RESEARCH PAPER | Biotechnology | Volume : 2 | Issue : 3 | December 2012 | ISSN - 2249-555X

Biosorption: An Eco-Friendly Technique for the Removal of Heavy Metals

KEYWORDS Biosorption, Pre-treatment, Isotherms, Crab shells, tamarind seeds, heavy metals, bioaccumulation.

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ABSTRACT *The biosorption technique can be used for the removal of pollutants from waters, those are considered as non-biodegradable. One of the most serious threats today is the heavy metal pollution that occurs in the aquatic systems. Most of the pollutants present in the waste water possess a significant threat to both environment and public health as they contain xenobiotics and heavy metals which are non-biodegradable and persistent. They possess a health hazard due to the principle of biomagnification as they seem to further accumulate in food chains. A plethora of sustainable biological materials that comprises of algae, bacteria, yeast and fungi have received enormous attention for removal of heavy metal and its recovery. Biosorption technology has advantages that are effective to treat dilute solutions of waste water harbouring heavy metals, has a low operating cost and generates minimum effluent. The dead or the living biomass may sequester the metals by the process of biosorption from water samples. The technology of biosorption employs various kinds of biomass which helps to trap heavy metals in contaminated waters. Intensive work on microbial biomass has emerged as an alternative for developing economic and ecofriendly treatment processes for waste water. The chemical processes that exist today are not economical for the treatment of large volumes of water bodies. Hence biological materials are used by virtue of their good performance, low cost and large available qualities. Here the microbial biomass used acts as an ion exchanger because of the presence of various reactive groups present on the cell surface such as carboxyl, sulphate, phosphate, sulfhydryl, and imidazole. The biosorbents is prepared by modifying the biomass with the help of various processes like granulation, pre-treatment and immobilization, which results in the entrapment of heavy metals in bead like structures and by the process of desorption the beads are used to release the metal ions which can be recycled and reused for subsequent procedures. This paper summarises the great challenge for the development of the biosorption process for the metal removal by two trends using hybrid technology and immobilization technology. The present review focuses on the examination of biosorbents within real and current research on biosorption and its potential application.*

INTRODUCTION

Most of the heavy metal pollutants are introduced into the ecosystem as a result of various industrial operations. Processes such as mining, smelting, surface finishing industry, energy and fuel production, fertilizer and pesticide, metallurgy, iron and steel, leather working, atomic energy, photography etc. Metals as a resource is depleting and posses a huge concern for human health and in the ecosystem. These wastes incorporated with the water are considered as highly toxic and carcinogenic. Three kinds of heavy metals are considered hazardous including toxic metals, precious metals, and radio nuclides (Wang and Chen, 2006). Among these that reaches hazardous levels are the heavy metals which comprise of lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, nickel, copper (Regine and Volesky-2000). Ahalya et al., 2003).

Taking into consideration the health hazards the heavy metals pose (Table 1) (Alluri et al) has become mandatory that all the effluents need to be assessed and require strict integrated pollution documentation before their final discharge which makes waste water treatment of utmost importance.

The traditional processes em ployed for the treatment of effluent are, chemical precipitation of hydroxides/sulphides, lime coagulation, reverse osmosis, solvent extraction and ion exchange (Rich and Cherry, 1987). The major disadvantage that we come across with the conventional processes is that the process is expensive and not eco-friendly, other disadvantages include incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal. (Ahalya et al., 2003). In view of these problems and legal constraints being imposed on discharge of effluents a need for an alternative and cost effective technology is essential. The search for novel technologies that involves the complete removal of the toxic heavy metals from waste water has lead to the discovery of the process of biosorption that relies on the metal binding capacities of various biological materials. The microbial biomass has proved to be a boon for developing economic and eco- friendly waste water treatment process.

Biosorption can be defined as the ability of biological materials to accumulate heavy metals (bioaccumulation) from waste water through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). It can also be defined as "a non directed physico-chemical interaction that may occur between metal/radio nuclide species and microbial cells" (Shumate and Stranberg, 1985). The process of bi-

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osorption includes a solid phase (sorbent or biosorbent, usually a biological material living/nonliving) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate), a metal ion. An enormous quantity of biological materials has been investigated as biosorbents. Algae, bacteria, fungi and yeast have proved to be potential metal biosorbents (Volesky, 1988).According to few investigations the possibility of the living organism to accumulate metallic elements could be toxic. Thus researchers have revealed that inactive or dead microbial biomass can passively bind metal ions via various physicochemical interactions. The mechanism is primarily due to the affinity between the sorbent and adsorbate. The mechanism understood is very limited and may be because of the combination of ion-exchange, complexation, coordination, adsorption, electrostatic interaction, chelation and micro precipitation (Wang and Chen 2006, Volesky, 2007, Vijayraghavan and Yun, 2008, Brady et al, 1994). Naturally occurring biomass or spent biomass have directed attention as the use of biosorbents as they can be effectively utilized. Biosorption offers advantages considering the low operating cost, minimization of the volume of chemical and /or biological sludge to be disposed, its high efficiency in dilute effluent, no requirement of nutrients and regeneration of biosorbents (Kratochvil and Volesky, 1998).

