REMOVAL OF CHROMIUM FROM WASTE WATER WITH THE HELP OF MICROBES: A REVIEW

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Abstract

Chromium VI (CrVI) is one of the highly toxic heavy metals. It is widely used in a number of industries like metallurgical, electroplating, paints, pigments, inks, fungicides and photography. It enters into the natural water bodies through the industrial effluents creating water pollution. In trace amounts it is useful for some of the metabolic activities like glucose, lipid, aminoacids and nucleic acid. However at higher concentration it becomes toxic for microbes, plants and humanbeings and causes a number of serious diseases. Therefore its removal from waste water is considered to be very important. In the present article chromium removal from waste water using bacteria by biosorption, reduction and transport was reviewed. Published literature suggests that immobilized, free and living cells, their extracellular metabolites even dead bacterial biomass play an important role in chromium removal from waste water. Reduction of Cr (VI) is one of the important mechanisms for its detoxification from waste water.It was shown by the work published so far that chromium reduction was carried out by aerobic and anaerobic bacteria and iron and sulphate reducing bacteria. pH inside the bacterial cells plays an important role in the reduction of Cr (VI). Review of literature suggests that different factors like pH, temperature, redox potential and presence of other metals play an important role in the removal of Cr (VI) from waste water using bacteria. We have carried out work in our laboratory on Cr (VI) uptake from waste water by Bacillus mycoides and the results obtained are also discussed in this communication.

Key words: Chromium; biosorption; reduction; uptake; regulating factors

1. Introduction

Industrilization and urbanization have been resulting in pollution of the environment. One of the consequences of pollution is the entry of toxic heavy metals into the water bodies creating water pollution. Release of heavy metals without treatment causes significant threat to public health due to their nondegradable and persistant nature. These metals have the property of biomagnification and accumulate in the food chain from unspecific compounds inside the cells causing toxicity at cellular level (Gupta and Mohapatra. 2003, Rajendran et al., 2003). Chromium is a heavy metal, which performs a number of important physiological functions through it's involvement in a variety of metabolic processes like glucose, lipid, amino acid and nucleic acid synthesis (Singh et al., 1994). Removal of heavy metals from polluted water bodies is a major problem and challenge at global level for the scientists. In metal industries widespread use of chromium and subsequent contamination problems have led to lot

of interest in this metal. Chromium concentration in different environmental components as reported in the literature is given in (Table1.).

Metallic chromium and salts are widely used in industry in a variety of chemical processes. It is used in electroplating industry where it oxidizes electroplated metal surfaces to provide smooth, shiny and clean finishes. Some other products which contain chromium include paints, pigments, inks, fungicides, wood preservatives, rubber ceramics, photography and textiles from where it is discharged into natural water bodies of water and lands (Fairhurst and Minty, 1989). Major use of chromium is in the metallurgical industries where it is alloyed with iron, nickel and cobalt to enhance resistance to corrosion and oxidation. The other bulk application of chromium is in leather industry where it is used as a tanning agent (Chaudhary et al., 2003). Chromium in waste water exists in two oxidation states viz Chromium (III) which normally exist in the form of $Cr(OH)_2^+$, $Cr(OH)_4^-$ and chromium (VI) which exist in the form of $Cr_2O_7^{2-}$ and CrO_4^{2-} depending on the pH of the solutions (Volzone and Tavani, 1995, Greenwood and Earnshow,1984). Cr (VI) is considered to be highly toxic compared to Cr (III). Each of these oxidation states has different biocidal, medicinal and toxicological properties (Greenwood and Earnshow, 1984, Kendrick et al., 1992). More than 1, 70,000 tonnes of chromium wastes are discharged to the environment annually as a consequence of industrial manufacturing activities (Kamaludeen et al., 2003). Due to its high oxidation potential it can easily penetrate biological membranes and cause health hazards (Chaudhary et al., 2003).

Chromium (VI) is hazardous to health when its limit in potable water exceeds 0.05mg / L (Mehra. and Juneja, 2003). The oral human lethal dose for Cr (VI) is 71mg/ Kg , while according to the occupational safety and health association (OSHA): permissible exposure limit (PET) , time waited average (TWA) value is 1 mg /m^3 (Meena and Rajagopal, 2003).

