Reclamation of Cr(VI) rich water and wastewater by wollastonite

Y.C. Sharma [a,*], Uma [a], V. Srivastava [a], J. Srivastava [b], M. Mahto [c]

[a] *Environmental Engineering and Research Laboratories, Department of Applied Chemistry, Institute of Technology,*
Banaras Hindu University, Varanasi 221005, India
[b] *Department of Mining Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221005, India*
[c] *JSPCB, Ranchi 834003, India*

Abstract

Chromium exists in two forms mainly Cr(III) and Cr(VI) and out of the two forms the later one is highly toxic and is documented as high priority pollutant. It has attracted the attention of the scientific workers worldwide. The present work was addressed to the use of clay mineral, wollastonite in order to provide an economically viable treatment of Cr(VI) containing aqueous solutions and industrial effluents. The removal of chromium is found to be concentration dependent. The removal increased from 47.4 to 69.5% by decreasing the concentration from 2.0×10^{-4} to 0.5×10^{-4} M at pH 2.5, 0.01 M NaClO$_4$ ionic strength, 100 μm adsorbent particle diameter and 30 °C temperature. Rate of uptake of Cr(VI) was found to be 3.0×10^{-2} min^{-1} under optimum conditions and the process is governed by first order kinetic equation. The process of Cr(VI) removal from aqueous solutions and wastewater involves intraparticle diffusion and the coefficient of intraparticle diffusion, D, was found to be 3.5×10^{-4} cm^2 s^{-1} under favourable conditions. Thermodynamic parameters for the process of removal have also been calculated to understand the process better.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Cr(VI); Removal; Kinetics; Intraparticle diffusion; Thermodynamic parameters

1. Introduction

Chromium is distributed on the earth's crust at approximately 100 ppm levels. It exists in many valence states like metallic chromium, bivalent chromium, trivalent and hexavalent chromium but from environmental viewpoint, two of its forms, viz., trivalent Cr(III) and hexavalent Cr(VI) are important [1]. Its hexavalent form is well known highly toxic metal and is considered to be a priority pollutant [2,3]. The USEPA has classified Cr(VI) as a human carcinogen and currently its maximum contamination level has been fixed as 100 ppb as total chromium [4]. Exposure to Cr(VI) causes health problems including dermatitis, allergic skin reactions and ulceration of intestine. Chromium has also been reported to be a teratogen [5]. In order to detoxify water and wastewater rich in chromium, the commonly employed methods are solvent extraction, ion-exchange, reverse osmosis, precipitation, adsorption on activated carbon, etc. [6–8], but these technologies are cost intensive and are not suitable for developing nations. Ultrafiltration complexation has been reported to remove chromium from wastewater [9]. Significant removal of metal ions from water has also been reported by using tree fern [10]. And Deng and Bai [11] reported significant removal of both the forms of chromium by animated polyacrylonitrile fibres, efforts have also been made to prepare activated carbon by waste materials to bring down the cost of water treatment [12,13]. Erdem et al. [14] have reported removal of chromium by natural zeolites. Xu and Axe [15] have used iron oxide coated silica for removal of cadmium from wastewaters and economically prepared saw dust activated carbon has also been successfully used for reclamation of chromium rich water [16]. An important work on field observation of chromium on tannery sludge has been studied [17]. The present work addresses to the reclamation of Cr(VI) containing water and wastewaters by economically viable material, wollastonite, to make the process of treatment cost effective. The effect of various important parameters, viz., contact time and initial concentration, pH and temperature on the removal has been investigated. Kinetic modeling of the process of removal and possibility of intraparticle diffusion have been carried out.

* Corresponding author. Tel.: +91 542 2307025; fax: +91 542 2316428.
E-mail address: y_sharma_2002@rediffmail.com (Y.C. Sharma).

2. Experimental

All the chemicals used were of analytical reagent grade and were obtained from B.D.H., Mumbai (India). In order to maintain the cost effectiveness of the process, the adsorbent, wollastonite, was used in the experiment without any pretreatment after maintaining a mean particle size of 100 μm. It was analyzed chemically using Indian Standard Methods [18]. The BET method using a Quantasorb Surface Area Analyzer QS-7 (Quanta Chrome Corp., USA) was used to measure the surface area of the adsorbent [8]. pH_{zpc} was determined by electrophoretic method employing a Carlo Erba Series 200 and Ress-Hugill Flask method were used to determine the density of the sample.

