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REVIEW

A comparative review towards potential of microbial cells for heavy metal removal with emphasis on biosorption and bioaccumulation

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Abstract The threat of heavy metal pollution to environmental health is getting worldwide attention due to their persistence and non-biodegradable nature. Ineffectiveness of various physicochemical methods due to economical and technical constraints resulted in the search for a cost-effective and eco-friendly biological technique for heavy metal removal from the environment. The two effective biotic methods used are biosorption and bioaccumulation. A comparison between these two processes demonstrated that biosorption is a better heavy metal removal process than bioaccumulation. This is due to the intoxication of heavy metal by inhibiting their entry into the microbial cell. Genes and enzymes related to bioremoval process are also discussed. On comparing the removal rate, bacteria are surpassed by algae and fungi. The aim of this review is to understand the biotic processes and to compare their metal removal efficiency.

Keywords Bioaccumulation · Biosorption · Dead/inactive cells · Heavy metals · Living cells · Physicochemical methods

Introduction

Industrialization has improved the living conditions, however has also affected the environment due to the release of large volume of contaminants to it. There are two broad classes of contaminants: organic and inorganic. Organic pollutants, for example industrial solvents, insecticides, pesticides and food processing wastes can be degraded. Whereas, inorganic pollutants such as metals, fertilizers, industrial discharges, etc. are indelible and will be present indefinitely in the environment, which may result in potential accumulation and human exposure via food chain.

According to physiological point of view, metals are categorized into three main categories: (1) essential and non-toxic (e.g. Ca and Mg), (2) essential, but harmful above threshold limit (e.g. Fe, Mn, Zn, Cu, Co, Ni and Mo), and (3) toxic (e.g. Hg and Cd) (Dutton and Fisher 2011). Many metals seem to serve no biologically relevant function, causing damage due to their avidity for the sulfhydryl (–C–SH or –R–SH) groups of proteins, which they block and deactivate (Valls and De Lorenzo 2002). Therefore, it has become indispensable for metal contaminated environment to find an eco-friendly option to clean up and preserve the health of the deteriorating ecosystem.

The demand for environmental protection and removal/recovery of heavy metals has resulted in the application of various methods. Mainly abiotic and biotic methods have been employed for the elimination of heavy metals from the environment. The abiotic methods consist of several conventional processes which are summarized in Table 1. These methods are ineffective in terms of process cost, energy and chemical products consumption, generation of toxic sludge and disposal problems (Wang and Chen 2009).

The disadvantages and complexities of abiotic methods resulted in an alternative technique, which is both economical and efficient. Bioremediation, an inexpensive and socially acceptable biotic method, involves the use of biological materials to deal with heavy metal problems in an environment-friendly manner (Volesky 2001). Biological methods are advantageous due to their low operative

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Table 1 Advantages and disadvantages of physicochemical methods applied for metal recovery (O'Connell et al. 2008)

Method	Advantages	Disadvantages
Chemical precipitation and filtration	Simple	Difficult separation
	Inexpensive	Large amount of sludge production
	Suitable for most metals	Suitable for high metal concentrations
		Disposal problems
Chemical oxidation or reduction	Mineralization	Chemicals required are not universal
		Slow biological system
		Climate sensitive
Electrochemical treatment	No consumption of chemicals	Suitable for high metal concentrations
	Pure metals can be obtained	Expensive
Reverse osmosis	Pure effluent metal recovery for recycle	Requires high pressures
		Membrane scaling
		Expensive
Ion exchange	Effective	Sensitive to particles
	Possibility of pure effluent metal recovery	Less number of metal ions recovery
		Only effective for <10 mg/L
	High regeneration of materials	pH dependent (2–6)
	No sludge disposal required	Pretreatment required
		Expensive resins
Adsorption using active carbon	Suitable for most metals	No regeneration possible
	High efficiency (>99 %)	Performance depends upon adsorbent
		Expensive
Coagulation–flocculation	Good sludge settling	pH dependent (11–11.5)
	Dewatering	Large amount of sludge production
		Only treats metal concentrations <100 or >1000 mg/L
		Large consumption of chemicals
		Expensive
Membrane technologies	Less solid waste produced	Low flow rates
	Less chemical consumption	Recovery decrease with the presence of other metals
	High efficiency (>95 % for single metal)	Expensive

cost, selectivity for specific metal, minimization of the volume of chemical and biological sludge and high efficiency in detoxifying very dilute effluents. Among the different biological methods, biosorption and bioaccumulation have been demonstrated as an economical alternative to conventional methods, possessing good potential for metal removal (Chojnacka 2010). This review emphasizes on the comparison between biosorption and bioaccumulation processes in order to determine the most efficient technique between these two. Their use in wastewater treatment process was also discussed.