On contact chromium (VI) causes irritation , corrosion of skin and respiratory tract and lung carcinoma.When chromium is ingested , epigastric pain , nausea , vomiting and severe diarrhoea are noticed.The primary routes of entry for animal exposure to chromium compounds are inhalation, ingetion and for hexavalent compounds , skin penetration. This last route is more important in industrial exposures. Over exposure to Cr (VI) may lead to inflammation and irritation of the eyes , skin and mucous membranes associated with the respiratory and gastrointestinal tracts. Skin ulcers and perforations of nasal septa were observed in some industrial workers after prolonged exposure to certain chromium (VI) compounds. The target organ for acute systemic toxicity is the kidney. Usually poisoning by chromium (VI) results in acute tubular necrosis of the kidney, and death. Prolonged contact with certain chromium compounds may produce allergic reaction and dermatitis in some individuals (Mehra and Juneja , 2003, Mondal and Das, 2003).

Various physico – chemical procedures are available for chromium removal from aqueous solutions, viz; precipitation, oxidation, reduction, filtration, electrochemical evaporation and ion exchange resins. However these procedures have disadvantages such as incomplete metal removal, high reagent or energy requirements or generation of toxic sludge and are generally very expensive to operate at low concentrations present in the waste waters.

Given the toxicity of Cr (VI) and its widespread occurance in various environmental matrics, a number of research papers have been published for the removal of chromium using bacteria. In this communication, we reviewed the removal methods of chromium using bacteria from waste water.The results obtained from our study on Cr (VI) uptake from waste water by *Bacillus mycoides* are also dissussed.

2. Cr (VI) removal by biosorption

 Bacterial biomass can be used as an economical option for removing heavy metals by the phenomenon of biosorption. Biosorption is a passive process of metal uptake using biomass (Volesky and Holan, 1995). It is a non-directed physico-chemical complexation reaction between dissolved metals and charged cellular components, which involves sorption and / or complexing of metals to living or dead cells (Kamaludeen et al., 2003). Biosorption process can be used for the removal of Cr (III) and (VI) . The advantage of biosorption process is that desorption of the metal is possible if desired. Further, it can be used for the metabolic processes of different microorganisms like bacteria, algae, fungi and plants. Thus recovery and reuse of the metal and bacteria is possible. Both living and dead cells of bacterial biomass can be used for biosorption. Besides chromium removal the bacterial biomass also can be used for the removal of a number of other metals. The bacterial biomass of *Bacillus coagulans* also can be used to bind dissolved Cr (VI) and for the biosorption of Cr (VI) in different matrices (Srinath et al., 2003, Kratochvil et al., 1998, Gadd and White, 1993, Hu and Reeves, 1997). Biosorption of Cr (VI) by free *Bacillus coagulans* was compared with biomass immobilized in different matrices. It was highly influenced by pH and maximum biosorption was found to be at pH 2.5. Thus the stability of the matrix during biosorption is essential without hampering Cr (VI) sorption efficiency. Immobilization of biomass in agarose and polyacrylamide had least effect on Cr (VI) sorption and the matrix was highly stable. Similarly, Uchiama et al (Uchiyama et al., 1994) found that agarose maintained its intigrity at acidic pH. However agar and calcium alginate showed low stability for Cr (VI) biosorption. Owing to its cationic cross nature alginate lost its integrity due to the presence of acidic conditions and anion like chromate (Hu and Reeves, 1997). Agarose and polyacrylamide are known to provide good resistance to hydrostatic pressure and mechanical degradation (Gadd and White, 1993). Polyacrylamide was found to be comparatively less resistant to mechanical stress (Hu and Reeves, 1997). Agarose was chosen as immobilization matrix for further studies. After equilibriation of the biomass agarose for 24 hours with Cr (VI) solution, around 70% of bound chromium was eluted, where as the elution efficiency of free biomass was 86.11% (Srinath et al., 2003). Influence of an aerobic selector on copper and Cr (VI) biosorption by activated sludge was carried out. Work carried out by Alkan et al suggested   that some microorganisms present in activated sludge treatment produce extracellular polymers which can adsorb and remove soluble metals from wastewater. In this study it was observed that Cr (VI) adsorption decreases with increasing pH (Alkan et al., 2002).

