



## Living and Non-Living microorganisms as adsorbents for the removal of chromium from waste water-A Review

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### ARTICLE INFO

#### Article history:

Received: 31 July 2013;

Received in revised form:

24 January 2014;

Accepted: 14 February 2014;

#### Keywords

Biosorption,  
Hexavalent Chromium,  
Metal uptake,  
Adsorption isotherm,  
Kinetic models.

### ABSTRACT

The contamination of water by toxic heavy metals is a worldwide problem. The presence of hexavalent chromium in waste water is a potential hazard to aquatic life and humans. Biosorption of heavy metals is an important technique used in the removal of toxic metals from various sources like industrial waste, aqueous systems and municipal waste waters. Metal removal technique using non-conventional adsorbents such as microorganisms are cheap because of the low cost of adsorbents used and many represent a practical replacement to conventional processes. There are various mechanisms such as kinetic models and adsorption isotherms employed for the efficient removal of hexavalent chromium from various sources. The present review discusses brief findings of hexavalent chromium removal with the maximum metal uptake by using living and non-living microorganisms as adsorbents.

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### Introduction

Water contamination with heavy metals is a very severe problem all over world [1-3]. The world production of chromite ore is several millions of tons in a year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (the aluminothermic process) or by electrolysis of either  $\text{CrO}_3$  or chrome alum solutions. Chromium and its compounds are extensively used in industry with important sources from metal finishing, leather tanning, electroplating, textile industries, and chromate preparation [4]. In aqueous phase chromium mostly exists in two oxidation states, namely, trivalent chromium ( $\text{Cr}^{+3}$  and  $\text{Cr}(\text{OH})^{2+}$ ) and hexavalent chromium ( $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$ , etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic. For example it was reported that  $\text{Cr}_2\text{O}_7^{2-}$  can cause lung cancer [5, 6].

Chrome plating, the result of which is often referred to simply as chrome is a technique of electroplating a thin layer of chromium on to a metal [7]. The chromed layer is attractive and provides corrosion resistance, easy cleaning and surface hardness. There are two types of chrome plating baths; hexavalent and trivalent, although the latter are not common. Hexavalent chromium baths are widely used.. About 35% of used chromium is discharged in the effluent as trivalent and hexavalent chromium.

Chromium(III) and Cr (VI) have major environmental significance because of their stability in the natural environment, Cr (VI) is known to have 100 fold more toxicity than Cr (III) because of its high water solubility and mobility as well as easy reduction [8]. International agency for Research on cancer has determined that Cr (VI) is carcinogenic to humans [9]. Therefore, the World Health Organization (WHO) recommends that the toxic limits of chromium (VI) in waste water at the level of 0.05mg/L, while total Cr containing Cr(III), Cr(VI) and other species of chromium is regulated to be discharged below 2mg/L [9]. The toxicological effect of Cr (VI) originates from the

action of this form itself as an oxidizing agent as well as the formation of free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell [10].

Hexavalent chromium shows adverse effects on growth parameters and also causes accumulation of chromium in plants [11-14]; via plants, it enters the food chain. Chromium also shows toxicity towards different animals. Studies have shown the toxicity of chromium picolinate in renal impairment, skin blisters and pustules, anemia, hemolysis, tissue edema, liver dysfunction, neural cell injury, impaired cognitive, perceptual and motor activity, enhanced production of hydroxyl radicals, chromosomal aberration, depletion of antioxidant enzymes and DNA damage in mice [15].

Several methods are used to remove chromium from the wastewater. These include reduction followed by chemical precipitation [16], ion exchange [17], reduction [18], electrochemical precipitation [19], solvent extraction [20], membrane separation [21], evaporation [22] and foam separation [23]. The chemical precipitation method involves a two step process. The first step is the reduction of Cr (VI) under acidic conditions, followed by the precipitation of Cr (III) hydroxide. Commonly used reducing agents are sulfur dioxide, sodium sulfite, sodium bisulfate and ferrous sulfate. The process requires addition of other chemicals, which finally leads to the generation of a high water content sludge, the disposal of which is cost intensive. An ion exchange is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The anion exchange sorption process is used for the removal of hexavalent chromium from the waste water. Chromium removal efficiencies by electrochemical precipitation are greater than 99% and the residual chromium concentration is less than 0.5 mg/L. Electrochemical precipitation consumes huge amounts power. In solvent extraction of chromium, several ion-association systems have been used such as triphenylsulfonium, ammonium,

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triphenylphosphonium, tetraphenylstibonium and triphenylselenium cations [24]. The solvents used for the extraction of Cr (VI) are diethylether, isobutyl ketone, ethylacetate, hexane, tri-n-butylphosphate and chloroform [24].

