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ADSORPTIVE REMOVAL OF Cr (VI) FROM AQUEOUS SOLUTION USING RUBBER SEED SHELL CHARCOAL

BINDU SUNIL, NAMITA DAS, MOHAN THOMAS, MATHEW T. V. AND K.C. PHILIP*

Department of Chemistry, St.Berchmans College, Changanacherry 686 101, Kerala, India
[2]Department of Environmental Science, University of Kashmir, Srinagar 190 006, J & K, India

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ABSTRACT

Charcoal samples were prepared from rubber seed shell, an agricultural waste, for the removal of Cr (VI) ions. The adsorption characteristics of chromium (VI) ions from aqueous solution on to activated rubber seed shell charcoal (RSC), acid treated rubber seed shell charcoal (ARSC), chitosan coated rubber seed shell charcoal (CRSC), and chitosan coated acid treated rubber seed shell charcoal (CARSC) were investigated. The effect of pH of chromium solution, adsorbent dosage and contact time on adsorption rates were studied in batch experiment. Results showed that chemically modified adsorbents with oxidizing agents or chitosan have better chromium (VI) removal capabilities than the untreated ones. The removal efficiency was found to be in the order (CARSC)> (CRSC)> (ARSC) > (RSC). The optimum pH was found to be between 1.0 and 2.0. The equilibrium data for the adsorption of chromium (VI) were analyzed in the light of Langmuir and Freundlich isotherm models.

INTRODUCTION

In recent years, the levels of heavy metals in water systems have substantially increased over time due to rapid industrialization. The chemical contamination of water from a wide range of toxic derivatives, in particular, heavy metals is a serious environmental problem owing to their potential human toxicity (Richardson, 2003). Polluted water is one of the main causes of irreversible ecosystem degradation (An et al. 2001). Therefore, there is a need to introduce cleaner technologies to minimize pollution and to protect the degrading environment.

Heavy metals generally occur in water in low concentrations as a result of geological processes. But they cause direct toxicity, both to human and other living beings due to their presence beyond the specified limits. The extensive use of chromium containing compounds in different industries like leather, textile, metal, electroplating, ceramics and photography has resulted in the discharge of chromium compounds into aquatic ecosystem (Pehlivan and Altun, 2008). Chromium (Cr) occurs most frequently as Cr (VI) or Cr (III) in aqueous solutions. Both valencies of chromium are potentially harmful but hexavalent chromium has a greater risk due to its carcinogenic properties (Babel

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***Address for correspondence - Email :** drkcphilip@gmail.com

and Kurniawan, 2004.). Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2}) and dichromate ($Cr_2O_7^{2-}$), possess significantly higher levels of toxicity in comparison with other valence states (Hossain et al. 2005). Toxicity of hexavalent chromium, even in small concentrations, has been well documented (Babel and Kurniawan, 2003). The maximum concentration limit for Cr (VI) for discharge into inland surface waters is 0.1mg/ L and potable water is 0.05mg/L (EPA).

Various methods are available to isolate and remove heavy metals from the environment. The important technologies include chemical precipitation, coagulation, electro dialysis, ion exchange ultra filtration and reverse osmosis. But these methods are generally expensive, complicated and require skilled personnel. Adsorption has advantages over the other methods because of simple design with a sludge free environment and can involve low investment in terms of both initial cost and land requirement (Kurniawan *et al.* 2006). Usage of commercial activated carbon (CAC) is recognized as a highly effective adsorbent in removing heavy metals but the high cost and difficulty in procuring has stimulated the search for cheaper alternatives like the activated carbons derived from the agricultural wastes (Demir and Arisoy, 2007; Minamisawa *et al.* 2004; Saeed and Iqbal, 2003).

Rubber seed shell is an agricultural waste, disposal of which often causes serious local environmental problems. Conversion of rubber seed shell, representing an unused resource, into activated carbon, which can be used as an adsorbent in water purification, provide a potentially inexpensive alternative to CAC. Worldwide, the solid waste from processing of shellfish, crabs, shrimps and lobsters constitute large amount of chitinaceous waste. Chitosan is produced commercially by deacetylation of chitin, a polysaccharide consisting predominantly of unbranched chains of β-(1$\rightarrow$4)-2-acetamido-D-glucose. It has recently been recognized as a biopolymer with significant potential for use as biosorbent for removal of metal ions from waste water (Babel and Kurniawan, 2003). Chitosan is soft and soluble in acid and neutral solutions and has a tendency to form a gel in aqueous solution. The present investigation relates to the development of specifically modified granular carbon from agricultural waste products that possess enhanced adsorption properties with regard to uptake of metal ions. Adsorbents were prepared by coating chitosan on the surface of chemically modified rubber seed shell charcoal not only to improve its acidic stability but also to inhibit gel formation and also to enhance adsorption properties with regard to uptake of metal ions from aqueous solution. Cr removal efficiency of rubber seed shell charcoal, acid treated rubber seed shell charcoal, chitosan coated rubber seed shell charcoal, and chitosan coated acid treated rubber seed shell charcoal from synthetic waste water were studied.

