant of reduced thioredoxin and a substrate for mammalian thioredoxin reductase. Journal of Biochemistry. 1992;**267**:8030-8034

[144] USEPA. Final Report-Selenium Treatment/Removal Alternatives Demonstration Project. 2001. Available from: http://www.epa.gov/nrmrl/std/mwt/a3/mwtp191.pdf

[145] Chung J, Rittmann BE, Her N, Lee SH, Yoon Y. Integration of H_2-based membrane biofilm reactor with RO and NF membranes for removal of chromate and selenate. Water, Air, and Soil Pollution. 2010;**207**:29-37. DOI: 10.1007/s11270-009-0116-7

[146] Van Ginkel SW, Yang Z, Kim BO, Sholin M, Rittmann BE. The removal of selenate to low ppb levels from flow gas desulfurization brine using the H_2-based membrane biofilm reactor (MBfR). Bioresource Technology. 2011;**102**:6360-6364. DOI: 10.1016/j.biortech.2011.03.010

[147] Ontiveros-Valencia A, Penton CR, Krajmalnik-Brown R, Rittmann BE. Hydrogen-fed biofilm reactors reducing selenate and sulfate: Community structure and capture of elemental selenium within the biofilm. Biotechnology and Bioengineering. 2016;**113**:1736-1744. DOI: 10.1002/bit.25945

[148] Lay CY, Wen LL, Shi LD, Zhao KK, Wang YQ, Yang X, Rittmann BE. Selenate and nitrate bioreductions using methane as the electron donor in a membrane biofilm reactor. Environmental Science & Technology. 2016;**50**:10179-10186. DOI: 10.1021/acs.est.6b02807

[149] Bhunia P, Ghangrekar M. Required minimum granule size in UASB reactor and characteristics variation with size. Bioresource Technology. 2007;**98**:994-999. DOI: 10.1016/j.biortech.2006.04.019

[150] North American Metal Council (NAMC). Review of Available Technologies for Removal of Selenium from Mater. 2010. Available from: http.//www.namc.org/docs/00062756.PDF

[151] Lenz M, van Hullebusch ED, Hommes G, Corvine PF, Lens PNL. Selenate removal in methanogeic and sulfate-reducing upflow anaerobic sludge bed reactors. Water Research. 2008;**42**:2184-2194. DOI: 10.1016/j.watres.2007.11.031

[152] Lenz M, Janzen N, Lens PNL. Selenium oxyanion inhibition of hydrogenotrophic and acetoclastic methanogenesis. Chemosphere. 2008;**73**:383-388. DOI: 10.1016/j.chemosphere.2008.05.059

[153] Lenz M, Smit M, Binder P, van Aelst AC, Lens PNL. Biological alkylation and colloid formation of selenium in methanogenic UASB reactor. Journal of Environmental Quality. 2008;**37**:1691-1700. DOI: 10.2134/jeq2007.0630

[154] Dessì P, Jain R, Singh S, Seder-Colomina M, van Hullebusch ED, Rene ER, Ahammad SZ, Carucci A, Lens PNL. Effect of temperature on selenium removal from wastewater by UASB reactors. Water Research. 2016;**94**:146-154. DOI: 10.1016/j.watres.2016.02.007

[155] Gali A, Dosta P, Lopez M, Alvarez M. SBR technology for high ammonium loading rates. Water Science and Technology. 2008;**58**:467-472. DOI: 10.2166/est.2008.408

[156] Rege MA, Yonge DR, Mendoza DP, Petersen JN, Bereded-Samuel Y, Johnstone DL, Apel W, Barnes JM. Selenium reduction by a denitrifying consortium. Biotechnology and Bioengineering. 1999;**62**:479-484. DOI: 10.1002/(SICI)1097-0290(19990220)62:4<479::AID-BIT11>3.0CO;2-G

[157] Macy JM, Lawson S, DeMoll-Decker H. Bioremediation of selenium oxyanions in San Joaquin drainage water using Thauera selenatis in a biological reactor system. Applied Microbiology and Biotechnology. 1993;**40**:588-594. DOI: 10.1007/BF00175752

[158] Kashiwa M, Ike M, Mihara H, Esaki N, Fujita M. Removal of soluble selenium by a selenate-reducing bacterium *Bacillus* sp. SF-1. BioFactors. 2001;**14**:261-265. DOI: 10.1002/biof.5520140132

[159] Mal J, Nancharaiah YV, van Hullebusch ED, Lens PN. Biological removal of selenate and ammonium by activated sludge in a sequencing batch reactor. Bioresource Technology. 2017;**229**:11-19. DOI: 10.1016/j.biortech.2016.12.112

