



Chromium(VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste

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ABSTRACT

The objective of this study was to investigate the Cr(VI) removal efficiency of sunflower waste from aqueous system under different process conditions. Two adsorbents were prepared by pre-treating the sunflower stem waste. One adsorbent was prepared by boiling it and second adsorbent was prepared by treating it with formaldehyde. Batch mode experiments were carried out as a function of solution pH, adsorbent dosage, Cr(VI) concentration and contact time. FT-IR spectra and SEMs of the adsorbents were recorded to explore the number and position of functional groups available for the binding of Cr(VI) ions and morphology of the studied adsorbents. 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 sunflower stem adsorbent and formaldehyde-treated sunflower stem adsorbent for the removal of Cr(VI) were 81.7 and 76.5%, respectively for dilute solutions at 4.0 g/L adsorbent dose. The applicability of Langmuir, Freundlich and Dubinin–Radushkevich isotherms was also tested. The results revealed that the hexavalent chromium is considerably adsorbed on sunflower stem and it could be an economical method for the removal of hexavalent chromium from aqueous systems.

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1. Introduction

Chromium is a highly reactive element and exists in six oxidation states. Its two most stable states are Cr(III) and Cr(VI). But Cr(VI) is more toxic to living organisms than the Cr(III) [1]. Furthermore, Cr(III) has limited hydroxide solubility making it relatively immobile and less available for biological uptake. Chromium's threshold concentration, on inhibitory effect on heterotrophic organisms, is 10 mg/L for Cr(III) and 1 mg/L for Cr(VI). Hexavalent chromium is considered powerful carcinogenic agent that modifies DNA transcription process causing important chromosomal aberration by The International Agency for Research on Cancer [2,3]. The hexavalent chromium has also been classified as a group A carcinogen by USEPA based on its chronic effects [4]. Strong exposure of Cr(VI) causes cancer in digestive tract and lungs [5] and may cause epigastric pain, nausea, vomiting, severe diarrhoea and hemorrhage [6]. Chromium has adverse impacts on aquatic species as it accumulates in fish tissues and causes reduction in fish production at higher concentration [7,8]. The current maximum Bureau of Indian Standards (BIS) recommended limit for Cr (as total Cr) in drinking water

is 0.05 mg/L. According to Minimum National Standards given by Central Pollution Control Board, India, the permissible limit for hexavalent chromium for discharge of industrial effluents in different water bodies namely, Inland surface water, Public sewers and Marine coastal areas is 0.1, 2.0 and 1.0 mg/L, respectively.

Chromium metal and its compounds have wide applications in making alloys, chrome plating, leather tanning, batteries, refractories, dyes, paints, welding, catalysis and wood preservatives [9,10] and its use at present may not be curtailed. However, its removal from industrial wastewaters is essential before discharging it into hydrosphere. The tanning process is one of the major sources of chromium pollution at global scale. In the chromium tanning process, the leather takes up only 60–80% of the applied chromium, and the rest is usually discharged into the wastewaters causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to hexavalent form. Chromium may be removed from wastewaters by chemical precipitation, ion exchange, lime coagulation, reverse osmosis, solvent extraction [11,12]. These techniques are usually not used due to inhibitive cost, incomplete metal removal and generation of toxic sludge in developing nations or elsewhere too. Sorption technology has been employed in yesteryears for the removal of heavy metals including chromium from synthetic or actual wastewaters. The commercially available activated carbon in granular or

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powdered form is effective for the removal of various heavy metal ions because of its large surface area, microporous structure and high adsorption capacity. However, due to the prohibitive cost, its 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.

Agricultural biomass mainly consists of lignin, cellulose, hemicellulose and some proteins which make them effective bio-adsorbent for heavy metal cations. Various investigated biomasses for their possible application in wastewater treatment for heavy metal removal include peapod, cotton and mustard seed cakes [13], sawdust [14], *Ocimum basilicum* seeds [15], waste tea [16], *Cicer arietinum* husk [17], sugarcane bagasse, maize corncob and *Jatropha* oil cake [18]. New, economical, easily available and highly effective adsorbents are still needed. Sunflower (*Helianthus annuus*) is a commonly grown cash crop in dry and arid regions of India. The stem waste of this plant is usually used as a domestic fuel. It is available in plenty at zero or negligible price. As per bibliographic survey, yet the adsorption capacity of the sunflower biomass has not been explored in detail. There are only three reports on the adsorption capacity of sunflower biomass. Sun and Shi [19] have reported its adsorption capacity which was found to be 25.07 mg/g for trivalent chromium, 29.3 mg/g for copper, 42.18 mg/g for cadmium and 30.73 mg/g for zinc. In other reports its colour removal efficiency [20] and comparative adsorption capacity has been tested [21]. Sunflower stalks are cellulosic materials which have an inherent ability to adsorb waste chemicals such as metal cations in water due to coulombic interaction. A legion of biomass has been tested for adsorption process but studies using sunflower biomass do not seem to be available in the literature. The crop has been cultivated in Northern India on a large scale. An attempt has been made in this article to study the adsorption behavior of the sunflower biomass on synthetic waste water containing Cr(VI). In our laboratory, the investigations are in progress on the possibility of the use of various biomasses for industrial pollution control. This paper reports the feasibility of utilizing pre-treated sunflower stem waste for the removal of hexavalent chromium from aqueous system.