Metal removal using biotic methods

The metal removal process using biotic methods involves high affinity biomaterials and solvent containing metal ions. The high affinity of the biomaterials towards metal ions resulted in the interaction, binding in the cell wall and transport across the cell membrane. According to the cells' metabolism, biological processes may be classified into two types (Fig. 1):

- biosorption
- bioaccumulation

Biosorption

It is a quick, independent and metabolically passive process responsible for the selective sequestration of heavy metal ions by dead/inactive biomaterials. It is a simple physicochemical phenomenon resembling to conventional adsorption or ion exchange method. The only difference is the nature of sorbent which in this case is the material of biological origin known as biosorbent. Biosorbents may be viewed as natural ion-exchange materials that primarily

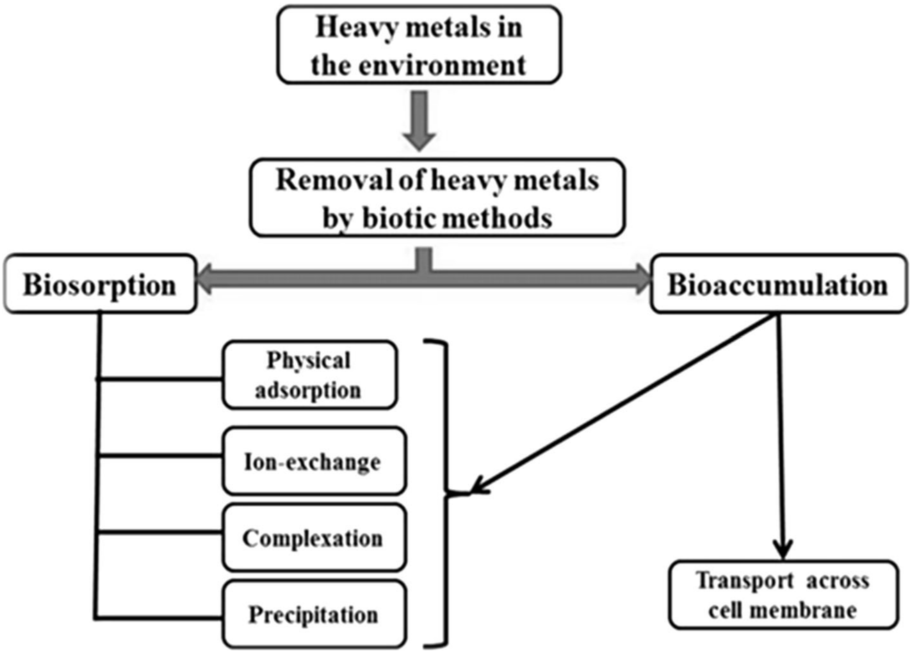

Fig. 1 Classification of biological processes according to cells' metabolism (Veglio and Beolchini 1997)

contain weakly acidic and basic groups, the chelation process being unspecific. These are the renewable biological materials responsible for the heavy metal removal from environment due to their metal sequestering properties (Wang and Chen 2009). Selection of biosorbent depends on the origin, availability and cost-effectiveness of biomass. They can be collected directly from the environment or specially developed by several modification processes (Dhankhar and Hooda 2011; Vijayaraghavan and Yun 2008).

Biosorbents can be modified physically, chemically or genetically to enhance their biosorptive properties. Physical modification such as heat treatment may results in better biosorption capacity of the biomass by removal of surface impurities and production of active metal binding sites via denaturation of cell wall protein (Cabuk et al. 2005). Khosa and co-workers reported that chemical modification of chicken feathers by esterification of –COOH functional groups have a maximum arsenic uptake of 85–90 % as compared to non-modified chicken feathers (Khosa et al. 2013). Modification offers several advantages including better reusability, high biomass loading and minimal clogging in continuous flow systems, however, care must be taken to avoid mass transfer limitations and additional process costs.

The advantages of an ideal biosorption process includes low cost, short operation time, absence of toxicity limitations, absence of requirements for nutrients, avoidance of sudden death of biomass and easy mathematical modelling of metal uptake by reactors (Ahluwalia and Goyal 2007). Biosorption or passive biosorption also has some disadvantages, such as early saturation and limitation in biological process.

Biosorption mechanism

Biosorption is a rapid mechanism of metal uptake on the cell surface, known as extracellular binding. In this process, metal adheres to surface molecules such as S-layer protein (SLP) (Gerbino et al. 2015). The binding occurs by any one or a combination of the processes includes: physical adsorption, van der Waals forces, ion exchange, complexation or inorganic microprecipitation (Fig. 2) (Srinath et al. 2002).

The first step, physical adsorption is associated with the presence of Van der Waal's forces (Crowell 1966). Ozer and Ozer (2003) reported that Pb(II), Ni(II) and Cr(VI) ions onto *Saccharomyces cerevisiae* is based on physical adsorption and exothermic nature of the reaction. Cell wall is the first component that comes in contact with the metal ions and also acted as a defense against metal toxicity. Therefore, the chemical makeup of the microbial cell wall is an important factor responsible for the adsorption of metal ions on the biomass' surface, which varies among different groups of micro-organisms results in significant difference in the metal binding type.