Foam separation is based on surface adsorption. It is a process in which solute substances adsorb at the gas-liquid interface between a dispersed phase and a liquid phase. This method can remove surface active agents or non-surface active materials which can adsorb or combine with surfactants. The foam is collected and collapsed in the bubble collector, and the collapsed formate solution containing chromium is much more concentrated in the surfactant than in the initial solution [25].

The above cited conventional chromium elimination processes are costly or ineffective at small concentrations and may also lead to environmental problems from waste disposal. In recent years biosorption research is focused on using readily available biomass that can remove heavy metals. This process involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. It is particularly the cell wall structure of certain fungi, bacteria, algae and plants that is responsible for this phenomenon. This process can be applied as a cost effective way of purifying industrial waste water whereby drinking water quality can be attained. A lot of research was focused on bio-adsorbent materials which can efficiently remove heavy metals from aqueous bodies. These materials are identified as bioadsorbents and the binding of metals by biomass is referred to as biosorption.

In this article, there are two approaches regarding the nature of adsorbents. One is conventional adsorbents and another is non-conventional adsorbents. The major advantage of biosorption over conventional process include easy available source, low cost, high effectiveness, ecofriendly, minimum waste disposal, etc. On this basis it is reviewed the literature of collection and analysis of data on hexavalent chromium (VI) using living and non-living microorganisms as adsorbents.

#### Biosorbent materials

A large number of materials have been investigated as biosorbent for hexavalent chromium removal. A fundamentally important characteristic of good adsorbents [26, 27] is their high porosity and consequent larger surface area with more specific adsorption sites. Most adsorbents which have been used in pollution control have porous structure. The porous structure not only increases surface area and consecutively adsorption but also the kinetics of the adsorption. A better adsorbent is one with large surface area and which requires less time for adsorption equilibrium. Hence, one generally looks to adsorbents with high surface area and faster kinetics for the removal of pollutants. Some of the important adsorbents used in pollution control and various industrial operations are discussed herein.

#### Living micro-organisms and non-living microorganisms as adsorbents

Both living and non-living microorganisms have the ability to remove the heavy metals and thereby making water contaminant free. Good evidence now exists showing that the biomass of filamentous fungi of the order Mucorales represents a good adsorbent material for a wide range of heavy metals. The metal binding sites are predominantly associated with the cell wall structure of these molds [28]. Both *Rhizopus arrhizus* and *Rhizopus nigricans* contain chitin and chitosan in their cell walls, which have been reported to play a role in the sequestration chromium metal ions from solution. Although chitin and chitosan have been reported to remove a number of

metal ions from solutions, among these are titanium, zirconium, hafnium, mercury, copper, and uranium [29], they do not seem to be the major metal binding compounds active in the complex sequestration of metals by adsorptions. However due to certain inherent disadvantages in the use of living microorganisms for metal removal, recovery is not generally feasible in all situations like industrial effluents contain high concentrations of toxic metals under widely varying PH conditions. These conditions are not always suitable to the growth and maintenance of an active microbial population.

Non-living microorganisms are several advantages over the living microorganism as adsorbents. The advantages are 1. Cheap source of biomass, 2. It is not subject to toxicity limitation by cells, 3. Because of it exhibit as ion exchange, the process is very rapid, 4. There is choice of wide range of operating conditions such as PH, temperature, and metal concentrations, because of cells are non-living. 5. Metals can be desorbed readily and then recovered. Chromium adsorption capacities for both living and non-living organisms are shown in Table 1 and Table 2.

#### Modeling of adsorption

Mathematical models can describe the behavior of the biosorption processes operating under different experimental conditions. They are very useful for scale up studies or process optimization. A number of models with varying degrees of complexity have been developed to describe the metal biosorption systems. These are of two types: kinetic models and equilibrium models.

#### Kinetic models

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbate uptake at the solid –solution interface. Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Sorption kinetics shows a large dependence on the physical and /or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ( $r^2$  values close or equal to one). A relatively high  $r^2$  value indicates that the model successfully describes the kinetic of Cr (VI) adsorption.

