The use of sulphuric acid-carbonization products of sugar beet pulp in Cr(VI) removal

H. Soner Altundogan, Nurdan Bahar, Buket Mujde, Fikret Tumen *

Department of Chemical Engineering, Firat University, 23279 Elazig, Turkey

Abstract

A carbon rich adsorbent prepared from the reaction of sugar beet pulp with sulphuric acid and gas formed during carbonization process have been studied for Cr(VI) removal from aqueous solutions. The SO_2 rich gas was shown to be an excellent Cr(VI) reductant. The equilibrium and kinetic studies were conducted by using the carbonaceous adsorbent derived from sugar beet pulp. The lower pH favoured Cr(VI) adsorption but substantial Cr(VI) reduction was observed. The Langmuir and Freundlich isotherm models were applied and the Langmuir model best fit the equilibrium isotherm data. The maximum adsorption capacity of chromium calculated from Langmuir isotherm is about 24 mg g^{-1} for 25 °C. The adsorption of Cr(VI) is an endothermic process and follows the pseudo-second-order rate kinetics. The sulphuric acid-carbonization is an economical method for particularly chromium removal because the gas generated during carbonization exhibits good Cr(VI) reduction properties and carbonaceous material obtained is an efficient Cr(VI) adsorbent.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Sugar beet pulp; Carbonization; Activated carbon; Cr(VI) reduction; Cr(VI) adsorption; Heavy metal removal

1. Introduction

Sugar beet pulp, a by-product left after the extraction of sugar from the sugar beet, is generated more than 14 million tonnes (in dry matter bases) each year in the European Community [1,2]. Sugar beet pulp is in polysaccharide structure and composed primarily of cellulosic and pectic substances. This product is mostly returned to the farmers to be used as animal feed, however, several potential ways to enhance its value such as the production of paper [3–5], detergents [6] dietary fibers [7,8] and pectins [9,10] have been investigated. Pectins in the sugar beet pulp contain polygalacturonic acids, which carry carboxyl groups and consequently exhibit high affinity towards metal cations [11,12]. Also, polysaccharides and their modified products adsorb cationic species from aqueous solutions [13–15]. From the standpoint of environmental pollution control, heavy metal adsorption of sugar beet pulp has also been studied [1,2,16–21].

The removal of various organic and inorganic pollutants from industrial wastewaters is considered as an important application of adsorption processes using suitable adsorbent. During recent years, interest has been primarily focused on the production of low-cost sorbents from agricultural wastes or by-products. Agricultural cellulosic materials are evaluated to be very economic precursors for the production of active carbons that has been used extensively in industrial processes for many purposes of separation and purification. Conversion of sugar beet pulp into activated carbon would add its economic value and thus, provide a potentially inexpensive alternative to the existing commercial active carbons. Starting from this idea, we have attempted to produce carbonized sugar beet pulp and reported some heavy metal adsorption characteristics of different type active carbons obtained from sugar beet pulp by pyrolysing techniques [22,23].

As known, concentrated sulphuric acid has a powerful affinity for water so much so that it removes the elements of water from many organic compounds by decomposing them to water, carbon and other simple products. Besides the methods based on pyrolysing and high temperature activation with various chemicals, sulphuric acid dehydration with or without heating at mild temperatures are applied as a carbonization method. Since it does not require high temperature procedures, this method seems to be a simple carbonization and probably is suitable for preparing

* Corresponding author. Tel.: +90 424 2370000/5523; fax: +90 424 2415526.
E-mail address: ftumen@firat.edu.tr (F. Tumen).

efficient and low-cost adsorbent from agricultural lignocellulosic waste materials. Heavy metals removals from aqueous solutions using various carbonaceous materials prepared by sulphuric acid carbonization method have been reported [24–29].

Chromium, one of the prior heavy metal pollutants, occurs in two stable oxidation states in aqueous solutions, Cr(VI) and Cr(III), that their properties are very different. Cr(VI) species, having mobile and strongly oxidant characters, are known as mutagen and potential carcinogen [30]. In contrast, Cr(III), having a limited hydroxide solubility and low toxicity, is generally regarded as non-dangerous pollutant. Because of these dramatic differences in physical and chemical properties of two chromium types and benign character of Cr(III), detoxification and immobilization processes of Cr(VI) is based on its reduction to Cr(III). Many different processes have been investigated for removing chromium from aqueous solutions. Principally, two types of treatment methods are differentiated for Cr(VI) removal. The first type of methods aim to remove Cr(VI) directly while the second type is based on the reduction of Cr(VI) to Cr(III). The precipitation of insoluble chromium hydroxide is a final step in the second type removal processes. The reduction–precipitation technique is abundantly practised for the treatment of chromium containing wastewaters [31,32]

In this study, a carbonaceous material was obtained from sugar beet pulp by carbonizing with concentrated sulphuric acid. The main objective of this study was to evaluate gas, liquid and solid products or co-products obtained during carbonization process for hexavalent chromium treatment in aqueous solutions. In this context, (a) hexavalent chromium reduction capability of the gas evolved during carbonization was determined, (b) characterisation of unreacted acid recovered by washing the carbonized product left after carbonization step was done, (c) carbonaceous adsorbent obtained was characterized and (d) hexavalent chromium adsorption characteristics of carbonaceous material obtained was determined.

2. Materials and methods

2.1. Preparation of sugar beet pulp

Sugar beet pulp was obtained from a local sugar factory in Elazig, Turkey. The coarse humidity of sugar beet pulp was removed by air blowing for 24 h. It was then dried in an oven at 50 °C for further 24 h. The dried pulp was grinded in a blender. The grinded material was sieved and the fraction of −30 + 50 mesh (600 μm < x < 300 μm) was used in the experiments. This sample was named as sugar beet pulp (SBP).

2.2. Preparation of adsorbent

SBP was mixed with two parts of concentrated sulphuric acid. The mixture was rapidly homogenized by stirring with a glass rod. A couple of minutes later, the mixture was immediately swelled by gas evolving. In a period of about 10 min, dark coloured and voluminous material was formed. The material was heated at the range of 140–150 °C for further 6 h. In this period, gas evolving continued for 40–60 min.