Stock suspensions of the wollastonite sample were prepared several weeks prior to experiments to ensure complete hydration of the solid surface. The batch adsorption experiments were then conducted by adding adequate quantity of distilled water, $NaClO_4$ (0.01 M) and aqueous solutions of chromium to a set of 250 ml polyethylene bottles. Wollastonite, the adsorbent (20 g l^{-1}) was then added from the stock suspension. pH of the solutions was adjusted to desirable levels by adding 1 M HCl/NaOH. The initial pH of the wollastonite suspension without addition of chromium solution was found to be 8.54. After pH adjustment, the sample bottles were agitated in a temperature-controlled thermostat at the desired temperature till equilibrium was achieved. After equilibrium time the surface of the adsorbent gets saturated and no further adsorption occurs on it. Moreover, this time is regarded as the 'reaction time'. At the end of the reaction time which is found to be 100 min in present studies, the solids were removed by centrifugation and the metal concentration of the supernatant was determined by Atomic Absorption Spectrophotometric Method [19].

3. Results and discussion

3.1. Chemical characterization of the adsorbent

The chemical characterization of wollastonite shows (Table 1) that silica and calcium oxide are its major constituents. The oxides of other metallic elements are present in traces. It is, therefore, anticipated that these two major species will be

Table 1
Characterization of the adsorbent

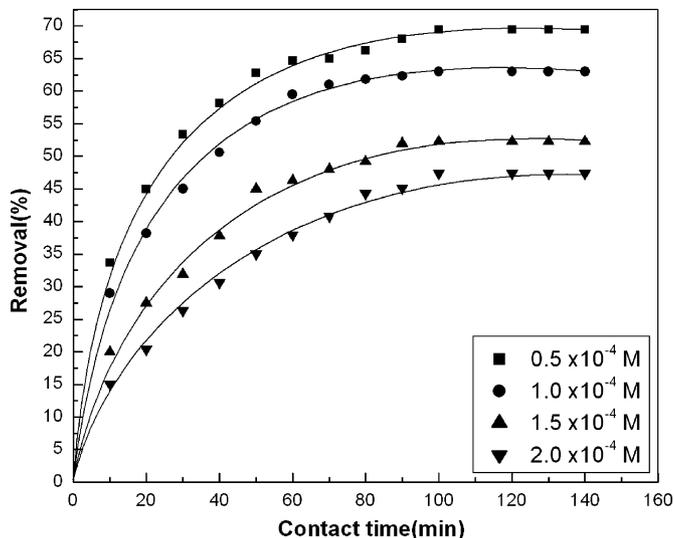| Constituents	% by weight
SiO_2	48.52
CaO_2	48.48
Al_2O_3	0.52
Fe_2O_3	0.26
Loss of ignition 2.50	
Surface area (m^2 g^{-1})	1.10
pH_{zpc}	2.60
Porosity	0.23
Density (gm^{-3})	2.21
Mean particle diameter (μm)	100.00

Fig. 1. Effect of contact time and initial concentration on removal of Cr(VI).

responsible for the removal of Cr(VI) from the aqueous solutions. Loss on agitation of the adsorbent was found to be 2.50% and the surface area 1.10 m^2/g. Values of other parameters are also presented in this table.

3.2. Effect of contact time and concentration

For complete understanding of the process of removal, the knowledge of effect of contact time and initial adsorbate concentration is very vital. A known amount of adsorbent (20.0 g l^{-1}) was added to a batch containing 50 ml solution of chromium in 250 ml polythene bottles and as already discussed after attainment of equilibrium, adsorbent was separated from solution by filtration or centrifugation.

During the experiments, the removal of Cr(VI) increased up to 100 min and then became constant (Fig. 1). This figure shows that the removal (%) increased from 47.4 to 69.5 at 2.5 pH, 30 °C temperature, 0.01 M $NaClO_4$ ionic strength by decreasing the Cr(VI) concentration from 2.0×10^{-4} to 0.5×10^{-4} M in aqueous solutions. The time of equilibrium, 100 min for the system is independent of concentration and other parameters. The curves of this figure are smooth and indicate the suitability of adsorption process for the present system. The higher (%) removal in low concentration range is of industrial application [20].

