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Review

CHROMIUM REMOVAL USING VARIOUS BIOSORBENTS

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ABSTRACT

Pollution of water due to presence of certain heavy metal ions is a severe socio-environmental problem caused by the discharge of industrial wastewater. In view of their toxicity, non-biodegradebility and persistent nature, their removal becomes an absolute necessary. Chromium is one of the major pollutants in the environment and is frequently present in wastewaters from various industrial units. Several conventional physical and chemical treatment techniques may be used for the removal of chromium. However, such processes are not only expensive and highly energy intensive, but also lead to production of harmful by-products and end-products, the ultimate disposal of which again causes secondary pollution. Hence, the potential application of microorganisms as biosorbent for the removal of chromium has been recognized as an alternative to the existing conventional physico-chemical methods. The aim of the present study is to review the removal of chromium from aqueous solution using various materials of agricultural and biological origin , which have been studied as potential chromium biosorbent (plant leaves, saw dust, sugar cane bagassa, sugar beet pulp, maize cob and rice hulls). Also reported cases on chromium removal from aqueous solution by using fungal, algal and bacterial biomass under the growing, resting and dead conditions in batch as well as in continuous bioreactors are reviewed.

Key words : Chromium; Biosorbents, Microorganisms, Metal removal

INTRODUCTION

Chromium as one of the major pollutants of the environment is available in nature as an odourless, steel grey hard metallic element. It is the seventh most abundant element on the earth and twenty first most abundant element in the rocks (McGrath and Smith, 1990). Elemental chromium is not usually found pure in nature and principally occurs as the mineral chromite $FeOCr_2O_3$ or chrome iron stone in which form it is extremely stable.

Chromium exists in nature as stable hexavalent and trivalent forms. The hexavalent form of chromium is more toxic than trivalent chromium and is often present in wastewater as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). This is of serious environmental concern as Cr(VI) persists indefinitely in the environment complicating its removal. The persistant nature makes it accumulate in the food chain which with time reach harmful levels in living beings resulting in serious health hazards such as irritation in lungs and stomach, cancer in digestive tract, low growth rates in plants and death of animals. Therefore, removal of Cr(VI) from wastewater prior to its discharge into natural water systems, adjoining landmasses and sewer systems. requires serious and immediate attention.

The conventional physico-chemical techniques used for the removal of Cr(VI) include chemical

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reduction followed by precipitation with caustic soda. This process requires a large excess of chemicals and produces voluminous sludges, disposal of which again create secondary pollution. Other available treatments include ion-exchange, electrolysis and reverse osmosis. which are not only expensive and high energy processes, but are also ineffective in removal of metal ions present at lower concentration in large volume of wastewaters (Bai *et al.,* 2000). Environmentally friendly processes, therefore, need to be developed to clean-up the environment without creating harmful waste by-products. Biosorption involves application of microorganisms in removal of heavy metals and has been recognized as a potential alternative to the conventional methods for treatment of contaminated wastewaters (Stratten,1987; Volesky, 1990).

The growing, resting and non-living cells of microorganisms are reported to remove Cr(VI) from aqueous solutions (Llovera *et al*., 1993), (Muter *et al*., 2001), (Sen *et al*, 2002), (Srinath *et al*., 2002), (Sen *et al*., 2005), (Sen *et al*., 2007), (Sen & Dastidar, 2007), (Sen *et al*., 2010). However, most of the works to remove Cr(VI) have been carried out using non-living fungal cells and a very little information is available on use of growing and resting cells. The application of non-living cells has advantages over growing and resting cells due to the absence of both toxicity limitations and requirements of growth media and nutrients. Both growing and resting cells can be maintained biochemically active. However, growing systems have the advantage over the non-living and resting cells that the simultaneous removal of metal is obtained during growth of the organism. On the other hand, the major limitation of using growing systems for biosorption of metals is that cell growth is inhibited when the metal concentration is high. This problem can be overcome by the use of metal tolerant organism. The tolerance and removal capacities are the essential characteristics of growing biomass used in a metal ion removal process .

The relation between the hexavalent and the trivalent states of chromium can be described by the following equation:

$$Cr_2O_7^{2-} + 14\ H^+ + 6e \rightarrow 2\ Cr(III) + 7\ H_2O + 1.33\ V \qquad (1)$$

The reduction–oxidation potential (1.33 V) of the two states indicates the strong oxidizing properties of hexavalent chromium (Cotton and Wilkinson, 1980). The oxidation state has important consequence on toxicity and bioavailability by the microbial biomass.