#### Pseudo-first order or Lagergen kinetic model

It is the first equation for sorption [62, 63] of liquid/solid system based on solid capacity. The pseudo first order equation is generally expressed as

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad [1]$$

Here  $q_e$  and  $q_t$  are the adsorption capacities at equilibrium and at time  $t$ , respectively (mg/g) and  $k_1$  is the rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ). Eq (1) can be arranged to obtain the more useful form

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad [2]$$

The values of  $\log(q_e - q_t)$  were linearly correlated with  $t$ . The plot of  $\log(q_e - q_t)$  vs  $t$  should give a linear relationship from which  $k_1$  can be determined from the slope. Eq (2) differs from a true first order equation in two ways: (i) the parameter  $k_1(q_e - q_t)$  does not represent the number of available sites, and (ii) the parameter  $\log q_e$  is the adjustable parameter and often it is found not equal to the intercept of the plot of  $\log(q_e - q_t)$  vs  $t$  where as in a true first order  $\log q_e$  should be equal to the intercept.

### Pseudo-second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad [3]$$

Where  $k_2$  is the rate constant of pseudo second order adsorption ( $\text{g}^{-1}\text{min}^{-1}$ ). Eq (3) can be rearranged to obtain more useful form as

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad [4]$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad [5]$$

And  $k_2$  is obtained from plot of  $t/q_t$  vs  $t$ . The model is best fit for hexavalent chromium removal by many agents.

### Intra-particle diffusion model

The adsorption of hexavalent chromium on a porous adsorbent is the combination of four consecutive steps [64]; diffusion in the bulk solution, then diffusion across the thin film surrounding the adsorbent particles, followed by intra-particle diffusion and adsorption within the particles [64]. According to Weber and Moris [65] if the rate limiting step is the intra-particle diffusion, then amount of adsorbed at any time should be directly proportional to the square root of contact time  $t$  and shall pass through the origin which is defined mathematically in Eq (6)

$$q_t = k_{id} t^{0.5} \quad [6]$$

A linearised form is Eq (6) where  $q_t$  is the amount of Cr (VI) adsorbed.  $t$  is the contact time.  $K_{id}$  is the intra-particle diffusion coefficient.

$$\log q_t = \log k_{id} + 0.5 \log t \quad [7]$$

A plot of  $\log q_t$  against  $0.5 \log t$  should give a straight line with a positive intercept for intra particle diffusion controlled adsorption process. The value of  $k_{id}$  can be calculated from intercept of such plot. Higher values of  $k_{id}$  illustrate an enhancement in the rate of adsorption. Intra particle diffusion coefficient values have been calculated by various workers to bring a better understanding of the process.

### Elovich kinetic equation

The Elovich Eq (8)] incorporates  $\alpha$  as the initial adsorption rate ( $\text{mg/g min}$ ),  $\beta$ ( $\text{g/mg}$ ) is the desorption constant related to the extent of the surface coverage and

$$\frac{dq}{dt} = \alpha e^{-\beta q_t} \quad [8]$$

$q_t$  is the amount of gas chemisorbed at time. Eq (8) can be simplified to Eq (9) by considering  $\alpha\beta \gg t$  and by applying the boundary conditions  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$  [144].

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad [9]$$

If the hexavalent chromium adsorption fits the elovich model, a plot of  $q_t$  vs  $\ln(t)$  should give a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $(1/\beta)\ln(\alpha\beta)$ .

### Equilibrium model

An adsorption isotherm is used to characterize the interaction of the metal ions with the adsorbents. This provides a relationship between the concentration of metal ions in the solution and the amount of metal ions adsorbed to the solid phase when the two phases are at equilibrium.

### Langmuir model

The Langmuir isotherm [66] was derived originally from studies on gas adsorption to activated carbon. The Langmuir isotherm model is used to estimate the adsorption of adsorbent used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir adsorption isotherm is represented as Eq (10).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad [10]$$

Here  $q_e$  is the metal concentration adsorbed in solid (biomass),  $C_e$  is the metal residual concentration in the solution.  $q_{\max}$  is the maximum specific uptake corresponding to sites saturation, and  $b$  is the ratio of adsorption/desorption rates. Two derivatives of the Langmuir equation are Eqs.(11) & (12).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad [11]$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \quad [12]$$

### Freundlich model

The Freundlich isotherm, first proposed in 1906, is based on multilayer adsorption with interaction between adsorbed molecules [67]. The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The Freundlich isotherm is the earliest known relationship describing the adsorption equation. The application of the Freundlich Eq (13) suggest that adsorption energy exponentially decreases on completion of the adsorptional centers of an adsorbent. For adsorption from solution, the Freundlich isotherm is represented by Eq (13).

$$q_e = K_f C_e^{1/n} \quad [13]$$

Here  $K_f$  is the Freundlich constant and is also known as Freundlich capacity and  $n$  stands for adsorption intensity.  $Q_e$  is the amount of chromium adsorbed at equilibrium and  $C_e$  is the residual concentration of Cr (VI) in solution. The Freundlich equation is expressed linearly as Eq (14).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad [14]$$

The values of  $K_f$  and  $n$  can be obtained from slope and intercept of a plot of  $\log q_e$  versus  $\log C_e$ . Both the parameters  $K_f$  and  $n$  affect the adsorption isotherm.