2. Experimental procedure

2.1. Adsorbents

2.1.1. Preparation of pre-boiled sunflower stem (BSS)

The sunflower stem waste was collected, at the time of harvesting, from agricultural fields of a village in Kurukshetra district (India). Stems were dried in sunlight until all the moisture evaporated. The dried mass was ground to fine powder without removing pith in a steel mill. The ground powder was boiled in distilled water at 100 °C for 5 h in the ratio of 1:5 (sunflower:distilled water, w/v). The mixture was filtered, washed with distilled water several times and kept in hot air oven at 100 °C for drying. The resulting material was sieved to get the adsorbent having size $\leq 300 \mu\text{m}$ and stored in air tight plastic containers.

2.1.2. Preparation of formaldehyde-treated sunflower stem (FSS)

The ground powder of sunflower stem (as given in Section 2.1.1) was treated with 1% formaldehyde in the ratio of 1:5 (sunflower:formaldehyde, w/v) at room temperature for 24 h to immobilize the colour and water soluble substances of sunflower [14]. The mixture was filtered out, washed with distilled water several times to remove free formaldehyde. The residue so obtained was kept in a hot air oven at 100 °C for drying. The resulting material was sieved to get the adsorbent having size $\leq 300 \mu\text{m}$ and stored in air tight plastic containers.

Fourier transform infrared spectroscopy (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 scanning electron microscopy (SEM) (model Quanta 200 FEG, FEI, Netherlands).

2.2. Batch experiment

A stock solution of hexavalent chromium (1000 mg/L) was prepared in deionized double distilled water using potassium dichromate. All working solutions of varying concentrations were obtained by successive dilution (AR grade). The pH of the solution was adjusted to required value by adding either 0.01 M HCl or 0.01 M NaOH using pH meter (Model pH_{ep}, Hanna Instruments, calibrated with buffers of pH 4.0, 7.0 and 9.2). Residual chromium concentration in the filtrate was determined by Atomic Absorption Spectrophotometer (Shimadzu 6300, Japan).

The batch mode operation was used to study the removal of Cr(VI) from synthetic wastewater. Adsorption experiments were carried out using 50 mL of chromium solution of desired concentration (100 mg/L) at initial pH 2.0, adsorbent dosage 0.2 g/50 mL in 150 mL Erlenmeyer flasks at temperature 26 ± 1 °C and agitation speed of 180 rpm on orbital shaker (Scigenics Biotech ORBITEK) for 180 min. At predetermined time interval, the samples were separated by centrifugation at 4000 rpm for 10 min. Residual chromium concentration in the supernatant was determined as stated above. Blank samples were run under similar conditions of concentration, temperature, pH without adsorbent in all cases to correct for any adsorption on the internal surface of flasks.

The per cent chromium removal (R , %) was calculated for each run by following expression:

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

where C_i and C_e were the initial and final concentration of chromium in the solution. The adsorption capacity 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 the following equation:

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

where C_i and C_e were the initial and final concentration of chromium 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

Sunflower stems are composed of polyol structures which have strong coulombic adsorption to cations such as organic bases as well as intrinsic adsorption to other materials such as acidic and anionic compounds [19]. Sunflower stems have relatively large surface areas that can provide intrinsic adsorptive sites to many adsorbates.

3.1. Fourier transform infrared analysis of adsorbents

The FT-IR spectra of BSS and FSS (before and after sorption of chromium) were used to determine the vibrational frequency changes in the functional groups in the adsorbents. The spectra of the adsorbents were measured within the range of 400–4000 cm^{-1} wave number. The spectra were plotted using the same scale on the

Table 1
FT-IR spectra of adsorbents and Cr(VI)-treated adsorbents

Adsorbents	O–H	C–H	C=O	–OCH ₃	Bending vibrations
BSS (native)	–	2356.85	1614.31	1031.85	667.32, 505.31
BSS–Cr(VI)	–	2360.71	1591.16	1031.85	655.75
FSS (native)	3352.05 (broad)	2813.95	1730.03	1107.06	707.83, 622.0
FSS–Cr(VI)	3382.91	2852.52	1739.67	1095.49	763.76

transmittance axis for all the adsorbents before and after adsorption. The FT-IR spectra of the adsorbents display a number of absorption peaks indicating the complex nature of studied adsorbents. Table 1 presents the fundamental peaks of the adsorbents before and after use. FT-IR spectra of both the adsorbents (native as well as chromium loaded) are given in Fig. 1(a)–(d).