In order to remove the unreacted acid, reaction product was mixed with distilled water in the ratio of 1/10 (w/w)[water/(SBP + H_2SO_4)], the mixture was agitated for half an hour and then filtered through vacuum. The first washing-water was set aside. The washing was repeated two times more. Then the material was soaked in 10% sodium bicarbonate solution overnight in the ratio of 1/10 (solid/liquid) to remove the remaining acid. After filtration, the residual solid was repeatedly washed with distilled water, until the washing water does not practically contain sodium. The presence of sodium in washing water was determined by a flame photometer (Eppendorf). The pH of the last washing water was about 8. The product obtained was dried at 105 °C for 24 h. Dried material was roughly grinded in a mortar and sieved through 100 mesh screen. The final materials were referred to as carbonized sugar beet pulp (CSBP) and stored in a tightly capped glass jar and used in adsorption studies.

2.3. Characterisation of recovered acid

In order to determine the acid recovery, washing-water obtained in first washing was analyzed by titration of liquor by NaOH solution.

2.4. Preparation of Cr(VI) solution

A stock solution containing 1000 mg/l of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in distilled water. Working solution of desired concentrations, if required, was prepared by diluting of stock solution. The pH of Cr(VI) solutions was adjusted by using NaOH and H_2SO_4 solutions.

2.5. Cr(VI) reduction by using the gas evolved during carbonization

In the study dealing with Cr(VI) reduction by carbonization gas, various SBP/sulphuric acid (96%, by weight) ratios (1, 1.5, 2.0 and 2.5 w/w) were applied.

Four grams of SBP and a predetermined amount of concentrated sulphuric acid (96%, by weight) were mixed in a glass reactor. Initially, an immediate reaction and an intensive gas evolving were occurred in a few minutes. During this period, the temperature of product rose up to approximately 120 °C. The temperature of the product was then kept at the range of 140–150 °C by heating the reactor with an electrical heater. The gas evolved during the carbonization and the following heating, was successively passed through four impingers containing dichromate solutions of 1000 mg Cr(VI) l^{-1}, the volume and height of which are 125 ml and 10 cm each (Fig. 1). As a result of reduction of Cr(VI) to Cr(III), the colour of solutions turned from orange to green. When the solution in the first impinger turned green, it was removed from system and a new impinger is added as fourth. After the gas evolving ended, the system was demounted and all solutions were mixed. The resulting solution was agitated for 15 min before Cr(VI) analysis was made. The amount of reduced Cr(VI) was determined based on the Cr(VI) concentration measured after and before treatment. The amount of reduction at the end of treatment, q_r (reduced Cr(VI) per gram
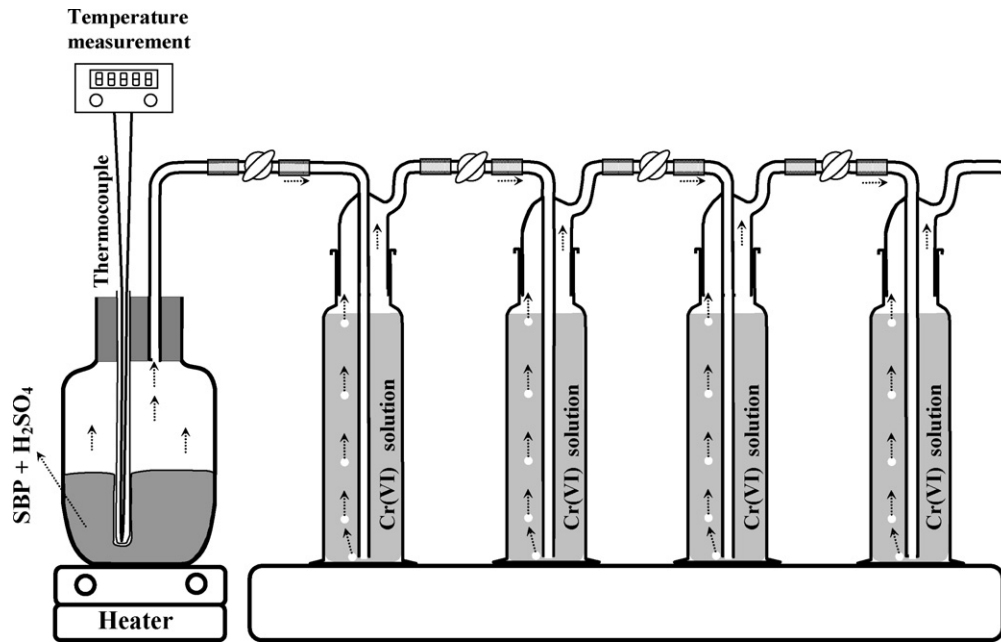
Fig. 1. Schematic diagram of experimental apparatus for the measurement of reduction capability of gas evolved during carbonization.

of H_2SO_4)(mg g^{-1}), was calculated as follows:

$$q_r = \frac{V}{0.96m}(C_i - C_f) \qquad (1)$$

where C_i and C_f are the initial and final Cr(VI) concentrations (mg l^{-1}) of solutions used in reduction experiment, V the volume of the total solution (l), and m is the weight of the H_2SO_4 (96%) (g) used in carbonization experiment.

2.6. Adsorption study

The first set of batch adsorption experiments were performed to determine equilibrium time for different initial Cr(VI) concentration. For this purpose, 1 g of CSBP was added to 200 ml Cr(VI) solution with a predetermined concentration (50, 100, 150 and 200 mg l^{-1}) and initial pH (2.00, 2.25, 2.50 and 3.00 (± 0.05)) in 300 ml Erlenmeyer flasks. The flasks placed in an temperature controlled orbital shaker (Selecta-Rotabit) with constant shaking at 200 rpm, at varying temperature in the range of 25–70 °C (± 1 °C). Samples were periodically withdrawn and the solutions were separated by a suction filter through an Advantec (no. 6) filter paper. In the supernatant, final pH was measured, Cr(VI) and, in some cases, in order to control the reduction of Cr(VI) during adsorption, total Cr were determined.

The amount of adsorbed chromium was determined based on the chromium concentration measured after and before equilibration. The amount of adsorption at equilibrium, q (mg g^{-1}), was obtained as follows:

$$q = \frac{V}{m}(C_i - C_e) \qquad (2)$$

where C_i and C_e are the initial and equilibrium liquid phase concentrations (mg l^{-1}), V the volume of the solution (l) and m is the weight of the CSBP used (g).

