



A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons

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ABSTRACT

This paper reports the feasibility of using agricultural waste and timber industry waste carbons to remove Cr(VI) from synthetic wastewater under different experimental conditions. For this, rice husk and saw dust have been used as adsorbent after sulphuric acid treatment. Effect of various process parameters, namely, pH, adsorbent dose, initial chromium concentration and contact time has been studied in batch systems. Maximum metal removal was observed at pH 2.0. The efficiencies of rice husk carbon (RHC) and saw dust carbon (SDC) for Cr(VI) removal were 91.75% and 94.33%, respectively for aqueous solutions (250 mg L⁻¹) at 20 g L⁻¹ adsorbent dose. The experimental data was analyzed using Freundlich, Langmuir, Dubinin–Redushkevich (D–R) and Temkin isotherm models. It was found that Langmuir, D–R and Temkin models fitted well. The results revealed that the hexavalent chromium is considerably adsorbed on RHC and SDC and it could be an economical method for the removal of hexavalent chromium from aqueous systems. FTIR and SEM of the adsorbents were recorded in native and Cr(VI)-loaded state to explore the number and position of various functional groups available for Cr(VI) binding onto studied adsorbents and changes in adsorbent surface morphology. The surface area of RHC and SDC was 1.12 and 1.16 m² g⁻¹, respectively.

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1. Introduction

Growing attention is being given to health hazards caused by the existence of heavy metals in the aqueous environment and their accumulation in living tissues poses a serious health problem. Hexavalent chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [1]. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries, inorganic chemicals production, etc. [2]. Chromium is one of the contaminants which exist in hexavalent and trivalent forms. Hexavalent form is more toxic than trivalent and requires more concern. Strong exposure to Cr(VI) may cause epigastric pain, nausea, vomiting, severe diarrhoea, haemorrhage and cancer in the digestive tract and lungs [3]. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg L⁻¹ and in potable water is 0.05 mg L⁻¹ [4,5]. It is therefore essential to remove Cr(VI) from wastewater before disposal. In wastewater treatment, various methods applied to remove chromium include chemical precipitation [6], ion exchange [7],

electrochemical precipitation [8], reduction [9], adsorption [10], solvent extraction [11], membrane separation [12], concentration [13], evaporation, reverse osmosis and biosorption [14–16]. However, most of these processes have considerable disadvantages, such as, incomplete metal removal, expensive equipment, regular monitoring system, reagent or energy requirements or producing toxic sludge or other disposal waste products [17–19]. Adsorption onto activated carbon (granular or powdered) has been reported to be an important technology for the removal of toxic pollutants from wastewaters, but it is too expensive. So there is a need to develop low cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment. Several types of biomasses have been investigated for their use in wastewater treatment for chromium removal. The various biomasses tested in past include raw rice bran [20], ethylenediamine-modified rice hull [21], coconut husk fibers [22], hazelnut shell [23], saw dust, sugar beet pulp, maize cob, sugarcane baggase [24], coniferous leaves [25], pine needles, olive cake, wool, almond, soya cake [26], maple saw dust [27], saw dust activated carbon [28] and sugarcane bagasse [29], etc. The biosorption efficiency of these adsorbents is given in Table 1. The authors have found that in most of the reported studies, biosorbents have not been characterised, whereas it is essential to characterise the adsorbent to have the repeatability of the results. So, further studies on biosorption are still needed.

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Table 1
Adsorption capacity of different biomasses for Cr(VI) removal from aqueous systems.

Biomass	Adsorption capacity (mg g ⁻¹)	pH	Reference
Raw rice bran	0.07	5.0	[20]
Ethylenediamine-modified rice hull	23.40	2.0	[21]
Coconut husk fibers	29.0	2.0	[22]
Hazelnut shell	170	1.0	[23]
Saw dust	39.7	2.0	[24]
Sugar beet pulp	17.2	2.0	
Maize cob	13.8	1.5	
Sugarcane baggase	13.4	2.0	
Coniferous leaves	6.3	3.0	[25]
Pine needles	21.5	2.0	[26]
Olive cake	33.4		
Wool	41.2		
Almond	10.6		
Soya cake	0.00028		
Maple saw dust	5.1	6.0	[27]
Saw dust activated carbon	65.8	2.0	[28]
Sugarcane bagasse	103	3.0	[29]

Present work was planned to develop new activated carbons from rice husk and saw dust and evaluate their capacity to remove Cr(VI) from different aqueous solutions. Batch adsorption process has been used to evaluate the maximum adsorption capacity of two carbons produced from rice husk and saw dust. The main process parameters considered were pH, initial Cr(VI) concentration, adsorbent dose and contact time.

2. Materials and methods

2.1. Preparation of adsorbents

Rice husk and saw dust used in the study were procured from local rice mill and saw mill, respectively located at Kurukshehra (Haryana). The collected rice husk/saw dust was dried under sun and impurities were separated manually. Dried rice husk and saw dust were washed with deionized water until all leachable impurities were removed. The samples were then treated with H₂SO₄ (50%) in a ratio of 2:1 (acid volume:weight of rice husk/saw dust) and allowed to get carbonized at 150 °C in hot air oven for 24 h and soaked with deionized water until solution pH was stable. Afterwards, the carbon so obtained was soaked in 2% NaHCO₃ (w/v) till any residual acid left was removed. Finally, the samples were dried in hot air oven at 110 °C, cooled, ground and sieved in the size of 300 μm and stored in airtight containers for further use [30]. FTIR spectra of native and chromium-loaded adsorbents were recorded on Fourier transform infrared spectrum (FTIR, FTIR-8400S, Shimadzu, Japan). The surface morphology of the adsorbents was visualized via scanning electron microscope (SEM) [model Quanta 200 FEG, FEI, Netherlands]. Surface area of the adsorbents was determined using surface area analyzer (Micro Meritics, Chemisorb-2720). The particle size was in the range of 1–300 μm.

2.2. Preparation and testing of synthetic wastewater

Aqueous solution of chromium (1000 mg L⁻¹) was prepared by dissolving potassium dichromate (AR grade) in double distilled water. The aqueous solution was diluted with distilled water to obtain the Cr(VI) synthetic wastewater of desired concentrations. pH of the solutions was adjusted using 0.01 M NaOH/HCl using pH meter (Model pHep, Hanna Instruments, calibrated with buffers of pH 4.0, 7.0 and 9.2). The Cr(VI) concentration was determined by Atomic Absorption spectrophotometer (Shimadzu 6300, Japan).

Table 2
FTIR spectra of untreated and Cr(VI) treated adsorbents.

Adsorbents	O–H	C–H	C=O	–CH ₃	Bending vibrations
RHC (native)	3629.78	3039.6	1664.45	1330.79	649.97, 798.47
RHC–Cr(VI)	3643.28	3047.32	1658.67	–	742.54, 792.69
SDC (native)	3460.06	2941.24	1587.31	1350.08	669.25, 763.76
SDC–Cr(VI)	3639.43	–	1658.75	–	721.33, 800.4

2.3. Adsorption experiments

Batch experiments were carried out at various pH (2–7), adsorbent dose (4–20 g L⁻¹) and stirring speed (180 rpm) for a contact time of 180 min. For each batch experiment, 100 ml Cr(VI) solution of 250 mg L⁻¹ concentration was used. After adding adsorbent pH was adjusted to desired value and the mixture was agitated on orbital shaker for 180 min at predetermined temperature. After that the mixture was filtered to separate the adsorbent from supernatant. The residual concentration of chromium in supernatant was determined as stated in Section 2.2. All experiments were replicated thrice and results were averaged.

