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Biosorption of Chromium (VI) from an aqueous solution using *Azadirachta indica.* A. Juss. (Neem) and activated charcoal: A comparative study

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ABSTRACT : Industrial water pollution is a potential threat to human health mainly because of the non-biodegradable, hazardous heavy metals. Among these heavy metals Chromium is of considerable concern. Various methods adopted for removal of heavy metals include chemical precipitation, membrane separation, ion exchange and adsorption. In case of adsorption, the generally used adsorbents like activated carbon, silica, alumina, etc. are expensive. This has prompted the use of natural materials as adsorbents in order to develop cheaper alternatives, which can be disposed off without regeneration due to their lower cost. And so, *Azadirachta indica* (Neem) leaf powder was tried for the removal of Chromium. The newly developed adsorbents should be as effective as (or more than) the conventional ones. Hence in the present work, Azadirachta indica (Neem) leaf powder and Activated charcoal are compared for their adsorptive capacity to remove Chromium (VI) from aqueous solution. The equilibrium studies were systematically carried out in a batch process covering various process parameters that include agitation time, adsorbent dosage, initial concentration of Chromium, volume of aqueous solution and pH of aqueous solution. Adsorption behaviour was found to follow the Freundlich's Adsorption Isotherm in case of both the adsorbents but the Neem powder was proved to be more promising than Charcoal in the removal of Chromium.

Keywords : Adsorption, neem, chromium, charcoal, kinetics, isotherm.

INTRODUCTION

Advances in science and technology have brought tremendous progress in many spheres of development, but in the process, also contributed to degradation of environment all over the globe due to very little attention paid to the treatment of industrial effluents. The discharge of non-biodegradable Heavy metals like Cu, Zn, Ni, Pb, Cd, and Cr into water stream is hazardous because the consumption of polluted water causes various health problems. Among these heavy metals, pollution by chromium is of major concern as the metal is used in electroplating, leather tanning, metal finishing, and chromate preparation.

Chromium exists in +3 and +6 oxidation states, as all other oxidation states are not stable in aqueous solutions. Both valences of chromium are potentially harmful (Dakiky *et al*., 2002).When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhoea, corrosion of skin, respiratory tract and lung carcinoma are noticed. The discharge limit from industry is less than 1 mg/L. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L.

Conventional methods for removing Cr(VI) ions from industrial wastewater include reduction (Kim *et al*., 2002), reduction followed by chemical precipitation (Ozer *et al*.,1997), adsorption on activated carbon (Lotfi and Adhoum, 2002), solvent extraction (Mauri *et al*., 2001), freeze separation, reverse osmosis (Padilla and Tavani, 1999), ion exchange (Rengaraj *et al*., 2003) and electrolytic methods (Namasivayam and Yamuna, 1995). This has prompted the use of natural materials as adsorbents in order to develop cheaper alternatives.

Biosorption refers to passive metal uptake by different forms of biomass, which may be dead or alive. It is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. Fly ash from thermal power plant (Panday *et al*., 1984), waste slurry from a fertiliser plant (Srivastava et al., 1989) and Fe(III)/Cr(III) hydroxide obtained from the petrochemical industry (Namasivayam and Ranganathan, 1993), blast furnace flue dust (Patnaik and Das, 1995) and photo film waste sludge (Selvaraj *et al*., 1997) have been examined for the removal of hexavalent chromium. The adsorption of Cr(VI) on bituminous coal (Rawat and Singh, 1992), sphagnum peat moss (Sharma and Forster, 1993), coconut husks and palm pressed fibres (Tan *et al*., 1993), sawdust (Dikshit 1989), sugarcane bagasse, sugarbeet pulp and maize cob (Sharma and Forster, 1994) has been reported.

And so, *Azadirachta indica A. Juss (*Neem*)* leaf powder was tried for the removal of Chromium.

The presence of niacin, praline, glutamic acid, aspartic acid, glutamine, tyrosine and alanine which contain polar groups like $-NH_2$, $-COOH$, $-OH$ etc. in neem powder contribute to the negative surface charge. The ingredients contribute an electronegativity of 35.1%.

This study aims at comparative evaluation of neem leaf powder and activated charcoal for removal of Cr (VI) from aqueous solution.