Cellulose is the major component of algal cell wall. So, the potential binding groups in this class of microbes are carboxylates, amines and imidazoles (Ozer and Ozer 2003). However, chitin and chitosan (contains amino, amido and hydroxyl groups) isolated from fungus has a great potential of heavy metal removal in polluted

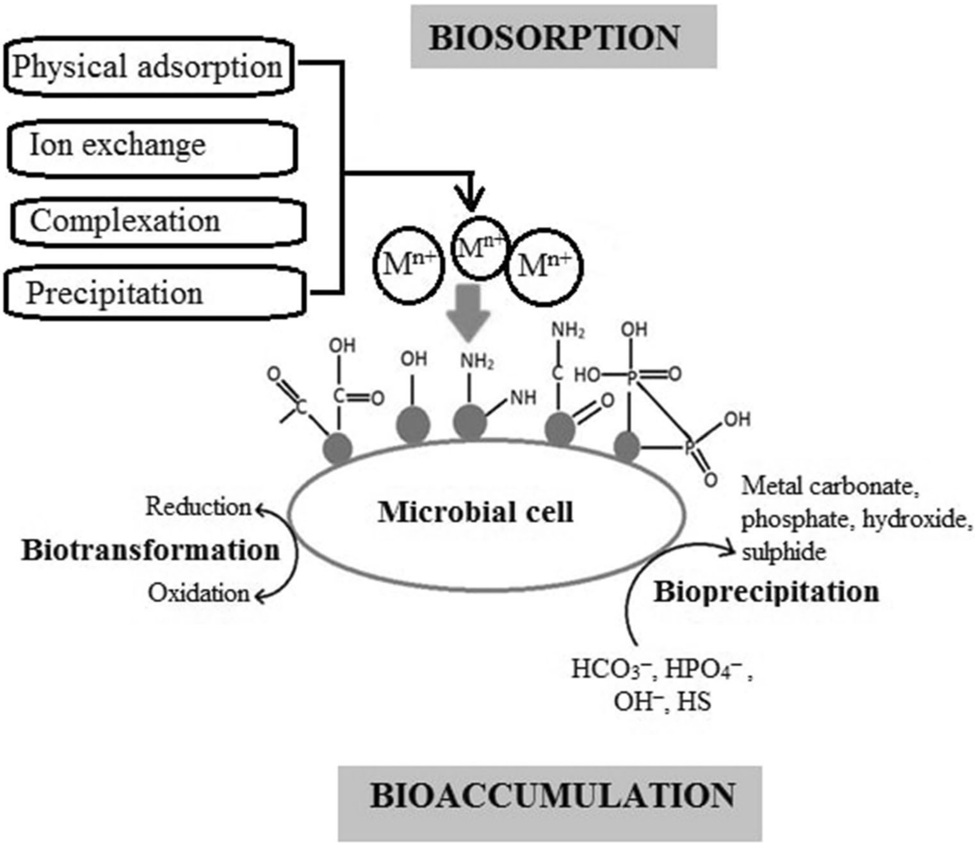

Fig. 2 The mechanism of biosorption and bioaccumulation of a microbial cell (Veglio and Beolchini 1997)

environment (Franco et al. 2004). Bacteria make excellent biosorbents because of their high surface to volume ratios and presence of potentially active chemiosorption sites (teichoic acids) in their cell walls (Beveridge 1989; Vijayaraghavan and Yun 2008). Gram-positive bacterial cell wall has teichoic acids containing phosphoryl and hydroxyl groups, which deprotonate into negative charge in alkaline condition acting as cation adsorption site. In gram-negative bacteria, the phosphate groups within lipopolysaccharides (LPSs) and phospholipids have been demonstrated to be the primary sites for metal interaction (Remacle 1990).

Huang and Liu (2013) and Davis et al. (2003) reported that surface binding is the principle phenomenon for biosorption of metal ions, which occurs due to ion-exchange mechanism of biomass. Ion exchange involves competition between protons and metal cations for the binding sites. Matheickal et al. (1997) reported that dominant mechanism of Cu(II) biosorption by *Ecklonia radiata* is ion exchange mechanism involves exchange of Ca^{2+} and Mg^{2+} ions present in their cell wall.

The metal removal from solution may also take place by complex formation on the cell surface after the interaction between metal cations and active groups present on the cell surface (Han et al. 2006). Gadd and Griffiths (1978) reported that complexation of metals such as copper, cadmium, and zinc is possible with polygalacturonic acid, an important constituent of the outer layers of bacterial cells. Aksu et al. (1992) hypothesized that uptake of Cu(II) by *Chlorella vulgaris* and *Zoogloea ramigera* takes place through both adsorption and formation of coordination bonds between metals and amino (–RNH_2) and carboxyl (–RCOOH) groups of cell wall polysaccharides. Complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and mercury accumulation by *Pseudomonas syringae* (Cabral 1992).

Bioaccumulation

Bioaccumulation is the complex process of metal removal by means of living cells. The process occurs in two steps, the first step is identical with biosorption, is metabolism independent and quick mechanism of metal uptake on the cell surface, known as extracellular binding. The second step is metabolism dependent, relatively slow mechanism responsible for the penetration/transport of metal ions into the cell membrane released from binding sites of the surface and bound to intracellular structures termed as intracellular binding (Chojnacka 2010).

