

# Mechanisms of heavy metal removal using microorganisms as biosorbent

Vahid Javanbakht, Seyed Amir Alavi and Hamid Zilouei

## ABSTRACT

Release and distribution of heavy metals through industrial wastewaters has adverse effects on the environment via contamination of surface- and ground-water resources. Biosorption of heavy metals from aqueous solutions has been proved to be very promising, offering significant advantages such as low cost, availability, profitability, ease of operation, and high efficiency, especially when dealing with low concentrations. Residual biomasses of industrial microorganisms including bacteria, algae, fungi, and yeast have been found to be capable of efficiently accumulating heavy metals as biosorbent. This paper presents and investigates major mechanisms of biosorption and most of the functional groups involved. The biosorption process includes the following mechanisms: transport across cell membrane, complexation, ion exchange, precipitation, and physical adsorption. In order to understand how metals bind to the biomass, it is essential to identify the functional groups responsible for metal binding. Most of these groups have been characterized on the cell walls. The biosorbent contains a variety of functional sites including carboxyl, imidazole, sulfhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide, and hydroxyl moieties that are responsible for metal adsorption. These could be helpful to improve biosorbents through modification of surface reactive sites via surface grafting and/or exchange of functional groups.

**Key words** | biosorption, heavy metals, mechanism, pretreatment, wastewater

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## INTRODUCTION

Heavy metals, being toxic and non-biodegradable, come to the environment mainly through industrial, mining, and agricultural activities (Majumdar *et al.* 2008). Industrial wastewaters are heavily loaded with different types of inorganic and organic pollutants in either soluble or insoluble forms (Javaid & Bajwa 2008; Kumar *et al.* 2008). They also have increased the biogeochemical cycling of toxic heavy metals. This has resulted in a significant deposition of heavy metals into natural aquatic and terrestrial ecosystems (Senthilkumaar *et al.* 2000; Abou Zeid *et al.* 2009). As heavy metals cannot be degraded, they are deposited, assimilated, or incorporated in water, sediment, and aquatic ecosystems' thus causing heavy metal pollution in water bodies. Therefore, heavy metals can be bioaccumulated and biomagnified via the food chain, and finally be assimilated by human consumers, resulting in health risks (Abdel-Baki *et al.* 2011). Exposure to heavy metals causes different adverse effects including growth inhibition, cancer, organ damage, nervous system damage, and, in the extreme case,

death. The metals of most immediate concern are Cr, Mn, Fe, Cu, Zn, Hg, Pb, and Cd, which are toxic even at low concentrations (Akpör & Muchiem 2010).

The development and implementation of cost-effective processes for the removal of metals and the detoxification of metal-contaminated wastewaters is essential to improve the competitiveness of industrial processes and to minimize the environmental hazard of toxic metal-containing effluents (Volesky & Naja 2007). However, the removal of heavy metals is a major consideration for all environmental protection agencies. The economic consideration of treatment based on volume, concentration of metals, and salinity and characteristics of wastewaters makes it impossible to use conventional technologies such as precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, cementation, coagulation, flocculation, electrochemical treatment, membrane processes, and evaporation (Ahn *et al.* 2009; Patrón-Prado *et al.* 2010). Most of these methods are too expensive or

incapable of meeting treatment objectives (Zayat & Smith 2010). The precipitation method is used in most electroplating industries, ending up with the loss of valuable resources, and consequently dumping the resources at landfills. Membrane separation processes are quite promising for commercial applications. The application of high-pressure membrane operation, i.e. reverse osmosis, is limited to wastewater treatment due to the high pressure requirement and low water permeability. Microfiltration and ultrafiltration, on the other hand, have a low rejection potential (Muthukrishnan & Guha 2006). Adsorption on activated carbon is a recognized method for the removal of heavy metals from wastewater; however, the high cost of activated carbon limits its application. Conventional methods for removing heavy metals suffer from a few major disadvantages such as high energy consumption, incomplete metal removal, and the generation of toxic sludge which needs proper disposal, in addition to financial constraints (Yan & Viraraghavan 2001; Hawari & Mulligan 2006; Zafar *et al.* 2007; Li *et al.* 2008).

The search for low-cost and easily available adsorbents has led to the investigation of materials of agricultural and biological origin as potential metal sorbents. The application of biological resources for the metal removal, defined as biosorption, has been recommended as a simple, economic, efficient, and environmentally friendly technique. The low cost and the relatively higher efficiency of metal removal from diluted solutions are among the main advantages of biosorption (Javanbakht *et al.* 2011). The process features a high selectivity and cost-effectiveness for low metal concentrations, compared to the common methods, even in drinking water treatment (Hasan *et al.* 2010; Hasan *et al.* 2012). Also, there would be no hazardous sludge by-product and biosorbents can be easily regenerated for multiple reuses (Volesky 2001; Diniz *et al.* 2008). The biosorption process represents an effective sequestration of organic or inorganic pollutants by certain types of biomasses. For practical application considerations, it is important to select either naturally abundant biomass types or industrial biomass wastes, especially from fermentation or seaweed processing plants. Using biomass for adsorption and removal of heavy metals can have revenue for industries presently wasting the biomass. Moreover, the biomass can be grown using simple fermentation methods and inexpensive growth media. Also, in the case where using waste biomass is not a priority from the economical point of view, the microbial cultures and growth can be amenable to genetic and morphological manipulations which may result in better adsorbent material (Wang & Chen 2009).

