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Biosorption of Copper by Bacterial Adsorbents: A Review

Arti Hansda, Vipin Kumar and Anshumali
Centre of Mining Environment, Department of Environmental Science and Engineering, Indian School of Mines, Dhanbad, Jharkhand, 826004, India

Corresponding Author: Vipin Kumar, Centre of Mining Environment, Department of Environmental Science and Engineering, Indian School of Mines, Dhanbad, Jharkhand, 826004, India Tel: +91-9471191352

ABSTRACT

Anthropogenic activities have resulted in release of significant amount of heavy metals in soil and water. Though, copper is an essential micronutrient for the cellular metabolism but, beyond threshold limit, it is toxic for the flora and fauna of the surrounding. Several conventional methods have been developed for the removal of copper contaminants from aqueous medium but were considered as ineffective due to economical and technical constraints. To avoid such environmental problem, biotic processes are getting momentum for the decontamination of pollutants from aqueous medium. Biosorption is a cost effective and eco-friendly technique for decontamination of metal ions with the help of biologically derived materials. This review summarizes the biosorption processes, mechanism of copper ion adsorption and different studies found in literature concerning reduction of copper contamination from the environment.

Key words: Adsorbent, biosorption, bacteria, metals, copper

INTRODUCTION

Industrial development has improved the living conditions but has also affected the basic amenities of life, such as air, soil and water, due to the release of large amounts of contaminants to the environment. There are two broad classes of contaminants: Organic and inorganic. Organic pollutants include industrial solvents, insecticides, pesticides and food processing wastes. Inorganic pollutants include metals, fertilizers, industrial discharges, etc. Agricultural practices are frequently a source of heavy metals contamination originate from atmospheric deposition and from different soil amendments such as sewage sludge (used as an organic amendment, manure and compost), fertilizers, liming materials, pesticides, manures and compost (Alloway, 1995; Kabata-Pendias, 1995). Metals are indirect sources of water pollution that enters the water supply from soil/ground water systems and from the atmosphere via rain water.

Among the important metals, mercury, lead, cadmium and chromium (VI) are considered as toxic, whereas others, such as copper, nickel, cobalt and zinc are not as toxic, however, their widespread usage and increasing levels in the environment are of serious concerns. Copper (Cu) is an essential micronutrient required in the growth of both flora and fauna. It affects many important functions of plants such as oxidation, photosynthesis, protein and carbohydrate metabolism, nitrogen fixation and cell wall metabolism (Kabata-Pendias and Pendias, 2001). The general values for the average total copper (Cu) contents in soils of different types all over the world are reported to range between 20 and 30 mg kg^{-1} (Alloway, 1995), whereas for drinking water the maximum permissible limit is 2.0 mg L^{-1} (WHO). At elevated levels, Cu harmfully affects the environment (Alloway, 1995). Copper (II) has been considered as one of the most harmful ions due to its toxicity to human body and its abundance and wide occurrence in the environment especially in waste-waters (Liu *et al*., 2013). It is extensively used in mining, materials processing, paper making, printing, electroplating, paint, metal finishing, mining operations, chemical manufacturing, fertilizer (Mermut *et al*., 1996), bactericides, fungicides (Epstein and Bassein, 2001) and pigment industries. They discharge untreated effluents resulting in the copper pollution in aquatic system.

Abiotic and biotic methods have been employed for the elimination of heavy metals from aqueous medium. Frequently applied abiotic methods include chemical precipitation, chemical reduction, carbon adsorption, ion exchange, solvent extraction, reverse osmosis, membrane process, evaporation and electrochemical processes. These methods are considered as ineffective due to some technical restrictions such as sludge production, operational intricacy or economic constraints (Crini, 2006). Therefore, the research has been focused towards biotic methods due to its potential applications in environmental protection and recovery of toxic or strategic heavy metals (Chang *et al*., 1997).

Among the different biotic methods, bioaccumulation and biosorption have been demonstrated to possess good potential for the removal of metals (Volesky and Holan, 1995; Das *et al*., 2008). Bioaccumulation is the active uptake of toxicants by living cells, however, biosorption mechanism is the passive uptake of toxicants by dead/inactive biological materials. Both living and dead microbial biomaterials have offered potential economical alternative to conventional absorbents (Lo *et al*., 2014).

BIOSORPTION

Biosorption is a metabolism independent process responsible for the selective sequestration of heavy metal ions or other molecules onto certain biological materials. It is the passive uptake of toxicants by dead/inactive biomaterials from very dilute complex solutions with high efficiency. The biosorption process involves a solid phase (biosorbent) and a liquid phase (solvent) containing species to be sorbed (metal ions). The high affinity of the sorbent towards metal ions resulted in the interaction and binding in the cell wall by different mechanisms. The process continues till the establishment of equilibrium between amount of solid bound sorbate and the remaining sorbate in the solution. It is carried out by various mechanisms that take place in cell wall, where the mechanism for pollutant uptake will take place according to the biomass type. Biosorption is considered as a potential mechanism for the removal of metals from solutions, not only for toxic metals but also for precious metal recovery (Das, 2010).

History of biosorption: The use of microbes for heavy metal accumulation was observed in early 18th and 19th centuries (Modak and Natarajan, 1995). The earliest technological applications of biosorption techniques were involved in sewage and waste treatment (Ullrich and Smith, 1951). Muraleedharan *et al*. (1991) reported that 1st quantitative study on copper biosorption was done by *L. hecke* by fungal spores of *T. tritici* and *U. crameri* in 1902. He also stated that Pichler and Wobler (1922) worked on uptake of Ag, Cu, Ce and Hg by corn smut. Various research reports have been published from toxicological points of view but these were concerned with the accumulation due to the active metabolism of living cells and the consequences of accumulation on the food chain (Volesky, 2001). Further research revealed that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. Researchers have understood and explained that biosorption depends not only on the type or chemical composition of the biomass but also on the external physicochemical factors. Many investigators explained the mechanisms responsible for biosorption which may be single or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and microprecipitation (Veglio and Beolchini, 1997). Goodman and Roberts (1971) reported that biosorption technology may be used for the monitoring of trace heavy metals in the environment.