In native FSS, the broad absorption peak at 3352.05 cm⁻¹ is indicative of the existence of bonded hydroxyl group. The absorption peak around 2813.95, 1730.03 and 1107.06 cm⁻¹ is assigned to –CH, C=O and C–O stretching, respectively. The additional peak at 707.83 and 622 cm⁻¹ can be assigned to bending modes of aromatic compounds (Fig. 1(a) and (b)). The –OH absorption peak was observed to shift to 3382.91 cm⁻¹ when FSS is loaded with Cr(VI). The –CH stretching peak also shifted to 2852.5 cm⁻¹. It seems that these functional group participates in metal binding. In native BSS, the peaks observed at 2356.85 cm⁻¹ can be assigned to stretching vibration of the C–H group. The peaks around 1614.31 cm⁻¹ corresponds to C=C stretching that may be attributed to the lignin aromatic groups (Fig. 1(c)). The strong C–O band at 1043.42 cm⁻¹ due to –OCH₃ group also confirms the presence of lignin structure in boiled sunflower stem. The additional peak at 667.32 and 505.31 cm⁻¹ can be assigned to bending modes of aromatic compounds. The C–O absorption peak was observed to shift to 1591.16 cm⁻¹ when BSS is loaded with Cr(VI) (Fig. 1(d)). It seems that this functional group participates in metal binding. 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 FT-IR spectra confirm the complexation of Cr(VI) with functional groups present in the adsorbents.

3.2. Scanning electron microscopy (SEM)

The scanning electron micrographs enable the direct observation of the surface microstructures of different adsorbents. The micrographs illustrated in Fig. 2(a)–(d) clearly indicated the presence of new shiny bulky particles over the surface of metal loaded adsorbents which are absent from the original adsorbents before loading metal ions. It can be observed from Fig. 2(a)–(d) that the surface morphology is different of the chromium loaded adsorbents.

3.3. Effect of pH

The pH is amongst one of the important parameters for adsorption process as it controls the adsorption capacity due to its influence on the adsorbent surface properties and ionic forms of metal ions in the solution. Adsorption experiments were carried out in the pH range of 2.0–7.0 keeping all other parameters constant (chromium concentration = 50 mg/L; adsorbent dose = 0.2 g/50 L; stirring speed = 180 rpm; contact time = 180 min; temperature = 26 ± 1 °C). Fig. 3 shows that maximum Cr(VI) removal by BSS and FSS was 32.4 and 31.3%, respectively, at pH 2.0. Thereafter, there was a sharp decline in percent adsorption with increase in pH of the aqueous solution. Chromium removal

decreased from 32 to 19% in BSS and 31 to 17% in FSS, respectively, as pH increased from 2 to 7. As maximum Cr(VI) removal was at pH 2.0, hence, it was taken as the optimal pH value for further adsorption experiments. The pH dependence of chromium adsorption can largely be related to the type and ionic state of functional groups present on the adsorbent and chromium speciation in solution [22,23]. Chromium exhibits different types of pH dependent equilibria in aqueous solution. As the pH is shifted, the equilibria will also shift. In the pH range of 2–6, HCrO₄⁻ and Cr₂O₇²⁻ ions are in equilibrium and at lower pH values, Cr₃O₁₀²⁻ and Cr₄O₁₃²⁻ species are formed [24,25]. At lower pH, there is an increase in H⁺ on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and negatively charged chromate ions. Lesser adsorption of Cr(VI) at pH ≥ 6 may be due to dual competition of both anions (CrO₄²⁻ and OH⁻) to be adsorbed on the surface of adsorbent [23,26–28]. The plausible explanation for higher adsorption in acidic region is that the Cr(VI) ion is oxidized to Cr(III). Being small in size, it gets easily replaced by the positively charged species [26].

