Equilibrium and kinetic studies for sequestration of Cr(VI) from simulated wastewater using sunflower waste biomass

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ARTICLE INFO

ABSTRACT

In the present work, potential of sunflower head (BSH) [an agricultural waste biomass] to remove Cr(VI) from simulated wastewater has been evaluated under different process conditions such as pH, metal concentration, adsorbent dose and contact time. A contact time of 120 min and pH 2.0 were found to be optimum. Chromium removal decreased from 90.0 to 45.2% as its concentration increased from 10 to 70 mg/L. The Cr(VI) removal increased from 31.4 to 52.4% as adsorbent dose increased from 4.0 to 20.0 g/L using a test solution having 100 mg/L Cr(VI) concentration. Adsorption isotherms were employed to evaluate the maximum adsorption capacity. Adsorption data fitted well to Langmuir isotherm and pseudo-second order model as indicated by high values of correlation coefficient (0.9882 and 0.999) respectively. The adsorption capacity calculated from Langmuir isotherm was 8.177 mg/g.

1. Introduction

Inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have probable carcinogenic effect [1]. One of such pollutant is chromium which is a highly reactive transition metal having variously coloured compounds and occurs in variable oxidation states ranging from 0 to 6, out of which Cr(III) and Cr(VI) are most stable oxidation states. Cr(VI), which is highly soluble (e.g., the oxyanions $HCrO_4^-$ and CrO_4^{2-}), and Cr(III), which behaves as a "hard" Lewis acid and can form insoluble $Cr(OH)_3$ and $Fe_xCr_{1-x}(OH)_3$ precipitates. Cr(III) is relatively non-toxic and an essential micronutrient, whereas Cr(VI) is considered to be a health hazard because of its high solubility, non-biodegradability and carcinogenic properties. It has been considered as a group A carcinogen by WHO [2]. Like other heavy metals, Cr(VI) also undergoes the process of bioaccumulation in biological systems resulting in high chromium laden biological sludge from biological treatment units, which is the cause of worry. The common sources of Cr(VI) in environment are electroplating, tanning, pigment, dye, anodizing, photography and chemical manufacturing. The maximum permissible limit of Cr(VI) in wastewater is 0.1 mg/L [3]. The Ministry of Environment and Forest, Government of India has set Minimal National Standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water [4]. So,

to comply with these limits, it is essential that industries treat their effluents to reduce Cr(VI) concentration in water and wastewater to acceptable levels before its disposal into natural environment.

At present, various physico-chemical methods such as reduction, precipitation, ion exchange, coagulation, membrane filtration and biosorption are available for removing hexavalent chromium from industrial wastewaters, but, biosorption is considered to be an attractive process in view of its ease and efficiency with which it can be applied to wastewater treatment. Activated carbon adsorption remains a competitive and effective process for removal of heavy metals but its use is curtailed in developing countries due to its high cost. Therefore, there is a need to develop new and cost effective methods which are more environment friendly. In recent years, investigations have been carried out for the effective removal of Cr(VI) from wastewater using low cost, non-conventional adsorbents [5]. Alibadi et al. [6] have found that lignocellulosic solid wastes have good chromium binding abilities. Hasan et al. [7] have found that maize bran could be an economically viable and potential biosorbent for removal of Cr(VI) ions from aqueous solution. In addition, Lytle et al. [8] found that wetland plants have the ability to reduce toxic Cr(VI) to more stable Cr(III) species. However, the literature is still insufficient to cover this problem and more work and investigations are needed to deal with other locally available and economically cheaper adsorbents to eliminate Cr(VI) from industrial wastewater with different compositions and characteristics.

Sunflower (*Helianthus annuus*) commonly known as *Surajmukhi* is grown in Northern India for oil production. The residual material from sunflower head after threshing out seed is used as

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Nomenclature

BSH	boiled sunflower head
Cr(VI)	hexavalent chromium
Cr(III)	trivalent chromium
g/L	gram/litre
mg/L	milligram per litre
min	minutes
h	hour
V	volume of solution (mL)
MINAS	Minimal National Standards
R (%)	percent removal
q_e (mg/g)	metal uptake loading capacity
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray Spectroscopy
Q_0	maximum adsorption capacity (mg/g)
b	Langmuir constant (L/mg)
R_L	dimensionless constant
R^2	coefficient of correlation
SSE	sum of error squares
WHO	World Health Organization
C_i	initial concentration of Cr(VI) in solution (mg/L)
C_e	equilibrium concentration Cr(VI) in solution (mg/L)
K_f	adsorption capacity (mg/g)
n	Freundlich constant, intensity of adsorption
q_t	amount of Cr(VI) adsorbed at any time 't'
k_1	pseudo-first order equilibrium rate constant (min^{-1})
k_2	pseudo-second order equilibrium rate constant (g/mg/min)
k_{id}	intra-particle diffusion rate constant (mg/g min$^{0.5}$)
C	intercept, thickness of the boundary layer
N	number of data points

feed stuff. The composition of deseeded head (in percentage) is dry matter = 88.27, protein = 8.86, fat = 3.16, carbohydrates = 46.42, fibers = 18.19 and ash content = 11.62 [9]. A bibliographic survey has shown that, no information is available on Cr(VI) removal from aqueous solution by dried sunflower head biomass. This paper reports the removal of Cr(VI) from aqueous solution by sunflower head biomass. This low cost material may be particularly suitable for application in small scale industries and developing countries. The various adsorption isotherms have been applied to the data to elucidate the equilibrium adsorption behaviour.