HISTORY OF BIOSORPTION

Biosorption has been considered as eco-friendly and may be used as a filtering technique for the environmental samples. The biosorption technique was first introduced by the Ames Crosta Mills & Company Ltd in 1973. According to investigations application of living biomass was used for the removal of metals from aqueous solutions in early 18th and 19th centuries (Modak and Natarajan, 1995, Ulrich and Smith, 1951). In early 1900's Arden and Lockett used certain types of living bacterial biomass to clean up the raw sewage and recover nitrogen and phosphorus in an aeration tank (Yan and Vijayraghavan, 2000)(Zhou and Kiff,1991). The first quantitative study was done by L. Hecke on the copper uptake by fungal spores on metal biosorption of T. tritici and U. crameri in 1902 (Muraleedharan et al, 1991).

BIOSORBENTS

Before endeavouring into the biosorption field, it is of prime importance to select the most promising type of biomass from a varied pool of readily available and inexpensive biomaterials (Kratochvil and Volesky, 1998). Metal biosorption by biomass depends on the various components of the cell especially through cell surface and the structure of the cell wall. The various chemical components of the bacterial cell surface that proves to be important for metal biosorption are peptidoglycan, teichoic acids and lipoteichoic acids. Various polysaccharides and proteins also proved to be involved in metal binding in certain kinds of biomass. The polysaccharides include, chitin, glycan, cellulose etc, which exist in fungi or algae cell walls.

The most common source of biosorbents can be the waste material from the industries as in comparison with the application of biomass from large scale fermentation processes, e.g. Yeast by- products from beer production or the use of Streptomyces and filamentous fungi from pharmaceutical production (Hughes and Pooley, 1989).The major criteria to be taken into consideration while selecting the biomass is its origin. As stated earlier, biomass can be obtained from activated sludge or fermentation waste from industries from those of food, dairy and starch. Microorganisms categorised as e.g. bacteria, yeast and fungi that are retrieved from their natural habitats are good source of biomass. Fast growing organisms like crab shells, sea weeds, tamarind seeds, fibrous plant wastes are specifically cultivated for biosorption process (Regine and Volesky, 2000). Other than microorganisms as a source of agricultural products, such as rice straw, coconut husks, peat moss, wool, are put in use for the biosorption process (Dakiky et al.,2002). Other abundantly available low cost adsorbents used are, waste tea, wheat bran, hard wood (Dalbergiasisso), saw dust, pea pod, cotton and mustard seed cakes (Ahluwalia and Goyal, 2005) , (Saeed et al, 2002). Biosorption can also be performed using cheap and abundantly available materials such as citrus peels which can prove to be a cost effective method for removing heavy metals from wastewater. Non living biomass is most commonly used in comparison to the use of the living microorganism because of its advantages. Non living things can be obtained with much lower cost, it is not subject to metal toxicity, the nutrient supply is not necessary, greater binding capacities to toxic metals has been reported as in the case of the removal of cadmium (Kratochvil andVolesky, 1998).Pine bark was one of the biosorbents which was cost effective and environment friendly and adsorbed two ions, Cu (II) and Zn (II) from its aqueous solutions. The optimum sorption pH for both the ions Cu (II) and Zn (II) were found to be in the range of 4.5-5. The study indicates that the sorption behaviour of both Cu (II) and Zn (II) on the pine bark was found to satisfy both Langmuir assumption and also Freudlich's assumption. (Amalinei et.al, 2012)

A much more cost effective method is the use of citrus peels for biosorption purpose which makes the process cheap and much more efficient. Pectin present in the citrus peels has an efficient metal binding capacity and its role was further investigated by using citrus peels, native orange peels, protonated peels, depectinated peels and extracted pectic acid. The binding capacity was found to be significantly higher for pectic acid. Protonated peels and native peels showed moderate metal binding capacity whereas depectinated peels showed the least metal binding capacity. (Schiewer S, Iqbal M. 2010). Table 2, represents the various types of abundantly available naturally biosorbents material used for the removal of heavy metal ions.

For efficient performance of the biosorbents, the ionic state of the biomass plays an important role, hence, biosorbents can be obtained with different ionic forms such as protonated (H+ form) or saturated cations, such as, Na+, Ca2+, Mg2+, etc. This is done by pretreating the biomass with mineral acids, bases and/or salts. Treatment process varies for different types of biomass and metal ions which are to be biosorbed. In order to develop an effective biosorbent and for its subsequent reuse (desorption process) the study of mechanism of metal binding is very important. Adsorption process contained a lot of activated carbon which was the most commonly used adsorbent, in comparison with biological waste water treatment, proved to be more efficient because it contained Extracellulary polymeric substances (EPS). EPS being a biopolymer compound contained many functional groups. EPS was found to adsorb various substances like, colour, metals, organic compounds and other compounds. Due to these positive effects EPS was extracted from activated sludge process and used as biosorbents (Junaidi, Sarwoko Mangkoedihardjo) (2011).