2.7. Analytical methods

The solutions were analyzed for hexavalent and total chromium. Cr(VI) was analyzed spectrophotometrically using the 1,5-diphenylcarbazide method [33]. Analysis of total chromium was done by atomic absorption spectrophotometer (AAS). The difference between concentration of total and hexavalent chromium was taken as the concentration of trivalent chromium. The AAS measurements were compared to the measurements made with the Cr(VI)-diphenylcarbazide method on etalon samples. Analytical measurements made by the two techniques were always comparable within 5%. All experiments were carried out in duplicate and mean values were reported or taken for calculations. Maximum deviation was 5%.

3. Results and discussion

The H_2SO_4 treatment process yielded a stable, granular adsorbent that was black in colour. Table 1 shows some characteristics of carbonized sugar beet pulp (CSBP). The washing

Table 1
Some characteristics of the adsorbent

Parameter	Value
Moisture content (%)	3.3
Ash content (%)	15.4
Specific gravity (g ml^{-1})	1.21
Conductivity (μS cm^{-1})	52.30
pH (1% solution)	7.5
Surface area (N$_2$-BET) (m^2 g^{-1})	37.8
Particle size (μm)	<150
Iodine number (mg g^{-1})	193
COD[a] (mg O$_2$ l^{-1})	92.2
Acid insoluble inorganic material (%)	9.5

[a] Value for water (100 ml) contacted with 1 g material for 24 h.

Table 2
The results of acid recovery in first washing of carbonized product (washing time: 30 min)

Parameter	Values			
SBP used (g)	2.0	2.0	2.0	2.0
H_2SO_4 (96%) used (g)	2.0	3.0	4.0	5.0
H_2SO_4 (96%)/DSBP ratio (w/w)	1.0	1.5	2.0	2.5
H_2SO_4 in H_2SO_4 (96%) used (g)	1.92	2.88	3.84	4.80
The amount of water used in first washing (ml)	20	20	20	20
0.1N NaOH solution consumed per ml of first washing water (ml)	5.5	8.6	14.5	20.6
Recovered H_2SO_4 in first washing (g)	0.539	0.843	1.421	2.019
Recovery of H_2SO_4 used (%)	28.07	29.27	37.01	42.07

water of carbonized material constitutes a diluted acid solution. Preliminary tests showed that the gas evolved during the carbonization process is a good reductant for Cr(VI). The results of the studies conducted by gas, liquid and solid products are given in following sections.

3.1. Reduction of Cr(VI) using carbonization gas

During the carbonization process, on one hand, concentrated sulphuric acid decomposes the organic materials and converts into carbon rich substances, on the other hand, a SO_2-rich gas is evolved. SO_2 is formed as a result of reduction of H_2SO_4. The Cr(VI) reduction capacity of gas evolved during carbonization was determined through the system schematized in Fig. 1. The results of Cr(VI) reduction performed by the gas evolved during carbonization process is summarized in Table 2.

Formation of SO_2 can be roughly depicted as in Eq. (3).

$$\text{Organic substance} + H_2SO_4$$
$$\rightarrow \text{C-rich substances} + SO_{2\uparrow} + CO_{2\uparrow} + H_2O \quad (3)$$
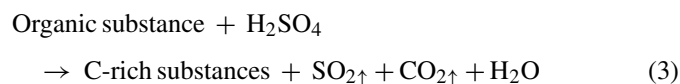
SO_2 is an efficient reductant for Cr(VI) that is reduced to Cr(III) according to following equation:

$$Cr_2O_7^{2-} + 3SO_2 + 2H_3O^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 3H_2O \quad (4)$$
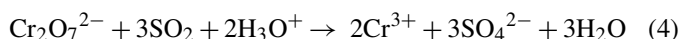
Required H_3O^+ can be met by the acidity formed by dissolution of SO_2 and ionization of H_2SO_3 in aqueous system as described in Eqs. (5) and (6). While initial pH value of standard Cr(VI) solution (1000 mg l^{-1}) is 3.70, final pH of the reduced solutions is measured as low values less than 1.5.

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad (5)$$

$$H_2SO_3 + H_2O \rightarrow H_3O^+ + HSO_3^- \quad (6)$$
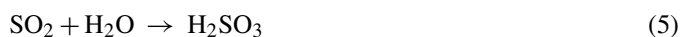
It was observed that gas evolving continued for 30–60 min depending on acid content of mixture. As can be seen from Table 3, the gas formed during carbonization could reduce 158.5 mg Cr(VI) per gram SBP used in a solution of 1000 mg l^{-1} Cr(VI) when 1 g of H_2SO_4 (96%) is used for 1 g of SBP in carbonization. The more acid amount the longer gas evolving and the more Cr(VI) is reduced. When the amount of H_2SO_4 96% is increased to 2-folds, Cr(VI) reduction efficiency is achieved to 286.5 mg. Calculation the reduction capacity based on sulphuric acid gives rather constant values. For example, on increasing the H_2SO_4/SBP ratio from 1.0 to 2.5, Cr(VI) reducing capacity calculated based on H_2SO_4 weight varied from 165.1 to 141.7 mg g^{-1} while reducing capacity calculated based on SBP weight varied from 158.5 to 340.0 mg g^{-1}. From these results, it may be concluded that SO_2 is the main reducing agent in reduction process.

Consequently, the Cr(VI) reduction capability of SO_2-rich carbonization gas evolved during carbonization process provides an advantage to the activation method.

