Bacteria and Fungi as Alternatives for Remediation of Water Resources Polluting Heavy Metals

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Classical methods which used for removal of heavy metals from contaminated water are adsorption, precipitation, coagulation, ion exchange resin, evaporation, and membrane processes. Microbial biosorption can be used for the removal of contaminated waters with pollutants such as heavy metals and dyes which are not easily biodegradable. Microbial biosorbents are inexpensive, eco friendly and more effective for the removal of toxic metals from aqueous solution. In this review, the bacterial and fungal abilities for heavy metals ions removal are emphasized. Environmental factors which affect biosorption process are also discussed. A detailed description for the most common isotherm and kinetic models are presented. This article reviews the achievements and the current status of bacterial and fungal biosorption technology for heavy metals removal and provides insights for further researches.

Key words: Biosorption, Microbial biomass, Fungi, Bacteria, Heavy metals

Introduction

The pollution of heavy metals into aquatic ecosystems has become a complex problem in over the world the last few decades. Presence of heavy metals even in small amounts is toxic to both flora and fauna. Many industries are responsible for this pollution such as mining, surface finishing, energy and fuel producing, fertilizer, pesticide, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leather, photography, electric appliance manufacturing, and metal surface treating. Moreover, the aerospace, atomic energy installations, and wastes containing metals are directly or indirectly being discharged into the environment causing serious environmental pollution (Wang and Chen 2009). Removal and Controlling toxic heavy metal discharges from water bodies has become a challenge for the twenty-first century.

The classical techniques of heavy metals removal such as chemical precipitation, chemical oxidation and reduction, ion-exchange, filtration, electrochemical treatment, and reverse osmosis give rise to several problems such as unpredictable metal ions removal and generation of toxic

sludges which are often difficult to dewater and require extreme caution in their disposal (Xia and Liyuan, 2002). Moreover, these classical techniques for heavy-metal removal are extremely expensive cost due to the high reagent or energy requirements (Xia and Liyuan, 2002). The need for economical, effective and safe methods for removing heavy metals from wastewater has resulted in search for unconventional methods that may be useful in reducing the levels of accumulated heavy metals in the environment. Recently, using microbial biomass as biosorbents for heavy metal removal from industrial waste streams has been considered as a potential alternative technology. Most microbial biomasses have a negative charge owing to the presence of negatively charged groups of atoms on the cell membrane and cell wall. The charged groups or ligands are responsible for the adsorption of positively charged metal ions in solution. The adsorption is typically rapid, reversible and independent of temperature and energy metabolism. This phenomenon is known as biosorption. Biosorption, using biomaterials such as bacteria, fungi, yeast and algae, is regarded as a cost-effective biotechnology for the treatment of high volume and low concentration complex wastewaters containing heavy metal(s). Currently, several adsorbents are being used including seaweeds, molds, yeast, bacteria, crabshells, agricultural products which are by-products of agriculture

and industries. It has been demonstrated that some fungal and bacterial species are typically associated with heavy metal rich substrata and can be even considered as hyper accumulators of heavy metals (Purvis and Halls, 1996, Gadd 1993). Fungi offer a wide range of chemical groups that can attract and sequester heavy metals in their biomass. Potential of filamentous fungi in bioremediation of industrial effluents and waste waters containing heavy metals has been increasingly reported from different parts of the world (Gadd, 1993).

Heavy Metals Removal by Microorganisms

Metal biosorption by microorganisms is a complex process that depends on the chemistry of the metal ions, cell wall composition of microorganisms, cell physiology, and physicochemical factors such as pH, temperature, time, ionic strength and metal concentration (Hassan et al., 2009; Gabr et al., 2008; Tuzen et al., 2008; Godlewska-Zylkiewicz, 2006; Mapoletoet al., 2005; Chaisuksant 2003; Goyalet al., 2003; Volesky 2003; Klimmeket al., 2001; Leung et al., 2001). Removal of toxic heavy metal ions from polluted waste waters by bacterial biomass has been studied extensively in the last few decades (Joo et al., 2010, Hassan et al., 2009; Tuzen et al., 2008; Akhtar et al., 2007; Kadukova and Vircikova 2005; Chaisuksant, 2003; Leung et al., 2001; Veglio et al., 1997; Akthar and Mohan, 1995; Fourest et al., 1994; Volesky, 2003; 1994; 1990). Microbial biomass have the ability to remove heavy metals from contaminated sites by two process; (1) biosorption "an energy-independent binding of metals to cell wall", and (2) bioaccumulation "an energy-dependent process of metal uptake into the cells" (Karna et al., 1999; Gadd, 1992). Both living and non-living microbial biomass of bacteria, fungi and algae have been used in removing toxic metal ions (Kumar et al., 2008; Karna et al., 1999; Kumar et al., 1998; Volesky, 1990; 1994). Metabolism-independent or biosorption essentially involves adsorption process such as ionic and physicochemical adsorption and is considered as the main mechanism present in the case of non-living biomass. A variety of functional groups located on the bacterial cell walls are known to be included in metal biosorption. These involved carboxyl, amine, hydroxyl, phosphate and sulfhydryl groups. The removal of heavy metals by living and non-living biosorbents have been studied (Joo et al., 2010; Kadukova and Vircikova, 2005; Mapoletoet al., 2005; Chaisuksant 2003; Pardo et al., 2003; Goyalet al., 2003; Volesky, 2003; Veglio et al., 1997; Fourest et al., 1994).