Microorganisms including bacteria, algae, fungi, and yeast have been found to be capable of efficiently accumulating heavy metals in both living and dead states. The performance of living biomass in binding metal ions depends not only on the nutrient and environmental status, but also on the cell age. In addition, living cells are subject to the toxic effect of heavy metals that can reach a certain level and can result in cell death (Yan & Viraraghavan 2000). There are many advantages in using non-viable biomasses. There is no need for maintenance and nutrition; there is no toxic effect on microorganisms and their sorption capacity; the biosorbents can be stored for long periods of time without any adverse effect on their performance; and finally, no metabolic toxin is released that would endanger the public (Zhou 1999). However, the fate of residual biosorbent in fact remains relatively unanswered. Different techniques such as precipitation and electrowinning have been applied to recover metals from concentrated solution. However, the final disposal of these materials should also be addressed properly, because some procedures like landfill or incineration have their technical or environmental problems (Das *et al.* 2008). Environmental factors that may influence the metal-binding capacity of microorganisms include temperature, type and concentration and oxidation state of metal, composition and pH of wastewater, type of microorganisms and mechanism of metal removal, concentration of biosorbent and metal co-ions, both cationic and anionic, simultaneous presence of inorganic and organic components, and presence of dissolved and volatile species, colloids, emulsions, and particles (Eccles 1999; Zouboulis *et al.* 1999; Gadd 2001; Kulbat *et al.* 2003).

Kinetic studies yield more accurate information on sorbate uptake rates. Rapid sorption reactions are usually not the rate-controlling step in the biosorption process. It has been widely recognized and confirmed that it is actually the intraparticle mass transfer rate which represents the bottleneck and is thus controlling the rate of the entire sorption process. The particle size and its structures are thus very important (Volesky 2001). Models have been developed to determine both the number of adsorption sites required to bind each metal ion and the rate of adsorption, using a batch reactor mass balance and the Langmuir theory of adsorption to surfaces or continuous dynamic systems (Gavrilescu 2004).

The aim of this paper is to review different mechanisms involved in biosorption of heavy metals using microorganisms as biosorbent. Recent studies have increased our understanding of the underlying mechanisms followed in this research. Understanding the mechanism by which

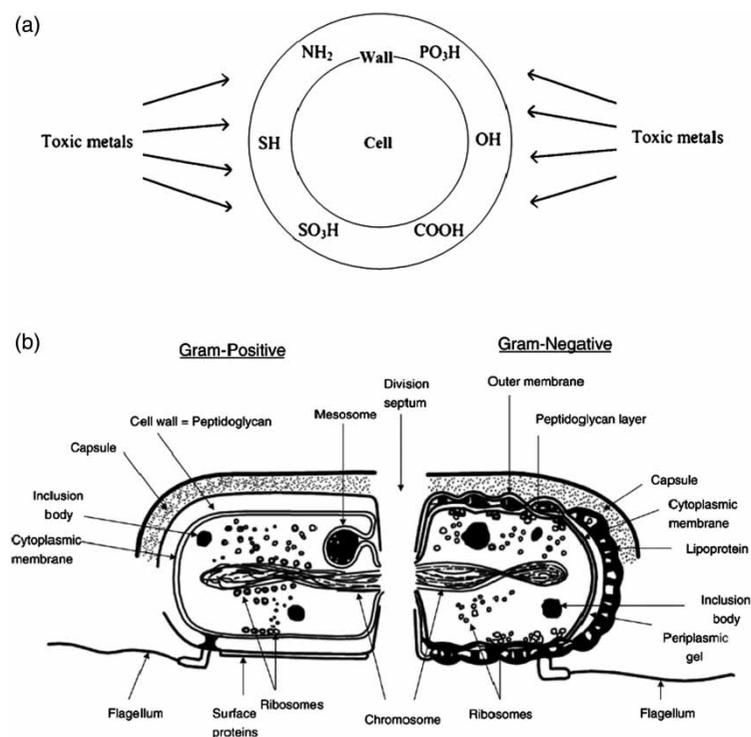
microorganisms accumulate metals is crucial to the development of microbial processes for concentration, removal and recovery of metals from the aqueous solutions (Ahluwalia & Goyal 2007). It also helps to improve biosorbents in order to increase the process efficiency using both biosorbent materials and process conditions.