3.3. Kinetic modeling

The kinetic modeling of the removal of Cr(VI) by adsorption on wollastonite was carried out by Lagergren's model [21]:

$$\log(q_e - q) = \log q_e - \left(\frac{K_{ad}}{2.303}\right) t \tag{1}$$

where q_e and q (both in mg g^{-1}) are amounts of Cr(VI) adsorbed at equilibrium and at any time, respectively, and K_{ad} is the rate constant of Cr(VI) removal. K_{ad} was determined graphically from the graph of "log $(q_e - q)$ versus t" (Fig. 2). The value of
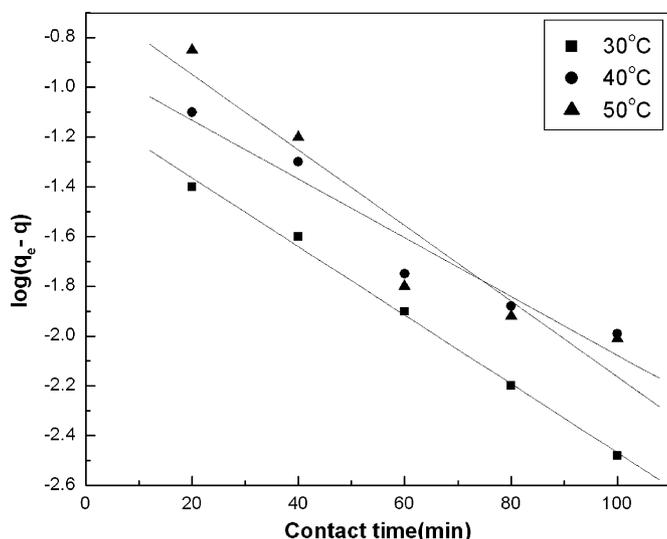
Fig. 2. Lagergren's plot for kinetic modeling of the process of Cr(VI) removal by adsorption on wollastonite.

Fig. 3. Maximum removal of Cr(VI) by adsorption on wollastonite at different pH values.

the rate constant of the process of removal is very vital and indicates the utility of the process for the system. Its value for the present system was found to be 3.0×10^{-2} min^{-1} at 0.5×10^{-4} M Cr(VI) concentration, 30 °C, 2.5 pH, 100 μm particle diameter, 100 rpm and 0.01 M NaClO$_4$ ionic strength. This value of K_{ad} is quite adequate and indicates that the adsorbent can be used successfully for Cr(VI) removal.

3.4. Activation energy study

The study of activation energy deciphers the nature of the processes. In the present studies, value of activation energy for the present system was calculated graphically by help of Fig. 2 and using well known Arrhenius equation [22]. Its value for the present system was found to be 0.69 kcal mol^{-1}. A low value of activation energy is indicative of flat nature of the energy barrier and also the exothermic nature of the process undertaken.

3.5. Intraparticle diffusion study

There are many ways by which the mass from bulk can go on to the solid surface and if the adsorbent is porous in nature, there exists a strong possibility of transfer of the dissolved mass onto the solid surface by the process of intraparticle diffusion. The present system was examined for this possibility and intraparticle diffusion was found to play a role in the process of removal. The rate of the process of diffusion is indicated by the coefficient of intraparticle diffusion [22,23]:

$$D = \frac{0.03}{t_{1/2}} r_0^2 \qquad (2)$$

where D (cm^2 min^{-1}) is the coefficient of intraparticle diffusion, $t_{1/2}$ (min^{-1}) time for half adsorption of Cr(VI) on wollastonite, and r_0 (cm) is radius of the adsorbent particles. The value of D was calculated to be 3.5×10^{-10} cm^2 s^{-1} at 0.5×10^{-4} M Cr(VI) concentration, 30 °C and at other optimum conditions.
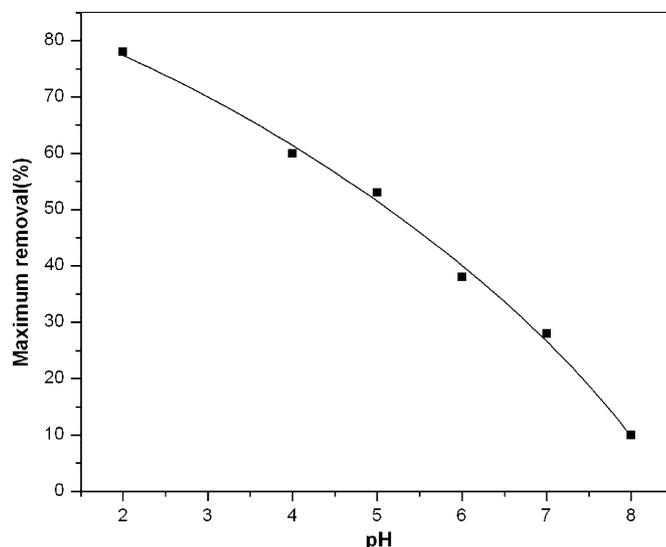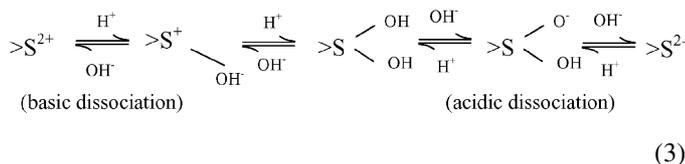
This value of the coefficient suggests that intraparticle diffusion is rate controlling step for the present system. Our findings are supported by earlier workers [22].