2. Experimental procedure

The sunflower head waste was collected, at the time of harvesting, from agricultural fields of a village in *Kurukshetra* district, Haryana (India). It was continuously washed with distilled water to remove surface adhered particles and water soluble materials and then dried in sunlight until all the moisture evaporated. The dried mass was ground to fine powder in steel mill. The ground powder was boiled in distilled water for 5 h in the ratio of 1:5 (sunflower:distilled water, w/v) to remove the colour and other leachable impurities. The mixture was filtered, washed with distilled water several times and kept in hot air oven at 80 °C for drying. The resulting material was sieved to get the biosorbent having size ≤300 μm and stored in air tight plastic containers for further use. The wastewater obtained while preparing the adsorbent is having colour and COD and free from any toxic substance. Colour and COD of the wastewater can be removed by biological process.

Aqueous solution of Cr(VI) (1000 mg/L) was prepared by dissolving potassium dichromate (AR grade) in water distilled twice. The aqueous solution was diluted with distilled water to obtain the working solutions of desired concentration. The pH of the solution was adjusted after adding the biosorbent using 0.01 M HCl/0.01 M NaOH. Residual chromium concentration in the filtrate was determined by Atomic Absorption Spectrophotometer (Shimadzu 6300, Japan). All experiments were conducted in triplicate and the percent error in the results was with in ±3%. The mean values of the results are given in this paper.

The batch studies were performed to study the removal of Cr(VI) from synthetic wastewater. A known amount of biosorbent was equilibrated with 50 mL of chromium solution of known concentration in 250 mL Erlenmeyer flasks at 25 ± 1 °C and stirring speed of 180 rpm in thermostatic orbital shaker (Scigenics Biotech ORBITEK) for 180 min. At predetermined time interval, the samples were separated by centrifugation at 4000 rpm for 10 min. The percent chromium removal (R%) was calculated for each run using Eq. (1):

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

where C_i and C_e were the initial and final concentration of chromium in the solution in mg/L.

The metal uptake loading capacity (mg/g) of BSH for each concentration of Cr(VI) ions at equilibrium was determined 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 are the initial and equilibrium metal ion concentration (mg/L) respectively, V is the volume of the solution in mL and M is the mass of the adsorbent (g).

To give qualitative and preliminary analysis of the main functional groups that might be involved in metal uptake, FT-IR analysis in solid phase was performed using Fourier Transform Infrared Spectrum (FTIR, FTIR-8400S, Shimadzu, Japan). 5–10 mg of finely ground sample was mixed homogeneously with dry potassium bromide in the ratio of 1:20 by weight and made pellets in disc by applying pressure. Sample was finely ground to reduce scattering. The surface morphology of the adsorbents was visualized via Scanning Electron Microscope (SEM) [model Quanta 200 FEG, FEI, Netherlands]. The particle size was in the range of 1–300 μm.

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX)