## PARAMETERS INFLUENCING BIOSORPTION

Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption–complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation, and surface adsorption. It is a recognized fact that a combination of several mechanisms, each functioning independently, contributes to the overall metal uptake (Brown *et al.* 2000). Metal biosorption is rather a complex process affected by several factors. The status of biomass (living or non-living), types of biomaterials, chemistry or chemical properties of metal solution, and ambient/environmental conditions such as pH and temperature influence the mechanism of metal biosorption (Das *et al.* 2008). On the other hand, pH affects the selectivity of biomass and binds a variety of metals. While binding sites

remain different at different pH levels, it is necessary to identify which functional groups are participating in metal binding in order to understand the mechanisms involved. Most of these groups have been found in cell wall (Brown *et al.* 2000; Demirbas 2008). Thus, a detailed investigation of chemical structures of microbial cells is necessary in order to understand the mechanism of interaction (Kumar *et al.* 2010). Also, the actual nature of association between the charged surface and the counter-ions depends on the mechanism of retention of the counter-ions with the surface, i.e., the extent of adsorption depends on either the respective charges on the adsorbing surface and the metallic cation or the intrinsic formation constants of the complexation reactions (Al-Hamdan & Reddy 2006).

Chemical modification and spectroscopic studies have shown that the cellular components including carboxyl, hydroxyl, sulfate, sulfhydryl (thiol), phosphate, amino, amide, imine, thioether, phenol, carbonyl (ketone), imidazole, phosphonate, and phosphodiester have potentials and properties of metal binding (Figure 1) that can act as the functional groups in biomass (Gardea-Torresdey *et al.* 2004). In fact, most microbial surfaces are negatively charged because of the ionization of the functional groups, thus contributing to metal binding (Yan & Viraraghavan 2003).



**Figure 1** | (a) A schematic of metal binding by functional groups on the cell wall of biomass. (b) Cell wall structure in bacteria (reprinted from Vijayaraghavan & Yun (2008) with permission from Elsevier).

## Microbial biomass as biosorbent

Both living and dead biomasses can accumulate heavy metals by a variety of mechanisms and practical potentials. Dead biomass has more advantages than living material as the former can be obtained inexpensively as waste, is not subjected to metal toxicity or adverse operating conditions, and is not dependent on nutrition supply. Table 1 reviews some studies on biosorption of different heavy metals and compares the performance of living and dead biomasses. On the other hand, biosorption represents the sum of all passive interactions of the cell wall with metal ions, including adsorption reactions, ion exchange reactions with functional groups at the cell surface, and surface complexation reactions (Sahmoune & Louhab 2010).

Based on the dependence on metabolism, biosorption mechanisms can be divided into metabolism-dependent

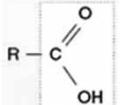
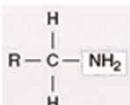
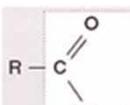
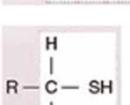
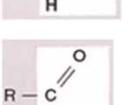
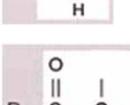
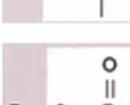
and metabolism-independent mechanisms. Depending on the location where the metal removal from solution happens, biosorption can be classified as extracellular accumulation/precipitation, cell surface adsorption/precipitation, and intracellular accumulation. Transport of the metal across the cell membrane, which results in intracellular accumulation, is dependent on the cell metabolism. This type of biosorption may take place only with viable cells, which are often associated with an active defence system of microorganisms (Ahalya et al. 2003; Ahluwalia & Goyal 2007).

Metabolism-independent biosorption using dead biomasses is the result of physicochemical interaction between the metal and the functional groups present on the microbial cell surface. This type of biosorption is relatively rapid and usually reversible. Some typical mechanisms are physical adsorption, ion exchange, and chemical sorption, which are