MATERIALS AND METHODS

Preparation of the charcoal

Rubber seed shell, sun dried for a week was allowed to smoulder in a pit in a limited supply of air. The resultant carbonaceous matter was ground and sieved using a sieve shaker to 80 -140 mesh particles.

Chemical modification of charcoal by oxidizing with sulphuric acid

RSC was conditioned by a method described previously (Demir and Arisoy, 2007). RSC was washed with deionised water until any leachable impurities due to free acid and adherent powders were removed. The samples were then sulphonated by treating them with 2.0% H_2SO_4 (v/v) in an incubator at 110°C for 24 h and soaked with deionised water until the solution pH remained stable. The adsorbent was further soaked in 2.0% $NaHCO_3$ (w/v) till any residual acid left was removed. Finally, the samples were dried over night in an oven at 110°C, cooled at room temperature and stored in desiccators.

Surface coating of charcoal with chitosan.

Chitosan powder (>85 % deacetylated) was supplied by Marine chemicals, Cochin -5, Kerala, India, was made into a gel by slowly adding 25g of chitosan to 500 mL of 10 wt % oxalic acid and heating to 40-50°C. The chitosan oxalic acid mixture formed a whitish viscous gel at room temperature. About 500 mL of gel was diluted with water (~500mL) and heated to 40-50°C. To this diluted gel, about 500g of acid treated charcoal was slowly added and mechanically agitated for 24h at 150rpm. The gel coated ARSC was then washed with deionised water and dried. This process was repeated several times to form a thick coating of chitosan on the ARSC surface. The chitosan coated activated beads were neutralized by treating with 0.5% NaOH solution for 3h. Finally, it was extensively washed with deionised water [4]. Hereafter, it was called chitosan coated acid treated rubber seed shell charcoal (CARSC). Likewise RSC was also coated with chitosan and was called chitosan coated rubber seed shell charcoal (CRSC).

Batch adsorption experiments.

Adsorption studies were conducted in batch mode at constant temperature to get optimum conditions of all pertinent factors such as dose, pH and contact time (Wang *et al.* 2008). Subsequent adsorption experiments were carried out with only optimized parameters. Synthetic waste water was prepared by dissolving 0.747g potassium chromate (K_2CrO_4) in 10,000 mL of deionised water. Studies were carried out using 250 mL conical flasks containing 100mL of synthetic waste water of known concentration with the adsorbent. The reaction mixture was agitated at a rate of 150 rpm using a rotary shaker. The pH of Cr solution was measured using a pH meter (Toshniwal CC-54). For determining the optimum pH corresponding to the maximum removal efficiency, the pH of the synthetic metal solution was adjusted using 0.1N NaOH or 0.1N H_2SO_4, after adding 4g of adsorbent for the 100mL of sample and agitated for 2h. For determining the optimum dose of adsorbent, the quantity of adsorbents was varied while the pH of the chromium solution was optimized and the samples were agitated at 150 rpm for 2 h at room temperature. Kinetic study was also conducted with optimized dose of adsorbent and pH. The samples were taken out at 30, 60, 90, 120, 150, 180, 210, 240 and 300 minutes.

After equilibrium period, the contents of the beakers were filtered using Whatman no. 1 filter paper. The concentration of Cr (VI) remaining in the supernatant liquid was analyzed using atomic adsorption spectrophotometer (Perkin-Elmer instruments AA 100). The removal efficiency (E) of adsorbent on Cr (VI) was defined as

$$E\ (\%) = (C_0 - C_1)100/C_0,$$

Where, C_o and C_1 are the initial and equilibrium concentration of Cr solution (mg/L) respectively.

All the batch experiments were carried out in duplicate and the mean values of the two data sets are presented. When the relative error exceeded the relative standard deviation by more than 1.0%, the data were disregarded and a third experiment was conducted until the relative error fell within the acceptable range.