3.4. Effect of initial concentration with time

Effect of initial concentration on Cr(VI) removal by BSS and FSS was studied by carrying out the experiments at different initial concentrations (10, 30, 50 and 70 mg/L) keeping pH (2.0), adsorbent dose (4.0 g/L), stirring speed (180 rpm), temperature (26 ± 1 °C) constant and varying the contact time (10, 20, 30, 45, 60, 90, 120 and 180 min). The removal of Cr(VI) by BSS and FSS increased with time and attains a maximum value at about 120 min and thereafter, it remains almost constant. The per cent chromium removal decreased with increase in initial concentration (Fig. 4(a) and (b)), but adsorption capacity increased from 1.2 to 4.9 mg/g for BSS while for FSS, adsorption capacity increased from 1.4 to 5.1 mg/g (Table 2). Thus, the removal of Cr(VI) was dependent on the initial concentration. Further, the adsorption is rapid in early stages and then attains almost constant value for larger adsorption time. The results show that Cr(VI) removal is not up to 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 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 BSS. Higher adsorption capacity at higher metal ion concentration can be attributed to increased rate of mass transfer due to increased concentration of driving force [29–31]. On the other hand, changing adsorbent from BSS to FSS, 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 twofold increase in the metal ion concentration of metal ions did not lead to a doubling of the equilibrium adsorption capacity.

3.5. Effect of adsorbent dose with contact time

The removal of Cr(VI) by BSS and FSS was studied by varying the adsorbent dose (0.2, 0.4, 0.6, 0.8 and 1.0 g/50 mL) in aqueous

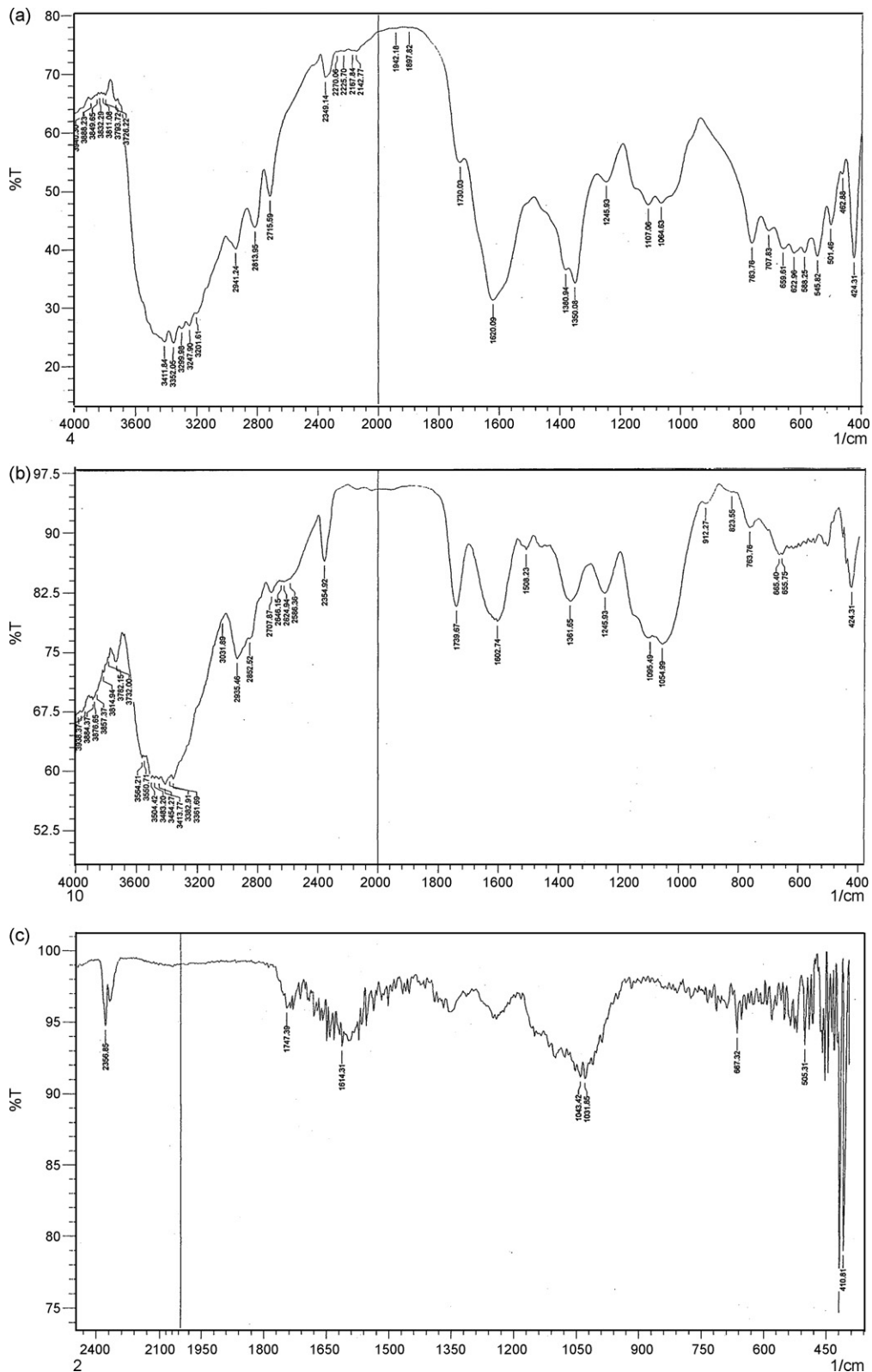


Fig. 1. (a) FT-IR spectra of native FSS, (b) FT-IR spectra of Cr(VI)-loaded FSS, (c) FT-IR spectra of native BSS and (d) FT-IR spectra of Cr(VI)-loaded BSS.