**Table 1** | Comparison of live and dead biomass for removal of different heavy metals

Type of biomass	Heavy metal	Initial concentration (ppm)	PH	Removal efficiency (% or mg/g unless)		Reference
				Live biomass	Dead biomass	
<i>Bacillus sphaericus</i>	Cu(II)	5	7	63.25%	82.2%	Al-Daghistani (2012)
	Ni(II)	5	7	52.7%	59.46%	
	Cr(VI)	5	7	66.6%	76.5%	
<i>Chlamydomonas reinhardtii</i> (Alga)	Pb(II)	200	6	8%	40%	Flouty & Estephane (2012)
	Cu(II)	200	6	28%	55%	
<i>Tetraselmis suecica</i> (Alga)	Cd(II)	6	7.8	23.08% (24 h) 56.04% (72 h)	76.92% (24 h) 56.04% (72 h)	Pérez-Rama et al. (2010)
<i>Streptomyces ciscaucasicus</i>	Zn(II)	150		57%	73%	Li et al. (2010)
<i>Fusarium</i> spp.	Zn(II)	80	6	18%	12%	Velmurugan et al. (2010)
<i>Bacillus cereus</i>	Cr(VI)	100	2	86.79%	89.87%	Sultan et al. (2012)
<i>Bacillus pumilis</i>	Cr(VI)	100	2	87.79%	89.23%	Sultan et al. (2012)
<i>Pantoea agglomerans</i>	Cr(VI)	100	3	83.64%	85.5%	Sultan et al. (2012)
<i>Mucor rouxii</i> (treated with NaOH)	Pb(II)	10	5	35.69	25.22	Yan & Viraraghavan (2003)
	Zn(II)	10	5	11.09	16.62	
	Cd(II)	10	5	8.46	8.36	
	Ni(II)	10	5	7.75	6.34	
<i>Aspergillus niger</i>	Pb(II)	100	7	79.4%	28.9%	Awofolu et al. (2006)
<i>Penicillium austurianum</i>	Pb(II)	100	7	75.57%	98.85%	Awofolu et al. (2006)
Ureolytic mixed culture	Ni(II)	100	6	17%	13%	Isik (2008)
<i>Saccharomyces cerevisiae</i>	Pb(II)	100	7	61.2%	88.68%	Awofolu et al. (2006)
<i>Mucor arcindloides</i>	Pb(II)	100	7	62.91%	93.13%	Awofolu et al. (2006)
Anaerobic mixed culture biomass	Pb(II)			35	51.56	Sulaymon et al. (2012)
		50	4			
		50	4	13.6	29	
		50	4			
<i>Trichoderma reesi</i>	Pb(II)	100	7	35.31%	80.7%	Awofolu et al. (2006)

**Table 2** | Some identified and studied functional groups related to the biosorption of heavy metals (Symbol R represents an alkyl radical such as CH<sub>2</sub>–, CH<sub>3</sub>CH<sub>2</sub>–) (Wang & Chen 2009)

Formula of functional group	Name	Class of compounds
	Hydroxyl	Alcohols, carbohydrates
	Carboxyl	Fatty acids, proteins, organic acids
	Amino	Proteins, nucleic acids
	Ester	Lipids
	Sulfhydryl	Cysteine (amino acid), proteins
	Carbonyl (terminal end)	Aldehydes, polysaccharides
	Carbonyl (internal)	Ketones, polysaccharides
	Phosphate	DNA, RNA, tissue plasminogen activator

not dependent on cell metabolism. *Tay et al. (2010)* found that chemisorption contributes to the mechanism of copper(II) biosorption to a large extent. Microbial cell walls, mainly composed of polysaccharides, proteins, and lipids such as glucans, chitin, mannans, and phospho-mannans, have abundant metal-binding groups such as carboxyl, sulfate, phosphate, and amino groups. These ligands are known to be involved in metal chelation (*Ahalya et al. 2003; Ahluwalia & Goyal 2007*). Some functional groups related to the biosorption are illustrated in *Table 2*.

### Functional groups on the surface of microorganisms

There is some evidence to confirm that the O–, N–, S–, or P–containing groups directly participate in binding a certain metal. Some active sites, involved in the metal uptake, have been identified using different techniques. Examples are titration, infrared and Raman spectroscopy, electron dispersive spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy, nuclear magnetic resonance, X-ray diffraction analysis, and X-ray absorption fine structure spectroscopy (*Wang & Chen 2009*). *Table 3* summarizes different techniques which have been applied to identify functional groups dominant in biosorption of heavy metals.

The information obtained from Fourier transform infrared (FTIR) spectral data by *Zvinowanda et al. (2010)* has shown that –OH and possibly –NH<sub>2</sub> groups were present on the surface of *Zea mays* tassel powder and might be responsible for the uptake of Pb(II) ions on the tassel. These functional groups are known to act as very active ligands, and therefore tend to bind readily with metal ions. FTIR studies have also indicated the involvement of carboxyl, hydroxyl, and amine groups present on the biomass surface of

**Table 3** | Some studies identifying functional groups related to the biosorption of heavy metals

Technique	Metal	Biosorbent	Functional group	Author
FTIR	Pb(II)	<i>Zea mays</i> tassel	–OH, –NH <sub>2</sub>	<i>Zvinowanda et al. (2010)</i>
FTIR	Pb(II)	<i>Aeromonas hydrophila</i>	Carboxyl, hydroxyl, amine	<i>Hasan et al. (2009)</i>
AFM, FTIR, SEM-EDX, SEM	Cu(II)	<i>Mucor rouxii</i>	Amino, carboxyl, phosphate	<i>Shraboni et al. (2008)</i>
FTIR	As(V)	Acid-washed crab shells	Amide	<i>Niu et al. (2007)</i>
FTIR, SEM, EDAX	Zn(II)	<i>Botrytis cinerea</i>	–OH, –NH	<i>Tunali &amp; Akar (2006)</i>
Infrared spectra	Fe(III)	<i>Cicer arientinum</i>	Hydroxyl, carboxyl, amide	<i>Ahalya et al. (2006)</i>
IR analysis	Pb(II)	<i>Streptomyces rimosus</i>	–COO, –C–O, –NH, –C = O, –OH	<i>Selatnia et al. (2004)</i>

FTIR: Fourier transform infrared; AFM: atomic force microscopy; SEM-EDX: scanning electron microscopy–energy dispersive X-ray spectroscopy; EDAX: energy-dispersive X-ray spectroscopy; IR: infrared.

