Journal of Hazardous Materials 162 (2009) 312–320

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk

Manjeet Bansal[a], Umesh Garg[b], Diwan Singh[a], V.K. Garg[c,*]

[a] Department of Civil Engineering, National Institute of Technology, Kurukshetra 136119, India
[b] Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal 148106 (Punjab), India
[c] Department of Environmental Science and Engineering, Guru Jambheshwar University of Science and Technology, Hisar 125001 (Haryana), India

ARTICLE INFO

Article history:
Received 4 March 2008
Received in revised form 8 May 2008
Accepted 8 May 2008
Available online 15 May 2008

Keywords:
Chromium(VI)
Rice husk
Adsorption
FTIR
SEM

ABSTRACT

This paper reports the feasibility of using pre-consumer processing agricultural waste to remove Cr(VI) from synthetic wastewater under different experimental conditions. For this, rice husk, has been used after pre-treatments (boiling and formaldehyde treatment). Effect of various process parameters, namely, pH, adsorbent dose, initial chromium concentration and contact time has been studied in batch systems. The removal of chromium was dependent on the physico-chemical characteristics of the adsorbent, adsorbate concentration and other studied process parameters. Maximum metal removal was observed at pH 2.0. The efficiencies of boiled and formaldehyde treated rice husk for Cr(VI) removal were 71.0% and 76.5% respectively for dilute solutions at $20\,\mathrm{g\,l^{-1}}$ adsorbent dose. The experimental data were analyzed using Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models. It was found that Freundlich and D–R models fitted well. The results revealed that the hexavalent chromium is considerably adsorbed on rice husk and it could be an economical method for the removal of hexavalent chromium from aqueous systems. FTIR and SEM were recorded, before and after adsorption, to explore number and position of the functional groups available for Cr(VI) binding on to studied adsorbents and changes in adsorbent surface morphology.

1. Introduction

Disposal of effluents containing heavy metals, produced by process industries, is a challenging task for environmental engineers due to their non-degradable and persistant nature. Chromium, as environmental contaminant, can enter into the ecosystem from electroplating, metal finishing, chromate preparation, leather tanning, cooling towers of heavy industry, atomic power plants, mining, metallurgy operations etc. Chromium exists in nature mainly in two oxidation states, +3 and +6. It is bio-element in +3 oxidation state but mutagenic in +6 oxidation state. The hydrolysis behavior of Cr(III) is complicated and it produces mononuclear species $\mathrm{Cr(OH)^{2+}}$, $\mathrm{Cr(OH)^{4-}}$, neutral species $\mathrm{Cr(OH)_3}$, and polynuclear species $\mathrm{Cr_2(OH)_2}$ and $\mathrm{Cr_3(OH)_4}^{5+}$. Chromium sulphate [Cr(III)] is used as tanning agent, resulting in severe groundwater contamination around tanneries, which is transformed into chromium(VI) [1].

Hexavalent form is more toxic than trivalent and requires more concern. Strong exposure of Cr(VI) causes cancer in the digestive tract and lungs [2] and may cause epigastria, nausea, vomiting, severe diarrhea and hemorrhage [3]. It is therefore, essential to remove Cr (VI) from wastewater before disposal. The permissible limit of Cr(VI) for industrial effluents to be discharged to surface water varies from 0.05 to 0.1 $\mathrm{mg\,l^{-1}}$ in different countries [4]. Numerous treatment methods such as ion exchange [5], chemical reduction [6], chemical precipitation [7], membrane separations [8,9], electrochemical precipitation [10], photo-catalytic reduction [11], adsorption [12–14], and biosorption [15,16] have been tested for chromium laden wastewater remediation in yesteryears. Most of these technologies are quite satisfactory in terms of purging chromium from wastewater but many of these produce sludge containing important concentrations of toxic compounds like chromium, cadmium, nickel etc whose final disposal is still a problem [17]. Authors have observed that there are not designated land-fill sites for hazardous sludges/chemicals in several States of India. As a result, either industries are storing the hazardous sludge in their premises or disposing the sludges in open which may contaminate soil, surface water, groundwater or other components of the environment. The situation of sludge disposal and manage-

---

* Corresponding author. Tel.: +91 1662 275375; fax: +91 1662 276240.
E-mail address: vinodkgarg@yahoo.com (V.K. Garg).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.05.037

ment in other developing countries is also not different and may perhaps exist elsewhere too. So there is a need to develop such treatment methods which are simple, economical and addresses the local resources and constraints.

The commercially available activated carbon in granular or powder form is effective for the removal of various heavy metal ions. However, due to prohibitive cost their use is limited in developing countries like India. So there is a need to develop low cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment. India is an agrarian country and pre-consumer processing agricultural waste is available in abundance. The biomasses may be effective in the removal of heavy metals due to their specific characteristics [18]. In recent years, several agricultural wastes have been tested for their heavy metals removal efficiency from synthetic wastewaters. Several agricultural wastes studied for the adsorption efficiencies in recent past include Indian rosewood saw dust [19], maize corn cobs, jatropha oil cake, sugarcane bagasse [20] etc. Several authors have reported the efficacy of rice husk as an adsorbent for the individual removal of Cd(II), Ni(II) and Zn(II) metal ions from aqueous solutions [21,22]. The present investigation is devoted to study the removal of Cr(VI) from synthetic aqueous wastewaters by using rice husk in its natural form and treated (with formaldehyde) form. This agricultural by-product is available in large amount in India and other countries. It is either used as fuel in brick kilns or a packing material and available at negligible price. The effects of pH, adsorbent dose, concentration of metal ions and contact time have been investigated. The data obtained may be useful for environmental engineers in designing heavy-metal-containing wastewater treatment systems.

2. Materials and methods

2.1. Materials and reagents

2.1.1. Preparation of pre-boiled rice husk (BRH)

Rice husk was collected from a pre-consumer agricultural product process industry located at Kurukshetra (Haryana). The collected rice husk was dried under sun and impurities were separated manually. It was boiled with distilled water for 5 h to make it free from colored compounds and filtered. The residual material so obtained was dried at 80 °C in hot air oven for 24 h, and then the material was grinded and sieved through the sieves of 300 μm size. The material was stored in airtight plastic container for further use.