[160] Prakash NT, Sharma N, Prakash R, Acharya R. Removal of selenium from Se enriched natural soils by a consortium of *Bacillus* isolates. Bulletin of Environmental Contamination and Toxicology. 2010;**85**:214-218. DOI: 10.1007/s00128-010-0061-6

[161] Sura-de Jong M, Reynolds RJB, Richterova K, Musilova L, Staicu LC, Chocholata I, Cappa JJ, Taghavi S, van der Lelie D, Frantik T, Dolinova I, Strejcek M, Cochran AT, Lovecka P, Pilon-Smits EAH. Selenium hyperaccumulators harbor a diverse endophytic bacterial community characterized by high selenium resistance and plant growth promoting properties. Frontiers in Plant Science. 2015;**6**:113. DOI: 10.3389/fpls.2015.00113

[162] Vallini G, Di Gregorio S, Lampis S. Rhizosphere-induced selenium precipitation for possible applications in phytoremediation of Se polluted effluents. Zeitschrift für Naturforschung. 2005;**60c**:349-356. DOI: 10.1515/znc-2005-3-419

[163] Ramos-Ruiz A, Field JA, Wilkening JV, Sierra-Alvarez R. Recovery of elemental tellurium nanoparticles by the reduction of tellurium oxyanions in a methanigenic microbial consortium. Environmental Science & Technology. 2016;**50**:1492-1500. DOI: 10.1021/acs.est.5b04074

[164] Ramos-Ruiz A, Sesma-Martin J, Sierra-Alvarez R, Field JA. Continuous reduction of tellurite to recoverable tellurium nanoparticles using an upflow anaerobic sludge bed (UASB) reactor. Water Research. 2017;**108**:189-196. DOI: 10.1016/j.watres.2016.10.074

[165] Mal J, Nancharaiah YV, Maheshwari N, van Hullebusch ED, Lens PN. Continuous removal and recovery of tellurium in an upflow anaerobic granular sludge bed reactor. Journal of Hazardous Materials. 2017;**327**:79-88. DOI: 10.1016/j.jhazmat.2016.12.052

[166] Barnaby S, Frayne S, Fath K, Banerjee I. Growth of Se nanoparticles on kinetin assemblies and their biocompatibility studies. Soft Materials. 2011;**9**:313-334. DOI: 10.1080/1539445X.2010.516302

[167] Srivastava N, Mukhopadhyay M. Biosynthesis and structural characterization of selenium nanoparticles mediated by *Zooglea ramigera*. Powder Technology. 2013;**244**:26-29. DOI: 10.1016/j.powtec.2013.03.050

[168] Zhao A, Zhang L, Yang Y, Ye C. Ordered tellurium nanowire arrays and their optical properties. Applied Physics A: Materials Science & Processing. 2005;**80**:1725-1728. DOI: 10.1007/s00339-003-2452-6

[169] Araki K, Tanaka T. Piezoelectric and elastic properties of single crystalline Se-Te alloys. Applied Physics Express. 1972;**11**:472-479. DOI: 10.1143/JJAP.11.472

[170] Ingale AG, Chaudhari AN. Biogenic synthesis of nanoparticles and the potential applications: An EcoFriendly approach. Journal of Nanomedicine & Nanotechnology. 2013;**4**:165. DOI: 10.4172/2157-7439.1000165

[171] Presentato A, Piacenza E, Anikovskiy M, Cappelletti M, Zannoni D, Turner RJ. *Rhodococcus aetherivorans* BCP1 as cell factory for the production of intracellular tellurium Nanorods under aerobic conditions. Microbial Cell Factories. 2016;**15**:204. DOI: 10.1186/s12934-016-0602-8

[172] Filippo E, Manno D, Serra A. Characterization and growth mechanism of selenium microtubes synthesized by a vapor phase deposition route. Crystal Growth & Design. 2010;**10**:4890-4897. DOI: 10.1021/cg1012632

[173] Zeng X, Zhang W, Xie Y, Xiong D, Chen W, Xu X, Wang M, Cheng YB. Low-cost porous $Cu_2ZnSnSe_4$ filmremarkably superior to noble Pt as counter electrode in quantum dot-sensitized solar cell system. Journal of Power Sources. 2013;**226**:359-362. DOI: 10.1016/j.jpowsour.2012.11.023

[174] Qin D, Zhou J, Luo C, Liu Y, Han L, Cao Y. Surfactant-assisted synthesis of size-controlled trigonal Se/Te allow nanowires. Nanotechnology. 2006;**17**:674. DOI: 10.1088/0957-4484/17/3/010

[175] Wang R, Da H, Wang H, Ji S, Tian Z. Selenium functionalized carbon for high dispersion of platinum-ruthenium nanoparticles and its effect on the electrocatalytic oxidation of methanol. Journal of Power Sources. 2013;**233**:326-330. DOI: 10.1016/j.jpowsour.2013.01.143