*Aeromonas hydrophila* in the sorption of Pb(II) (Hasan *et al.* 2009). In order to understand the interaction of copper ions with *Mucor rouxii* biomass, an AFM study was carried out by Shraboni *et al.* (2008). It was revealed from the FTIR and SEM-EDX study and blocking experiments that amino, carboxyl, and phosphate groups, present on the cell surface of the biomass, are involved in chemical interaction with copper ions. Both SEM and AFM micrographs have revealed the formation of a metal nanostructure on the biomass surface due to copper adsorption. Biomass surface modification has indicated the major involvement of an amino functional group for binding, probably through chelation (Majumdar *et al.* 2008). Niu *et al.* (2007) concluded that arsenic biosorption was mainly through arsenate binding on the amide groups in acid-washed crab shells (AWCS). Because the dense structure of AWCS and its low swelling extent prevent arsenic species from accessing all functional groups available on the AWCS, further arsenic uptake improvement may be possible by modifying the structure of the AWCS. The cell wall of dead bacterial *Streptomyces rimosus* biomass contains anionic groups such as  $-\text{COO}^-$ ,  $-\text{C}-\text{O}^-$ ,  $-\text{NH}_2$ ,  $-\text{C}=\text{O}$  and  $-\text{OH}$  whose adsorbent ability towards  $\text{Pb}^{2+}$  ions was obtained to be fairly high (Selatnia *et al.* 2004). The interactions between Zn(II) ions and functional groups such as  $-\text{OH}$  and  $-\text{NH}_2$  on the cell wall surface of the fungal *Botrytis cinerea* biomass were confirmed by FTIR, SEM, and EDAX analysis (Tunali & Akar 2006). Both *Aspergillus niger* and *Mucor rouxii* species contain chitin and chitosan, which provide prominent metal adsorption ability, in such a way that the wall of *A. niger* is in the chitin-glucan group and the wall of *M. rouxii* is in the chitosan-chitin group (Lo *et al.* 1999). The infrared spectra of *Cicer arietinum*, before and after treatment with Fe(III), has revealed that hydroxyl, carboxyl, and amide bonds are involved in the uptake of Fe(III) ions (Ahalya *et al.* 2006).

## MECHANISMS OF METAL UPTAKE

### Physical adsorption

The phenomenon through which ions are transferred from a liquid phase to a solid phase usually involves the following three steps: (i) boundary layer mass transfer across the liquid film surrounding the particle; (ii) internal diffusion/mass transport within the particle boundary as pore and/or solid diffusion; and (iii) adsorption within the particle and on the external surface (Poots *et al.* 1976). According to Allard *et al.* (1987), there are two further pathways by which

sorption may occur on the surface: (i) physical adsorption, which is rapid and reversible and is due to the non-specific attraction forces (e.g. Van der Waals forces); and (ii) electrostatic adsorption due to the coulombic attraction forces between charged solute species and adsorbing phase, which is usually rapid and largely reversible (Won *et al.* 2008; Sahmoune & Louhab 2010; Sutherland & Venkobachar 2010). Kuyucak & Volesky (1988) showed that biosorption of uranium, cadmium, zinc, copper, and cobalt by dead biomasses of algae, fungi, and yeasts takes place through electrostatic interactions between metal ions in solutions and microbial cell walls. The electrostatic interactions have been found to be responsible for copper biosorption by bacterium *Zoogloea ramigera* and alga *Chlorella vulgaris* and also for chromium biosorption by fungi *Ganoderma lucidum* and *Aspergillus niger* (Ahalya *et al.* 2003).

### Transport across microbial cell wall

Different cations can be shifted into cells by diffusion across the cell wall. Cell membrane permeability would greatly influence the cations' uptake (Mane *et al.* 2011). Transport of heavy metals across microbial cell membranes, known as intracellular accumulation, may be mediated by the same mechanism used to convey metabolically important ions such as potassium, magnesium, and sodium. Cation transport systems may become confused by the presence of heavy metal ions of the same charge and ionic radius associated with essential ions. This kind of mechanism is not associated with metabolic activity. Basically, biosorption by living organisms consists of two steps: first, a metabolism-independent binding, where metals are bound to the cell walls; and second, metabolism-dependent intracellular uptake, where metal ions are transported across the cell membrane (Sag & Kutsal 2001). Price *et al.* (2001) found that the mechanism of copper removal by *Aspergillus niger* is mainly due to an active metabolic process leading to internal absorption of the metal. Metal accumulation inside the cell may result from bioaccumulation, a slow metabolic-dependent removal mechanism (Hamza *et al.* 2010). The adsorption and accumulation mechanism of macrophytes can clean a water body of heavy metal contamination (Mane *et al.* 2011).

