Eco-friendly remediation of industrial effluents via biosorption technology - An overview

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Abstract: The mankind strives ever for the refinement of its life and civilization and the task is achieved by reaping the natural resources through industrialization. The chief threat of industrialization is emanation of large volumes of effluents, especially as aqueous discharges. The discharges generally are loaded with heavy metals that are persistent. Though most of these ions are "essential elements" required in traces for the biota, their presence in excess amounts harms many forms of life and proves catastrophic to the environment in the long run. Thus, environmental health governs the standard of human life as well as the prosperity of the biosphere. Biosorption is rapid phenomenon of passive metal sequestration by the biomass. Biological resources such as Bacteria, Cyanobacteria, yeasts, Algae and fungi are identified as potential sorbent candidates of toxic heavy metals from the aqueous medium. Either live or dead biomass can be employed as a sorbent material because of ease in harvesting and valorizing them. This article provides a selective overview of past achievements and present scenario of Biosorption studies carried out on some promising natural biosorbents (algae, fungi, bacteria, yeast) and some waste materials which could serve as an economical means of treating effluents charged with toxic metallic ions

Keywords: algae, fungi, yeast, bacteria, heavy metal, biomass, wastewater.

1. Introduction

A large number of industries including plating, petroleum refinery, battery manufacturing, pigments and mining release heavy metals in waste streams which have negative effects on water bodies. The chief threat of industrialization is emanation of large volumes of effluents, especially as aqueous discharges. The discharges generally are loaded with heavy metals that are persistent. Though most of these ions are "essential elements" required in traces for the biota, their presence in excess amounts harms many forms of life and proves catastrophic to the environment in the long run [1,2]. Thus, environmental health governs the standard of human life as well as the prosperity of the biosphere. Effective removal of heavy metal ions from aqueous solution is important in the protection of environmental quality and public health because heavy metal ions are not biodegradable. As almost all nations around the world are increasingly concerned about the raising levels of toxic heavy metals in the environment, their removal especially from aqueous systems occupies top priority among the various environmental issues. Several methods are being used for the removal of heavy metal ions from aqueous wastes (chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, etc)[3]. Each of these methods has its own merits and demerits. Chemical precipitation and electrochemical treatments are ineffective, especially when metal ion concentration in aqueous solution is lower than 50 mg/L. moreover; such treatments produce large amounts of sludge to be treated with great difficulties. Ion exchange, membrane technologies and activated carbon adsorption processes are extremely expensive. Therefore, the search for new cost-effective technologies for the removal of heavy metals from wastewaters has been directed towards Biosorption, which is known for the last few decades. Algae, bacteria, fungi and yeasts have provide to be potential metal biosorbent, due to metal sequestering properties and can decrease the concentration of heavy metal ions in solution[4]. The first step, passive Biosorption, is metabolism independent and proceeds rapidly by any one or a combination of the following metal binding mechanisms: coordination, complexation, ion exchange, physical adsorption (e.g. electrostatic) or inorganic micro precipitation. Passive Biosorption is a dynamic equilibrium of reversible adsorption-desorption. Metal ions bound on the surface can be eluted by other ions, chelating agents or acids. In the second step, due to active Biosorption, metal ions penetrate the cell membrane and enter into the cells.

(a) Factors Affecting Biosorption:

The major factors that affect the Biosorption processes are (i) initial metal ion concentration, (ii) pH, (iii) temperature, and (iv) biomass concentration in solution. Aksu et al [16] reported that temperature does not influence the Biosorption processes in the range of 20-35^{0}C. However, pH seems to be the most important parameter in the Biosorption processes. It affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of the metallic ion [18]. Biomass concentration in the solution seems to influence the specific uptake: for lower values of biomass concentration leads to interference between the binding sites. Fourest the Roux [19] invalidated this hypothesis attributing the responsibility of the specific uptake decrease due to metal concentration shortage in solution. Hence, this factor needs to be taken into consideration in any application of microbial biomass as biosorbent.