Although, metal biosorption by bacterial biomass occurs through complexation, coordination, physical adsorption, chelation, ion exchange, inorganic precipitation and/or a combination of these process (Akhtar et al., 2007; Chen et al., 2005; Tsezos et al., 1995). Such process includes the active participation of several anionic ligands present on the biomass, like phosphoryl, carboxyl, carbonyl, sulfydryl and hydroxyl groups, was used to immobilize metal ions (Volesky, 2003). Also, the ability of any biosorbent depends on biomass characteristics, physicochemical properties of the heavy metals and the environmental conditions i.e., the solution pH, temperature, and interaction with other ions etc (Volesky, 2003).

Bioaccumulation and Biosorption

It is important to distinguish between active, metabolically mediated metal uptake "an energy-dependent process of metal uptake into the cells" by living cells as opposed to passive metal uptake by non-living biomass "an energy-independent binding of metals to cell wall". The terms bioaccumulation is an intracellular metal accumulation by living cells (Malik, 2004). This process involves metal binding on intracellular compounds, metal binding proteins, intracellular precipitation, methylation and other mechanisms. The uptake process usually involves adsorption of heavy metal ions at the microbial cell wall or cell membrane through interactions with various functional groups and/or transport into the cell with subsequent transformation. It has been proved that, in some cases, growing cells are able to remove metals continuously through internal detoxification mechanisms (Malik, 2004).

While biosorption can be defined as the ability of biological materials to adsorb heavy metals from aqueous solution through physico-chemical pathways of uptake or a property of certain types of inactive, non-living microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution (Volesky, 2003; Fourest and Roux, 1992). Biological materials (bacteria, fungi, algae and plant biomass) are known for their potential to adsorb heavy metals (Kratochvil and Volesky, 1998; Chang and Hong, 1994). Mechanisms of cell surface sorption are independent of cell metabolism; they are based upon physicochemical interactions between heavy metal ions and functional groups of the cell wall of microorganisms.

Biosorption is usually a rapid process responsible for metal removal by non-living biomass. It does not depend on temperature, metabolic energy, or the presence of metabolic inhibitors. Biosorbents in the waste materials discarded either from fermentation industries or from rubber plantaions or marine biomass as a source of raw biosorptive materials. Therefore, the biomass can be either living or non-living but non living is preferred as its easy to handle, and the processes is not growth independent as well as it has no physiological constraints. The use of dead microbial biomass for metal removal and sequestration offers some advantages over living cells in that it the dead microbial biomass is less sensitive to toxic heavy metals, and biosorption may not be inhibited by their presence. Because of there is no metabolic activity, it can be easily control the operating conditions such as pH, temperature, time and metal concentration. Moreover, we can improve the efficiency of biosorption by pre treatment of the microbial biomass. Also, metal recovery and regeneration of the biosoorbent is applicable.

Factors Affecting Biosorption

Biosorption is presented as an alternative to traditional physicochemical means for removing toxic metals from ground-waters and wastewater. The investigation of the efficacy of biosorption "the metal uptake by the microbial biomass" is essential for the industrial application of biosorption, as it gives information about the equilibrium of the process which is necessary for the design of the equipment. The major factors affecting the biosorption process are (1) the contact time (2) initial metal ion concentration, (3) temperature, (4) pH, and (5) biomass concentration in solution (Tomko, 2006).

Contact time effect   Contact time is very important parameter for successful biosorption application. The biosorption process of heavy metal by bacterial biomass usually completes rapidly. The biosorption of metals as cadmium, cobalt, copper, zinc, lead, nickel, chromium and uranium by nonliving cells of bacterial biomass, is a rapid process and often reaches equilibrium within several minutes (Özer and Özer, 2003; Kapoor and Viraraghavan, 1997). However, passive uptake of heavy metals by fungi is thought to be physical adsorption or ion exchange at the cell surface, reaching the adsorption equilibrium within 30-40 min (Das et al, 2008). Equilibrium adsorption levels

of lead(II) and copper(II) by filamentous fungi present on the corncob surfaces were attained after about 90 minutes of exposure (Jonglertjunya, 2008). *Trametes versicolor* is a good cadmium biosorbent, as it removes all Cd(II) ions within 2 hours (Jarosz-Wilkolazka et al., 2002). This appears to be an energy-independent surface binding process that occurs at a rate of about 2 mg Cd(II) per gram of mycelial dry weight. *Rhizopus* sp. biosorbed 80% of Ni(II) within 2 hours at an initial concentration of 10 ppm (Mogollon et al., 1998). It is necessary to optimize the contact time, considering the efficiency of desorption and regeneration of the biomass. Gabr et al. (2008) optimized the sorption time for Pb(II) and Ni(II) by heavy metal resistant strain *Pseudomonas aeruginosa* ASU 6a. Besides, the results showed that a 30 min sorption period was the best option to ensure the metal removal from solution and good recovery from biosorbent. Similar results were observed by Hassan et al. (2009) who concluded that the optimum time for biosorption of Cu and Cd by *P. stutzeri* was 30 min.