The removal percentage (*R*(%)) of chromium was calculated for each run by using Eq. (1):

$$R(\%) = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \quad (1)$$

where *C_i* and *C_e* were the initial and final concentration of chromium in the solution. The adsorption capacity (*q_e*) of an adsorbent, which is obtained from the mass balance on the sorbate in a system with solution volume *V*, is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of Cr(VI) ions at equilibrium were calculated using Eq. (2):

$$q_e (\text{mg g}^{-1}) = \left[\frac{C_i - C_e}{M} \right] \times V \quad (2)$$

where *C_i* and *C_e* were the initial and final concentration of chromium (mg L⁻¹) in the test solution, respectively. *V* is the volume of solution (L) and *M* is the mass of adsorbent (g) used.

3. Results and discussion

3.1. Fourier transform infrared analysis of adsorbents

Fourier transform infrared (FTIR) was used to determine the changes in vibration frequency in the functional groups of the adsorbents due to metal sorption. The spectra of the dry adsorbents were measured within a range of 500–4000 cm⁻¹. The FTIR spectra of native and metal loaded rice husk carbon (RHC) and saw dust carbon (SDC) adsorbents are given in Fig. 1a–d). The FTIR spectra reveal complex nature of the adsorbents as evidenced by the presence of a large number of peaks. Table 2 presents the fundamental peaks of all the adsorbents before and after use. In native RHC an absorption peak around 3629.78 cm⁻¹ indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed at 3039.6 cm⁻¹ can be assigned to stretching vibration of the C–H group. The peaks around 1664.45 cm⁻¹ corresponds to the C=O stretching that may be attributed to the lignin aromatic groups (Fig. 1a). The additional peak at 649.97, and 798.47 cm⁻¹ can be assigned to bending modes of aromatic compounds. The C=O absorption peak shifted to 1658.67 cm⁻¹ when RHC is loaded with Cr(VI) (Fig. 1b). Similarly there are shifts in other peaks also which indicate the participation of these groups in metal binding. In native SDC (Fig. 1c), a broad adsorption band has been observed around 3460.06 cm⁻¹ which can be attributed to the bonded –OH groups present in the structure. The other prominent peaks are due

to C–H, C=O and –CH₃ (2941.24, 1587.31 and 1350.08 cm⁻¹, respectively) groups. The additional peak at 669.25, and 763.76 cm⁻¹ can be assigned to bending modes of aromatic compounds. However in case of Cr(VI)-loaded SDC (Fig. 1d), there is remarkable shift in positions of –OH and C=O group peaks indicating Cr(VI) binding mostly with –OH and C=O groups. It has been reported by Basha et al. [31] that during biosorption of hexavalent chromium by *Cystoseira indica*, –OH and C=O groups bind with hexavalent chromium. Similarly the bending modes of aromatics have also shifted, indicative

of association with the aromatic ring. The changes in FTIR spectra confirm the complexation of Cr(VI) with functional groups present in the adsorbents.

3.2. Scanning electron microscopy

The SEM enables the direct observation of the surface microstructures of different adsorbents. Studies are available which have reported the utilization of the scanning electron microscopy

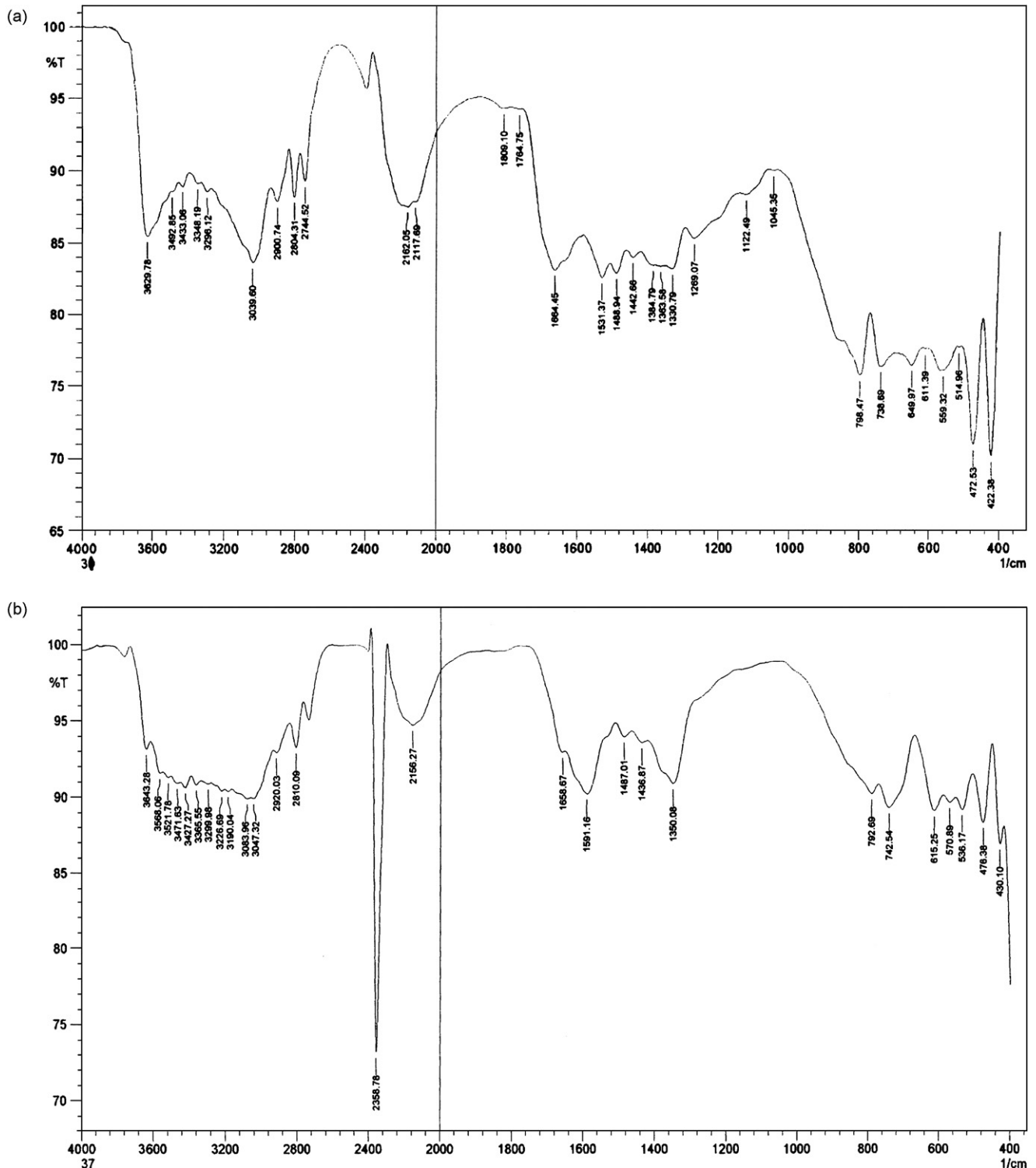


Fig. 1. (a) FTIR spectra of native RHC, (b) FTIR spectra of Cr(VI)-loaded RHC, (c) FTIR spectra of native SDC, and (d) FTIR spectra of Cr(VI)-loaded SDC.