MATERIAL AND METHODS

Preparation of Adsorbents

Neem: The biomaterial, mature Neem leaves *(Azadirachta indica. A. Juss)* belonging to family Meliaceae, were collected (2009) and were washed thrice with water to remove dust and water soluble impurities and were dried until the leaves became crisp. The leaves were powdered and the resulting neem powder was stored in glass bottle and used as an adsorbent.

Activated Charcoal: Commercially available powdered activated charcoal (PAC) was directly used as an adsorbent.

Experimental Procedure

1000 mg/L of Chromium stock solution was prepared from which a working standard of 300 ppm was prepared. 25 ml of the aqueous solution containing 60 mg/L chromium (VI) was treated with 1 g of adsorbent in 100 ml conical flask for 30 min by shaking on a Rotary Shaker at 160 rpm at room temperature (28°C). The sample was allowed to settle and then filtered through Whatman filter paper No. 1. The filtrate of the sample was analyzed using a spectrophotometric method of analysis of chromium (APHA, 1985) for the final concentration of chromium in aqueous solution. The percentage removal of chromium (VI) was calculated as

% Removal = Co-Ct × 100/Co

Where, Co: Initial Chromium concentration

Ct: Chromium concentration at equilibrium after treatment with adsorbent.

The same experimental procedure was repeated for different agitation times. The agitation time established between the solution and adsorbent was noted. The effects of other parameters such as initial concentrations of chromium in aqueous solution, volume and pH of aqueous solution on % removal of chromium (VI) are obtained at the equilibrium agitation time by following the procedure described above. This procedure is followed for both the adsorbents. The values of variables studied in this investigation are shown in Table 1.

Table 1: Experimental conditions investigated.

Parameters	Values investigated for neem	Values investigated for charcoal
Agitation time, t (min)	30 – 360	15 – 120
Adsorbent dose, m (g/L)	8 – 40	8 – 96
Initial Cr conc. in aq. soln., Co (mg/L)	20 – 300	20 – 100
Vol. of the aq. soln., v (ml)	25 – 125	25 – 125
pH of aqueous solution	3 – 9	3 – 9

RESULTS AND DISCUSSION

Effect of agitation time

Kinetic experiments were carried out to evaluate the potential of the adsorbents for the commercial applications. In order to estimate the adsorption capacity of the adsorbent accurately, it is very much important to allow significant time for the experimental solution to attain equilibrium.

As the time increases, the amount of solute, chromium getting adsorbed by the adsorbent increases, but at a particular point of time, the solution attains equilibrium. The equilibrium agitation time is defined as the time required for the heavy metal concentration to reach a constant value.

The equilibrium agitation time is determined by plotting the % removal of chromium against agitation time for a particular adsorbent

Results obtained for effect of agitation time with neem and charcoal as adsorbents are shown in Table 2.

Table 2: Effect of agitation time on the removal of chromium.

Neem		Charcoal	
Charcoal Time (min)	% Removal	Agitation Time (min)	% Removal
30	86.70	15	78.33
60	90.00	30	80.00
90	93.30	45	81.67
120	96.67	60	81.67
150	98.33	75	83.33
180	100.0	90	83.33
210	100.0	105	83.33
240	100.0	120	83.33
270	100.0	135	83.33
300	100.0	150	83.33
330	100.0	165	83.33
360	100.0	180	83.33

The % removal of chromium increases upto 180 minutes of agitation time and after that no further increase was recorded for chromium removal by neem leaf powder as shown in Fig. 1

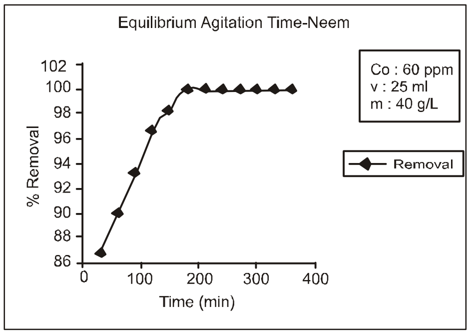

Fig. 1 : Effect of Equivalent Agitation Time on the removal of chromium using Neem.

