Alkali-treated Carbonized Rice Husk for the Removal of Aqueous Cr(VI)

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Rice husk was chemically modified for the preparation of activated carbon. Rice husk was treated with nitric acid and carbonized at 700 °C. After carbonization, the resulting rice husk char was treated with NaOH at room temperature. The 5 M NaOH-treated rice husk had the highest surface area (750 m^2/g). Proximate analysis of activated carbon confirmed that NaOH treatment removed silica completely. Temperature programmed decomposition (TPD) graphs showed that the total gas contents (CO and CO_2) liberated by CRH and H_2O-treated CRH and CRH5M were 2l5 µmol/g, 390 µmol/g, and 970 µmol/g, respectively. The adsorption studies of the activated carbon during Cr(VI) removal from the aqueous medium indicated that CRH5M showed the highest rate of adsorption. The effect of adsorbent dosage, Cr(VI) concentration, pH, and temperature were studied to determine the best removal efficiency. With a decrease in pH from 4.4 to 2, the adsorption capacity increased from 3 mg/g to 25.2 mg/g. The adsorption of Cr(VI) followed pseudo-second-order behaviour. The changes in Gibbs free energy, enthalpy, and entropy affected by thermodynamic parameters were found to be negative, which confirmed that the adsorption of Cr(VI) on CRH5M is spontaneous, exothermic, and favours low temperatures.

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INTRODUCTION

Chromium and its ionic compounds are toxic aqueous pollutants. Chromium enters water bodies from many industrial processes such as metal finishing, electroplating, wood preservation, paint manufacturing, leather tanning, pigment manufacturing, chemical manufacturing, and agricultural runoff (Gupta *et al*. 2010). In the aquatic environments, chromium occurs in two predominant oxidation states, Cr(VI) and Cr(III). Hexavalent chromium is more toxic than the trivalent ion and has mutagenic and carcinogenic properties. Its consumption by humans may cause adverse effects such as vomiting, nausea, epigastric problems, diarrhea, *etc*. (Tiravanti *et al*. 1997).

There are several tested methods for the removal of chromium from aquatic environments, including precipitation (Zhou *et al*. 1993), chemical reduction (Seaman *et al*. 1999), ion exchange (Petruzzelli *et al*. 1995), electrochemical precipitation (Kongsricharoern and Polprasert 1996), membrane separation (Kozlowski and Walkowiak 2002), adsorption (Srivastava *et al*. 1997), biosorption (Aravindhan *et al*. 2004), and photocatalytic reduction (Testa *et al*. 2004). Most of these techniques have drawbacks such as high costs and/or the incomplete removal of toxic metals (Demirbas *et al*. 2004). Of

these techniques, adsorption appears to be commercially suitable. Activated carbon (AC) is an effective material in removing hazardous compounds such as pesticides, heavy metal ions, *etc.* (Huang and Wu 1977; Ouki *et al*. 1997; Demirbas *et al*. 2004). Even though AC is widely tested, its production costs are high and there is a need to develop low-cost, tailor-made ACs.

Agricultural biowaste materials have been tested for the removal of heavy metal ions from water, including sawdust (Garg *et al*. 2004), bamboo (Dula *et al*. 2014), neem leaves (Babu and Gupta 2008), olive cake (Dakiky *et al*. 2002), green coconut shell (Pino *et al*. 2006), groundnut husk (Dubey and Gopal 2007), and peanut shell (Romero *et al*. 2004). Biowaste is a suitable candidate for the preparation of AC because of its underutilization and/or availability in large quantities (Garg *et al*. 2007). Carbonized rice husk has been tested for the removal of metal ions such as Cr(VI), Ni(II), Zn(II), and Cd(II) ions from aqueous streams (Srivastava *et al*. 2007), but most reports do not deal with the choice of AC source, role of surface chemistry, *etc.* There is a need to understand the influence of the surface chemistry of AC on the adsorption capacity. In the present study, AC was prepared from rice husk and it was tested for the removal of Cr(VI) from an aqueous medium. The kinetics of metal ion removal were measured and the thermodynamic parameters were determined.

EXPERIMENTAL METHODS

Preparation of Adsorbents

Rice husk was collected from the Srinivasa Rice Mill (Hyderabad, India), washed with distilled water, and dried overnight at 100 °C. Fifty grams of dried rice husk was mixed with 500 mL of 5M HNO_3 solution and heated at 60 °C for 24 h with continuous stirring. HNO_3-treated rice husk was filtered, washed with distilled water, and dried at 100 °C for 5 h. HNO_3-treated rice wash was carbonized by placing the rice husk in a tubular furnace and heating it at 700 °C for 5 h under a N_2 flow rate of 20 mL/min. After carbonization, the product was allowed to cool in an N_2 atmosphere.

Carbonized acid-treated rice husk (CRH) was then treated with different concentrations of NaOH. For this purpose, 100 mL of 0.5 M NaOH solution was added to 10 g of carbonized rice husk, and this mixture was stirred for 24 h. After the 0.5 M NaOH treatment, the carbonized rice husk was filtered, washed with distilled water until the filtrate was neutral, and dried at 60 °C for 10 h. For identification, 0.5M NaOH-treated rice husk was denoted as CRH0.5M. Similarly, 1 M, 3 M, and 5 M NaOH-treated rice husk was denoted as CRH1M, CRH3M, and CRH5M, respectively.