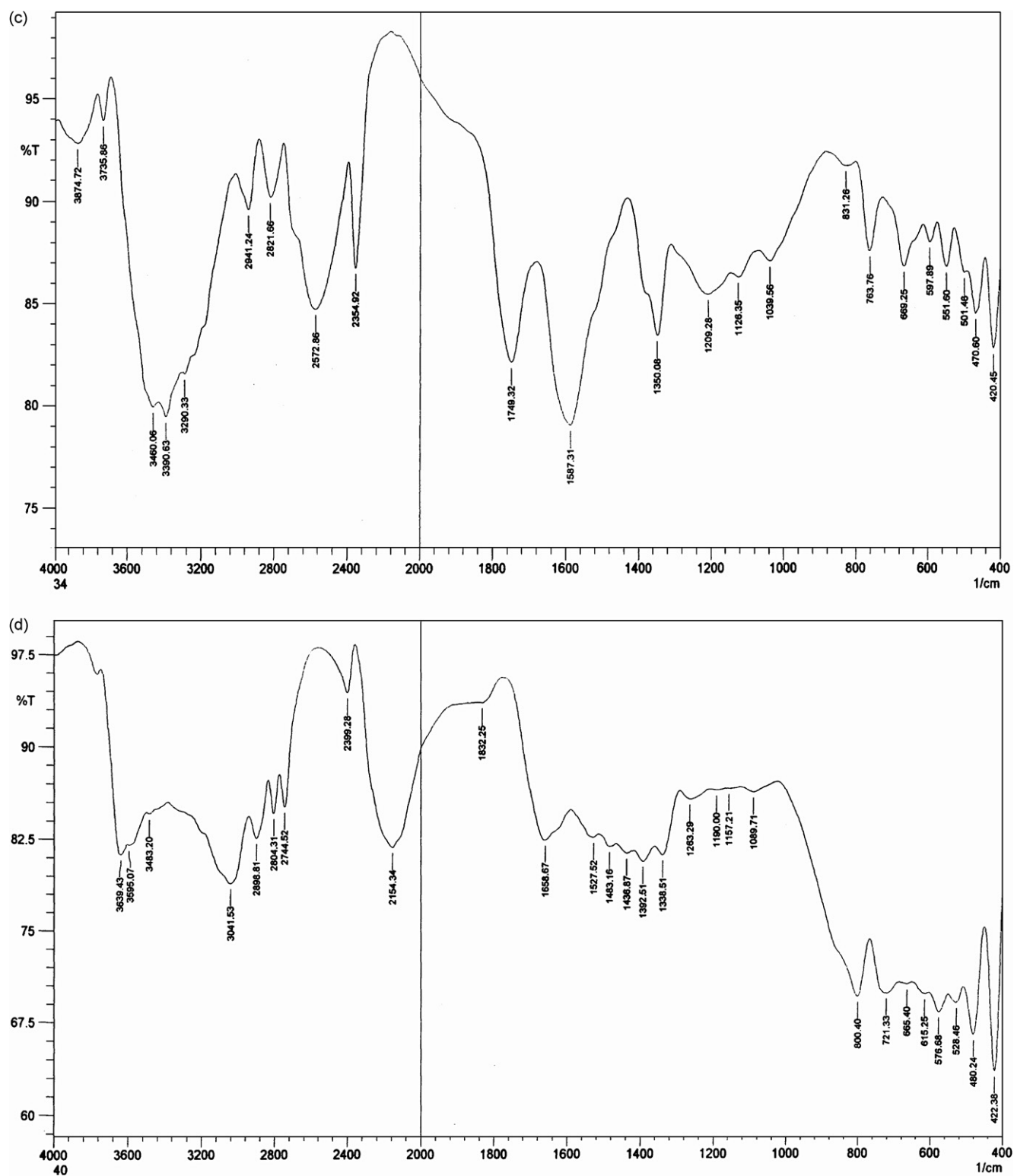


Fig. 1. (Continued).

analysis for showing morphology of different adsorbent. SEM micrographs obtained before and after Cr(VI) adsorption onto RHC (Fig. 2a and b) and SDC (Fig. 3a and b) are given. The sulphuric acid treated biosorbents (RHC and SDC) have porous structure with greater homogeneity, which can be clearly seen in the magnified view of the scanning electron micrograph (Figs. 2a and 3a). The SEMs illustrated in Figs. 2b and 3b clearly indicate the presence of

hexavalent chromium ions in the form of new shiny bulky particles and layer over the surface of metal loaded biosorbents which are not seen in the native biosorbents. Further, the porousness is also lesser in the metal loaded biosorbents.

The surface area of a porous material is one of the most useful microstructural parameters for defining its properties. The specific surface area of the RHC was $1.12 \text{ m}^2 \text{ g}^{-1}$ and SDC was $1.16 \text{ m}^2 \text{ g}^{-1}$.

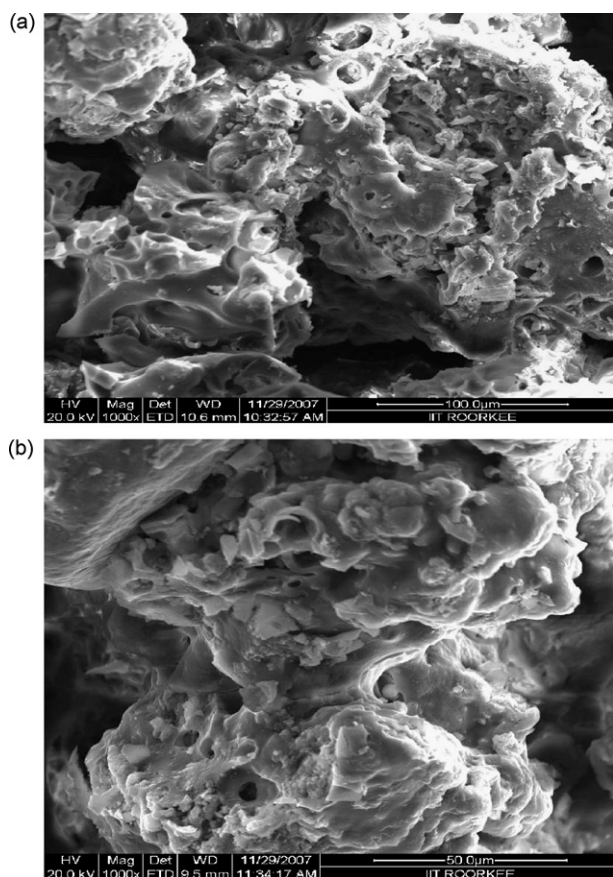


Fig. 2. (a) SEM of native RHC and (b) SEM of Cr(VI)-loaded RHC.

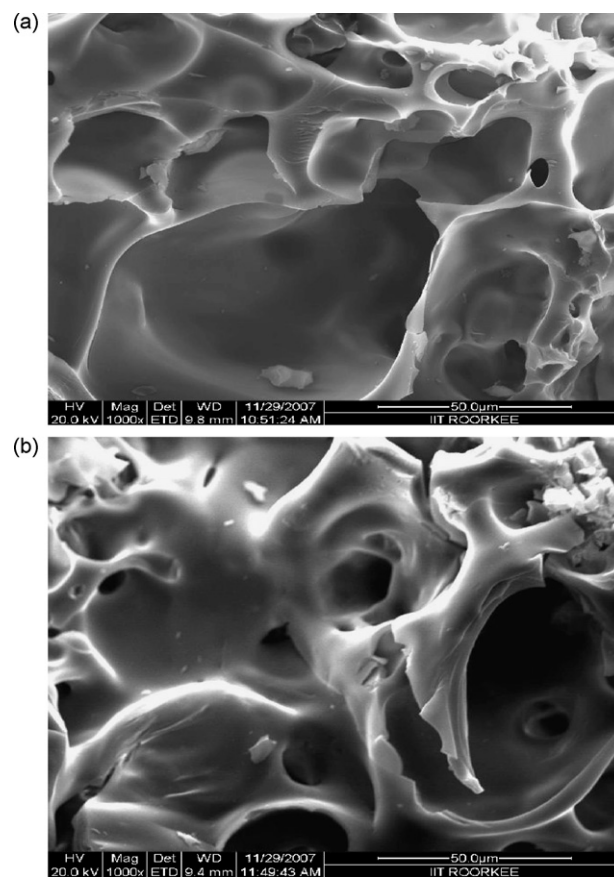


Fig. 3. (a) SEM of native SDC and (b) SEM of Cr(VI)-loaded SDC.