2.1.2. Preparation of formaldehyde treated rice husk (FRH)

To immobilize the color and water-soluble substances the ground rice husk was treated with 1% formaldehyde in the ratio of 1:5 (rice husk:formaldehyde, w/v) at room temperature (27 ± 3 °C) for 24 h. The rice husk was filtered, washed with distilled water to remove free formaldehyde and dried at 80 °C in a hot air oven for 24 h. The resulting material was ground sieved through the sieves of 300 μm size. The material was stored in airtight plastic container for further use.

FT-IR spectra of native and chromium-loaded adsorbents were recorded on FTIR-8400S, Shimadzu, Japan. The surface morphology of the adsorbents was visualized via SEM (model Quanta 200 FEG, FEI, Netherlands)

2.1.3. Preparation and testing of synthetic waste water

Aqueous solution of chromium (1000 mg l^{-1}) was prepared by dissolving potassium dichromate in double distilled water. The aqueous solution was diluted with distilled water to obtain the Cr(VI) synthetic wastewater of desired concentration. pH of the solutions was adjusted using 0.01 M NaOH/0.01 M 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 1

FT-IR spectra of adsorbents and Cr(VI) treated adsorbents

Adsorbents	O—H	C—H	C=O	–CH$_3$	Bending vibrations
BRH (native)	3660.6	3076.2	1664.4	1332.7	848.6, 750.2
BRH-Cr(VI)	3654.8	–	1589.2	–	891.0, 867.9, 734.8
FRH (native)	3438.8 (broad)	2908.4	1554.5	1026.0	862.1, 686.6
FRH-Cr (VI)	3411.8	2810.0	1533.3	–	746.4

2.2. 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 100 mg l^{-1} concentration was used. After setting pH and adding desired amount of adsorbent the mixture was agitated on mechanical shaker for 180 min. 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 2.1.3. All experiments were replicated thrice for all the adsorbents and results were averaged. The removal percentage (R%) of chromium was calculated for each run by following expression:

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

where C_i and C_e were the initial and final concentration of chromium in the solution. The adsorption capacity 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 chromium(VI) ions at equilibrium were calculated using Eq. (2).

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

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

3. Results and discussion

Rice husk is an agricultural waste, obtained from the rice mills. It accounts for about one-fifth of the annual gross rice production of 545 million metric tons, of the world [21]. Structurally agricultural materials consist of lignin, cellulose, hemi-cellulose and some proteins, which make them effective biosorbents for heavy metal cations. Rice husk contains 43.3% cellulose, 32–33% sugars and 22% lignin [23]. Generally rice husk has an average length of 4–5 mm and bulk densities 96–160 kg/m^3. Since rice husk is available in plenty and it has very high potential as an adsorbent, the present study has been undertaken to report its adsorption characteristics for hexavalent chromium ions from aqueous solutions.

3.1. Fourier transform infrared analysis of adsorbents

The FTIR spectra of BRH and FRH (before and after sorption of chromium) were used to determine the vibrational frequency changes in the functional groups in the adsorbent. The spectra of adsorbents were measured within the range of 500–4000 cm^{-1} wave number. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents before and after adsorption. The FTIR spectra of the adsorbent display a number of absorption peaks, indicating the complex nature of the studied adsorbent. Table 1 presents the fundamental peaks of all the adsorbents before and after use. The spectra display a number of absorption peaks, indicating the complex nature of the examined adsorbents. In native BRH the absorption peak around 3660.6 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed at 3076.2 cm^{-1} can be assigned to stretching vibration of the C—H group. The peaks around 1664.4 cm^{-1} corresponds to the C=O stretching that may be attributed to the lignin aromatic groups (Fig. 1a). The additional peak at 848.6 and 750.2 cm^{-1} can be assigned to bending modes of aromatic compounds. The C=O absorption peak was observed to shift to 1589.2 cm^{-1} when BRH is loaded with Cr(VI) (Fig. 1b). It seems that this functional group participates in metal binding. In native FRH, a broad adsorption band has been observed around 3438.8 cm^{-1} can be attributed to the bonded —OH groups present in the structure. The other prominent peaks are due to C—H, C=O and C—O (2908.4, 1554.5 and 1026.0 cm^{-1} respectively) groups. The additional peak at 862.1 and 686.6 cm^{-1} can be assigned to bending modes of aromatic compounds (Fig. 1c). However in case of Cr(VI) loaded FRH, there is remarkable shift in positions and shapes of —OH and C=O group peaks indicating Cr(VI) binding mostly with —OH and C=O groups (Fig. 1d). Similarly the bending modes of aromatics have also shifted, indicative of association with the aro-