Bacteria are having the property of utilizing the organic load present in the waste water. The functional groups present in the organic compounds go to the bacterial cell surface. Functional groups play a major role in biosorption of heavy metals like Cr, Cu, and Pb .Presence of a number of functional groups on the outer surface of bacteria depends on the nature of the organic chemicals and pH. Number of functional groups

present on the outer surface of the biomass vary from one organism to another organism and also depend on the type of organic compounds utilized by the microorganism (Eccles, 1999, Paknikar et al, 2003). Phosphate functional group plays an important role in binding the heavy metals. If the organism is grown in an organic compound containing phosphate, the phosphate is absorbed by the cell which in turn will be very useful for absorption of heavy metals like chromium. Sulphate containing organic waste is generally utilized by the microorganisms by converting it for the synthesis of sulphur rich cystine amino acid containing protein.

3. Cr (VI) reduction by anaerobic and aerobic bacteria

It is known that Cr (VI) is many times more toxic than the Cr (III). Therefore reduction of Cr (VI) to Cr (III) by bacteria is a very important phenomenon in terms of environmental pollution control. Microbial reduction of Cr (VI) to Cr (III) was studied extensively (Tynecka et al., 1981).The process followed by bacteria for the reduction of Cr (VI) is different in aerobic and anaerobic bacterial cells.

Viamajala et al observed that toxicity effects of Cr (VI) on bacteria were also different for aerobic and anaerobic conditions (Viamajala et al., 2004). Immediately after exposure to Cr (VI) aerobic cultures were found to have higher resistance to Cr (VI) than anaerobic cultures. *Enterobacter cloacae* were observed to be Cr (VI) resistant (Ohtake et al., 1990). Growth of *Shewanella MR-1* was inhibited at 0.035 mmol Cr (VI) under aerobic conditions and at 0.015 mmol Cr (VI) under anaerobic conditions (Viamajala et al., 2004).

Mid log phase *Shewanella spp* cultures continued to grow at a reduced growth rate after the addition of 0.035 mmol Cr (VI), while under anaerobic conditions, growth stopped, immediately after Cr (VI) addition. Thus Cr (VI) toxicity was found to be different in aerobic condition when compared to the anaerobic condition of microbial biomass (Viamajala et al., 2004).

Shewanella spp were found to reduce Cr (VI). *Shewanella spp* could be used as a model for metal reducing bacteria to develop an understanding of the fundamental processes involved in metal reduction (Venkateswaran et al., 1999, Myers and Nealson, 1990, Truex et al., 1997). *Shewanella spp* was found to be potentially applicable for use in the remediation of toxic Cr (VI) and other metal contaminants (Myers et al, 2000, Caccavo et al, 1996) while the rapid rate of direct and Fe (II) mediated Cr (VI) reduction by *Shewanella spp* (Wielinga et al., 2001, Viamajala. et al., 2002) appear to make it a useful option for use in chromate bioremediation.

Sulphate and iron reducing bacteria were observed to indirectly reduce Cr (VI) by their anaerobic metabolic end products hydrogen sulfide (HS-) and Fe (II) respectively (Petterson et al., 1997, Pettine et al., 1998, Pettine et al., 1994, Saleh et al., 1989, Sedlak and Chan, 1997). The study of Fude et al, 1994 showed that sulphate reducing bacteria were found to reduce 20 mmol Cr (VI). Marsh et al, 2000, compared Cr (VI) reduction in aquifer sediment slurries with different electron acceptors. Results indicated that the reduction of Cr (VI) in sandy sediment samples with sulphate or ferric iron resulted in sulfidogenesis or ferric iron reduction and appeared to be mediated by microorganisms.

Many facultative and strictly anaerobic bacteria commonly found in soils and marine sediments were capable of reducing Cr (VI) to Cr (III) (Francis et al., 2000, Venkateswaran, 1999, Ohtake et al., 1990, Tebo and Obraztsova, 1998).

Some bacteria such as *Desulfomacculum reducens* and *Pantoea agglomerans* strain sp-1 might use Cr (VI) as an electron acceptor for anaerobic growth (Francis et al., 2000, Tebo and Obraztsova, 1998), while others have cytochromes (Bae et al., 2000, Mc Lean et al., 2001, Park et al., 2000, Suzuki et al., 1992) viz, several *Pseudomonas species*, *Escherichia coli* and *Shewanella oneidensis* strain MR-1 that reduce Cr (VI).

