RICE BRAN CARBON: AN ALTERNATIVE TO COMMERCIAL ACTIVATED CARBON FOR THE REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION

Deeksha Ranjan and Syed Hadi Hasan*

Rice bran carbon (RBC) prepared from rice bran (an agricultural waste) was successfully utilized for the removal of hexavalent chromium from aqueous solution. The potentiality of RBC was tested and compared with commercial activated carbon (CAC), and it was found that RBC removed 95% of hexavalent chromium at pH 2, 1000 µM Cr(VI) concentration, temperature 30 °C, and adsorbent dose of 2 g/L. The maximum uptake of total chromium obtained by applying the Langmuir isotherm model was 138.88 mg/g for RBC, which was found comparable to that obtained by utilizing CAC (116.28 mg/g) at 40 °C. The removal of Cr(VI) was found maximum at a proton to chromium ratio of 10 and chromium to carbon ratio of 0.052, and these ratios were found to be applicable over a range of Cr(VI) concentrations. The removal of Cr(VI), at low pH (< 2.0), was not only due to sorption of Cr(VI) but also because of reduction of Cr(VI) into less toxic Cr(III), which was also adsorbed on the surface of the sorbent. The rate of reduction removal of Cr(VI) followed pseudo-first order kinetics, whereas the sorption of total chromium followed pseudosecond order kinetics for both the types of activated carbons.

Key words: Rice bran carbon; Hexavalent chromium; Removal; Adsorption; Sorption kinetics

Contact information: a: Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi - 221005, U.P., India; *Corresponding author: shhasan.apc@itbhu.ac.in

INTRODUCTION

Chromium is one of the heavy metals that has been a major cause of concern in wastewater treatment. The main industrial sources of chromium in water are leather tanning, electroplating, metal processing, wood preservatives, paint and pigments, textile manufacture, dyeing, steel fabrication, and the canning industry (Karthikeyan et al. 2004; Das et al. 2004; Garg et al. 2004; Rais et al. 2005). Chromium exists in both trivalent and hexavalent forms in industrial discharge (Khezami and Capart 2005). The trivalent form is relatively innocuous, whereas hexavalent chromium is toxic, carcinogenic, mutagenic, and teratogenic in nature (Bai and Abraham 2001). Hexavalent chromium is highly mobile in soil and aquatic systems; it is a strong oxidant and capable of being adsorbed by the skin (Ahalya et al. 2005). The concentrations of Cr(VI) in industrial wastewaters range from 0.5 to 270.000 mg/L. However, according to the United States Environmental Protection Agency (1990), the permissible limit of Cr(VI) for industrial effluents to be discharged to surface water is 0.1 mg/L and in potable water is 0.05 mg/L (Demirbas et al. 2004). It is therefore essential to remove hexavalent chromium from industrial effluents before discharging them into aquatic environments or onto land. Among the

various treatment techniques available for removal of hexavalent chromium, the most commonly used are, reduction and precipitation, lime coagulation, ion exchange, solvent extraction, and reverse osmosis. However, most of these processes have technical and/or economical constraints (Singh et al. 2005; Mungasavalli et al. 2007; Sumathi et al. 2005). In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent material is activated carbon. As proved by many authors, removal of heavy metals by activated carbon is economically favorable and technically easier (Khezami and Capart 2005). However, the use of commercial activated carbons is not suitable for developing countries because of their low availability and high cost. Therefore, there is a need to produce activated carbon from cheaper and readily available materials that can be economically viable on large scale and to compare its adsorbent capacity with its commercially prepared counterpart. The present work aims to synthesize rice bran carbon (RBC) from rice bran, which is a byproduct of rice milling. The carbon prepared was thermally activated and then used for the removal of hexavalent chromium from an aqueous solution. The sorption capacity of RBC was tested and compared with a commercially available activated carbon. The mechanism of removal of hexavalent chromium has been discussed in detail. Further kinetic and equilibrium studies have also been carried out.

