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Bacteria Mediated Biosorption of Hexavalent Chromium - A Review

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ABSTRACT

A good living standard is always a major priority of every human being in this world. The continuous industrialization, urbanization, and an increase in population has directly or indirectly accounted for the endless mass pollution of various basic needs such as water, air, and land. This has created a significant havoc in the global environment leading to several health issues both for humans as well as other life forms. Hence, there is an imperative need for environment friendly approaches towards the removal of heavy metals from the ecosystem. Among the various processes, biosorption has been considered as one of the most promising and attractive approach for the removal of heavy metals from different industrial wastewaters. Recently, there is a huge interest in utilizing the biosorption approach for the removal of hexavalent chromium using various biosorbents. The major advantage of such a biological process includes good efficiency in nature and application of low cost biosorbents which can be reused. The present chapter provides an overview of the removal of hexavalent chromium using different types of bacteria extracted from various environments.

Keywords: *Biosorption, Biosorbents, Biomass, Hexavalent chromium, Pollution, Wastewater*

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INTRODUCTION

There are numerous human induced contaminants present in the environment and the major segments of those are the heavy metal wastes generated from the industries. The occurrence of such wastes in the air, water or soil even in trivial amounts can threaten the long- term health of all living beings [25]. Trace metals such as lead, mercury, cadmium and chromium are of substantial consideration due to their ability to build up through the tropic levels of the ecosystem inducing a harmful ecological impact [6].

The massive industrial utilization of the non-biodegradable heavy metal Chromium (VI) is a serious environmental concern as it can accumulate in living organisms. This makes it imperative to treat such wastes prior to releasing them into the atmosphere. In order to serve this purpose efficiently and cost-effectively, the biosorption method can be employed [12]. Biosorption is identified as a process accomplished with the help of active/inactive microbial biomass called biosorbents that bind and concentrate the heavy metals. This approach when used for removal of Cr (VI) is prompt, reversible, passive and promising in contrast to the other conventional methods used like chemical precipitation, reverse osmosis, ion exchange, solvent extraction, etc.. The cell wall components of the microorganisms assist them in carrying out the biosorption process by adsorbing the inorganic contaminants. Major contribution to biosorption is attributable to the anionic ligand groups such as carbonyl, hydroxyl, phosphoryl and sulfhydryl [40].

HEXAVALENT CHROMIUM

The most prevalent heavy metal contaminants include cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn). Out of these Chromium (Cr) is of major concern to life. It occurs naturally in soil, plants, animals, rocks, gases and dust particles. It subsists in a range of oxidative states with valency from +2 to +6, of which 0, +3 and +6 are accounted to be the most stable states. Human activities are accountable for the rising concentration of the trivalent and hexavalent forms in the environment. Chromium contaminants in ground water are present in the form of oxyacids and oxyanions of hexavalent chromium, which is very soluble, toxic and mobile in its oxidation state. Hexavalent chromium can be carcinogenic depending on its chemical form, valency and solubility under certain conditions [28].

Hexavalent chromium intake is possible by all cell types wherein it is reduced to the trivalent form inside the cells. This trivalent chromium is capable of directly binding to the DNA besides formation of DNA-protein cross linkages resulting in mutagenesis. Furthermore, hexavalent chromium ion reduction within the cells drives the synthesis of unstable compounds like Cr(V) and Cr(IV) and thiol radicals. Reaction of hexavalent chromium with oxygen leads to the formation of ROS (reactive oxygen species) particularly hydroxyl and hydrogen peroxide radicals. All these conditions, finally direct towards DNA damage and gene mutations [26].

The limitation for maximum authorized discharge levels into surface and portable water set by regulatory authorities is below 0.05 mg. Exposing humans to Cr (VI) are linked to respiratory cancers. Man-made contamination of fresh water resources occurs when industrial effluents are released into them without appropriate treatment. Chromium attracts attention since it is used in several industrial processes including plating, petroleum refining, leather, tanning, wood preserving, textile manufacturing and pulp processing. It is also employed in the fabrication of steel and metal alloys, cement, galvanized plastic, tanneries, paints, fertilizers and fungicides. Research anticipates that Cr (VI) is approximately a hundred times more toxic than Cr (III) which is a crucial component required in human metabolism for the maintenance of glucose, cholesterol and triglyceride levels. Cr (III) is very much capable to oxidize into Cr (VI), the more toxic form [14].