(b) Biosorption Mechanisms

The Biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the later is attracted and removed by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution.

The major advantages of Biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and biological sludge, and regeneration of biosorbent and possibility of metal recovery [5]. The disadvantages of Biosorption are (i) early saturation i.e., when metal interactive sites are occupied, metal desorption is necessary prior to further use; (ii) the potential for biological process improvement (e.g. through genetic engineering of cells) is limited because cells are not metabolizing [6].

The mechanism of metal Biosorption is a complicated process. The status of biomass (living or nonliving), types of biomaterials, properties of metal solution, environmental conditions such as pH, influence the mechanism of metal Biosorption. The metal Biosorption process by living cells is a two step process. In the first step, metal ions are adsorbed to the surface of cells by interactions between metals and functional groups displayed on the surface of cells. All the metal ions before gaining access the cell wall. The cell wall contains of a variety of polysaccharides and proteins and hence offers a number of active sites capable of binding metal ions. Difference in the cell wall composition among the different groups of microorganisms, viz., algae, bacteria, Cyanobacteria and fungi, cause significant differences in the type and amount of metal ion binding to them. The potential metal binding groups in this class of microbes are *carboxylates*, amines, *imidazoles*, phosphates, sulfhydryls, sulfates and hydroxyls. Of these amines and imidazoles are positively charged when protonated and may build negatively charged metal complexes. In E. coli K12, *peptidoglycan* was found to be potent binder of the metals tested and carboxylate groups were the principal components involved in metal binding. Fungal cell walls contain chitin and *chitosan*, which have been shown to sequester metal ions [9, 10].

Metal uptake by non-living cells is mainly in passive mode [11-14]. By investigating the Biosorption of Cr (VI) and Fe (III) recovery of heavy metals are very important with respect to environmental on Streptococcus *S.cerevisiae equisimils,* and *Aspergillus niger*, Goyal et al confirmed that the metal uptake by microorganisms occurs in two stages: passive uptake which takes place slowly. The first stage is thought to be physical adsorption or ion exchange at the cell surface, reaching the adsorption equilibrium within 30-40 min. therefore, and passive mode is independent of energy, mainly through chemical functional groups of the material, comprising the cell and particularly cell wall whereas active mode is metabolism dependent and related to metal transport and deposition.

(c) Biosorption equilibrium models:

Preliminary testing of solid-liquid adsorption system is based on two types of investigations: a) equilibrium batch sorption test and b) dynamic continuous flow sorption studies. The equilibrium of the Biosorption process is often described by fitting the experimental points with models [20] usually used for the representation of isotherm adsorption equilibrium. The two widely accepted and linearised equilibrium adsorption isotherm models for single solute system are given by the following equations:

Langmuir: $q = q_{max}bC_{eq}/1+bC_{eq}$

Where q is in milligrams of metal 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 ratio of adsorbtion and desorption rates. This is a theoretical model for monolayer adsorption.

Another empirical model for monolayer adsorption is

Freundlich: $q = K_F\, C_{eq}^{1/n}$

Where K_F and n are constants.

These models can be applied at a constant p_H, and used for modeling of Biosorption equilibrium in the presence of one metal.

Recently, some biosorbents have emerged as an eco-friendly, effective and low cost material options [13,21]. These biosorbents include some agricultural wastes, fungi, algae, bacteria and yeast. Studies using biosorbents have shown that both living and dead microbial cells are able to uptake metal ions and offer potential inexpensive alternative to conventional absorbents. In addition dead cells require less care and maintenance, and are cheaper[26]. Furthermore, dead biomass could be easily regenerated and reused.

(d) Algae as biosorbent

Use of algae biomass as a biosorbent is emerging as an attractive, economical and effective proposition because of certain added advantages of algae over others [27]. Algae have low nutrients requirements, being autotrophic they produce a large biomass, and unlike other biomass and microbes, such as bacteria and fungi, they generally do not produce toxic substances. Binding of metal ions on algal surface depends on different conditions like ionic charge of metals ion, algal species and chemical composition of the metal ion solution.