Characterization of Adsorbents

The specific surface area of NaOH-treated samples was measured with the BET-N_2 adsorption method using a NOVA 2200e (Quantachrome Instruments, Florida, USA). Moisture content was estimated from the weight loss after heating 1 g of the sample in a ceramic crucible at 120 °C, whereas ash content was estimated by burning the sample at 550 °C. The proximate analysis was estimated using the following equations,

$$Moisture\ content\ (\%) = \frac{W_i - W_M}{W_i} \times 100 \qquad (1)$$

$$Ash\ content\ (\%) = \left[\frac{W_i - W_A}{W_i} \times 100\right] - (Moisture\ content(\%)) \qquad (2)$$

$$Carbon\ content\ (\%) = 100 - [(\%\ moisture + \%\ ash\ content)] \qquad (3)$$

where W_i is the initial weight of the sample, W_M is the weight of the sample after the removal of moisture, and W_A is the weight of the final ash.

A temperature programmed decomposition (TPD) study was performed to understand the functional groups formed on the surface of the carbons during chemical treatment. TPD was performed using a Quantachrome gas sorption analyzer (Quantachrome Instruments, Florida, USA), which has both a thermal conductivity detector (TCD) and a quadrapole mass spectrometer (RGA PRIS MA PLUS 200 AMU). For TPD measurements, 0.1 g of the sample was placed in a quartz reactor and purged with helium gas with the appropriate flow rate at room temperature. Later, the sample was heated gradually from room temperature to 900 °C at a heating rate of 10 °C/min in helium flow with simultaneous quantification of CO and CO_2, which indicate the decomposition of acidic and basic groups, respectively (Subrahmanyam *et al*. 2005; Manoj Kumar Reddy *et al*. 2013).

Adsorption Study

The adsorption study was performed during the removal of Cr(VI) from the aqueous medium. A 100-mg/L stock solution of Cr(VI) was prepared by dissolving 0.283 g of $K_2Cr_2O_7$ into 1000 mL of distilled water, and 10 mg/L, 30 mg/L, 50 mg/L, 70 mg/L, and 100 mg/L Cr(VI) test solutions were prepared from the stock solution. A total of 100 mL of each test solution was placed in a 250-mL conical flask containing 0.1 g of NaOH-treated rice husk and stirred at room temperature. The concentration of Cr(VI) was analyzed every 10 min using a UV-Visible spectrophotometer (PG Instruments, Ltd, Leicestershire, UK). The intensity of the Cr(VI)-1,5 diphenylcarbazide complex was measured by estimating the maximum absorbance at 542 nm. For this purpose, 2 mL of 10% H_2SO_4 solution and 2 mL of 0.02 M 1,5-diphenylcarbazide solution were added to 1 mL of Cr(VI) solution and diluted into a 50-mL volumetric flask. The adsorption percentage of Cr(VI) was determined using Eq. 4

$$Adsorption\ (\%) = \frac{C_o - C_t}{C_o} \times 100 \qquad (4)$$

where C_o is the initial concentration of Cr(VI) (mg/L) in the solution and C_t is the concentration of Cr(VI) ions (mg/L) at time t (min). Furthermore, adsorption studies were carried out by varying the adsorbent dosage, temperature, and pH. The pH was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH and read with a digital pH meter (Systronics, Ahmedabad, India).

RESULTS AND DISCUSSION

The physico-chemical characteristics of the CRH, CRH0.5M, CRH1M, CRH3M, and CRH5M samples are summarized in Table 1, which confirmed that surface area increased with NaOH treatment. The surface area of NaOH-treated carbonized rice husk varied from 380 m^2/g to 750 m^2/g on increasing NaOH concentration from 0.5 M to 5 M,

respectively. The proximate analysis of moisture, carbon, and ash contents of carbonized rice husks is shown in Table 2. CRH5M had the highest fixed carbon content and almost no ash content, probably because silica was removed by 5 M NaOH. TPD quantified the surface functional groups that decomposed to give CO_2 and CO (Eq. 5):

$$(-COOH, >CH-OH, >C=O) \longrightarrow CO_2, CO \qquad (5)$$
$$\text{Functional groups}$$

BET Surface Area Analysis

Table 1 lists the BET surface area and porosity characteristics of ACs prepared at different concentrations of NaOH. The textural properties of AC produced from RHs, especially the surface area and pore volumes, significantly improved with increasing concentration of NaOH up to 5 M. At the low concentration, the pore structure was inadequately developed, indicating that only a mild reaction occurred between the char and activating agent. In contrast, at 5 M, the sample showed remarkably improved porosity when compared with the other activation temperatures, with a maximum Brunauer–Emmett–Teller surface area and total pore volume of 750 m^2/g and 0.56 cm^3/g, respectively was obtained.

Table 1. Surface Area and Pore Volume of NaOH-treated Carbonized Rice Husks

Carbonized Rice Husk	BET Surface Area (m^2/g)	Micropore volume (cc/g)	Mesopore volume (cc/g)	Total pore volume (cc/g)
CRH	315	0.18	0.07	0.25
CRH0.5M	380	-	-	-
CRH1M	465	-	-	-
CRH3M	535	0	0.38	0.38
CRH5M (5 h)	570	-	-	-
CRH5M	750	0	0.56	0.56

Table 2. Proximate Analysis of Carbonized Rice Husks

Carbonized Rice Husks	Moisture Content (%)	Carbon Content (%)	Ash Content (%)
CRH	6.8	45	48 .2
CRH0.5M	6.5	79.3	14.2
CRH1M	5.7	83.6	10.7
CRH3M	5	88.0	7.0
CRH5M	4.8	94.6	0.6

The TPD graphs of CRH, H_2O-treated CRH, and CRH5M are shown in Fig. 1(a). For comparison, the H_2O-treated CRH sample was prepared by passing H_2O vapors along with N_2 gas through the tubular furnace containing CRH at 700 °C for 1 h. The mass spectra of the CO and CO_2 liberated during the TPD of CRH5M are shown in Fig. 1(b). The total gases liberated (quantified by TCD) and individual CO and CO_2 gases (measured by mass spectrometer) are summarized in Table 3. The total gas evolution by CRH was 215 μmol/g, which was consistent with the values for individual CO (180 μmol/g) and CO_2 (45 μmol/g). Similarly, CRH5M showed the highest gas liberation (970 μmol/g), out of which 615 μmol/g was CO and 410 μmol/g was CO_2. The TPD value of H_2O-treated CRH was slightly higher than that of CRH, but less than that of CRH5M due to additional functional groups created from the presence of H_2O.