The equilibrium agitation time for adsorption of chromium by charcoal was reported as 75 minutes as shown in Fig. 2

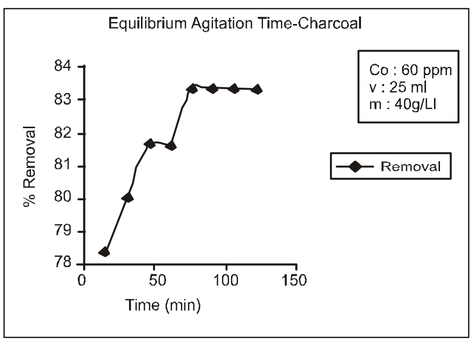

Fig. 2 : Effect of Equivalent Agitation Time on the removal of chromium using Charcoal.

Effect of Adsorbent Dosage

The % removal of chromium increased with the increase in adsorbent dosage.

In case of Neem, the % removal increased from 36.67% to 100% as the amount of neem powder was increased from 8 gm/L to 40 gm/L as shown in Fig.3

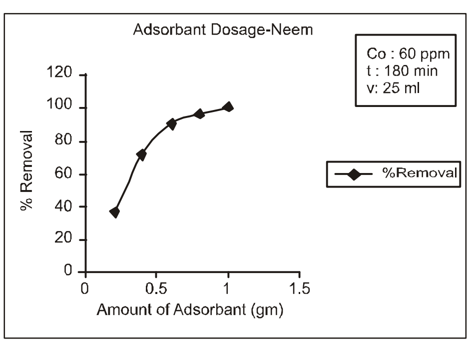

Fig. 3 : Effect of Adsorbent Dosage on the removal of chromium using Neem.

In case of Charcoal, the % removal was increased from 30% to 83.3% with the increase in amount of charcoal from 8 gm/L to 40 gm/L. For getting 100% removal, 96 g/L of Charcoal was required as shown in Fig. 4.

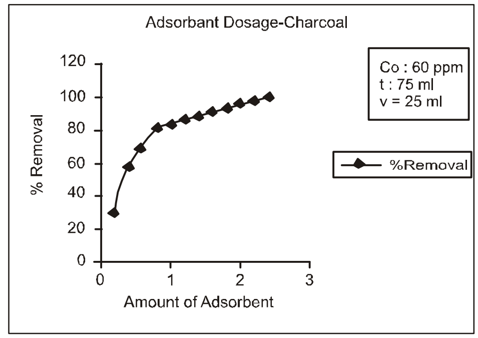

Fig. 4 : Effect of Adsorbent Dosage on the removal of chromium using Charcoal.

Thus, for 100% removal, quantity of neem required was less than that of charcoal. The increase in percentage adsorption with increase in adsorbent dosage is due to the increase in the number of adsorption sites. (Sharma and Forster, 1993; Selvaraj et al., 1997).

Results obtained for the effect of adsorbent dosage with neem and charcoal as adsorbents are shown in Table 3.

Table 3: Effect of Adsorbent Dosage on the removal of chromium.

Neem		Charcoal	
Adsorbent Dose(gm/l)	**% Removal**	**Adsorbent Dose(gm/l)**	**% Removal**
8	36.67	8	30.00
16	71.67	16	58.33
24	90.00	24	68.33
32	96.67	32	81.67
40	100.0	40	83.33
	48	86.70	
	56	88.33	
	64	91.67	
	72	93.33	
	80	96.67	
	88	98.33	
	96	100.0	

Effect of Initial Concentration of Chromium

As the initial concentration of chromium increased, the % removal of chromium decreased.

In case of Neem, the % removal decreased from 100% to 81.67% with the increase in initial chromium concentration from 20 mg/L to 300 mg/L as shown in Fig. 5.

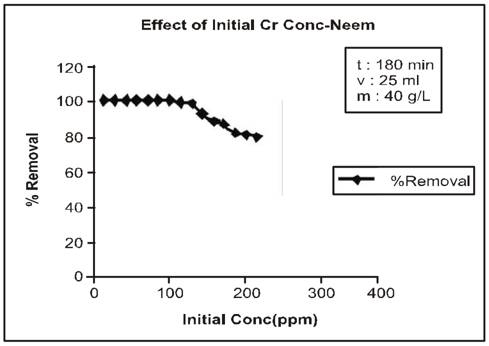

Fig. 5 : Effect of Initial Concentration on the removal of chromium using Neem.