Recently, numerous approaches have been made for the development of low-cost sorbents from industrial and agricultural wastes. Of these activated sludge (Al-Qodah, 2006), rice husks (Chuah et al; 2005), egg shell (Vijayraghavan et al; 2005b), wood bark and peat moss (Sharma and Froster; 1993), sea food processing waste, peanut shell waste, waste ashes deserve particular attention.

Metal Binding

The chemical groups that attract and sequester the metals in biomass are the acetamido groups of chitin, structural polysaccharides of fungi, amino and phosphate groups in nucleic acids, amido, amino, sulfhydryl and carboxyl groups in proteins, hydroxyls in polysaccharides and mainly carboxyls and sulphates in polysaccharides of marine algae. The presence of some functional groups may not always guarantee biosorption perhaps due to steric, conformational or other hindrances. (Ahalya et al., 2003). Metal binding appears to occur in two steps where the first is a stoichiometric interaction between the metal and the reactive chemical groups in the cell wall and the second is an inorganic deposition of increased amounts of metal(s). Before reaching the plasma membrane and cell cytoplasm all metal ions have to come across the cell wall and the cell wall has a number of active sites capable of binding metal ions. This mechanism is similar

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to the complex ion exchanger in a commercial resin. Table 3, represents the various reactive functional groups present in different microbial cell (Talaro and Talaro, 2002). The difference in cell wall composition can cause a significant difference in the type and amount of metal ion binding to them. Among the photoautotrophs eukaryotic algal cell walls are mostly cellulosic. The potential metal binding groups of these classes of microbes are carboxylate, amine, imidazole, phosphate, sulfhydryl, sulphate and hydroxyl. Among these amine and imidazoles are positively charged and may produce negatively charged metal complexes (Crist et al., 1981). Certain other compounds such as chitosan in the cell wall of Penicillium chrysogenum has been shown to have high metal ion adsorption capacity which accounts for 3-40% of cell wall. (Galun et.al, 1986). The cell walls of brown algae contain fucoidin and alginic acid. The alginic acid gives anionic carboxylate and sulphate sides at neutral pH. Many fresh water forms contain galaturonic acid and its polymer pectin which also has anionic sides to which metals can bind by electrostatic attractions. The amino and carboxyl groups, and nitrogen and oxygen of the peptide bonds are also present for coordination bonding with metal ions like lead, copper or chromium. Such bond formation is shown to be accompanied by proton displacement and involves the extent of protonation which is determined by the pH. . (Gadd et al, 1988; Gourdon et al, 1990; Gadd, 1990; Horikoshi et al,1981). Different groups involved in metal binding have been shown to use the modification or blocking of the groups. Taking a look into the Hard and Soft Acid Base principle, hard ions which bind to F- strongly such as Na+,Ca2+,Mg2+ could form stable bonds with OH-, HPO42-, CO32+etc, which are oxygen containing ligands . In contrast to hard ions, soft ions example-heavy metal ions such as mercury and lead forms strong bonds with CN-, R-S-, -SH-, NH2-and imidazole contain nitrogen and sulphur atoms. Borderline metal like zinc and copper are less toxic. Hard ions show ionic nature and soft ions binding exhibit covalent degree. (Nieboer and Richardson, 1980; Pearson, 1963; Remacle, 1990)

BACTERIAL BIOSORBENTS - STRUCTURE AND MECHANISM

There exist a great deal of heterogeneity among different bacterial species considering the various surface binding sites, binding strength for different ions and the binding mechanism. (Paknikar et al., 2003). These are the most abundant and versatile microorganisms which constitute an enormous fraction of the entire living terrestrial biomass approximately 1018gm. (Mann 1990). The primary components of the cell walls of bacteria and cyanobacteria are peptidoglycans which consist of linear chains of disaccharides N- acetyl glucosamine, β- 1,4-N-Acetly muramic acid with peptide chains. The gram positive bacteria have a negative charge on their cell walls and surfaces by virtue of the peptidoglycan network which is a macro molecule consisting of strands with alternating glucosamine and muramic acid residues, which are often N- acetylated. Carboxylate groups at the carboxyl terminus of individual strands provide bulk of anionic character to the cell walls. The ion exchange capacity of the cell walls is provided by the phosphor diesters of teichoic acid and the carboxyl groups of teichuronic acid. (Paknikar et al., 2003). The cell wall as the first component in contact includes carboxyl, phosphonate and hydroxyl groups. Bacteria are most commonly used as biosorbents owing to their small size, their ubiquity, their ability to grow under controlled conditions, and their resilience to a wide range of environmental situations. (Urrutia 1997).Bacillus polymyxahas been shown to adsorb high quantities of copper.(Phillip and Venkobachr, 2001).The results of Fein et al, on Bacillus subtilis quantified the deprotonation constants for organic functional groups on the bacterial cell wall and the stability constants for adsorption of Cu, Cd, Pb, and Al metals(Dakiky,2002;Volesky , 2000).The FT-IR spectroscopy and chemical analysis revealed that the neutral-carbohydrate, uronic acid and protein contents are present in EPS. The results highlight the potential Hg-tolerant killed bacterial biomass when incubated in presence of HgCl2 , is sequestered mercury extracellularly as spherical or amorphous deposits. (Vijayraghavan and Yun,2008; Volesky and Holan,1995).Biosorptive efficiencies of different bacterial strains have been reported on many review papers by Vijayraghavan and Yun 2008. Fig 2.Represents the structure of the Bacterial cell wall (Volesky 2000).