Certain points should be considered for selection of micro-organisms for bioaccumulation process, such as:

- isolation from polluted environment because bioaccumulation by adapted microorganisms is more efficient than by non-adapted microorgainsms (Donmez and Kocberber 2007)
- resistant to high loads of pollutants and do not have mechanisms for protection from excessive accumulation inside the cell and (Donmez and Kocberber 2007)
- presence of mechanism for intracellular binding.

Bioaccumulation is an advantageous process as it does not require separate biomass cultivation or harvesting model. In bioaccumulation, it is possible to reach lower residual concentration of sorbate because cells offer binding sites on the surface and inside the cell. Bioaccumulation processes have some disadvantages, such as the cells' metabolism responsible for the intracellular accumulation may result in interruption to the bioaccumulation process by death of biomass.

Bioaccumulation mechanism

Bioaccumulation is the intracellular uptake of metal ions via ATP-driven active transport and/or via bioprecipitation (release of sulfide or phosphate ions) associated with metabolic functions or biotransformation (oxidation, reduction, methylation and demethylation) (Fig. 2) (Dhankhar and Hooda 2011; Yilmazer and Saracoglu 2009). Bioaccumulation may involve localization of the metal ions within specific organelles; enzymatic detoxification and efflux pump (Srinath et al. 2002). The concentration of the internalized metal is regulated by metal homeostasis system, which involves complexation of ligands and proteins to avoid the reaction of metal ions with biomolecules. Cells form complexation of unwanted metal and sequester it into intracellular organelles for eventual export from the cell by efflux systems. Toxic effects may occur such as deterioration of biomolecules which may change the properties of carriers and the plasma membrane and thus the internalization of the metal. Microorganisms also excrete compounds responsible for complex formation of metal ions in the extracellular medium in order to reduce their bioavailability and bioaccumulation (Hassler et al. 2004).

The first step of bioaccumulation involves biosorption process i.e. binding of metal ions to the functional groups of cell's surface, exchange of ions, complexation, and precipitation. The second step, transport of metals across the cell membrane is dependent on the cells' metabolism associated with active defense system of the microorganisms. Heavy metal transport across microbial cell membranes may be mediated by the same mechanism used to convey metabolically important ions such as potassium, magnesium and sodium. The metal transport systems may become confused by the presence of heavy metal ions of the same charge and ionic radius associated with essential ions.

Bioprecipitation of metals results from the excretion of special proteins (thiol groups rich special proteins or low molecular weight proteins namely metallothioneins and phytochelatins) from living bacteria that chemically reacts with metals present in solution (metal ions) to produce an insoluble metal compounds (hydroxides, carbonates, phosphates and sulfides). The overexpression of metallothioneins in bacterial cells induced by metal stress may result in an enhanced metal binding and sequestration (Bae et al. 2000). Special proteins segregate out the pollutants as complexes, thus restricting them from interfering with the normal metabolic processes (Martin-Gonzalez et al. 2006). Brierley (1990) observed that the enzymatically produced HPO_4^{2-} by *Citrobacter* sp. has been shown to precipitate metals as phosphates. The precipitation of metals with H_2S produced by sulphate reducing bacteria (SRB) has been proposed as an alternative process for the treatment of metal-bearing effluents (Foucher et al. 2001).

Biotransformation of a metal is an important speciation parameter because it can drastically affect its toxicity and mobility. Metals can be transformed via reduction/oxidation or alkylation reactions by microorganisms. For example, many aerobic and anaerobic bacteria reduce Cr(VI) to the less toxic and less soluble Cr(III). Mercuric reductase (the product of the *merA gene*) is responsible for the metal detoxification and enzymatic transformation of mercury (Hg^{2+}) into less toxic and volatile Hg^0 species (Misra 1992).

Factors affecting biosorption and bioaccumulation

The bioremoval of pollutants is a complex process and depends upon several factors, such as, type of biomass, pH, temperature and presence of other competing ions. Therefore, description of the factors affecting biosorption and bioaccumulation processes is important for the optimization of the operating conditions of the biomass (Table 2).

Apart from the factors mentioned in Table 2, there are some other factors affecting biosorption and bioaccumulation, such as ionic strength, contact time, presence of other pollutants and many more. Donmez and Aksu (2002) observed that increase in the ionic strength of the solution reduces the removal of pollutants by competing with the adsorbate for binding sites on the biosorbent. It was found that increasing the concentration of pollutant which is to be accumulated poses changes in morphology and physiology of cells (de Siloniz et al. 2002). By considering various factors, it was observed that biosorption has certain advantages over bioaccumulation. Table 2 demonstrated