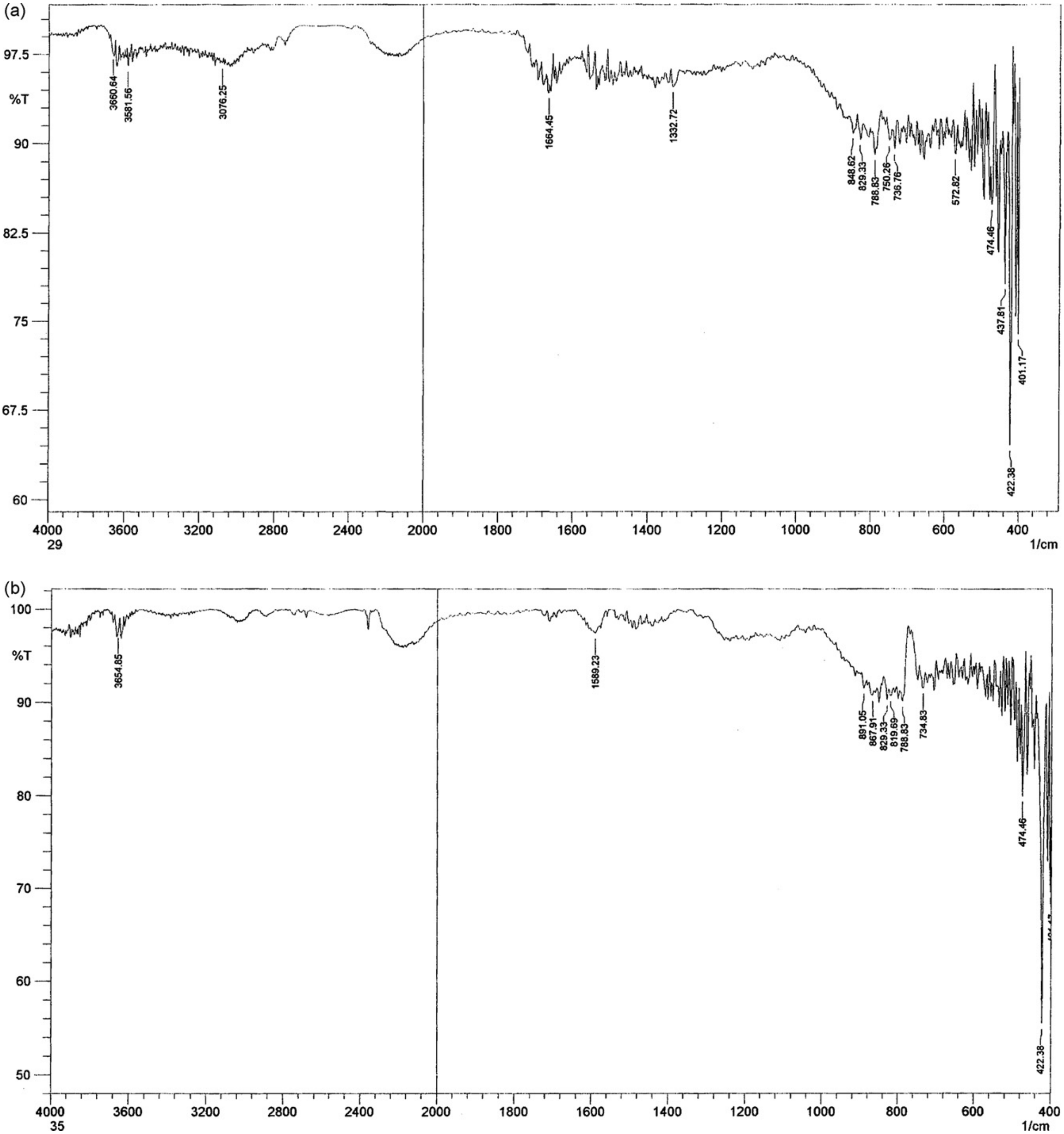

Fig. 1. (a) FT-IR spectra of native BRH, (b) FT-IR spectra of Cr(VI)-loaded BRH, (c) FT-IR spectra of native FRH and (d) FT-IR spectra of Cr(VI)-loaded FRH.

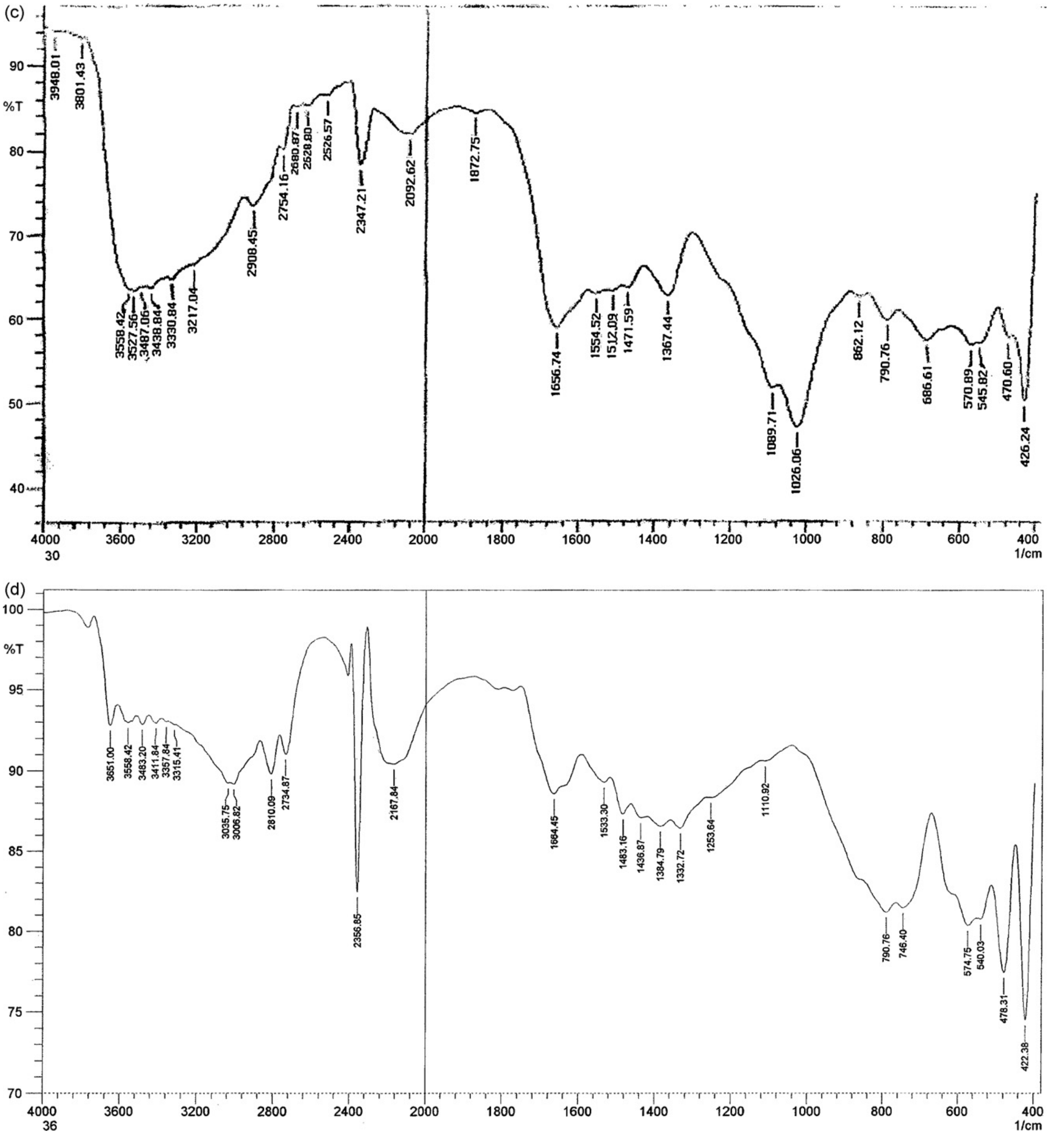

Fig. 1. (*Continued*)

matic ring. The possible adsorption on these adsorbents may be due to physical adsorption, complexation with functional groups, ionic exchange, surface precipitations and chemical reaction with surface sites. 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 analysis for showing morphology of different adsorbent. SEM micrographs obtained before and after Cr(VI) adsorption onto BRH (Fig. 2a and b) and FRH (Fig. 3a and b) are given. These micrographs indicated clearly the presence of new shiny bulky particles over the surface of metal loaded BRH and FRH.