The uptake of Pb by dried biomass of green algae, Chlorella vulgaris was investigated in a single –staged batch reactor in the concentration range of 250200 mr/L. Sorption phenomenon at different pH values and temperatures was expressed by the Freundlich adsorption isotherm. Increased Pb uptake values at higher pH values and temperature were observed. Holan and Volesky reported the Biosorption of Pb and Ni by biomass of marine algae. The multi metal sorption system was investigated by De Carvalho etal with brown marine algae. *Ascophyllum nodosum*. Using two metal systems comprising either (Cu+Zn), (Cu+Cd), or (Zn+Cd), they found that each of the metals inhibited the sorption of others. Biosorption of Cr (VI) from aqueous solution by green algae *spirogyra* had also been reported. The brown seaweed, *Sargassum Sp.(Chromophyta)* was used as a biosorbent for Cu ions. The influence of different experimental parameters such as initial pH, shaking rate, sorption time, temperature, equilibrium conditions and initial concentration of Cu ions on Cu uptake was evaluated.

(e) Fungi as biosorbent

Biomaterials like fungi have been proved efficient and economical for the removal of toxic metals from dilute aqueous solutions by Biosorption because fungal biomass offers the advantage of having a high percentage of cell wall material, which shows excellent metal binding properties [19]. 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.

Aspergillus niger had been found capable of removing heavy metals, Pb, Cd, and Cu. The role played by various functional groups in the cell wall of *A.niger* was investigated. The biomass was subjected to chemical treatments to modify the functional groups, carboxyl, amino and phosphate and to study their role in Biosorption of heavy metals. The effect of pretreatment on the heavy metal Biosorption capacity of *Pencillium lanosa-coeruleum* was investigated by Llhan et al. they found that heat, NaOH and detergent pretreatments significantly improved Biosorption of Pb and Cu whereas gluteraldehyde increased Ni biosorption. Kogej and Pavko reported the Biosorption of Pb from aqueous solutuion in a batch stirred tank reactor and a continuous packed bed column using self immobilized *Rhizopus nigricans* as biosorbent. The effect of pretreatment on Pb Biosorption capacity of fungal biomasses such as *Aspergillus versicolor, Metarrhizium anisopliae Var. anisopliae and Pencillium verrucosum* was investigated by Cabuk et al. Fungal biomasses were subjected to physical treatments like heat and autoclaving, and chemical treatments viz. NaOH, formaldehyde, gluteraldehyde, acetic acid, H_2O_2, commercial laundry detergent, orthophosphoric acid and dimethyl sulfoxide. Biosorption of Pb was increased when biomass of A. versicolor was pretreated with dimethyl sulfoxide, H_2O_2 and gluteraldehyde. Preetha and Viruthagiri investigated the absorption of Zn (II) ions by *Rhizopus arrhizus*, a filamentous fungus, in a batch reactor. Batch adsorption studies were carried out by varying biomass loading. Specific Zn (II) uptake decreased with the increase in biomass loading and these results were analysed in the light of Lagergren equation and the process followed a second order rate kinetics.

Biosorption of heavy metals by macrofungi or mushroom is a known phenomenon now-a-days but not much work has been done. Since mushrooms grow under natural habitats, heavy metal pollutants present in the soil or in the natural substrates are taken up by the fruiting bodies of mushrooms resulting in accumulation of metals in the *mycelia* and *sporocarps*. Size, texture and other physical characteristics are conducive for their development into absorbents without the need for immobilization or development of sophisticated reactor configuration as needed in the case of microorganisms.