EXPERIMENTAL

Preparation of Carbon from Rice Bran

Rice bran is a byproduct of rice milling plants. It was collected from M/s Manoj Industries (rice mill), Chunar, Mirzapur (UP). Rice bran was carbonized by treating it with concentrated sulphuric acid (weight ratio 4:3) for 24 h at 150 °C in an air oven. The material obtained was washed with water in order to remove the excess acid present on the material, and it was dried at 110 °C for half an hour. Subsequently, this carbonized material was activated using thermal activation process in which the dried material was kept at 850 °C in a continuous flow of carbon dioxide (75 mL/min) for half an hour (Mohan and Pittman Jr. 2006). The rice bran carbon (RBC) prepared was then finally ground and sieved to 200 mesh, and the product was used throughout the study.

The sample of commercial activated carbon (CAC) was obtained from S.D. Fine Chemicals, Mumbai, India. The material was ground, and particles of similar sizes were separated and used.

Reagents

All of the chemicals used were of analytical grade. Potassium dichromate, KMnO₄, NaOH, HCl, H₂SO₄, and other necessary chemicals were purchased from E. Merck India Ltd., Mumbai, India. The stock solution containing 1040 ppm of Cr(VI) was prepared by dissolving 1.471 g quantity of AR grade $K_2Cr_2O_7$ in 500 mL deionized, double distilled water. Required initial concentrations of Cr(VI) standards were prepared daily by appropriate dilution of the above stock Cr(VI) standard solution.

Equipment

The surface area of the sorbent (Rice Bran Carbon) was determined by a threepoint N_2 gas adsorption method using a Quantasorb Surface Area Analyzer (model Q5-7, Quanta chrome Corporation, USA). The bulk density of the RBC was determined by densitometer. The porosity of RBC was determined with a porositometer (model H: M7V, NGRI, Hyderabad, INDIA). Percentage of volatile matter, ash, and moisture were determined (Jeffery et al. 1989). The physicochemical charaterisation of CAC used in the present study for the removal of hexavalent Cr were taken from (Mor et al. 2007) and are given in Table 1, whereas physicochemical characterisation of RBC are given in Table 2.

For the determination of chromium content in the standard and treated solutions, a spectrophotometer, (Spectronic 20, Bausch and Lomb, USA) was used. The pH of the solution was measured with a pH meter (CAT No. CL-54, Toshniwal, India).

Table 1. Physicochemical Characteristics of Commercial Activated Carbon (CAC)

Properties	Quantitative value		
Raw material	Coconut shell		
Surface area (m ² g ⁻¹) (based on BET)	1000		
Bulk density (g cm ⁻³)	5000		
Particle density (kg m ⁻³)	850		
Ash content (on dry basis) (%)	3.59		
Moisture content (%)	5.0		
pH _{ZPC}	5.3		
Conductivity (µS cm ⁻¹)	94.0		

Table 2. Physicochemical Characteristics of Rice Bran Carbon (RBC)

Properties	Quantitative value
Bulk density (g cm ⁻³)	0.387
Moisture, (%)	15.56
Ash, (%)	31.18
Matter soluble in water, (%)	2.46
Surface area (m ² g ⁻¹)	651.64
Porosity (%)	16.35

Batch Experiments

Using the different amounts of sorbents (CAC or RBC) in a 250 mL stoppered conical flask containing 50 mL of test solution, batch sorption studies were carried out at desired initial pH value, temperature and sorbate concentration. Different initial concentrations of Cr(VI) solution were prepared by proper dilution from stock 1040 ppm Cr(VI) standard, and the initial pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as required. The necessary amount of sorbent was then added, and the contents of the flask were shaken for the desired contact time (2 h) in an electrically thermostated reciprocating shaker at 125 rpm. The contents of the flask were separated from the sorbent by centrifugation at 15000 rpm and were analyzed for the remaining

Cr(VI) concentration in the sample. The amount of Cr(VI) sorbed per unit mass (mg/g) of the sorbent, q_t was evaluated by using following equations,

$$q_t = (C_i - C_t) X V/W \tag{1}$$

where C_i and C_t are the Cr(VI) concentrations in mg/L initially and at a given time t, respectively; V is the volume of the Cr(VI) solutions in mL; and W is the weight of activated carbon in mg.