BIOSORBENTS

Biosorbents are the biological materials (e.g., bacteria, algae, fungi, yeasts, agricultural wastes and other polysaccharide materials) responsible for the removal of heavy metals due to their metal sequestering properties (Volesky, 1986). When choosing the biomass for metal biosorption, its origin, availability and cost-effectiveness are major factors to be concerned. Potent metal biosorbents of bacteria include the genus of *Bacillus* (Tunali *et al*., 2006), *Pseudomonas* (Chang *et al*., 1997; Uslu and Tanyol, 2006) and *Streptomyces* (Mameri *et al*., 1999). Some of the important results of copper biosorption using bacterial biomass are illustrated in Table 1. Likewise,

Table 1: Important results on biosorption of copper by various bacterial species along with operating conditions

	Operating conditions					
Bacterial species	pH	Temperature (°C)	Biomass dosage (g L^{-1})	Equilibrium time (h)	Metal adsorbed (mg g^{-1})	References
Bacillus sp. ATS-1	5.0	25	2	2	16.3 (E)	Tunali *et al.* (2006)
Micrococcus luteus IAM 1056	5	25	0.5	1	33.5 (L)	Nakajima *et al.* (2001)
Enterobacter sp. J1	5.0	25	NA	24	32.5 (L)	Lu *et al.* (2006)
Pseudomonas aeruginosa PU21	5.0	NA	1-2	24	23.1 (L)	Chang *et al.* (1997)
Pseudomonas cepacia	7	30	NA	NA	65.3 (L)	Savvaidis *et al.* (2003)
Pseudomonas putida	5.5	30	1	24	96.9 (L)	Uslu and Tanyol (2006)
Pseudomonas putida CZ1	4.5	30	1	24	15.8 (L)	Chen *et al.* (2005)
Sphaerotilus natans[b]	6	NA	3	0.5	60 (E)	Beolchini *et al.* (2003)
Sphaerotilus natans	5.5	30	NA	NA	5.4 (L)	Beolchini *et al.* (2006)
Thiobacillus ferrooxidans[a]	6.0	37	0.2	2	198.5 (L)	Ruiz-Manriquez *et al.* (1997)
Thiobacillus thiooxidans[a]	5.0	40	300	2	39.84 (L)	Liu *et al.* (2004)
Streptomyces coelicolor	5	25	1	8	66.7 (L)	Ozturk and Ayar (2004)
Active sludge bacteria	5	25	0.5	NA	50	Aksu *et al.* (1991)
Zoogloea ramigera	5.5	NA	0.83	NA	270	Norberg and Persson (1984)
Zoogloea ramigera	4	25	NA	NA	29	Aksu *et al.* (1992)
Pseudomonas syringae	NA	22	0.28	NA	25.4	Cabral (1992)
Streptomyces noursei	5.5	30	3.5	NA	9	Mattuschka and Straube (1993)
Arthrobacter sp.	3.5-6	30	0.4	NA	148	Veglio *et al.* (1997)
Bacillus firmus	4	25	NA	NA	381 (L)	Salehizadeh and Shojaosadti (2003)
Geobacillus toebii	4.0	60	2.5	1	48.5 (L)	Ozdemir *et al.* (2009)
Geobacillus thermoleovorans	4.0	60	2.5	1	41.5 (L)	Ozdemir *et al.* (2009)
Bacillus sp. FM1	5	NA	NA	1	78.125	Masood and Malik (2011)
Arthrobacter sp.	5	30	NA	NA	175.87 (L)	Hasan and Srivastava (2009)
Pantoea sp. TEM18	5	NA	0.01	0.25	30.1 (L)	Ozdemir *et al.* (2004)
Zoogloea ramigera	4	45	NA	NA	52.3 (L)	Sag and Kutsal (1995)
Bacillus sp. F19	4.8	25	NA	0.1	89.62 (L)	Zheng *et al.* (2008)

NA: Not available, L: Uptake predicted by the Langmuir model, E: Experimental uptake, [a]Chemically modified, [b]Immobilize important fungal biosorbents include *Aspergillus* (Binupriya *et al.*, 2006), *Rhizopus* (Bai and Abraham, 2002) and *Penicillium* (Tan and Cheng, 2003), etc. Recently, numerous approaches have been made for the development of low-cost sorbents from industrial and agricultural wastes. Of these, crab shells (Vijayaraghavan *et al.*, 2006), brown seaweed (Davis *et al.*, 2003), activated sludge (Al-Qodah, 2006), rice husks (Chuah *et al.*, 2005), eggshell (Vijayaraghavan *et al.*, 2005) and peat moss (Sharma and Forester, 1993) deserves particular attention.

Bacterial biosorbents-cell wall structure and biochemistry: Bacteria are a major group of unicellular living organisms, ubiquitous in soil and water. They constitute a significant fraction of the entire living terrestrial biomass of ~10^{18} g. They make excellent biosorbents because of their high surface to volume ratios and presence of potentially active chemiosorption sites (e.g., teichoic acid) in their cell walls (Beveridge, 1989).

Bacterial cell wall is a well-defined polymeric matrix located just outside the plasma membrane of a cell, providing mechanical strength and resistance to cell. It is the first cellular structure that comes in contact with the soluble metal species in the extracellular environment. Bacterial cell wall shape and strength is due to a polysaccharide called peptidoglycans; which consist of linear chains of the disaccharide N-Acetyl Glucosamine (NAG), N-Acetyl Muramic acid (NAM). Peptidoglycan contains several amino acids, three of which are D-glutamic acid, D-alanine and mesodiaminopimelic acid. Peptide chains of amino acids are connected to carboxyl groups by NAM. The carboxyl group of the D-alanine is often connected directly to the amino group of mesodiaminopimelic acid (Prescott *et al.*, 2002).