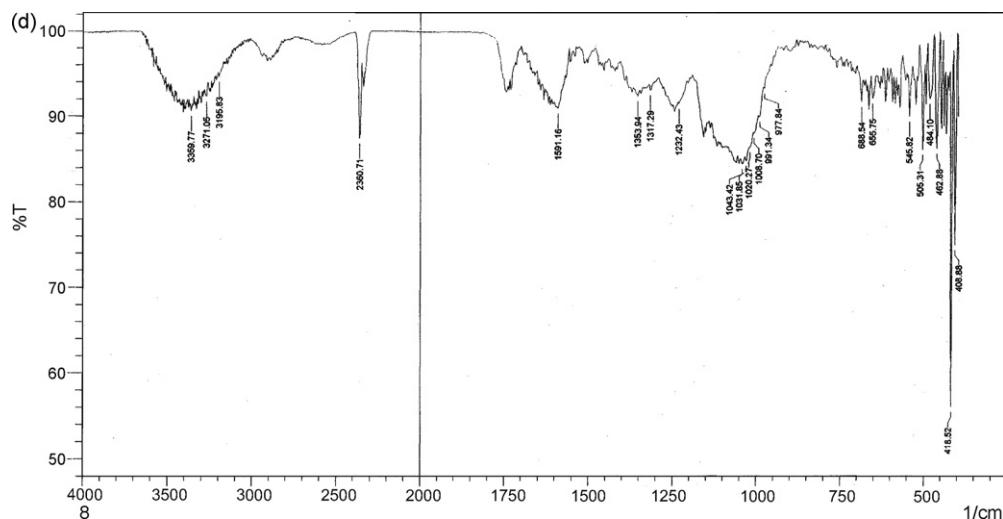


Fig. 1. (it Continued)

system while keeping initial metal concentration (100 mg/L), temperature ($26 \pm 1^\circ\text{C}$) and pH (2) constant at pre-determined contact times. Measurement of percentage Cr(VI) removal as a function of time at different doses indicate that removal of Cr(VI) increased

with increasing adsorbent dose (Fig. 5(a) and (b)). The adsorption increased from 30.9 to 54.8% in case of BSS while it increased from 29.2 to 38.7% in FSS as dose increased from 0.2 to 1.0 g/50 mL. Maximum Cr(VI) removal was achieved within 120 min after which