The percentage removal of Cr(VI) was calculated as follows;

Percentage removal of
$$\operatorname{Cr}(\operatorname{VI}) = (C_i - C_t)/C_i \times 100$$
 (2)

Chromium analysis

Chromium(VI) analysis

A pink colored complex was formed when 1,5-diphenylcarbazide was added into Cr(VI) in acidic solution, and the concentration was determined spectrophotometrically at 540 nm by Spectronic 20 (Bausch and Lomb, U.S.A.) (Park et al. 2004).

Chromium(III) analysis

For the determination of Cr(III) concentration, Cr(III) (formed due to the reduction of Cr(VI) into Cr(III) during the sorption process) was again converted to Cr(VI) by the addition of excess potassium permanganate at high temperature (130 to 140°C), after which 1,5-diphenycarbazide was added. The pink colored complex formed gives the concentration of Cr(VI) plus Cr(III), which is total chromium. The Cr(III) concentration was then calculated by the difference of the total chromium and Cr(VI) concentrations measured above (Park et al. 2004).

RESULTS AND DISCUSSION

In order to investigate the effect of carbon dosage at various pHs on the percentage of total chromium and hexavalent chromium removal, experiments were performed by varying carbon dosages from 0.4 to 6 g/L in hexavalent chromium solution of 1000μ M, for the initial pH range of 1 to 6 using both types of carbons (RBC and CAC) at 30 °C. The results thus obtained are explained below.

Effect of Carbon Dose and pH on the Removal of Total Chromium

Figure 1(a) (CAC) and 1(b) (RBC) shows that the percentage removal of total chromium initially increased with the increase in carbon dose up to 2 g/L, and thereafter it became constant with further increase in carbon dose. It was also observed that there was an increase in percentage removal of total chromium from approx 75% to 85% with an increase in pH from 1 to 2. Thereafter, the percentage removal started decreasing from 40 to 20% in case of CAC and 40 to 30% in case of RBC with an increase in pH from 3 to 6. Furthermore, the maximum removal of total chromium was achieved at pH 2 (104 μ M H⁺) and carbon dose of 2 g/L for both the types of carbon.



Fig. 1. Effect of carbon dose and initial pH on total chromium removal for (a) CAC and (b) RBC. Conditions: Cr(VI) 50 mL of 104 mg/L, Equilibration time- 2 h, pH range- 1-6, carbon dose- 0.4 to 6 g/L.

Effect of Carbon Dose and pH on the Removal of Hexavalent Chromium

Plots for the percentage of unadsorbed hexavalent chromium in the solution for various carbon dosages over the pH range (1-6) are given in Fig. 2(a) (CAC) and Fig. 2(b) (RBC). The figures show that the percentage of unadsorbed hexavalent chromium in the solution at higher pH values (4-6) was almost unchanged with the increase in carbon dose, while at low pH levels (1-3) there was a decrease in the percentage of unadsorbed hexavalent chromium in the solution up to 2 g/L carbon dose. At pH 3 the percentage of unadsorbed hexavalent chromium was unchanged after 2 g/L carbon dose, while at pH 1 and 2 the percentage of unadsorbed chromium found in the solution was almost zero after 2 g/L carbon dose.



Fig. 2. Hexavalent chromium removal as a function of carbon dosage for (a) CAC and (b) RBC. Conditions: Cr(VI) 50 mL of 104 mg/L, Equilibration time- 2 h, pH range- 1-6, carbon dose- 0.4 to 6 g/L.