3.3. Effect of pH on Cr(VI) removal

The pH of the medium has a significant effect on the sorption of metal ions on different adsorbents. This is partly due to the fact that the hydrogen ion itself is a strong competing adsorbate, and partly due to the chemical speciation of metal ions under the influence of the solution pH. At acidic pH, the predominant species of Cr are

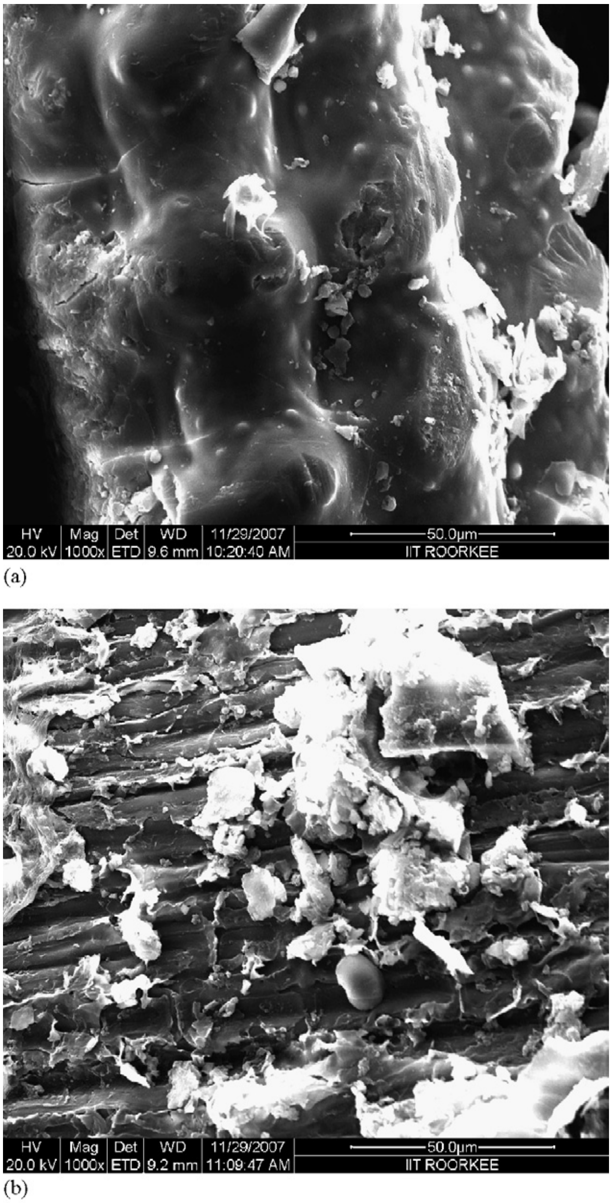

Fig. 2. (a) SEM of native BRH and (b) SEM of Cr(VI)-loaded BRH.

$Cr_2O_7{}^{-2}$, $HCrO_4{}^{-1}$, H_2CrO_4, $Cr_3O_{10}{}^{-2}$ and $Cr_4O_{13}{}^{-2}$. The adsorption of metal ions depends both upon the nature of the adsorbent surface and the species distribution of the metal ions in the aqueous solution. For adsorption of Cr(VI), experiments were carried out by varying pH from 2 to 7. The results presented in Fig. 4 indicate that Cr(VI) removal is considerably affected by the pH. The maximum adsorption of chromium(VI) metal ions was observed at pH 2 for both adsorbents viz; 35% and 39.6% for BRH and FRH respectively (Fig. 5). Initial pH of Cr(VI) solution was increased after the equilibrium time (3 h). The pH increase was lesser at lower initial pH values. It may be due to hydrolysis of the adsorbent in water, which will create positively charged sites [24]. At initial pH of 2.0, the adsorbent surfaces might be highly protonated which favor the uptake Cr(VI) in the predominant anionic form ($HCrO_4{}^{-}$) [25]. With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased [26]. Furthermore, as pH increases, there is competition between OH^{-} and chromate ions. Hence, adsorption of Cr(VI) on the adsorbent was not significant