Other authors have also reported the surface areas of different biomasses in this range.

3.3. Effect of pH on Cr(VI) removal

Hexavalent chromium removal by the RHC and SDC adsorbents was found to be pH-dependent as shown in Fig. 4. Equilibrium chromium sorption was favoured by acidic pH range of 2–3 and maximum adsorption was observed at pH 2.0. Increase in pH resulted in the decrease of chromium adsorption by both adsorbents. Cr(VI) exists as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ in solution at optimum sorption pH [32–34]. The dominant form of hexavalent chromium at acidic pH is HCrO_4^- which arises from the hydrolysis reaction of the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) and with increasing pH will shift the concentration of HCrO_4^- to $\text{Cr}_2\text{O}_7^{2-}$ and other forms as CrO_4^{2-} . At initial pH of 2.0, the adsorbent surfaces might be highly protonated which favour the uptake Cr(VI) in the predominant anionic form (HCrO_4^-). Maximum biosorption at pH 2.0 indicates that chromium in solution is present in HCrO_4^- form. Maximum Cr(VI) removal at pH 2.0 (76.63% by RHC and 84.95% by SDC) and hence it was taken as the optimal value for further adsorption studies.

3.4. Effect of adsorbent dose with contact time

The removal of Cr(VI) by RHC and SDC was studied by varying the adsorbent doses (0.4, 0.8, 1.2, 1.6, 2.0 g 100 ml⁻¹) in aqueous system, while keeping initial Cr(VI) concentration (250 mg L⁻¹), temperature (26 °C) and pH (2) constant at predetermined contact times varying from 10 to 180 min. Measurement of Cr(VI) removal percentage as a function of time at different doses indicates that removal of Cr(VI) increased with increasing adsorbent doses for

both RHC and SDC (Fig. 5a and b). The adsorption increased from 76.63% to 91.75% in case of RHC while in SDC, it increased from 84.95% to 94.33% as dose increased from 0.4 to 2.0 g 100 ml⁻¹. Maximum Cr(VI) removal was achieved within 120 min after which Cr(VI) concentration in the test solution became constant. This can be explained due to the fact that higher the dose of adsorbent in the solution, greater the availability of exchangeable sites for metal ions and greater the surface area. However, uptake capacity showed a reverse trend, as it is a measure of the amount of Cr(VI) ions bound by unit weight of adsorbent and therefore, its magnitude decreased with increment in adsorbent dose 4–20 g L⁻¹. Adsorption capac-

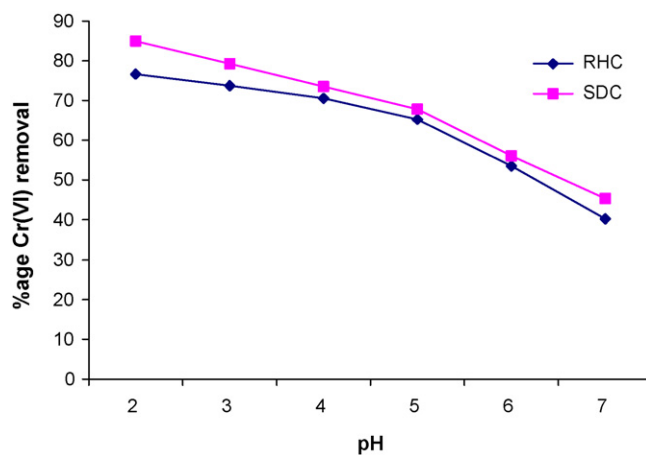


Fig. 4. Effect of pH on Cr(VI) removal by RHC and SDC [Cr(VI) conc. = 250 mg L⁻¹; adsorbent dose = 4 g L⁻¹; contact time = 180 min; stirring speed = 180 rpm; temp. = 25 °C].

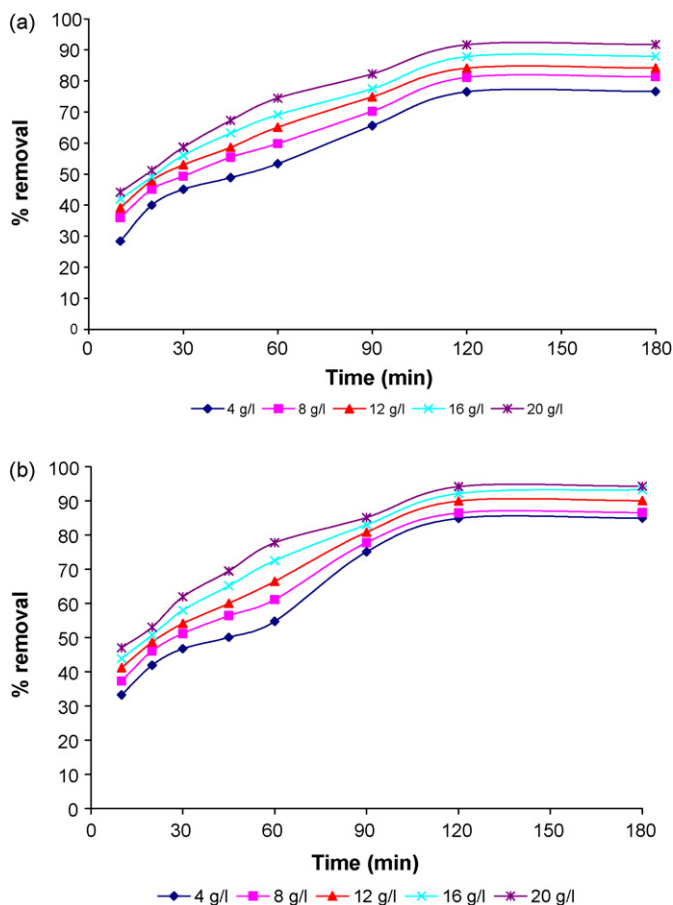


Fig. 5. (a) Effect of adsorbent dose with contact time on Cr(VI) removal by RHC and (b) effect of adsorbent dose with contact time on Cr(VI) removal by SDC.

ity was decreased from 47.89 to 11.47 mg g^{-1} for RHC and 53.09 to 11.79 mg g^{-1} for SDC, respectively (Table 3). This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [35].

3.5. Effect of initial metal ion concentration with contact time

The effect of initial Cr(VI) concentration and contact time on chromium removal, while keeping the adsorbent dose ($0.4 \text{ g } 100 \text{ ml}^{-1}$), pH (2.0) and stirring speed (180 rpm) constant at $25 \pm 1 \text{ }^\circ\text{C}$ has been encapsulated in Fig. 6a and b. The removal of Cr(VI) by RHC and SDC has increased with time and attains a maximum value at about 120 min and thereafter, it remains almost constant. On changing the initial concentration of Cr(VI) solution from 100 to 250 mg L^{-1} , for RHC and SDC, the percent adsorption decreased with increase in initial metal ion concentration but adsorption capacity increased from 24.4 to 47.89 mg g^{-1} for RHC while for SDC, the adsorption capacity increased from 24.96 to 53.09 mg g^{-1} (Table 4). Thus, the removal of Cr(VI) was dependent on the initial concentration. At low concentration, the ratio

Table 3
Adsorption capacity of RHC and SDC at different adsorbent doses.