Biological treatment techniques

Biosorption of Cr(VI) using fungal, algal or bacterial biomass (growing, resting and dead cells) and biological and agricultural waste materials has been recognized as a potential alternative to the existing conventional methods for detoxification of industrial wastewaters. The major advantages of the biosorption process over the conventional treatment methods include:

- Low cost
- Increased metal removal
- Regeneration of biosorbent
- Possibility of metal recovery

The removal of Cr(VI) from the wastewaters using biological materials have long been used. Several authors have studied the adsorption of Cr(VI) from aqueous solution using cellulosic, lignocellulosic and agricultural waste materials, briefly reported in Table 1.

Higher plants have been used for many years as bioindicator of metal due to their bioaccumulation properties. Living plants have been used for the decontamination of both water and soil. Water hyacinth (*Eichhornia Crassipes*) has been shown to remove Cr(VI) from water (Lytle *et al*.,1998), while terrestrial plants such as maize have been presented to adsorb Cr(VI).

Many higher plants biomass materials such as plant, parts of the plants or derivatives have been shown to have good biosorbent properties. These include maize cob (Sharma & Forster, 1994), leaves (Mahvi *et al*., 2007; Gholami *et al*., 2006), saw dust (Sharma and Forster,1994), sugar cane baggase (Sharma and Forster, 1994) and rice hulls (Cici and Keles, 1990). The cellulosic materials of Chitin and Chitosan have considerable potential for Cr(VI) binding.

The relation between the amount of metal adsorbed by the adsorbent and unadsorbed component in solution at a constant temperature can be represented by both Langmuir and

Table 1 : Cr(VI) biosorption using various cellulosic, lignocellulosic and agricultural waste materials

Biosorbent	Reactor/conditions	Initial Cr(VI) Conc. (mg/L)	Maximum Cr(VI) removed	Reference
Plataneus Orientalis leaves	Batch reactor pH= 3.0-9.0 Dose=2.0 g/L, 20-30^{0}C 300 rpm, 30-240 min	2.0-40	5.01 (mg/g) (pH= 7.0, 24^{0}C, 120 min) Q^0=5.7, b=0.29, R^2= 0.956 K_F =2.02, n = 2.0, R^2=0.646	Mahvi *et al*., 2007
Plant *Ulmus* leaves	Batch reactor pH= 3.0-9.0 Dose=2.0 g/L, 20-30^{0}C 300 rpm, 30-240 min	2.0-40	0.9 (mg/g) 5.0 (mg/g) (pH= 6.0, 24^{0}C, 60 mins)	Gholami *et al*., 2006
Lignocellulosic material peat	Batch reactor pH= 2.0-7.0 Dose=1.0 g/L, 30^{0}C	10-200	30.16 (mg/g) (pH= 6.0)	Dean and Tobin 1999
Plant water hyacinth: (*Eichhornia Crassipes*)	Batch reactor pH= 2.0-6.0 30^{0}C, 8h	10	6.0 (mg/g) (pH= 6.0)	Lytle *et al.,* 1998
Cellulosic materials: Sugar cane bagasse Sawdust Sugar beet pulp Maize cob	Batch reactor pH =1.5-10.0 Dose=4.0 g/L, 24 h, 25^{0}C 100 rpm	10-1000	13.4 39.7 (mg/g) 17.2 (mg/g) 13.8 (mg/g) (pH= 2.0)	Sharma & Forster, 1994
Rice hulls	Batch reactor pH=2.0-8.0 30^{0}C	20-200	99- 38 % (pH =2.0)	Cici and Keles, 1990

(Q^o,b) and (Kf,n) are Langmuir and Freunlich coefficients.