RESULTS AND DISCUSSION

The results of the experiments carried out for the removal of Cr (VI) from the synthetic samples using charcoal derived from rubber seed are discussed below.

Characteristics of the adsorbent

The characteristics of the rubber seed shell carbon are presented in Table 1.

Table 1. Charactristics of rubber seed shell charcoal.

Properties	Value (%)
Fixed carbon	68.26
Moisture content	4.1
Volatile matter	24.64
Ash content	3.0

Effect of pH

The pH of the solution is an important controlling parameter since it affects the surface charge of the adsorbate, degree of ionization and speciation of adsorbate (Kurniawan *et al.* 2006). To examine the effect on Cr removal, the pH of the solution was varied from 1.0 to 11.0. Figure 1 shows that the optimum removal efficiency occurs at pH 1.0 for both ARSC and CRSC and then declining at higher pH. The other two adsorbents, RSC and CARSC showed optimum removal efficiency at pH 2.0 and then declines at higher pH. This can be attributed to the fact that a lower pH increases the availability of negatively charged groups on the surface of charcoals which lead to the higher Cr uptake (Babel and Kurniawan, 2004).

At higher pH, the presence of oxygen containing functional groups make the adsorbent surface negatively charged and hence there is repulsive electrostatic interaction between the adsorbent and the anions (Meena *et al.* 2008).

Effect of dose of the adsorbent

The effect of the amount of adsorbent on the removal of Cr (VI) for all the four types of adsorbents is shown in Figure 2. The effect was studied by varying the adsorbent dose while keeping the other parameters constant. It is observed that with an increase in the amount of adsorbent the removal of Cr ion also increases and after a certain value there is no further increase of adsorption. This suggests that after a certain dose of adsorbent, the groups make the

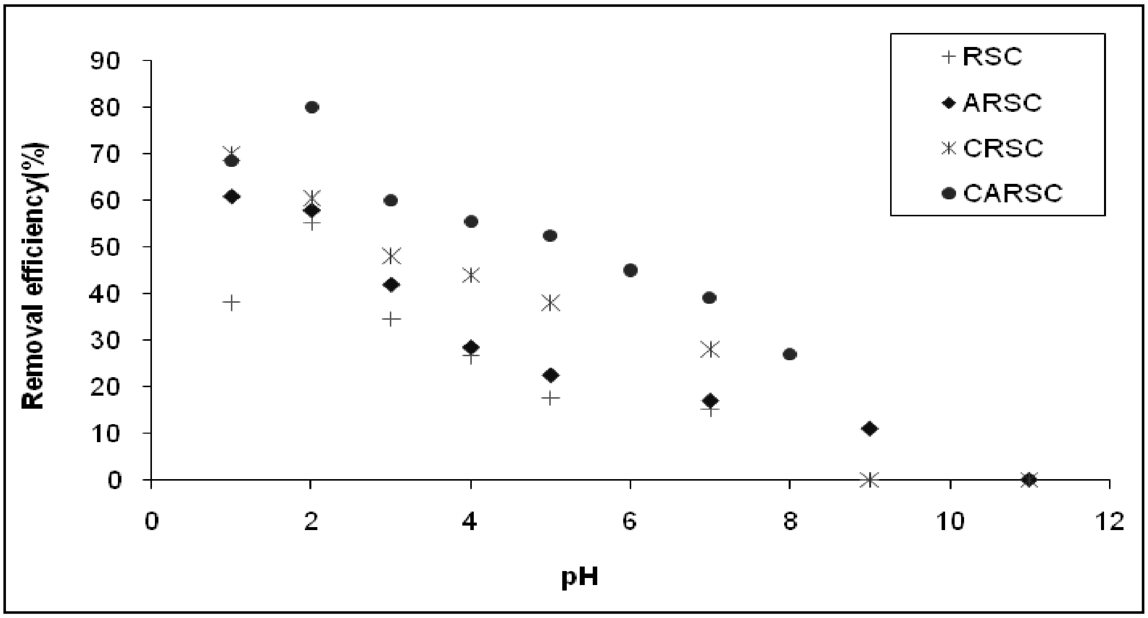

Fig. 1 Effect of pH on the removal efficiencies of Cr (VI). Cr (VI) concentration: 20 mg/L, Adsorbent dose = 4g/100mL, Agitation speed: 150 rpm, Contact time: 2 h

Fig. 2 Effect of dose on the removal efficiencies of Chromium. (Cr (VI) concentration: 20 mg/L, pH: Optimum, Contact time: 2 h)

adsorbent surface negatively charged and hence there is repulsive electrostatic interaction between the adsorbent and the anions. From Figure (2), removal efficiencies are observed to be 80.5%, 72%, 64% and 58.5% respectively for CARSC, CRSC, ARSC and RSC at the optimum doses. So it is concluded that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent (Nomanbhay and Palanisamy, 2005).