Thus if same quantity of neem and charcoal are taken, then neem is effective for larger range of initial concentration of chromium than charcoal.

Results obtained for the effect of initial concentration of chromium with neem and charcoal as adsorbents are shown in Table 4.

Table 4: Effect of Initial concentration on the removal of chromium.

Neem		Charcoal	
Initial Cr Con.(mg/L)	**% Removal**	**Initial Cr Con.(mg/L)**	**% Removal**
20	100.0	20	90.00
40	100.0	40	90.00
60	100.0	60	83.33
80	100.0	80	77.50
100	100.0	100	72.00
120	100.0	120	
140	100.0	140	
160	99.38	160	
180	98.33	180	
200	93.00	200	
220	89.54	220	
240	88.33	240	
260	83.46	260	
280	82.85	280	
300	81.67	300	

Effect of Volume. As the volume of aqueous chromium solution increased, the % removal of chromium decreased.

In case of neem, % removal decreased from 100% to 38.33% with increase in the volume of aqueous solution from 25 ml to 125 ml as shown in Fig. 7

Whereas in case of charcoal, the % removal was decreased from 90% to 72% with the increase in initial chromium concentration from 20 mg/L to 100 mg/L as shown in Fig. 6.

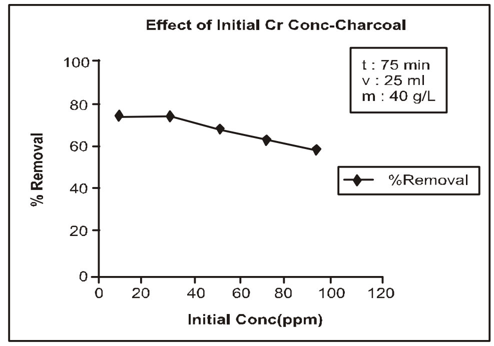

Fig. 6 : Effect of Initial Concentration on the removal of chromium using Charcoal.

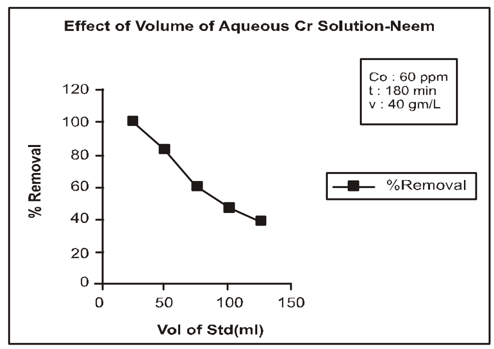

Fig. 7 : Effect of Volume of Aqueous Solution on the removal of chromium using Neem.

Similarly in case of Charcoal also % removal decreased from 83.33% to 30% with increase in the volume of aqueous solution from 25 ml to 125 ml as shown in Fig. 8

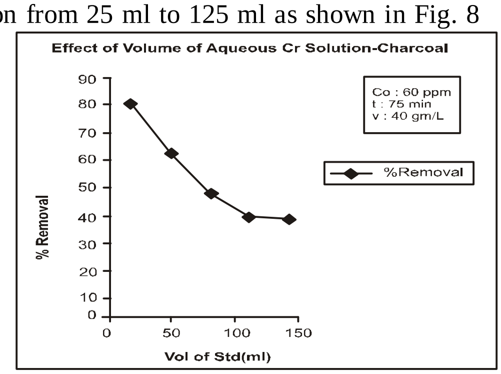

Fig. 8 : Effect of Volume of Aqueous Solution on the removal of chromium using Charcoal.

The reason may be attributed to an increase in chromium metal concentration with an increase in volume of the water and the unchanged area of contact of the adsorbent.

Results obtained for the Effect of Volume of Aqueous Solution with neem and charcoal as adsorbents are shown in Table 5.

Table 5: Effect of Volume of Aqueous Solution on the removal of chromium.

Neem		Charcoal	
Volume of Aqueous Solution (ml)	% Removal	Volume of Aqueous Solution (ml)	% Removal
25	100.0	25	83.33
50	81.67	50	60.00
75	60.00	75	41.67
100	46.67	100	31.67
125	38.33	125	30.00

Effect of pH

pH is an important factor controlling the process of adsorption as it affects the surface charge of the adsorbents, the degree of ionization and the species of adsorbate.