Adsorbent dose (g L^{-1})	RHC (q_e , mg g^{-1})	SDC (q_e , mg g^{-1})
4	47.89	53.09
8	25.43	27.07
12	17.54	18.76
16	13.74	14.42
20	11.47	11.79

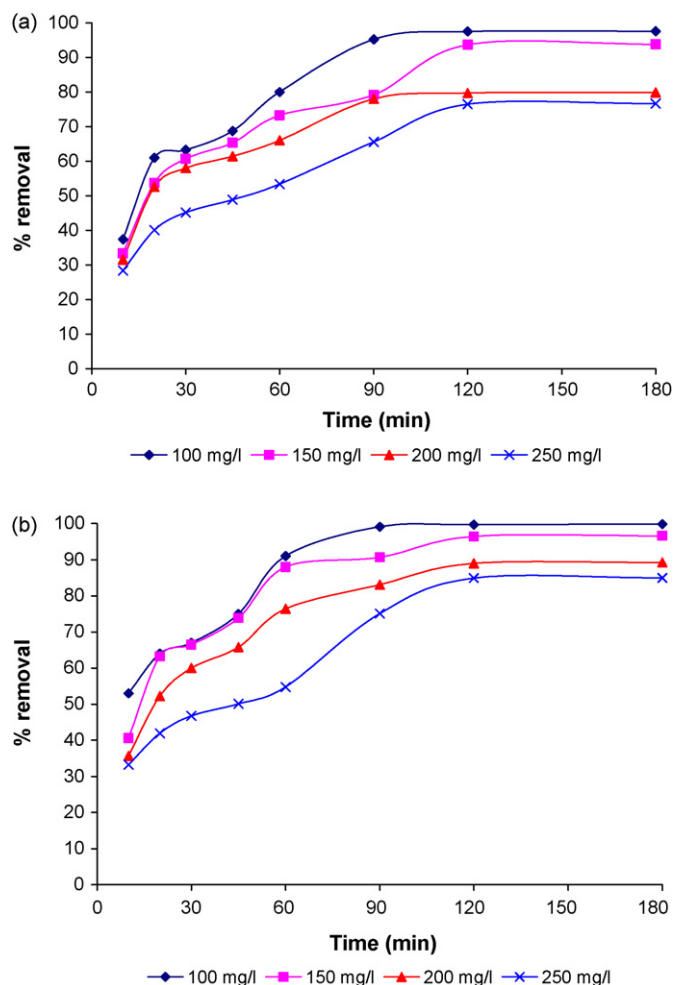


Fig. 6. (a) Effect of initial metal concentration and contact time on Cr(VI) removal by RHC and (b) effect of initial metal concentration and contact time on Cr(VI) removal by SDC.

of available surface to the initial Cr(VI) concentration is larger, so the removal is higher. However, in case of higher concentrations this ratio is low; hence the percentage removal is also lesser. Increasing metal ion concentration increased adsorption capacity for each adsorbent, could be attributed to increased rate of mass transfer due to increased concentration of driving force [36]. On the other hand, changing adsorbent from RHC to SDC, adsorption capacity increase could be due to increased diffusivity of the adsorbate (metal ion) across the liquid film formed on the adsorbent at increasing initial metal ion concentrations. Also, the results showed that although the equilibrium adsorption increased with increasing metal ion concentration, the extent of this increase was not proportional to the initial metal ion concentration, i.e., a two-fold increase in the metal ion concentration of metal ions did not lead to a doubling of the equilibrium adsorption capacity. This can be explained in terms of the surface area of the adsorbent on which the competitive adsorption of metal ions occurred [37,38].

Table 4
Adsorption capacity of RHC and SDC at different initial concentrations of Cr(VI).

Initial Cr(VI) conc. (mg L^{-1})	RHC (q_e , mg g^{-1})	SDC (q_e , mg g^{-1})
100	24.4	24.96
150	35.18	36.22
200	39.95	44.6
250	47.89	53.09

Table 5
Freundlich and Langmuir models regression constants for RHC and SDC.

Adsorbents	Freundlich isotherms			Langmuir isotherms		
	K_f (mg g^{-1})	n (L mg^{-1})	R^2	Q_0 (mg g^{-1})	b (L mg^{-1})	R^2
RHC	21.61	5.36	0.9387	48.31	0.27	0.9850
SDC	0.96	7.75	0.9680	53.48	0.56	0.9871

3.6. Adsorption isotherms

The Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin models have been employed as adsorption isotherm models. These isotherms relate the amount of solute adsorbed at equilibrium per unit weight of adsorbent, x/m (mg g^{-1}), to the adsorbate concentration at equilibrium, C_e (mg L^{-1}). The Freundlich isotherm is the most widely nonlinear sorption model. This model proposes a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules. The general form of this model is presented as:

$$q_e = K_f C_e^{1/n} \quad (3)$$

where K_f stands for adsorption capacity (mg g^{-1}) and n stands for adsorption intensity. The Freundlich equation is expressed linearly as:

$$\log q_e = \log_{10}(K_f) + \left(\frac{1}{n}\right) \log_{10}(C_e) \quad (4)$$

where q_e is the amount of chromium adsorbed at equilibrium (mg g^{-1}) and C_e is the residual concentration of Cr(VI) in solution (mg L^{-1}). The values of K_f and n were obtained from the slope and intercept of a plot of $\log q_e$ versus $\log C_e$. Both the parameters K_f and n affect the adsorption isotherm. The larger the K_f and n values, the higher the adsorption capacity.

The Langmuir isotherm was applied to estimate the adsorption capacity of adsorbents used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The linear form of the Langmuir adsorption isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (5)$$

where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), and q_e is the amount of Cr(VI) adsorbed per gram at equilibrium (mg g^{-1}). Q_0 (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e . Results of the modelling of the isotherms of Cr(VI) sorption by RHC and SDC, according to Langmuir and Freundlich models, are summarized in Table 5. According to the coefficient of correlation obtained, we deduced that the model of Langmuir correlated the experimental data well and better than the Freundlich model for both the adsorbents (Figs. 7 and 8). The adsorption capacities of the RHC and SDC indicates potential for the removal of the Cr(VI) from dilute wastewaters, with the order $\text{SDC} > \text{RHC}$. Value of slope found to be lesser than unity implied that significant adsorption took place at low metal ion concentration [39]. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [40] which is defined as given below:

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

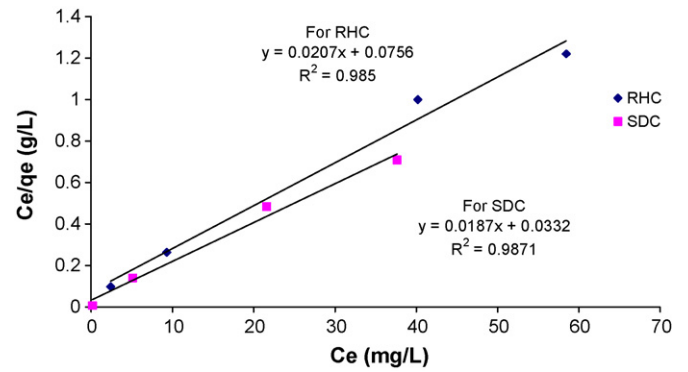


Fig. 7. Langmuir plot for Cr(VI) adsorption on RHC and SDC.