Table 2 Factors affecting biosorption and bioaccumulation of microbial cell

Factors	Biosorption	Bioaccumulation	References
Agitation speed	Directly proportional to the biosorption capacity of biosorbents, due to minimization of mass transfer resistance	Directly proportional	Park et al. (2010)
Biomass	Biomass is usually inactive	Live cells are used for this process	Kapoor and Viraraghavan (1995)
Biomass size	Reversible relation with biosorption process	Reversible relation	Park et al. (2010)
Biomass dosage	Reversible relation with biosorption process	Directly proportional with bioaccumulation capacity	Li et al. (2014)
Initial metal ion concentration	Directly proportional to the biosorption capacity of biosorbents, due to the elevated surface area of the biosorbent, which in turn increases the number of binding sites	Inversely proportional to bioaccumulation process	Li et al. (2014)
Nutrient	Not required due to presence of dead/inactive biomass	Directly proportional to bioaccumulation process	Aksu and Donmez (2005)
Other pollutant concentration	Inversely proportional to the biosorption capacity of biosorbents, due to complex formation with other pollutants	Inversely proportional	Li et al. (2010)
pH	Directly proportional to biosorption process. However, the process can be operated under a wide range of pH conditions	The living cells are strongly affected under extreme pH conditions during metal uptake	Park et al. (2010)
Temperature	Not influenced as the biomass is inactive	Severely affected due to active biomass	Veglio and Beolchini (1997)
Time	Directly proportional to biosorption activity	Directly proportional to bioaccumulation activity	Li et al. (2014)

that there are several factors which affect the extraction efficiency of bioremoval processes. Optimization of these factors can improve the efficiency of the process.

Comparison between biosorption and bioaccumulation

An efficient biological process is necessary not only to detoxify metal-bearing effluents but also to recover metal ions for recycling back to the consumers for its reuse. The main attraction of biosorption is the potential ability to regenerate the biomass, through the process called desorption. It can influence the price of the whole process and the possibility of metal recovering from liquid phase as well, which is very important for practical use of the process.

It is possible to remove ions from cell surfaces after biosorption by simple non-destructive methods, but in bioaccumulation, the metal ions can only be removed by destructive methods like incineration or dissolution into strong acids or alkalis. This is due to the toxicity of metal ions towards biomass, resulting in a drop in the metal removal capacity of the biomass following regeneration (Vijayaraghavan and Yun 2008). For this reason, the choice between living or dead biomass systems is important for later metal recovery. In contrast, extracellular precipitation of metals makes it easier to harvest the metals by collecting the insoluble metal precipitates.

Biosorption and bioaccumulation are considered as the potential methods for heavy metal removal. Both these processes take place by means of biological materials; however there are several differences in their features (Table 3) and factors affecting their bioremoval ability (Table 2). By comparing their features, it was observed that biosorption has certain advantages over bioaccumulation in terms of cost, maintenance, metal ions uptake, regeneration, toxicant recovery and many more. When comparing both these processes, bioaccumulation although performed in simpler installations, requires difficult cultivation of the biomass in the presence of contaminants that may pose toxicity to the biomass itself.

Some research works have been reported in the context that biosorption is better bioremoval process than bioaccumulation (Table 4). Probably due to intoxication, live cells partially lose their binding capacity and small amount of metal subsequently released back into solution. But after a few hours, a strong intoxication likely caused the death of some cells, and because of that, the ratio between the living and dead cells changed.

On the contrary, other authors describe opposite results (Al-Garni et al. 2009; Zucconi et al. 2003) probably as a

Table 3 Comparative features of biosorption and bioaccumulation of microbial cell (Dhankhar and Hooda 2011; Vijayaraghavan and Yun 2008)

Features	Biosorption	Bioaccumulation
Cellular growth	No cellular growth	Cellular growth occurs
Cost	Generally low as the biosorbents used are mainly industrial, agricultural and other type of waste biomass	Usually high. The process involves living cells and; hence, cell maintenance is cost prone
Degree of uptake	Extremely high	As living cells are sensitive to high toxicant concentration, uptake is usually low
Maintenance/Storage	Easy to store and use as the biomass is inactive	External metabolic energy is needed for maintenance of the culture
Metabolism	Not controlled by metabolism due to use of inactive biomass	Controlled by metabolism due to the presence of active cells
Metal binding surface	Metals are bound to the cell surface	Metals are bound to cellular surface and interior structures
Process	Single stage passive process	Double stage active process
Rate of uptake	Most biosorption mechanisms are rapid due to extracellular accumulation	Usually slower than biosorption. Since intracellular accumulation is time consuming.
Reaction mode	Adsorption	Absorption
Regeneration and reuse	High possibility of biosorbent regeneration, with possible reuse over a number of cycles	The chances are confined as most toxicants are accumulated intracellularly
Selectivity	Poor. However, selectivity can be improved by modification/processing of biomass	Better than biosorption
Surface area	Large	Small
Toxicant affinity	High under favorable conditions.	Depends on the toxicity of the pollutant
Toxicant recovery	With proper selection of elutant, toxicant recovery is possible. Several instances proved that acidic or alkaline solutions are an efficient medium to recover toxicants	Even if possible, the biomass cannot be utilized for the next cycle
Versatility	Reasonably good. The binding sites can accommodate a variety of ions	Inflexible. Prone to be affected by high metal/salt conditions