3.2. Recovery of unreacted acid

If the carbonaceous adsorbent is used in hexavalent chromium treatment, unreacted H_2SO_4 can partially be recovered as diluted acid by washing and this acid solution can be utilized in Cr(VI) adsorption that occurs in acidic media. Alkalimetric titration analyses of first washing waters showed that about 28 to 42% of H_2SO_4 used can be recovered in first washing conducted with 10 ml water per gram of SBP. Acid recovery conditions and the results of washing experiments are given in Table 2. The sum of H_2SO_4 amounts corresponded to SO_2 and recovered after carbonization roughly give the H_2SO_4 used in carbonization process. Thus, H_2SO_4 consumed

Table 3
The results of reduction of Cr(VI) using carbonization gas (initial pH of Cr(VI) solution is 3.7)

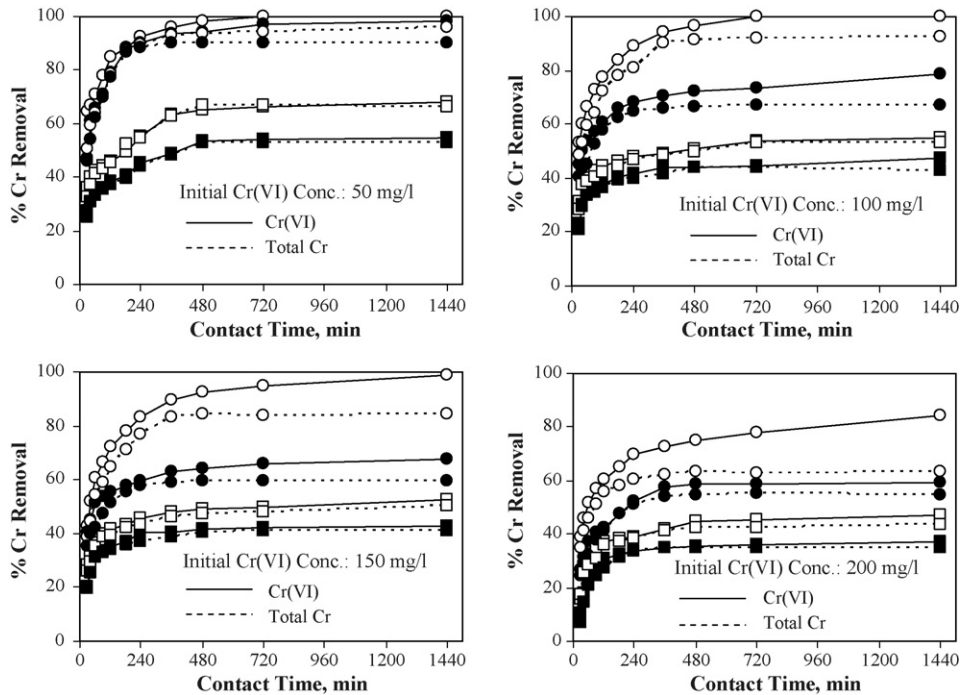| DSBP used (g)	H_2SO_4 (96%) used (g)	CSBP obtained (g)	CSBP yield (%)	Cr(VI) reduced (mg)	Cr(VI) reducing capacity	
					mg Cr(VI)/g DSBP	mg Cr(VI)/g H_2SO_4
2	2	1.14	57.00	317	158.5	165.1
2	3	1.05	52.50	457	228.5	158.7
2	4	0.95	47.50	573	286.5	149.2
2	5	0.90	45.00	680	340.0	141.7

Fig. 2. Effect of contact time on the removal of Cr(VI) by using of CSBP ((○) pH 2.0, (●) pH 2.25, (□) pH 2.50, (■) pH 3.0)) (adsorbent dosage: 5 g/l; temperature: 25 °C).

in carbonization process may be used for another purpose, i.e., Cr(VI) reduction while unreacted H_2SO_4 recovered through a simple washing may be utilized in acidifying the Cr(VI) solution.

3.3. Cr(VI) adsorption of CSBP

3.3.1. Equilibration time and pH study

Fig. 2 shows the time curves of Cr(VI) removed from the aqueous solution during the experiment performed with four different pH and four different initial Cr(VI) concentrations. The results indicated that the adsorption process is rather quick. Nearly 80% of the adsorption capacity was reached within 4 h and an approximate equilibrium state could be reached after 6 h of contact time for all concentration and pH studied.

The pH of the aqueous solutions is an important parameter in the heavy metal adsorption processes. Its role on the removal of hexavalent chromium from aqueous solution by using CSBP is seen in Fig. 2. The solution pH and initial concentration of hexavalent chromium affected the removal rate of chromium. As expected, lower pH favoured Cr(VI) adsorption because surface is covered with positive charge as a result of protonation and Cr(VI) in anionic forms is well binded by surface. In fact, the results clearly show that the adsorption of hexavalent chromium increased with the decrease of solution pH from 3.0 to 2.0. In more acidic cases, the concentration of trivalent chromium increases in the solution, which indicates that the removal of hexavalent chromium proceeds contributing a reduction process. Further pH decrease was not conducted due to the possibility of Cr(VI) reduction in high amount at much lower pH, in addition, very low pH is not practical for a removal process.

3.3.2. Temperature study

The temperature affects the rate and extent of adsorption. Furthermore, temperature dependence of adsorption provides thermodynamic and mechanistic information about the sorption process. The effect of temperature on Cr(VI) adsorption on to CSBP was studied in the range of 25–70 °C for a contact period of 6 h in the solutions the initial concentrations of which are varied in the range of 50–200 mg l^{-1}. The results are shown in Fig. 3.

3.3.3. Kinetic study

Mostly, the kinetics of adsorption by any material is tested for the first-order expression of Lagergren [34]. However, a
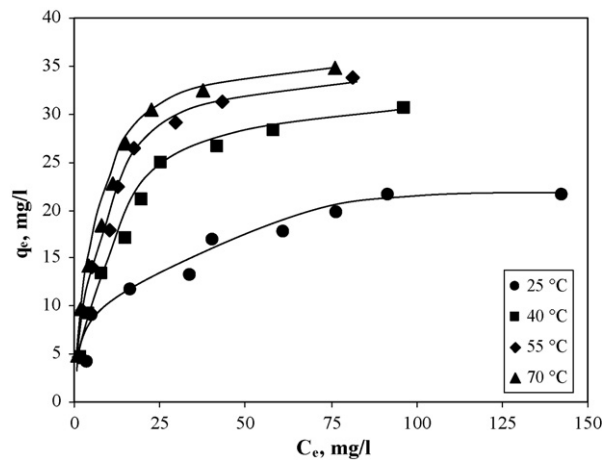