Water pollution is a chief environmental crisis as a consequence of the hydrological cycle. Manufacturing industries release toxic chemicals and contaminants from different sources at diverse levels. Hexavalent chromium Cr (VI) is one of the major water pollutants. It proves to be toxic even in parts per billion (ppb) levels. Its properties are so advantageous that it stay for prolonged periods in various physical and chemical constituents of the ecosystem. The species of chromium generated by each anthropogenic source are contrasting [30].

Conventional methods applied to remove hexavalent chromium from the industrial effluents include processes such as reverse osmosis, solvent extraction, lime coagulation, ion exchange and chemical precipitation. These techniques accompany some drawbacks including greater energy requirements, insufficient removal of metals and production of large volumes of toxic sludge waste attributed to the chain of reagents used in the treatment processes. As a result, seeking a suitable substitute solution and developing techniques that help in the exclusion of these contaminants is a necessity. The application of bisorbents in coupled or uncoupled form is currently being used to eliminate Cr (VI) [40].

BIOSORBENTS

A biosorbent used must be predominantly aim at immobilizing the metal ions. Therefore, the selection of a pertinent biosorbent is considered as the primary phase in formulating biosorbents. The elemnets governing the selection criteria include rigidity, ability to endure intense operating conditions, cost of material and treatment, provision and steady supply. In other words, the process designed must be cost-effective and the origin of the biomass used for the metal biosorption must be scrutinized. In certain cases where the biomasses are cultivated to exploit their biosorption ability, the expense and unpredictability in retaining a constant supply of biomass must be taken into account. Even the waste generated from certain industries like food, fermentation and pharmaceuticals can be utilized to treat the metal wastes using the potent microbial species of *Saccharomyces, Corynebacterium* and *Streptomyces* [41].

The high surface to volume ratio and electronegative charges on microbial cell walls result in brilliant nucleation sites. Native microorganisms isolated and studied from areas polluted by heavy metals are believed to be the beginning point for all research activities. It is therefore crucial to isolate bacteria with unique metabolic competencies [2].

The mechanism governing the biosorption process relies on several other intrinsic and extrinsic conditions. For treatment of heavy metals, choosing a suitable biosorbent is the foremost requirement, followed by other features like viability of the cell, metabolic products, specific growth velocity, nutrient/substrate needs, and growth environment involving temperature, pH and dissolved oxygen. Besides the type and concentration of the metallic species, the type of the effluent compounds and their configuration must also be investigated. A large part of the microorganisms displays a biphasic response, which is symbolized by the inducement of cell growth when presented to low concentrations and growth inhibition, supposedly due to the minimal inhibitory concentration (MIC). This corresponds to the lowest amount of the contaminant that can lead to the suppression of microbial growth, and can consequently influence their population demographics, diversity and biological activity [40].

Optimization of Biosorption

Significant studies have exploited the biosorption ability of different bacterial biosorbents for hexavalent chromium from aqueous environment. The presence of various physiochemical parameters plays vital role in the maximum uptake of chromium ions from the environment. It is very much essential to the understand the effect of various factors that affect the biosorption process which could provide a clear view on their impact and further help to design the process to achieve a maximum metal ion removal ability. The understanding these parameters also aid in the wise utilization of biosorbent which can further reused and recycled efficiently.

Biosorption is a rapid and reversible process in which binding of ions from aqueous solution is based on the different functional groups present on the biomass surface. The biosorption process is independent of cellular metabolism and can be used against any type of metal removal [10]. Biosorption has several advantages compared to other bioremediation process, where the former can be performed in a wide range of pH from 1 to 9 whereas the latter requires specific pH depending upon the microbial growth. Similarly, temperature can also be employed as it is non-metabolic and desorption can be achieved within a short span of time. The major advantage of the biosorption process is cost-effective, where inexpensive agricultural waste and industrial wastes of bio origin such as residual biomass can also be employed [22]. Another important feature of the biosorption process includes biosorbent regeneration, recovery of metal ions and there is no need of any additional nutrient to perform this process [18].