consequence of the method used to prepare the dead biomass and the experimental conditions, which affect significantly the efficiency of the biosorbent. Suh et al. (1998) observed that live cells of *Saccharomyces cerevisiae* and *Aureobasidium pullulans* are more efficient for metal removal than dead cells. This is due to the decrease in number of binding sites of Pb^{2+} by autoclaving in case of *S. cerevisiae*, whereas, in case of *A. pullulans*, existence of extracellular polymeric substances on cell surface resulted in difficulty in penetration into inner cellular parts. Doshi et al. (2007) reported that both dead and live *Spirulina* sp. are excellent biosorbent for cadmium, however, the live species is found to be more potent for bioremediation. Tangaromsuk et al. (2002) studied the uptake of Cd(II) by *Sphingomonas paucimobilis* biomass and reported that the cadmium removal capacity of live cells was markedly higher than that of dead cells, probably due to intracellular uptake of metal ions.

Genes and enzymes in heavy metal removal

The most representative class of enzyme used in the remediation of polluted environments are hydrolases, dehalogenases, transferases and oxidoreductases; mainly obtained from bacteria, fungi, plants and microbe plant associations (Rao et al. 2010). A particular gene is responsible for production of a particular enzyme. A list of genes and enzymes related with metal removal are listed in Table 5.

Biological processes in heavy metal removal from wastewater

Most heavy metal ions are water soluble and get dissolved in wastewater, which results in health hazards and harmful biochemical effects on human beings (Batayneh 2012). Therefore it is essential to remove heavy metals in industrial wastewater and the environment to an acceptable level. The non-living biomass of algae, waste biomass originated from plants and mycelial wastes from fermentation industries are potential biosorbents for removal of heavy metals from industrial effluents. Atkinson et al. (1998) classified the industrial effluents into two broad categories: (a) low pollutant concentration in large volume and (b) high TDS values in small volumes. For the first case, a biosorbent with strong affinity towards the

Table 4 Comparative results of biosorption and bioaccumulation potential of microbial cells

Microorganisms	Metals	Bioaccumulation (mg/g)	Biosorption (mg/g)	References
Bacteria				
Bacillus cereus RC-1	Cd	24.01	31.95	Huang et al. (2013)
Bacillus megaterium (A)	Cr	15.7	30.7	Srinath et al. (2002)
Bacillus coagulans (181)	Cr	23.8	39.9	Srinath et al. (2002)
Pseudomonas aeruginosa ASU 6a	Pb	79.0	123.0	Gabr et al. (2008)
P. aeruginosa ASU 6a	Ni	70.0	113.0	Gabr et al. (2008)
Streptomyces ciscaucasicus	Zn	42.75	54.0	Li et al. (2010)
Bacillus sphaericus OT4b31	Cr(VI)	25*	44.5*	Velasquez and Dussan (2009)
B. sphaericus IV(4)10	Cr(VI)	32*	45*	Velasquez and Dussan (2009)
Fungi				
Trichoderma SP2F1	Cu	19.60	28.75	Ting and Choong (2009)
Aspergillus niger MTCC 2594	Cr(VI)	75*	83.3*	Mala et al. (2006)
A. niger MTCC 2594	Cr(III)	78*	78.7*	Mala et al. (2006)
Lentinus edodes	Zn	33.7	57.7	Bayramoglu and Arica (2008)
L. edodes	Cd	78.6	274.3	Bayramoglu and Arica (2008)
L. edodes	Hg	336.3	403.0	Bayramoglu and Arica (2008)
Pichia stiptis	Cr(III)	9.10	19.2	Yilmazer and Saracoglu (2009)
P. stiptis	Cu	15.85	16.89	Yilmazer and Saracoglu (2009)
Trichoderma asperellum	Cu	5.69	12.42	Tan and Ting (2014)
Lentinus edodes	Hg	336.3	403.0	Bayramoglu and Arica (2008)
Algae				
Spirulina platensis	Cd	44.56	47.89	Murugesan et al. (2008)
Chlorella kessleri	Cu	1.9	2.8	Kadukova and Vircikova (2005)
Chlamydomonas reinhardtii	Cu	0.056	0.109	Flouty and Estephane (2012)
C. reinhardtii	Pb	0.057	0.286	Flouty and Estephane (2012)
Aulacoseira varians	Cu	2.29	3.03	Tien et al. (2005)
Ceratium hirundinella	Cu	2.3	5.75	Tien et al. (2005)
Chlorella vulgaris	Cu	3.63	4.26	Tien et al. (2005)
C. vulgaris	Ni	15.4	15.6	Al-Rub et al. (2004)

* Bioaccumulation and biosorption capacity in percent

contaminant is mandatory; whereas the latter case requires a biosorbent with high uptake capacity. Biosorption processes are applicable to effluents containing low concentrations of heavy metals for an extended period. The application of biosorption in the purification of wastewater offers a high potential for large scale exploitation. The potential of natural, abundant, and cheap microbial biomass can be used successfully in selective removal of metal ions from solutions. Very few instances are present regarding commercialization of biosorption processes by using biosorbents, for example., AMT-BioclaimTM, BIO-FIX and AlgaSORB. List of microorganisms used for wastewater treatment and their removal rate are summarised in Table 6.