3.6. Effect of pH

pH has been reported to be an important parameter and is termed as 'master variable' in many adsorption processes. In the present experiments the extent of removal decreases from 77.3 to 11.8% by increasing the pH from 2.5 to 8.5 (Fig. 3) at initial chromium concentration of 0.5×10^{-4} M, 0.01 M NaClO$_4$ ionic strength and 30 °C.

It is clear from the characterization of the adsorbent that it is rich in various oxides (Table 1). These oxides undergo surface hydroxylation forming surface hydroxyl compounds. As a result of their subsequent dissociation these give negatively or positively charged surfaces as follows [23]:

$$>S^{2+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} >S^+ \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} >S\genfrac{}{}{0pt}{}{OH}{OH} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} >S\genfrac{}{}{0pt}{}{O^-}{OH} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} >S^{2-}$$

(basic dissociation)   (acidic dissociation)

$$(3)$$

where 'S' stands for Si, Ca, Fe, etc. It is clear from the above scheme that with decrease in pH of the solution, the positive charge density on the adsorbent surface increases and hence the adsorption of Cr(VI) also increases.

Further, the pH$_{zpc}$ of the adsorbent is 2.6 (Table 1) and this indicates that the surface of the adsorbent is positively charged at a pH of approximately 2 and will be quite favourable for the removal of dominating HCrO$_4^-$ species. Significant adsorption at neutral and negatively charged surface, however, cannot be explained on the basis of electrostatic attraction only. Specific chemical interactions and surface complexation have also been suggested to describe the removal of adsorption of Cr(VI) from aqueous solutions and wastewater. The adsorption beyond 4.5

will include CrO_4^{2-} ions and the following surface complexation scheme has been suggested [24]:

$$SOH_2 + \quad 2H^+ \quad + \quad CrO_4^{2-} \Leftrightarrow \quad \begin{matrix} SOH_2 \\ \\ SOH_2 \end{matrix} > CrO_4^{2-} \tag{4}$$
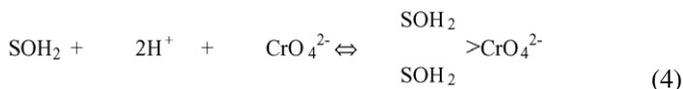
Such type of model has also been reported by Davis and Leckie [25]. An alternative scheme based on chemisorption includes $HCrO_4^-$ and CrO_4^{2-} for chromium removal [26,27].

3.7. Effect of temperature and adsorption isotherm

Most adsorption processes occurring in the environment are exothermic in nature and the cases of endothermic adsorption processes are rather scanty [28]. In all cases temperature has a pronounced effect on the process of adsorption. The experimental results for the present system revealed an endothermic nature of the process of removal of Cr(VI) by adsorption on wollastonite. The results obtained have been presented in Fig. 4. The removal increased from 69.5 to 91.7% by increasing the temperature from 30 to 50 °C at 0.5×10^{-4} M Cr(VI) concentration, 2.5 pH and at an ionic strength of 0.01 M $NaClO_4$. The increasing trend of the removal at higher values of temperature indicates endothermic nature of the process of Cr(VI) removal. The graphs of Fig. 4 are smooth and indicate a significant removal by adsorption.