A wide range of facultative anaerobes were able to reduce Cr (VI) to Cr (III) including *Escherichia coli, Pseudomonas*, *Shewanella oneidensis* and *Aeromonas* sp (Wang, 2000). Anaerobic condition is generally required to induce maximum activity against Cr (VI) , but it was observed by Suzuki et al and Park et al that some enzyme systems like the soluble NADPH dependent reductases of *Pseudomonas ambigua* G -1 (Suzuki, 1992) and *Pseudomonas putida* (Park et al., 2000) operated under aerobic conditions. Membrane fraction of anaerobically grown *S. putrefaciens* were able to reduce Cr (VI) into less toxic intermediate form (Myers et al., 2000). Thus Cr (VI) bioremediation seems to be initiated by a one electron transfer from the reductase. Obligate anaerobes were also able to enzymatically reduce Cr (VI) and anaerobic growth coupled to Cr (VI) reduction was reported for a sulphate reducing bacterium (Tebo and Obraztsova, 1998). Thus sulphate reducing bacteria were particularly well studied (Lloyd et al., 2001) and were showed to be catalysed by cytochrome C3. Most studies were focused on planktonic cells but more recent studies showed that biofilms of sulphate reducing bacteria can reduce and precipitate Cr (VI). Cr (VI) reduction was thought to be enzymatic; reduction by sulfide was discounted because sulphate reduction was inhibited dramatically in the presence of chromate (Smith and Gadd, 2000).

In addition to sulfide, a variety of organics and Fe (II) can also nonenzymatically reduce Cr (VI) (Eary and Rai, 1991, Masscheleyn et al., 1992, Palmer and Wittbrodt, 1991). Numerous bacterial genera including *Pseudomonas, Bacillus, Enterobacter, Deinococcus, Desulfovibrio, Rhodobacter*, *Shewanella, Microbacterium* and *Escherichia* were reported under both aerobic and anaerobic conditions and the two processes were shown to be redox sensitive. *Desulfovibrio vulgaris* was used for Cr (VI) reducing activity by its soluble and membrane fractions (Lovley and Phillips, 1994). In *Desulfovibrio vulgaris* Cr (VI) reduction was catalysed by cytochrome C3 (Lovley et al., 1993) , which might be functioning as Cr (VI) reductase.

Enterobacter cloacae (anaerobic) (Wang et al., 1989) and *Desulfovibrio vulgaris* (anaerobic) (Lovley and Phillips, 1994) was found to reduce Cr (VI) to Cr (III). Membrane bound NADPH was observed to act as electron donors. *Pseudomonas ambiqua* (aerobic) (Suzuki et al., 1992) and *Pseudomonas putida* (aerobic) (Ishibashi et al., 1990) also were studied for the reduction of Cr (VI) to Cr (III).NADPH was responsible for the reduction which was in soluble form. *Bacillus sp* (aerobic and anaerobic) (Campos-Garcia et al., 1997) was able to reduce Cr (VI) to Cr (III) by its soluble NADH. *Pseudomonas fluorescens* (aerobic and anaerobic) (Bopp and Ehrlich, 1988) and *Escherichia coli* (aerobic and anaerobic) (Shen and Wang, 1993) was also capable of reducing Cr (VI) to Cr (III).

Immobilized cells of *Bacillus* sp. (Chirwa and Wang, 1997) and *Pseudomonas fluorescens* LB 300 (Chirwa and Wang, 1997) were also used to treat Cr (VI) contaminated water. *Bacillus sp.* QCI-2, a chromium tolerant strain isolated from a chromium polluted zone, reduced (VI) to Cr (III).

There is an evidence for Cr (VI) reduction by both aerobic and anaerobic reduction systems with different microbes.Anaerobic chromate reduction occurs with a membrane preparation. Aerobic chromate reductase activities (probably involving soluble proteins) were found in other bacteria. Cr (VI) reductase activity by a soluble protein fraction from *Pseudomonas putida* was studied. Chromate reduction required either NADH or NADPH for maximum activity, where as a previous report showed activity specific for NADH. Hg and Ag were shown as strong inhibitors for Cr (VI) reduction in *Pseudomonas putida* in a non competitive manner (Bopp and Ehrlich, 1988, Horitsu et al., 1987, Shimada and Matsushima, 1983, Gvozdyak et al., 1986, Kvasnikov et al., 1985, Lebedeva and Lyalikova, 1979, Romanenko and Korenkov, 1977).