Freundlich adsorption isotherms, which provide the equilibrium data required for the designing of the adsorption system. The Langmuir adsorption isotherm, which is applicable to monolayer sorption onto a surface having homogeneously distributed identical binding sites over the surface sorbent , is given by

$$q_e = \frac{Q^o\, b\, C_e}{1 + b\, C_e} \qquad (2)$$

or

$$\frac{1}{q_e} = \frac{Q^o\, b\, C_e}{1 + b\, C_e} \qquad (2a)$$

or:

$$\frac{C_e}{q_e} = \frac{1 + b\, C_e}{Q^o\, b} = \frac{1}{Q^o\, b} + \frac{C_e}{Q^o} \qquad (2b)$$

where : q_e is the amount of metal adsorbed per gram of dried biomass at equilibrium (mg Cr(VI)/g of dried biomass) and C_e is the residual (equilibrium) metal concentration in the solution after sorption [mg Cr(VI)/L]. The Langmuir constants, Q^o and b, indicate the maximum amount of metal ion bound per g of adsorbent to form a monolayer (mg/g) and the adsorption affinity (l/mg) for binding of Cr(VI) on the adsorbent sites, respectively. The values

of Q^o and b can be calculated from the slope and intercept of the plot C_e / q_e against the residual concentration , C_e (Aksu *et al*., 2001; Gupta *et al*., 2001).

The Freundlich adsorption isotherm is applicable to adsorption of Cr(VI) on a heterogeneous surface and is expressed as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

or :

$$\log q_e = \log K_F + \frac{1}{n} Ce \quad (3a)$$

where: K_F and n are the Freundlich constants and are related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. Equation (2) can be linearized in logarithmic form and Freundlich constants n and K_F can be determined from the slope and intercept which are equal to 1/n and K_F, respectively (Aksu *et al*., 2001). Bacteria, fungi, yeast and algal biomass under growing, resting and dead conditions have been reported to remove Cr(VI) from aqueous solution in substantial quantities (Tzezos, 1996; Sudha Bai and Abraham, 2000; Solisio *et al*., 2000; Gupta *et al.,* 2001; Muter *et al*., 2001; Aksu *et al*., 2001; Muter and Rapport., 2001; Srinath *et al*., 2002; Sen *et al*., 2002; Dursan *et al*., 2003; Sen *et al*., 2005; Sen *et al*., 2007; Sen and Dastidar, 2007; Sen *et al*., 2010).

The use of bacterial species as biosorbents (Table 2) has raised the possibility of using these microorganisms as a biotechnological tool for removal of Cr(VI) from wastewaters because of their small size, their ubiquity and their ability to grow under wide range of environmental situations.

The complexity of microorganisms structure implies that there are many ways for the metal to be captured by the cell. Various mechanisms involved in metal removal by bacteria include cell surface binding, extra cellular precipitation, intra-cellular accumulation, oxidation and reduction and methylation/demethylation. The ability of bacterial cells to bind metal ions is associated with its cell envelop, which is formed by many layers and it separates the cell protoplasm from the surrounding area.

Several types of structures may form the cell envelop. The most important one is the cell walls, on which capsules, S-layers and sheaths are commonly found to be superimposed. The metal binding to the surface occurs through a passive mechanism which involves stoichiometric interaction of the metal with the reactive chemical groups, followed by the intracellular accumulation of metal due to the simultaneous effects of growth and surface biosorption.

Algae

Algae are photosynthetic organisms. Both growing and non-living cells of algae are capable of removing Cr(VI) and shown in Table 3.

The cell surface binding is the first step involved in the binding of Cr(VI) ions to algal species. This is a rapid process and is metabolized independently. This is followed by the second step of intracellular accumulation of metal due to the simultaneous effect of growth and surface biosorption. This step is metabolism dependent and is a much slower process.

Fungi

Fungi and yeasts are the eukaryotic organisms which are used as biosorbents for the removal of heavy metals due to the production of high yields of biomass. They grow easily under wide range of environmental situations and can also be modified genetically to produce enzymes (reductase, DNA polymerase etc.), which are helpful in higher metal removal from the wastewaters. The fungal organisms, in general, are resistant to higher metal ion concentrations. Heavy metals such as zinc, copper, manganese, nickel and cobalt in trace amount serve as micronutrients for the growth of the fungus. The fungi can also accumulate non-nutrient metals such as cadmium, mercury, lead, uranium, silver and gold in substantial amounts.

