Int. J. Chem. Sci.: 11(3), 2013, 1371-1384
ISSN 0972-768X
www.sadgurupublications.com

INDUSTRIAL WASTES AS ADSORBENTS FOR THE REMOVAL OF CHROMIUM FROM WASTE WATER : A REVIEW

G. RAVI KISHORE, R. PADMA SREE[a] and D. KRISHNA[*]

Department of Chemical Engineering, M. V. G. R. College of Engineering,
VIZIANAGARAM – 535005 (A.P.) INDIA
[a]Department of Chemical Engineering, A. U. College of Engineering (A),
VISAKHAPATNAM – 535005 (A.P.) INDIA

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 industrial waste as adsorbents 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 industrial waste as adsorbents.

Key words: Biosorption, Hexavalent chromium, Industrial wastes, Adsorption isotherm, Kinetic models.

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 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 (Cr^{+3} and $Cr(OH)^{2+}$) and haxavalent chromium ($HCrO_4^-$, CrO_4^{2-} or

---

[*]Author for correspondence; E-mail: d_krishna76@rediffmail.com

$Cr_2O_7^{2-}$, etc). Most of the hexavalent compounds are toxic, carcinogenic and mutagenic. For example, it is reported that $Cr_2O_7^{2-}$ 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.

Cr (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 0.05 mg/L, while total Cr containing Cr (III), Cr (VI) and other species of chromium is regulated to be discharged below 2 mg/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, 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, 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 reviwed the literature of collection and analysis of data on hexavalent Cr (VI) removal from waste water using industrial waste 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.

Industrial wastes as adsorbents

Wide spread industrial activities are producing large amount of solid waste materials. Some of these materials are being put to use while others find no proper utilization and are dumped elsewhere. The industrial waste material is available almost free of cost and causes major disposal problem. If the solid wastes could be used as low cost adsorbents, it will provide a two-fold advantage in reducing the pollution. Firstly, the volume of waste materials could be partly reduced and secondly the developed low cost adsorbent can reduce the pollution of wastewaters at a reasonable cost. With this view, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal pollutants from wastewaters. Important industrial wastes with their metal uptake such as fly ash waste slurry, blast furnace slags etc are shown in Table 1.

Table 1: Reported adsorption capacities (mg/g) for various industrial wastes

Material	Cr (VI), mg/g	Isotherms followed	Kinetics followed	Reference
Iron (III) hydroxide	0.47	Langmuir, Freundlich	---	[28]
Blast furnace slag	7.5	Langmuir, Freundlich	1st order	[29]
Activated red mud	1.6	Langmuir, Freundlich	---	[30]
Bagasse fly ash	260	Langmuir, Freundlich	---	[31]
Tea factory waste	54.65	Langmuir, Freundlich	1st order, I-P-Model	[32]
Tannery waste	177-217	Langmuir,	2nd order	[33]
Chestnut tannins	42	Langmuir	2nd order	[34]
Mimosa tannins	38	Langmuir	2nd order	[34]
Oak wood & Oak bark char	4.93 & 7.51	Langmuir, Freundlich, R-P-Model, Sips model, Toth model, Radke Model	2nd order	[35]
Clarified sludge	26.31	Langmuir, Freundlich	2nd order I-P-Diffusion model	[36]

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[37,38] of liquid/solid system based on solid capacity. The pseudo first order equation is generally expressed as –

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad \ldots(1)$$

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 (min^{-1}). Eq (1) can be arranged to obtain the more useful form.

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t \qquad \ldots(2)$$

The values of $\log(q_e-q_t)$ were linearly correlated with t. The plot of $\log(q_e-q)$ 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 -

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \qquad \ldots(3)$$

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad \ldots(4)$$

The linear form is -

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \qquad \ldots(5)$$

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[39]; 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[39]. According to Weber et al.[40], 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).

$$q_t = k_{id} t^{0.5} \qquad \ldots(6)$$

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.

$$\log q_t = \log k_{id} + 0.5 \log t \qquad \ldots(7)$$

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 α as the initial adsorption rate (mg/g min), β (g/mg) is the desorption constant related to the extent of the surface coverage and

$$\frac{dq}{dt} = \alpha e^{-\beta q_t} \quad \ldots(8)$$

q_t is the amount of gas chemisorbed at time. Eq. (8) can be simplified to Eq (9) by considering $\alpha\beta >> t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$.[48]

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

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/β) and an intercept of (1/β) ln(αβ).