Other studies have also implicated the involvement of cytochromes in Cr (VI) reduction by bacteria cytochrome C in *Enterobacter cloacae* and cytochrome b and d in *Escherichia coli* (Wang et al., 1989, Shen and Wang, 1993). Cr (VI) reduction was associated with membrane in some species and with soluble cell fraction in other species. However Cr (VI) reduction is a nonspecific reaction in which a variety of enzymes might play a role in the transfer of electrons to Cr (VI).

Viamajala et al observed that the presence of nitrite inhibited Cr (VI) reduction processes and therefore denitrification might not be the most effective way to stimulate bacterial growth for Cr (VI) reduction, especially when nitrate to nitrite reduction leads to accumulation of nitrite (Pettine et al., 1998).

Bacterial respiration utilizes a number of inorganic compounds as terminal electron acceptors, including O_2, NO2, NO3 SO_4, Fe (III) and Mn (VI). Under anaerobic conditions Cr (VI) may also act as a terminal electron acceptor through a membrane bound reductase activity. Studies with *Enterobacter cloacae* implicated the respiratory chain in the transfer of reducing equivalents to Cr (VI) through cytochrome C. However there is no evidence to show that electron transport to Cr (VI) through respiratory chain could conserve enough energy to support anaerobic growth because fermentable organic compounds were always used in the metabolism (Jones, 1983, Lovley, 1991, Wang et al., 1989, Wang et al., 1990, Wang et al., 1991).
Cr (VI) reduction in *E.coli ATCC 33456* may occur largely on the cell surface, although minor intracellular reduction of Cr (VI) may also take place. Published work revealed that microbial Cr (VI) reduction occurs most likely on the cell surface. The formation of insoluble Cr (III) on the cell surface was though offer protection of cells from   the toxicity of Cr (VI).The finding that Cr (VI) reductase reduced Cr (VI) in the absence of any external electron donors indicated that the reductases can ulilize endogenous reserve as electron donor for chromium reduction. However, it was shown that the activity of Cr (VI) reduction catalyzed by the reductase was enhanced by the addition of   NADH, an external electron donor (Imai and Gloyna, 1990, Wang et al., 1990, Williams and Silver, 1984).

Shen and Wang presented information that stimulation of Cr (VI) reductase activity in aerobic and anaerobic intact cell cultures by 2, 4 DNP suggests that other intracellular Cr (VI) reduction mechanisms were also involved in addition to the predominant extracellular dissimilatory Cr (VI) reduction. The presence of the uncopular, 2-4 DNP greatly increased the permeability of the inner membrane to H+ by carrying protons through the cell membrane and thus stimulated aerobic respiration following the reaction $4H^+ +4e^- + O_2 \Leftarrow X$ $2H_2O$. Similarly, an increase in H^+ concentration inside cells might also lead to an increase in Cr (VI) reduction through the respiratory chain linked activity by the reaction. Therefore the results indicated that inner Cr (VI) reduction activity associated with the respiratory chain was likely, although Cr (VI) reduction in *E coli ATC* 33456 was largely due to soluble reductase activity. Reduction of 1 mol of Cr (VI) requires 8 mol of H^+. Hence, Cr (VI) reduction occurring on the cell surface results in a great reduction of the H^+ gradient across the membrane, which is the driving force for oxidation phosphorylation in cells. Therefore, the energy produced through Cr (VI) reduction on the cell surface by the soluble Cr (VI) reductase activity can not be conserved. The depletion of H^+ on the cell surface by the soluble reductase activity also restricts the penetration of protons into cells, yielding a higher pH inside the cells.The higher pH inside inturn confines Cr (VI) reduction through respiratory chain linked electron transport (Shen and Wang, 1995).