Table 3. CO and CO_2 Quantification by TPD

Sample	CO (μmol/g)	CO_2 (μmol/g)	Total (μmol/g)
CRH	180	45	215
H_2O-treated CRH	385	11	390
CRH5M	615	410	970
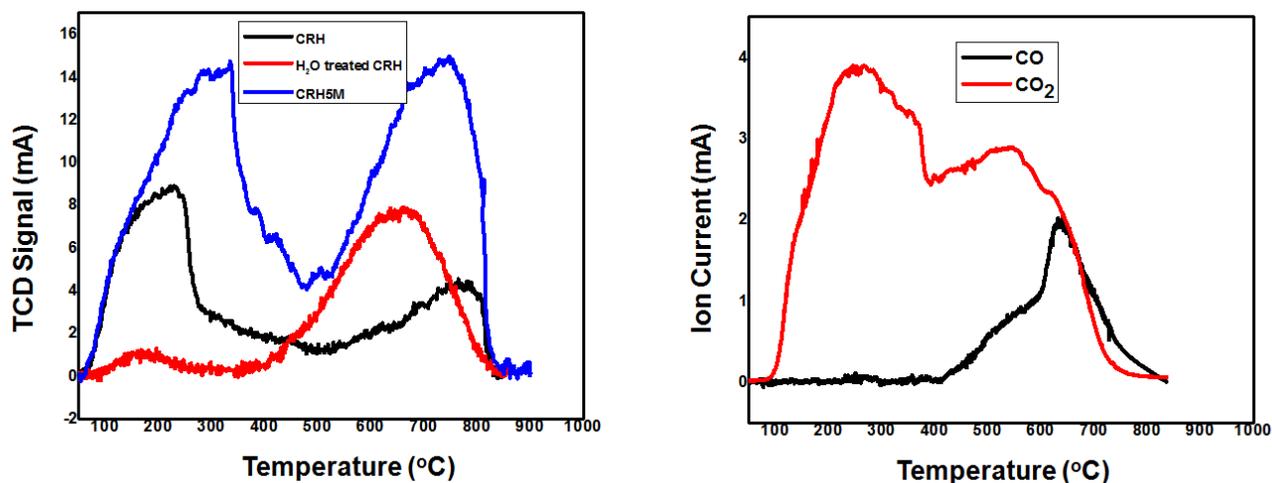
Fig. 1. (a) Temperature programmed decomposition of CRH, H_2O-treated CRH, and CRH5M; (b) mass spectra of CO and CO_2 gases evolved by CRH5M

SEM

Figure 2 shows the scanning electron microscopy (SEM) micrographs of ACs prepared at different concentrations of NaOH. SEM micrographs of (a) carbonized rice husk (CRH), showing the more silica content, (b) a magnified image of Fig. 2(a) showing that silica was present in the CRH, (c) an image showing that 3M NaOH treatment of RH (CRH3M) removes all of the silica present in the CRH, and (d) CRH 5M showing more pores inside the carbon.

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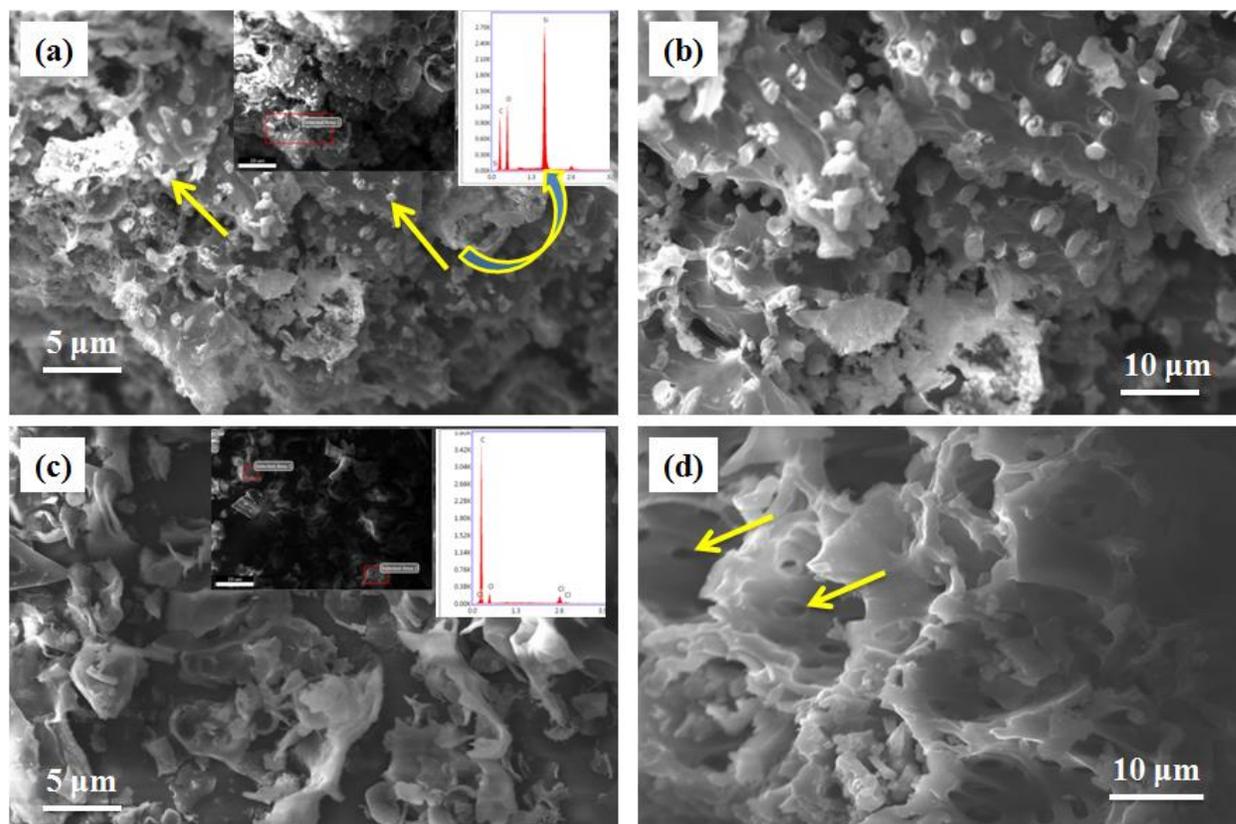
Fig. 2. Scanning electron microscopy (SEM) micrographs of (a) carbonized rice husk (CRH), showing the more silica content (shown by EDAX spectrum) (b) magnified image of Fig. 2(a), (c) 3M NaOH treated RH (CRH3M) has removed whole silica present in the CRH (no Si peak in the EDAX spectrum), and (d) CRH 5M showing more pores inside the carbon (indicated by arrows).