The removal efficiencies of the 4 types of adsorbents are different from one another due to the extent of surface modification. The sorption properties of RSC are due to the presence of some functional groups such as carboxylic, hydroxyl and lactone which have a high affinity for metal ions (Minamisawa *et al.* 2004). The removal efficiency increased when the rubber seed shell charcoal was treated with sulphuric acid. This may be due to the generation of more oxygen containing surface functional groups and also due to large surface area available for metal uptake by improving its pore structure. The coating of chitosan on rubber seed shell charcoal further increased the adsorption efficiency because the NH_3^+ group on the chitosan is chiefly responsible for Cr (VI) adsorption and the composite adsorbent is stable under acidic conditions. The chitosan coated charcoal showed lower adsorption capacity than chitosan coated and acid treated charcoal probably due to the less efficient coating of chitosan on RSC, which has lesser acidic surface oxides. The interaction may not be very strong and chitosan may agglomerate to a certain degree and become more soluble at low pH and hence reduces the availability of active binding sites on the chitosan for adsorption of Cr (VI) (Nomanbhay and Palanisamy, 2005). The superior adsorption capability of CARSC is the strong electrostatic interaction between the charcoal and the chitosan.

Effect of contact time

The effect of period of exposure of adsorbents to the metal solution on adsorption efficiency was studied for a period of 10 to 330 minutes at optimum conditions of pH of solution, dose of adsorbent and agitation speed while temperature was kept at 27° C. From contact time data (Figure 3), it may be seen that RSC and ARSC showed increase in removal efficiency as time increases and maximum removal sets in at 210 and 180 minutes respectively, thereafter adsorption decreases. A similar trend of variation can be observed with the CRSC as well as with CARSC. The optimum contact time for both CRSC and CARSC was found to be 150 minutes. The removal efficiency remained constant after 150 minutes. Results, in general have revealed that chitosan coated charcoal requires a shorter contact time. Greater availability of various functional groups on the surface of chitosan which are required for interaction with ions significantly improved the binding capacity and the process proceeded rapidly (Nomanbhay and Palanisamy, 2005). This result is important as equilibrium time is one of the important parameters for an economical waste water treatment system.

Adsorption Isotherm

Adsorption isotherms have been of colossal importance for environmentalists dealing with research work on waste water treatment by adsorption technique since they provide approximate estimation of adsorption, capacity and the nature of adsorption (Eren and Afsin, 2009). Several adsorption isotherm models have been extensively used for the interpretation of adsorption data. Because of the simplicity and

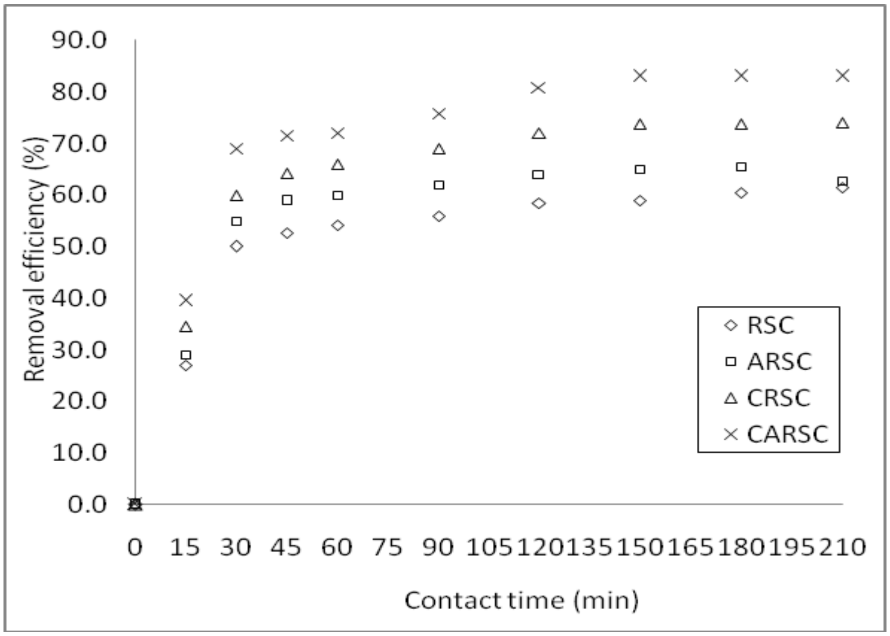

Fig. 3 Effect of contact time on the removal efficiencies of Cr using different types of adsorbents (Cr (VI) concentration: 20 mg/L, Dose and pH: Optimum)