The fungi and yeasts (*A. niger, T. reessii, R. arrhizus, R. nigricans, S. cerevisiae*, etc.) are used in a variety of industrial fermentation processes (Volesky, 1990) and can serve as an economical

Table 2: Biosorption of Cr(VI) using various bacterial biomass

Biosorbent (Bacterial species)	Reactor/conditions	Initial Cr(VI) Conc.	Maximum Cr(VI) removed	Reference
Bacillus circulans biofilm	Batch adsorption non-living cells, pH=2.0-7.0, 30 °C, 24-96 h, 120 rpm	50-500 mg/L	48 % pH=7.0, 96 h	Khanafari *et al.*, 2008
Distillery sludge	Batch reactor non-living cells, dose = 1-20 g /L, pH=3.0-10.0, 30°C,150 min	10-40 mg/L	64 % pH=3.0, 5g/L, 105 min Q^0=5.7, b=0.49 K_F=2.05, n= 3.91	Selvaraj *et al.*, (2003)
Shewanella oneidensis MR-1 (facultative Gram-negative bacteria)	Batch reactor, growing cells, 30 °C, 200 rpm, aerobic condition	60 - 400 µm	100 µm	Sarah *et al*., (2003)
Bacillus circulan Bacillus megaterium Bacllus coaglans	Batch reactors, resting cells, 2.5 pH=150 rpm,24 h, 28 °C	0-100 mg/L	34.5 (mg/g) 32 (mg/g) 23.8 (mg/g)	Srinath *et al*., (2002)
Bacillus coagulans & Bacillus megaterium	Batch reactor non-living cells, pH=2.5, 28°C, 150 rpm, 24 h	100 mg/L	39.9 (mg/g) 30.7 (mg/g)	Srinath *et al*., (2002)
Microbacterium liquuefaciens MP30	Batch bioreactor resting cells immobilised in (PVA) alginate beads, 100 rpm, 30°C, 4d Continuos flow bioreactor, flow rate=0.95 mL/h, 20 d	100 µm 50 µm	Complete removal (90 % removal)	Pattanapipit Paisa *et al.*, (2001)
Dried activated sludge	Batch reactor non-living cells, pH=1.0-6.0, 25°C, dose = 0.5 g /L, 150 rpm, 24 h,	25-500 mg/L	27.7 (mg/g) pH=1.0 K_F=4.99, n= 1.55 R^2 = 0.994	Aksu *et al*., (2001)
Bacillus sp. QC1-2	Batch reactor resting cells, 30°C, 20 h, Cell conc=1x10^9 cells/mL	0.3 mM	Complete removal	Campos *et al*., (1995)
Zoogloea ramigera	Batch bioreactor, non-living cells, pH=2.0, 100 rpm, 25°C, 60 min)	0-75 (mg/L)	3.40 (mg/g/min) K_F=2.02, n = 2.0	Nourbaksh *et al*., (1994)
Agrobacterim radiobacter EPS-916	batch reactor resting cells pH=5.0-8.0, 10-40°C, 6 h	0.5 mM	Complete removal 25 - 30 °C, pH=7.0-7.5	Llovera *et al.*, (1993)

and constant supply of biomass for biosorption of heavy metals. They can also be grown using inexpensive media and unsophisticated fermentation techniques. Therefore, the cost of a biosorbent (obtained from an industrial fermentation process in which biomass is

Table 3 : Biosorption of Cr(VI) using various algal biomass

Biosorbent (Algal species)	Reactor/conditions	Initial Cr(VI) Conc.	Maximum Cr(VI) removed	Reference
Sargassum Seaweed (marine algae)	Batch reactor non-living cells, dose=2.5 g/L , 22 ^{0}C, pH=3.5, 10-60 min	10-100 (mg/L)	60 mg/L, 40 min K_F=0.365, n=1.23 R^2 =0.99 Q^0=114, b=4.44 R^2 =0.99	Barkhordar and Ghaiseddin, 2004
Scenedesmus incrassalulus (green micro algae)	Continuous flow system growing cells, sterile condition irradiance of (200µmol/m^2/s), operation volume of 1.6 L, 200 rpm, air injection (600mL/min), 25 ºC , cell density=3.75 X 10^6 cells/mL, 16 d	1.2 (mg/L/d)	52.7 % (Under steady state conditions)	Penacastro *et al.,* (2004)
Sptrogyra species (green filamentous algae)	Batch reactor non-living cells, 25-35 ^{0}C, pH= 1.0-6.0, 180 min , dose=1-15 g/L	1-25 (mg/L)	90%, (pH=2.0, 120 min , 5 g/L) Q^0= 14.70 b=0.2 , R^2 =0.99	Gupta *et al.,* (2001)
Chlorella vulgaris *Scenedesmus accutus* (filamentous algal)	Fluidized bed packed bed Kappacarragenan (natural biopolymer), Polyurethane foam (cells immobilized in columns)	50 (mg/L)	48% 34% 36 % 31%	Travieso *et al.*, (1999)
Chlorella vulgaris *Chlorella crispate*	Batch reactor non-living cells, 25-35 ^{0}C, pH= 1.0-5.0, 30-60 min	0-200 (mg/L)	2.98 (mg/g/min) pH=1.0-2.0, 35 $^\circ$C K_F=4.99, n=2.23 6.20 mg/g/min (pH=1.0-2.0, 25 $^\circ$C) K_F =3.86, n = 2.02	Nourbakash *et al.,* (1994)