FTIR

FT-IR spectra were recorded for qualitative identification of surface functional groups formed during the activation. The spectra of activated carbons indicating considerable amounts of carboxyl groups, as shown in Fig. 3.
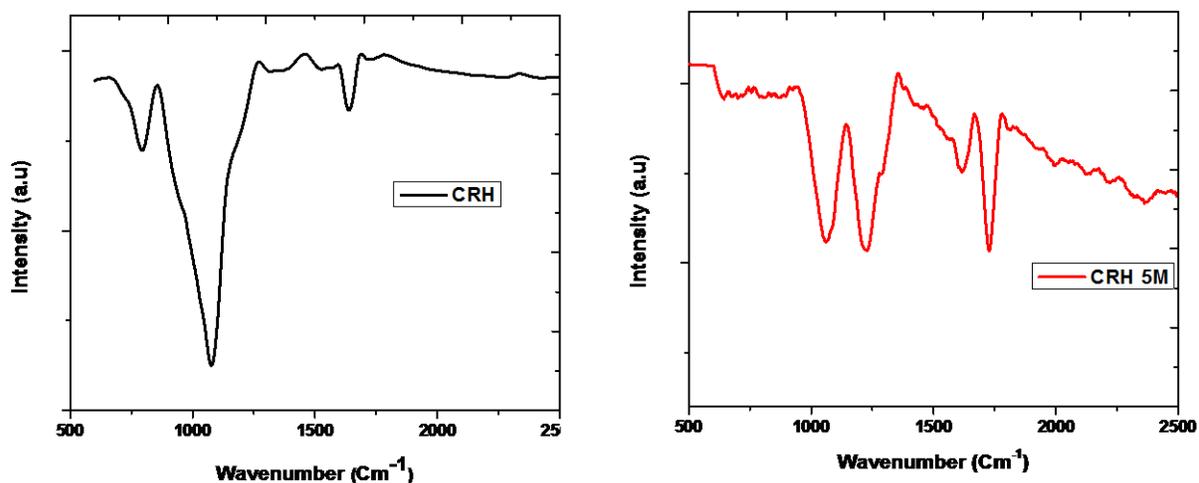
Fig. 3. FT-IR spectrum of CRH and CRH 5M

For CRH the peak around 1095 cm^{-1} is due to Si–O-Si asymmetric stretching vibration. The peak at 967 cm^{-1} is due to Si–OH stretching vibration. The peaks appearing at 819 cm^{-1} are due to Si–O–Si symmetric stretching and the band at 1640 cm^{-1} due to O-H bending vibration (Rahim *et al.* 2015). FTIR spectra of CRH 5M shows carbonyl C=O (1719 cm^{-1}), aromatic C=C (1620 cm^{-1}), carboxyl O=C-O (1356 cm^{-1}), epoxy C-O (1217 cm^{-1}), and alkoxy C-O (1049 cm^{-1}) stretching vibrational modes.