In case of Neem, the% removal was found to increase from 83.33% to 100% with an increase in pH from 3 to 7. At pH 7 it showed maximum % removal i.e.100% as shown in Fig.9

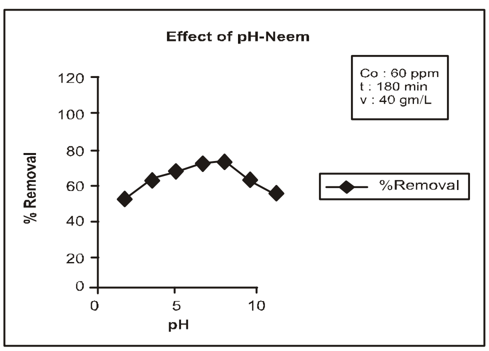

Fig. 9 : Effect of pH on the removal of chromium using Neem.

In contrast to neem, Charcoal showed maximum removal at pH 3 as shown in Fig.10.

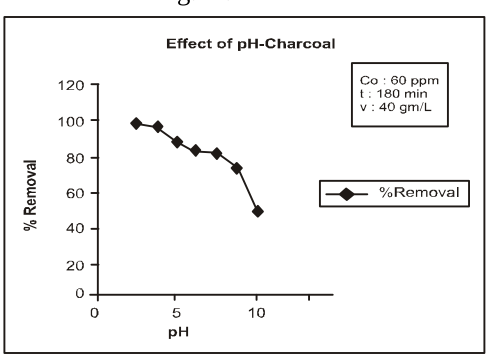

Fig. 10 : Effect of pH on the removal of chromium using Charcoal.

It was confirmed that adsorption increased with the decrease in acidity. At low pH, hydrogen ions compete with chromium ions for appropriate sites on the adsorbent. As pH approaches 7, hydrogen ions become negligible and more chromium ions are bound to the adsorbent. The % removal decreased as pH increased beyond 7. Similar results were reported by Donmez and Aksu (2002), Dakiky *et al.* (2002), Selvaraj *et al.* (2003), Yu *et al.* (2003), Ucun *et al.* (2002), Hu *et al.* (2003) and Gupta *et al.* (2001).

The greater the interaction the higher the adsorption of heavy metal. The neem leaf powder contains 35.1% electronegative components. In the present investigation, the maximum %removal of chromium by neem is 100%. The reason can be attributed to the higher electronegativity of the adsorbent, the neem leaf powder.

Results obtained for the effect of pH with neem and charcoal as adsorbents are shown in Table 6.

Table 6: Effect of pH on the removal of chromium.

Neem		Charcoal	
pH	% Removal	pH	% Removal
3	83.33	3	98.33
4	91.66	4	96.67
5	95.00	5	88.33
6	98.33	6	83.33
7	100.0	7	81.67
8	91.66	8	73.33
9	85.00	9	48.33

Freundlich Adsorption Isotherm

Every kind of carbon has its own adsorption isotherm and in the water treatment business this isotherm is defined by the function of Freundlich. The Freundlich adsorption isotherm (Freundlich, 1907) was also applied for the adsorption of Cr(VI).

The function of Freundlich:

$x/m = k_f C_e^n$

x/m = adsorbed substance per gram active carbon

=(Co-Ce)/m

Ce = equilibrium adsorbate concentration

Kf, n = specific constants

The above equation can be written as, $q_e = k_f C_e^n$

The empirical Freundlich relationship does not indicate a finite uptake capacity. This relationship can be reasonably applied to the low or intermediate concentration ranges.

The above equation is linearised (Rao *et al.*, 2006) as

$\log q_e = \log k_f + n \log Ce$

The present data, when plotted shows good linearity for Freundlich relationship (correlation coefficient, R^2=0.9874) in case of neem. The slope of isotherm (n) also satisfies the condition of 0<n<1 for favourable adsorption.

The following equation is obtained for neem as shown in Fig.11.