### Langmuir-Freundlich model

In this model [55], the surface of the sorbent is considered to be homogeneous and sorption is a cooperative process due to adsorbate-adsorbate interaction. The Langmuir-Freundlich model is represented in Eq (15).

$$q_e = \frac{q_{\max} b C_e^{1/n}}{1 + b C_e^{1/n}} \quad [15]$$

### Tempkin model

The Tempkin isotherm model contains a factor that takes care of the adsorbent-adsorbate interactions [68]. Tempkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. Tempkin noted experimentally that heats of adsorption would more often decrease than increase with increasing coverage.

**Table 1. Reported adsorption capacities (mg/g) for living microorganisms**

Biomass type	Biomass class	Metal up take, mg/g	Isotherms it follows	Kinetics it follows	References
Chlorella Vulgaris	algae	23.6	Freundlich		[30]
Ochrobactrum anthropi	Bacteria	86.2	Langmuir, Freundlich	2 <sup>nd</sup> order	[31]
Aeromonas caviae	Bacteria	124.46	Langmuir, Freundlich	2 <sup>nd</sup> order	[32]
Dunaliella 1 and 2	Bacteria	58.3 & 45.5	Langmuir, Freundlich	2 <sup>nd</sup> order	[33]
Bacillus thuringiensis	Bacteria	89.03	Langmuir, Freundlich	---	[34]
Pseudomonas fluorescens TEM08	algae	40.8	Langmuir	---	[35]
Sargassum sp	algae	19.06	Langmuir, Freundlich	---	[36]
Spent/fresh Spirulina platensis and Chlorella vulgaris	Bacteria	213 & 189	Langmuir, Freundlich	Initial zero order, 1 <sup>st</sup> order	[37]
Type-I, type-II Mucor hiemalis	Bacteria	53.5	Langmuir	2 <sup>nd</sup> order	[38]
S.equisimilis, B.coagulans and E. Coli,	Bacteria	5.82, 5.35 & 4.12	Freundlich, RP-Model for E.Coli	---	[39]
Rhizopus arrhizus	Fungus	23.92	Freundlich, R-P-Model	2 <sup>nd</sup> order	[40]
Nostoc muscorum	cyanobacterium	22.92	Langmuir, Freundlich	1 <sup>st</sup> order, 2 <sup>nd</sup> order	[41]
Biofilm of E.Coli supported on carbon	Bacteria	97.7	Langmuir, Freundlich	---	[42]
Pseudomonas Sp	Bacteria	95	Langmuir, Freundlich	---	[43]
Phormidium Sp.	Bacteria	22.8	Langmuir	2 <sup>nd</sup> order	[44]
Staphylococcus xylosus	Bacteria	143	Langmuir, Freundlich	---	[43]
Aspergillus flavus	Fungus	0.335	---	----	[45]
Aspergillus sydoni	Fungus	9.07	Langmuir, Freundlich	---	[46]
Aspergillus niger	Fungus	17.61	Langmuir, Freundlich	---	[46]
Penicillium Janthinellum	Fungus	9.35	Langmuir, Freundlich	----	[46]
Rhizopus nigricans	Fungus	47	Langmuir, Freundlich	1 <sup>st</sup> order, 2 <sup>nd</sup> order	[47]
Chlorella Vulgaris	algae	79.3	Langmuir, Freundlich	---	[49]
L.Japonica	algae	59.35	Freundlich	2 <sup>nd</sup> order	[50]
Oedogonium hatei	algae	31.0	Langmuir, Freundlich	1 <sup>st</sup> order	[51]
Scenedesmus obliquus	algae	58.8	Langmuir, Freundlich	---	[49]