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[41] 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).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad \ldots(10)$$

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 satuation, and b is the ratio of adsorption/desorption rates. Two derivatives of the Langmuir equation are Eq. (11) and Eq. (12).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad \ldots(11)$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \qquad \ldots(12)$$

Freundlich model

The Freundlich isotherm, first proposed in 1906, is based on multilayer adsorption with interaction between adsorbed molecules[42]. 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).

$$q_e = K_f C_e^{\frac{1}{n}} \qquad \ldots(13)$$

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).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \ldots(14)$$

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[43], 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).

$$q_e = \frac{q_{\max} b C_e^{1/n}}{1 + b C_e^{1/n}} \qquad \ldots(15)$$

Tempkin model

The Tempkin isotherm model contains a factor that takes care of the adsorbent-adsorbate interactions[44]. 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. The nonlinear form of Tempkin equation is given by Eq. (16) and the linear form in Eq. (17).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \qquad \ldots(16)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad \ldots(17)$$

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[45,46]. It is described in Eq (18).

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{b_R}} \qquad \ldots(18)$$

The linearised form is Eq. (19)

$$\ln \frac{K_R C_e}{q_e - 1} = b_R \ln(C_e) + \ln(\alpha_R) \qquad \ldots(19)$$

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

BET model

The Brunauer, Emmer and Teller (BET) model is an extension of the Langmuir model[47], and 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).

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

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.

CONCLUSION

Industrial wastes as 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 industrial wastes as adsorbents were investigated utilizing 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, Biotechnology Prog., **11**, 235 (1995).
2. F. Veglio and F. Beolchini, Removal of Metals by Biosorption: A Review, Hydrometallurgy, **44**, 301 (1997).
3. Z. Kowalshi, Treatment of Chromic Tannery Wastes, J. Hazard Materials, **39**, 137 (1994).
4. A. E. Sikaily, A. E. Nemr, A. Khaled and O. Abdelwahab, Removal of Toxic Chromium from Waste Water using Green Alga Ulva Lactuca and its Activated Carbon, J. Hazard. Mater., **148**, 216 (2007).

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**, 6271 (2008).

6. D. E. Paul, J. T. Black and A. R. Kohser, Materials and Process in Manufacturing, 9th Ed, Wiley New York (2003) p. 793.

7. V. Gomez and M. P. Callo, Chromium Determination and Speciation Since 2000, Trends Anal. Chem., **25**, 1006 (2006).

8. World Health Organisation, Guidelines for Drinking Water Quality, 3rd Ed., Genrva **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**, 121 (2002).

10. A. K. Das, Micellar Effect on the Kinetics and Mechanism of Chromium (VI) Oxidation of Organic Substrates, Coord. Chem. Rev., **248**, 81 (2004).

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**, 335 (1992).

12. I. M. Zeid, Responses of Phaseolus Vulgaris Chromium and Cobalt Treatment, Biol., Plant, **44**, 111 (2001).

13. M. Faisal and S. Hasnain, Bacterial Cr (VI) Reduction Concurrently Improves Sunflower (*Helianthus Annuus L.*) Growth, Biotechnology, Lett., **27**, 943 (2005).

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**, 615 (2005).

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**, 5 (2002).

16. X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake and S. Shinoda, A Process Monitoring/controlling System for the Treatment of Waste Water Containing Chromium (VI), Water Res., **27**, 1049 (1993).

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**, 197 (1997).

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**, 938 (1999).

19. N. Kongsricharoern and C. Polprasert, Chromium Removal by a Bipolar Electro-Chemical Precipitation Process, Water Sci. Technol., **34**, 109 (1996).

20. K. R. Pagilla, L. W. Canter, Laboratory Studies on Remediation of Chromium – Contaminated Soils, J. Environ. Eng., **125**, 243 (1999).

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**, 59 (1995).

22. Z. Aksu, D. Ozer, H. I. Ekiz, T. Kutsal and A. Calar, Investigation of Biosorption of Chromium (VI) on Cladophora Crispata in Two-Staged Batch Reactor, Environ. Technol., **17**, 215 (1996).

23. S. D. Huang, C. F. Fann and H. S. Hsiech, Foam Separation of Chromium (VI) from Aqueous Solution, J. Colloid. Interface Sci., **89**, 504 (1982).

24. P. Venkateswaran and K. Palanivelu, Solvent Extraction of Hexavalent Chromium with Tetrabutyl Ammonium Bromide from Aqueous Solution, Sep. Purif. Technol., **40**, 279 (2004).