The values of rate constants of adsorption for the removal of Cr(VI) at the selected values of temperature were determined and the results obtained are plotted in Fig. 2. The values of the rate constants for the removal process were found to be 2.4×10^{-2}, 2.6×10^{-2} and 3.5×10^{-2} min^{-1} at 30, 40 and 50 °C, respectively. The increasing trend of the values of rate constants at higher temperatures is indicative of endothermic nature of the process.

In order to understand the equilibrium behaviour of the process, the equilibrium data was examined using Langmuir's
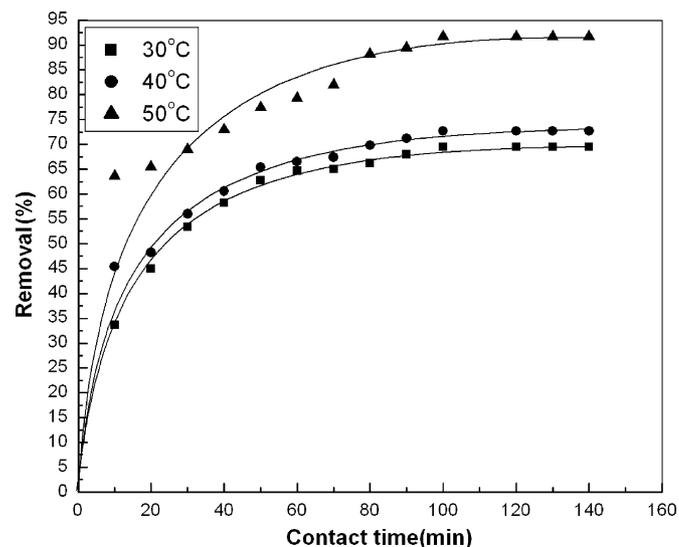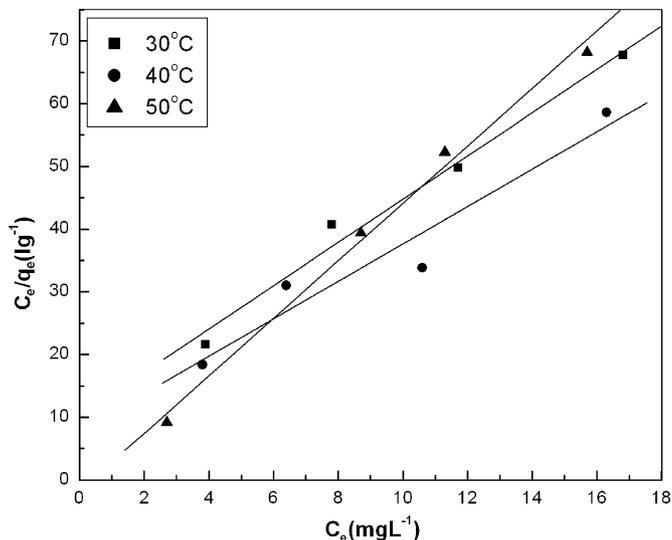
Fig. 5. Langmuir's isotherm for the removal of Cr(VI) by adsorption on wollastonite.

model [29]:

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \tag{5}$$

where C_e (mg l^{-1}), q_e (mg g^{-1}) are the concentration of chromium and amount of chromium adsorbed at equilibrium, respectively. Q° (mg g^{-1}) and b (l g^{-1}) are the terms related to capacity and energy of adsorption, respectively, and are known as Langmuir's constants. For equilibrium studies, adsorption experiments were conducted for all the selected adsorbate concentrations at the various values of temperature, viz., 30, 40 and 50 °C. Then the equilibrium data was plotted for 'C_e/q_e versus C_e' (Fig. 5).

The linear plots of Fig. 5 in the concentration range studied confirm the validity of the above model for the present system. The values of the two constants are determined by the slopes and intercepts of these plots and are recorded in Table 3. It is clear from this table that the values of both the parameters are in increasing pattern with temperature and this further confirms the endothermic nature of the removal. It is therefore suggested that for better removal of Cr(VI) high temperature should be employed.

3.8. Thermodynamic studies

Thermodynamic studies were undertaken to elucidate the mechanism involved in the process of removal of Cr(VI) by adsorption on the selected adsorbent. The following thermodynamic parameters, namely variation of free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined for the present studies [30]:

$$\Delta G^\circ = -RT \ln K \tag{6}$$

$$\Delta H^\circ = R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{K_2}{K_1} \right) \tag{7}$$

Fig. 4. Removal of Cr(VI) by adsorption on wollastonite at different values of temperature.