pH effect   The pH seems to be the most important parameter in the biosorption process. Solution pH value strongly influences not only the site dissociation of the biomass surface, but also the solution chemistry of the heavy metals as hydrolysis, complexation by organic and/ or inorganic ligands, redox reactions, precipitation, the speciation and the biosorption availability of the heavy metals (Esposito et al., 2001; Wang et al., 1997). Also, it affects the activity of the functional groups in the biomass and the competition of the metalic ions (Friis and Keith, 1998; Galun et al. 1987). It has been attributed to protonation or poor ionization of acidic functional group of cell wall at low pH, inducing a weak complexation affinity between the cell wall and the metal ions (Chergui et al., 2007). Therefore, at low pH values the cell surface becomes more positively charged, then reducing the attraction between metal ions and functional groups on the cell wall. In contrast, higher pH results in facilitation of the metal biosorption, since the cell surface is more negatively charged. The biosorptive capacity of metal cations increases with increasing pH of the sorption system, but not in a linear relationship. On the other hand, extreme pH value can cause precipitation of metal complexes, so it should be avoided during experiments. As pH increases, functional sites on the microbial surface become deprotonated and may bind cationic metals instead. This results in the

common trend of increasing accumulation with increasing pH. However, in many cases, the accumulation starts to decrease again at higher pH. The metals will transform into hydroxide complexes at high pH values, however, it could not be considered as a biosorption behavior of the cells. Mapoleto and Torto (2004) proved that the biosorption capacity of Cd^{2+}, Cr^{3+}, Cr^{6+}, Cu^{2+}, Pb^{2+} and Zn^{2+} is dependent on pH. For all studied metal ions, the optimum pH values in all cases were found to be greater than 5. The optimum pH for Cd^{2+} and Pb^{2+} biosorption is 5.8. Also, Özer and Özer (2003) reported that optimal pH value for Pb(II) and Ni(II) ion uptake is 5.0 by *S. cerevisiae*. Cr(VI) and some other metals such as arsenic are known to exist as anions meaning that the metal carry negative charge. These anions exhibit different pH features from metal cations. The biosorption was favourable at low pH for these anions. In this concern, cell wall ligands of bacterial biomass are protonated at low pH values, and compete significantly with metal binding. With pH increase, more ligands such as amino and carboxyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to the cell surface. As the pH increased further, the overall surface charge on cells could become negative and therefore, biosorption of anions decreased again (Khambhaty et al., 2009; Wang and Chen 2006; Park et al., 2005; Tewari et al., 2005).

Metal concentration and Ionic strength   There is evidence that at high metal ion concentration, the number of ions sorbed is more than at low metal concentration, where more binding sites were free for interaction (Mukhopadhyay et al., 2007). Most of light metals bind weakly to the negatively charged biomass particles, through electrostatic attraction in which a significant ionic strength effect may be observed in the presence of high concentration of light metals. Kaewsarn (2002) reported that effect of Na^+ on Cu(II) uptake was negligible at a concentration of 10 mM, and K^+, Mg^{2+} and Ca^{2+} reduced the removal efficiency by 4%, 11% and 13%, respectively. Since Na, K, Ca, Mg are present in many industrial waste waters, it is useful to estimate the extent and interferes of light metals with biosorption of heavy metal by microbial biomass (Goyal et al., 2003; Volesky 2003; Esposito et al., 2001; Pagnanelli et al., 2000). Calcium, which may form specific, coordinate bonds, might be having stronger effect on heavy metal biosorption (Goyal

et al., 2003; Volesky, 2003; Esposito et al., 2001; Pagnanelli et al., 2000). However, the effect of ionic strength can be explained via the competition of light metals with the heavy metals for electrostatic binding to the biomass. In addition, Chang and Hong, (1994) noted that the mercury uptake by *P. aeruginosa* decreased with the increment of ionic strength. Also, Cho et al. (1994) showed that no significant decrease in the binding of Cd^{2+} and Zn^{2+} occurred up to the ionic strength of 10^{-3}M. In contrast, Chaisuksant (2003) illustrated that the presence of light metal ions (Na^+, K^+, Mg^{2+} and Ca^{2+}) in solution had an insignificant effect on cadmium and copper sorption capacity by pretreated biomass of marine alga *Gracilaria fisheri*. In general, the increase of ionic strength decreased biosorption efficiency because of the increment of electrostatic charge (Volesky, 2003).

Microbial biomass and surface area effect   Biosorption generally decreased with increase in biosorbent particle size and its concentration (Zhou, 1999). Fourest and Roux (1992) invalidated this hypothesis attributing the responsibility of the specific uptake decrease due to metal concentration shortage in solution. Biomass concentration in the solution seems to influence the specific uptake; for lower values of biomass concentration lead to interference between the binding sites (Das et al. 2008). Moreover, large quantity of fungal biomass is available from the antibiotic- and food-industries. Ultimately, the biosorption results not only in metal removal but also provides an eco-friendly environment. Hence, this factor needs to be taken into consideration in any application of microbial biomass as biosorbent (Ahalya et al. 2003). The passive part of microbial metal accumulation can be influenced by surface properties such as charge and orientation of the metal binding functional groups on the cell surface. Microorganisms have a high surface area-to-volume ratio as their small size, and therefore this high surface area provide a large contact area that can interact with metals in the surrounding environment. Microbial metal accumulation has received much attention during the last years due to the potential use of microorganisms for cleaning metal-polluted water. However, less attention has been paid to the role of microorganisms for metal mobility in soil even though the same processes might occur there. Metal accumulation by microorganisms is influenced by the surface characteristics of microorganisms, but also themselves can lead to changes in the surface properties such as charge changes (Ivanov et

al., 1996; Chen and Ting, 1995; Collins and Stotzky 1992).