From the above results, it can be explained that the maximum removal of chromium was acheived when the initial hexavalent chromium concentration was 1000 μ M (104 mg/L), the pH was 2 (104 μ M H⁺), and the carbon dosage was 2 g/L of chromium solution. In other words, for maximum removal of chromium at an initial chromium(VI) concentration of 1000 μ M, the proton to chromium ratio (proton/Cr(VI)) required was 10, and that of chromium to carbon ratio (Cr(VI)/ carbon) was 0.052. The applicability of these ratios for the maximum removal of total chromium from aqueous solution, was further confirmed by performing experiments using various initial Cr(VI) concentrations [1,000 μ M (104 mg/L) to 10,000 μ M (1040 mg/L)], while maintaining the proton to Cr(VI) ratio at 10 and Cr(VI) to carbon ratio at 0.052. The results thus obtained are presented in Fig. 3, which shows a linear relationship between initial chromium concentration and total chromium removal at constant proton to Cr(VI) and Cr(VI) to carbon ratios, showing that both the ratios were applicable for all the concentrations of Cr(VI) studied. The applicability of the ratio of Cr(VI) to carbon could be explained on the basis that if only sorbate concentration was increased for a fixed carbon dose, the number of active sites to accomodate sorbate ions remain unchanged, hence the percentage of removal goes down. Thus, to maintain a high percentage of metal ions, there must be a suitable increase in the adsorbent dosage when the metal ion concentration is increased.



Fig. 3. Total chromium removal as a function of chromium(VI) concentration, for both the carbons CAC and RBC. Conditions: Cr(VI) concentration from 1000 μ M (104 mg/L) to 10,000 μ M (1040 mg/L), proton to Cr(VI) ratio at 10 and Cr(VI) to carbon ratio at 0.052.

The applicability of the proton to chromium(VI) ratio can be explained that when there was an increase in the initial Cr(VI) concentration, a suitable decrease in pH (i.e. increase in proton concentration) was essentially required that permitted more adsorption of Cr(VI) in the form of oxyanions $HCrO_4^-$ and $Cr_2O_7^{2-}$ at the surface of the sorbent. Another observation was that when the pH of the solution decreased, the concentration of trivalent chromium increased. This was because hexavalent chromium in acidic medium acts as a powerful oxidant, and the functional groups present on the surface of the adsorbent became oxidized and Cr(VI) itself was reduced, forming trivalent chromium. As a result, the equilibrium pH of the solution was observed to increase.

The formation of Cr(III) was further confirmed by experiments performed at low pH (1, 2, and 3) at Cr(VI) concentration of 1000 μ M by varying the carbon dose (0.4 to 6 g/L), and the results are given in Fig. 4(a) (CAC) and Fig. 4(b) (RBC). It was observed from the results that the formation of Cr(III) to an extent of approx. 10-15 % took place at pH 2.0 and 3.0. In addition to this it is also evident from the results Fig. 4(a) and Fig. 4(b) that at lower pH conditions (< 2.0) the percentage of Cr(III) formed in the solution increased with the increase in carbon dosage.



Fig. 4. Extent of chromium(VI) reduction, for (a) CAC and (b) RBC. Conditions: Cr(VI) 50 mL of 104 mg/L, Equilibration time- 2 h, pH range- 1-3, carbon dose- 0.4 to 6 g/L.

Removal Mechanism

The overall mechanism of removal of Cr(VI) from aqueous solution by activated carbon could be explained as when the carbon was activated thermally at high temperatures, there was formation of surface oxides of C_xO and C_xO_2 (Mor et al. 2007; Srinivasan et al. 1988). These surface oxides reacted with water and resulted in a increase in the pH of the solution due to the following hydrolytic reaction of water molecules,

$$C_x O + H_2 O \rightarrow C_x^{+2} + 2OH^-$$

$$C_x O_2 + H_2 O \rightarrow C_x O^{+2} + 2OH^-$$
(3)

The carbon surface due to above reaction acquires a positive charge and interacts with negatively charged chromate ions, which are the predominant species in solution of hexavalent chromium at pH < 7.0. Thus its removal is expected according to the following equation:

$$C_x^{+2} + HCrO_4^{-} \rightarrow C_xO HO_3Cr^+$$

$$C_xO^{+2} + HCrO_4^{-} \rightarrow C_xO_2 HO_3Cr^+$$
(4)

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Combining equations (3) and (4) gives the overall reaction involved for the removal of hexavalent chromium:

$$C_{x}O_{2} + H_{2}O + HCrO_{4}^{-} \rightarrow C_{x}O HO_{3}Cr^{+} + 2OH^{-}$$

$$C_{x}O_{2} + H_{2}O + HCrO_{4}^{-} \rightarrow C_{x}O_{2} HO_{3}Cr^{+} + 2OH^{-}$$
(5)

Furthermore, it can also be observed from the above reaction that for every mole of chromate ion adsorbed on the carbon surface, two moles of hydroxyl ions are released in the aqueous solution. Thus, the ratio of chromate ion adsorbed to hydroxyl ion released (represented as R) should be 0.5 under the optimal conditions for the adsorption of hexavalent chromium from aqueous solution.