The changes in the functional groups and surface properties of the adsorbent after adsorption were confirmed by FT-IR spectra (Fig. 1a and b). The FT-IR spectra evidence the presence of amino, carboxylic, hydroxyl and carbonyl groups on the adsorbent. The spectra of the native and Cr(VI) loaded biosorbents were measured in the range of 4000–400 cm^{-1} wave number. The FT-IR spectra of BSH has intense peaks at frequency level 3400–3100 cm^{-1} representing –OH group stretching, stretching of carboxylic group and stretching of –NH groups thus showing the presence of hydroxyl and amine group as indicated by the peaks at 3409.91 and 3400.27 cm^{-1} [10] and those around 2948.96 and 2943.17 cm^{-1} of alkyl chains indicating the existence of CH$_2$ asymmetric stretching vibrations. The strong band within 1100–1000 cm^{-1} is due to C–O stretching which is the characteristic peak of polysaccharides and is indicated by the presence of peaks at 1022.20 in native BSH and 1018.34 cm^{-1} in chromium loaded BSH.
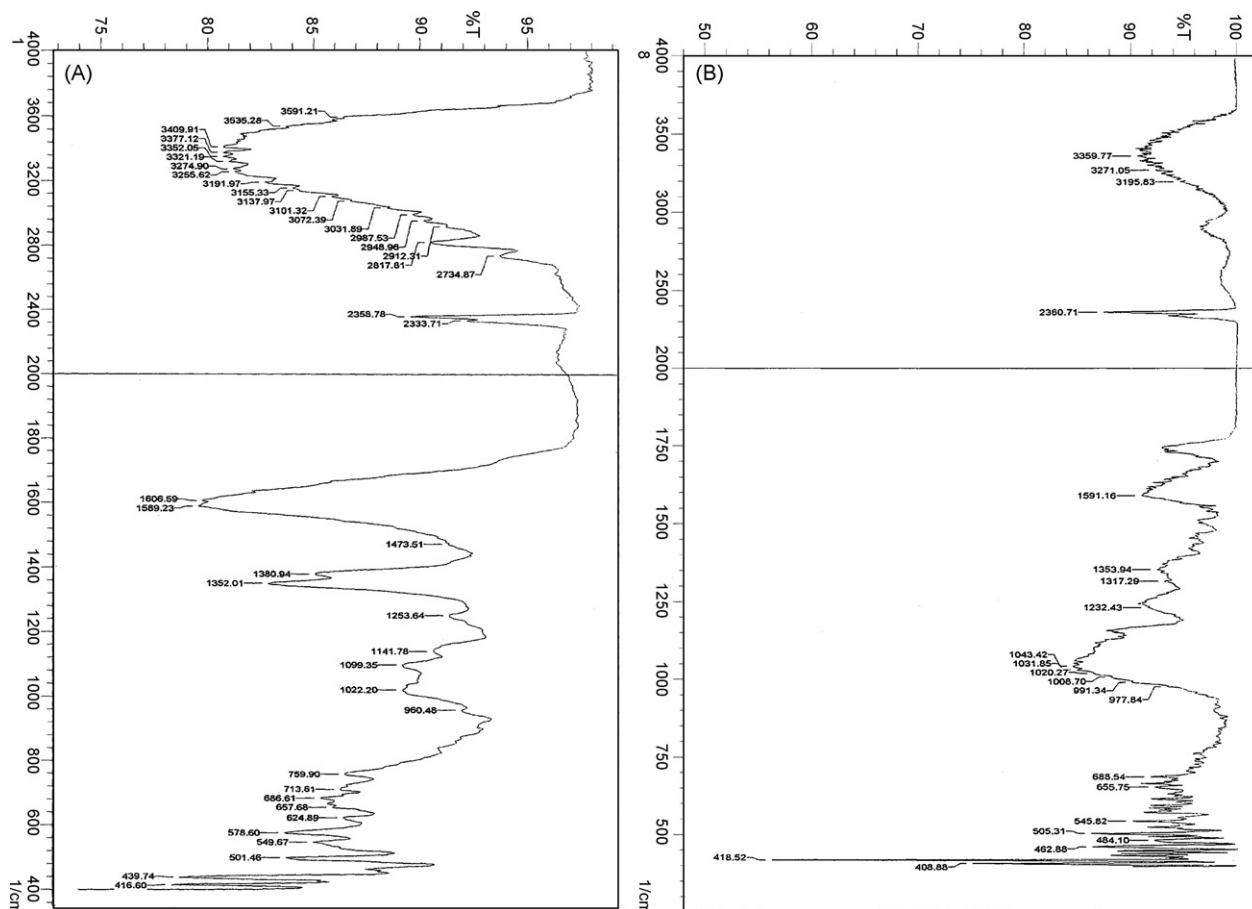
Fig. 1. (a) FT-IR spectra of native BSH. (b) FT-IR spectra of Cr(VI) loaded BSH.

The absorbance of peaks in Cr(VI) loaded BSH is subsequently lower than those in native biosorbent. This indicates that bond stretching occurs to a lesser extent due to presence of chromium and subsequently peak absorption is attenuated [11].

Scanning Electron Microscopy along with Energy Dispersive X-Ray analysis (model Quanta 200 EFG, FEI, Netherlands) has been used as a tool for biosorbent characterization and elucidation of probable mechanism involved in sorption process. Electron micrographs of native BSH (Fig. 2a) shows that its surface before adsorption is irregular and porous and there can be good probability for Cr(VI) ions to be trapped and adsorbed into these pores. It is evident from SEM of Cr(VI) loaded BSH (Fig. 2b) that its surface has become shiny due to deposition of chromium ions after adsorption.

The Energy Dispersive X-Ray analysis is an analytical technique used for the qualitative and quantitative elemental analysis. This technique is used in conjunction with SEM and is not a surface science phenomenon. It provides elemental information through analysis of X-Ray emission caused by a high energy electron beam. The spectra recorded indicate the presence of C, Ca, and O in native BSH (Fig. 3a). These signals are due to X-Ray emissions from cellulose and proteins present on the cell wall of the biomass. Additional signals of chromium are noted in EDX of Cr(VI) loaded BSH indicating the binding of metal ions on the biomass.