4. Chromium uptake by bacteria

Metal uptake is an energy dependent process. Through uptake process bacteria are able to accumulate different types of metals inside the cell. Some times they use it as a constituent of enzyme and for some other metabolic processes. Chromium uptake in sulfate taking bacteria *Alcaligenes eutrophus* A E 104 were studied by Nies and Silver, 1989.The uptake of chromate by strain *Alcaligenes eutrophus* AE 104 was competitively inhibited by sulphate and uptake of sulphate was competitively inhibited by chromate. This result may support the existence of a secondary transport system.

Ohtake et al reported that SO_4^{-2} and $CrO4^{-2}$ accumulations by *Pseudomonas fluorescens* in minimal medium followed the Michaelis Menton Kinetics. It appeared that $CrO4^{-2}$ and $SO4^{-2}$ were competitive inhibitors of each others transport. The ability of $SO4^{-2}$ to protect growing cells from the inhibitory effects of $CrO4^{-2}$ suggested that a direct competition between $SO4^{-2}$ and $CrO4^{-2}$ uptake followed Michaelis Menton Kinetics, and line weaver- Burk plots showed that $SO4^{-2}$ and $CrO4^{-2}$ were competitive inhibitors of $CrO4^{-2}$ and $SO4^{-2}$ uptake respectively (Ohtake et al., 1987).

In microbial systems, Cr (VI) was believed to enter the cell cytoplasm through sulphate uptake mechanism due to the structural similarity of sulphate and chromate anions (Silver et al., 1981, Silver and Misra, 1984, Paknikar et al., 2003).

Cr (VI) uptake by SO_4^{-2} taking bacteria was studied (Singh et al., 2006) in our laboratory. Maximum Cr (VI) uptake by *Bacillus mycoides* was found to be 15.06µg of Cr (VI) mg^{-1} dry wt at pH 7 within 60 minutes in absence of $SO4^{-2}$. In the same way maximum SO_4^{-2} uptake in absence of Cr (VI) by *Bacillus mycoides* was 11.66 µg of SO_4^{-2} mg^{-1} dry wt within 60 min (Singh et al., 2006). However in the presence of

the same concentration of SO_4^{-2} and Cr (VI) in the solution the uptake of Cr (VI) by *Bacillus mycoides* was inhibited. Lineweaver-Burk plot showed that SO_4^{-2} acted as a non competitive inhibitor for Cr (VI) transport system of *Bacillus mycoides*. Na_2SO_4 type of $SO4^{-2}$ salt was used for $SO4^{-2}$ uptake and with the Cr (VI) to study its interaction with Cr (VI) uptake by bacteria. This is highly toxic form of Cr (VI) salt for water and even plants also. Therefore its removal from waste water is very important before its use for irrigation purpose.

5. Factors affecting the removal of chromium

Environmental factors that affect Cr (VI) reduction were reviewed which include competing electron acceptors, pH, temperature, redox potential and the presence of other metals (Wang, 2000). A recent study also demonstrated that the presence of complexing agents can promote Cr (VI) reduction, possibly through protection of the metal reductase by chelation of Cr (III) or the intermediate formed. The type of electron donor, supplied can also have an effect on the rate and extent of Cr (VI) reduction. Optimal electron donar for metal reduction processes are low molecular mass carbohydrates, amino acids and fatty acids. Degradation of a range of aromatics including phenol, p- cresol and benzene by *Pseudomonas putida DMP -1* was also coupled to the reduction of Cr (VI) by *E coli* 33456 in coculture (Shen and Wang, 1995). Similar results were also reported for a mixed culture of phenol degrading microorganisms and the Cr (VI) reducing E.coli strain (Chirwa and Wang, 2000).

Mc Lean and Beveridge observed that G+ bacteria exhibit enhanced metal binding capacity than G⁻ bacteria (Mc Lean and Beveridge, 1990). G⁻ Cell wall and surfaces have a negative charge density oweing to the peptidoglycon network, a macromolecule consisting of strands of alternating glucosamine and muramic acid residues, which are often N- acetylated. Carboxylate groups at the carboxyl terminus of individual strands provide bulk anionic character to the cell wall. In comparison to ion exchange process bacteria poses higher metal binding capacity (MBCs) attributed to nucleation reaction (Hancock, 1986). The cell envelops of G⁻ bacteria are structurally more complex than that of G+ bacteria. The wall structure consisted of two membranes separated by periplasm. The major anionic character in G⁻ cell walls was due to the phosphate in the outer and inner membranes and thin peptidoglycon layer (Mc Lean et al., 1996). In G⁻ bacteria, the metal ions bind to phosphoryl ligand of lipopolysaccharide (Ferric and Beveridge, 1986).