The cell walls of Gram-positive bacteria is thick due to presence of thick peptidoglycan layer (20-80 nm) containing teichoic acid and lipoteichoic acid in them (Beveridge, 1981) as shown in Fig. 1. Peptidoglycan accounts for 50% or more of the dry weight of the wall of some Gram-positive species. Teichoic acid appears to extend to the peptidoglycan surface and as they are negatively charged, helpful to give the Gram-positive cell wall a negative charge. The phosphoryl groups of secondary polymers and the carboxyl groups of the peptide chains provide negatively charged sites in the Gram-positive cell wall, helps in cation sequestering mechanism (Prescott *et al.*, 2002).

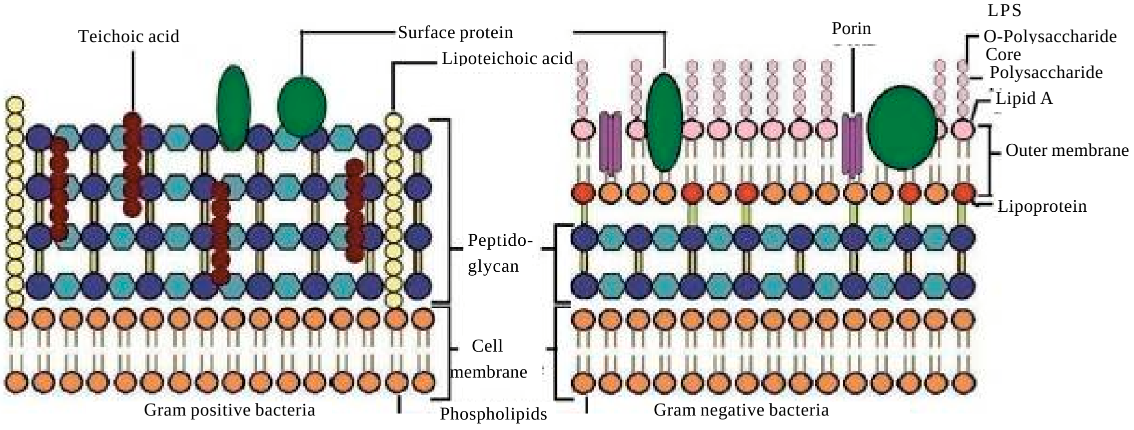

Fig. 1: Bacterial cell-wall structure (adapted and modified from Murphy *et al.*, 2008)

Gram-negative bacteria are thinner than Gram-positive containing monolayer peptidoglycan (10-15 nm thick), Lipopolysaccharide (LPS), phospholipids and surface protein (Beveridge, 1981). The phosphate groups within LPSs and phospholipids have been demonstrated to be the primary sites for metal interaction (Remacle, 1990; Prescott *et al.*, 2002).

BIOSORPTION MECHANISM

Chemical makeup of microbial cells is responsible for the strong biosorbent behavior of microbial biomass towards metal ions (Volesky and Holan, 1995). Functional groups responsible for the attraction and sequestration of pollutants include carboxylate, hydroxyl, carbonyl, carboxyl, imine, imidazole, sulfonate, sulfhydryl, thioether, phenolic, amide, amine, phosphate and phosphodiester groups present within the cell-wall components, such as polysaccharides, lipids and proteins (Gupta *et al.*, 2000). The importance of any given group for biosorption of a certain metal by a certain biomass depends on factors, such as: The number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the site (i.e., availability) and affinity between site and metal (i.e., binding strength) (Vieira and Volesky, 2000). The biosorption mechanism is a complex process (Fig. 2), influenced by the status of biomass (living or non-living, cell wall composition), types of biomaterials, properties of metal solution chemistry and ambient/environmental conditions (such as pH, temperature, biosorbent dosage, etc.).