Cr(VI) adsorption changed as a function of time on SiO$_2$ (CRH ash), CRH, CRH1M, CRH3M, and CRH5M (Fig. 4). Because CRH5M showed the highest adsorption capacity, it was chosen for subsequent experiments varying Cr(VI) concentration, adsorbent dosage, and pH.
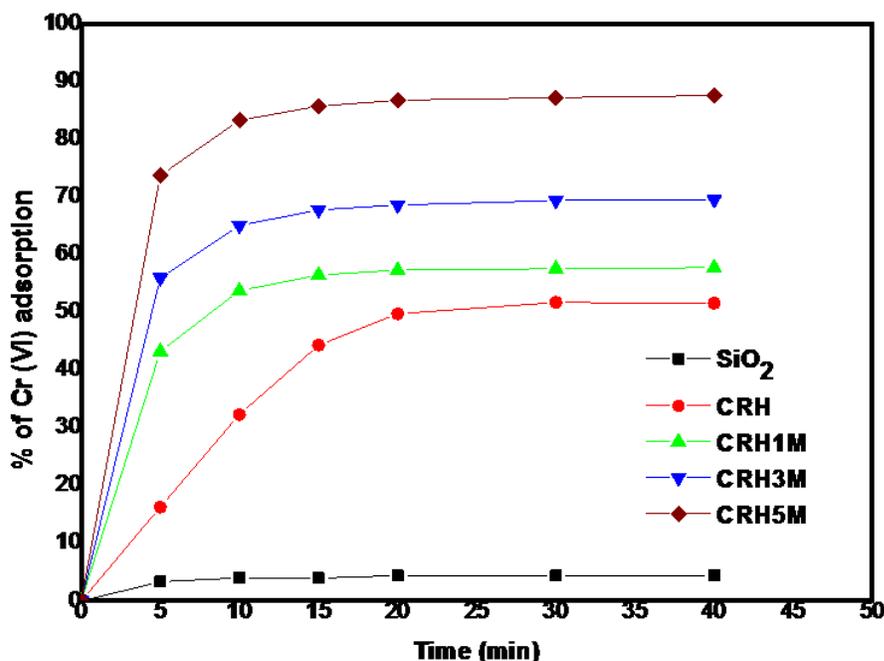
Fig. 4. Effect of Cr(VI) adsorption percentage on differently treated carbonized rice husks. Conditions: 1 g carbonized rice husk and 100 mL 10-mg/L Cr(VI) solution
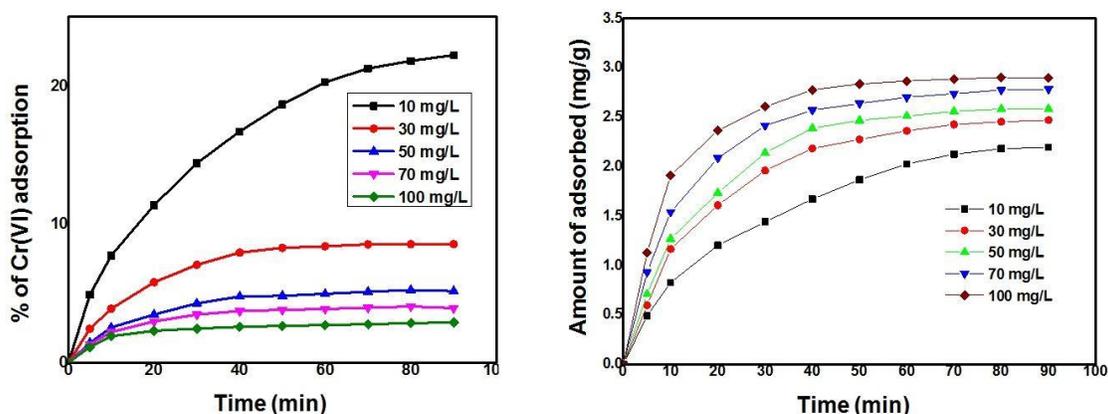
Fig. 5. (a) Efficiency of Cr(VI) adsorption and (b) amount of Cr(VI) adsorbed onto CRH5M with different concentrations of Cr(VI) solution, using 0.1 g of carbonized rice husk and 100 mL of Cr(VI) solution

Cr(VI) adsorption and the adsorption capacity of CRH5M for different Cr(VI) concentrations are shown in Fig. 5. The adsorption of Cr(VI) by CRH5M increased with time reaching equilibrium at 90 min. The removal of Cr(VI) depends on Cr(VI) initial concentration. By changing the initial concentration from 10 mg/L to 100 mg/L, the adsorption percentage decreased from 22.5% to 3%, whereas the adsorption capacity of CRH5M increased from 2.25 mg/g to 3 mg/g after 90 min. The adsorbent dosage also affected Cr(VI) removal efficiency (Fig. 6). When the amount of adsorbent increased from 100 mg to 400 mg, the percentage of Cr(VI) adsorption efficiency also increased from 22.5% to 39% within 90 min.
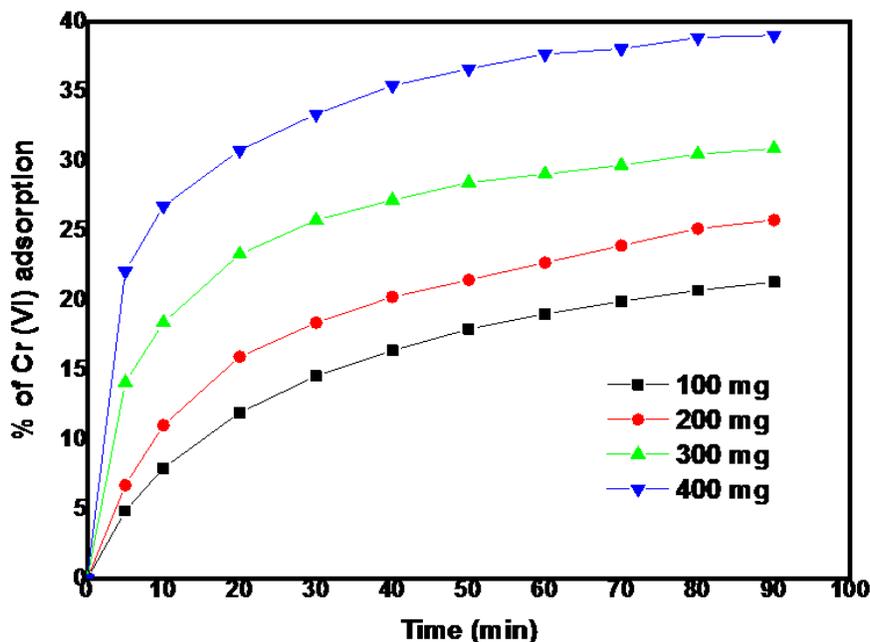
Fig. 6. Efficiency of Cr(VI) adsorption using different amounts of CRH5M and 100 mL of 10 mg/L Cr(VI) solution

The pH of the test solution is an important factor governing adsorption capacity, as it alters the surface chemistry of the adsorbent. The adsorption behaviour of CRH5M was studied in the pH range 2 to 10 (Fig. 7(a)). Because 100 ppm Cr(VI) solution is acidic (pH 4.4), the pH of pure water was adjusted to 4.4, which increased to 5.4 with the addition of 0.1 g of adsorbent. Under the same experimental conditions, the pH of 100 ppm of the Cr(VI) solution increased only to 4.8 with the addition of CRH5M. A positively charged surface has a higher adsorption capacity for $HCrO_4^-$ than for $Cr_2O_7^{2-}$ (Dean and Tobin 1999; Rodrigues *et al*. 2010).