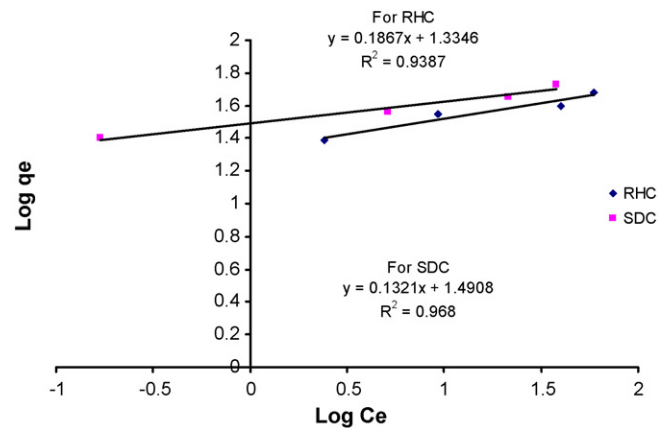


Fig. 8. Freundlich plot of Cr(VI) adsorption on RHC and SDC.

where b is the Langmuir constant (L mg^{-1}) and C_0 (mg L^{-1}) is the initial concentration of Cr(VI). Thus, R_L is a positive number whose magnitude determines the feasibility of the adsorption process. The R_L value between 0 and 1 indicates favourable adsorption of Cr(VI) onto studied adsorbents. The values of R_L for the studied system at different initial concentrations were found to be in between 0 and 1 which indicate favourable adsorption of Cr(VI) onto the adsorbents (Table 6). Langmuir model represents the monolayer adsorption onto a homogeneous surface with a finite number of active sites whereas D–R model does not assume homogeneous surface. The D–R adsorption isotherm is represented as:

$$\log_{10} q_e = \log_{10} q_D - 2B_D R^2 T^2 \log_{10} \left(1 + \frac{1}{C_e}\right) \quad (7)$$

where q_D is theoretical saturation capacity (mg g^{-1}) and B_D is a constant related to adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$), R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The slope of the plot $\log_{10} q_e$ versus $\log_{10}(1 + 1/C_e)$ gives the q_D and B_D values. The constant B_D gives an idea about the mean free energy E_D (kJ mol^{-1}) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calcu-

Table 6
Separation factor (R_L) of RHC and SDC at different initial concentrations of Cr(VI).

Initial Cr(VI) conc. (mg L^{-1})	RHC	SDC
100	0.036	0.024
150	0.024	0.016
200	0.018	0.012
250	0.015	0.0097

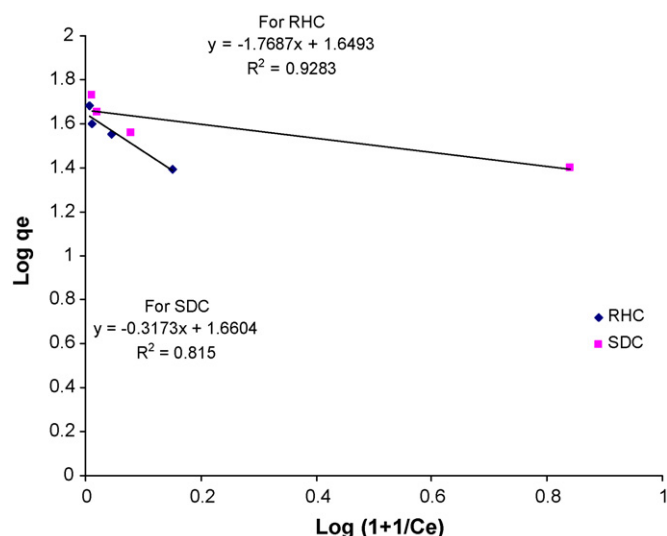


Fig. 9. D–R sorption model for adsorption of Cr(VI) onto RHC and SDC.

lated from the D–R isotherm constant B_D using following equation [41]:

$$E_D = \frac{1}{\sqrt{2B_D}} \quad (8)$$

The results so obtained are given in Fig. 9 and Table 7. The calculated E_D values were found to be 1.86 kJ mol^{-1} for RHC and 4.39 kJ mol^{-1} for SDC. E_D value less than 8 kJ mol^{-1} as indicated by our results shows that the adsorption process of Cr(VI) on RHC and SDC follows physical adsorption [42]. Temkin isotherm equation contains a factor that explicitly takes into account adsorbing species–adsorbate interactions. It assumes that: the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate repulsions and the adsorption is uniform distribution of maximum binding energy [43]. In addition, it assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. It has commonly been written in Eq. (9) [44]:

$$q_e = \frac{RT}{b_T} \log(A_T C_e) \quad (9)$$

where $b_T = (RT)/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The constant b_T is related to the heat of adsorption; A_T is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy [45]. The adsorption data can be analyzed according to Eq. (9). A plot of q_e versus $\log C_e$ enables the determination of the isotherm constants A_T and b_T and represented in Fig. 10 and the value of constants and correlation coefficients are reported in Table 7. The correlation coefficients obtained are $R^2 \geq 0.94$ (RHC) and $R^2 \geq 0.92$ (SDC), which indicates that the Temkin isotherm fit well the equilibrium data obtained for the adsorption of Cr^{6+} onto both adsorbents. However, based on the R^2 value, the Temkin isotherm appears to be more applicable. A list showing the adsorption capacity of different adsorbents for the adsorption of hexavalent chromium from aqueous solutions is given in Table 8, where it is observed that the adsorption

Table 7
Dubinin–Radushkevich and Temkin models' constants for RHC and SDC.

Adsorbent	D–R isotherms				Temkin isotherm		
	q_D (mg g^{-1})	B_D ($\text{mol}^2 \text{ kJ}^{-2}$)	E_D (kJ mol^{-1})	R^2	a (L g^{-1})	b (kJ mol^{-1})	R^2
RHC	44.6	0.14	1.86	0.9283	18.97	0.165	0.9398
SDC	45.75	0.026	4.39	0.815	21.22	0.226	0.9243

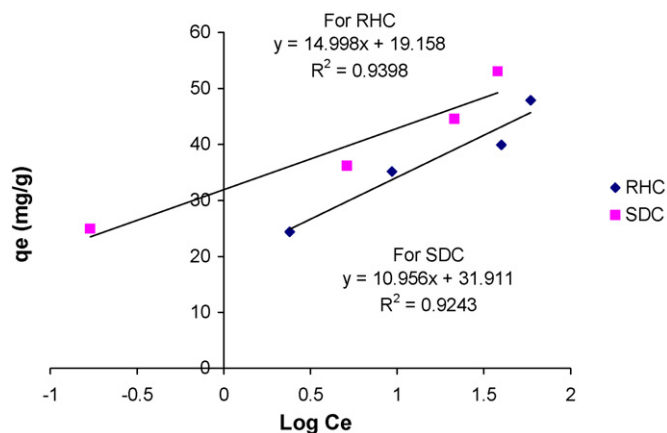


Fig. 10. Temkin sorption model for adsorption of Cr(VI) onto RHC and SDC.

Table 8
Comparison of adsorption capacities of different adsorbents for Cr(VI).

Adsorbent	Adsorption capacity (mg g^{-1})	pH	Model used to calculate adsorption capacity	Reference
Sugarcane bagasse	13.4	2.0	Langmuir	[46]
Larch bark	31.3	3.0	Langmuir	[47]
Almond shell	2.40	4.0	Langmuir	[48]
Fly ash	1.4	2.0	Langmuir	[49]
Saw dust	1.50	–	Freundlich	[50]
Cactus	7.08	2.0	Langmuir	[51]
Rice husks	0.6	–	Freundlich	[50]
Wool	41.2	2.0	Langmuir	[52]
Distillery sludge	5.7	3.0	Langmuir	[53]
Pine needles	21.5	2.0	Langmuir	[52]
Almond	10.6	2.0	Langmuir	[52]
Saw dust	2.2	2.0	Langmuir	[54]
RHC	48.31	2.0	Langmuir	This work
SDC	53.48	2.0	Langmuir	This work

capacity of RHC and SDC for hexavalent chromium is comparable with other low-cost adsorbents. The differences noted in the adsorption capacities towards chromium ions may be ascribed to the difference in various properties such as structure, functional groups and surface areas of the adsorbents.