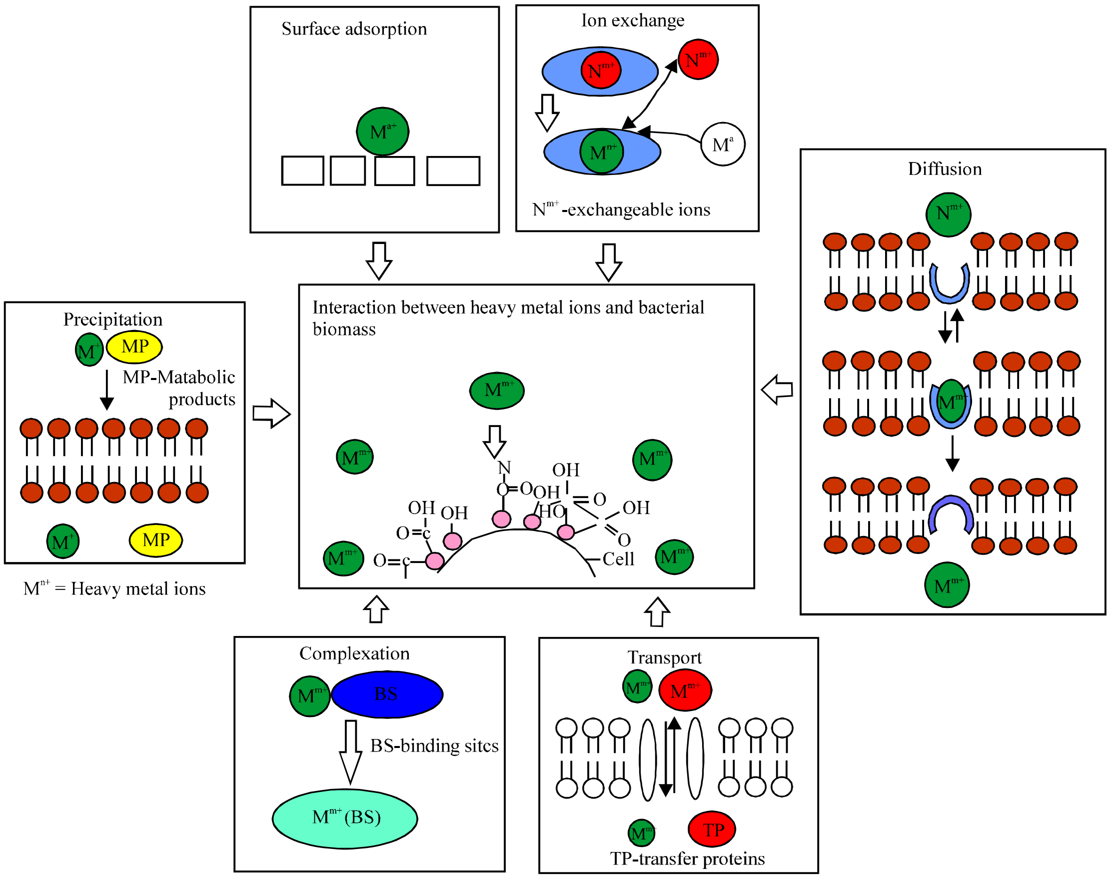

Fig. 2: Mechanism for heavy metal biosorption process (adapted and modified from Sud *et al.*, 2008; He and Chen, 2014)

From the literature, it has been reported that no single mechanism is able to describe the sorption mechanism of copper. The binding occurs by any one or a combination of the physicochemical attractions between the metal ions and functional groups present on the cell wall surface. It includes, coordination, complexation, ion exchange, physical adsorption or inorganic microprecipitation (Sud *et al.*, 2008).

Biosorption mechanism is a two step process: Passive biosorption and active biosorption. The first step, passive biosorption is metabolism independent and rapid mechanism of metal uptake on the cell wall surface, known as extracellular binding. Occurrence of binding is due to the interaction between metal ions and functional groups present on the cell wall. The second step, active biosorption is metabolism dependent, relatively slow mechanism responsible for the penetration of metal ions into the cell membrane, termed as intracellular binding (Goyal *et al.*, 2003). These complex bindings are dependent on the metal ions and the biological system. Though functional groups are responsible for binding of metals, however, the presence of functional groups does not assure successful biosorption; as steric, conformational, or other barriers may also be present (Volesky, 1986).

ANALYTICAL TECHNIQUES IN BIOSORPTION RESEARCH

A number of analytical techniques (Fig. 3) have been used to elucidate the biosorption processes, including Atomic Absorption Spectrophotometry (AAS), potentiometric titrations, Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy

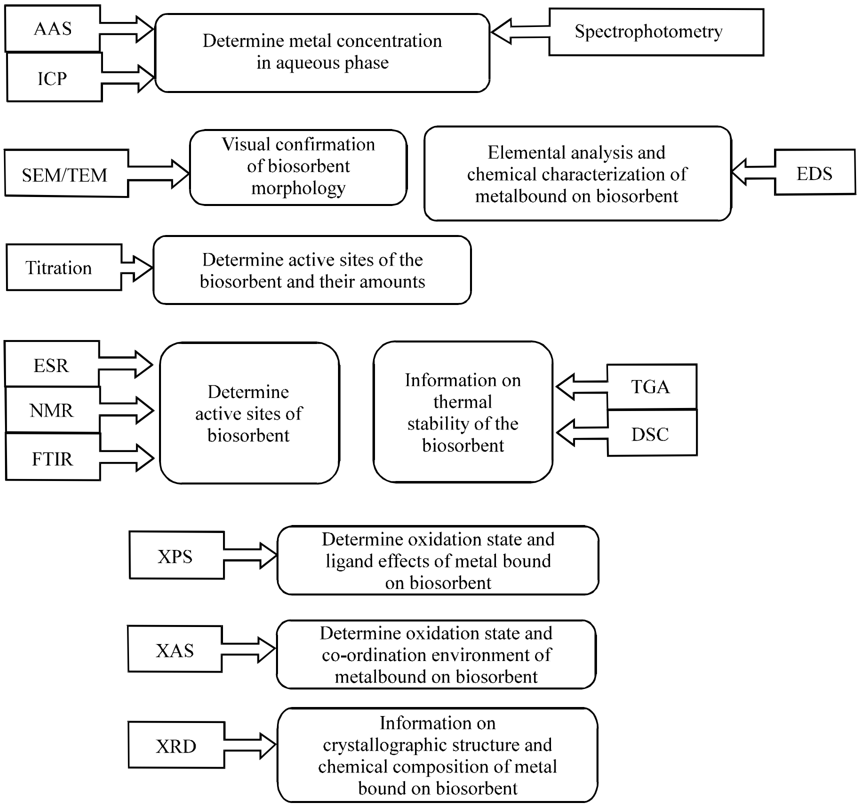

Fig. 3: Analytical techniques in biosorption research and their characteristics (Park *et al.*, 2010)

(SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), Electron Spin Resonance spectroscopy (ESR), Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC), X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Spectroscopy (XAS), Thermo-Gravimetric Analysis (TGA) among others (Wang and Chen, 2006; Park *et al.*, 2010). All these techniques complement each other in giving insights into the mechanisms of biosorption.