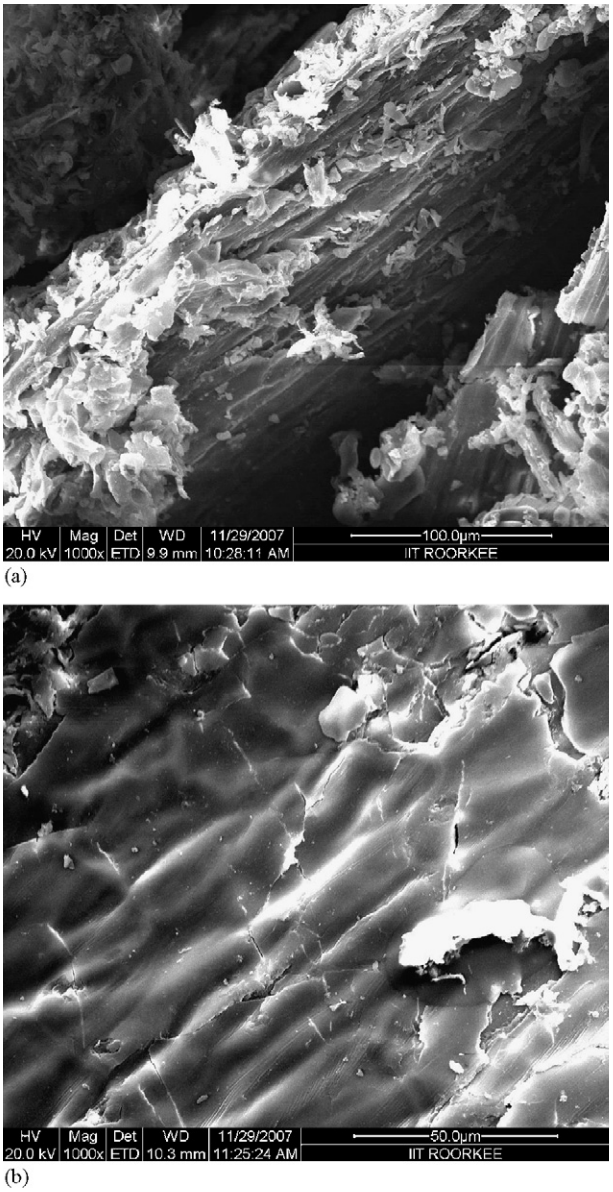

Fig. 3. (a) SEM of native FRH and (b) SEM of Cr(VI)-loaded FRH.

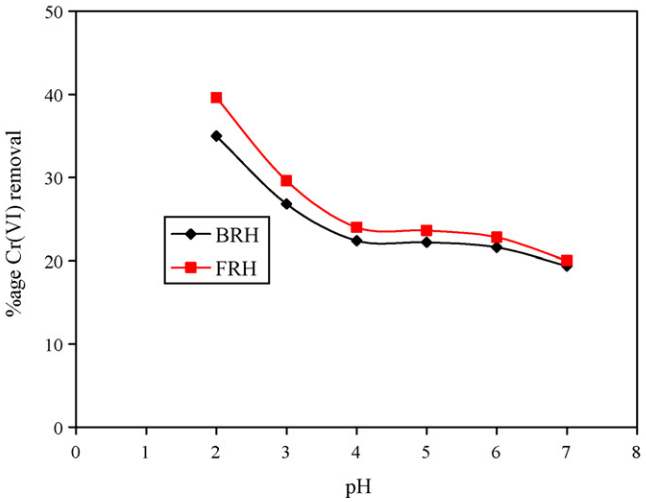

Fig. 4. Effect of pH on Cr(VI) removal by BRH and FRH.

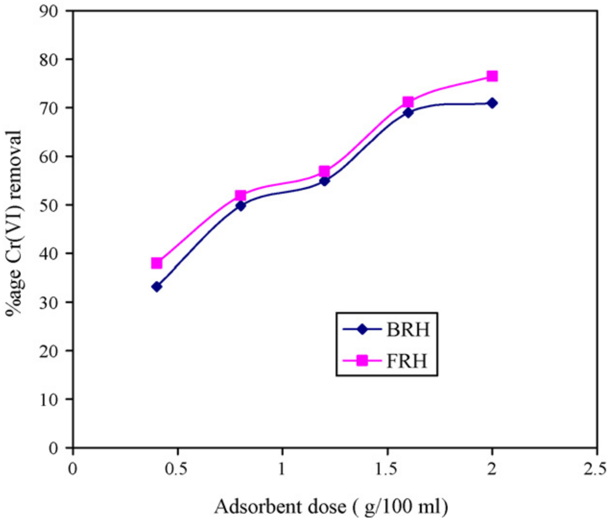

Fig. 5. Effect of adsorbent dose on Cr(VI) removal.

at greater pH values due to dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominant. Maximum adsorption occurs at pH 2.0 and hence it was taken as the optimal value for further adsorption studies.

3.4. *Effect of adsorbent dose*

The removal of metal ions is a function of adsorbent dosage, so the efficiency of BRH and FRH adsorbents was evaluated at different adsorbent doses for the percent removal of chromium. The experiments were conducted at constant initial Cr(VI) concentration (100 mg l^{-1}), contact time (180 min), pH 2, temp. (25 ± 1 °C), stirring speed (180 rpm) with varying adsorbent doses (4–20 g l^{-1}). Measurement of percentage Cr(VI) removal as a function of time at different doses indicates that removal of Cr(VI) increased with increasing adsorbent dose (Fig. 5). Increase in chromium removal with adsorbent dose can be attributed to increased surface area and the availability of more adsorption sites [27]. The removal of Cr(VI) by BRH ranged from 33.2% to 71% at the equilibrium time with various adsorbent doses of 4.0 g to 20.0 g l^{-1}. The removal of Cr(VI) by FRH ranged from 38% to 76.5% with various dose of 4.0 g to 20.0 g l^{-1}. But adsorption efficiency of both the adsorbents decreased with increase in adsorbent dose (Table 2). For BRH, adsorption efficiency was decreased from 8.30 to 3.55 mg g^{-1} as the dose increased from 4.0 to 20.0 g l^{-1} in the tested wastewater. For FRH, adsorption efficiency was decreased from 9.50 to 3.83 mg g^{-1}. This may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles [28].