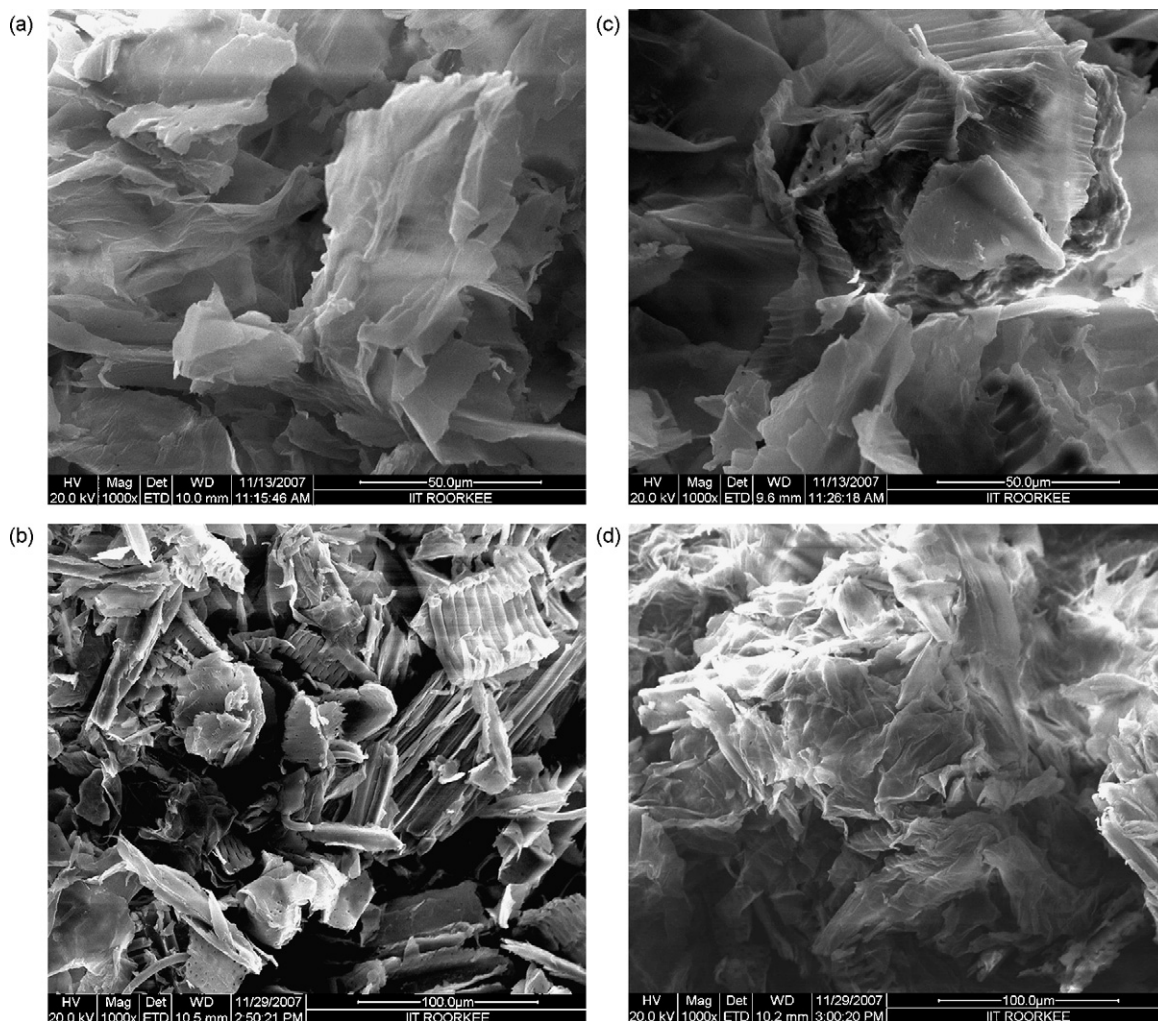


Fig. 2. (a) SEM of native BSS, (b) SEM of Cr(VI)-loaded BSS, (c) SEM of native FSS and (d) SEM of Cr(VI)-loaded FSS.

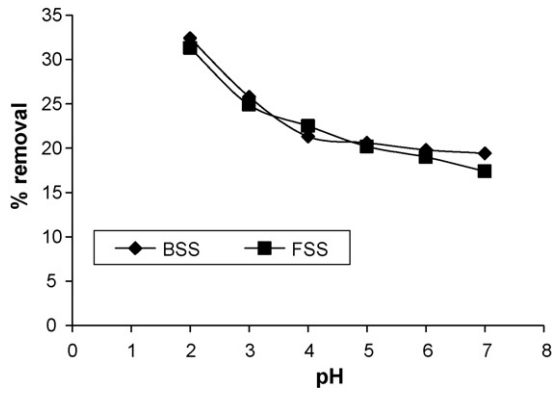


Fig. 3. Effect of pH on Cr(VI) removal by BSS and FSS.

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 [14]. But adsorption capacity decreased with increase in adsorbent dosage (Table 3). This may be

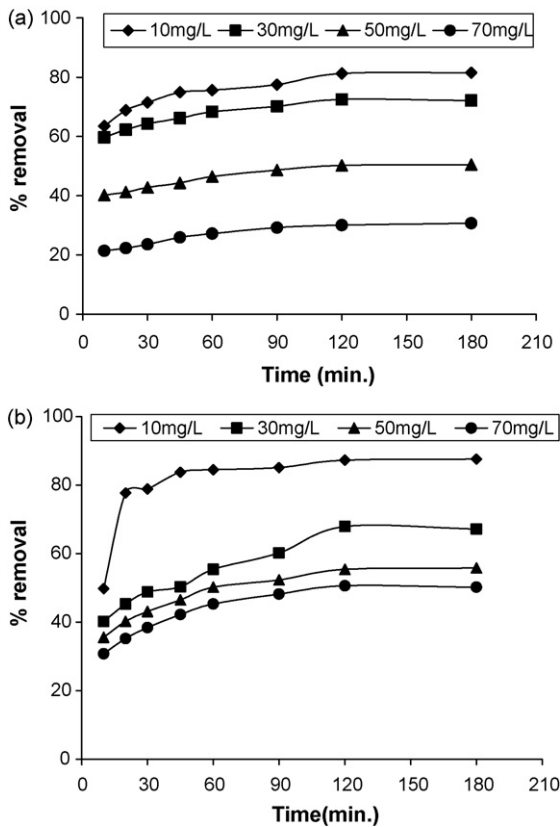


Fig. 4. (a) Effect of initial concentration and contact time on Cr(VI) removal by BSS and (b) effect of initial concentration and contact time on Cr(VI) removal by FSS.