[176] Hurt RH, Harmburg SP, Sarin L, Kulaots I. Nanostructured Sorbent Materials for Capturing Environmental Mercury Vapor. 2009 U.S. Patent WO 108220,A1

[177] Bhavani P, Nenavathu AVR, Rao K, Goyal A, Kapoor A, Dutta RK. Synthesis, characterization and enhanced photocatalytic degradation efficiency of Se doped ZnO nanoparticles using trypan blue as a model dye. Applied Catalysis A: General. 2013;**459**:106-113. DOI: 10.1016/j.apcata.2013.04.001

[178] Wang T, Yang L, Zhang B, Liu J. Extracellular biosynthesis and transformation of selenium nanoparticles and application in H_2O_2 biosensor. Colloids and Surfaces. B, Biointerfaces. 2010;**80**:94-102. DOI: 10.1016/j.colsurfb.2010.05.041

[179] Suchand Sandeep CS, Samal AK, Pradeep T, Philip R. Optical limiting properties of Te and Ag_2Te nanowires. Chemical Physics Letters. 2010;**485**:326-330. DOI: 10.1016/j.cplett.2009.12.065

[180] Sharma YC, Purohit A. Tellurium based thermoelectric materials: New directions and prospects. J Integr. Science and Technology. 2016;**4**:29-32

[181] Wang H, Zhang J, Yu H. Elemental selenium at nano size posseses lower toxicity without compromising the fundamental effect on selenoenzymes: Comparison with selenomethionine in mice. Free Radical Biology & Medicine. 2007;**42**:1524-1533. DOI: 10.1016/j.freeradbiomed.2007.02.013

[182] Tran PA, Webster TJ. Selenium nanoparticles inhibit *Staphylococcus aureus* growth. International Journal of Nanomedicine. 2011;**6**:1553-1558. DOI: 10.2147/IJN.S21729

[183] Piacenza E, Presentato A, Zonaro E, Lemire JA, Demeter M, Vallini G, Turner RJ, Lampis S. Antimicrobial activity of biogenically produced spherical Se-nanomaterials embedded in organic material against *Pseudomonas aeruginosa* and *Staphylococcus aureus* strains on hydroxyapatite-coated surfaces. Microbial Biotechnology. 2017. DOI: 10.1111/1751-7915.12700

[184] Ahmad MS, Yasser MM, Sholkamy EN, Ali AM, Mehanni MM. Anticancer activity of biostabilized selenium nanorods synthesized by *Streptomyces bikiniensis* strain Ess_amA-1. International Journal of Nanomedicine. 2015;**10**:3389-3401. DOI: 10.2147/IJN.S82707

[185] Huang W, Wu H, Li X, Chen T. Facile one-pot synthesis of tellurium Nanorods as antioxidant and anticancer agents. Chemistry, an Asian Journal. 2016;**11**:2301-2311. DOI: 10.1002/asia.201600757

[186] Zonaro E, Lampis S, Turner RJ, Qazi SJS, Vallini G. Biogenic selenium and tellurium nanoparticles synthetized by environmental microbial isolates efficaciously inhibit bacterial planktonic cultures and biofilms. Frontiers in Microbiology. 2015;**6**:584. DOI: 10.3389/fmicb.2015.00584

[187] Cremonini E, Zonaro E, Donini M, Lampis S, Boaretti M, Disu S, Melotti P, Lleo MM, Vallini G. Biogenic selenium nanoparticles: Characterization, antimicrobial activity and effects on human dendritic cells and fibroblast. Microbial Biotechnology. 2016;**9**:758-771. DOI: 10.1111/1751-7915.12374

[188] Alivisatos AP. Perspectives on the physical chemistry of semiconductor nanocrystals. The Journal of Physical Chemistry. 1996;**100**:13226-13239. DOI: 10.1021/jp9535506

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Municipal and industrial wastewaters contain a wide spectrum of pollutants. Their effective removal presents a challenge for water treatment technology. Biosorption of nutrients and pollutants has been used in sewage treatment since the discovery of the activated sludge process. It is a passive uptake process by which pollutants are adsorbed on the surface of cell walls and/or dissolved in structures of microorganism cells that are present in sludge. Sorbed pollutants remain in the sludge and can be potentially released back into the environment depending on their condition and the reversibility of the pollutant-sludge interaction. An overview of typical biosorption applications for the removal of nutrients, organic pollutants, and metals in wastewater treatment is provided in different areas of their use for the protection of aquatic ecosystems and human health. This book will be of interest to operators of wastewater treatment plants and sludge treatment and disposal facilities as well as to researchers and university students in the field of environmental engineering.

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