FUNGAL BIOSORBENTS

Fungi are a large and diverse group of eukaryotic microorganism. Molds, yeasts, and mushrooms are the three groups of filamentous fungi which have major practical importance in the process of biosorption. Majority of the fungi have filamentous or hyphal growth. Cell walls of the fungi show a multi laminate architecture, where, up to 90% of the dry mass is composed of amino or non amino polysaccharides. The cell wall consists of two phase system with a chitin framework embedded on an amorphous polysaccharide matrix. (Yan and Vijayraghavan, 2000). Fungal biomass proves to be advantageous in having a high percentage of cell wall materials which offers excellent metal binding properties (Luef et al, 1991; Mann, 1990; Muraleedharan et al 1991). Most of the fungi and yeast have shown excellent potential of metal biosorption particularly the genera Rhizopus, Aspergillus, Streptoverticillum and Sacharomyces (Nieboer and Richardson,1980;Pearson, 1963; Paknikar et al, 1993; Puranik and Paknikar,1997; Philip and Venkobachr,2001; Paknikar et al.,2003; Rosenberger,1975).The biomass from the fungi can be cheaply and easily obtained in rather substantial quantities also as a by product from fermentation processes from industries which can be used for the biosorption of heavy metals and radio nuclides, which makes the fungi a very useful raw material that is used for production of biosorbents. Heavy metal ions and radio nuclide removal by filamentous fungi such as Penicillium spp, Aspergillus spp, Rhizopus spp has been shown from aqueous solutions. R.arrhizus and R.javanicus has been discovered to show relatively good sequestering properties (Volesky 1990). Fungus Aspergillus niger has shown a very good affinity for binding copper, zinc, and nickel ions in a single composition system, while in a multi component solution, it occurred only for copper and zinc. The yeast biomass has been successfully used as a biosorbent for the removal of heavy metals such as Ag, Au, Co, Cu, Cd, Ni, Pb, U, Zn, and Th from aqueous solutions. Yeasts of the genera Saccharomyces, Candida, Pichia have proved to be efficient biosorbents for heavy metal ions. (Filipovic-Kovacevic et al., 2000); (Denise MesquitaVieir et al 2007) aimed to study the biosorption of lead by Sargassum filipendula in batch and continuous systems, obtaining equilibrium parameters in a static system to aid the dynamic operation of bioreactors for the treatment of ionic lead in high concentrations.

(Regine et al, 2000) has extensively worked on three different species of Sargassum like Sargassum vulgare ,Sargassum fluitans & Sargassum filipendula biomass for the heavy metal uptakes of Cd & Cu from the aqueous solutions using sorption isotherms.

CRAB SHELL AS BIOSORBENTS

The fibrous shell is composed of nanocrystalline calcite, which gives the structure very high strength. The top surface (reddish) is fibrous with metal nanoparticle segregation, while the bottom layer is composed of layered nanohole array similar to air-dielectric photonic lattice structure (Kuyucak and Volesky,1988).Crab shells favor the removal of different heavy metal ions, especially under acidic pH conditions, because of the presence if CaCO3 and chitin in the biosorbent chitin or chitosan itself if nontoxic, readily biodegradable and hence environmentally acceptable (Chui et al 1996). Chitin acts as an anion exchanger in acidic medium . The poor solubility of chitin is the major limiting factor in the utilization, whereas chitosan has a natural selectivity for heavy metal ions and is useful for the treatment of waste water (Ravikumar 2000).

Hence there exists a potential use of shell particles of crab for removal of different heavy metals like copper, chromium, nickel, zinc, manganese, arsenic(v) and also some of the anionic metal species like gold, cyanide, anionic vanadate from aqueous solution was investigated on the basis of systematic equilibrium and kinetics studies.(Wang and Chen,2006)

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TAMARIND FRUIT SHELL AS A BIOSORBENT

Tamarind fruit shells, a waste product of tamarind pulp industry, are used for the removal of heavy metal ions like chromium from aqueous solutions. Tamarind fruit shell was also used as a low cost biosorbent for the removal of different dyes from aqueous solutions. (Srinivasa Rao Popuri et al, 2007).