Uptake of Cd, Pb, Co, Cu by *mycelia* and *sporocarps* of an adible mushroom, Volvariella volvacea, was reported by Purkayastha and Mitra. Metal (Cu II) uptake potential, mechanism and application of *mushroom, Ganoderma lucidium*, as a biosorbent had been reported. Uptake of heavy metal pollutants by edible mushrooms and its effect on their growth, productivity and mammalian system was also studied. Fruiting bodies of nine non-edible mushrooms viz. *Coriolopsis strumosa, Daedalea tenuis, Lentinus strigosus, Lenzites malaccenis, Phellinus xeranticus, Rigidoporus, Trametes lactenia, Ganoderma Lucidium* were screened for copper uptake potential. Garcia et al reported the potential use of *Agaricus macrrosporus* for bioextraction of heavy metals from contaminated wastes. The data indicated that *A.macrosporous* effectively extracted Cd, Hg and Cu from contaminated substrates.

(f) **Bacteria as Biosorbent:**

Numerous studies have identified a number of potential bacterial species capable of accumulating metals from aqueous environment. Amoung the *bacterium, Bacillus sp. has* been identified as having a high potential of metal sequestration and has been used in commercial biosorbent preparation. Besides, there are reports on the Biosorption of metals using *Pseudomonas sp., Zoogloea ramigera* and *streptomyces sp*. A study of the application of bacteria for the recovery of heavy metals from aqueous environments was carried out by Seki et al. The Biosorption characteristics of Cd and Pb ions were determined with purple non-sulfur bacteria *Rhodobacter sphaeroides,* and hydrogen bacteria, *Alcaligenes eutrophus* H16 IIhan et al reported the removal of Cr, Pb and Cu ions from industrial waste waters by *Staphylococcus saprophyticus*; the optimum pH values for Cr, Pb and Cu Biosorption were found to be 2.0, 4.5 and 3.5 respectively [24]. The Biosorption properties of bacterial biomass and the effects of environmental factors (pH, metal concentration, contact time, temperature etc...) on Cr, cd and cu Biosorption were explored by Ozdemir et al. They reported that a species of Gram negative bacterium, Pantoea TEM18 isolated from waste water treatment of a petrochemical industry along with other microorganisms exhibited the greatest Cu tolerance. Cell walls of Gram negative bacteria are somewhat thinner tan the Gram positive ones and are also not heavily cross-linked. They have an outer membrane, which is composed of an outer layer of lipopolysaccharide (LPs), phospholipids and proteins. Gourdon et al compared Cd^{2+} Biosorption capacities o Gram positive and Gram negative bacteria. Glycoproteins present on the outer side of gram positive bacterial cell walls were suggested to have more potential binding sites for Cd^{2+} than the phospholipids and LPs and hence are responsible for the observed difference in capacity.

Rabbani et al reported Biosorption of Cr (III) by 17 bacterial strains isolated from Ramsar warm spring, Iran. A new strain of gram positive *coccobacilli bacteria (NRC_BT_2)* was found to be highly capable for the Biosorption of Cr (III). In the batch experiments with various initial concentrations of Cr ions to obtain the sorption capacity and isotherms, the Biosorption of Cr (III) and Cr(VI) onto the cell surface of *Pseudomonas aeruginosa* was investigated[28].

(g) Yeast as Biosorbent:

Among the promising biosorbents for heavy metal removal, which have been researched during the past decades, yeast (*Saccharomyces cerevisiae*) has received increasing attention due to its unique nature in spite of the mediocre capacity for metal uptake. *S. Cerevisiae* in different forms has been studied in Biosorption research. For example, living cell/dead cell, immobilized cell/free cell, wild type/mutant type, flocculent/non-flocculent cell, engineered and non-engineered cell, laboratory culture/waste cells from different industries.