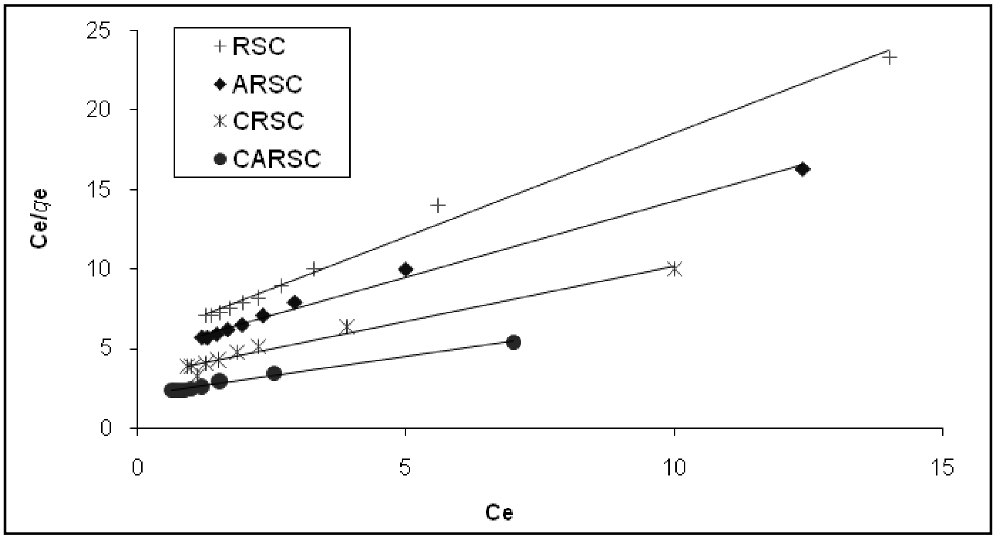

Fig. 4 Langmuir isotherms for Cr adsorption by different types of adsorbents

Fig. 5 Freundlich isotherms for Cr adsorption by different types of adsorbents

reproducibility of results Langmuir and Freundlich adsorption isotherms are most commonly used. The Langmuir model assumes that the uptake of metal ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The isotherm data were correlated using the Langmuir adsorption model which is applied in the form

$C_e/q_e = (1/K_L) + (a_L/K_L)C_e$

Where C_e is the solution phase metal ion concentration, qe (mg/g) is the amount of metal ions adsorbed into the unit mass of the adsorbent, K_L is the Langmuir equilibrium constant which is related to the affinity of binding sites and a_L is the Langmuir constant. The values of a_L and K_{L-} were determined from the slope and intercept of the plot C_e/q_e versus $C_{e-.}$ Further the essential characteristics of Langmuir isotherms can be described by a separation factor R_L, which is defined by:

$R_L = 1/(1+K_LC_0)$

Where, C_{0-} is the initial concentration of metal ion. The value of R_L indicated the type of Langmuir isotherm to be irreversible (R_L=0), favorable ($0<R_L<1$), linear (R_L=1) or unfavorable ($R_L>1$).

Freundlich isotherm assumes that the uptake of metals occurs on a heterogeneous surface by multilayer adsorption and is expressed as

$\text{Ln}\, q_e = b \ln C_e + \ln a$

where, a and b are Freundlich constants to be

Table 2. Langmuir and Freundlich isotherm constants for Cr adsorption

Adsorbent	Langmuir isotherm		Freundlich isotherm		Recommended Isotherm			
	KL	aL	R^2	RL	a	B	R^2	
RSC	0.1827	0.2380	0.9917	0.2148	- 1.7475	0.4883	0.98	Langmuir
ARSC	0.2118	0.2018	0.9929	0.1909	-1.5979	0.5425	0.9933	Freundlich
CRSC	0.3088	0.2150	0.9723	0.1393	-1.3247	0.5909	0.9945	Freundlich
CARSC	0.4782	0.2280	0.9917	0.0946	-0.9617	0.6577	0.9912	Langmuir

determined from the plot of lnq_e versus lnC_e. The Freundlich model as observed in Figure 5 was also found to be linear which showed that Freundlich isotherm was also representative for the Cr adsorption by all types of adsorbent tested. In this study, Freundlich isotherm is more applicable in the case of ARSC and CRSC whereas Langmuir isotherm is more fitting in the case of RSC and CARSC. The calculated Langmuir and Freundlich constants together with correlation coefficients (R^2) and separation factor (R_L) are presented in Table 2.