3.2. Effect of pH

The pH is an important factor that controls the sorption of heavy metals from wastewater. The percent removal of Cr(VI) as a function of pH for initial chromium concentration = 50 mg/L; stirring speed = 180 rpm; contact time = 2 h; biosorbent dose = 4 g/L; tem-

perature = 25 ± 1 °C and varying pH in the range of 2.0–7.0 is given in Fig. 4. The results show that maximum Cr(VI) removal was 55% at pH 2.0. Thereafter, there was a decline in Cr(VI) removal with increase in pH of test solution. As maximum adsorption was observed at pH 2.0, hence, it was taken as the optimal pH value for further adsorption experiments. The dominant form of Cr(VI) at aforesaid pH is $HCrO_4^-$ [12,13] which arises from the hydrolysis reaction of dichromate ion $(Cr_2O_7^{2-})$ according to the equation:

$$Cr_2O_7^{2-} + H_2O \rightarrow 2HCrO_4^- \quad pK_a = 14.56 \quad (3)$$
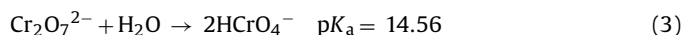
Increasing the pH will shift the concentration of $HCrO_4^-$ to $Cr_2O_7^{2-}$ and other forms like CrO_4^-. More adsorption at acidic pH might be due to increase in number of protons on biosorbent surface which in turn neutralizes the negatively charged hydroxyl group (–OH) on adsorbed surface thereby reducing the hindrance to the diffusion of dichromate ions. At higher pH values, the reduction in adsorption may be possible due to abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions.

Different mechanisms such as electrostatic forces, ion exchange, chemical complexation must be taken into account when examining the effect of pH on Cr(VI) sorption. One of the common proposed mechanisms is electrostatic attraction/repulsion between sorbent and sorbate. Thus, the increase in Cr(VI) sorption at acidic pH may be due to electrostatic attraction between positively charged groups of biomaterial surface and the $HCrO_4^-$ anion, which is the dominant species at low pH. Moreover, the decrease in sorption with increasing pH could also be due to decrease in electrostatic attraction and competition between the chromium anionic species ($HCrO_4^-$ and CrO_4^-) and OH^- ions in the bulk for the adsorption on active sites of the sorbent [14].
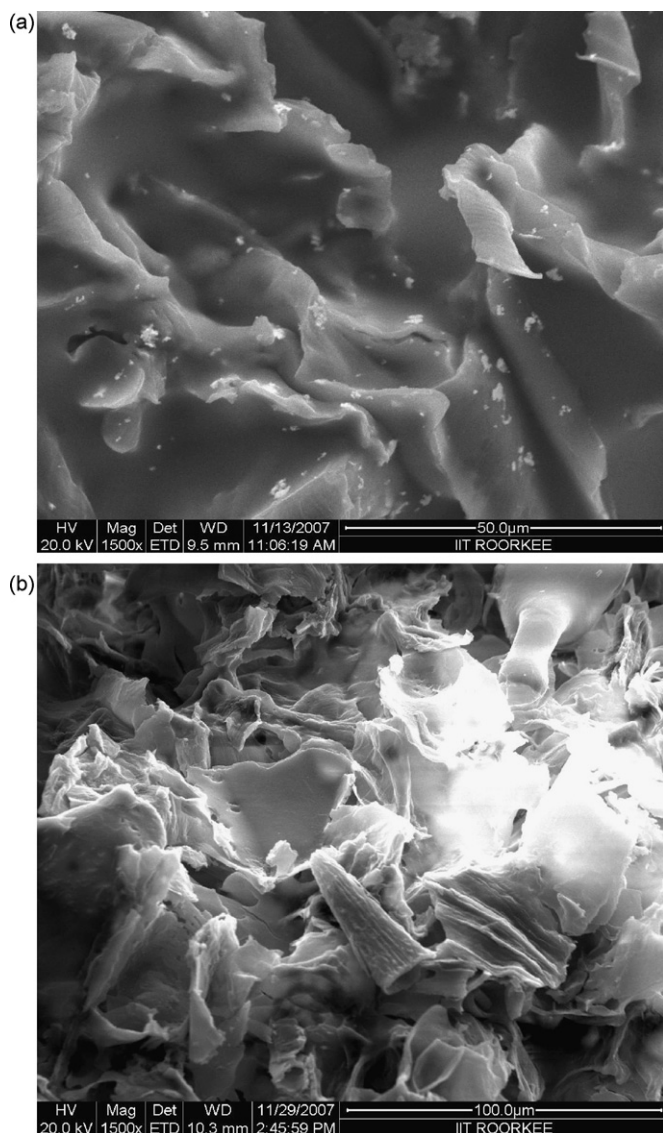
(a)

(A)

(b)

(B)

Fig. 3. (a) EDX of native BSH. (b) EDX of Cr(VI) loaded BSH.

Fig. 2. (a) SEM of native BSH. (b) SEM of Cr(VI) loaded BSH.

70 mg/L (Table 1). This might be due to the fact that increasing metal ion concentration increased the number of collisions between the adsorbent and metal ions thus leading to increased metal uploading capacity [17].