Comparative results of metal biosorbent capacities between *S. cerevisiae* and other microorganisims has been investigated by Bakkaloglu et al . They investigated various types of microorganisms including bacteria *(S. rimosus*), yeast *(S.cerevisiae*), fungi *(P.chrysogenum*), activated sludge as well as marine algae (*F. vesiculosus* and *A. nodosum*) for Biosorption of metals[23]. They compared the removal efficiency for Zn, cu and Ni ions at the stage of Biosorption, sedimentation and desorption. The results showed that *S. cerevisiae* has a mediocre efficiency for one or multi metal Biosorption systems. By comparing the index q_{max} of Langmiur equation with seven types of waste biomass for the removal of Pb ion, Kogej and Pavko indicated that Pb uptake capacity by *S. cerevisae* is in the middle, in comparision to other six biomaterials used[19]. Vianna et al studied the Biosorption capability for Cu, Cd, and Zn, using three kinds of waste biomass from fermentation industries, that is *Bacillus lentus, Aspergillus oryzae* and *S. cerevisiae*. The results showed that protonated B. lentus had the highest sorption capacity for Cu and Cd, followed by protonated biomass of *A. oryzae* and *S. cerevisiae*. Donmez and aksu studied Cu ion bioaccumulation by adapted and growing cells of *S. cerevisiae, Kluyceromyces* and *marxianus*, *Schizosaccharomyces pombe* and *candida sp*. They found that the biosorptive capacity for Cu^{2+} decreased in the following order: *S. cerevisiae* (7.11)>

K. marxianus (6.44)>*Candida sp*. (4.80)>*S.pombe* (1.27). However, the results indicated that *Candida sp and K. marxianus* were more efficient than *S. cerevisiae and S.pombe* for heavy metal resistance and Cu(II) bioaccumulation at higher concentrations[16-18].

In *S. cerevisiae*, free cells appear unsuitable in practical application, largely due to solid/liquid separation problem. However, Veglio and Beolchini pointed out that investigation on the performance of free cells for metal uptake can provide fundamental information on the equilibrium of the Biosorption process, which is useful for practical application. Meanwhile, flocculating cell has been suggested for Biosorption, attempting to overcome the separation problem of freecells. Brady et al proved that the cells of *S. cerevisiae* treated with hot alkali were capable of accumulating a wide range of heavy metal cations (Fe^{3+}, Cu^{2+}, Cr^{3+}, Hg^{2+}). Some toxic metal ions studied in *S. cerevisiae* Biosorption are pb, Cu, Zn. Mapolelo and Torto proved that Biosorption of Cd(II), Cr(III), Cr(VI), Cu(II), Pb(II) and Zn(II) by *S.cerevisiae* is dependent on optimum pH values above 5.

(h) Waste materials of food and Agricultural Industry as Biosorbents

Agricultural by-products have been widely studied for metal removal from water. Peat, bark, banana pith, soybean and cotton hulls, rice bran, saw dust, wool orange peel have been demonstrated to remove heavy metals from waste water. These agricultural waste biosorbents are inexhaustible, cheap and non-hazardous materials, which are specifically selective for heavy metals and can be easily disposed by incineration [15].

The feasibility of using bio-waste obtained from fruit juice industry for the removal of toxic heavy metals, Hg(II), Pb(II), Cd(II), Cu(II), Zn(II), and Ni(II) from wastewaters was explored by Senthilkumaar et al. Fruit residues and phosphate which the latter showed higher Biosorption capacity. The pH of solution was identified as the most important variable influencing metal adsorption on biosorbents. Removal and recovery of Pb(II) from single and multi metal (Cd, Cu, Ni and Zn) solutions by crop milling waste (black gram husk) was reported by Saeed et al. Selectivity order of the biosorbent for metals was Pb> Cd> Zn>Cu>Ni. Complete desorption of Pb and other metals in single and multi metal solution was achieved with 0.1 M HCl in both shake flask and fixed bed column studies.

Biosorption characteristics of dried sugar beet pulp for removing Cu(II) from aqueous solutions revealed that at 250 mg L^{-1} initial Cu(II) concentration and pH 4, highest cu(II) uptake capacity (28.5 mg/g) at 25^0c was observed. The capacity of raw rice bran to remove Cr and Ni from aqueous solutions was investigated by Oliveria et al. The adsorption equilibrium was modeled using the Langmuir and Freundlich isotherm and the experimental data were well fitted to the Freundlich equation. The possibility of utilization of the rice bran for sorption of Cu ions from aqueous solutions was also studied by Wang and Qin . The experimental results were fitted to the Langmuir, Freundlich, Temkin and Redlich-Peterson isotherms to obtain the characteristic parameters of each model. Except Freundlich, the sorption data fitted well in other three isotherms models.