FACTORS INFLUENCING BIOSORPTION PROCESS

Analysis of factors influencing biosorption is important for evaluation of the biosorption potential of any biomaterial. The important factors include:

pH: pH affects the solution chemistry of pollutants and the activity of the functional groups of the biomass surface (Galun *et al.*, 1987; Esposito *et al.*, 2002). The range of pH between 3 to 6 has been found favourable for biosorption, because of the presence of negatively charged carboxyl groups on cell wall which are responsible for the extracellular binding of metal cations (Gadd and de Rome, 1988). However, higher solution pH complicates the sorption process due to the decrease in solubility of metal complexes. For cationic metal species like Cu, Cd, Ni, Co and Zn, the biosorption activity is reduced at lower pH whereas for anionic metals like CrO^{4-}, $Au(CN)^{2-}$ vice-versa i.e., higher biosorption occur at low pH (Gadd and White, 1985).

Temperature: Temperature influences biosorption process to a lesser extent within the range from 20-35°C (Aksu *et al.*, 1992; Veglio and Beolchini, 1997). An increase in temperature is responsible for the reduction in biosorption capacity of the biosorbent as well as physical damage to the biosorbent due to the exothermic nature of some adsorption processes (Mameri *et al.*, 1999).

Ionic strength: Ionic strength influences the adsorption of solute to the biomass surface (Daughney and Fein, 1998; Borrok and Fein, 2005). Ionic strength is the competition between ions or the changes in metal activity. When two phases, e.g., biomass surface and solute in aqueous solution are in contact, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction. Thus, adsorption decreases with increase in ionic strength (Donmez and Aksu, 2002).

Biosorbent dosage: The biosorbent dosage strongly influences the extent of biosorption. Lower biosorbent dosages yield higher uptakes due to high surface area and availability of more sorption sites (Vijayaraghavan *et al.*, 2006). Conversely, with increase in biosorbent dosage, the decrease in adsorption capacity may be observed due to unsaturated binding sites and reduction in the effective surface area (Esposito *et al.*, 2001; Aksu and Cagatay, 2006).

Initial solute concentration: The initial solute concentrations have an impact on biosorption. Higher solute concentration (initial) resulting in a high solute uptake (final), due to the elevated surface area of the biosorbent which in turn increases the number of binding sites (Ho and McKay, 1999a, b, 2000). However, at higher concentrations, the sites available for sorption become fewer compared to the moles of solute present and hence, the removal of solute is strongly dependent upon the initial solute concentration (Vijayaraghavan and Yun, 2008). Oves *et al.* (2013) demonstrated that rate of biosorption decreased with an increase in metal ion concentration of copper. The maximum biosorption of copper was recovered at a low initial metal ion concentration for example it was 91.8% at 25 mg L^{-1} while it was 82.7% at 150 mg L^{-1}.

BIOSORPTION ISOTHERM MODELING AND SORPTION KINETICS

Biosorption isotherms: The quality of a biosorbent is judged by how much sorbate it can attract and retain in an immobilized form. The amount of metal adsorbed by adsorbent was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = (C_i - C_{eq})\frac{V}{M}$$

Where:

q = Metal uptake (mg g^{-1})
C_i = Initial metal concentrations in the solution (mg L^{-1})
C_{eq} = Equilibrium metal concentrations in the solution (mg L^{-1})
V = Solution volume (L)
M = Mass of biosorbent (g)

Appropriate models are useful in analysis of experimental data, prediction of experimental behavior, concluding the process mechanisms and optimization processes. Gadd (1988) stated that, the equilibrium of the biosorption process is often described by providing the experimental points with models usually used for the representation of isotherm adsorption equilibrium. Table 2 represents the widely accepted and linearized equilibrium adsorption isotherm models.

Where:

b = Ratio of adsorption and desorption rates
K_F and n are constants
C_s = Saturation concentration of the solute
B = Constant relating to the energy of interaction with the surface and other symbols are as previously described

Table 2: Widely accepted isotherm equations and specific characteristics

Isotherm models	Equation	Characteristics	References
Langmuir	$q = \frac{q_{max} bC_{eq}}{1 + C_{eq}}$	For monolayer sorption onto surface and finite number of identical sites Extensively used for dilute solutions Applied only at constant pH	Langmuir (1918), McKay (1982)
Freundlich	$q = KFC_{eq}^{1/n}$	For heterogeneous surface Extensively used for dilute solutions Applied only at constant pH	Freundlich (1907), McKay (1982)
BET	$q = \frac{q_{max} BC_{eq}}{(C_s - C_{eq})[1 + (B-1)(C_{eq} / C_s)]}$	For multilayer adsorption	Brunauer *et al.* (1938)

Sorption kinetics: Sorption kinetics and operation control are very important for effective biosorption process, as they provide information on the rate of metal uptake and hydrodynamic parameters (Azizian, 2004). The kinetics describe the solute uptake that finally controls the residence time of a sorbate at the solid-solution interface which in turn provides insight into the reaction pathways and the mechanism of the sorption reaction (Ho and McKay, 2000).

The kinetics of the adsorption data can be analyzed by using two kinetic models, pseudo-first order and pseudo-second order. The pseudo-first order equation is generally expressed by Lagergren *et al.* (1898), Vijayaraghavan and Yun (2008) and Park *et al.* (2010):

$$\log = (q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303} t$$

Where:

q_{eq} = Amount of metal ion adsorbed at equilibrium (mg g^{-1})
q = Amount of metal ion adsorbed at time t (mg g^{-1})
k_1 = Pseudo first-order rate constant (min^{-1})

The pseudo-second order kinetics was calculated by (Ho and Mckay, 1999a):

$$\frac{t}{q} = \frac{1}{k_2 q^2_{eq}} + \frac{1}{q_{eq}} t$$

k_2 = Second-order equilibrium rate constant (g mg^{-1} min)

The researchers calculated the rate of the second, third and fourth stages, according to the pseudo-second-order model. The rate for these steps decreased sequentially and was related to the ratio of the metal ion concentration to the sorbent concentration.