From the tables (Tables 4, 6), it was observed that algae and fungi are better biosorbents than bacteria for removal of heavy metal ions from aqueous medium. Algae and fungi are also surpassing bacteria in terms of availability. They are easily available from industrial waste in large volume, which is one of the essential factors for good biosorbents.

Use of biofilms is the another approach towards heavy metal removal and recovery from wastewater stream (Costley and Wallis 2001). It can be defined as an assemblage of bacteria, algae, fungi and protozoa enclosed in a matrix consisting of a mixture of polymeric compounds, primarily polysaccharides generally referred as extracellular polymeric substances (EPS). Use of biofilms is efficient for bioremediation process, as it absorb, immobilize and degrade various environmental pollutants. Biofilms contain advantages, such as protection from surrounding environment, ability to communicate and exchange genetic

Table 5 Genes and enzymes/proteins responsible for bioremoval of heavy metal ions in microorganisms

Metals	Microorganisms	Genes	Enzymes/proteins	References
Cr	*Ochrobactrum tritici* 5bvl1	*chrR, chrB, chrA, chrC and chrF*	Chromate reductase	Morais et al. (2011)
	Bacillus cereus SJ1 species	*azoR, nitR*	Azoreductase, nitroreductase	He et al. (2010)
	Bacillus subtilis BYCr-1	*nfrA*	NfrA	Zheng et al. (2015)
	Pseudomonas aeruginosa	*chrR*	–	Aguilar-Barajas et al. (2008)
	Serratia sp.	*ChrT*	chromate reductase	Deng et al. (2015)
	Cupriavidus metallidurans	*chrA*	–	Branco et al. (2008)
	P. putida	–	EcdA (Soluble chromate reductase)	Park et al. (2000)
	Escherichia coli	*KefF*	Nitroreductase	Prosser et al. (2010)
	Escherichia coli	*chrR*	Quinone reductase	Eswaramoorthy et al. (2012)
	P. putida	*chrR*	Flavoenzyme	Park et al. (2000)
	P. aeruginosa	*chrA*	Flavoprotein family of reductases	Díaz-Pérez et al. (2007)
	Rhodobacter sphaeroides	*chr*	NADH-dependent	Nepple et al. (2000)
	Escherichia coli	–	YieF (chromate reductase)	Ackerley et al. (2004)
	Saccharomyces carlsbergensis	–	OYE enzyme	Saito et al. (1991)
	Vibrio harveyi	–	Flavin reductase P	Zenno et al. (1998)
	Escherichia coli	*nemA*	NemA	Robins et al. (2013)
	Escherichia coli	*azoR*	Azoreductase	Robins et al. (2013)
	Escherichia coli	–	NfsA (Nitroreductase)	Ackerley et al. (2004)
	V. harveyi	–	NfsB (Nitroreductase)	Kwak et al. (2003)
	Bacillus subtilis	–	YcnD (FMN reductase)	Morokutti et al. (2005)
	P. putida	–	EcdA (Soluble chromate reductase)	Park et al. (2000)
	Shewanella strain ANA-3	*chrBAC*	Efflux transporter	Aguilar-Barajas et al. (2008)
	Vibrio (or *Photobacterium*) *fischeri*	–	FRase I (FMN reductase)	Zenno et al. (1994)
Cu	*Pseudomonas* sp. NA	*cop*	Cell free Copper reductase	Andreazza et al. (2011)
	P. syringae	*copABCD, copR, copS*	Copper reductase	Mills et al. (1993)
	Escherichia coli	*pcoABCDE, pcoR, pcoS*	Copper reductase	Brown et al. (1995)
	P. syringae	–	CopD, CopB, CopA, CopC	Cha and Cooksey (1991)
	Enterococcus hirae	*copA, copB*	CopA, CopB	Odermatt et al. (1993)
	Synechococcus PCC 7942	*smtA and smtB*	Metallothioneins (MT)	Blindauer (2011)
	Debaryomyces hansenii	–	Cell surface copper reductase	Wakatsuki et al. (1991)
	Hebeloma cylindrosporum	*HcMT1*,*Hc*MT2	–	Ramesh et al. (2009)
	Gigaspora margarita	*GmarCuZnSOD*	Superoxide dismutases	Lanfranco et al. (2005)
	G. intraradices	*GintCuZnSOD*	Superoxide dismutases	
Cd and Zn	*Escherichia coli*	*o732*	–	Goldberg et al. (1999)
	P. aeruginosa CMG103	*czr*	CzrC, CzrB, CzrA	Hassan et al. (1999)
	Pseudomonas aeruginosa WI-1	*bmtA*	–	Naik et al. (2012)
Cd, Zn and Co	*Alcaligens eutrophus* CH34	*czc*	CzcA, CzcB, CzcC	Nies (1995)
Cd	*Staphylococcus aureus*	*cadA*	–	Nucifora et al. (1989)
	B. subtilis	*cadA*	–	Tsai et al. (1992)
	Streptococcus thermophilus Strain 4134	*cadCSt, cadASt*	CadCSt, CadASt	Schirawski et al. (2002)
Cd, Zn and Pb	*Staphylococcus aureus*	*cadAC*	CadC	Busenlehner et al. (2003)