generated as waste) will be significantly lowered as compared to the cost of the conventional adsorbent.

A wide range of fungal species under non-living condition have been studied by different researchers for the removal of Cr(VI) from the wastewaters. The fungal cells can be killed for biosorption by physical and chemical methods. The physical methods include boiling, autoclaving, vaccum and freeze drying, and mechanical disruption (Galun *et al*, 1983a ; Townsley *et al.*, 1986). The chemical methods include the treatment of biomass with various organic and inorganic compounds (Kapoor *et al.,* 1999). Table 4 shows the Cr(VI) biosorption potential of various fungal biomass under growing, resting and non-living conditions.

Metal ion uptake by fungal biomass similarly takes place as discussed in algal cells. The first uptake mode involves the surface binding of Cr(VI) ions to the cell wall and extra-cellular material, which is metabolism independent. The second mode of Cr(VI) uptake into the cell across the cell membrane is dependent on the metabolic activity and is referred to as intra cellular accumulation. The first mode of metal uptake is common both in dead and living cells. Cr(VI) uptake by the second process, which is metabolism dependent, occurs only in the living cells.

To date the biosorption mechanism of Cr(VI) ions by fungal biomass has been studied largely in relation to chitin, its deacylated derivatives, chitosan and cellulose. The fungal cell wall also contain glycan, proteins, lipids, polyuronids and melanin. The role played by the cell wall fraction and structural polysaccharides is not fully understood and needs to be studied in greater detail.

Table 4 : Biosorption of Cr(VI) using various fungal biomass

Biosorbent (Fungal species)	Reactor/conditions	Initial Cr(VI) Con	Maximum Cr(VI) removed	Reference
Aspergillus sp. (filamentous)	Batch reactors, non-living cells, pH=2.0-6.0, dose= 4.5 g/L 150 rpm, 8h, 30^{0}C	50-500 (mg/L)	10-27.5 mg/g (pH=2.0, 2 h) Q^0= 29.2, b = .03 R^2 =0.954, K_F=6.8, n= 4.5 R^2 =0.987	Sen *et al.* (2010)
Aspergillus sp. (filamentous)	Batch reactors, resting cells, pH=2.0-6.0, 180 rpm, 30^{0}C dose= 2.4-5.2 g/L culture age 12-48 h	0-500 (mg/L)	34.8 (mg/g) pH=2.0, 4.5 g/L, 36 h	Sen and Ghosh Dastidar, (2007)
Fusarium sp. (filamentous)	Batch bioreactor growing cells pH=5.0, 30°C, 180 rpm	100-500 (mg/L)	18.2-71.0(mg/g)	Sen *et al.,* (2007)
	Continuous flow bioreactor (single & multistage), dilution rates=0.01-0.04/h, pH=5.0, 30°C	50-500 (mg/L)	40 mg/L, 0.02/h 420 mg/L, 0.01/h	
Fusarium sp. (filamentous)	Batch reactors, non-living cells, pH=1.0-6.0, dose=4 g/L 150 rpm, 8h, 30°C	50-500 (mg/L)	12.5-47.5(mg/g) (pH=2.0, 2h) Q^0= 50.25, b=0.03 R^2=0.975 K_F =7.90, n=3.12 R^2 =0.996	Sen *et al.,* (2005)
Candida utilis.	Batch bioreactor resting cells (immobilised in PVA alginate beads) 100 rpm, 30°C, 4d	100 µm	Complete removal	Pattanapipit Paisa *et al.,* (2001)
	Continuous flow bioreactor, flow rate= 0.95 mL/h, 20 d	50 µm	(90 %)	
R. arrhizus *S. cerevisiae*	Batch reactors, non-living cells, pH=1.0-5.0, 25-30°C, 30-60 min	0-100 (mg/L)	8.40 (mg/g/min) pH=1.0-2.0, 35°C, 60 min K_F=4.53, n = 1.78 4.30 (mg/g/min) pH=1.0-2.0, 35°C, 60 min K_F=1.59, n=1.82	Prakasham *et al.,* (1998)
Zygomycetes (Mucor heimalis MP/92/3/4)	Batch reactor resting cells, pH=1.0-5.5, 30°C, metal enrichment time= 1000 min	50 (mg/L)	4.3 (mg/g) pH= 1.0, 30°C, 1000 min	Pillichshanmer *et al.*, (1995)
Candida utilis & different species of yeast	Batch reactor resting dehydrated cells 30 °C, 72 h (dehydrated to different moisture level) & intact cells 75% of moisture (without dehydration)	150 (mg/L)	9.0 (mg/g) dehydrated cells	Rapport & Muter, (1994)