Hossian and Kumita sudied the dynamic characteristics of Cr(VI) sorption using black tea leaves as biosorbent. Batch experiments were conducted to evaluate the effects of Cr(VI). Experimental and calculated kinetics data for equilibrium were expressed by Langmuir effect on the adsorption rate. The potential to remove Cr(VI) from aqueous solutions through Biosorption using the husk of Bengal gram (Cicer arientinum) was investigated in batch experiments by Ahalya et al. The results showed 99.9% removal of Cr from 10 mg/L Cr solution; the biomass required at saturation was 1 g/mg. the adsorption data fitted well with the Langmuir and Freundlich isotherms models. Vijayaragavan et al investigated the Biosorption of cu(II) and Co(II) by crab sell. At optimum particle size (0.767 mm), biosorbent dosage (5 g/L) and initial pH of solution (pH 6), the biosorbent recorded 243.9 and 322.6 mg/g, uptakes of Cu and Co, respectively according to Langmuir model. Yohimbe bark and grape stalks waste were used as ligands in composite and PVC-based membranes for the development of Cr(VI) and Hg(II) selective electrodes by Fiol et al.

(i) Commercial Applications of Biosorption Technology:

By critical analysis of various microbial masses, a few potential metal sequestering biosorbents have been commercialized. Bio-Fix biosorbent was developed using biomass from a variety of sources like *cyanobacterium* (*Spirulina)*, yeast, algae, and plants (*Lemma sp. Sphagnum Sp.*). The biomass was blended with xantham and guar gums to give a consistent product and many attractive features including selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operational costs.

AlgaSorb^{TM}, a potent algal biosorbent was developed using a fresh water alga, Chlorella vulgaris, to treat wastewater. It efficiently removed metallic ions from dilute solutions. Another metal sorption agent, AMT-BIOCLAIM^{TM} (MRA), was developed using Bacillus biomass to manufacture granulated material for wastewater treatment and metal recovery. This can accumulate metal cautions with efficient removal of more than 90% from dilute solutions.

(j) Immobilization of Microbial Biomass for Bioreactors:

In order to retain the ability of microbial biomass to adsorb metals during the continuous industrial process, it is important to utilize an appropriate immobilization technique. The free cells can provide valuable information in the laboratory experimentation but are not suited for column packing in industrial applications. The free cells generally have low mechanical strength and small particle size and therefore, excessive hydrostatic pressures are required to generate suitable flow rates. High pressures can cause disintegration of free biomass. These problems can e avoided by the use of immobilized cell systems. Immobilized biomass offers many advantages including better reusability, high biomass loading and minimal clogging in continuous flow systems.

In accordance with the process mechanism, kinetics, uptake capacity and physical characteristics of the biosorbents, many reactor configurations have been suggested in both batch and continuous mode. The typical reactor configurations suggested are: a) batch stirred tank reactor, b) continuous flow stirred tank reactor, c) fixed packed bed contactor, d) pulsating bed contactor, e) fluidized bed contactor, and f) multiple bed contact arrangement.

II Conclusions:

Research over the past decade has provided a better understanding of metal Biosorption by certain potential biosorbents. The group of cheap biosorbent materials based on natural and waste biomasses constitutes the basis for a new cost-effective technology that can find its largest application in the removal of metal contaminated industrial effluents. Application aspects of Biosorption are being aimed at Biosorption process optimization. Mathematical models are helpful in this regard in order to guide further experimental work and provide predictions of the performance of the Biosorption process under different operating conditions. To attract more usage of biosorbent technology, some strategies have to be developed where further processing of biosorbent can be done to renerate the biomass and then convert the recovered metal into usable form.

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