**Table 2. Reported adsorption capacities (mg/g) for non- living microorganisms**

Biomass Type	Biomass class	Metal up take, mg/g	Isotherms it follows	Kinetics it follows	Reference
Rhizopus arrhizus	Fungus	23.88	Freundlich	---	[52]
Spirulina Sp	Cyanobacteria	4.7	Langmuir	----	[53]
Spirogyra Sp	Filamentous algae	14.7	langmuir		[54]
Dried Rhizopus arrhizus	Fungus	78	Langmuir, Freundlich, Langmuir-Freundlich model, R-P.Model	2 <sup>nd</sup> order	[55]
Parmelina tiliaceae	Fungus	52.11 for Cr(III)	Langmuir, Freundlich, D-R-Model	2 <sup>nd</sup> order	[56]
Rhizopus arrhizus	Fungus	108.9	Langmuir-Freundlich Model	2 <sup>nd</sup> order	[55]
Aspergillus niger	Fungus	117.33	Langmuir	2 <sup>nd</sup> order	[57]
Hylocomium splendens	Fungus	42.1 Cr(III)	Langmuir, Freundlich	2 <sup>nd</sup> order	[58]
Ceramium virgatum	Fungus	26.5	Langmuir, Freundlich, D-R.Model	2 <sup>nd</sup> order	[59].
Aspergillus niger	Fungus	30.1	Freundlich	2 <sup>nd</sup> order	[60]
Fusarium Sp	Fungus	50.25	Langmuir, Freundlich	---	[61]
Rhizopus oryzae	Fungus	23.5	----	1 <sup>st</sup> order	[48]
Saccharomyces cerevisiae	Fungus	44.2	----	1 <sup>st</sup> order	[48]

The nonlinear form of Tempkin equation is given by Eq (16) and the linear form in Eq (17).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad [16]$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad [17]$$

Here  $B_T = (RT/b_T)$ .  $T$  is the absolute temperature.  $R$  is the universal gas constant. Constant  $b_T$  is related to the heat of adsorption.  $A_T$  is the equilibrium binding constant corresponding to the maximum binding energy. A plot of  $q_e$  versus  $\ln C_e$  at a fixed temperature will give Tempkin isotherm constants,  $A_T$  and  $b_T$ .

#### Redlich-Peterson model

The Redlich-Peterson isotherm contains three parameters which may be used to represent adsorption equilibrium over a wide concentration range, and can be applied either in homogeneous or heterogeneous systems due to its versatility [69, 70]. It is described in Eq (18).

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{b_R}} \quad [18]$$

The linearised form is Eq (19)

$$\ln \frac{K_R C_e}{q_e - 1} = b_R \ln(C_e) + \ln(\alpha_R) \quad [19]$$

It has three isotherm constants  $K_R$ ,  $\alpha_R$ , and  $b_R$ . The Redlich-Peterson isotherm constants cannot be obtained using graphical methods because of the three unknown parameters. A professional graphics software package is ideal for this.

#### BET model

The Brunauer, Emmet and Teller (BET) model is an extension of the Langmuir model [71]. It represents the isotherm with a multilayer adsorption at the adsorbent surface. It assumes that the Langmuir equation is applicable to each layer and a given layer may not be completely formed before the next layer forms Eq (20).

$$q_e = \frac{q_{\max} B C_e}{C_s - C_e} \left[ 1 + (B - 1) \frac{C_e}{C_s} \right] \quad [20]$$

Where  $C_s$  is the saturation concentration of the solute.  $B$  is a constant relating to the energy of interaction with the surface and other symbols are as previously described.

#### Conclusions

Both conventional and non-conventional adsorbents are cheap for the removal chromium from waste water, those represents an efficient and potential and also a practical replacement to the conventional processes. In spite of profile use of activated carbon in wastewater treatment, its use is sometimes restricted because of its high cost. To replace the expensive activated carbon, a wide range of inexpensive bioadsorbents were investigated utilizing naturally occurring materials and waste products of different industries. Some of them were found to be quite satisfactory. However, it is utmost important to dispose of the spent adsorbents in an environment friendly. Only limited information is available in the literature about safe disposal of spent adsorbents. More efforts should be made in this direction.

#### References

1. B.Volesky, and Z.R.Holan, Biosorption of heavy metals, *Biotechnol. Progr.* 11 (1995) 235.
2. F.Veglio and F.Beolchini, Removal of metals by biosorption: a review, *Hydrometallurgy.* 44 (1997) 301.