### Ion exchange

Polysaccharide is one of the main constituents of the cell wall of microorganisms in which bivalent metal ions are

exchanged with counter ions of polysaccharides. Ion-exchange is an important concept in biosorption, because it explains many observations made during heavy metal uptake experiments (Tables 3 and 4). The term ion exchange does not explicitly identify the mechanism of heavy metal binding to biomass, because the precise mechanism(s) may range from physical binding (i.e. electrostatic or London–van der Waals forces) to chemical binding (i.e. ionic and covalent) (Uluozlu *et al.* 2008; Li *et al.* 2009). Biosorption of Pb(II) and Cd(II) on *A. rubescens* and *L. scrobiculatus* biomasses took place due to chemical ion exchange (Anayurt *et al.* 2009; Sar & Tuzen 2009).

The term sorption refers to the binding of a metal cation to a free site as opposed to that previously occupied by another cation. Higher biosorbent dosages resulted in a higher removal of Cd(II) and Pb(II) due to good availability of sorption sites and exchanging ions (Vimala & Das 2009). The relevance of electrostatic attraction to biosorption depends on the types and amount of sites present in the biomass and whether they are ionized or occupied by protons or other ions. That, in turn, depends on the pH and the  $pK_a$  of the respective group. Amine groups are positively charged in their protonated form and neutral when they are deprotonated. Carboxyl, sulfate, and phosphate groups are neutral when they are protonated, and are negatively charged when they are deprotonated (Naja *et al.* 2009).

The alkaline treatment is expected to remove proteins from the biomass and to contribute to deacetylate chitin-based material present in the cell wall of these microorganisms. The alcohol treatment does not contribute to the reinforcement of accessibility and availability of sorption sites and solely induces denaturing of protein fractions. Decreasing the pH of metal solution during sorption, when the initial pH was in a certain range, indicates that protons are released during metal uptake, revealing a mechanism of ion exchange on carboxylic functions (Svecova *et al.* 2006). Verma *et al.* has indicated that during metal sorption on biomasses of *Eichhornia crassipes*, *Vallisneria spiralis* and *Pistia stratiotes*, there is a strong ionic balance between adsorbed acidic agent ( $H^+$ ) and metal ions ( $M^{2+}$ ) onto the biomass compared to released ions ( $Na^+$  and  $K^+$ ) from the biomass. Further, the adsorption of targeted metal ions from multi-metal solution remains unaffected in the presence of other metal ions, helping to explain the metal adsorption mechanism, i.e., ion exchange from a multi metal system such as industrial wastewater (Verma *et al.* 2008). Tables 5 and 6 summarize the influence of different types of pretreatment on the surface characteristics and biosorption behaviour of algae and fungi, respectively.

Surface modification of biosorbent has been used as a new technique to use natural and raw sources of sorbents to improve their adsorption capacity and selectivity. This modification has been continued, in recent years, by combination of the surface properties of biomass with advanced technologies such as nanomagnetite, reactive nanoparticles and photocatalysts.

The technique of SEM, coupled with X-ray dispersion analysis, has shown that  $Pb^{2+}$  has exchanged with  $K^+$  and  $Ca^{2+}$  on the cell wall of *Mucor rouxii*, thereby suggesting ion exchange as one of the dominant mechanisms of metal biosorption for this fungal strain. Both *Aspergillus* and *Mucor* species contain chitin and chitosan, which provide prominent metal adsorption ability (Lo *et al.* 1999). Using measurement of pH in the wastewater effluent with protonated biomass and metal ions in the effluent of the biosorption process, the main mechanism of uranium biosorption by *Cystoseira indica* biomass was investigated, similar to that by Ghasemi *et al.* (2011). Monitoring pH in the effluent of the biosorption process presented the simultaneous release of  $H^+$  and the uptake of heavy metals. Hence, ion exchange was confirmed to be one of the main biosorption mechanisms (Ghasemi *et al.* 2011).

## Complexation

The metal removal from solution may also take place by a complex formation on the cell surface after the interaction between metal and the active groups on the cell wall. Some of these groups are carboxyl, amino, thiol, hydroxy, phosphate, and hydroxy-carboxyl that can interact in a coordinated way with heavy metal ions (Sag & Kutsal 2001). Complexation plays an important role in metal–ligand and sorbate–sorbent interactions (Table 4). A complex compound is a poly-atomic molecule that consists of one or several central atoms (usually metal cations) surrounded by and attached to ligands (other atoms or groups, usually of negative or neutral charges). Complex compounds can be neutral, or positively or negatively charged. The number of coordinating atoms (in the ligands) directly attached to the central atom is called the *coordination number* and can be larger than the valence of the central atom (most common coordination numbers are 4 and 6, but 2 and 8 also occur frequently). If one ligand is attached to the central atom through two or more coordinating atoms, the complex is called chelate (Naja *et al.* 2009). Complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper, and mercury accumulation by *Pseudomonas syringae*.