Table 2
Value of Langmuir's constants for the removal of Cr(VI) by adsorption on wollastonite at different temperatures

Temperature ($\pm 0.5\,^\circ$C)	Q° (mg g^{-1})	b (l g^{-1})
30	0.686	0.224
40	0.746	0.315
50	0.826	0.323

Concentration of solution 0.5×10^{-4} M, 2.5 pH and 0.01 M NaClO$_4$ ionic strength.

Table 3
Thermodynamic parameters for the removal of Cr(VI) by adsorption on wollastonite

Temperature (K)	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS° (kcal/mol)
303	−3.26	+0.50	+13.0
313	−3.57		
323	−3.71		

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \qquad (8)$$

where 'R' (cal/mol K) is the gas constant, K_1 and K_2 are the equilibrium constants at temperatures T_1 and T_2 (K), respectively. K is Langmuir's constant which is equal to the product of 'Q°' and 'b' (Table 2). The values of the above three thermodynamic parameters calculated are given in Table 3. It is clear from this table that all the values of ΔG° are negative suggesting that the adsorption process involved is spontaneous with high preference to Cr(VI).The values of ΔG° also suggest that the adsorption is physical in nature as a value of ΔG° less than 3.82 suggests that the process of adsorption is accompanied by electrostatic attraction between sites and the adsorbed species and that is physical in nature. On the other hand, if value of ΔG° is more negative than −7.82 kcal/mol, it indicates the adsorption attachment of the species with coordinate bonds [31]. The values of ΔG° involved in the present process are in the range of −3.26 to −3.71 kcal/mol suggesting that physical adsorption is involved in the process of removal. The values of ΔH° and ΔS° are 0.50 and 13.0 kcal/mol and are positive suggesting that the adsorption is spontaneous and endothermic in nature. Weng et al. [32] reported significant results on adsorption of Cr(VI) onto TiO$_2$ from aqueous solutions. In another study authors have carried out adsorption of chromium onto hydrous concrete particles [33]. Results of the present work are supported by these scientific workers.

4. Conclusions

The studies on the removal of Cr(VI) by adsorption on wollastonite provide important information. Broadly the conclusions may be drawn as follows:

(i) The adsorbent shows significant removal of Cr(VI) from aqueous solutions and higher removal has been obtained at low concentration ranges.
(ii) The process of removal follows first order rate kinetics.
(iii) Intraparticle diffusion plays an important role in Cr(VI) removal.
(iv) Higher removal is obtained at low pH ranges.
(v) Temperature studies show that the unlike most adsorption processes, the present process is endothermic in nature and thus, higher removal can be obtained at higher temperature.

Further, as the adsorbent is naturally available, it incurs no extra financial burden on the users and hence it can always be recommended for the treatment of Cr(VI) containing waters and wastewaters.