SEAWEEDS AS BIOSORBENTS

Seaweeds comprises a large group of marine benthic algae. Because of their large surface area they are very useful for their biosorption process. They contain many polyfunctional metal binding sites suitable for both cationic and anionic metal complexes. The potential metal cation binding sites of algal cell components include, carboxyl, amine, imidazole, phosphate, sulphate, hydroxyl, sulfhydryl, and chemical functional groups contained in cell proteins and sugars (Crist et al., 1991). Taking into consideration some results (Crist et al., 1988), the biosorption of heavy metals undergoes two phases: a fast surface reaction and a much slower metal uptake (2h). The first phase results due to surface adsorption mainly based on anion exchange with the participation of the carboxyl groups of uronic acids. The second phase represents the diffusion of ions into the cell structure. (Crist et al, 1991) not only demonstrated that copper was adsorbed by ion exchange but also by additional covalent bonding with the carboxyl groups of Vaucheria pectins.

MECHANISM OF BIOSORPTION

Biosorption that is applied for the effective removal of the dissolved heavy metals from the aqueous wastewater is based on several mechanisms, the most important being physical adsorption , ion exchange, surface complexation and surface precipitation. These Mechanisms may involve various different pathways like the binding of the metal cations on to the cell surface or within the cell and the formation of metal containing precipitates by reaction with extra cellular polymers. In the second case, the enhancement of metals occurs by direct microprecipitation. These mechanisms in biosorption are classified based on various criteria which are as follows- based on cell metabolism, they are of two types, metabolism dependent and non metabolism dependent.

According to the location where the metal removed from the solution is found, biosorption can be classified as: extracellular accumulation/precipitation, cell surface sorption/precipitation and intracellular accumulation (Ahalya et al., 2003).The transport of the adsorbed ions across the membrane occurs by the same mechanism by which metabolically important ions such as potassium, magnesium and sodium are taken up. The transport of the metal across the cell membrane leads to intracellular accumulation which depends on the cell's metabolism. Such a kind of biosorption will take place only with viable cells. This mechanism is often associated with an active defence system of microorganisms, when the microorganisms are found in the presence of toxic metals. During non metabolism dependent biosorption, the metal uptake is due to physico-chemical interaction between the metal and the functional groups present on the microbial cell surface. This phenomenon has its basis on the principle of physical adsorption, ion exchange and chemical sorption which are not dependent on the cell's metabolism. Such a type of biosorption is rapid and reversible. (Kuyucak and Volesky, 1988). In the case of precipitation, the metal uptake may take place both in solution and on the cell surface (Ercole et al., 1994). Precipitation process maybe dependent on the cell's metabolism. The process of precipitation is favoured in the presence of certain compounds produced by the microorganism in the presence of toxic metals. The process of precipitation can also be considered non dependent on the cell's metabolism if it occurs after a chemical interaction between the metal and cell surface. The process of physical adsorption has been demonstrated in the case of electrostatic interaction responsible for copper biosorption by the bacterium Zooglea ramigera and alga Chlorella vulgaris. (Aksu et al, 1992). The various biosorption methods mentioned above can take place in combination/simultaneously. Pre-treatment and immobilization are considered to increase efficiency of metal uptake. The adsorbed metal is removed by desorption process and the biosorbent can be used for further treatments.

EFFECT OF PRETREATMENT ON BIOSORPTION

Since the biosorption process involves mainly cell surface sequestration, the modification of cell wall can greatly enhance metal binding. Various methods have been employed to modify the cell wall of the microbes in order to help metal binding capacity of the biomass. Biosorbents are prepared by pretreating the biomass by different methods. Effective biosorption of certain metals by a certain biomass depends on various factors like, a number of sites in the biosorbent material, easy accessibility of the site, the chemical nature of the site and the binding site between site and metal.(Ahluwalia and Goyal, 2005). These modifications can be introduced, either during the growth of the micro organism or in the pre grown biomass. The cell surface phenomenon is greatly affected by the condition in which the micro organism grows. Biomass can be pre-treated directly, but if it is larger in size (sea weeds) they are sized into fine particles or granules. The physical treatments involved in the modification of the cell walls include, heating/boiling, freezing/thawing, drying and lyophilisation. The various chemical treatments used for the modification of biomass include, washing the biomass with detergents, cross linking with organic solvent, alkali or acid treatments. These pre- treatments could modify the characteristic of cell surface, either by removing or masking the groups or by exposing more metal binding sites (Vieira and Volesky, 2000). (Leuf, Prey and Kubicek,. 1991), reported that Aspergillus niger biomass grown in potassium hexacyanoferate obtained in large amount form citric acid fermentation plant showed very high biosorption due to change in the cell wall composition. As the cell wall plays an important role in the biosorption by the non viable cells biosorption can be enhanced by heat or chemical sterilization or by crushing. Thus the degraded cells offer a larger available surface area and expose intra cellular components and more surface binding sites because of the destruction of the cell membranes (Errasquin and Vazquez, 2003).