Fig. 3. Adsorption isotherms obtained for Cr(VI) removal by CSBP (adsorbent dosage: 5 g/l; initial Cr(VI) concentration: 25–250 mg/l; pH 2.25; contact time: 360 min).
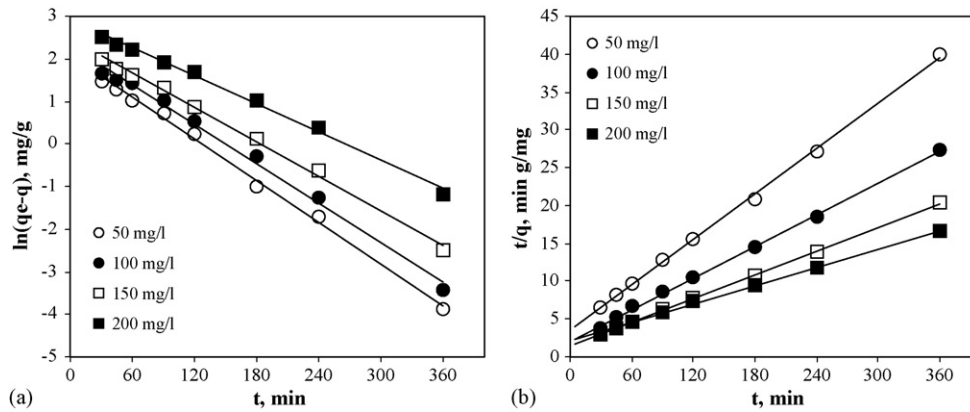
Fig. 4. Application of equilibration data to the Lagergren first order (a) and pseudo-second-order (b) rate expressions.

pseudo-second-order approach can sometimes provide a good description of the adsorption kinetics [35]. The first-order Lagergren equation is:

$$\ln(q_e - q) = \ln q_e - kt \tag{6}$$

The pseudo-second-order equation is:

$$\frac{t}{q} = \frac{1}{k'q_e^2} + \frac{t}{q_e} \tag{7}$$

where q_e (mg g^{-1}) and q (mg g^{-1}) is the mass of metal adsorbed at equilibrium and at time t, respectively, k (min^{-1}), and k' (g mg^{-1} min^{-1}) is the first-order and pseudo-second-order rate constants of adsorption.

The plot of $\ln(q_e - q)$ versus t for first-order Lagergren model and the plot of t/q versus t for pseudo-second-order model are shown in Fig. 4a and b, respectively. k and k' values can be calculated from the slope and intercept of the lines. Also, q_e values for both models can be extracted from corresponding slope and intercept values. Besides the regression coefficients, it is possible to determine the most suitable kinetic model by comparing the actual and the estimated values of q_e. Whole kinetic parameters for both models are shown in Table 4. As seen from Fig. 4 and Table 4, kinetic data fit well to both model. But, correlation coefficients calculated for pseudo-second-order model are higher than those of Lagergren model. Also, estimated q_e values for pseudo-second-order model are closer than those of Lagergren model. Thus, it can be concluded that the pseudo-second-order model is most suitable model for the data and this suggests that the rate-limiting step may be chemical sorption rather than diffusion.

3.3.4. Isotherm study

The sorption data obtained at different temperatures were analyzed by fitting the Freundlich and Langmuir isotherm models [36,37].

The Freundlich isotherm is most frequently used to describe the adsorption of heavy metal ions in solution. Freundlich isotherm assumes that the uptakes of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The equilibrium data were analyzed using the following linearised Freundlich equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{8}$$

where K_f is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. K_f and $1/n$ can be determined from the linear plot of $\ln q_e$ versus $\ln C_e q_e$ is the amount of Cr(VI) sorbed (mg g^{-1}) on CSBP at equilibrium and C_e is the Cr(VI) concentration (mg l^{-1}) of solution at the equilibrium.

The best known of all sorption isotherms is the Langmuir model that is applicable to sorption processes. In this model, the sorption of each sorbate molecule onto the surface has equal sorption activation energy. The linearised Langmuir sorption isotherm can be used to describe sorption of an ionic species such as Cr(VI) from an aqueous solution as

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{9}$$

where C_e is equilibrium concentration of Cr(VI) (mg l^{-1}), q_e the amount of Cr(VI) adsorbed per unit mass of sorbent (mg g^{-1})

Table 4
Calculated kinetic parameters for first-order Lagergren and pseudo-second-order models

| Initial Cr(VI) concentration (mg l^{-1})	Actual q_e values (mg g^{-1})	First-order Lagergren model			Pseudo-second-order model		
		k (min^{-1})	Estimated q_e values (mg g^{-1})	R^2	k' (g mg^{-1} min^{-1})	Estimated q_e values (mg g^{-1})	R^2
50	9.011	0.0162	7.768	0.9964	0.0028	10.000	0.9988
100	13.242	0.0154	10.175	0.9926	0.0024	14.368	0.9988
150	17.811	0.0134	11.648	0.9961	0.0019	19.157	0.9995
200	21.944	0.0110	18.239	0.9935	0.0009	24.814	0.9988
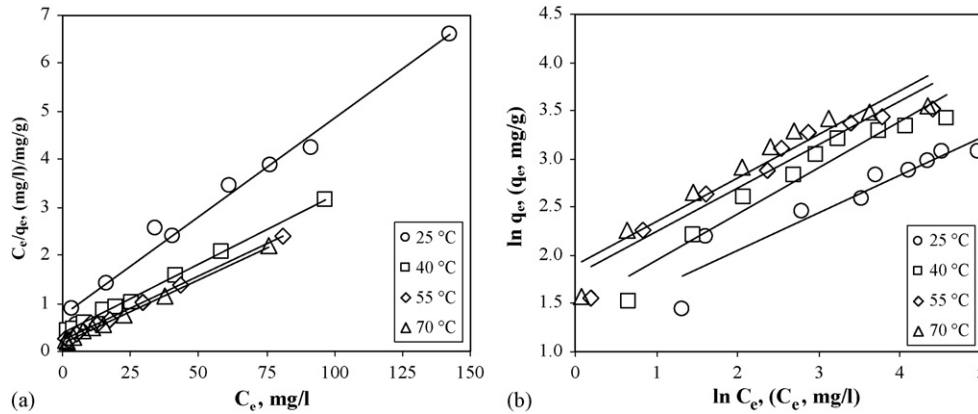
Fig. 5. Langmuir (a) and Freundlich (b) plots for Cr(VI) adsorption by CSBP.

and q_{max} is the maximum sorption capacity $(mg\,g^{-1})$. $b\,(l\,mg^{-1})$ is a constant related to the affinity of binding sites or bonding energy. q_{max} represents a practical limiting sorption capacity when the surface of sorbent is completely covered with sorbate. If a plot of C_e/q_e versus C_e gives a straight line with a slope $1/q_{max}$ and intercepts $1/bq_{max}$, this indicates that the sorption process follows the Langmuir model. Langmuir and Freundlich plots for Cr(VI) adsorption by CSBP are shown in Fig. 5. Also, calculated isotherm parameters and correlation coefficients are depicted in Table 5. As can be seen, Langmuir model is better correlated the data obtained at 25, 40, 55 and 70 °C than the Freundlich model.