pH had an influence on the removal of chromium from waste water . Cr O^{-2} anion of metals in aqueous solution exhibits higher uptake in the acidic pH range. Boiling water, sodium hydroxide, formaldehyde and acetone act as cleansers to improve metal binding (Paknikar et al., 1993, Puranik and Paknikar, 1997). Heat treatment and detergent washing expose additional metal binding groups (Gadd et al., 1988).

Some of the complex anions like sulphate, chloride and phosphates are also present in many industrial effluents in addition to metal ions (Tobin et al., 1987). Such anions make a complex with the metal cations present in effluent and reduce the binding of metals with microbial cell surface and alternatively reduce the metal adsorption and uptake from effluents (Lin and Benjamin, 1992). Thus some anions and metal complexes affect the metal removal by bacteria from waste water. Results suggested that anion and biosorbent interaction in some cases might increase the metal removal.

Metal anion complexes are formed that are more strongly adsorbed than the free metal resulting in enhanced metal uptake (Zhou and Kiff, 1991).

Biomass of lower cell densities absorbs more metals than the biomass of higher cell densities (Modak and Natarajan, 1995). Cells having biosorption sites got interferences due to increase in biomass and thus removal of metals gets affected (De Rome and Gadd, 1987). Biomass of lower cell densities resulted in more exposure sites for the binding and uptake of metals. In the same way metal concentration also affected the removal capacity of microorganisms.Thus for higher metal uptake cations which compete with metals also play an important role in the enhancement of metal uptake (Modak and Natarajan, 1995).

Acid, acetate, acetone, methanol, S-acetyl mercaptosuccinic anhydride modify functional surface groups such amino, carboxyl, phosphate, hydroxyl, phenolic etc (Brady and Duncan, 1994, Drake et al., 1996). Enzyme increased surface sorption efficiency by destroying the unwanted component of the bacterial surface (Ting and Teo, 1994).

Thus physical/chemical pretreatment also affects permeability and surface charges of the biomass and exposes effectively metal binding groups for remediation purpose.

6. Conclusions

Microorganisms are capable of treating organic and inorganic contaminents in waste water. The organics present in effluent are utilized as nutrients for the microorganisms which in turn reduce Cr (VI) to Cr (III) leading to the removal of Cr (VI) from the environment.

Literature review revealed that extensive studies were carried out in the application of bacteria for the removal of chromium from industrial waste water. *Bacillus coagulans, Desulfomacculum reducens , Escherichia coli, Pseudomonad , Pseudomonas ambigua* G -1, *Pseudomonas putida , Enterobacter cloacae , E.coli ATCC 33456 , Alcaligenes eutrophus* AE 104 , *Pseudomonas fluorescens , Bacillus mycoides* strains were used for the bioremediation of Cr (VI) from industrial waste water. Removal of Cr (VI) by bacteria is ecofriendly and economical when compared to chemical methods. Further research in this direction may provide the bioremediation of chromium from industrial waste waters at commercial scale.

It is observed that most of the work was carried out by growing bacteria in synthetic solutions for chromium bioremediation. An approach by growing bacteria in organic effluent could enhance the efficiency of bioremediation. Bacteria by oxidation of different organic compounds present in the effluent can provide electrons for reduction of Cr (VI) and can accumulate various types of functional groups on its cell surface to enhance metal biosorption and accumulation of different anionic organic compounds inside its cell and can make complex with different metal cations including chromium. Bacteria grown in synthetic solution having fixed and limited organic compounds is comparatively expensive process for the bioremediation of metals in comparision to bacteria grown in effluent.

Acknowledgements

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Table 1. Chromium concentration in different environmental components (Kamaludeen et al, 2003)

Environmental component	Concentration of chromium
Continental crust	80-200 mg/ kg
Soil	10-150 mg/kg
Fresh water	0.1- 6.0 mg/L
Sea Water	0.2- 50.0 mg/L
Drinking water	0.05 mg/L
Air sample	0.015- 0.03 mg/m^3