For CRH5M, the decrease in pH was not significant, and the adsorption of Cr(VI) ions was higher. Similarly, the adsorption of Cr(VI) ions at pH 8 was lower compared with the adsorption at pH 4 because of the presence of more hydroxide ions, which block the CrO_4^{2-} species from adsorbing onto the surface of the adsorbent. The effect of pH during the adsorption of Cr(VI) is shown in Fig. 7(b). As the pH decreased from 4.4 to 2, the adsorption capacity increased from 3 mg/g to 25.2 mg/g; under basic conditions at pH 10, the adsorption of Cr(VI) ions decreased to 1.2 mg/g.
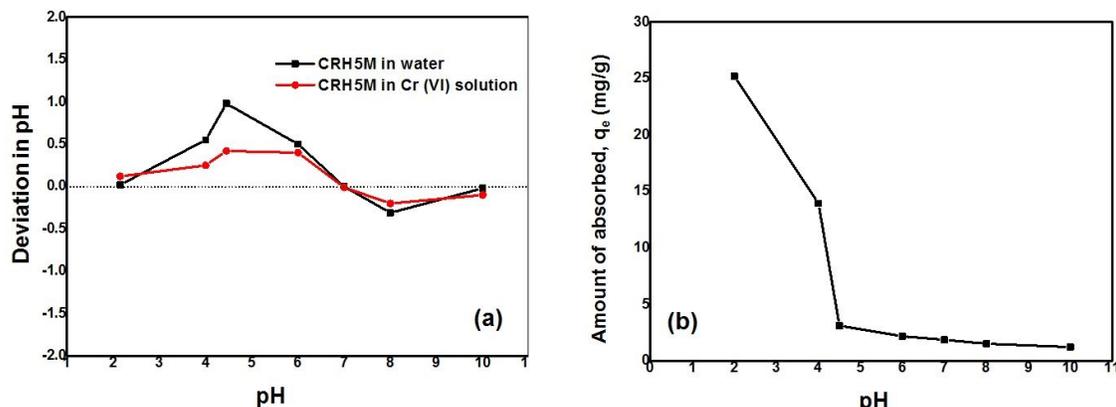
Fig. 7. (a) Change in pH with the addition of CRH5M in water and Cr(VI) solution; (b) amount of Cr(VI) adsorbed with varying pH values of the solution

Table 4. Comparison of Adsorption Capacities of the Adsorbents for the Removal of Cr(VI) with those of other Adsorbents

S.No	Adsorbent	Adsorption Capacities (mg/g)	Reference
01	Almond	10.62	Dakiky *et al.* 2002
02	Hazelnut shell	17.70	Cimino *et al.* 2000
03	Paper mill sludge	7.40	Calace *et al.* 2002
04	Coal	6.78	Dakiky *et al.* 2002
05	Pine needles Almond	21.50	Dakiky *et al.* 2002
06	Sago waste activated carbon	5.78	Vennilamani *et al.* 2005
07	Saw dust	15.82	Dakiky *et al.* 2002
08	Fly ash	23.86	Bhattacharya *et al.* 2008
09	Saw dust	20.70	Bhattacharya *et al.* 2008
10	Neem bark	19.60	Bhattacharya *et al.* 2008
11	Rice husk ash	25.64	Bhattacharya *et al.* 2008
12	walnut hull	24.00	Wang *et al.* 2009
13	Rice husk carbon (5M NaOH)	25.2	Present study

In order to understand the mechanism of adsorption on CRH5M, the experimental data for various concentrations of Cr(VI) was fit into several kinetic models, including first-order (Hossain *et al.* 2005), pseudo-first-order (Annadurai *et al.* 2002), second-order (Sparks 1989), and pseudo-second-order models (Rengaraj *et al.* 2003) (Fig. 8). The data did not fit well into first, pseudo-first, or second-order rate expressions, but the coefficient of determination (R^2) value of the pseudo-second-order model was nearly 1 (Table 5). Hence, the adsorption of Cr(VI) by carbonized NaOH-treated rice husk displayed pseudo-second-order kinetic behavior.