3. Z.Kowalshi, Treatment of chromic tannery wastes, *J.Hazard Materials.* 39 (1994) 137.
4. A.E.Sikaily, A.E.Nemr, A.Khaled, O.Abdelwahab, Removal of toxic chromium from waste water using green alga *Ulva Lactuca* and its activated carbon, *J.Hazard.Mater.*, 148 (2007) 216.
5. H.Li, Z.Li, T.Liu, X.Xiao, Z.Peng and L.Deng, A novel technology for biosorption and recovery hexavalent chromium in waste water by bio-functional magnetic beads, *Bioresour. Technol.* 99 (2008) 6271.
6. D.E.Paul, J.T.Black and A.R.Kohser, *Materials and Process in Manufacturing*, 9 th ed, Wiley New York, 2003, p793.
7. V.Gomez and M.P.Callo, Chromium determination and speciation since 2000, *Trends Anal.Chem.* 25 (2006) 1006.
8. World Health Organisation, *Guidelines for drinking water quality*, 3<sup>rd</sup> ed., Genva Vol.1. 2004, p 334.
9. A.Baral and R.D.Engelken, Chromium based regulations and greening in metal finishing industries in the USA, *Environ.Sci.polocy.* 5 (2002) 121.
10. A.K.Das, Micellar effect on the kinetics and mechanism of chromium (VI) oxidation of organic substrates, *Coord.Chem.Rev.* 248 (2004) 81.
11. F.H.Hsu and H.C.Chou, Inhibitory effects of heavy metals on seed germination and seedling growth of *Miscanthus* species, *Bot.Bull, Acad.Sin.*33(1992)335.
12. I.M.Zeid, Responses of phaseolus *Vulgaris* chromium and Cobalt treatment, *Biol, plant* 44 (2001) 111.
13. M.Faisal and S.Hasnain, Bacterial Cr (VI) reduction concurrently improves sunflower (*Helianthus Annuus L.*) growth, *Biotechnology, Lett.* 27 (2005) 943.
14. M.Faisal, A.Hameed and S.Hasnain, Chromium resistant bacteria and cyanobacteria: Impact on Cr(VI) reduction potential and plant growth, *J.Ind. Microbiol. Biotechnol.* 32 (2005) 615.
15. D.Bagchi, S.J.Stohs, B.W.Downs, M.Bagchi and H.G.Preuss, Cytotoxicity and oxidative mechanisms of different forms of chromium, *Toxicology* 180 (2002) 5.
16. X.Zhou, T.Korenaga, T.Takahashi, T.Moriwake and S.Shinoda, A process monitoring/controlling system for the treatment of waste water containing (VI), *Water Res.* 27 (1993) 1049.
17. G.Tiravanti, D.Petruzzelli and R.Passino, Pretreatment of tannery wastewaters by an ion-exchange process for Cr (III) removal and recovery, *Water.Sci.Technol.* 36 (1997), 197.
18. J.C.Seaman, P.M.Bertsch and L.Schwallie, "In-Situ Cr (VI) reduction within coarse -textured oxide-coated soil and aquifer systems using Fe(II) solutions", *Environ.Sci.Technol.* 33 (1999) 938.
19. N.Kongsricharoern and C.Polprasert, Chromium removal by a bipolar electro-chemical precipitation process, *Water.Sci.Technol.* 34 (1996) 109.
20. K.R.Pagilla and L.W.Canter, Laboratory studies on remediation of Chromium -contaminated soils, *J.Environ.Eng.* 125 (1999) 243.
21. A.K.Chakravathi, S.B.Chowadary, S.Chakrabarty, T.Chakrabarty and D.C.Mukherjee, Liquid membrane multiple emulsion process of chromium (VI) separation from waste waters, *Colloids,Surf.A* 103(1995)59.
22. Z.Aksu, D.Ozer, H.I.Ekiz, T.Kutsal and A.Calar, Investigation of biosorption of Chromium (VI) on *Cladophora Crispata* in Two-Stage Batch reactor, *Environ.Technol.*, 17(1996)215.
23. S.D.Huang, C.F.Fann and H.S.Hsieh, Foam separation of Chromium (VI) from aqueous solution, *J.Colloid.Interface.Sci.*, 89(1982)504.