In order to strengthen the above finding that two moles of hydroxyl ions were released for per mole of chromate adsorption, experiments were performed to observe the change in pH (Δ pH) in the presence and absence of Cr(VI) solution for both the carbons. For these experiments, the Cr(VI) concentration was varied from 1000 to 5000 µM, keeping the proton to chromium ratio (proton/Cr(VI)) at 10. The results thus obtained are presented in Table 3. The values of ΔpH were calculated from the equation $\Delta pH = pH_a$ or $pH_b - pH_i$, where pH_a and pH_b are the change in the pH of the solution in the absence and presence of Cr(VI), respectively, after 2 hrs of equilibration, and pH_i refers to initial pH of the solution. The table shows that the R values remained almost constant (0.5 \pm 0.050) over the initial Cr(VI) concentration range of 1000 to 4000 µM for both the carbons. It was also found that the expected value of 'R' (0.5 ± 0.050) was much deviated at 5000 μ M of initial Cr(VI) concentration. Actually this deviation in the expected value of 'R' was because of the occurance of a competing proton-consuming reaction in the media that leads to a large decrease in the pH values. At such high concentration of Cr(VI) (5000 μ M) to maintain a proton to Cr(VI) ratio of 10, a proton concentration of 50,000 μ M had to be provided, and these conditions will lead to the formation of CrO₃, as shown in the following reaction: AT T+

$$2 \text{ H}^{+} + 2 \text{ HCrO}_{4}^{-} \rightarrow 2 \text{ H}_{2}\text{CrO}_{4} \rightarrow 2 \text{ H}_{2}\text{O} + \text{Cr}_{2}\text{O}_{7}^{-2} \rightarrow 2 \text{ CrO}_{3} + 2 \text{ H}_{2}\text{O}$$
 (6)

Thus, under highly acidic conditions there will be formation of chromium oxide species, and as the pH lowers more polymerised chromium oxide species will be formed (Mohan and Pittman Jr. 2006; Mor et al. 2007). These oxy species (in +6 oxidation state) act as very powerful oxidants and thus will oxidise the carbon surface, due to which all these oxy chromium species themselves will get reduced into the Cr(III) form as follows (Park et al. 2005; Daneshvar et al. 2002; Dupont and Guillon 2003; El- Shafey 2005):

$$Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$$
 (7)

$$HCrO_4^- + 7 H^+ + 3 e^- \rightarrow Cr^{3+} + 4 H_2O$$
 (8)

Thus, it is clear that at an optimum pH (2.0) $Cr_2O_7^{2-}$ and $HCrO_4^{-}$ were the predominant species that became adsorbed on the carbonaceous sorbent surface. At high

initial Cr(VI) concentrations, it becomes necessary to increase the acidity of the aqueous medium so that the proton to chromium ratio could be maintained at the optimum level of 10, and the reduction of Cr(VI) is the most favored reaction on the carbon surface. Thus, in the presence of carbonaceous sorbent, which also acts as a reducing agent, the amount of Cr(VI) becoming reduced into Cr(III) increases with the increase of the concentration of protons (i.e. low pH).

Hence, it can be concluded that the removal of Cr(VI) from the aqueous solution occurs via two mechanisms, one is the direct sorption of Cr(VI) on the surface of the sorbent, and other is the reduction of Cr(VI) into Cr(III) at low pH, and the sorption of Cr(III) on the surface of the sorbent.