3.3. Effect of initial Cr(VI) concentration and contact time

Cr(VI) removal as a function of initial metal ion concentration and contact time is given in Fig. 5. The initial metal ion concentration was varied from 10 to 70 mg/L while time was varied from 10 to 180 min at constant adsorbent dose of 4.0 g/L; pH 2.0; stirring speed = 180 rpm and temperature 25 ± 1 °C. The maximum Cr(VI) removal was attained within 2 h after that further removal was negligible which may be due to quick exhaustion of adsorption sites after that. After the formation of one molecule thick layer of metal ion on the adsorbent, the capacity of adsorbent gets exhausted and then the uptake rate is controlled by the rate at which the sorbate is transported from exterior to the interior sites of the adsorbent. The data indicates that the initial metal ion concentration determines the equilibrium concentration and also determines the uptake rate of metal ion and its kinetic character [15]. Cr(VI) removal decreased from 90% to 45.2% as initial Cr(VI) concentration increased from 10 to 70 mg/L. This may be due to the saturation of sorption sites in the adsorbent for complexation of Cr(VI) ions at higher concentration [16]. But, the behaviour of adsorption capacity was opposite to that of percent removal. Adsorption capacity (mg/g) increased from 2.3 to 7.9 mg/g as initial chromium concentration increased from 10 to
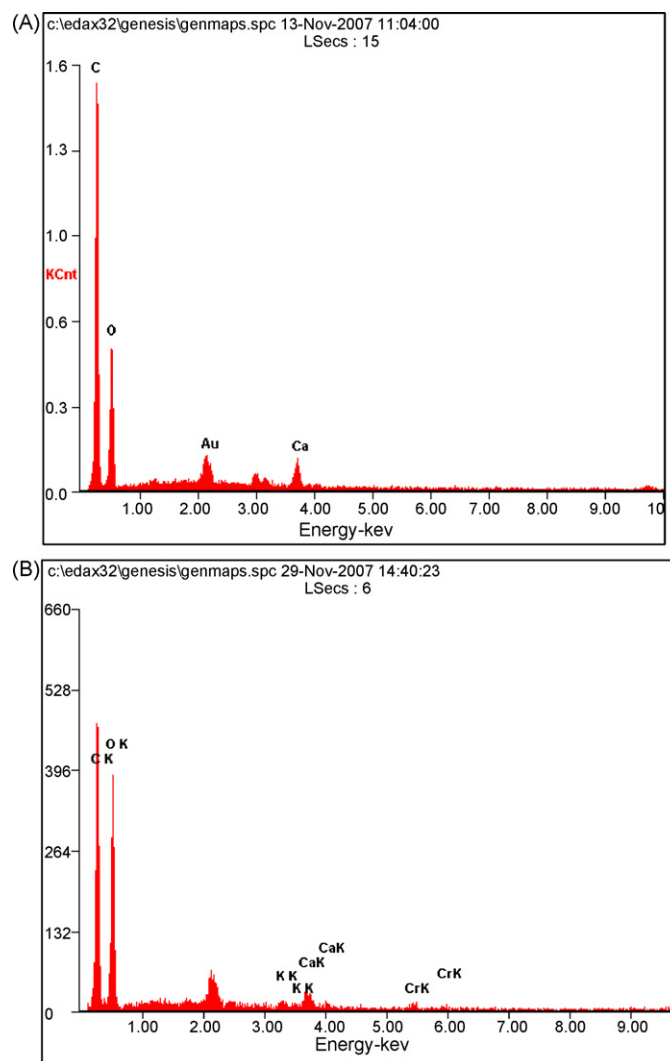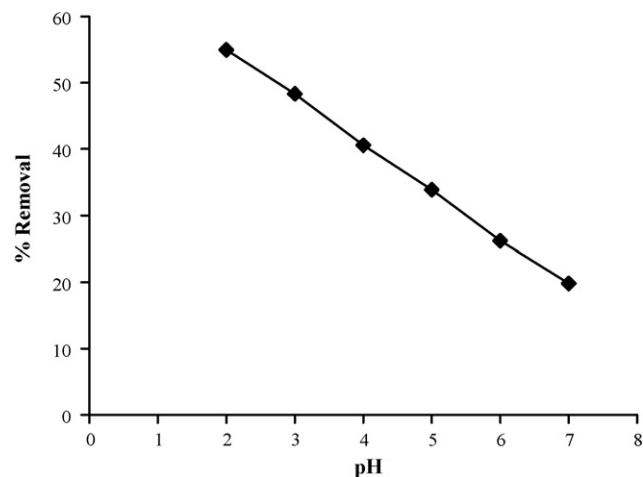