24. P.Venkateswaran and K.Palanivelu, Solvent extraction of hexavalent chromium with tetrabutyl ammonium bromide from aqueous solution, *Sep.Purif.Technol.* 40 (2004) 279.
25. C.S.Jiao and Y.Ding, Foam separation of chromium (VI) from aqueous solution, *J.Shanghai, Univ.* 13 (2009) 263.
26. C.Tien, Adsorption calculations and modeling (Butterworth-Heinemann, Boston), 1994.
27. B.G.Linsen, Physical and chemical aspects of adsorbents and catalysts, Academic Press, London, 1970.
28. J.Remacle and B.Volesky, Biosorption of heavy metals CRC Press: Boca Raton, F.L. 1990, 83-92.
29. R.A.A.Muzzarelli, Chitin and its derivatives: New trends of applied research, *Carbohydrate Polymers*, 3 (1983) 53.
30. Z.Aksu, U.Acikel and T.Kutsal, Investigation of simultaneous biosorption of copper (II) & Chromium (VI) on dried *Chlorella Vulgaris* from binary metal mixtures: application of multicomponent adsorption isotherm, *Sep.Sci.Technol.* 34 (1999) 501.
31. G.Ozdemir, D.Ozurk, N.Ceyhan, R.Isler and T.Cosar, Heavy metal biosorption by biomass of *ochrobactrum anthropi* producing exopolysaccharide in activated sludge, *Bioresour.Technol.* 90 (2003) 71.
32. M.X.Loukidou, A.I.Zouboulis, T.D.Karapantsios and K.A.Mastis, Equilibrium and kinetic modeling of chromium (VI) biosorption by *Aeromonas Caviae*, *Colloid.Surf.A, Physicochem.Eng.Aspects*, 242 (2004) 93-104.
33. D.Gonul and Z.Aksu, Removal of Chromium (VI) from saline wastewaters by *Dunaliella* species, *J.Hazard.Mater.* 38 (2002) 751.
34. Y.Sahin and A.Ozturk, Biosorption of Chromium (VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*, *J.Process.BioChemistry.* 40 (2005) 1895.
35. A.Uzel, Metal biosorption capacity of the organic solvent tolerant *Pseudomonas fluorescens TEM08*<sup>®</sup>, *Bioresour.Technol.* 100 (2009) 542.
36. M.G.V.Viera, R.M.Oisiovici and M.L.Gimenes, "Biosorption of chromium (VI) using a *Sargassum* Sp, packed-bed column, *Bioresour.Technol.* 99 (2008) 3094.
37. S.V.Gokhale, K.K.Jyoti and S.S.Lelekinetic, Equilibrium modeling of chromium (VI) biosorption on fresh and spent *Spirulina platensis/Chlorella vulgaris* biomass, *Bioresour. Technol.* 99 (2008) 3600.
38. N.Tewari, P.Vasudevan and B.K.Gupta, Study on biosorption of Cr (VI) by *Mucor hiemalis*, *Biochem.Eng.J.* 23 (2005) 185.
39. C.Quintelas, B.Fernandes, J.Castro, H.Figueiredo and T.Tavares, Biosorption of Cr (VI) by three different bacterial species supported on granular activated carbon: a comparative study, *J.Hazard.Mater.* 153 (2008) 799.
40. B.Preetha and T.Viruthagiri, Batch and continuous biosorption of chromium (VI) by *Rhizopus arrhizus*, *Sep.Purif.Technol.* 57 (2007) 126.
41. V.K.Gupta and A.Rasogi, Sorption and desorption studies of chromium (VI) from nonviable cyanobacterium *Nostoc muscorum* biomass, *J.Hazard.Mater.* 154 (2008) 347.
42. R.M.Gabr, S.M.F.Gad-Elrab, R.N.N.Abskharon, S.H.A.Hasan and A.A.M.Shoreu, Biosorption of hexavalent chromium using biofilm of *E.Coli* supported on granulated activated carbon, *World J.Microbiol.Biotechnol.* 25 (2009) 1695-1703.
43. M.Ziagova, G.Dimitriadis, D.Aslandou and X.Papaioannou, Comparative studies of Cd (II), and Cr (VI) biosorption, *Bioresour.Technol.* 98 (2007) 2859-2865.
44. Z.Aksu, S.Ertugrul and G.Donmez, Single and binary chromium (VI) and Ramazol Black B biosorption properties of *Phormidium* Sp, *J.Hazard.Mater.* 168 (2009) 310.
45. K.K.Deepa, M.Sathishkumar, A.Binupriya, G.S.Murugesan, K.Swaminathan and S.E.Yun, Sorption of Cr (VI) from dilute solutions and waste water by live and pretreated biomass of *Aspergillus flavus*, *Chemosphere*, 62 (2006) 833-840.
46. R.Kumar, N.R.Bishnoi and K.G.Bishnoi, Biosorption of chromium (VI) from aqueous solution and electroplating industry using fungal biomass, *Chem..Eng.J.*, 135 (2008) 202-208.
47. R.S.Bai and T.E.Abraham, Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*, *Bioresour.Technol.* 79 (2001) 73-81.
48. D.Park, Y.S.Yun and J.M.Park, Use dead fungal biomass for the detoxification of hexavalent chromium: screening and kinetics, *Process Biochem*, 40 (2005) 2559-2565.
49. G.C.Donmez, Z.Aksu, A.Ozturk and T.Kutsal, A comparative study on heavy metal biosorption characteristics of some algae, *Process Biochem*, 34 (1999) 885-892.
50. X.S.Wang, Z.Z.Li and C.Sun, Removal of chromium (VI) from aqueous solution by low cost biosorbents: marine macroalgae and agriculture by products, *J.Hazard.Mater.*, 153 (2008) 1176-1184.
51. V.K.Gupta and A.Rastogi, Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions, *J.Hazard.Mater.*, 163 (2009) 396-402.
52. R.S.Prakasham, J.S.Merrie, R.Sheela, N.Saswathi and S.V.Ramakrishna, Biosorption of Chromium (VI) by free and immobilized *Rhizopus arrhizus*, *Environ.Pollut.* 104 (1999) 421.
53. K.Chojnackaa, B.Chojnackaa and H.Gorecka, Biosorption of Cr (III), Cd (II) and Cu (II) ions by blue-green algae *Spirulina* Sp: Kinetics, equilibrium and the mechanism of the process, *Chemosphere*, 59 (2005) 75.
54. V.K.Gupta, A.K.Shrivastava and N.Jain, Biosorption of Chromium (VI) from aqueous solutions by green algae *spirogyra* species, *Water.Res.*, 35 (2001) 4079.
55. Z.Aksu and E.Balibek, Chromium (VI) biosorption by dried *Rhizopus arrhizus*: Effect of salt (NaCl) concentration on equilibrium and kinetic parameters, *J.Hazard.Mater.* 145 (2007) 210.
56. D.U.Ozgun, A.Sari, M.Tuzen and M.Soylak, Biosorption of Pb (II) and Cr (III) from aqueous solution by lichen (*Parmelia tiliaceae*) biomass, *Bioresour.Technol.* 99 (2008) 2972.
57. K.Yamin, M.Kalpana, S.Basha and B.Jha, Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*, *Chem.Engg.J.* 145 (2009) 489.
58. A.Sari, M.Durali, M.Tuzen and M.Soylak, Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass: Equilibrium, kinetic and thermodynamic studies, *Chem.Engg.J.* 144 (2008) 1.
59. A.Sari and M.Tuzen, Biosorption of total chromium from aqueous solution by red algae (*Ceramium Virgatum*): Equilibrium, kinetic and thermodynamic studies, *J.Hazard.Mater.* 160 (2008) 349.
60. D.P.Mungasavalli, T.Viraraghavan and Y.C.Jin, Biosorption of chromium from aqueous solution by pretreated *Aspergillus niger*: Batch and column studies, *Colloid Sur. A*, 301 (2007) 214-223.
61. M.Sen, M.G.Dastidar and P.K.R.Choudhury, Biosorption of chromium (VI) by nonliving *Fusarium* Sp. Isolated from soil, *Hazard Radio act Waste Manage.*, 9 (2005) 147-151.