Initial Cr (VI) Initial pH (pH _i) pH of the solution pH of the solution Change in pH Change in						
concentratior	n of the solution	after 2 hrs. of	after 2 hrs. of	for carbon	pH for F	R= <u>B - A</u>
(µM)		equilibrium of	equilibrium of	(pH _a -pH _i)	Cr (VI)	Α
		carbon with	carbon with		solution	
		distilled water	Cr (VI) solution	on (pH _b -pH _i)		
		(pH _a)	(pH _b)	(A)	(B)	
CAC						
1000	2.00	2.39	2.60	0.39	0.60	0.538
2000	1.70	2.12	2.31	0.42	0.61	0.452
3000	1.52	1.89	2.07	0.37	0.55	0.486
4000	1.40	1.72	1.89	0.32	0.49	0.531
5000	1.30	1.61	1.85	0.31	0.55	0.774
RBC						
1000	2.00	2.56	2.82	0.56	0.82	0.464
2000	1.70	2.13	2.33	0.43	0.63	0.465
3000	1.52	1.76	1.91	0.24	0.36	0.500
4000	1.40	1.58	1.68	0.18	0.28	0.550
5000	1.30	1.41	1.53	0.11	0.21	0.909

Table 3. Effect of Initial Cr (VI) Concentration on the Ratio of Chromate Ion to

 Hydroxyl Ion (R)

Adsorption Kinetics

For kinetic study a series of experiments was performed at different initial Cr(VI) concentrations viz., 100, 500, and 1000 μ M and time intervals (from 5 to 180 min.) at a temperature of 30 °C and pH 2.0 for both the carbons. It was found that the concentration of both Cr(VI) and total chromium in solution decreased with time. The decrease in concentration appeared to be faster and more significant for Cr(VI) than for total chromium, for both the carbons. The difference between total chromium and Cr(VI) concentrations with time is apparently due to unadsorbed Cr(III) that was produced as a result of Cr(VI) reduction.

The removal of Cr(VI) was found to occur via two processes, i.e. reduction and adsorption. The kinetic data for reduction as well as sorption of chromium were examined via first order reversible, pseudo-first order and pseudo-second order models for both CAC and RBC. The correlation coefficients, presented in Table 4, of pseudo-first order model for reduction removal and pseudo- second order model for sorption

removal were found to be much better as compared with other models applied; hence only these models will be discussed in detail. The reduction removal model is based solely on the reduction of Cr(VI) to Cr(III) in the aqueous solution, regardless the extent of chromium sorption. The pseudo-first order equation (Eq. 9) was applied to the data obtained by following the Cr(VI) concentration with time in order to predict the reduction rate (El- Shafey 2005),

$$\log C = \log C_o - k_1 \cdot t / 2.303 \tag{9}$$

where C is the Cr(VI) concentration at any time t, C_o is the initial concentration of Cr(VI), and k_I is the rate constant of Cr(VI) reduction removal. The straight- line plots of log C vs. t (min.) for both the carbons were tested to obtain the pseudo-first-order rate constant at different initial concentrations of Cr(VI). Linear fits were observed for all concentrations with good correlation coefficients, indicating that the reduction reaction can be approximated by the pseudo-first order kinetic model.

Removal via sorption is based on the uptake of total chromium on the adsorbent with time. The rate of sorption was attained by following total chromium concentration with time in the aqueous solution during the experiment.

This model is expressed as (Ho and McKay 1999),

$$t/q_t = 1/k_2 q_e^2 + 1/q_e.t \tag{10}$$

$$h = k_2 \dot{q}_e^2 \tag{11}$$

where k_2 is the equilibrium rate constant and *h* is the initial sorption rate, and q_e and q_t are the amount of chromium sorbed at equilibrium and at any time *t* per unit weight of the sorbent (mg/g) respectively. The linear plots of t/q_t vs. t were used to determine the rate constants. Good correlation coefficients showed a good fitting of the model for the sorption of chromium on both the carbons.