From Table 5, the value of q_{max} and b increases by the temperature. Thus, on increasing the temperature from 25 to 70 °C, the adsorption capacity increased from 24.154 to 38.168 $mg\,g^{-1}$. Consequently, it is clear that adsorption equilibrium is temperature-dependent. The K_f represents similar trend. This situation shows that the Cr(VI) adsorption process by CSBP has an endothermic nature. Increasing the adsorption ability by increasing the temperature may be due to widening the pores of the adsorbent. In addition, endothermic nature of sorption process may reveal to the Cr(VI) uptake of CSBP is mainly chemical sorption. In a previous study [18], it has been observed that the process of Cr(VI) sorption on depectinated sugar beet pulp is endothermic and that a large fraction of Cr(VI) is reduced to trivalent form. Cr(III) and Cr(VI) sorption capacities were reported as 1.19 and 0.40 $mg\,g^{-1}$, respectively, for depectinated sugar beet pulp [17,18]. The positive values in enthalpy change for the Cr(VI) adsorption were also found in the studies conducted by rice bran [38], composite alginate-geothite beads [39] and activated carbons derived from hazelnut shell [29] and *Hevea Brasilinesis* sawdust [40].

Reddad et al. [41] have reported that the reduction of Cr(VI) into Cr(III) took place in solution by contact with sugar beet pulp due to it contains carboxylic and hydroxyl groups which probably play a role as electron donors. It has been proved that Cr(III) sorption took place with a Ca^{2+} exchange. The Langmuir adsorption capacity of sugar beet pulp for Cr(III) was reported as about 10 $mg\,g^{-1}$ in the study mentioned. In a previous study [21], it has been indicated that iron (III)-hydroxide-loaded sugar beet pulp exhibited about 5 $mg\,g^{-1}$ Cr(VI) sorption. By comparing these values with the result of 24.154 $mg\,g^{-1}$ found in present study, it can be concluded that the carbonaceous adsorbent obtained by sulphuric acid dehydration of sugar beet pulp is a good deal of advantageous.

Recently, several studies related to chromium adsorption from wastewater have been carried out. It is needed to compare the results from the studies using activated carbons or carbonized materials and adsorbents derived from sugar beet pulp in a wide perspective. In such studies, however, the parameters such as adsorbent dosage, adsorbent properties, chromium species, concentration range and equilibration time are very different from each other. In addition, chromium adsorption fits different isotherms by various correlations in those studies. Therefore, the better comparisons can be made by using the adsorption capacities calculated from isotherms. Table 6 compares chromium adsorption capacities of adsorbents derived from sugar beet pulp and various activated carbons reported in previous studies. As seen activated carbons generally have a high adsorption capacity for chromium. Carbonized sugar beet pulp shows a higher

Table 5
Calculated isotherm parameters for Cr(VI) adsorption by CSBP

Temperature (°C)	Langmuir isotherm				Freundlich isotherm		
	$q_{max}\,(mg\,g^{-1})$	$b\,(l\,mg^{-1})$	R^2	R_L[a]	$K_f\,(mg\,g^{-1})(l\,mg^{-1})^n$	$1/n$	R^2
25	24.154	0.058	0.985	0.079	3.588	0.389	0.889
40	34.722	0.079	0.998	0.060	4.211	0.480	0.932
55	37.175	0.120	0.998	0.040	5.966	0.454	0.921
70	38.168	0.146	0.999	0.033	6.586	0.456	0.907

[a] Calculated values for the initial concentration of 200 $mg\,l^{-1}$.

Table 6
The adsorptive capacities of some sugar beet based adsorbents and various activated carbons

Adsorbent	Cr species studied	Capacity (mg g^{-1})	Reference
Sugar beet pulp	Cr(III)	10.04	[41]
Depectinated sugar beet pulp	Cr(III)	0.19	[17]
Depectinated sugar beet pulp	Cr(VI)	0.40	[18]
Iron III hydroxide loaded sugar beet pulp	Cr(VI)	5.12	[21]
Carbonized sugar beet pulp	Cr(VI)	24.15	Present study
AC made from *Hevea Brasilinesis* (rubber wood) sawdust	Cr(VI)	44.05	[40]
Different granulated and fibrous ACs	Cr(III)	3.52–13.31	[42]
AC from coconut tree sawdust	Cr(VI)	3.46	[26]
Commercial ACs	Cr(VI)–Cr(III)[a]	48.70–57.70	[43]
ACs made from coconut shell	Cr(VI)–Cr(III)[a]	68.30–73.90	[43]
AC from hazelnut shell	Cr(VI)	170.77	[29]
AC from coconut shell and its oxidised products	Cr(VI)	4.72–10.44	[44]
AC from fir wood slabs	Cr(VI)	180.3	[45]
AC from *Terminalia Arjuna* nut	Cr(VI)	28.43	[46]

[a] Real wastewater.

adsorption capacity than sugar beet pulp and its depectinated product and it has comparable capacity to some activated carbons (Table 6).

In some earlier studies [45,47], authors have suggested that using a dimensionless separation factor is suitable for evaluation of sorption data. For the Langmuir type sorption process, the isotherm shape can be classified by a term R_L, dimensionless constant separation factor, which is defined as in Eq. (10).

$$R_L = \frac{1}{(1 + bC_0)} \tag{10}$$

where R_L is dimensionless separation factor, C_0 initial metal concentration (mg l^{-1}) and b is Langmuir constant (l mg^{-1}). The parameter R_L indicates the shape of the isotherm accordingly:

$R_L > 1$ (unfavourable), $\quad R_L = 1$ (linear),

$0 < R_L < 1$ (favourable), $\quad R_L = 0$ (irreversible)

The R_L values for Cr(VI) sorption by CSBP, were calculated from Langmuir constant b for various temperatures and initial metal concentration range of 50–200 mg l^{-1} and the values calculated for highest concentration of 200 mg l^{-1} are listed in Table 5. Since all calculated R_L values are between 0 and 1, it can be stated that the process of metal sorption by CSBP is favourable.