Several findings have been reported that pH can affect the charge of the functional groups on the biomass surface which in turn affects the biosorption process. Based on the pH dependency of biosorption process, researchers have suggested that the binding of metal ions to the biosorbent may occur through an ion exchange type of phenomenon [24]. Contrastingly, other researchers have concluded that the binding of metal ions to the biosorbent takes place predominantly through the functional groups such as amide, carboxyl and hydroxyl present on the cell wall of the biomass. In this present study, the maximum biosorption was prevailed at pH 4, consistent to the findings of Lin *et al.* [23] who have also reported that the hydrogen ion concentration greater than 4 deprotonated the carboxyl group present in the cell wall and in turn enhances the uptake of metal ions.

When the pH was maintained at lower values, transfer of H^+ ions from the functional group has indicated that the binding sites for the metal ions were occupied. On the other hand, during increase in pH, the H^+ ions concentration decreases and leads the positively charged metal ions to bind with the surface of negatively charged biomass [10].

Goyal *et al.* [15] who have investigated the effect of temperature on biosorption of hexavalent chromium metal ions using *S. cerevisiae.* They have also found that increasing the temperature from 25 to 45 °C increases the metal uptaking ability of *S. cervisiae* due to higher affinity or increasing binding sites for metal ions on the biomass surface. On the other hand, during very high temperature, the metal adsorption tend to be decreased due to the distortion of binding sites on the cell surface [6,7, 16, 23-29] have also found that temperature has major effect on the fungal biosorption which influences the enzymatic systems as well as the metal solubility in the effluents and its adsorption rate. Yu *et al.* [44] have also suggested that increase in temperature beyond a certain level may also affect the integrity of the cell membrane, development of ionization of chemical moieties of the cell wall of biomass and also the stability of metal complex depending on the binding sites.

As the biomass concentration increases, more and more absorption of metal ions on the surface of biosorbent occurs resulting in increased adsorption yield [9, 10, 11]; however in some cases, partial cell aggregation may occurr at higher concentrations, resulting in the decrease of number of active sites [13].

Based on the results, Al-Qodah [4]) has concluded that the increase in agitation speed to a certain limit decreases the biosorption of heavy metals due to the increased turbulence. As a result, there could be decrease in external mass transfer resistance thickness over the adsorbent applied when the rate of agitation was increased. In addition, when the speed of agitation is increased, the rate of mixing also increases, resulting in an improper contact between the binding sites of biosorbent and the metal ions thereby reduces the biosorption efficiency [3, 4].

CHARACTERIZATION OF BIOSORBENTS

Data on the active sites responsible for the binding of the toxic metal pollutants is investigated using certain sophisticated analytical tools. For instance, Fourier transformed infrared spectroscopy (FTIR) helps to locate the binding sites of the bisorbents and the Scanning Electron Microscopic (SEM) technique helps to visually observe and confirm surface morphology of the bisorbents [1].

Based on the results of SEM analysis from various researches, it is found that untreated bacterial biomass revealed smooth cell surface. In contrast to these results, a rough surface accompanied by surface depression was observed in the hexavalent chromium treated biomass. These variations can be attributed to the adsorption of chromium on the biomass cell surface. The micrographs obtained from the SEM analysis results assist the researchers to evaluate cell surface morphology prior to and also after performing biosorption [5].