Table 5 continued

Metals	Microorganisms	Genes	Enzymes/proteins	References
Zn and Co	*Staphylococcus aureus*	*zntA*	–	Xiong and Jayaswal (1998)
Zn	*Saccharomyces cerevisiae*	*ZRT1, ZRT2*	Zrt1p, Zrt2p	Zhao and Eide (1996)
	Synechococcus PCC 7942	*smtA, smtB*	Metallothioneins (MT)	Blindauer (2011)

Table 6 Use of microorganisms for heavy metal removal from wastewater

Microorganisms	Metals	IMC (mg/L)	Removal rate (%)	References
Bacteria				
Bacillus sp. JDM-2-1	Cr(VI)	100	86	Zahoor and Rehman (2009)
Staphylococcus capitis	Cr(VI)	100	89	Zahoor and Rehman (2009)
Geobacillus thermodenitrificans	Cr(VI)	20.22	39.2	Chatterjee et al. (2010)
G. thermodenitrificans	Cu	9.24	13.03	Chatterjee et al. (2010)
G. thermodenitrificans	Cd	0.73	35.88	Chatterjee et al. (2010)
G. thermodenitrificans	Zn	–	9.02	Chatterjee et al. (2010)
G. thermodenitrificans	Fe	1.08	43.94	Chatterjee et al. (2010)
G. thermodenitrificans	Pb	–	18.22	Chatterjee et al. (2010)
G. thermodenitrificans	Co	–	11.43	Chatterjee et al. (2010)
Fungi				
Aspergillus caespitosus	Pb	3.95	93	Aftab et al. (2014)
Aspergillus niger	Cr(VI)	47	71.18	Kumar et al. (2008)
A. sydoni	Cr(VI)	47	65.32	Kumar et al. (2008)
Penicillium janthinellum	Cr(VI)	47	62.59	Kumar et al. (2008)
Algae				
Spirogyra condensate	Cr(III)	8.26	55	Onyancha et al. (2008)
S. condensate	Cr(III)	3356.7	32	Onyancha et al. (2008)
Rhizoclonium hieroglyphicum	Cr(III)	8.26	65	Onyancha et al. (2008)
R. hieroglyphicum	Cr(III)	3356.7	43	Onyancha et al. (2008)
Chlorella miniata	Cr(III)	100	75	Han et al. (2008)
C. miniata	Cr(VI)	100	100	Han et al. (2008)
Spirogyra neglecta	Pb	75	>70	Singh et al. (2007)
Pithophora odeogonia	Pb	75	>70	Singh et al. (2007)
Sargassum sp.	Cu	30	87	Jacinto et al. (2009)
Chlorococcum sp.	Cr	2	67	Jacinto et al. (2009)
Chlorella sp.	Cd	–	65	Matsunaga et al. (1999)

IMC initial metal concentration

material, nutrient availability and persistence in different metabolic states (Costerton 1999). Biofilm based reactors are commonly used for the treatment of large volume of industrial and municipal wastewaters. Based on the reports, it may be concluded that biofilms have the potentiality to remove heavy metals from wastewaters and natural waters containing low levels of pollutants. Biofilms are also applied as tools for monitoring and assessment of heavy metal pollution in water as structure and physiological alterations of biofilms occur rapidly in presence of toxicant (Fuchs et al. 1997). Further research area needs to be extended on the focus of gene transfer within biofilms.

Study of biofilm communities and gene transfer within biofilms would facilitate the development of better techniques for the bioremediation of polluted sites and wastewaters.

Conclusions

Decontamination of heavy metals from the environment is very much essential for the maintenance of a healthy and safe environment. Although physicochemical methods are often used for similar purposes, biological processes namely biosorption/bioaccumulation seems to be a promising alternative method from the perspective of costs, technology requirement, metal recovery efficiency, energy requirement and environmental impacts. However, when biosorption and bioaccumulation were compared, the former proved to be advantageous due to the use of dead/inactive biomaterials; which inhibits the internalization of metal through the cell wall. A comparison among bacteria, algae and fungi showed that algae and fungi are proved to be better biosorbents due to their high metal uptake capacity, easy availability and high biomass generation capacity. There is still a challenge for specific adsorption due to the heterogeneity of microbial cell surface. Furthermore, when living cells are used for heavy metal removal, genetic engineering might be needed to enhance the metal tolerances of microbial strains. More studies should be carried out for better understanding of heavy metal removal by these two processes.

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