CONCLUSIONS AND FUTURE DIRECTIONS FOR BIOSORPTION RESEARCH

There are several modes of metal decontamination, though they have been considered as ineffective due to technical restrictions. Biosorption has been emerged as a potential alternative for removal of metals with the help of biomaterials. Biosorption researches have exposed the intricacy of the process, its dependence on physicochemical and biological factors and uncertainty about the mechanisms involved.

Though the biosorption process has been well studied and developed, yet its application is limited. The two major factors behind this may be the shortcomings of the biosorption technology and less knowledge about the mechanism. Biosorption processes are still at the stage of laboratory-scale study in spite of unquestionable progress. Thus, much work in this area is necessary to demonstrate its possibilities on an industrial scale.

Common suggestions for future research directions:

- Development of more comprehensive and specific biosorbent models for complex biosorption systems
- Recognition of biosorption mechanisms

- Development of hybrid technology for removal of pollutants i.e., use of several biotechnological processes for decontamination
- Involvement of genetic engineering, to identify the mechanism at molecular level which will help in the construction of engineered organisms with higher sorption capacity
- Biosorption research has mainly aimed for the removal of pollutants, however, precious metal recovery by biosorbents is getting paid attention because of the increasing rate and limited deposits of the precious metals
- Although, the pretreatment enhances the biosorption capacity but they increase the overall cost of biosorption process. So, it is necessary to develop new methods which will drop the overall costs for pretreatments

REFERENCES

Aksu, Z. and S.S. Cagatay, 2006. Investigation of biosorption of Gemazol Turquise Blue-G reactive dye by dried *Rhizopus arrhizus* in batch and continuous systems. Sep. Purif. Technol., 48: 24-35.

Aksu, Z., T. Kutsal, S. Gun, N. Haciosmanoglu and M. Gholaminejad, 1991. Investigation of biosorption of Cu(II), Ni(II) and Cr(VI) ions to activated sludge bacteria. Environ. Technol., 12: 915-921.

Aksu, Z., Y. Sag and T. Kutsal, 1992. The biosorption of copper by *C. vulgaris* and *Z. ramigera*. Environ. Technol., 13: 579-586.

Al-Qodah, Z., 2006. Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination, 196: 164-176.

Alloway, B.J., 1995. The Origins of Heavy Metals in Soils. In: Heavy Metals in Soils, Alloway, B.J. (Ed.). Blackie Academic and Professional, London, UK., ISBN-13: 9780751401981, pp: 38-57.

Azizian, S., 2004. Kinetic models of sorption: A theoretical analysis. J. Colloid Interface Sci., 276: 47-52.

Bai, R.S. and T.E. Abraham, 2002. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. Water Res., 36: 1224-1236.

Beolchini, F., F. Pagnanelli, L. Toro and F. Veglio, 2003. Biosorption of copper by *Sphaerotilus natans* immobilised in polysulfone matrix: Equilibrium and kinetic analysis. Hydrometallurgy, 70: 101-112.

Beolchini, F., F. Pagnanelli, L. Toro and F. Veglio, 2006. Ionic strength effect on copper biosorption by *Sphaerotilus natans*: Equilibrium study and dynamic modelling in membrane reactor. Water Res., 40: 144-152.

Beveridge, T.J., 1981. Ultrastructure, chemistry and function of the bacterial wall. Int. Rev. Cytol., 72: 229-317.

Beveridge, T.J., 1989. Role of cellular design in bacterial metal accumulation and mineralization. Ann. Rev. Microbial., 43: 147-171.

Binupriya, A.R., M. Sathishkumar, K. Swaminathan, E.S. Jeong, S.E. Yun and S. Pattabi, 2006. Biosorption of metal ions from aqueous solution and electroplating industry wastewater by *Aspergillus japonicus*: Phytotoxicity studies. Bull. Environ. Contam. Toxicol., 77: 219-227.

Borrok, D.M. and J.B. Fein, 2005. The impact of ionic strength on the adsorption of protons, Pb, Cd and Sr onto the surfaces of Gram negative bacteria: Testing non-electrostatic, diffuse and triple-layer models. J. Colloid Interface Sci., 286: 110-126.

Brunauer, S., P.H. Emmett and E. Teller, 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc., 60: 309-319.

Cabral, J.P.S., 1992. Selective binding of metal ions to *Pseudomonas syringae* cells. Microbios, 71: 47-53.

Chang, J.S., R. Law and C.C. Chang, 1997. Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU21. Water Res., 31: 1651-1658.

Chen, X.C., Y.P. Wang, Q. Lin, J.Y. Shi, W.X. Wu and Y.X. Chen, 2005. Biosorption of copper(II) and zinc(II) from aqueous solution by *Pseudomonas putida* CZ1. Colloids Surf. B: Biointerfaces, 46: 101-107.

Chuah, T.G., A. Jumasiah, I. Azni, S. Katayon and S.Y.T. Choong, 2005. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview. Desalination, 175: 305-316.

Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal: A review. Bioresour. Technol., 97: 1061-1085.

Das, N., 2010. Recovery of precious metals through biosorption: A review. Hydrometallurgy, 103: 180-189.

Das, N., R. Vimala and P. Karthika, 2008. Biosorption of heavy metals: An overview. Indian J. Biotechnol., 7: 159-169.

Daughney, C.J. and J.B. Fein, 1998. The effect of ionic strength on the adsorption of H^+, Cd^{2+}, Pb^{2+} and Cu^{2+} by *Bacillus subtilis* and *Bacillus licheniformis*: A surface complexation model. J. Colloid Interface Sci., 198: 53-77.

Davis, T.A., B. Volesky and A. Mucci, 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res., 37: 4311-4330.

Donmez, G. and Z. Aksu, 2002. Removal of chromium(VI) from saline wastewaters by *Dunaliella* species. Process Biochem., 38: 751-762.