3.7. Adsorption kinetic study

In the present study, two kinetic models have been tested in order to predict the adsorption data of Cr(VI) as a function of time using a pseudo-first-order and pseudo-second-order kinetic models at different concentrations. The first-order-model can be expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (10)$$

where q_e (mg g^{-1}) is the mass of Cr(VI) adsorbed at equilibrium, q_t (mg g^{-1}) the mass of Cr(VI) at any time and k_1 ($1/\text{min}$) is the equilibrium rate constant of pseudo-first-order adsorption. The values of k_1 and q_e are determined from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t , respectively (Fig. 11a) and are given

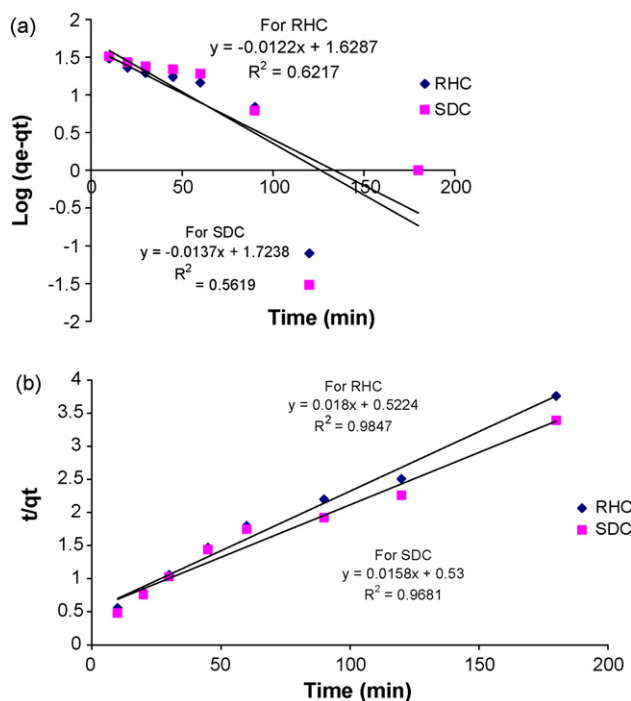


Fig. 11. (a) Pseudo-first-order kinetic plot for Cr(VI) adsorption on RHC and SDC and (b) pseudo-second-order kinetic plot for Cr(VI) adsorption by RHC and SDC.

in Table 9. The pseudo-second-order model, which leads to the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where k_2 is the pseudo-second-order rate constant (g/mg/min). The value of q_e is determined from the slope of the plot of t/q_t versus t (Fig. 11b). The correlation coefficients for the linear plot are very high (>0.96). The calculated q_e value from the pseudo-second-order model is in good agreement with experimental q_e value. This suggests that the sorption system followed the pseudo-second-order model. The values of kinetic constants and q_e values of Cr(VI) sorption onto RHC and SDC are given in Table 8.

3.8. Desorption studies

Desorption studies are helpful to explore the possibility of recycling the adsorbents and recovery of the metal resource. Desorption experiments were done at contact time of 60 min. Different concentrations of KI and HCl ranging from 0.0125 to 0.150 M were tested to remove Cr(VI) from both adsorbents. Desorption of Cr(VI) by KI and HCl is shown in Fig. 12a and b. The results showed that Cr(VI) desorption from RHC and SDC was 55.48% and 53.03% by KI solution and 65.04% and 68.84% by HCl solution at 0.15 M concentration.

Table 9

Kinetic parameters for the removal of Cr(VI) by RHC and SDC.

Pseudo-order	Parameter	RHC	SDC
Pseudo-first-order	q_e , exp. (mg g ⁻¹)	47.89	53.09
	k_1 (1/min)	0.028	0.032
	q_e , cal. (mg g ⁻¹)	55.55	63.29
	R^2	0.6217	0.5619
Pseudo-second-order	q_e , exp. (mg g ⁻¹)	47.89	53.09
	k_2 (g/mg/min)	0.00062	0.00047
	q_e , cal. (mg g ⁻¹)	42.53	52.94
	R^2	0.9847	0.9681

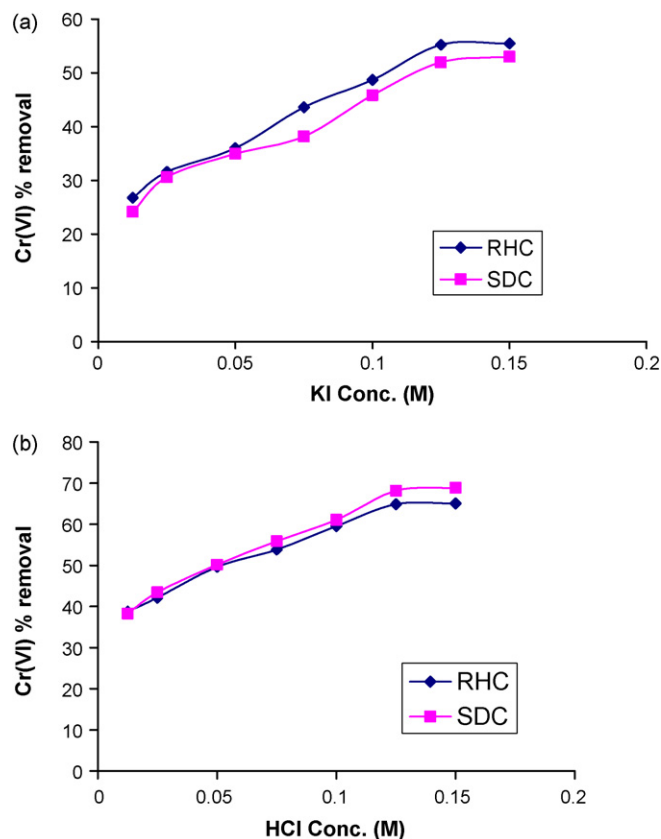


Fig. 12. (a) Desorption plot of the Cr(VI) bound on the RHC and SDC by KI and (b) desorption plot of the Cr(VI) bound on the RHC and SDC by HCl.

4. Conclusion

RHC and SDC could be suitable adsorbents for the removal of Cr(VI) from wastewaters. The adsorption was found to be strongly dependent on pH, adsorbent dose, contact time and initial Cr(VI) concentration. Maximum metal removal was observed at pH 2.0. The efficiencies of RHC and SDC for Cr(VI) removal were 91.75% and 94.33%, respectively for dilute solutions at 20 g L⁻¹ adsorbent dose. The experimental data was analyzed using Freundlich, Langmuir, Dubinin–Redushkevich (D–R) and Temkin isotherm models. It was found that Langmuir, D–R models and Temkin isotherm fitted well. FTIR and SEM characterisation of the adsorbents has shown a clear difference in the native and Cr(VI)-loaded adsorbents. It is also evident from the results that there is no much difference in the adsorption capacity of RHC and SDC at equilibrium time. So both adsorbents could be attractive options for the small scale industries located in countryside. Rice husk and saw dust are readily available in developing nations, so this data can be used by small scale industries having low concentrations of Cr(VI) in wastewater using batch or stirred-tank flow reactors where standard material, such as activated carbon, is not available.

References

- J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, et al., Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (Oat) biomass, J. Hazard. Mater. B 80 (2000) 175–188.
- Y.-T. Wang, C. Xiao, Factors affecting hexavalent chromium reduction in pure cultures of bacteria, Water Res. 29 (1995) 2467–2474.
- 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.
- EPA, Environmental Protection Agency, Environmental Pollution Control Alternatives, EPA/625/5-90/025, EPA/625/4-89/023, Cincinnati, US, 1990.