References

[1] J.O. Nriagu, A silent epidemic of metal poisoning, Environ. Pollut. 50 (1988) 139–161.
[2] K. Kannan, Fundamentals of Environmental Pollution, S. Chand & Co., New Delhi, 1995.
[3] C. Raji, T.S. Anirudhan, Chromium adsorption by sawdust carbon kinetics and equilibrium, Indian J. Chem. Technol. 4 (1996) 228–236.
[4] http://www.oehha.ca.gov/water/phg/, Cal/EPA Office of the Environmental Health Hazard Assessment, 2001.
[5] A.G. Mukherjee, Environmental Pollution and Health Hazards: Causes and Control, Galgotia Publications, New Delhi, 1986.
[6] G. McKay, M.S. Otterburn, A.G. Sweeny, Surface mass transfer process during colour removal from effluents using silica, Water Res. 15 (1981) 327–331.
[7] J.Y. Hu, T. Aizawa, Y. Magara, Evaluation of adsorbability of pesticides in water on powdered activated carbon using octanol–water partition coefficient, Water Sci. Technol. 35 (1997) 219–226.
[8] Y.C. Sharma, Effect of temperature on interfacial adsorption of Cr (VI) on wollastonite, J. Colloid Interface Sci. 233 (2001) 265–271.
[9] R. Molinari, S. Gallo, P. Argurio, Metal ions removal from washing water from contaminated soils by ultrafiltration–complexation, Water Res. 38 (2004) 593–600.
[10] D.E. Girani, Removal of copper ions from aqueous solution by tree fer, Water Res. 38 (2004) 453–458.
[11] S. Deng, R. Bai, Removal of trivalent and hexavalent chromium with animated polyacrylonitrile fibre: performance and mechanisms, Water Res. 38 (2004) 2424–2432.
[12] M. Ahmedna, W.E. Marshall, A.A. Husseiny, R.M. Rao, I. Goktepe, The use of nutshell carbons in drinking waterfilters for removal of trace metals, Water Res. 38 (2004) 1062–1068.
[13] M. Ahmedna, W.E. Marshall, A.A. Husseiny, R.M. Rao, I. Goktepe, Granular activated carbons from sugarcane bagasse: production and uses, Int. Sugar J. 102 (2000) 147–151.
[14] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.
[15] Y. Xu, L. Axe, Synthesis and characterization of iron oxide-coated silica and its effect on metal adsorption, J. Colloid Interface Sci. 282 (2005) 373–379.
[16] T. Karthikeyen, S. Rajgopal, L.R. Miranda, Chromium (VI) adsorption from aqueous solutions by *Hevea Brasilinesis* saw dust activated carbon, J. Hazard. Mater. 124 (2005) 192–199.
[17] A.D. Apte, S. Verma, V. Tare, P. Bose, Oxidation of Cr(III) in tannery sludge to Cr(VI): field observations and theoretical assessment, J. Hazard. Mater. 121 (2005) 215–222.
[18] Indian Standard Methods of Chemical Analysis of Fire Clay and Silica Refractory Materials, IS: 1527, 1960.
[19] Standard Methods for Examination of Water and Wastewater, 18th ed., APHA/AWWA/WPCF, Washington DC, 1992.
[20] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by fly ash, Water Res. 19 (1985) 869–873.

[21] S.K. Srivastava, R. Tyagi, N. Pant, Studies on removal of some toxic metal ions Part II (removal of lead and cadmium by montmorillonite and kaolinite), Environ. Technol. Lett. 10 (1989) 275–282.

[22] G.S. Gupta, G. Prasad, V.N. Singh, Removal of colour from wastewater by sorption for water reuse, J. Environ. Sci. Health A23 (1988) 205–218.

[23] S.M. Ahmed, Studies of the dissociation of oxides surfaces at the liquid–solid interface, Can. J. Chem. 44 (1966) 1663–1670.

[24] W. Stumm (Ed.), Aquatic Surface Chemistry, Wiley-Interscience, NY, 1987.

[25] J.A. Davis, J.O. Leckie, Adsorption of chromium on activated carbons, J. Colloids Interface Sci. 74 (1980) 32–37.

[26] S. Deng, R. Bai, J.P. Chen, Behaviours and mechanisms of copper adsorption to hydrolyzed polyacrylonitrile fibers, J. Colloid Interface Sci. 260 (2003) 265–272.

[27] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes II. The case of chromium(VI) and cadmium(II), J. Hazard. Mater. 95 (2002) 275–290.

[28] Y.C. Sharma, G. Prasad, D.C. Rupainwar, Treatment of Cd(II) rich effluents(kinetic modeling and mass transfer), Int. J. Environ. Anal. Chem. 45 (1991) 11–18.

[29] J. Rodriguez, L. Castrillon, E. Maranon, H. Sastre, E. Fernandez, Removal of non-biodegradable organic matter from landfill lechates by adsorption, Water Res. 38 (2004) 3297–3303.

[30] C.H. Weng, Y.F. Pan, Adsorption characteristics of methylene blue from aqueous solution by sludge ash, Colloids Surf. A: Physicochem. Eng. Aspects 274 (2006) 264–273.

[31] M. Horsfall, A.A. Abiba, A.I. Spiff, Kinetic Studies on the adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions by cassava (Manihot sculenta Cranz) tuber bark waste, Bioresour. Technol. 97 (2006) 283–291.

[32] C.H. Weng, J.H. Wang, C.P. Huang, Adsorption of TiO_2 from dilute aqueous solutions, Water Sci. Technol. 35 (1997) 55–62.

[33] C.H. Weng, C.P. Huang, H.E. Allen, P.F. Sanders, Cr(VI) adsorption onto hydrous concrete particles from ground water, J. Environ. Eng., ASCE 27 (2001) 1124–1131.