Epstein, L. and S. Bassein, 2001. Pesticide applications of copper on perennial crops in California, 1993 to 1998. J. Environ. Qual., 30: 1844-1847.

Esposito, A., F. Pagnanelli, A. Lodi, C. Solisio and F. Veglio, 2001. Biosorption of heavy metals by *Sphaerotilus natans*: An equilibrium study at different pH and biomass concentrations. Hydrometallurgy, 60: 129-141.

Esposito, A., F. Pagnanelli and F. Veglio, 2002. pH-related equilibria models for biosorption in single metal systems. Chem. Eng. Sci., 57: 307-313.

Freundlich, H., 1907. Ueber die Adsorption in Loesungen. Z. Phys. Chem., 57: 385-470.

Gadd, G.M. and C. White, 1985. Copper uptake by *Penicillium ochrochloron*: Influence of pH on toxicity and demonstration of energy-dependent copper influx using protoplasts. Microbiology, 131: 1875-1879.

Gadd, G.M. and L. de Rome, 1988. Biosorption of copper by fungal melanin. Applied Microbiol. Biotechnol., 29: 610-617.

Gadd, G.M., 1988. Heavy Metal and Radionuclide by Fungi and Yeasts. In: Biohydrometallurgy, Norris, P.R. and D.P. Kelly (Eds.). Rowe, Chippenham, UK.

Galun, M., E. Galun, B.Z. Siegel, P. Keller, H. Lehr and S.M. Siegel, 1987. Removal of metal ions from aqueous solutions by *Penicillium* biomass: Kinetic and uptake parameters. Water Air Soil Pollut., 33: 359-371.

Goodman, G.T. and T.M. Roberts, 1971. Plants and soils as indicators of metals in the Air. Nature, 231: 287-292.

Goyal, N., S.C. Jain and U.C. Banerjee, 2003. Comparative studies on the microbial adsorption of heavy metals. Adv. Environ. Res., 7: 311-319.

Gupta, R., P. Ahuja, S. Khan, R.K. Saxena and H. Mohapatra, 2000. Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solutions. Curr. Sci., 78: 967-973.

Hasan, S.H. and P. Srivastava, 2009. Batch and continuous biosorption of Cu^{2+} by immobilized biomass of *Arthrobacter* sp. J. Environ. Manage., 90: 3313-3321.

He, J. and J.P. Chen, 2014. A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry and modeling simulation tools. Bioresour. Technol., 160: 67-78.

Ho, Y.S. and G. McKay, 1999a. Pseudo-second order model for sorption processes. Proces. Biochem., 34: 451-465.

Ho, Y.S. and G. McKay, 1999b. The sorption of lead (II) ions on peat. Water Res., 33: 578-584.

Ho, Y.S. and G. McKay, 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res., 34: 735-742.

Kabata-Pendias, A. and H. Pendias, 2001. Trace Elements in Soils and Plants. 3rd Edn., CRC Press, Boca Raton, FL., USA., ISBN-13: 9781420039900, Pages: 432.

Kabata-Pendias, A., 1995. Agricultural Problems Related to Excessive Trace metal Contents of Soil. In: Heavy Metals (Problems and Solutions), Salomons, W., U. Forstner and P. Mader (Eds.). Springer-Verlag, New York, USA., ISBN-13: 9783540585084, pp: 3-18.

Lagergren, S., 1898. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga Svenska Vetenskapsakademiens Handlingar, 24: 1-39.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1403.

Liu, H.L., B.Y. Chen, Y.W. Lan and Y.C. Cheng, 2004. Biosorption of Zn(II) and Cu(II) by the indigenous *Thiobacillus thiooxidans*. Chem. Eng. J., 97: 195-201.

Liu, Y., M. Chen and H. Yongmei, 2013. Study on the adsorption of Cu (II) by EDTA functionalized Fe_3O_4 magnetic nano-particles. Chem. Eng. J., 218: 46-54.

Lo, Y.C., C.L. Cheng, Y.L. Han, B.Y. Chen and J.S. Chang, 2014. Recovery of high-value metals from geothermal sites by biosorption and bioaccumulation. Bioresour. Technol., 160: 180-190.

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

Mameri, N., N. Boudries, L. Addour, D. Belhocine, H. Lounici, H. Grib and A. Pauss, 1999. Batch zinc biosorption by a bacterial nonliving *Streptomyces rimosus* biomass. Water Res., 33: 1347-1354.

Masood, F. and A. Malik, 2011. Biosorption of metal ions from aqueous solution and tannery effluent by *Bacillus* sp. FM1. J. Environ. Sci. Health Part A: Toxic/Hazard. Subst. Environ. Eng., 46: 1667-1674.

Mattuschka, B. and G. Straube, 1993. Biosorption of metals by a waste biomass. J. Chem. Technol. Biotechnol., 58: 57-63.

McKay, G., 1982. Adsorption of dyestuffs from aqueous solutions with activated carbon I: Equilibrium and batch contact-time studies. J. Chem. Technol. Biotechnol., 32: 759-772.

Mermut, A.R., J.C. Jain, L. Song, R. Kerrich, L. Kozak and S. Jana, 1996. Trace element concentrations of selected soils and fertilizers in Saskatchewan, Canada. J. Environ. Qual., 25: 845-853.

Modak, J.M. and K.A. Natarajan, 1995. Biosorption of metals using nonliving biomass: A review. Miner. Metall. Proces., 12: 189-196.

Muraleedharan, T.R., L. Iyengar and C. Venkobachar, 1991. Biosorption: An attractive alternative for metal removal and recovery. Curr. Sci., 61: 379-385.

Murphy, K., C. Janeway, P. Travers and M. Walport, 2008. Janeway's Immunobiology. 7th Edn., Garland Science, USA., ISBN: 9780815341239, Pages: 887.