3.5. *Effect of initial metal ion concentration and contact time*

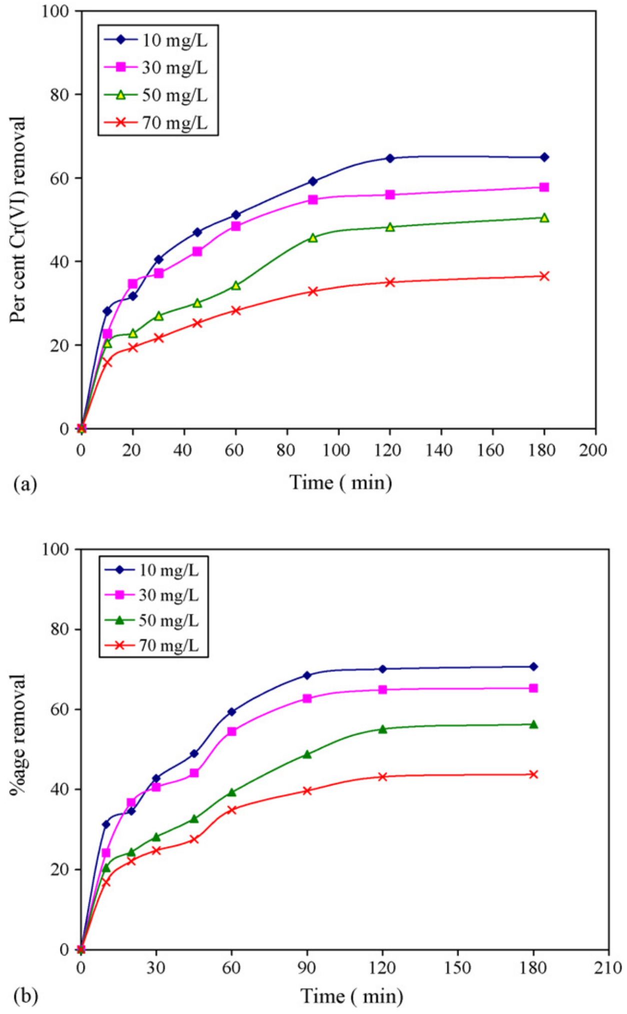

Fig. 6. (a) Effect of initial concentration and contact time on Cr(VI) removal by BRH and (b) effect of metal concentration and contact time on Cr(VI) removal by FRH.

The effect of changing the initial concentration of the adsorbate and contact time on adsorption, while keeping the adsorbent dose (4.0 g l^{-1}), pH (2.0) and stirring speed (180 rpm) constant at 25 ± 1 °C illustrated in Fig. 6a and b. The removal of Cr(VI) by BRH and FRH 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 10 to 70 mg l^{-1}, for BRH and FRH, the percent adsorption decreased with increase in initial metal ion concentration but adsorption capacity increased from 1.63 to 6.39 mg g^{-1} for BRH while for FRH, the adsorption capacity increased from 1.77 to 7.67 mg g^{-1} (Table 3). The results shows that Cr(VI) removal is not upto the permissible disposal limit as prescribed by National Standards. But as the removal of Cr(VI) is dependent on pH, initial Cr(VI) concentration and adsorbent dose, so when initial concentration of Cr(VI) is low, adsorbent dose is higher and pH is optimum, then the permissible levels of Cr(VI) can be achieved in the effluents. At low concentration, the ratio of available surface to the initial Cr(VI) concentration

Table 2
Adsorption capacity of BRH and FRH at different adsorbent doses

Adsorbent dose (g l^{-1})	BRH (q_e, mg g^{-1})	FRH (q_e, mg g^{-1})
4	8.3	9.5
8	6.23	6.49
12	4.58	4.74
16	4.31	4.45
20	3.55	3.83

Table 3
Adsorption capacity of BRH and FRH at different initial concentrations of Cr(VI)

Initial Cr(VI) conc. (mg l^{-1})	BRH (q_e, mg g^{-1})	FRH (q_e, mg g^{-1})
10	1.63	1.77
30	4.33	4.90
50	6.31	7.04
70	6.39	7.67

Table 4
Freundlich and Langmuir models regression constants for different adsorbents

Adsorbent	Freundlich isotherms			Langmuir isotherms		
	K_f ($l\,g^{-1}$)	n	R^2	q_0 ($mg\,g^{-1}$)	b ($l\,mg^{-1}$)	R^2
BRH	0.883	1.75	0.931	8.5	0.079	0.974
FRH	1.053	1.71	0.943	10.4	0.080	0.986

is larger, so the removal is higher. However, in case of higher concentrations this ratio is low; hence the percentage removal is also lesser. The plots are smooth and continuous suggesting the possible monolayer adsorption of chromium on the surface of BRH and FRH. 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 (Table 3) [20,29,30]. On the other hand, changing adsorbent from BRH to FRH, 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.

3.6. *Adsorption isotherm*

The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) 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 non-linear sorption model. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active