- [5] Indian Standard, Drinking water—specification (first revision), IS 10500, 1991.
- [6] X. Zhou, T. Korenaga, T. Takahashi, T. Moriwake, S. Shinoda, A process monitoring/controlling system for the treatment of wastewater containing chromium(VI), *Water Res.* 27 (1993) 1049–1054.
- [7] G. Tiravanti, D. Petruzzelli, R. Passiono, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, *Water Sci. Technol.* 36 (1997) 197–207.
- [8] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, *Water Sci. Technol.* 34 (1996) 109–116.
- [9] J.C. Seaman, P.M. Bertsch, L. Schwallie, In situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions, *Environ. Sci. Technol.* 33 (1999) 938–944.
- [10] N. Calace, D.A. Muro, E. Nardi, B.M. Petronio, M. Pietroletti, Adsorption isotherms for describing heavy metal retention in paper mill sludges, *Ind. Eng. Chem. Res.* 41 (2002) 5491–5497.
- [11] K. Pagilla, L.W. Canter, Laboratory studies on remediation of chromium contaminated soils, *J. Environ. Eng.* 125 (1999) 243–248.
- [12] A.K. Chakravarti, S.B. Chowdhury, S. Chakrabarty, T. Chakrabarty, D.C. Mukherjee, Liquid membrane multiple emulsion process of chromium(VI) separation from wastewaters, *Colloids Surf. A: Physicochem. Eng. Aspects* 103 (1995) 59–71.
- [13] C.F. Lin, W. Rou, K.S. Lo, Treatment strategy for Cr(VI) bearing wastes, *Water Sci. Technol.* 26 (1992) 2301–2304.
- [14] Z. Aksu, T. Kutsal, A comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*, *Environ. Technol.* 11 (1990) 979–987.
- [15] Z. Aksu, D. Ozer, H. Ekiz, T. Kutsal, A. Calar, Investigation of biosorption of chromium(VI) on *C. crispata* in two staged batch reactor, *Environ. Technol.* 17 (1996) 215–220.
- [16] I. Ortiz, M.F.S. Roman, S.M. Corvalan, A.M. Eliceche, Modeling and optimization of an emulsion pertraction process for removal and concentration of Cr(VI), *Ind. Eng. Chem. Res.* 42 (2003) 5891–5899.
- [17] B. Volesky, *Biosorption of Heavy Metals*, CRC Press, Boston, USA, 1990, ISBN 0849349176, p. 408.
- [18] M.C. Basso, E.G. Cerrella, A.L. Cukierman, Empleo de algas marinas para la biosorción de metales pesados de aguas contaminadas, *Avances en Energías Renovables Medio Ambiente* 6 (2002).
- [19] Z. Aksu, F. G'onen, Z. Demirçan, Biosorption of chromium(VI) ions by Mowital B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon, *Process. Biochem.* 38 (2002) 175–186.
- [20] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. Nobrega, M.C. Rollemberg, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran, *Process. Biochem.* 40 (2005) 3485–3490.
- [21] P.L. Tang, C.K. Lee, K.S. Low, Z. Zainal, Sorption of Cr(VI) and Cu(II) in aqueous solution by ethylenediamine modified rice hull, *Environ. Technol.* 24 (2003) 1243–1251.
- [22] C.P. Huang, M.H. Wu, The removal chromium(VI) from dilute aqueous solution by activated carbon, *Water Res.* 11 (1977) 673–679.
- [23] M. Kobya, Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies, *Bioresour. Technol.* 91 (2004) 317–321.
- [24] D.C. Sharma, C.F. Forster, A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, *Bioresour. Technol.* 47 (3) (1994) 257–264.
- [25] M. Ayoama, T. Sugiyama, S. Doi, N.S. Cho, H.E. Kim, Removal of hexavalent chromium from dilute aqueous solution by coniferous leaves, *Holzforchung* 53 (1999) 365–368.
- [26] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.* 6 (4) (2002) 533–540.
- [27] L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, Adsorption of chromium from aqueous solutions by maple sawdust, *J. Hazard. Mater.* 100 (1–3) (2003) 53–63.
- [28] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea brasiliensis* sawdust activated carbon, *J. Hazard. Mater.* 124 (1–3) (2005) 192–199.
- [29] L.H. Wartelle, W.E. Marshall, Chromate ion adsorption by agricultural by-products modified with dimethyloldihydroxyethylene urea and choline chloride, *Water Res.* 39 (13) (2005) 2869–2876.
- [30] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, *Sep. Purif. Technol.* 24 (2001) 497–505.
- [31] S. Basha, Z.V.P. Murthy, B. Jha, Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*, *Chem. Eng. J.* 137 (2008) 480–488.
- [32] C. Namasivayam, R.T. Yamuna, Adsorption of Cr(VI) by a low cost adsorbent: biogas residual slurry, *Chemosphere* 30 (1995) 561–578.
- [33] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of lead(II) by adsorption using treated granular activated carbon: batch and column studies, *J. Hazard. Mater. B* 125 (2005) 211–220.
- [34] Z. Aksu, U. Acikel, E. Kabasakal, S. Tezer, Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, *Water Res.* 36 (2002) 3063–3073.
- [35] C. Namasivayam, K. Kadirvelu, M. Kumuthu, Removal of direct red and acid brilliant blue by adsorption onto banana pith, *Bioresour. Technol.* 64 (1998) 77–79.
- [36] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach, *Bioresour. Technol.* 99 (5) (2008) 1325–1331.
- [37] Y.S. Ho, C.C. Chiang, Y.C. Hsu, Sorption kinetics for dye removal from aqueous solution using activated clay, *Sep. Sci. Technol.* 36 (11) (2001) 2473–2488.
- [38] G. McKay, M.S. Otterburn, A.G. Sweny, Surface mass transfer processes during colour removal from effluent using silica, *Water Res.* 15 (1981) 327–331.
- [39] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, *Bioresour. Technol.* 92 (2004) 79–81.
- [40] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Indian Eng. Chem. Fundam.* 5 (1966) 212–218.
- [41] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, *J. Hazard. Mater.* 140 (2007) 60–68.
- [42] S.M. Hasany, M.H. Chaudhary, Sorption potential of Hare River sand for the removal of antimony from acidic aqueous solution, *Appl. Radiat. Isotopes* 47 (1996) 467–471.
- [43] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, *Bioresour. Technol.* 98 (2007) 14–21.
- [44] C. Aharoni, D.L. Sparks, Kinetics of soil chemical reactions—a theoretical treatment, in: D.L. Sparks, D.L. Suarez (Eds.), *Rate of Soil Chemical Processes*, Soil Science Society of America, Madison, WI, 1991, pp. 1–18.
- [45] C.I. Pearce, J.R. Lloyd, J.T. Guthrie, The removal of colour from textile wastewater using whole bacterial cells: a review, *Dyes Pigments* 58 (2003) 179–196.
- [46] Z. Aksu, U. Acikel, A single-staged bioseparation process for simultaneous removal of copper(II) and chromium(VI) by using *C. vulgaris*, *Process. Biochem.* 34 (6/7) (1999) 589–599.
- [47] M. Aoyama, M. Tsuda, Removal of Cr(VI) from aqueous solutions by larch bark, *Wood Sci. Technol.* 35 (5) (2001) 425–432.
- [48] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, *Bioresour. Technol.* 97 (2006) 949–956.
- [49] S.S. Banarjee, M.V. Joshi, R.V. Jayaram, Removal of Cr(VI) and Hg(II) from aqueous solutions using fly ash and impregnated fly ash, *Sep. Sci. Technol.* 39 (7) (2004) 1611–1629.
- [50] K.M.S. Sumathi, S. Mahimairaja, R. Naidu, Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent, *Bioresour. Technol.* 96 (2005) 309–316.
- [51] N. Daneshvar, D. Salari, S. Aber, Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake, *J. Hazard. Mater.* 94 (1) (2002) 49–61.
- [52] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.* 6 (4) (2002) 533–540.
- [53] K. Selvaraj, S. Manonmani, S. Pattabhi, Removal of hexavalent chromium using distillery sludge, *Bioresour. Technol.* 89 (2) (2003) 207–211.
- [54] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, *Chem. Eng. J.* 84 (2001) 95–105.