Fig. 4. Effect of pH on Cr(VI) removal by sunflower head [pH = 2, concentration = 50 mg/L, dose = 4 g/L, time = 120 min].
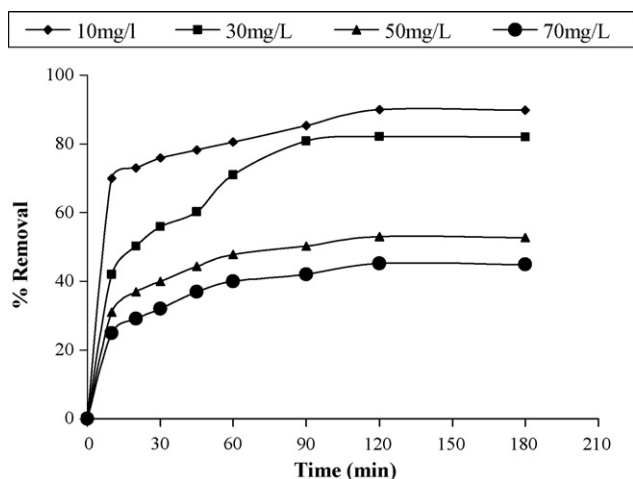
Fig. 5. Effect of initial concentration with contact time on Cr(VI) removal by BSH [pH = 2, dose = 4.0 g/L, temperature = 25 °C, time = 120 min].

Table 1
Adsorption capacity of BSH at different initial chromium concentrations and different adsorbent doses.

Parameter	Adsorption capacity (q_e, mg/g)
Initial chromium concentration (mg/L)	
10	2.30
30	6.20
50	6.60
70	7.90
Adsorbent dose (g/L)	
4	7.90
8	4.70
12	3.50
16	2.90
20	2.60

3.4. Effect of adsorbent dose and contact time

The removal of Cr(VI) was studied by varying the biosorbent dose in aqueous solution while keeping initial Cr(VI) concentration (100 mg/L), temperature (25 ± 1 °C) and pH (2.0) constant. The adsorption increased and equilibrium time decreased with increase in biosorbent dosage (Fig. 6). The biosorption increased from 31.4 to 52.4% as adsorbent dose increased from 4.0 to 20.0 g/L at 120 min while adsorption capacity decreased from 7.9 to 2.6 mg/g with increasing adsorbent dose (Table 1). Maximum Cr(VI) removal was
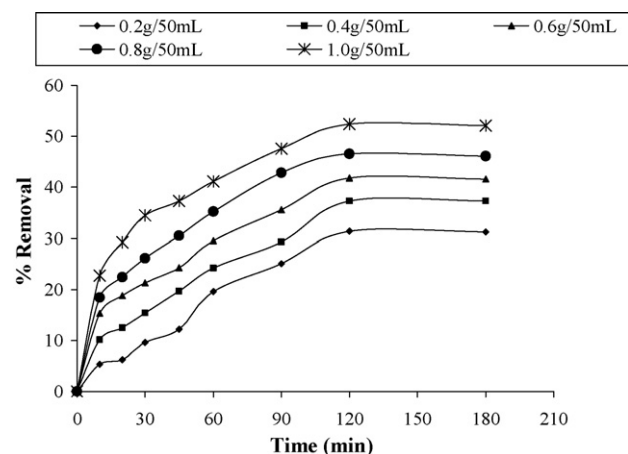

Fig. 6. Effect of adsorbent dose with contact time on Cr(VI) removal by BSH [pH = 2, concentration = 100 mg/L, time = 120 min, temperature = 25 °C].

Table 2
Freundlich and Langmuir model constants for BSH.

Parameter	Value
Freundlich constants	
K_f (mg/g)	2.63
n (L/mg)	3.12
R^2	0.8598
Langmuir constants	
Q_0 (mg/g)	8.177
b (L/mg)	0.36
R^2	0.9882

achieved within 2 h after which it became constant in the test solution. Removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbent and adsorbate at operating conditions. Before attainment of equilibrium, the enhancement of metal sorption could be due to increase in electrostatic interaction between the two. When an optimum amount has been sorbed, rate of adsorption decreased and desorption comes into play which considerably reduced the overall rate of removal. The adsorbed ions either blocked the access to initial pores or caused particles to aggregate, thereby reducing the active site availability. This can be explained due to the fact that at higher biosorbent dose, greater number of exchangeable sites is available for metal ions adsorption [18].

3.5. Adsorption isotherms

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. The linearized Freundlich model isotherm was applied for the adsorption of Cr(VI) and is expressed as Eq. (4).

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

where q_e is the amount of 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). Values of K_f and n were calculated from the intercept and slope of the plot and are given in Table 2. 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 simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not the adjacent sites are occupied. This is in accordance with the Langmuir model which assumes that the uptake of metal ions occur 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 linearized form of Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{5}$$

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 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) follows Langmuir isotherm model for BSH 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 2.

Further analysis of Langmuir equation can be made on the basis of dimensionless constant called separation factor (R_L) which indicates the favorability of the adsorption and is determined by the following equation:

$$R_L = \frac{1}{1 + bC_i} \tag{6}$$

where, b is the Langmuir constant which indicates the nature of adsorption and indicates the shape of the isotherm and C_i is the initial Cr(VI) concentration (mg/L). The R_L values for each of the initial concentration was found to be between 0 and 1 thus indicating favorable adsorption of Cr(VI) onto BSH. The values of R_L calculated were found to be 0.22, 0.08, 0.05 and 0.04 for 10, 30, 50, and 70 mg/L respectively and showed that the adsorption process was favorable for the studied adsorbent.