Table 2 Adsorption capacity of different adsorbents at different initial chromium concentration

Cr(VI) concentration (mg/L)	FSS (q_e) (mg/g)	BSS (q_e) (mg/g)
10	1.4	1.2
30	4.3	2.3
50	4.9	3.6
70	5.1	4.9

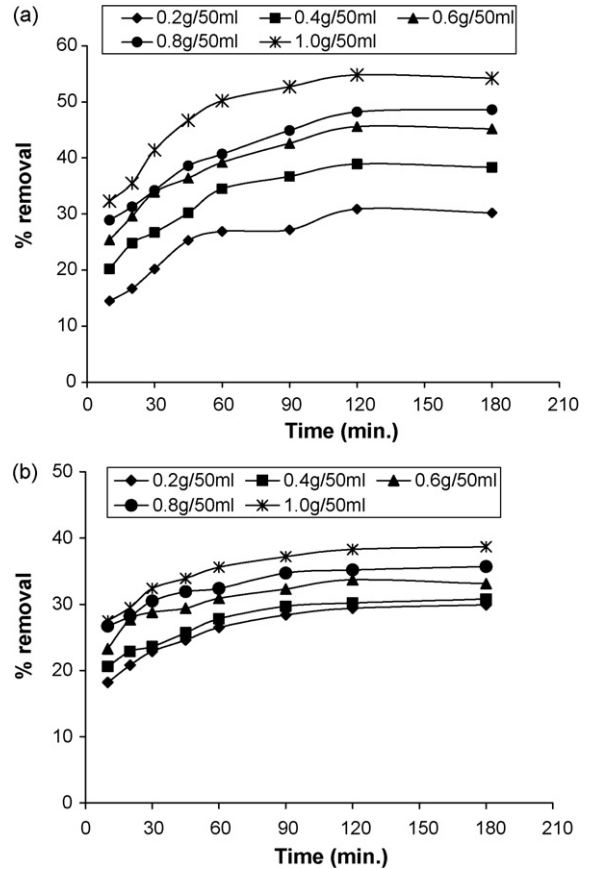


Fig. 5. (a) Effect of adsorbent dose and contact time on Cr(VI) removal by BSS and (b) effect of adsorbent dose and contact time on Cr(VI) removal by FSS.

due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles [32].

3.6. Adsorption isotherms

Adsorption equilibrium data which expresses the relationship between mass of adsorbate per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate are represented by adsorption isotherms and provide important design data for adsorption system. The Freundlich isotherm assumes that the uptake of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. It is widely used in environmental engineering practice to model adsorption of pollutants from aqueous medium empirically. It is most widely used non-linear sorption model. The linearized Freundlich model isotherm was applied for the adsorption of Cr(VI) and is expressed as

$$\log q_e = \log_{10}(K_f) + \left(\frac{1}{n}\right) \log_{10}(C_e) \tag{3}$$

Table 3 Adsorption capacity of different adsorbents at different adsorbent doses

Adsorbent dose (g/L)	BSS (q_e) (mg/g)	FSS (q_e) (mg/g)
4	7.7	7.4
8	4.9	3.8
12	3.8	2.8
16	3.0	2.2
20	2.7	1.9

Table 4
Langmuir and Freundlich parameters obtained for the studied systems

Adsorbent	Langmuir parameters			Freundlich parameters		
	Q_0 (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n	R^2
BSS	5.37	0.109	0.934	0.86	1.78	0.617
FSS	4.81	0.071	0.808	0.562	2.0	1.0

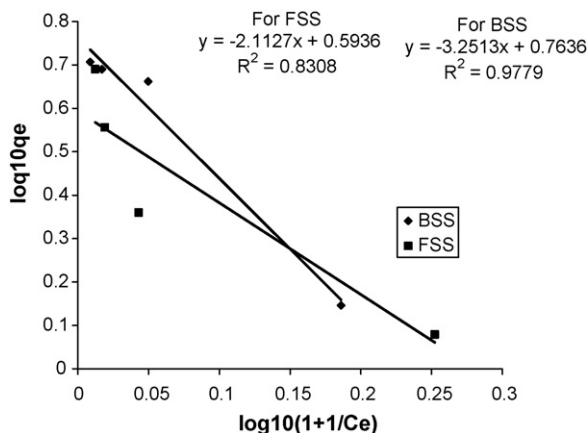


Fig. 6. D–R sorption model for Cr(VI) ions onto BSS and FSS.