Nakajima, A., M. Yasuda, H. Yokoyama, H. Ohya-Nishiguchi and H. Kamada, 2001. Copper biosorption by chemically treated *Micrococcus luteus* cells. World J. Microbiol. Biotechnol., 17: 343-347.

Norberg, A.B. and H. Persson, 1984. Accumulation of heavy metal ions by *Zoogloea ramigera*. Biotechnol. Bioeng., 26: 239-246.

Oves, M., M.S. Khan and A. Zaidi, 2013. Biosorption of heavy metals by *Bacillus thuringiensis* strain OSM29 originating from industrial effluent contaminated North Indian soil. Saudi J. Biol. Sci., 20: 121-129.

Ozdemir, G., N. Ceyhan, T. Ozturk, F. Akirmak and T. Cosar, 2004. Biosorption of chromium(VI), cadmium(II) and copper(II) by *Pantoea* sp. TEM18. Chem. Eng. J., 102: 249-253.

Ozdemir, S., E. Kilinc, A. Poli, B. Nicolaus and K. Guven, 2009. Biosorption of Cd, Cu, Ni, Mn and Zn from aqueous solutions by thermophilic bacteria, *Geobacillus toebii* sub. sp. *decanicus* and *Geobacillus thermoleovorans* sub. sp. *stromboliensis*: Equilibrium, kinetic and thermodynamic studies. Chem. Eng. J., 152: 195-206.

Ozturk, A., T. Artan and A. Ayar, 2004. Biosorption of nickel(II) and copper(II) ions from aqueous solution by *Streptomyces coelicolor* A3(2). Colloids Surf. B. Biointerfaces, 34: 105-111.

Park, D., Y.S. Yun and J.M. Park, 2010. The past, present and future trends of biosorption. Biotechnol. Bioprocess. Eng., 15: 86-102.

Pichler, F. and A. Wobler, 1922. Advances in Pest Control Research. Vol. 2, Interscience Publishers Inc., New York, USA.

Prescott, M., J.P. Harley and D.A. Klein, 2002. Industrial Microbiology and Biotechnology in General Microbiology. 5th Edn., McGraw-Hill, New York, USA.

Remacle, J., 1990. The Cell Wall and Metal Binding. In: Biosorption of Heavy Metals, Volesky, B. (Ed.). CRC Press, Boca Raton, ISBN-13: 9780849349171, pp: 83-92.

Ruiz-Manriquez, A., P.I. Magana, V. Lopez and R. Guzman, 1997. Biosorption of Cu by *Thiobacillus ferrooxidans*. Bioprocess. Eng., 18: 113-118.

Sag, Y. and T. Kutsal, 1995. Biosorption of heavy metals by *Zoogloea ramigera*: Use of adsorption isotherms and a comparison of biosorption characteristics. Chem. Eng. J. Biochem. Eng. J., 60: 181-188.

Salehizadeh, H. and S.A. Shojaosadati, 2003. Removal of metal ions from aqueous solution by polysaccharide produced from *Bacillus firmus*. Water Res., 37: 4231-4235.

Savvaidis, I., M.N. Hughes and R.K. Poole, 2003. Copper biosorption by *Pseudomonas cepacia* and other strains. World J. Microbiol. Biotechnol., 19: 117-121.

Sharma, D.C. and C.F. Forester, 1993. Removal of hexavalent chromium using sphagnum moss peat. Water Res., 27: 1201-1208.

Sud, D., G. Mahajan and M.P. Kaur, 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions: A review. Bioresour. Technol., 99: 6017-6027.

Tan, T. and P. Cheng, 2003. Biosorption of metal ions with *Penicillium chrysogenum*. Applied Biochem. Biotechnol., 104: 119-128.

Tunali, S., A. Cabuk and T. Akar, 2006. Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. Chem. Eng. J., 115: 203-211.

Ullrich, A.H. and M.W. Smith, 1951. The biosorption process of sewage and waste treatment. Sewage Ind. Wastes, 23: 1248-1253.

Uslu, G. and M. Tanyol, 2006. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature. J. Hazard. Mater., 135: 87-93.

Veglio, F. and F. Beolchini, 1997. Removal of metals by biosorption: A review. Hydrometallurgy, 44: 301-316.

Veglio, F., F. Beolchini, A. Gasbarro, S. Lora, B. Corain and L. Toro, 1997. Polyhydroxoethylmethacrylate (polyHEMA)-trimethylolpropanetrimethacrylate (TMPTM) as a support for metal biosorption with *Arthrobacter* sp. Hydrometallurgy, 44: 317-320.

Vieira, R.H. and B. Volesky, 2000. Biosorption: A solution to pollution? Int. Microbiol., 3: 17-24.

Vijayaraghavan, K., J. Jegan, K. Palanivelu and M. Velan, 2005. Removal and recovery of copper from aqueous solution by eggshell in a packed column. Miner. Eng., 18: 545-547.

Vijayaraghavan, K., K. Palanivelu and M. Velan, 2006. Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles. Bioresour. Technol., 97: 1411-1419.

Vijayaraghavan, K. and Y.S. Yun, 2008. Bacterial biosorbents and biosorption. Biotechnol. Adv., 26: 266-291.

Volesky, B., 1986. Biosorbent materials. Biotechnol. Bioeng. Symp., 16: 121-126.

Volesky, B., 2001. Detoxification of metal-bearing effluents: Biosorption for the next century. Hydrometallurgy, 59: 203-216.

Volesky, B. and Z.R. Holan, 1995. Biosorption of heavy metals. Biotechnol. Prog., 11: 235-250.

Wang, J.L. and C. Chen, 2006. Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review. Biotechnol. Adv., 24: 427-451.

Zheng, Y., X. Fang, Z. Ye, Y. Li and W. Cai, 2008. Biosorption of Cu(II) on extracellular polymers from *Bacillus* sp. F19. J. Environ. Sci., 20: 1288-1293.