If,

$R_L > 1$, unfavorable
$R_L = 1$, linear
$0 < R_L < 1$, favorable
$R_L = 0$, irreversible

3.6. Adsorption kinetics

The kinetics of the adsorption describes the rate of uptake of chromium ions onto adsorbent and this rate controls the equilibrium time. The kinetics of Cr(VI) on BSH was analyzed by pseudo-first order, pseudo-second order and intra-particle diffusion models. The experimental data and model predicted data were compared based on regression coefficient (R^2) and are shown in Table 3. The specific rate constant, k_{ad}, for the adsorption of Cr(VI) was calculated using the pseudo-first order Lagergren equation and pseudo-second order equation. The pseudo-first order Lagergren equation is represented as [19]:

$$\log_{10}(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

where q_e and q_t (both in mg/g) are the amounts of Cr(VI) adsorbed at equilibrium time and at any time 't' (min), respectively and k_1 is the equilibrium rate constant of pseudo-first order equation (min^{-1}). 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 time and values of k_1 and q_e are given in Table 3.

Table 3
Kinetic and intra-particle diffusion constant parameters for adsorption of Cr(VI) on BHS.

Parameter	Value
Pseudo-first order	
q_e (mg/g) (exp)	6.63
q_e (mg/g) (cal)	3.34
k_1 (min^{-1})	0.0223
R^2	0.8044
SSE%	0.92
Pseudo-second order	
q_e (mg/g) (exp)	6.63
q_e (mg/g) (cal)	7.03
k_2 (g/mg/min)	0.0138
R^2	0.999
SSE%	0.61
Intra-particle diffusion	
k_{id}	0.3469
C	3.0415
R^2	0.964

Table 4
Adsorbent capacity of different adsorbents for hexavalent chromium.

Adsorbent	Adsorption capacity (mg/g)	Reference
Pomegranate husk	10.59	[22]
CTAB treated *A. niger*	10.60	[23]
Treated sawdust of Indian rosewood	10.0	[18]
Mangrove leaves	8.87	[24]
Termitomyces clypeatus	8.77	[25]
Boiled sunflower head	7.9	This study
Groundnut husk carbon	7.01	[26]
Cactus leaves	7.08	[12]
Eichhornia crassipes	6.98	[27]
Pine needles	5.36	[12]
Iron (III) hydroxide loaded sugar beet pulp	5.12	[28]
Coconut tree sawdust	3.46	[5]

The experimental data was also analyzed using the pseudo-second order model [20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

where k_2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg/min). If pseudo-second order kinetic is applicable to the system under study, the plot of t/q_t versus time of Eq. (8) should give a linear relationship. The second order sorption rate constant and q_e were determined from the slope and intercept of plot t/q_t versus time. The correlation coefficients for the linear plot are very high (0.999). 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 BSH are given in Table 3.

Intra-particle diffusion is another model to study the rate determining step for Cr(VI) adsorption onto BSH and is of major concern because it is the rate limiting step in the liquid adsorption systems. The metal ions are most probably transported from the bulk of the solution onto the solid phase by intra-particle diffusion. The possibility of intra-particle diffusion is explored by using the following equation [21].

$$qt = k_{id}t^{1/2} + C \tag{9}$$

where, q_t is the amount adsorbed (mg/g) at time t (min), k_{id} (mg/g min$^{0.5}$) is the rate constant of intra-particle diffusion. The intra-particle diffusion rate constant was determined from the slope of the linear gradient of plot q_t versus $t^{1/2}$. The R^2 value given in Table 3 is close to unity confirming that the rate limiting step is actually the intra-particle diffusion process. The value of intercept C in the table provides information about the thickness of the boundary layer that is resistant to external mass transfer. The larger the value of intercept, the higher is the external mass transfer.

Besides the value of R^2, the applicability of the kinetic models is verified by the sum of error squares (SSE%). The adsorption kinetics of Cr(VI) on BSH was tested at 50 mg/L at different times. The validity of each model was determined by sum of error squares (SSE%) given by Eq. (10).

$$SSE\% = \frac{\sqrt{\sum (q_{e_{cal}} - q_{e_{exp}})^2}}{N} \tag{10}$$

where N is the number of data points. The higher the value of R^2 and lesser the value of SSE%, the better is the goodness of fit. The calculated results are given in Table 3. A comparison of the adsorption capacity of different adsorbents is given in Table 4. The table shows that the adsorption capacity of BSH is comparable with other adsorbents studied in yesteryears.