Temperature effect   As the temperature increases, the rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increases (Ho and McKay, 1998). The temperature range of 20-45℃ apparently exhibited no significant influence on biosorption potential of test fungal species (Javaid et al., 2010). In addition, metal biosorption by non-living biomass is a metabolism independent process and it is not ruled by physiological restriction.

Pretreatment and its effect on the biosorption of heavy metals   Many findings have been reported regarding the use of pre-treated biomass for biosorption of metals. Physical and chemical treatments such as autoclaving, drying, and boiling may affect binding properties, also chemical treatments such as alkali or ethanol treatment can elevate the biosorption capacity, especially evident in some fungal systems because of deacetylation of chitin to form chitosan- glucan complexes with higher metal affinities (Wang and Chen 2006). Pre-treating the fungal biomass can help shed light on the role played by functional groups in biosorption of lead (Parvathi, 2007). The bioadsorption capacity of autoclaved *Mucor rouxii* decreased as compared to the live fungus, attributed to the loss of intracellular uptake (Yan and Viraraghavan, 2000). On the other hand, Ahuja et al. (1999) found that the use of acid-pretreated *Oscillatoria anguistissima* resulted in a decline in cobalt adsorption while metal sorption remained unchanged after alkali pretreatment. More detailed studies are required to understand why enhancement or reduction in adsorption capacity occurs under specific pretreatment conditions (Kapoor and Viraraghavan, 1998). Göksungur et al. (2005) suggested that higher metal uptake by ethanol pretreated cells was due to the increase in the availability of binding sites. Arica et al. (2005) added that denaturation of protein molecules and degradation of polysaccharide compounds of the cell wall components also produce additional available binding sites.

Biosrption Isotherms

Several studies on metal accumulation by microorganisms have been used the adsorption isotherms as a way to describe metal accumulation process. The relationship between the amount of metal ion which adsorbed on the microbial biomass (q_{eq}) and the metal ion concentration remaining in solution (C_{eq}), is described by an isotherm equation. Also, the isotherm represents the equilibrium distribution of metal ions between the aqueous and solid phase. Thereby, the equilibrium distribution is an important in determination the maximum biosorption capacity. Several isotherm models are available to describe this equilibrium distribution such as Freundlich, Langmuir, Redlich-Paterson, BET, and the Sips equation. The two most commonly used models for describing this type of system are those given by Langmuir and Freundlich.

Langmuir isotherm   The most widely applied isotherm for equilibrium data modeling. Langmuir adsorption isotherm is based on some assumptions, mainly, the adsorption is limited to monolayer coverage, all surface sites are energetically equivalent, each site can hold one ion, and the adsorption is localized. The Langmuir equation can be written in the following form:

$$q_{eq} = \frac{q_{max}bC_e}{1+bC_e} \tag{1}$$

While, the linear form of Langmuir equation is

$$C_{eq}/q = 1/q_{max}b + C_{eq}/q_{max} \tag{2}$$

Where q_{max} is the Langmuir constant (mg/g) reflect the maximum adsorption capacity of the metal ion per unit weight of microbial biomass to form a complete monolayer on the surface bound at high C_{eq}. The value of Langmuir constant b (L/mg), represents a ratio of adsorption rate constant to desorption rate constant, which also gives an indication of the affinity of the metal for binding sites on the biosorbent, q_{max} and b can be determined from the linear form of Langmuir equation (2) by plotting C_{eq}/q_{eq} vs C_{eq} (Hassan et al., 2009; Norton et al., 2004; Volesky, 2003; Aksu and Dönmez 2001; Puranik and Paknikar 1999; Veglio et al., 1997; Chong and Volesky, 1995; Volesky and Holan, 1995). Langmuir model was chosen to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. On the other hand, Freundlich model was chosen to estimate the adsorption intensity of the biosorbent towards the biomass.

Freundlich adsorption isotherm   Freundlich expression is an empirical equation based on the sorption on a heterogeneous surface. It models monolayer adsorption

on a heterogeneous surface and the equation is written as:

$$q_{eq} = KC_{eq}^{1/n} \qquad (3)$$

The linearized form of this model is;

$$\ln q_{eq} = \ln K_f + 1/n \ln C_{eq} \qquad (4)$$

where K_f and n are the Freundlich constants characterizing of the system. Equation 3 can be linearized in logarithmic form (eq. 4) and Freundlich constants can be determined.

Freundlich isotherm is also more widely used but provide no information on the monolayer adsorption capacity. In contrast to Langmuir model, Freundlich equation measures the adsorption capacity K_f, and the intensity of adsorption (n). (Hassan et al., 2009; Goyal et al., 2003; Volesky, 2003; Chong and Volesky, 1995; Mattuschka and Strauble, 1993; Aksu and Dönmez 2001; Puranik and Paknikar, 1999).