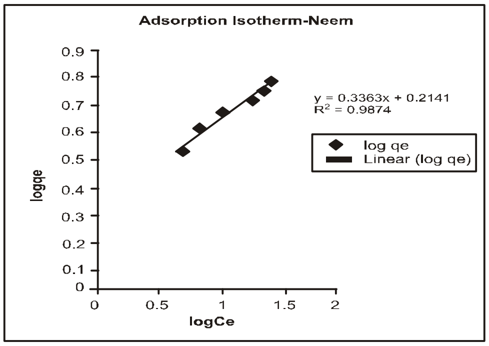

Fig. 11 : Freundlich Adsorption Isotherm (Neem).

$\log q_e = 0.2141 + 0.3363 \log Ce$

In case of Charcoal, the slope of isotherm (n) satisfies the condition of 0<n<1 for favourable adsorption but linearity of the data present here is lower than that of neem (correlation coefficient, R^2= 0.9408).

The following equation is obtained for charcoal as shown in Fig.12.

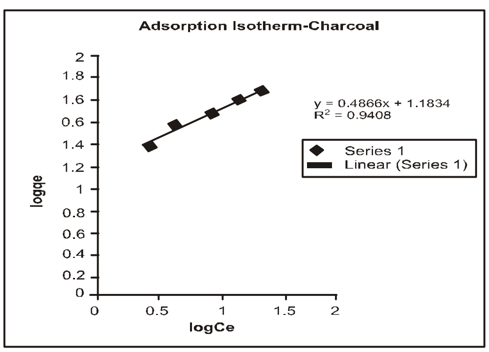

Fig. 12 : Freundlich Adsorption Isotherm (Charcoal).

$\log q_e = 1.1834 + 0.4866 \log Ce$

The good linearity of an isotherm indicates strong binding of adsorbate ions to the surface of adsorbent.

DISCUSSION

The equilibrium agitation time for the adsorption of chromium using neem as adsorbent is 180 minutes, whereas chromium is adsorbed maximum by charcoal in 75 minutes. So the charcoal is superior when time considerations are taken into account.

The % removal of chromium in aqueous solution is increased with an increase in adsorbent dosage in both the cases- neem and charcoal, but for 100% removal of chromium, 96 g/L charcoal is required as compared to much lower amount of neem required i.e. 40 g/L . Considering the economic aspects, neem is a better option as it is required in less quantity as well as it is cheaper to obtain.

The increase in initial chromium concentration and volume of aqueous solution results in a decrease in the % removal of chromium.

But neem can remove chromium efficiently upto the larger initial concentration range than charcoal. So when initial chromium concentration is higher, then it is better to take neem into action.

The maximum chromium removal by neem is observed. So when effluents are acidic, then charcoal is better and when effluents have higher pH, then neem is better.

The adsorption data fit in Freundlich adsorption isotherm**.** But the neem adsorption isotherms show better linearity than the charcoal isotherm. Using the equations obtained by plotting adsorption isotherms, we can determine what amount of adsorbent would be required for treatment of effluent containing known amount of initial chromium concentration.

CONCLUSION

Hence by considering all the aspects of requirements like, the time which can be spent for particular volumes of effluent treatment, efficiency required, the initial chromium concentration, the economic aspect, quality of effluent regarding its pH, an industry can choose the adsorbent, either neem or charcoal.

REFERENCES

APHA (1985) *Standard Methods for the Estimation of Waste and Wastewater*, 16th ed., American Public Health Association, Washington, DC.

Dakiky, M., Khami, A., Manassra, A. and Mer'eb, M. (2002) 'Selective adsorption of chromium (VI) in industrial wastewater using low cost abundantly available adsorbents', *Advances in Environmental Research*, **6**(4)**:** 533–540.

Dikshit, V.P. (1989) 'Removal of chromium (VI) by adsorption using sawdust', *National Academy of Science Letters*, **12**(12)**:** 419–421.

Donmez, G. and Aksu, Z. (2002) 'Removal of chromium (VI) from wastewaters by Dunaliella species', *Process Biochemistry*, **38**(5)**:** 751–762.

Freundlich, H. (1907) 'Ueber die adsorption in Loesungen', *Zeitschrift fr Physikalische Chemie*, **57:** 385–470.

Gupta, V.K., Shrivastava, A.K. and Jain, N. (2001) 'Biosorption of chromium (VI) from aqueous solutions by green algae Spirogyra species', *Water Research*, **35**(17)**:** 4079–4085.