Table 5. Comparison of Adsorption Kinetic Models

Concentration (mg/L)	Coefficient of Determination (R^2)			
	First-order	Pseudo-first-order	Second-order	Pseudo-second-order
10	0.93801	0.97206	0.95443	0.99834
30	0.74919	0.96774	0.75627	0.99996
50	0.7502	0.97654	0.75488	0.99998
70	0.68993	0.9804	0.69201	1
100	0.64235	0.96024	0.64563	1
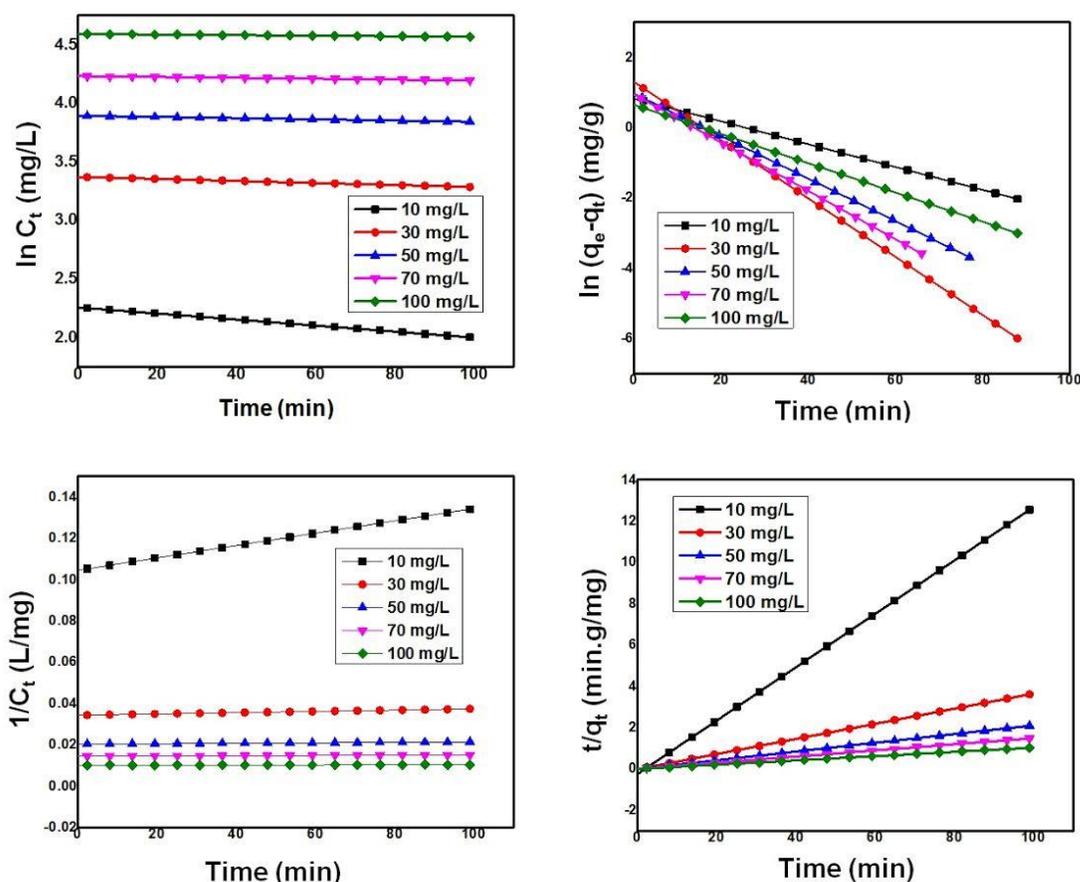
Fig. 8. Plots of (a) first-order, (b) pseudo-first-order, (c) second-order, and (d) pseudo-second-order adsorption kinetics of Cr(VI) on CRH5M with different initial concentrations

Thermodynamic parameters determine the nature of Cr(VI) adsorption on the adsorbent. The change in Gibb's free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS) were calculated using the following expressions (Ramaraju *et al*. 2014),

$$K_d = q_e/C_e \tag{6}$$

$$\Delta G = - RT\, ln\, K_d \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

where K_d is the distribution constant, q_e is the amount adsorbed at equilibrium (mg/g), C_e is the concentration of Cr(VI) in solution at equilibrium (mg/L), R (8.314 J/mol·K) is the universal gas constant, and T (K) is the absolute temperature.

To determine thermodynamic parameters, the adsorption capacity of Cr(VI) was followed on CRH5M at different temperatures, and the percentage of Cr(VI) adsorption *vs.* time was plotted (Fig. 9). The pseudo-second-order plot for different temperatures is shown in Fig. 10, and the reciprocal slope of each curve determined the amount adsorbed at equilibrium (q_e). The free energy changes at different temperatures are summarized in Table 6. The negative values of ΔG from -2.705 kJ/mol (25 °C) to -0.905 kJ/mol (55 °C) indicated the spontaneity of the Cr(VI) adsorption on CRH5M. The intercept and slope of