Biosorption Kinetics

Kinetic studies of heavy metal biosorption is probably one of the most important factorin biosorption system design being the residence time and the reactor dimensionscontrolled by the system kinetics. For batch kinetics of heavy metal biosorption are generallycharacterized by an initial rapid diminution of heavy metal concentration in the liquid phase followed by a second slower and insignificant decrease. The study of biosorption kinetics for heavy metals removal from water ecosysten is significant as it provides valuable insights for the reaction directions and into the reaction mechanisms. Monitoring a kinetic experiment enables us to see how the sorption system is affected by process variables and to understand the steps which limit sorption. Also, the kinetics describes the solute uptake rate which in turn controls the residence time of sorbate accumulated at the solid-solution interface, determination the sorption processes. So, it is necessary to be able to expect the reaction rate at which heavy metals is removed from aqueous solutions in order to design appropriate sorption treatment plant. There are numerous biosorption kinetics models have been studied in order to investigate the biosorption processes. Some of these kinetic models included the pseudo-first-order kinetic model, and the pseudo-secondorder kinetic model. Other models also used for description of kinetic studies such as

Elvoich kinetic model, and the Weber and Morris (WM) sorption kinetic model. In the review we will focus for the first two models.

The pseudo-first-order kinetic model The Lagergren rate equation is one of the most widely used sorption rate equations for the sorption of a solute from a liquid solution. Lagergren's first-order rate equation described the adsorption rate on the base of the biosorption capacity t may be represented as

$$dq_t/dt = k_1(q_{eq} - q_t) \qquad (5)$$

where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min), q_e is the amount of metal ions adsorbed (mg/g) at equilibrium and K_1 is the rate constant of pseudo-first-order reaction rate constant for biosorption (min^{-1}).

Integration by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\log(q_{eq}/q_{eq} - q_t) = (k_1 t)/2.303 \qquad (6)$$

A plot of log $(q_{eq} - q_t)$ against t should give a straight line to confirm the applicability of the first-order kinetic model. In a true first order process log q_{eq} should be equal to the intercept of a plot of log $(q_{eq} - q_t)$ against t. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time of heavy metals biosorption. Pseudo-first order model have been applied to many biosorption kinetic studies (Febrianto et al., 2009).

The pseudo-secondorder kinetic model A pseudo-second-order model proposed by Ho and McKay (1999) was then used to explain the biosorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorptions and predicts the behavior over the whole range of concentration and is in agreement with an adsorption mechanism being the rate controlling step. Other assumptions for description of the type of kinetic model are almost similar to Langmuir adsorption isotherm model, such as;

(1) A monolayer of heavy metal ions on the surface of sorbent will be formed.
(2) The energy of biosorption for each metal ion is equivalent and independent of surface coverage.

Table 1. Important results from the literature for metal biosorption by various bacterial biomass.

Metal	Biosorbent	pH	q_{max} (mg/g)	References
Copper	*Bacillus sp. (ATS-1)*	5	16.3	Tunali et al., 2006
	Bacillus subtilis IAM 1026	5	20.8	Nakajima et al., 2001
	Enterobacter sp. J1	5	32.5	Lu et al., 2006
	Micrococcus luteus IAM 1056	5	33.5	Nakajima et al., 2001
	Pseudomonas aeruginosa PU21	5	23.1	Chang et al., 1997
	Pseudomonas cepacia	7	65.3	Savvaidis et al., 2003
	Pseudomonas putida	6	6.6	Pardo et al., 2003
	Pseudomonas putida	5.5	96.9	Uslu and Tanyol, 2006
	Pseudomonas putida CZ	4.5	15.8	Chen et al., 2005
	Pseudomonas stutzeri IAM 12097	5	22.9	Nakajima et al., 2001
	Sphaerotilus natans	6	60	Beolchini et al., 2006
	Streptomyces coelicolor	5	66.7	Öztürk et al., 2004
	Thiobacillus ferrooxidans	6	198.5	Ruiz-Manriquez et al., 1997
	Paenibacillus jamilae	6	7.8	Morillo et al., 2008
	Pseudomonas pseudoalcaligenes	5	48.4	Leung et al., 2001
	Pseudomonas aeruginosa AT18	5	113.64	Pérez Silva et al., 2009
	Pseudomonas stutzeri	5	33.16	Hassan et al., 2009
Cadmium	*Aeromonas caviae*	7	155.3	Loukidou et al., 2004
	Bacillus circulans	7	26.5	Yilmaz and Ensari, 2005
	Enterobacter sp. J1	6	46.5	Lu et al., 2006
	Pseudomonas aeruginosa PU21	6	42.4	Chang et al., 1997
	Pseudomonas putida	6	8	Pardo et al., 2003
	Pseudomonas sp.	7	278	Ziagova et al., 2007
	Staphylococcus xylosus	6	250	Ziagova et al., 2007
	Streptomyces pimprina	5	30.4	Puranik et al., 1995
	Paenibacillus jamilae	6	20.4	Morillo et al., 2008
	Pseudomonas aeruginosa	8.5	6.18	Tuzen et al., 2008
	Streptomyces rimosus	8	64.9	Selatnia et al., 2004
Lead	*Bacillus sp. (ATS-1)*	3	92.3	Tunali et al., 2006
	Corynebacterium glutamicum	5	567.7	Choi and Yun, 2004
	Enterobacter sp. J1	5	50.9	Lu et al., 2006
	Pseudomonas aeruginosa	5	79.5	Chang et al., 1997
	Pseudomonas aeruginosa	5	0.7	Lin and Lai, 2006
	Pseudomonas putida	5.5	270.4	Uslu and Tanyol, 2006
	Pseudomonas putida	6.5	56.5	Pardo et al., 2003
	Streptomyces rimosus	6.5	135	Selatnia et al., 2004
	Streptoverticillium cinnamoneum	4	57.7	Puranik and Paknikar, 1997
	Paenibacillus jamilae	Not available	303.03	Morillo et al., 2008
	Pseudomonas aeruginosa	8.5	6.07	Tuzen et al., 2008
	Pseudomonas pseudoalcaligenes	5	271.7	Leung et al., 2001
	Pseudomonas aeruginosa ASU 6a	6	123	Gabr et al., 2008
Nickel	*Streptomyces coelicolor*	8	11.1	Öztürk et al., 2004
	Streptomyces rimosus	6.5	36	Selatnia et al., 2004
	P. aeruginosa ASU 6a	7	113.6	Gabr et al., 2008
	Pseudomonas aeruginosa	8.5	5.25	Tuzen et al. 2008
	Escherichia coli	7	34.3	Kao et al., 2008
	Paenibacillus jamilae	6	17.6	Morillo et al., 2008
Zinc	*Paenibacillus jamilae*	6	12.31	Morillo et al., 2008
	Escherichia coli	7	659	Kao et al., 2008
	Pseudomonas aeruginosa AT18	7.-7.2	87.72	Pérez Silva et al., 2009
	Pseudomonas putida	7	6.9	Pardo et al., 2003
	Pseudomonas putida	5	17.7	Chen et al., 2005
	Streptomyces rimosus	3	30	Mameri et al., 1999
	Streptomyces rimosus	3	80	Mameri et al., 1999
	Streptoverticillium cinnamoneum	5.0-6.0	21.3	Puranik and Paknikar, 1997