BIOSORBENT IMMOBILIZATION

An essential requirement of an industrial sorption system requires the sorbent to be utilized as a fixed or expanded bed and should not cause much pressure drop across the bed. In order to maintain the ability of the microbial biomass to sorb metals during continuous industrial process, it is important to utilize an appropriate immobilization technique, although cell entrapment imparts mechanical strength and resistance to chemical and microbial degradation upon biosorbents the cost of immobilising agents cannot be ignored. Free microbial cells used for the immobilisation process are basically small particles which have low density, poor mechanical strength and little rigidity, which may come up with the solid-liquid separation problems, possible biomass swelling, inability to regenerate/reuse and the development of high pressure drop in the column mode in real application. Now these problems can be avoided by the use of immobilised cell systems. Support matrices that are commonly used for biomass immobilization include alginate, polyacrylamide, polyvinyl alcohol, poly sulfone, silica gel, cellulose and glutaryl aldehyde. (Wang 2000). Biosorbents are hard enough to withstand the application of pressure, water retention capacity, porous and/or to metal ion sorbate species, and have high and fast sorption uptake even after repeated regeneration cycles. Also, the immobilization technique helps the biosorbent to have a better shelf life and offers easy and convenient usage compared to the free biomass which is easily biodegradable (Volesky and May- Phillips, 1995).

EFFICIENCY OF BIOSORPTION

Assessment and preliminary testing of solid liquid sorption system are based on two types of tests.

(1) Equilibrium batch sorption test and (2) Dynamic continuous flow sorption studies. The equilibrium of the biosorption process is described by fitting the experimental points with

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models (Gadd, etal. 1988) used for the representation of isotherm adsorption equilibrium. The two widely accepted and linearized equilibrium adsorption isotherm models for single solute are given by the following equation:

$$q = \frac{q_{max} b C_{eq}}{l + b C_{eq}}$$

Where (q) is milligrams of metals accumulated per gram of the biosorbent material; (C_{eq}) is the metal residual concentration in solution; (q_{max}) is the maximum specific uptake corresponding to the site saturation and (b) is the ration of adsorption and desorption rates. This is a theoretical model for monolayer adsorption.

Another empirical model for monolayer adsorption is

$$q = K_F C_{eq}^{\frac{1}{n}}$$

Where (K_F) and n are constants.

These models can be applied at a constant pH. These models are used in literature for modelling of biosorption equilibrium in the presence of one metal. These values are plotted in a 2D line where the specific uptake rate q is reported as a function of the metal concentration (C_{eq}). The above mentioned adsorption isotherms can exhibits an irregular pattern due to the complex nature of both the sorbent material and its varied multiple sites as well as the complex solution chemistry of some metallic compounds (Volesky and Holan, 1995). Evaluation of equilibrium sorption performance needs to be supplemented by process oriented studies of its kinetics and eventually by dynamic continuous flow tests. (Ahalya et al. 2003).

KINETICS OF BIOSORPTION

In order to investigate the biosorption kinetics, the Lagergren first order (Lagergren, 1898) and pseudo second order kinetics models (Ho and Mckay, 1999) are applied.

The linearized form of Lagergren is given by the equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Where, k_1 is the Lagergren rate constant for adsorption (min^{-1}), qe is the amount of metal biosorbed at equilibrium ($mg\ g^{-1}$) and qt is the amount of metal biosorbent ($mg\ g^{-1}$) at any time t.

The equation of pseudo second order model is:

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{1}{qet}$$

Where, k_{is} equilibrium rate constant of second order kinetics model ($g\ mg^{-1}\ min^{-1}$), qe is the equilibrium capacity and qt is biosorption capacity at any time, t.

The values of k1and qe can be determined from the slope and intercept of the lines by plotting a graph of time t, against log (qe –qt) in the case of Lagergren kinetic model. The equilibrium rate constant, k2 and equilibrium capacity, qe can be determined from the slope and intercept of the lines by plotting a graph of time, t plotted against t/qt in the case of pseudo second order model.

The intra-particle diffusion kinetics model can also be used to examine the kinetics of biosorption process by using the intra-particle diffusion from the following equation:

$$q_t = k_{id}\sqrt{t} + C$$

Where, kid is the intra-particle diffusion rate constant (mol $s^{-1/2}\ g^{-1}$) and C is the intercept of the plot of qt versus $\sqrt{t}$.

DESORPTION AND METAL RECOVERY

The total biosorption process includes, sorption followed by desorption required to concentrate the solute. The efficiency of the biosorption process used for the removal of heavy metals depends upon the regeneration of the biosorbent after metal desorption. The regeneration of the biosorbent is crucially important to maintain a cost effective process and in recovering the metals extracted from the liquid phase. For this purpose it is desirable to desorb the sorbed metals and to regenerate the biosorbent materials to use for successive cycles of applications. Non destructive recovery by mild and cheap desorbing agents is appropriate for the regeneration of biomass. Appropriate eluants used for the desorption process depends on the type of the biosorbents and the mechanism of biosorption. Acidic and alkaline conditions were used for desorption. The eluants such as CaCl2 with HCl, NaOH, and HCl with EDTA were reported. (Vijayraghavan and Yun, 2008). Dilute mineral acids (HCl, H2SO4, HNO3) have been used for the removal of biomass.(Paknikar et al.,1993; Wang and Chen, 2006; Philip and Venkobachr,2001; Holan et al., 1993).The desorption data showed that nearly 99% of Cr was adsorbed on Mucorhiemalisx could be desorbed using 0.1N NaOH. (Tewari et al., 2005). Desorption with nitric acid showed the high elution efficiency and biosorptive property preservation for heavy metals like Chromium, cadmium, copper by blue green algae Spirulina spp.(Chojnacka et al.,2005) immobilization is a key aspect for the purpose of biosorption application as is it important to decrease the cost of immobilization and consequent distribution, regeneration and reuse of biosorbents. The efficiency of the desorbing agent or the eluant is often expressed taking into consideration S/L ratio i.e. the solid to liquid ratio. To make the process more economical, high values of S/L are desirable for complete elution (Gadd et al., 1988).This technology has certain economic heavy metals such as, silver, tellurium, cadmium etc. From waste cadmium, tellurium, photovoltaic cells, if disposed into landfill sites may pose severe environmental and health hazards. The technology can also be used to remove heavy metals like, mercury, arsenic, lead etc. Sequestered in food and food products caused due to metal biomagnification/ accumulation.