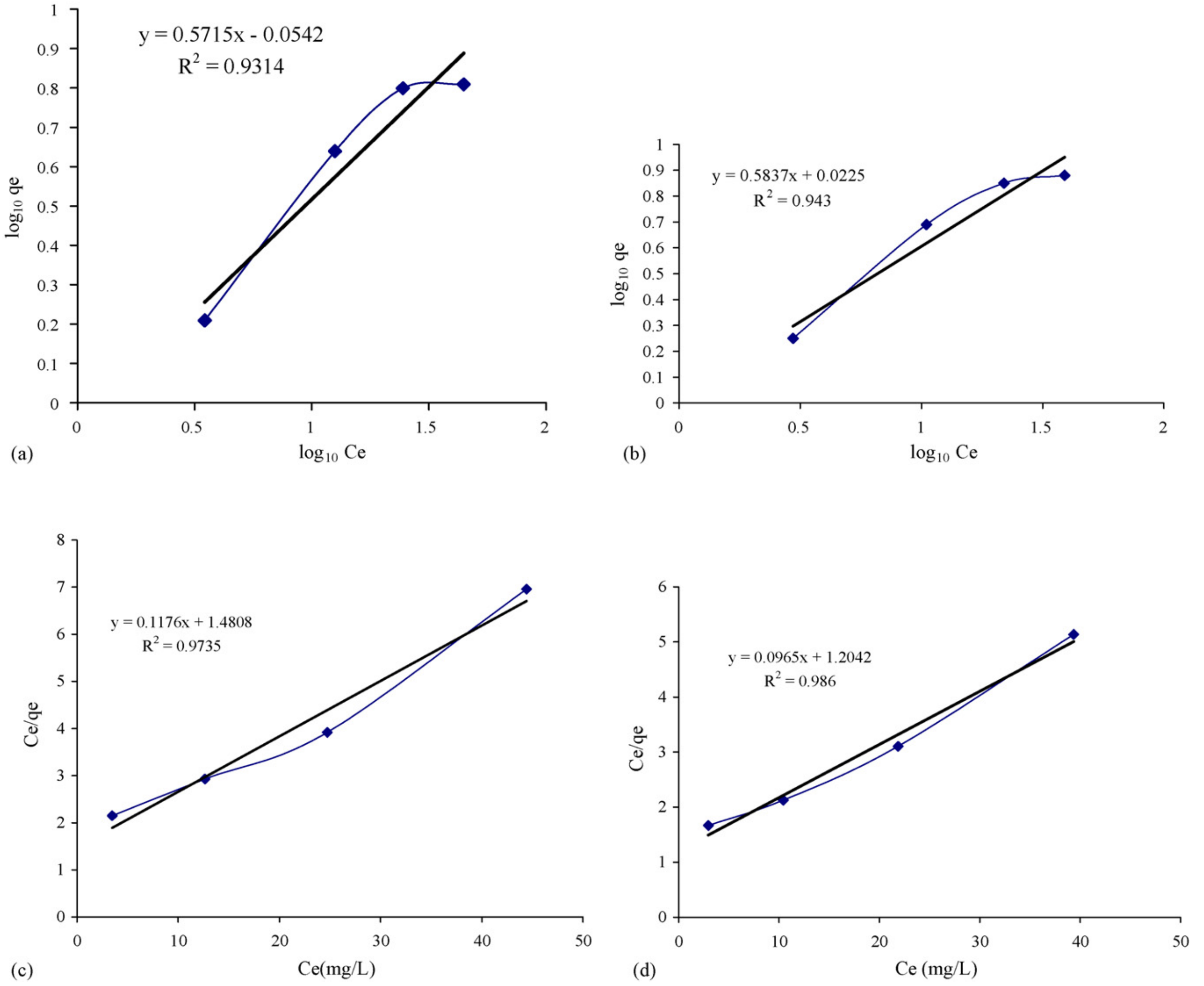

Fig. 7. (a) Freundlich plot of Cr(VI) adsorption on BRH, (b) Freundlich plot for Cr(VI) adsorption on FRH, (c) Langmuir plot for Cr(VI) adsorption on BRH and (d) Langmuir plot for Cr(VI) adsorption by FRH.

sites, accompanied by interaction between adsorbed molecules. The general form of this model is presented as:

$$q_e = K_f C_e^{1/n} \tag{3}$$

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

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

where q_e is the amount of chromium adsorbed at equilibrium ($\mathrm{mg\,g^{-1}}$) and C_e is the residual concentration of Cr(VI) in solution ($\mathrm{mg\,l^{-1}}$). 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:

$$\frac{C_e}{q_e} = \left[\frac{1}{Q_0 b} + \frac{C_e}{Q_0}\right] \tag{5}$$

where, C_e is the equilibrium concentration of adsorbate ($\mathrm{mg\,l^{-1}}$), and q_e is the amount of Cr(VI) adsorbed per gram at equilibrium ($\mathrm{mg\,g^{-1}}$). Q_0 ($\mathrm{mg\,g^{-1}}$) and b ($\mathrm{l\,mg^{-1}}$) 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 modeling of the isotherms of Cr(VI) sorption by BRH and FRH, according to Langmuir and Freundlich models, are summarized in Table 4. According to the coefficient of correlation obtained, we deducted that the model of Langmuir correlated the experimental data well and better than the Freundlich model for both the adsorbents (Fig. 7a–d). The adsorption capacities of the BRH and FRH indicate potential for the removal of the Cr(VI) from dilute wastewaters, with the order FRH > BRH. Value of slope found to be lesser than unity implied that significant adsorption took place at low metal ion concentration [20]. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [31] which is defined as given below:

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

where b is the Langmuir constant ($\mathrm{l\,mg^{-1}}$) and C_0 ($\mathrm{mg\,l^{-1}}$) 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 favorable 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 favorable adsorption of Cr(VI) onto the adsorbents. Langmuir model represents the monolayer adsorption on to 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:

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

where q_D is theoretical saturation capacity ($\mathrm{mg\,g^{-1}}$) and B_D is a constant related to adsorption energy ($\mathrm{mol^2\,kJ^{-2}}$), R is the gas constant ($\mathrm{kJ\,mol^{-1}\,K^{-1}}$) 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 ($\mathrm{kJ\,mol^{-1}}$) 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 calculated from the D–R isotherm constant B_D using following equation [32]:

$$E_D = \frac{1}{(2B_D)^{0.5}} \tag{8}$$

The results so obtained are given in Fig. 8 and Table 5. The calculated E_D values were found to be $1.0\,\mathrm{kJ\,mol^{-1}}$ for BRH and $1.06\,\mathrm{kJ\,mol^{-1}}$ for FRH. E_D value less than $8\,\mathrm{kJ\,mol^{-1}}$ as indicated by our results shows that the adsorption process of Cr(VI) on BRH and FRH follows physical adsorption [33]. A list showing the adsorption

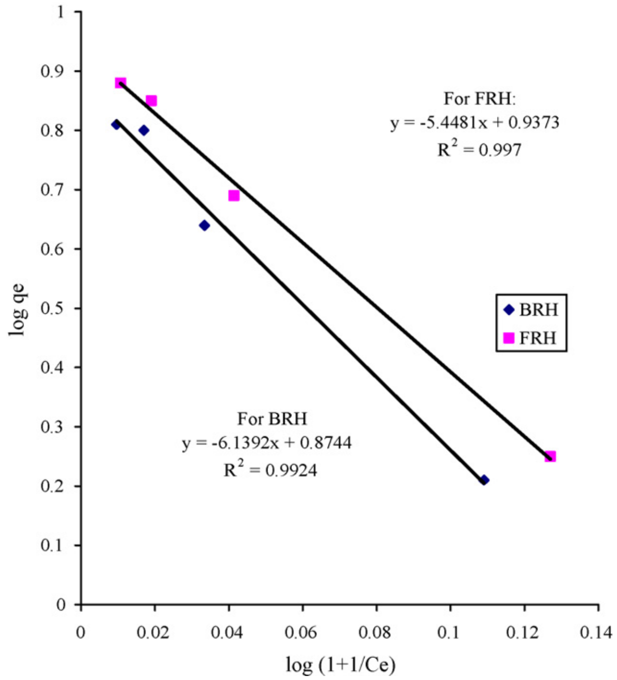

Fig. 8. D–R sorption model for adsorption of Cr(VI) onto BRH and FRH.