In order to perform the FTIR analysis, the bacterial biomass is usually mixed with 10 mL of Cr(VI) solution (100 mg/L) at pH 2.0. After a period of absorption of six hours, the pellets are separated and washed twice with double deionized water. Finally, they are dried using an air oven drier. Both dried Cr(VI) treated biomass and untreated biomass are ground with salts (KBr) individually using a mortar and pestle. The powder obtained is converted into a 7 mm die set separation disc by manual pressing. Lastly, the absorbance of the IR spectrum is recorded within 500 to 4000 cm-1. The FTIR examination of chromium exposed and unexposed biomass revealed certain absorption bands at differing wavelengths, indicating the existence of various functional groups like an amine (-NH2), bonded and non-bonded hydroxyl (O-H) groups, amide (-CONH-), carboxyl (-COOH), aromatic (C = C) ring, alkenes (C = C), aliphatic (-CH2) groups, etc. Slight variations in the peak intensities for the chromium treated and untreated biomass was seen. Meanwhile, a minor shifting of a few peaks was also established. Strong absorption bands were visualized at 3299.65 cm-1 for unexposed biomass, indicating the presence of amine N-H stretching or the presence of bonded or the non-bonded hydroxyl group (O-H) in that particular region. The similar absorption peaks of aliphatic (-CH2) groups at 2925 cm-1 and 2925 cm-1 for both the types of biomass showed the asymmetric stretching of proteins, lipids, nucleic acids, and polysaccharides in the biomass cell wall. Thus, it was concluded by the observations that the changes observed could be attributed to the interaction between chromium and the organic functional groups [17].

Zhang *et al.* [46] have also studied the changes in the functional moiety of the dead biomass of *Corynebacterium* strain SH09 using FTIR spectroscopy before and after the biosorption of metal ions. Several functional groups such as amide, especially C=O, C-N and ionized carboxyl corresponding to the spectral peaks 1651 cm^{-1}, 1537 cm^{-1} and 1385 cm^{-1}, respectively, were shifted in metal ions treated biomass, thus indicating their association in the biosorption process. Based on these studies, it is apparent that the functional groups such as carboxyl, carbonyl and secondary amines present in the fungal cell biomass have played a major role in the biosorption process. On the basis of FTIR spectral studies, various researchers have reported that shifting or group changes occurred in metal ions treated biosorbent during the biosorption of various heavy metals [32, 43, 21].

Scanning electron microscopic analysis is one the most important and widely used characterization techniques to study the surface properties and morphology of the biosorbent. Salunkhe *et al.* [32] have confirmed the presence of metal ions over the surface of the *C. lunatus* cell biomass during the biosorption process. Several other researchers have also investigated and characterized the presence of metal ions over the surface of cell biomass using scanning electron microscopy [33, 27, 19].

MECHANISM OF BIOSORPTION

Several researchers has studied the role of essential components responsible for the biosorption of chromium using bacterial biosorbents. It is very essential to understand the mechanisms of metal removal from the environment which enables to develop large scale technology. Studies reveals that the biosorption mechanism of hexavalent chromium was a complex process depends on various factors such as, metal structure and properties, nature and structural component of the biosorbent and also physiochemical conditions of the environment which plays crucial role in the successful biosorption process.

The common biosorption mechanism found in the removal of chromium metals includes metal chelating, ion exchange, metal adsorption on the surface, microprecipitation, metal diffusion through the cell walls of bacterial biosrobent and on to the membrane using membrane bound proteins. Studies also reveals that the major forces behind the interaction of metal with biosorbents includes electrostatic interactions, vander Waals forces and covalent bonding, or with different combinations when bound to the surface of bacterial biosorbent. The existence of various functional groups in the bacterial biosorbent such as amine, and negatively charged functional groups like, hydoxyl, carboxyl, phosphoryl groups tend to have electrostatic interaction during the absorption of metal ions [5, 42]. The ion exchange mechanism during the biosorption of copper and lead ions using Bacillus sp. (ATS-1) was reported [39]. Kalola and Desai [18] in their studies confirmed role of carboxyl and amide groups present in biosorbent of *Bacillus subtilis* SS-1 isolated from electroplating industry in biosorption process.