**Table 4** | The dominant mechanism presented in biosorption of heavy metals using different types of biomass and identified functional groups

Biomass	Heavy metal	Functional group	Mechanism	Reference
<i>Spirulina</i> sp.	Cr(III), Cd(II) Cu(II)	Carboxyl, hydroxyl, phosphate group	Physical adsorption, ion exchange	Chojnacka <i>et al.</i> (2005)
<i>Yarrowia lipolytica</i>	Ni(II)	Hydroxyl, carboxyl, carbonyl and amino groups	Ion exchange	Shinde <i>et al.</i> (2012)
Acidophilic bacterium	Cd(II)	Amine, carboxyl and hydroxyl groups	Electrostatic reaction and complex formation	Chakravarty & Banerjee (2012)
<i>Mesorhizobium amorphae</i> CCNWGS0123	Cu(II)	O–H, N–H, C–H, C = O, –NH, –CN, C–N, C–O, amide–I, –II, –III	Precipitation	Mohamad <i>et al.</i> (2012)
<i>Pseudomonas plecoglossicida</i>	Cd(II)	–NH, –OH, –CH, and –CONH	Ionic exchange, electrostatic interaction	Guo <i>et al.</i> (2012)
<i>Cyanobacteria microcystis</i>	Antimony(III)	Carboxyl, hydroxyl and amino groups	Complexation	Wu <i>et al.</i> (2012)
Pretreated <i>Rhizopus arrhizus</i>	Cr(VI)	Amino and carboxyl groups	Electrostatic attraction	Shroff & Vaidya (2012)
Inactivated fungal biomass	Hexavalent chromium	Carboxyl, phosphates, sulfhydryl, amines	Physical adsorption, ion exchange, complexation and electrostatic attraction	Ramrakhiani <i>et al.</i> (2011)
Alkali-modified sewage sludge	Cd(II)	Carboxyl group, hydroxyl group	Ion exchange, electrostatic attraction and complexation	Hu <i>et al.</i> (2012)
Aerobic granules and bacterial alginate	Pb(II)	Carboxyl (–COO–)	Ion exchange	Wang & Li (2012)
Fruiting body of jelly fungus	Cd(II), Cu(II) Pb(II)	Carboxyl, amine/hydroxyl, amino, phosphoryl, and C–N–C	Ion exchange and surface complexation	Huang <i>et al.</i> (2012)
Xanthate-modified magnetic chitosan	Pb(II), Cu(II) Zn(II)	Thiol amino group	Complexation	Zhu <i>et al.</i> (2012)
Magnetic PS-EDTA resin	Cr(VI)	Primary amine, secondary amine	Chelating electrostatic interaction	Mao <i>et al.</i> (2012)
<i>Cyanobacteria Microcystis</i>	Antimony(III)	Carboxyl, hydroxyl and amino groups	Complexation	Sun <i>et al.</i> (2011)
Barley straw	Cu(II), Pb(II)	Carboxylic, hydroxyl	Ion exchange, complexation	Pehlivan <i>et al.</i> (2012)
Rice straw	Aquatic Cd(II)	Carboxyl, hydroxyl, c = c	Ion exchange, chelation	Ding <i>et al.</i> (2012)
Green tomato husk	Fe(II), manganese	Carboxylic acid, phenolic groups	Ion exchange, complexation, precipitation	Garcia Mendieta <i>et al.</i> (2012)
Raw and treated agave bagasse	Cd(II), Pb(II) Zn(II)	Carboxylic groups	Ion exchange, complexation	Velazquez-Jimenez <i>et al.</i> (2013)
Soybean	Cr(III), Cu(II)	Carboxyl, hydroxyl	Ion exchange, chelation, precipitation	Witek-Krowiak & Kumar Reddy (2013)
Date pits/tea-waste	Cr(VI)	–COOH, –NH <sub>2</sub> , O–CH <sub>3</sub>	Complexation	Albadarin <i>et al.</i> (2013)
Watermelon rind	Cu, Zn, Pb	Amine groups, carboxyl (–COO–)	Ion exchange and micro-precipitation	Liu <i>et al.</i> (2012)