where q_e is the amount of Cr(VI) adsorbed at equilibrium (mg/g), and C_e is the equilibrium concentration of chromium in solution (mg/L). K_f and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity). Linear plots of $\log_{10} q_e$ versus $\log_{10} C_e$ show that adsorption follows Freundlich isotherm well for FSS. Values of K_f and n were calculated from the intercept and slope of the plot and are given in Table 4. 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 model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \left[\frac{1}{Q_0 b} + \frac{C_e}{Q_0} \right] \quad (4)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of Cr(VI) adsorbed at equilibrium time (mg/g) and Q_0 (mg/g) is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface whereas b is a constant related to the affinity of binding sites with the metal ions. The plots of C_e/q_e versus C_e are linear which shows that the adsorption of Cr(VI)

Table 7
Adsorption capacity of different adsorbents for hexavalent chromium

Adsorbent	Optimum dose (g/L)	Initial concentration (mg/L)	Optimum pH	q_e (mg/g)	Reference
Hazelnut shell	2.5	1000	1.0	170	[36]
Almond shell	2.4	100	2.0	10.62	[37]
Saw dust	2.4	100	2.0	15.82	[37]
Wool	2.4	100	2.0	41.15	[37]
Maple waste	50	10	5.0	5.1	[38]
Bagasse	4.0	100	6.0	0.03	[39]
Flyash	4.0	90	6.0	0.01	[39]
Wallastonite	20	10.4	2.5	0.52	[40]
Waste tea	–	–	–	1.55	[41]
BSS	4.0	50	2.0	4.9	This work
FSS	4.0	50	2.0	3.6	This work

Table 5
Langmuir dimensionless constant separation factor for different adsorbents

C_i (mg/L)	R_L	
	BSS	FSS
10	0.2	0.09
30	0.07	0.03
50	0.04	0.02
70	0.03	0.01

Table 6
D–R model constants for adsorption of Cr(VI) on BSS and FSS

Adsorbent	q_D (mg/g)	B_D (mol ² /kJ ²)	E_D (kJ/mol)	R^2
BSS	5.8	0.27	1.37	0.9779
FSS	3.9	0.17	1.70	0.8308

follows Langmuir isotherm model for BSS (Table 4) which indicates that the data fitted reasonably well to the Langmuir isotherm in the present adsorption studies. 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 and are reported in Table 4.

The essential characteristics of Langmuir isotherm can be explained in terms of dimensionless constant separation factor (R_L) which is expressed as [33]:

$$R_L = \left(\frac{1}{1 + bC_i} \right) \quad (5)$$

where b is the Langmuir constant (1/mg) and C_0 (mg/L) 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 values for each of the different initial concentrations used are between 0 and 1 indicating favorable adsorption of Cr(VI) onto differently modified sunflower stem (Table 5).

The sorption data was also subjected to Dubinin–Radushkevich model represented as follows [34]:

$$\log_{10} q_e = \log_{10} q_D - 2B_D R^2 T^2 \log_{10} \left(1 + \frac{1}{C_e} \right) \quad (6)$$

where q_D is the theoretical saturation capacity (mg/g), B_D is a constant related to adsorption energy (mol² kJ⁻²), R is the gas constant (kJ mol⁻¹ K⁻¹) and T is the temperature (K). The slope of $\log_{10} q_e$ versus $\log_{10}(1 + 1/C_e)$ gives q_D and B_D values (Fig. 6).

The constant B_D gives an idea about the mean free energy E_D (kJ mol^{-1}) of adsorption per molecule of adsorbate when it was transferred to the surface of solid from infinity in the solution and can be calculated from D–R isotherm constant B_D using following equation [35]:

$$E_D = \frac{1}{\sqrt{2B_D}} \quad (7)$$

The calculated E_D value was found to be 1.37 and 1.70 kJ mol^{-1} for Cr(VI) onto BSS and FSS, respectively (Table 6). E_D value less than 8 kJ mol^{-1} indicates that the physical adsorption is the process involved for adsorption of Cr(VI). D–R sorption isotherm is more general than Langmuir isotherm as its deviation is not based on ideal assumptions such as equipotential of sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level. A list showing the adsorption capacity of different adsorbents for the adsorption of hexavalent chromium from aqueous solutions is given in Table 7, where it is observed that the adsorption capacity of sunflower stem waste for hexavalent chromium is comparable with other low-cost adsorbents.

4. Conclusion

The adsorption of hexavalent chromium by BSS and FSS was strongly dependent on pH, adsorbent dose, contact time and initial Cr(VI) concentration. The Cr(VI) removal was maximum at pH 2.0 for both the adsorbents. The results obtained in this study showed good fit to Langmuir, Freundlich and D–R adsorption isotherms. FT-IR 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 BSS and FSS at equilibrium time. So, BSS could be an attractive option for the small scale industries located in country side as no chemical is required for the preparation of BSS. The data so obtained, 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.

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