(3) The bisorption occurs only on localized sites.

(4) No interactions between sorbed ions.

(5) The rate of reactions is almost negligible for the initial rate of biosorption processes.

The pseudo-second-order model can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{7}$$

Which have the linear form

$$(1/q_t) = (1/k_2 q_{eq} t) + (1/q_{eq}) \tag{8}$$

where q_t is the amount of metal ions adsorbed to dry biomass of *N. commune* (mg/g) at any given time t (min), q_e is the amount of metal ions adsorbed (mg/g) at equilibrium and K_2 is the second-order reaction rate constant for adsorption (g/(mg min). The rate constant (k_2) and adsorption at equilibrium (q_{eq}) can be obtained from the intercept and slope, respectively. Pseudo-second order kinetic model is generally more suitable than pseudo-first order model to represent kinetic data of heavy metal biosorption in batch models. In many biosorption studies the regression coefficients higher than 0.98 were obtained and the calculated amount the amount of metal ions adsorbed (mg/g) at equilibrium time (q$_e$) values agreed well with experimental ones (Febrianto et al. 2009). In recent study by Joo et al. (2010), for biosorption of Zn(II) by gram negative and gram positive bacteria, the biosorption processes fit well with pseudo-second order kinetic model than pseudo-first order model.

Bacterial Biosorption of Heavy Metals

Removal of toxic heavy metal ions may contribute to the detoxification of polluted environments. Therefore, the investigation of metal uptake by bacteria is fundamental for the application of biosorption, since it gives information about metal ions removal efficiency in the process (Veglió, and Beolchini, 1997). Different kinds of bacterial species were used for the biosorption and removal of heavy metal ions. Table 1 summarizes some of the important results of heavy metal biosorption using bacterial biomass.

Table 1 shows the maximum biosorption capacity of heavy metals by bacteria reported in literature. However, the direct comparison of experimental data is not possible, due to different in experimental conditions employed (such

as; pH, equilibrium time, temperature, biomass concentration, heavy metal concentrations and the bacterial biomass). Even so, Table 1 provides some information to evaluate the possibile usage of bacterial biomass for the removal of heavy metal ions. Also, the biosorption capacity is not only depends on the type of heavy metal ions, but also on the type of bacteria, due to the variations in cellular constituents.