**Table 5** | Influence of pretreatment and surface modification on biosorption behaviour of different algal biomass

Algae	Pretreatment	Effect	Metal ion	Reference
<i>Laminaria japonica</i>	Epichlorohydrin	Improves the surface characteristics of algae by cross linking	Cd Cu Ni	Luo <i>et al.</i> (2006)
<i>Oedogonium hatei</i>	HCl	Acid pretreatment can cause degradation of cellular compounds such as cell wall, proteins, and complex organic components of biomass	Ni	Gupta <i>et al.</i> (2010)
<i>Durvillaea potatorum</i>	CaCl <sub>2</sub>	Prevents leaching of alginate from the biomass and increases the stability of the biosorbent material	Cu Pb	Matheickal & Yu (1999)
<i>Cystoseira indica</i>	Formaldehyde Glutaraldehyde CaCl <sub>2</sub>	Prevents leaching of adsorptive components from biomass and increases the stability of the biosorbent material	Cd Ni Pb	Montazer-Rahmati <i>et al.</i> (2011)
<i>Padina australis</i>	Ferro cyanide Algal Sorbent type 1 (FASs1) Ferro cyanide Algal Sorbent type 2 (FASs2)	As selective ion exchanger	Cs	Jalali Rad <i>et al.</i> (2004)
<i>Sargassum glaucescens</i>	Polyethylene imine	Well known for its metal-chelating characteristic, and increases the adsorption capacity	Cd Ni Pb	Montazer-Rahmati <i>et al.</i> (2011)

**Table 6** | Influence of pretreatment and surface modification on biosorption behaviour of different fungal biomass

Fungi	Pretreatment	Effect	Metal ion	Reference
<i>Aspergillus niger</i>	NaOH	Improved metal ion removal was due to the changes in sorptive characteristics of the biomass	Pb Cu Cd	Kapoor <i>et al.</i> (1999)
<i>Aspergillus niger</i>	HCl & H <sub>2</sub> SO <sub>4</sub>	Acids destroyed the absorbing groups and their positive ions (H <sup>+</sup> ) may have covalently bonded to the absorbing surfaces	Cu Ni Cr	Javaid <i>et al.</i> (2011)
<i>Termitomyces clypeatus</i>	CaCl <sub>2</sub>	Calcium stabilized the biomass, causing the precipitation of inorganic substances present in the mycelium	Cr(VI)	Ramrakhiani <i>et al.</i> (2011)
<i>Penicillium verrucosum</i>	Glutaraldehyde	Cross-linking reagent with functional groups and increase biosorption	Pb Cd	Cabuk <i>et al.</i> (2005)
Tea fungus	FeCl <sub>3</sub>	Iron has an affinity towards arsenic-iron oxide	As(V)	Murugesan <i>et al.</i> (2006)

Microorganisms may also produce organic acids (e.g., citric, oxalic, gluconic, fumaric, lactic, and malic acids) which chelate toxic metals and cause the formation of metallo-organic molecules. These organic acids help with the solubilization of metal compounds and their leaching from their surfaces. Metals may become more complex by carboxyl groups found in microbial polysaccharides and other polymers (Ahalya *et al.* 2003).

Metal sequestration can be viewed as complexation (or coordination) of a central heavy metal to a multidentate ligand present on the surface of an alga, which can be treated as a polyfunctional macromolecule. Binding

of different metal ions on biomaterials with different functional groups depends on ionic properties such as electronegativity, ionization potential, ionic radius, and redox potential of the metals (Allen & Brown 1995). According to the final pH measurements, Sarioglu *et al.* (2009) showed that the main mechanism of copper removal should be the formation of insoluble complexes between Cu<sup>2+</sup> and anionic species such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and OH<sup>-</sup>, which takes place on the surface of biosorbent. The amount of copper adsorption was probably insignificant and the precipitation of copper with biosorbent was the primary removal mechanism.

## Precipitation

Initially, it was thought that, at higher pH values, metals may be accumulated inside the cells or on the cell walls by sorption-precipitation (Venkata et al. 2009). Precipitation may be either dependent on or independent of cellular metabolism (Ahalya et al. 2003). In the former case, the metal removal from solution is often associated with an active defence system of microorganisms. Precipitation, as shown in Table 4, is a result of the reaction between target metal(s) and compound(s) produced by microorganisms as a result of the defence system. For a cellular metabolism-independent precipitation, it may be a consequence of the chemical interaction between the metal and the cell surface (Ahalya et al. 2003). In the case of precipitation, the metal uptake may take place both in the solution and on the cell surface. Further, it may be dependent on cell metabolism if, in the presence of toxic metals, the microorganism produces compounds that favour the precipitation process. Precipitation may be independent of cell metabolism if it occurs after the chemical interaction between the metal and cell surface (Ahalya et al. 2003).

## CONCLUSION

Mechanisms involved in the biosorption process include transport across cell membrane, complexation, ion exchange, precipitation, and physical adsorption. Metabolism-independent metal binding to the cell walls and external surfaces is the only mechanism present in the case of non-living biomass. Metabolism-independent uptake essentially involves adsorption processes such as ionic, chemical and physical adsorption. Most functional groups, responsible for metal binding to the biomass, are found in cell walls. The biosorbent contains a variety of functional sites including carboxyl, imidazole, sulfhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide, and hydroxyl moieties that are responsible for metal adsorption. Therefore, biomass has been found as a natural source containing different functional sites, with the ability for adsorption of metal ions.

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