The use of non-living biomass in the removal of metal ions has the advantages due to the absences of toxicity limitations and adverse operating conditions (pH and temperature), but the most important limitation is that enzymatic reactions are no longer continued as the cells are dried.

Resting cells can sequester the metal through a combination of surface reactions, intracellular and extra cellular precipitation and extra cellular complexation reactions and can be maintained metabolically active using very low maintenance energy.

The use of growing cells for metal removal has the advantage that the simultaneous removal of metal is obtained during growth of the organism and separate biomass production processes e.g., cultivation, harvesting, drying, processing and storage can be avoided (Dursun *et al*., 2003). Also, the actively growing systems sequester metal through a combination of surface reactions, intracellular and extracellular precipitation and extracellular complexation reactions. However, major limitation of using growing systems for removal of metals is that cell growth is inhibited when the metal concentration is high, resulting in poor metal removal (Donmez & Aksu, 1999). This problem can be overcome by the use of metal tolerant organism. The tolerance and removal capacities are the essential characteristics of growing biomass used in a metal ion removal process.

Different researchers have reported different tolerances for Cr(VI) depending on the type of the fungal strain.

SUMMARY

Most of the studies reported in the literature to remove Cr(VI) have been carried out using non-living and resting cells of various microorganisms (algae, bacteria, fungi, etc.) and a very little information is available on the use of growing cells due to the toxicity limitations. However, actively growing system has a number of advantages. The simultaneous removal of metal is obtained during growth of the organism and therefore, separate production processes e.g., cultivation, harvesting, drying, processing and storage can be avoided. Moreover, the growing cells can be maintained enzymatically active to remove the metals from aqueous solution.

Different cell forms have different metal uptake capacities and sensitivities towards the potential toxic metals. Most of the studies in reported literature have been conducted using bacterial cells and scanty information is available on the use of fungal cells. The fungi, in general, have the higher tolerance levels for metals and hence studies are needed on their successful exploitation in biosorption processes.

Batch systems are mostly reported for Cr(VI) removal in the literature. However, the effluents are generated by the industries in very large quantities, treatment of which in the batch systems can no longer be applied. Therefore, a suitable operational strategy needs to be developed for continuous removal of Cr(VI) from the industrial effluents.

Most of the studies in reported literature have been conducted using synthetic Cr(VI) containing solution prepared in the laboratory and scanty information is available on treatment of actual industrial effluents. Keeping in mind large scale applications, studies are required to be carried out on metal removal from actual industrial effluents.

The reported literature information is available on Cr(VI) removal using bacteria, algae and fungus at lower concentrations of Cr(VI). There is a need to examine the tolerance level and the metal removal capacities of the organisms at higher metal ion concentrations.

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REFERENCES

Aksu, Z., Akpinar, D., (2001). Competitive biosorption of phenol and chromium (VI) from binary mixture onto dried anaerobic activate sludge. Biochemical Engineering., **7:** 183-193.

Bai, R. S., Abraham, T. E., (2001). Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigrificans*. Bioresources Technology., **79:** 73-81.