4. Conclusions

In this study, the potential of using boiled sunflower head biomass has been assessed for the removal of Cr(VI) from synthetic wastewater and it suggests that BSH can be an adsorbent for the removal of Cr(VI) from dilute aqueous solution. In batch mode study, adsorption was dependent on pH, initial metal ion concentration, biosorbent dose and contact time. The Langmuir model fitted the experimental data well. The BSH exhibits a maximum adsorption capacity of 7.9 mg/g. Adsorption followed pseudo-second order model as indicated by very high values of coefficient of correlation and calculated q_e results are comparable with experimental q_e. The intra-particle diffusion model suggests that, it played a significant role but it was not the main rate determining step during the process. Since, the raw material of sunflower is freely available in large quantities as a waste, the boiling treatment would be effective in removing soluble impurities. Removal of Cr(VI) from wastewater using natural material such as BSH will certainly have a positive effect on the ecosystem.

References

[1] P. Madoni, D. Davoli, G. Gorbi, L. Vescovi, Toxic effect of heavy metals on the activated sludge protozoan community, Water Res. 30 (1996) 135–142.
[2] World Health Organisation, Environmental Health Criteria 61, Chromium, WHO, Geneva, 1988.
[3] Central Pollution Control Board (CPCB), The Environmental (Protection) Rules, Pollution control series PCL/2/1992, Schedule 1, Delhi, 266, 1995.
[4] MINAS, Pollution Control Acts, Rules and Notification under Central Pollution Control Board, Ministry of Environment and Forest, Government of India, New Delhi, 2001.
[5] K. Selvi, S. Pattabhi, K. Kadirvelu, Removal of Cr(VI) from aqueous solution by adsorption on to activated carbon, Biores. Technol. 80 (2001) 87–89.
[6] M. Alibadi, K. Morshedzadeh, H. Soheyli, Removal of chromium from aqueous solution by lignocellulosic solid waste, Int. J. Environ. Sci. Technol. 3 (2006) 321–325.
[7] S.H. Hasan, K.K. Singh, O. Prakash, M. Talat, Y.S. Ho, Removal of Cr(VI) from aqueous solution using agricultural waste 'maize bran', J. Hazard. Mater. 152 (2008) 356–365.
[8] C.M. Lytle, F.W. Lytle, N. Yang, J.H. Qian, D. Hansen, A. Zayed, N. Terry, Reduction of Cr(VI) to Cr(III) by wetland plants: potential for in situ heavy metal detoxification, Environ. Sci. Technol. 32 (1998) 3087–3093.
[9] The Wealth of India, A Dictionary of Indian Raw Materials and Industrial Products, National Institute of Science Communication, CSIR, New Delhi, 2001.
[10] D.L. Pavia, G.M. Lampman, G.S. Kaiz, Introduction to Spectroscopy: A Guide to Students of Organic Chemistry, W.B. Saunders Company, 1987.
[11] L. Norton, K. Baskaran, T. Mckenzie, Biosorption of Zn from aqueous solution using biosolids, J. Adv. Environ. Res. 8 (2004) 629–635.
[12] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of Cr(VI) in industrial wastewater using low cost abundantly available adsorbents, J. Adv. Environ. Res. 6 (2002) 533–540.
[13] C. Namasivayam, R.T. Yamuna, Adsorption of Cr(VI) by low cost adsorbent: biogas residual slurry, Chemosphere 30 (1995) 561–578.
[14] E. Pehlivan, T. Altun, Biosorption of Cr(VI) ion from aqueous solutions using walnut, hazelnut and almond shell, J. Hazard. Mater. 155 (2008) 378–384.
[15] A. Shukla, Y. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. B95 (2002) 137–157.
[16] S.R. Bai, T.E. Abraham, Biosorption of Cr(VI) from aqueous solution by Rhizopus nigricans, Biores. Technol. 79 (2001) 73–81.
[17] Z. Aksu, Equilibrium and kinetic modeling of cadmium (II) biosorption by C. vulgaris in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2002) 285–294.
[18] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, Biores. Technol. 92 (2004) 79–81.
[19] Lagergren, S. Kungl. Sv. Vetensk. Handl. 24 (1898) 1–39.
[20] Y.S. Ho, G. Mckay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[21] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–60.
[22] A.E. Nemr, Pomegranate husk as an adsorbent in the removal of toxic chromium from wastewater, J. Chem. Ecol. 23 (2007) 409–425.
[23] D.P. Mungasavalli, T. Viraraghavan, Y.C. Jin, Biosorption of chromium from aqueous solutions by pretreated Aspergillus niger: batch and column studies, Colloids Surf. A: Physicochem. Eng. Aspects 301 (2007) 214–223.
[24] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of chromium species by aquatic weed, kinetic and mechanism studies, J. Hazard. Mater. 152 (2008) 100–112.
[25] S.K. Das, A.K. Guha, Biosorption of chromium by Termitomyces clypeatus, Colloids Surf. B: Biointerfaces 60 (2007) 46–54.
[26] S.P. Dubey, K. Gopal, Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: a comparative study, J. Hazard. Mater. 145 (2007) 465–470.
[27] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by Eichhornia crassipes, Chem. Eng. J. 117 (2006) 71–77.
[28] H.S. Altundogan, Cr(VI) removal from aqueous solution by iron (III) hydroxide-loaded sugar beet pulp, Process Biochem. 40 (2005) 1443–1452.