As expected, higher CSBP/solution ratios are required to treat the solutions having higher metal concentrations. Unnithan and

Table 7
Calculated CSBP dosages to achieve the 95 and 99% removal yield for Cr(VI)

Initial concentration (mg l^{-1})	Calculated m/V values (sorbent dosage) (g l^{-1})	
	For 95% removal	For 99% removal
150	19.48	76.87
200	21.44	78.92
250	23.41	80.97
500	33.25	91.22

Annirudhan [48] have suggested the Eq. (11) which the sorbent/solution ratio can be calculated from

$$\frac{m}{V} = \frac{C_0 - C_e}{(q_{max}bC_e)/(1 + bC_e)} \tag{11}$$

where the m/V is CSBP/solution ratio (in other term, sorbent dosage) (g l^{-1}) and the C_0 and C_e is initial and equilibrium sorbate concentrations (mg l^{-1}), respectively. In order to have an idea about the required CSBP amount for higher metal uptake, calculated CSBP dosages to achieve the removal yields of 95 or 99% for Cr(VI) by using Langmuir isotherm parameters obtained at 25 °C are shown in Table 7. Actual Cr(VI) sorption percentages for the initial concentration of 150 and 200 mg l^{-1} by using 5 g l^{-1} CSBP dosage were 63.3 and 57.7%, respectively. As shown from the table, these removal yields may be increased to 95 and 99% by increasing the CSBP dosages to 19.5 and 76.9 g l^{-1} for 150 mg l^{-1} and 21.4 and 78.9 g l^{-1} for 200 mg l^{-1}, respectively. Also, by this method, required CSBP dosages for the effective Cr(VI) removal from the solutions having the higher initial concentrations such as 250 or 500 mg l^{-1} can be estimated as in table.

The thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH) and entropy changes (ΔS) for the adsorption process can be determined using following equations:

$$\ln b = \ln b' - \frac{\Delta H}{RT} \tag{11}$$

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G}{RT} \tag{12}$$

$$\Delta S = \frac{\Delta H - \Delta G}{RT} \tag{13}$$

where the b' is energy parameter, T absolute temperature (K) and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The enthalpy change for chromium adsorption by CSBP determined from the slope of $\ln b$ versus $1/T$ was found to be 18.18 kJ mol^{-1} (Fig. 6). The positive value of ΔH confirms that the process is endothermic. Other thermodynamic parameters calculated depending on temperature are depicted in Table 8. The negative values of ΔG indicate that the nature of adsorption process is spontaneous. The values of entropy changes are small and positive for Cr(VI) adsorption process. Positive entropy change values may show that the some structural deformations occur in the adsorbent during the sorption process.
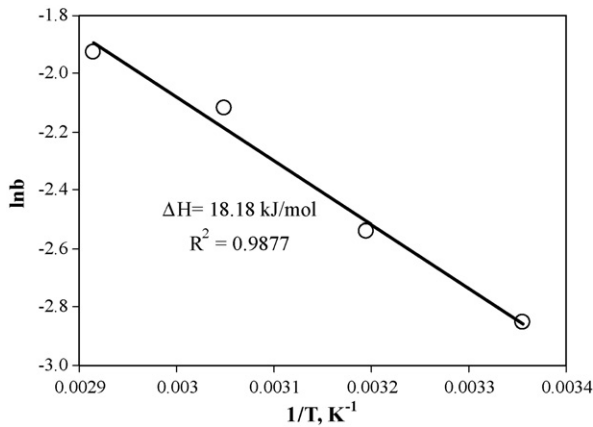
Fig. 6. ln *b* vs. 1/*T* plot for Cr(VI) adsorption on CSBP.

Table 8
Free energy and entropy changes for Cr(VI) adsorption by CSBP

Temperature (°C)	Thermodynamic parameters	
	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
25	−19.880	0.1331
40	−21.653	0.1325
55	−23.831	0.1331
70	−25.474	0.1321

4. Conclusions

The agroindustrial waste material, i.e., sugar beet pulp was converted into low cost carbon rich material by reacting with sulphuric acid. The gas evolved from the carbonization process has been used successfully as a Cr(VI) reducing agent. The carbonaceous material derived from sugar beet pulp could be used as an effective adsorbent for the treatment of Cr(VI). Further, unreacted H_2SO_4 is recovered as a diluted solution in first step of washing and may be used in Cr(VI) adsorption which is favoured in acidic media. In brief, as an alternative to much more expensive reagents and systems, solid and gas products of H_2SO_4 carbonization process may be used for the Cr(VI) treatment.

References

[1] C. Gerente, P. Couespel du Mesnil, Y. Andres, J.-F. Thibault, P. Le Cloirec, Removal of metal ions from aqueous solution on low cost natural polysaccharides—sorption mechanism approach, React. Funct. Polym. 46 (2000) 135–144.

[2] V.M. Dronnet, C.M.G.C. Renard, M.A.V. Axelos, J.-F. Thibault, Binding of divalent metal cations by sugar-beet pulp, Carbohyd. Polym. 34 (1997) 73–82.

[3] G. Vaccari, C. Nicolucci, G. Mantovani, A. Monegato, Process for manufacturing paper from sugar-beet pulp and paper thus obtained, European Patent (1994) 94114666.4.

[4] G. Vaccari, C. Nicolucci, G. Mantovani, A. Monegato, Utilization of beet pulp for paper manufacture, Int. Sugar J. 97 (1995) 556–559.

[5] G. Vaccari, G. Mantovani, E. Dosi, C. Nicolucci, A. Monegato, Paper manufacture using beet pulp and factory waste lime, Int. Sugar J. 99 (1997) 532–536.

[6] S. Petit, R. Ralainirina, S. Favre, R. De Baynast, World Patent (1993) 02092.

[7] C. Bertin, X. Rouau, J.-F. Thibault, Structure and properties of sugar beet fibres, J. Sci. Food Agric. 44 (1988) 15–29.

[8] F. Michel, J.-F. Thibault, J.-L. Barry, R. DeBaynast, Preparation and characterisation of dietary fibre from sugar beet pulp, J. Sci. Food Agric. 42 (1988) 77–85.