Fungal Biosorption of Heavy Metals

Fungi and yeasts have been shown to biosorb heavy metals metal ions from aqueous solutions (Singh 2006; Kapoor and Viraraghavan 1995). The most common species that used for heavy metals removal are, *Saccharomyces cerevisiae*, *Penicillium* sp., *Phanerochaete chrysogenum* was studied most. The species of *Penicillium* was observed to sorb uranium and lead well (Wang and Chen 2009). The living fungal cells of *A. niger*, *M. rouxii* and *R. arrhizus* have been shown to take up precious metals such as gold and silver (Mullen et al. 1992). The biosorption kinetics of heavy metals is depend on contact time. Also, the fungal biosorption of heavy metal ions is strongly depends on pH (Table 2). Biosorption of Ni, Cd, and Pb by *P. digitatum* was observed to be inhibited below pH 3.0 (Kapoor and Viraraghavan 1995). Heavy metals biosorption can take place by living cell or dead cell of fungal biomass. Table 2 shows the maximum biosorption capacity of heavy metals by fungi reported in literature. Fungi, such as *Aspergillus niger* and *Mucor rouxii* are capable of removing heavy metals from aqueous solutions (Yan and Viraraghavan, 2008). Basidiomycetes (wood rotting fungi) are useful source of mycelial biomass for biosorption of metal ions, being easy to cultivate, acquire high yield and generally regarded as safe. Therefore, biosorbents made from these fungi can be easily accepted by public when applied practically. The potential of wood rotting fungi to remove metal ions is limited to a few examples in comparison with micromycetes and the role of macromycetes in this field has been known only for few decades (Veit et al., 2005; Jarosz-Wilkolazka et al., 2006; Gonen et al., 2008; Vimala and Das, 2009).White-rot fungi are capable of accumulating high levels of heavy metals from the environment (Baldrian, 2003). In some cases, their ability to bind metals is same or even better, than that of lower fungi and yeast (Javaid and Bajwa, 2008). The ability of the basidiomycetes to adsorb and accumulate

Table 2. Important results from the literature for metal biosorption by various fungal biomass.

Metal	Biosorbent	pH	q_{max} (mg/g)	References
Au	*Aspergillus niger*	2.5	199	Kuyucak et al., 1988
	Rhizopus arrizus	2.5	160	Kuyucak et al., 1988
Ag	*Rhizopus arrhizus*	4.2	54	Tobin et al., 1984
	Sacchromyces cerevisiae	5.0	4.7	Brady and Duncan, 1993
Cd	*Candida tropicalis*	6.0	60	Mattuschka et al., 1993
	Aspergillus terreus	6.0	6.0	Massaccesi et al., 2002
	Pencillium chrysogenum	3.5	56	Holan and Volesky, 1995
	Penicillium chrysogenum	4.0-5.0	11	Niu et al., 1993
	Mucor rouxii	5.0	8.46	Yan and Viraraghavan, 2003
	Rhizopus arrhizus	4.2	30	Tobin et al., 1984
	Fusarium flocciferum	7.5-8.0	192	Delgado et al., 1998
	Aspergillus oryzae	8.0	10	Kiff and Little 1986
	Sacchromyces cervisiae	4.5	2-40	Volesky et al., 1993
	Rhizopus arrhizus	6.0	27	Fourest and Roux, 1992
	Rhizopus nigricans	3.5	19	Holan and Volesky, 1995
	Polyporus versicolor	6.0	12	Yetis et al., 1998
	Phanerochaeta chrysosporium	6.0	15	Yetis et al., 1998
	Penicillium chrysogenum	6.0	23	Say et al., 2001
	Penicillium chrysogenum	4.5	15.2	Li et al., 2004
	Fomitopsis pinicola	6.2	51	Gabriel et al., 1996
Cr(VI)	*Rhizopus arrhizus*	4.2	31	Tobin et al., 1984
	Rhizopus arrhizus	2.0	8.4	Sag and Kutsal, 2000
	Rhizopus nigricans	2.0	212	Bai and Abraham, 2002
	Candida tropicalis	6.0	4.6	Mattuschka et al., 1993
Cr(III)	*Mucor meihi*	4.0	45	Tobin and Roux, 1998
	Polyporus versicolor	6.0	18	Yetis et al., 1998
Cu	*Candida tropicalis*	6.0	80	Mattuschka et al., 1993
	Cladosporium resinae	6.0	18	Gadd et al., 1988
	Rhizopus arrhizus	6.0	16	Yin et al., 1999
	Saccharomyces crevisae	5.0	17-40	Mattuschka et al., 1993
	Penicillium chrysogenum	4.0-5.0	9	Niu et al., 1993
	Aspergillus oryzae	5.0	55	Huang, 1996
	Polyporus versicolor	6.0	7.5	Yetis et al., 1998
	Phanerochaete chrysosporium	6.0	15	Yetis et al., 1998
	Penicillium chrysogenum	6.0	20.2	Say et al., 2001
	Penicillium chrysogenum	6.0	100	Sing and Yu, 1998
	Ganoderma lucidum	5.0	64.4	Rao, et al., 1993
	Fusarium flocciferum	4.5	40	Delgado, 1998
	Mucor miehi	4.0	19	Brady, et al., 1999
	Penicillium digitatum	5.5	14.6	Galun, et al., 1987
	Aspergillus niger	5.0	10	Rao, et al., 1993
	Aureobasidium pullulans	5.5	6	Gadd et al., 1988
Pb	*Mucor miehi*	6.0	53.75	Tobin and Roux, 1998
	Rhizopus arrizus	6.0	126	Yin et al., 1999
	Penicillium chrysogenum	4.0-5.0	116	Niu et al., 1993
	Mucor rouxii	5.0	35.69	Yan and Viraraghavan, 2003
	Phomopsis sp.	6.0	180	Saiano et al., 2005
	Penicillium chrysogenum (Resting cells)	5.0	80	Yetis et al., 2000
	Penicillium chrysogenum	6.0	69.8	Say et al., 2001
	Penicillium chrysogenum	4.5	12.34	Li et al., 2004