Sharma and Singh [36] implied that the bacterial forms of Gram positive nature was majorly composed of peptidoglycan and teichoic acid which is basically a polymer of acetyl glucosamine, acetyl muramic acid and copyranosyl glycerol phosphate respectively, which in turns displays the following functional groups like, carboxyl, phosphate and hydroxyl groups could play vital role in the formation of bonding between the biomass and metals [38]. The presence of lipopolysaccharides, proteins and phospholipids in the cell wall of Gram negative bacterial cells found to displace phosphate and carboxyl groups in the outer surface proves to be an ideal site provides metal ion binding Cheung and Gu [8].

RECENT DEVELOPMENTS

The two main phenomenons towards the development of biosorption procedures are making use of the hybrid technology for the elimination of pollution, in particular using living cells and the advancement of biomaterial immobilization and optimization together with reuse and recycling. In addition, the market situation also plays a major role in the development of bisorption technology [5].

Biosorption procedures are successfully used for the treatment of industrial waste waters but they can also be used to serve other purposes. They can blend in various environmental applications where elimination of metal ions is necessary. Substantial research may also be conducted in conventional green roofs. Biosorption technology can be implemented to treat the green roof run off which contains moderate levels of metal pollutants. Inclusion of biomaterials such as seaweeds and crab shells in the green roof setup will serve the function of conventional fertilizers as well as biosorbents for heavy metal ions. Nonetheless, further research findings on biosorbents such as their mode of application, assessment of life cycle and control leaching of light metal ions has to be studied [42].

Similarly, the process can be explored to treat heavy metals obtained from comparatively dilute solutions such as effluents released from lab wastes. Given the perplexity of the wastes generated from laboratories, not much emphasis is given to their treatment. But laboratory wastes are considered as potential sources of suitable investigation field to explore the application of biosorption treatment machinery and to eliminate the contaminants, when there is no definite prerequisite for the removal of metal ions. Likewise, biosorption should be used to eradicate other sorts of pollutants as well. They must not be confined to certain areas and pollutants to perform control actions. With a clear primary knowledge of the science governing biosorption and a persistent technological survey, biosorption technology can be applied to non-confined areas and sources of water pollution. Biosorption can be applied to carry out the best managing practices (BMP) effectively. One such example is the development of storm water BMP's which have been implemented in the previous years [42].

Biosorbents can be engaged in the purification of ion based pharmaceuticals such as proteins, antibodies, and peptides. In order to obtain fine and pure products column chromatographic techniques need to be utilized instead of fixed or moving bed adsorption techniques. Other factors that need to be considered in pharmaceutical functions include consideration of the heat reactivity of biosorbents and monitoring the impurities released during autoclave sterilization and purification. The difficulties faced during biosorption usage act as driving forces by motivating researchers to apply other technologies like hybrid technology which integrates a range of methods for processing of waste water at large-scale [1].

A great step forward in the sorbent development is desirable in order to resolve the significant problem of removal and recovery of metal ions. On the other hand, to eradicate the toxic effects of the metal ions from aqueous solutions, there is a need for further development of state-of –art biosorbents of maximum exclusion ability. Since, biosorbents are biodegradable in nature, it might be challenging to store them and recycling is mandatory for cost effectiveness and remediation of the environment. Crystalline domains of cellulose are reported to lend strength, resistance to swelling and fibre stability. Therefore, studying the structural makeup of bisorbents can help us improvise on aspects related to their cost effective modifications and improved removal of toxic metal pollutants from aqueous solutions [14].

CONCLUSION

Bacterial biomass fall under the category of competent and promising bisorbents applied for the removal of metal ions from solution. The bacterial biomasses display a budding potential to contend with standard traditional technologies to treat toxic metal contaminated solutions. Such biomasses are cost-effective and are prepared from inexpensive raw materials that are eco-friendly as well. The one major drawback of this technology is the confinement of the range of research performed to laboratory conditions without really tackling the actual issues. With the existing knowledge on the key theory impacting the performance, mechanism, operation mode, capacity and relative experimental parameters, new progress has to be made in order to convert and apply this technique as a tool to scale-up and decode the potential employability of biosorbents leading to their adequate commercialization.

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CONFLICT OF INTEREST

The authors declare no conflict of interests.

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