[9] N. Arslan, Extraction of pectin from sugar-beet pulp and intrinsic viscosity molecular weight relationship of pectin solutions, Int. J. Food Sci. Technol. 32 (1995) 381–385.

[10] S. Levigne, M.-C. Ralet, J.-F. Thibault, Characterisation of pectins extracted from fresh sugar beet under different conditions using an experimental design, Carbohyd. Polym. 49 (2002) 145–153.

[11] V.M. Dronnet, C.M.G.C. Renard, M.A.V. Axelos, J.-F. Thibault, Characterisation and selectivity of divalent metal ions binding by citrus and sugar-beet pectins, Carbohyd. Polym. 30 (1996) 253–263.

[12] M.T. Kartel, L.A. Kupchik, B.K. Veisov, Evaluation of pectin binding of heavy metal ions in aqueous solutions, Chemosphere 38 (1999) 2591–2596.

[13] W.E. Marshall, L.H. Wartelle, D.E. Boler, M.M. Johns, C.A. Toles, Enhanced metal adsorption by soybean hulls modified with citric acid, Bioresource Technol. 69 (1999) 263–268.

[14] R.E. Wing, Starch citrate: preparation and ion exchange properties, Starch/Starke 48 (1996) 275–279.

[15] R.E. Wing, Cellulosic citrates: preparation and ion exchange properties, J. Polym. Mater. 14 (1997) 303–309.

[16] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, Bioresource Technol. 47 (1994) 257–264.

[17] A. Ozer, F. Tumen, M. Bildik, Cr(III) removal from aqueous solutions by depectinated sugar beet pulp, Environ. Technol. 18 (1997) 893–901.

[18] A. Ozer, F. Tumen, M. Bildik, Cr(VI) removal from aqueous solutions by depectinated sugar beet pulp, Chim. Acta Turc. 25 (1997) 113–118.

[19] V.M. Dronnet, M.A.V. Axelos, C.M.G.C. Renard, J.-F. Thibault, Improvement of the binding capacity of metal cations by sugar-beet pulp. 1. Impact of cross-linking treatments on composition, hydration and binding properties, Carbohyd. Polym. 35 (1998) 29–37.

[20] V.M. Dronnet, M.A.V. Axelos, C.M.G.C. Renard, J.-F. Thibault, Improvement of the binding capacity of metal cations by sugar-beet pulp. 2. Binding of divalent metal cations by modified sugar-beet pulp, Carbohyd. Polym. 35 (1998) 239–247.

[21] H.S. Altundogan, Cr(VI) removal from aqueous solution by iron (III) hydroxide-loaded sugar beet pulp, Process Biochem. 40 (2005) 1443–1452.

[22] A. Ozer, M.S. Tanyildizi, F. Tumen, Study of cadmium adsorption from aqueous solution on activated carbon from sugar beet pulp, Environ. Technol. 19 (1998) 1119–1125.

[23] A. Ozer, F. Tumen, Cd(II) adsorption from aqueous solution by activated carbon from sugar beet pulp impregnated with phosphoric acid, Fresen. Environ. Bull. 12 (2003) 1050–1058.

[24] C. Namasivayam, K. Kadirvelu, Agricultural solid wastes for the removal of heavy metals: adsorption of Cu(II) by coirpith carbon, Chemosphere 34 (1997) 377–399.

[25] C. Namasivayam, K. Kadirvelu, Uptake of mercury (II) from wastewater by activated carbon from an unwanted agricultural solid by-product: coirpith, Carbon 37 (1999) 79–84.

[26] K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon, Bioresource Technol. 80 (2001) 87–89.

[27] E. Demirbas, M. Kobya, S. Oncel, S. Sencan, Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies, Bioresource Technol. 84 (2002) 291–293.

[28] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, Bioresource Technol. 87 (2003) 129–132.

[29] M. Kobya, Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies, Bioresource Technol. 91 (2004) 317–321.

[30] J.W. Moore, S. Ramamoorthy, Heavy Metals in Natural Waters, Springer-Verlag Co., New York, 1984, pp. 100–120.

[31] W.W. Eckenfelder, Industrial Water Pollution Control, 2nd ed., McGraw Hill, New York, 1989.

[32] M. Sittig, Pollutant Removal Handbook, Noyes Data Co., NJ, 1973.

[33] Standard Methods for Examination of Water and Wastewater, 17th ed., American Public Health Association, APHA-AWWA-WPCF, Port City Press, Washington DC, 1989.

[34] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens, Handl. 24 (1898) 1–39.

[35] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[36] H. Freundlich, Ueber die adsorption in Loesungen, Z. Phys. Chem. 57 (1907) 385–470.

[37] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[38] K.K. Singh, R. Rastogi, S.H. Hasan, Removal of Cr(VI) from wastewater using rice bran, J. Colloid Interf. Sci. 290 (2005) 61–68.

[39] N.K. Lazaridis, Ch. Charalambous, Sorptive removal of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate-geothite beads, Water Res. 39 (2005) 4385–4396.

[40] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon, J. Hazard. Mater. B124 (2005) 192–199.

[41] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Mechanisms of Cr(III) and Cr(VI) removal from aqueous solutions by sugar beet pulp, Environ. Technol. 24 (2003) 257–264.

[42] D. Aggarwal, M. Goyal, R.C. Bansal, Adsorption of chromium by activated carbon from aqueous solution, Carbon 37 (1999) 1989–1997.

[43] Z. Hu, L. Lei, Y. Li, Y. Ni, Chromium adsorption on high-performance activated carbons from aqueous solution, Separ. Purif. Technol. 31 (2003) 13–18.

[44] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere 54 (2004) 951–967.

[45] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, J. Hazard. Mater. 123 (2005) 223–231.

[46] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride, Chem. Eng. Sci. 60 (2005) 3049–3059.

[47] Y.S. Ho, C.C. Wang, Pseudo-isotherms for the sorption of cadmium ion onto tree fern, Process Biochem. 39 (2004) 761–765.

[48] M.R. Unnithan, T.S. Anirudhan, The kinetics and thermodynamics of sorption of chromium (VI) onto the iron (III) complex of a carboxylated polyacrylamide-grafted sawdust, Ind. Eng. Chem. Res. 40 (2001) 2683–2701.