Continued

Metal	Biosorbent	pH	q_{max} (mg/g)	References
Ni	*Mucor miehi*	6.0	20.49	Tobin and Roux, 1998
	Fusarium flocciferum	7.5	52	Delgado et al., 1998
	Rhizopus arrizus	2.0	10.3	Sag and Kutsal, 2000
	Mucor rouxii	5.0	11.09	Yan and Viraraghavan, 2003
	Phomopsis sp.	6.0	6.4	Saiano et al., 2005
	Polyporus versicolor	6.0	27	Yetis et al., 1998
	Phanerochaete chrysosporium	6.0	13.5	Yetis et al., 1998
	Polyporus versicolor	5.0	57	Dilek et al., 2002
Zn	*Mucor miehi*	6.0	53.85	Tobin and Roux, 1998
	Rhizopus arrizus	6.0	34.66	Yin et al., 1999
	Mucor rouxii	5.0	7.75	Yan and Viraraghavan, 2003
	Aspergillus oryzae	2.0-5.0	17.6	Volesky, 1994
	Penicillium digitatum	5.5	17	Galun et al., 1987
	Trichoderma reesii	5.5	15.7	Volesky, 1994
	Rhizopus nigricans	5.5	14.4	Volesky, 1994
	Aspergillus niger	5.5	13.7	Volesky, 1994
	Endothia parasitica	4.0-5.0	9.8	Volesky, 1994
	Penicillium chrysogenum	4.5	6.2	Niu, et al., 1993
	Rhizopus arrizus	5.5	13.93	Zhou, 1999
	Phomopsis sp.	6.0	8.5	Saiano et al., 2005
Fe(III)	*Rhizopus arrizus*	2.0	3.9	Sag and Kustal, 2000
	Penicillium digitatum	5.5	15	Galun et al., 1987
Fe(II)	*Neurospora crassa*	5.1	295.3	Rashmi et al., 2004
	Penicillum citrinum	5.1	126.4	Rashmi et al., 2004
Co	*Aspergillus niger*	4.0-5.0	95	Kuyucak and Volesky, 1988
	Rhizopus arrizus	6.5	2.9	Sakaguchi and Nakajima, 1991
	Aspergillus niger	6.5	2.4	Sakaguchi and Nakajima, 1991
U	*Aspergillus niger*	5.8	220	Yakubu and Dudeney, 1986
	Rhizopus arrizus	4.0-5.0	180	Tsezos and Volesky, 1981
	Penicillium chrysogenum	2.0-5.0	165	Tsezos and Volesky, 1981
	Rhizopus nigricans	4.0-5.0	114	Kuyucak and Volesky, 1988
	Aspergillus niger	4.0-5.0	31	Tsezos and Volesky, 1981
	Trichoderma reesii	4.0-5.0	28.6	Kuyucak and Volesky, 1988
	Endothia parasitica	4.0-5.0	23.85	Kuyucak and Volesky, 1988
	Penicillium digitatum	5.5	10	Galun et al., 1987
	Aspergillus terreus	2.0-5.0	0.95	Tsezos and Volesky, 1981

metals together with excellent mechanical properties of fungal mycelia provides an opportunity to utilize such candidates in selective sorption of industrial heavy metal ions from polluted waters (Bayramoglu et al., 2007; Razmovski and Šćiban, 2008). Table 2 gives the biosorptive capacities of various fungal biomass to different heavy metals.

Conclusions and Future Perspectives

Bacterial and fungal biomass represents an efficient and an economically feasible technology for the removal of heavy metal ions from solutions. In this concern, bacterial and fungal biomass (living/non-living cells) can be applied to the mixed contaminated water for the removal of several heavy metals within short time. Several researchers identified superior biosorption performance of bacterial and fungal biomass compared to other adsorbents. Consequently, the application of biosorption using living cells has obtained attention compared to dead cells in addition to growing microbes as a useful alternative for heavy metal contaminants from industrial waste were recommended (Malik, 2004). The optimization of biosorption characteristics and physical conditions is required as additional trend for developing biomaterial immobilization as reuse, recycling and metal-microbes interactions (Wang and Chen, 2006).It is cleared

that biosorption of heavy metals is self-driven and don't disturb the sites in cleaning process. Also, biosorption could contribute to conventional methods as a second or pretreatments that enhanced the efficiency of heavy metal removal from industrial wastes and wastewater. Further researches are required to focus on low cost biosorbents as it is difficult to create a definite protocol that could be applied to any contaminated water and wastewater. So, each biosorbents must be customized and adapted to site-specific conditions. Modeling, regeneration and immobilization of biosorbents are required impressive investigations. The physico-chemical properties of the bacterial or fungal biosorbents need to be studied and how to improve the nature of bacterial and fungal cells for increasing the biosorption capacity of toxic metals ions needs to be developed. Techniques for biosorbent regeneration and their effects on the biosorbent quality should also be evaluated. The biosorption rate for heavy metals, and multi-ions biosorption, should be studied to serve as a basis for the design of biosorption treatment systems. Further studies in real stream water contaminated sites with pollutants should be conducted and finally preliminary design and economic studies should follow.

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