Barkhordar, B., Ghiasseddin., M., (2004). Comparision of Langmuir and Freundlich Equilibriums in Cr, Cu and Ni Adsorption by *Sargassum,* Iranian J Env Health Sci Eng,

1: 2, 58-64.
Campos, J., Martinez-Pacheco, M., Cervantes, C., (1995). Hexavalent chromium reduction by a chromate resistant Bacillus Sp. Strain. Antonie Van Leeuwenhoek, **68:** 203-208.
CiCi, Mechmet., Keles, E., (1990). Removal of Cr(VI) ions from solutions with active carbon prepared from rice husk. J. Sci. Ind. Res., **33(**8): 347-350.
Cotton, F. A., Wilkinson, G., (1980). Chemistry of the Transition element .Chichester Jjohn Willy and Sons, 719-735.
Dean ,S. A., Tobin , J. M ., (1999). Upake of Chromium cations and anions by milled peat . Resources Conservations and Recycling ., **27:** 151-156.
Donmez, G., Akshu Z., Ozturk A., Kustal, T., (1999). A comparative study on heavy metal biosorption characteristics of some algae. Processs Biochem., **34:** 885-892.
Dursan, A. Y., Ulsu, G., Cuci, Y., Aksu, Z., (2003). Bioaccumulation of cupper (II), lead (II) and chromium (VI) by growing *Aspergillus nige*, Process Biochemistry, **38**(10):1647-1651.
Gholami, F., Mahvi, A.H., Omrani, Gh. A.,Nazmara, Sh., Gashri, A., (2006). Removal of Chromium (VI) from aqueous solution by *ULMUS* leaves, Iranian J Env Health Sci Eng, **3** (2): 97-102.
Gulan, M., Keller, P., Malki, D., (1983 a). Removal of Uranium (VI) from solution by fungal biomass and fungal wall related biopolymer, Science, **219:** 285-286.
Gupta, V. K., Shrivastava, A. K., Jain, N., (2001). Biosorption of Chromium(VI) from aqueous solutions by green algae', *Spirogyra species,,* Water Res. **35:** 4079-4085.
Kapoor ,A., Viraraghavan, T., Roy Cullimore, D., (1999). Removal of heavy metals using the fungus *Aspergillus niger,* Bioresource Technology, **70:** 95-104.
Khanafari, A., Eshghdoost, S., Mashinchian, A., (2008). Removal of lead and chromium from aqueous solution by Bacillus circulans biofilm, Iran. J. Environ. Health. Sci. Eng., **5:** 3, 195-200.
Llovera, S., Bonet, R., Simon-Pujol , M. D., Congregado, F., (1993). Effect of culture medium ions on chromate reduction by resting cells of *Agrobacterium radiobacter,* Appl. Microbial. Biotechnol., **39:** 424-426.
Lytle, C. M., Lytle, F. M., Yang, N., Qian, J.H, Hansen, D., Zayed, A., Teroy, N., (1998). Reduction of Cr (VI) to Cr (III) by plants : potential for in situ heavy metal detoxification, Environmental Science Technology, **32:** 3087-3093.
McGrath, S. P., Smith, S., (1990). Chromium and nickel, In: Heavy Metals in soils (Alloway,B.J.,Ed.), Willy,New York, 125-150.
Mousumi, Sen., Dastidar, M.G., (2010). Adsorption-Desorption Studies on Cr(VI) Using Non-Living Fungal Biomass. Asian Journal of Chemistry, **22(**3):2331-2338.
Mousumi, Sen., Dastidar, M.G., Roychoudhury ,P.K., (2007). Comparative studies of batch and continuous biological treatment of Cr(VI) using Fusarium solani. Enzyme and Microbial Technology, **41**(1-2): 51-56.
Mousumi, Sen., Dastidar, M.G., (2007). Biosorption of Cr(VI) by resting cells of Aspergillus sp. Iran. J. Environ. Health. Sci. Eng.,.,.**4** (1): 9-12.
Mousumi, Sen., Dastidar, M.G., Roychoudhury , P.K., (2005). Biosorption of Cr(VI) using fungal strain of Fusarium sp. American Society of Civil Engineers (ASCE), *Prac.Period. Hazard.,Toxic Radioact. Waste Manag.,* **9**(3):147-151.
Mousumi, Sen., Dastidar ., M.G., Roychoudhury ,P.K., (2002).Biological Removal of Cr (VI) using an isolated fungal strain Water and Waste water Perspectives of Developing Countries (WAPDEC), Water Association, 1163-1169.