25. C. S. Jiao and Y. Ding, Foam Separation of Chromium (VI) from Aqueous Solution, J. Shanghai, Univ., **13**, 263 (2009).

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. C. Namasivayam and K. Ranganathan, Waste Fe (III)/Cr (III) Hydroxide as Adsorbent for the Removal of Cr(VI) from Aqueous Solution and Chromium Plating Industry Waste Water, Environ. Pollut., **82**, 255 (1993).

29. S. K. Srivastava, V. K. Gupta and D. Mohan, Removal of Lead and Chromium by Activated Slag-ablast-furnace Waste, J. Environ. Engg., **123**, 461 (1997).

30. J. Pradan, S. N. Das and R. S. Thakur, Adsorption of Hexavalent Chromium from Aqueous Solution by using Activated Red Mud, J. Colloid. Interface Sci., **217**, 137 (1999).

31. V. K. Gupta, D. Mohan, S. Sharma and K. T. Park, Removal of Chromium (VI) from Electroplating Industry Wastewater using Bagasse Fly Ash-A Sugar Industry Waste Material, The Environmentalist, **19**, 129 (1999).

32. E. Malkoc and Y. Nuhoglu, Potential of Tea Factory Waste for Chromium (VI) Removal from Aqueous Solutions: Thermodynamic and Kinetic Studies, Sep. Purif. Technol., **54**, 291 (2007).

33. J. Anandkumar and B. Mandal, Adsorption of Chromium (VI) and Rhodamine B by Surface Modified Tannery Waste: Kinetics, Mechanistic and Thermodynamic Studies, J. Hazard. Mater., **186**, 1088 (2011).

34. L. Chabaane, S. Tahiri, A. Albizane, M. EI Krati, M. L. Cervera and M. De La Guardia, Immobilization of Vegetable Tannins on Tannery Chrome Shavings and their use for the Removal of Hexavalent Chromium from Contaminated Water, Chem. Engg. J., **174**, 310 (2011).

35. D. Mohan, S. Rajput, V. K. Singh, P. H. Steele and Jr. C. U. Pittman, Modeling and Evaluation of Chromium Remediation from Water using Low Cost Bio-Char a Green Adsorbent, J. Hazard. Mater., **188**, 310 (2011).

36. A. K. Bhattacharya, T. K. Naiya, S. N. Mandal, S. K. Das, Adsorption, Kinetics and Equilibrium Studies on Removal of Cr (VI) from Aqueous Solution using Low Cost Adsorbents, Chem. Engg. J, **137**, 529 (2008).

37. S. Lagergren, K. Vetenskapsakad, About Theory of so called Adsorption of Soluble Substances, Handlingar, **24**, 1 (1898).

38. Y. S. Ho, Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions, Scientometrics, **59**, 171 (2004).

39. S. S. Baral, N. Das, G. Roy Choudary, S. N. Das, A Preliminary Study on the Adsorptive Removal of Chromium (VI) using Seaweed, Hydrilla Verticillata, J. Hazard. Mater., **171**, 358 (2009).

40. W. J. Weber, Jr. J. C. Morris and J. Sanit, Kinetics of Adsorption on Carbon from Solution, Eng. Div. Am. Soc. Civ. Eng., **89**, 31 (1963).

41. I. Langmuir, Adsorption of Gases on Glass, Mica, and Platinum, J. Am. Chem. Soc., **40**, 1361 (1918).

42. H. Freundlich, Veber Die Adsorption in Loesungen (Adsorption in Solution), Z. Phys. Chem., **57**, 385 (1907).

43. Z. Aksu and E. Balibek, Chromium (VI) Biosorption by Dried Rhizopus Arrtizus: Effect of Salt (NaCl) Concentration on Equilibrium and Kinetic Parameters, J. Hazard. Mater., **145**, 210 (2007).

44. M. J. Tempkin and V. Pyzhev, Recent Modifications to Langmuir Isotherms, Acta Physiochim, URSS, **12**, 217 (1940).

45. 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**, 83 (2009).

46. O. J. Redlich, D. L. Peterson, A useful Adsorption Isotherm, J. Phys. Chem., **63**, 1024 (1959).

47. S. Brunauer, P. H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, L. Am. Chem. Soc., **60**, 309 (1938).

48. H. C. Niu, B. Volesky, Biosorption of Chromate and Vanadate Species with Waste Crab Shells, J. Hydrometallurgy, **84**, 28 (2006).

Revised : 10.08.2013 *Accepted : 13.08.2013*