Hu, Z., Lei, L., Li Y. and Ni, Y. (2003) 'Chromium adsorption on high performance activated carbon from aqueous solution', *Separation and Purification Technology*, **31**(1)**:** 13–18.

Kim, S.D., Park, K.S. and Gu, M.B. (2002) 'Toxicity of hexavalent chromium to *Daphnia magna*: influence of reduction reaction by ferrous iron', *Journal of Hazardous Materials*, **93**(2)**:** 155–164.

Lotfi, M. and Adhoum, N. (2002) 'Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater', *Separation and Purification Technology*, **26**(2–3)**:** 137–146.

Mauri, R., Shinnar, R., Amore, M.D., Giordano, P. and Volpe, A. (2001) 'Solvent extraction of chromium and cadmium from contaminated soils', *American Institute of Chemical Engineers Journal (AIChE)*, **47**(2)**:** 509–512.

Namasivayam, C. and Rangnathan, K. (1993) 'Waste Fe (III)/Cr (III) hydroxide adsorbent for the removal of Cr (VI) from aqueous solution and chromium plating industry wastewater', *Environmental Pollution*, **82:** 255–261.

Ozer, A., Altundogan, H.S., Erdem, M. and Tunmen, F. (1997) 'A study on the Cr (VI) removal from aqueous solutions by steel wool', *Environmental Pollution*, **97**(1–2)**:** 107–112.

Padilla, A. and Tavani, E.L. (1999) 'Treatment of an industrial effluent by reverse osmosis', *Desalination*, **129**(1–3)**:** 219–226.

Panday, K.K., Prasad, G. and Singh, V.N. (1984) 'Removal of chromium from aqueous solution by adsorption on flyash wollostonite', *Journal of Chemical Technology and Biotechnology*, **34:** 367–374.

Patnaik, L.N. and Das, C.P. (1995) 'Removal of hexavalent chromium by blast furnace fluedust', *Indian Journal of Environmental Health*, **37:** 19–25.

Rawat, N.S. and Singh, C.D. (1992) 'Removal of Cr (VI) on bituminous coal', *Asian Environment*, **14:** 30–41.

Rengaraj, S., Joo, C.K., Kim, Y. and Yi, J. (2003) 'Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H', *Journal of Hazardous Materials*, **102**(2–3)**:** 257–275.

Selvaraj, K., Chandramohan, V. and Pattabhi, S. (1997) 'Removal of Cr (VI) from solution and chromium plating industry wastewater using photofilm waste sludge', *Indian Journal of Chemical Technology*, **18:** 641–646.

Selvaraj, K., Manonmani, S. and Pattabhi, S. (2003) 'Removal of hexavalent chromium using distillery sludge', *Bioresource Technology*, **89**(2)**:** 207–211.

Sharma, D.C. and Forster, C.F. (1993) 'Removal of hexavalent chromium using sphagnum moss peat', *Water Research*, **27:** 1201–1208.

Sharma, D.C. and Forster, C.F. (1994) 'A preliminary examinations into the adsorption of hexavalent chromium using low cost adsorbents', *Bioresource Technology*, **47:** 257–264.

Rao MM, Ramesh A, Rao GPC, Seshaiah K (2006). Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, *J. Hazard. Mater*. **129:** 123-129.

Srivastava, S.K., Tyagi, R. and Pant, N. (1989) 'Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plant', *Water Research*, **23:** 1161–1165.

Tan, W.T., Ooi, S.T. and Lee, C.K. (1993) 'Removal of Cr (VI) from solution by cocunut husk and palm pressed fiber', *Environmental Technology*, Vol., **14,** p277.

Ucun, H., Bayhan, Y.K., Kaya, Y., Cakici, A. and Algur, O.F. (2002) 'Biosorption of chromium (VI) from aqueous solution by cone biomass of *Pinus sylvestris*', *Bioresource Technology*, **85**(2)**:** 155–158.

Yu, L.J., Shukla, S.S., Dorris, K.L., Shukla, A. and Margrave, J.L. (2003) 'Adsorption of chromium from aqueous solutions by maple sawdust', *Journal of Hazardous Materials*, **B100:** 53–63.