	Reduction remova	•	Sorption removal				
Pseudo-first order model			Pse	Pseudo-second order model			
Adsorbent	Rate constant, k_1 (min ⁻¹)	r²	Rate constant, k_2' (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	r²		
CAC							
Initial Cr (VI) c	onc.						
100 µM	0.0265	0.998	0.0732	1.843	0.998		
500 µM	0.0233	0.997	0.0182	10.52	0.997		
1000 µM	0.0117	0.997	0.0114	22.93	0.998		
RBC							
Initial Cr (VI) conc.							
100 µM	0.0283	0.998	0.0742	1.891	0.998		
500 µM	0.0267	0.999	0.0173	9.921	0.997		
1000 µM	0.0149	0.997	0.0139	28.01	0.997		

Table 4. Rate Constants of Cr(VI) Reduction & Sorption Removal Kinetic Models

Sorption Isotherms

Various isotherm models have been utilized for describing sorption equilibrium for wastewater treatment. For the present work the Langmuir equation is being used in order to evaluate the sorption capacities of both the carbons. The Langmuir sorption isotherm describes that the uptake occurs on a homogeneous surface by monolayer sortion without interaction between sorbed molecules (Mohan and Pittman Jr. 2006; Padmesh et al. 2006). The linear form of the Langmuir isotherms may be represented as:

$$C_e/q_e = 1/Q^o b + C_e/q_e$$
(12)

where, C_e is the equilibrium concentration (mg/L) of solute in bulk solution, q_e is the amount of removed chromium per unit weight of sorbent (mg/g) at equilibrium, b is the Langmuir constant related to the free sorption energy (L/mg), and Q^o is the amount of chromium sorbed per unit weight of the sorbent required for the monolayer coverage of the surface, or monolayer capacity (mg/g).

The sorption data were represented in terms of chromium concentrations (104 to 1040 mg/L) at different temperatures (20 to 40 °C) to produce a sorption isotherm. The values of Q^o and b were calculated from the slope and intercept of the plot C_e/q_e vs. C_e respectively for both CAC and RBC (Fig. 5(a) and Fig. 5(b) respectively) and are given in Table 5.

The fitting of the Langmuir isotherm model for both the carbons as shown by good correlation coefficients (r^2) shows the same type of sorption mechanism of chromium on the surface of both the carbons. Value of Q^o was found to increase with the increase in temperature, showing that the increase in temperature favored the reaction.



Fig. 5. Langmuir sorption isotherm for (a) CAC and (b) RBC. Conditions: Equilibration time 2 h, Initial Cr(VI) concentration from 104-1040 mg/L and at different temperatures (20, 30 and 40 °C).

		CAC			RBC	
Temperature	Q^{o}	b	r ²	Q^o	b	r ²
	(mg/g)			(mg/g)		
20°C	107.52	0.015	0.997	120.48	0.016	0.998
30°C	111.11	0.017	0.998	131.57	0.014	0.997
40°C	116.28	0.018	0.998	138.88	0.015	0.997

Table 5. Langmuir Parameters for the Chromium Sorption

CONCLUSIONS

The following conclusion can be drawn:

- 1. Activated carbon prepared from low-cost agricultural byproduct rice bran showed almost comparable removal of Cr(VI) from aqueous solution as that of commercial activated carbon. Thus, it could be recommended for removal of Cr(VI) from wastewaters in developing countries in place of commercial activated carbon.
- 2. For the maximum removal of Cr(VI) from aqueous solution the proton to chromium(VI) ratio (proton/ Cr(VI)) required was 10, and the chromium to carbon ratio (Cr(VI) / carbon) was 0.052.
- 3. From the removal mechanism it was clear that the removal of hexavalent chromium at low pH (<2.0) from aqueous solution was governed by two processes; one was the sorption of Cr(VI) and other was the reduction of Cr(VI) to the less toxic form Cr(III), which itself becomes sorbed on the sorbent surface, with an overall increase in the solution pH.
- 4. The rate of reduction removal of the Cr(VI) followed pseudo-first order kinetics, while the sorption of total chromium followed pseudo-second order kinetics for both the types of sorbents.
- 5. Langmuir isotherm described well the sorption equilibrium for both the types of carbons, consistent with the model of monolayer sorption of chromium on the homogenous surface of the sorbent.

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