CONCLUSION

Biosorption not only has advantages which can be used as an alternative to conventional systems for the removal of toxic metals from industrial effluents it also has disadvantages like early saturation of biomass, little biological control over the characteristics of the biosorbents. Further investigation in a, view of modelling and regeneration of biosorbent material, testing of immobilised raw biomass with industrial effluents are required for enhancing biosorption process. Most of the biosorption studies usually deals with single metal uptake systems while multi metal sorption systems appear rarely. Which can be further investigated. There is a necessity to have more knowledge involved in the basic mechanism of biosorption in order to develop better and effective biosorbents. For the better application of biosorption in the future, there are two aspects of biosorption for metal removal that has to be taken into consideration. One of them is to use hybrid technology for the removal of pollutants with the help of living cells. Another way is to develop excellent commercial biosorbents in the form of an ion-exchange resin. The difficulties encountered in the process of biosorption advocate people to apply the hybrid technology, which consist of various processes that helps in the treatment of wastewater. Various biotechnology based processes such as biosorption, bioreduction, and bio precipitation were considered. Along with such bioprocesses, non-biotechnology based processes, for example chemical precipitation, floatation, electrochemical process, membrane technology will also prove useful for treating large scale effluents. Another trend requires the improvement of immobilization of biomaterials as well as standardizing the parameters involved in biosorption process and physico-chemical conditions including reuse and recycling. The future development of the biosorption process requires a thorough investigation in the direction of modelling, of regeneration and immobilization of biosorbents and of treating industrial effluents. While standardizing the biosorption process certain application have to be optimized in conjugation with industrial technicians and requires knowledge expertise in process engineering and developmental capital commitment. Various commercial microbial biosorbents are availa-

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ble for example alga sorb, AMT- Bioclaim and Bio-fix. Biosorption is regarded as a potential cost effective biotechnology process for the treatment of high volume low concentration complex waste waters containing heavy metals.

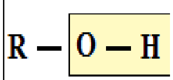
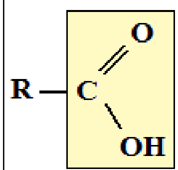
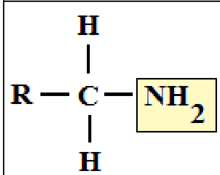
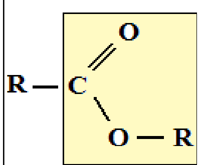
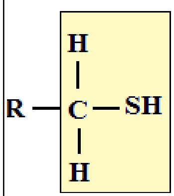
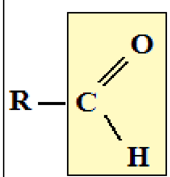
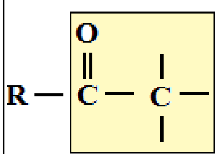
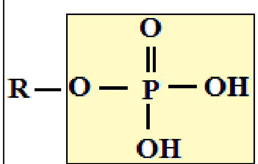
TABLE-1:- TYPES OF HEAVY METALS AND THEIR EFFECT ON HUMAN HEALTH

POLLUTANTS	MAJOR SOURCES	EFFECT ON HUMAN HEALTH	PERMISSIBLE LEVEL (ppm)
ARSENIC	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis	0.02
CADMIUM	Welding, electroplating, pesticides, fertilizers, Cd, Ni batteries, nuclear fission plant	Kidney damage, Bronchitis, gastrointestinal disorder, bone marrow, cancer.	0.06
LEAD	Paint, pesticides, smoking, automobile emission, mining, burning of coal.	Liver, kidney, gastrointestinal damage, mental retardation in children.	0.1
MANGANESE	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system	0.26
MERCURY	Pesticides, batteries, paper industry	Damage to the nervous system, protoplasm poisoning	0.01
ZINC	Refineries, brass manufacture, metal plating, plumbing.	Zinc fumes have corrosive effect on the skin, causes the damage to the nervous membrane	15

TABLE-2 DIFFERENT TYPES OF NATURALLY AVAILABLE MATERIAL USED FOR THE BIOSORPTION PROCESS (Park et al, 2010)