Table 5
Dubinin–Radushkevich model constants for different adsorbents

Adsorbent	q_D ($\mathrm{mg\,g^{-1}}$)	B_D ($\mathrm{mol^2\,kJ^{-2}}$)	E_D ($\mathrm{kJ\,mol^{-1}}$)	R^2
BRH	7.49	0.500	1.0	0.9924
FRH	8.65	0.445	1.06	0.9970

Table 6
Comparison of adsorption capacities of different adsorbents for hexavalent chromium

Adsorbent	Adsorption capacity ($\mathrm{mg\,g^{-1}}$)	pH	Model used to calculate adsorption capacity	Reference
Raw rice bran	0.07	5.0	Freundlich	[34]
Almond shell	2.40	4.0	Langmuir	[35]
Saw dust	1.50	–	Freundlich	[36]
Rice husks	0.6	–	Freundlich	[36]
Coir pith	0.2	–	Freundlich	[36]
Olive cake	33.3	2.0	Langmuir	[37]
Pine needles	21.5	2.0	Langmuir	[37]
Almond	10.6	2.0	Langmuir	[37]
Spirogyra algae	14.7	2.0	Langmuir	[15]
Saw dust	2.2	2.0	Langmuir	[38]
BRH	8.5	2.0	Langmuir	This work
FRH	10.4	2.0	Langmuir	This work

capacity of different adsorbents for the adsorption of hexavalent chromium from aqueous solutions is given in Table 5, where it is observed that the adsorption capacity of rice husk for hexavalent chromium is comparable with other low-cost adsorbents (Table 6).

4. Conclusion

BRH and FRH could be suitable adsorbents for the removal of Cr(VI) from dilute waste waters. 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 boiled and formaldehyde treated rice husk for Cr(VI) removal were 71.0% and 76.5% respectively for dilute solutions at $20\,\mathrm{g\,l^{-1}}$ adsorbent dose. The experimental data was analyzed using Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models. It was found that Freundlich and D–R models fitted well. FTIR and SEM characterization of the adsorbents has shown a clear difference in the native and Cr(VI) loaded adsorbents. It is evident from the results that there is not much difference in the adsorption capacity of BRH and FRH at equilibrium time. So BRH could be an attractive option for the small-scale industries located in country side as no chemical is required in its preparation. Rice husk is readily available in India, 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

[1] A. Blanco, B. Sanz, M.J. Llama, J.L. Serra, Biosorption of heavy metals to immobilised *Phormidium laminosum* biomass, J. Biotechnol. 69 (1999) 227–240.

[2] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, J. Hazard. Mater. 102 (2003) 257–275.

[3] G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, Water Sci. Technol. 36 (1997) 197–207.

[4] B.M. Braukman, Industrial solutions amenable to biosorption, in: B. Volesky (Ed.), Biosorption of Heavy Metals, CRC Press, USA, 1990, pp. 51–64.

[5] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, Ind. Eng. Chem. Res. 34 (1995) 2612–2617.

[6] 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.

[7] 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.

[8] H. Shaalan, M. Sorour, S. Tewfik, Simulation and optimization of a membrane system for chromium recovery from tanning wastes, Desalination 14 (2001) 315–324.

[9] C.A. Kozlowski, W. Walkowiak, Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes, Water Res. 36 (2002) 4870–4876.

[10] N. Kongsricharoern, C. Polprasert, Chromium removal by a bipolar electrochemical precipitation process, Water Sci. Technol. 34 (1996) 109–116.

[11] J.J. Testa, M.A. Grela, M.I. Litter, Heterogeneous photocatalytic reduction of chromium (III) over TiO_2 particles in the presence of oxalate: involvement of Cr(VI) species, Environ. Sci. Technol. 38 (2004) 1589–1594.

[12] S.K. Srivastava, V.K. Gupta, D. Mohan, Removal of lead and chromium by activated slag—a blast furnace waste, J. Environ. Eng. (ASCE) 123 (1997) 461–468.

[13] S.K. Srivastava, V.K. Gupta, D. Mohan, Kinetic parameters for the removal of lead and chromium from wastewater using activated carbon developed from fertilizer waste material, Environ. Model. Assess. 1 (1997) 281–290.

[14] V.K. Gupta, K.T. Park, S. Sharma, D. Mohan, Removal of chromium (VI) from electroplating industry wastewater using bagasse flyash—a sugar industry waste material, The Environmentalist 19 (1999) 129–136.

[15] V.K. Gupta, A.K. Shrivastava, N. Jain, Biosorption of chromium (VI) from aqueous solutions by green algae *spirogyra* species, Water Res. 35 (2001) 4079–4085.

[16] R. Arvindhan, B. Madhan, J.R. Rao, B.U. Nair, T. Ramasami, Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse, Environ. Sci. Technol. 38 (2004) 300–306.

[17] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresour. Technol. 76 (2001) 63.

[18] 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.

[19] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, Bioresour. Technol. 92 (1) (2004) 79–81.

[20] 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.

[21] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, J. Hazard. Mater. B134 (2006) 257–267.

[22] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA), Chem. Eng. J. 132 (1–3) (2007) 267–278.

[23] M. Patel, A. Karera, P. Prasanna, Effect of thermal and chemical treatment on carbon and silica contents in rice husk, J. Mater. Sci. 22 (1987) 2257–2464.

[24] 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 (2002) 533–540.

[25] S. Rao, P. Shashikant, G.S. Munjunatha, Kinetic studies on adsorption of chromium by coconut shell carbons from synthetic effluents, J. Environ. Sci. Health A 27 (1992) 2227–2241.

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

[27] K. Kadirvelu, C. Faur-Brasquet, P. Le Cloirec, Removal of Pb(II), Cu(II) and Ni(II) ions by adsorption onto activated carbon cloths, Langmuir 16 (2000) 8404–8409.

[28] C. Namasivayam, D. Prabha, M. Kumutha, Removal of direct red and acid brilliant blue by adsorption on to banana pith, Bioresour. Technol. 64 (1998) 77–79.

[29] 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.

[30] 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.

[31] 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.

[32] K.E. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, Indian Eng. Chem. Fund. 5 (1996) 212–223.

[33] S.M. Hasany, M.H. Chaudhary, Sorption potential of Hare River sand for the removal of antimony from acidic aqueous solution, Appl. Radiat. Isot. 47 (1996) 467–471.

[34] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. Nóbrega, 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.

[35] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium (VI) by *Tamarindus indica* seeds, Bioresour. Technol. 97 (2006) 949–956.

[36] 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.

[37] 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 (2002) 533–540.

[38] 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.