Mahvi, A. H., Nabizadeh, R., Gholami, F. , Khairi, A., (2007). Adsorption of chromium from wastewater by Platanus oriantalis leaves, Iran. J. Environ. Health. Sci. Eng., **4**(3): 191-196.
Muter, O., Patmalnieks, A., Rapoport, A., (2001). Interrelations of the yeast *Candida utilis* and Cr (VI): metal reduction and its distribution in the cell and medium, Process Biochemistry, **36:** 963-970.
Nourbaksh, M., Sag, Y., Ozer, Z., Aksu, Z., Kustal, T., Caglar, A., (1994). A comparative study of Various Biosorbent for Removal of Chromium (VI) Ions from Industrial Waste Waters', Process Biochemistry, **29:** 1-5.
Pattanapipitpaisal. P., Brown, N. L., Macaskie, L. E., (2001). Chromate reduction by Microbacterium liquefaciens immobilized in polyvinyl alcohol. Biotech Letter, **23:** 41-43.
Penacastro, J.M., Martinez-Jeronimo, F., Esparza-Garcia, F., Canizares-Villanueva, R.O., (2004). Heavy metals removal by the micro algae Sceneunus in crassatulus in continuous cultures. Bioresource Technology, **94** (2): 219-222.
Prakasham,R.S., Sheno, Merrie.,Sheela, J., Saswathi, N., Ramakrishna, S.V., (1998). Biosorption of chromium (VI) by free and immobilized Rhizopus arrhizus. Environmental pollution, **104:** 421-427.
Pillichshammer, M., Pumpel, T., Poder, R., Eller, K., Klima, J., Schinner, F., (1995). Biosorption of chromium to fungi., Biometals, **8:** 117-121.
Rapoport, A. I., Muter, O. A., (1994). Biosorption of Hexavalent Chromium by Yeasts, Process Biochemistry, **30** (2): 145-149.
Sag, Y., Kutsal, T., (1995). The Selective Biosorption of Chromium(VI) and Copper(II) Ions from Binary Metals Mixtures by *Rhizopus arrhizus,* Process Biochemistry, **31** (6): 561-572.
Sarah, S., Middleton, Rizlan., Bencheikh, Latmani., Mason, R., Mackey, Mark., H., Ellisman, Badley., M., Tebor, Craigs Criddle., (2003). Cometabolism of Cr(VI) by *Shewanella Oncendensis* MR-1 produced cell Associated reduced Chromium and inhibit Growth. Wiley Interscience.DOI:10.1002/bit, 10725.
Selvaraj, K.S., Manonmai, S., Pattabhi., (2003). Removal of hexavalent chromium usng distillery sludge. Bioresource Technology, **89:** 207-211.
Sharma, D. C., Forster, C. F., (1994). A preliminary examination into the adsorption of hexavalent chromium using low cost adsorbents, Biores. Technol, **47:** 257-264.
Solisio, C., Lodi, A., Converti, A., Del, M., (2000). The effect of acid pre treatment on the biosorption of chromium(III) by *Sphaeritilus natans* from industrial waste water, Water Res., **34:** 3171-3178.
Srinath, T., Verma, T., Ramteka, P.W., Garg, S.K., (2002). Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria, Chemophere, **48:** 427-435.
Stratten, G. W., (1987) Review, In environmental Toxicology ed. Hodson E., Elsiever, Amsterdam, 85-94.
Townsley, C. C., Rose, J. S., Atkins, A. S., (1986). Biorecovery of metallic residues from various industrial effluents using filamentous fungi, In Fundamental and Applied Bio hydrometallogy, eds R. W. Lawrence, R. M., R. Braneon and H. G. Enner. Elsevier, Amsterdam, 279-289.

Travieso, L., Canizarez, R. O., Borja, R., Benitez, F., Dominguez, A. R., Dupeyron, R. Valiente, V., (1999). Heavy metal removal by micro algae. Bull. Environ. Contam. Toxicol., **62:** 144-151.

Tzezos, M., (1996). Adsorption by microbial biomass in a process for removal of heavy metal ions from waste solutions, In Immobilization of Ions by Biosorption, eds, Eccles, H and Hunt, S., Ellis Horwood, Chichester, 201-218.

Volesky, B., (1990) .Biosorption and biosorbents in Biosorption of Heavy Metals, ed. B. Volesky, CRC press Inc, Boca Raton.