the ΔG *vs.* T plot (Fig. 11; Table 6) provided the values of ΔH and ΔS, respectively (-24.2 kJ/mol and -71.2 J/mol·K, respectively). These values confirmed that Cr(VI) adsorption on CRH5M is spontaneous, exothermic, and is favorable at low temperatures.
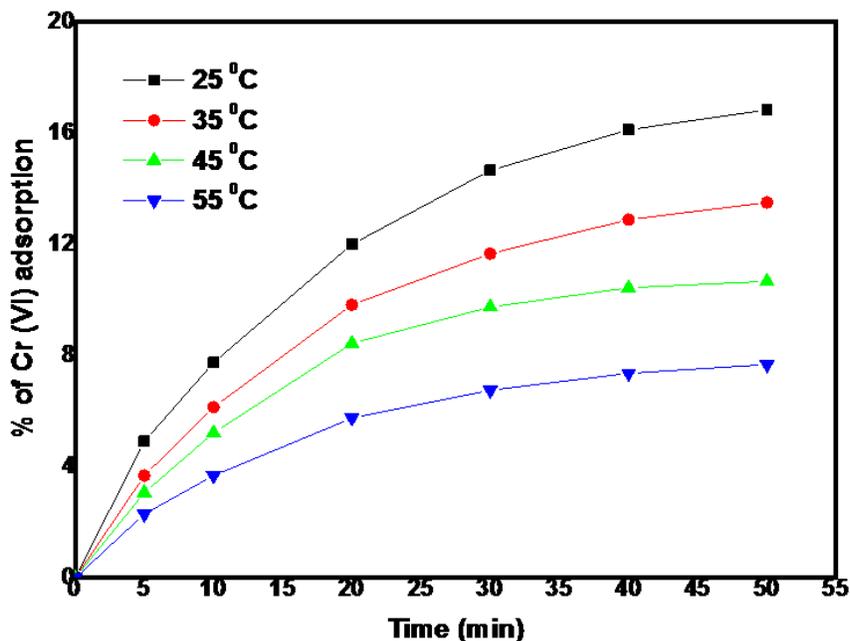
Fig. 9. Effect of Cr(VI) adsorption percentage on CRH5M at different temperatures, using 0.1 g of carbonized rice husks and 100 mL of 10 mg/L Cr(VI) solution
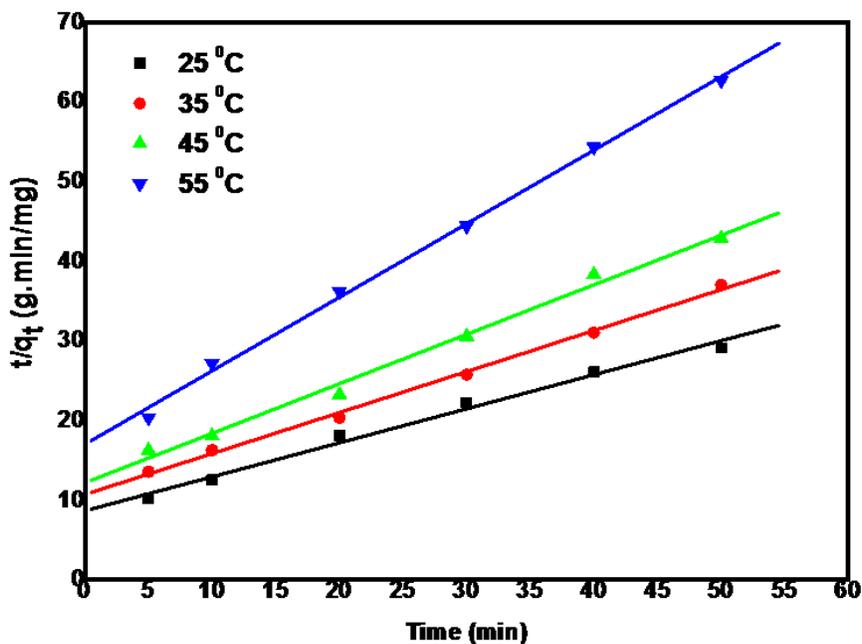
Fig. 10. Pseudo-second-order adsorption kinetics of Cr(VI) on CRH5M at different temperatures
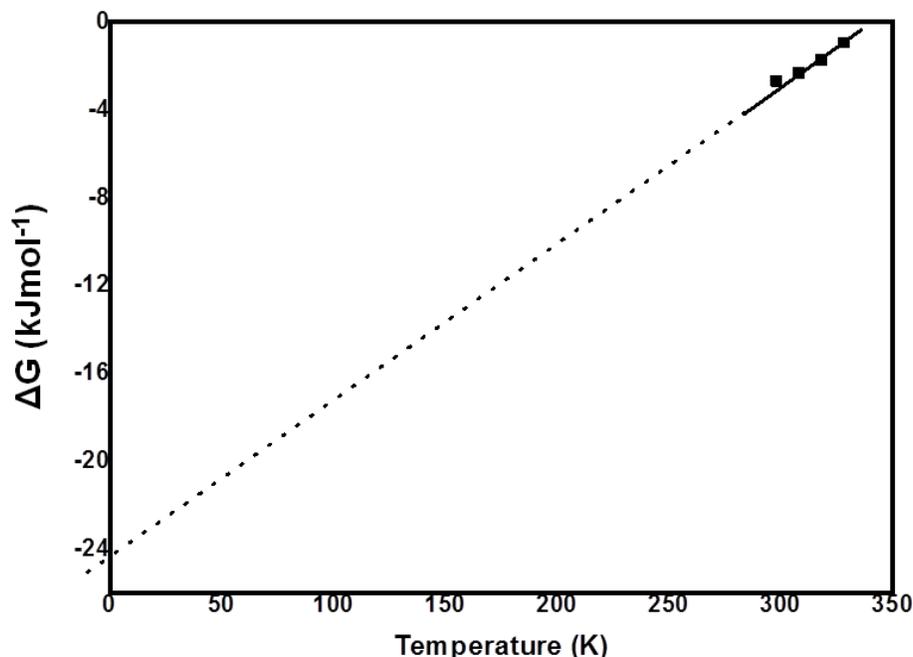
Fig. 11. ΔG *versus* T-plot of Cr(VI) adsorption on CRH5M with 100 mL of 10-mg/L concentration

Table 5. Thermodynamic Parameters of Cr(VI) Adsorption

Temperature (°C)	q_e (mol/g)	C_e (mol/L)	$K_d = q_e/C_e$	$\Delta G = -RT\ln K_d$ (kJ/mol)
25	4.41×10^{-4}	1.48×10^{-4}	2.98	−2.705
35	3.81×10^{-4}	1.54×10^{-4}	2.47	−2.315
45	3.10×10^{-4}	1.61×10^{-4}	1.92	−1.724
55	2.44×10^{-4}	1.71×10^{-4}	1.42	−0.956

Table 6. Change in Enthalpy (ΔH) and Entropy (ΔS) for Cr(VI) Adsorption

Sample	ΔS (J/mol·K)	ΔH (kJ/mol)
CRH5M	−71.2	−24.2

CONCLUSIONS

1. Rice husk was used to prepare activated carbon with a high surface area and treated sample was found to be effective in treating water contaminated by hexavalent chromium.

2. Sodium hydroxide treatment was crucial in order to obtain a high surface area AC. An increase in surface area as a consequence of alkali treatment is due to removal of SiO_2 and NaOH-treated carbonized rice husk showed the best performance during the removal of aqueous Cr(VI).

3. Increasing concentrations of Cr(VI) increased the adsorption efficiency. In a similar manner, increasing the adsorbent dosage increases Cr(VI) adsorption because of the availability of more surface active sites.

4. Acidic pH favors the best adsorption of Cr(VI). The adsorption of Cr(VI) on carbonized rice husk follows pseudo-second-order kinetics, whereas thermodynamic studies indicated the spontaneity and exothermic nature of the adsorption process.

ACKNOWLEDGMENTS

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