CONCLUSIONS

The adsorption of Cr (VI) ions from synthetic wastewater was investigated by the successful preparation of rubber seed shell charcoal. To evaluate its superior removal efficiency due to pretreatment with chemicals like acid and also coating with chitosan, four forms of rubber seed shell charcoals were used as adsorbents for comparison in batch adsorption experiments. The analysis of the results indicates that adsorption capacity strongly depends on pH of the solution. The sorption capacity is high at low pH values. The optimum pH is 1 for ARSC and CRSC and 2 for RSC and CARSC. From the optimization of adsorbent dosage study, it can be concluded that the percentage removal of Cr ions increased with increase in the adsorbent dose. The percentage adsorption of metal ions increases with the increase in agitation time. From the kinetic study, the equilibrium time obtained for RSC and ARSC is 210min and 180min respectively. For CRSC and ARSC the equilibrium time is 150min. The uptake of metal ions decreases after optimum time with RSC and ARSC whereas with CRSC and CARSC it remained constant. So it is possible to increase metal removal efficiency of rubber seed shell charcoal by treating with H_2SO_4 and also by coating with chitosan. Among the four types of adsorbents, CARSC and CRSC showed 83% and 74% removal efficiencies respectively within 2½ h of contact time whereas the removal efficiency of ARSC was 66% within 3 h. The removal efficiency of RSC is the lowest having 61.5% at 3.5h. From these studies it can be inferred that charcoal derived from rubber seed shell, an agricultural waste can effectively be used for effluent treatment for the removal of heavy metals like Cr (VI). The use of rubber seed shell with surface modification for heavy metal removal appears to be technically feasible, eco-friendly and economically attractive.

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REFERENCES

An, H.K., Park, B.Y. and Kim, D.S. 2001. Crab shell for the removal of heavy metals from aqueous solution. *Water Research.* 35 : 3551–3556.

Babel, S. and Kurniawan, T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.* B97 : 219-243.

Babel, S. and Kurniawan, T.A. 2004. Cr (VI) removal from synthetic waste water using coconut shell charcoal and commercial activated carbon modified with oxidizing agent and/or chitosan. *Chemosphere.* 54 : 951-967.

Demir, A. and Arisoy, M. 2007. Biological and chemical removal of Cr (VI) from waste water: Cost and benefit analysis. *J. Hazard. Mater.* 147 : 275-280.

Eren, E. and Afsin, B. 2009. Removal of basic dye using activated bentonite samples, *J. Hazard. Mater.* 166 : 830-835.

Hossain, M.A., Kumita, M., Michigami, V. and Mori, S. 2005. Optimization parameters for Cr (VI) adsorption on used black tea leaves. *Adsorption.* 11 : 561-568.

Kurniawan, T.A., Chan, G.Y.S., Lo, W. and Babel, S. 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci. Total Environ.* 366 : 409-426.

Meena, A.K., Kadirvelu, K., Mishra, G.K., Rajagopal, C.

and Nagar, P.N. 2008. Adsorptive removal of heavy metals from aqueous solution by treated sawdust (Acacia arabica). *J. Hazard. Mater.* 150 : 604-611.

Minamisawa, M., Minamisawa, H., Yoshida, S. and Takai, N. 2004. Adsorption behavior of heavy metals on biomaterials. *J. Agric. Food Chem.* 52 : 5606-5611.

Nomanbhay, S.M. and Palanisamy, K. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology*. 8 : 43-53.

Pehlivan, E. and Altun, T. 2008. Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. *J. Hazard. Mater.* 155 : 378-384.

Richardson, S.D. 2003. Water analysis: emerging contaminants and current issues. *Anal. Chem.* 75 : 2831-2857.

Saeed, A. and Iqbal, M. 2003. Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arientinum*). *Wat. Res.* 37 : 3472-3480.

Wang, X.S., Li, Z.Z. and Sun, C. 2008. Removal of Cr (VI) from aqueous solutions by low-cost biosorbents: Marine macroalgae and agricultural by-products. *J. Hazard. Mater.* 153 : 1176-1184.