Category	Examples
Bacteria	Gram Positive bacteria like (Bacillus sp., Corenybacterium sp., etc), Gram Negative bacteria like (Escherichia sp.,Pseudomonas sp., etc),,Cyanobacteria like (Anabaena sp., Synechocystis sp., etc.)
Fungi	Molds like (Aspergilllus sp., Rhizopus sp., etc.), Mushrooms like (Agaricus sp., Trichaptum sp., etc) Yeast like (Saccharomyces sp., Candida sp.,etc.)
Algae	Micro-algae like (Chlorellasp., Chlamydomonas sp.,etc.) Macro-algae like (green seaweed (Enteromorpha sp., Codiumsp.,etc.), brown seaweed (Sargassum sp., Eckloniasp.,etc) and red seaweed (Geildium sp., Porphyra sp., etc.))
Industrial wastes	Wastes from fermentation industry, food and beverage industry, activated, anaerobic sludges, etc.
Agricultural wastes	Wastes from fruit and vegetables like, Orange peels, wastes from fibrous plants, wheat bran, rice husk, soybean hulls, etc.
Natural residues	Plant residues, sawdust, tree barks, seaweeds, etc.
Others	Chitosan and cellulose driven materials etc.

TABLE 3: THE REPRESENTATIVE FUNCTIONAL GROUPS AND CLASSES OF ORGANIC COMPOUNDS IN BIOMASS

FORMULA OF THE FUNCTIONAL GROUP	NAME	CLASS OF COMPOUNDS
	Hydroxyl	Alcohols, Carbohydrates
	Carboxyl	Fatty acids, Proteins, Organic acids
	Amino	Proteins, Nucleic acids
	Ester	Lipids
	Sulfhydryl	Cysteine (amino acid), Proteins
	Carbonyl, terminal end	Aldehydes, Polysaccharides.
	Carbonyl, internal	Ketones, Polysaccharides
	Phosphate	DNA, RNA, ATP

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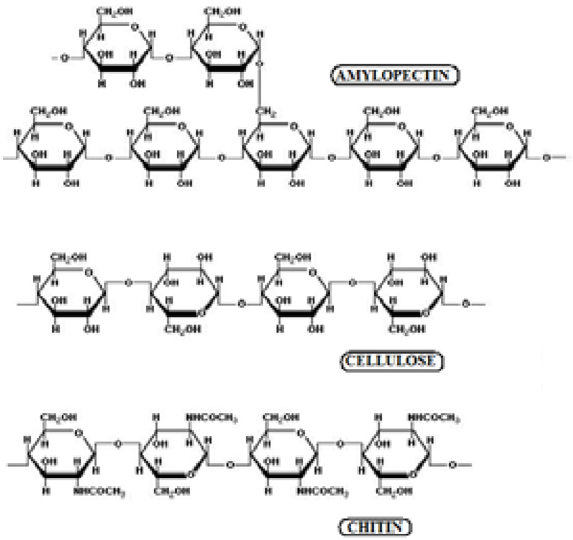

Fig. 1 CHEMICAL STRUCTURES OF VARIOUS METAL BINDING ADSORBENTS

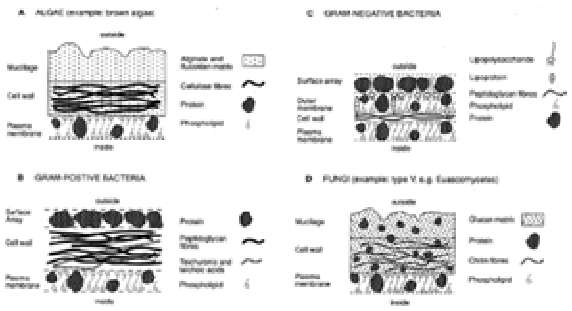

Fig. 2 Cell wall structure in A: algae (example: brown algae), B: Gram-positive bacteria (in part after Beveridge 1989 and Remacle 1990 C: Gram-negative bacteria (Beveridge 1989 and Remacle 1990, D: fungi (example: type V, e.g. Euascomycetes)

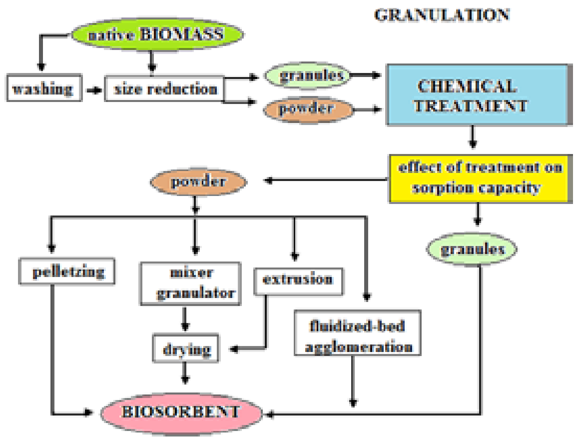

Fig. 3 Schematic diagram for processing of native biomass into biosorbents as suggested by Vieira and Volesky, 2000.

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