62. J.Qui, Z.Wang H.Li, L.Xu, J.Peng, M.Zhai, C.Yang, J.Li and G.Wei, Adsorption of Cr (VI) using silica based adsorbent prepared by radiation induced grafting, *J.Hazard.Mater.*, 166 (2009) 270-276.
63. Y.S.Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, *Scientometrics*. 59 (2004) 171.
64. S.S.Baral, N.Das, G.Roy Choudary and S.N.Das, A preliminary study on the adsorptive removal of Chromium (VI) using seaweed, *Hydrilla Verticillata*, *J.Hazard.Mater.* 171 (2009) 358.
65. W.J.Weber, Jr. J.C.Morris and J.Sanit, Kinetics of adsorption on carbon from solution, *Eng.Div.Am.Soc.Civ.Eng.* 89 (1963) 31.
66. I.Langmuir, Adsorption of gases on glass, Mica, and Platinum, *J.Am.Chem.Soc.* 40 (1918) 1361.
67. H.Freundlich, Veber die adsorption in loesungen (adsorption in solution), *Z.Phys.Chem.* 57 (1907) 385.
68. M.J.Tempkin and V.Pyzhev, Recent modifications to Langmuir Isotherms, *Acta Physiochim, URSS*, 12 (1940) 217.
69. M.Bansal, D.Singh and V.K.Garg, A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture waste carbons, *J.Hazard.Mater.* 171 (2009) 83.
70. O.J.Redlich and D.L.Peterson, A useful adsorption isotherm, *J.Phys.Chem.* 63 (1959) 1024.
71. S.Brunauer, P.H.Emmett and E.Teller, Adsorption of gases in multimolecular layers, *L.Am.Chem.Soc.* 60 (1938) 309.