Removal of Cr (VI) from aqueous solutions using wheat bran

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ABSTRACT

The possible use of 'wheat bran' as novel biosorbent has been successfully demonstrated in the removal of Cr (VI) from aqueous solution. The effect of different parameters (such as contact time, sorbate concentration, pH of the medium and temperature) were investigated, and maximum uptake of Cr (VI) was attained as $310.58 \, \text{mg} \, \text{g}^{-1}$ at pH 2.0, under the initial Cr (VI) concentration of $200 \, \text{mg} \, \text{L}^{-1}$ and temperature of $40\,^\circ\text{C}$. Effect of pH showed that wheat bran was not only removing aqueous Cr (VI) but also reducing it into less toxic Cr (III). When the sorption kinetics were tested with first-order reversible, pseudo-first-order, and pseudo-second-order reaction, Cr (VI) uptake process followed the pseudo-second-order rate expression. Mass transfer of Cr (VI) from bulk to the solid phase (wheat bran) was studied at different temperatures. Different thermodynamic parameters viz., ΔG°, ΔH° and ΔS° have also been evaluated, and the sorption was feasible, spontaneous, and endothermic in nature. The sorption equilibrium, when expressed by the Langmuir and Freundlich equations, indicated that the process was in compliance with Langmuir isotherm. The results of desorption studies also demonstrated that complete desorption of Cr (VI) took place at pH of 9.5.

1. Introduction

The presence of metal ions in natural or industrial wastewater and their potential impact has been a subject of research in environmental science for a long time. Among the various toxic heavy metals discharged in to the environment through various industrial wastewaters, constituting one of the major causes of environmental pollution, chromium is one of the most toxic and has become a serious health concern. Of its two most common and stable oxidation states, hexavalent chromium Cr (VI) species are known to be much more toxic and hazardous than trivalent chromium Cr (III) species. The main industrial sources of chromium pollution are leather tanning, electroplating, metal processing, wood preservatives, paints and pigments, textile, dyeing, steel fabrication and canning industry. According to Indian standards, the permissible limit of Cr (VI) for industrial effluents to be discharged to surface water is $0.1 \, \text{mg} \, \text{L}^{-1}$. So the removal of Cr (VI) from industrial effluents is important before discharging them in to aquatic environments or on to land. To solve this problem, biosorption can be part of the solution. Biosorption of heavy metals by biomass of bacteria, fungi or alga and agricultural waste have been recognized as a potential alternative to the existing technologies such as pre-

cipitation, ion exchange, solvent extraction and liquid membrane for removal of heavy metals from industrial wastewater, because these processes have the limitations of technical and/or economical viability [1–5].

The literature survey reveals two distinct approaches to the use of biosorbents, either of living microorganisms or non-viable (dead) biomass of microorganism or agricultural waste [6]. There are significant practical limitations to the method, which employ living microorganism systems. Perhaps the most significant limitation is that microbial growth is inhibited when the concentrations of metal ions are too high or when significant amount of metal ions are adsorbed by microorganisms. Thus, for metal removal applications, the use of dead biomass or agricultural waste may be preferable as large quantities are readily and cheaply available as a byproduct of various industries [7–20]. Therefore we have chosen agricultural byproduct wheat bran for the removal of chromium (VI) from wastewater, because it is easily available, economically viable, and biodegradable.

2. Theory

2.1. Sorption isotherm

Different isotherm models have been utilized for describing sorption equilibrium for wastewater treatment. Langmuir and Freundlich equations are being used for present work. The Langmuir

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sorption isotherm describes the surface as homogeneous assuming that all the sorption sites have equal sorbate affinity and that adsorption at one site does not affect sorption at an adjacent site [21]. The linear form of the Langmuir isotherms may be represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \tag{1}$$

The values of Q° and b can be calculated from the slope and intercept of the plot C_e/q_e versus C_e.

The Freundlich sorption isotherm (an empirical equation), however, describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. The linear form of Freundlich sorption isotherm can be represented as [22]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

where, n and K_F are Freundlich isotherm constants. The values of n and K_F can be calculated from the slope and intercept of the plot $\log q_e$ versus $\log C_e$.

2.2. Thermodynamic parameters

Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change of adsorption can be evaluated from the following equations [23,24]:

$$K_c = \frac{C_{A_e}}{C_e} \tag{3}$$

where, K_c is the equilibrium constant and C_{A_e} and C_e (both in mg L^{-1}) are the equilibrium concentrations for solute on the sorbent and in the solution, respectively. The K_c values are used in Eqs. (4) and (5) to determine the ΔG°, ΔH°, and ΔS°.

$$\Delta G^\circ = -RT \ln K_c \tag{4}$$

K_c may be expressed in terms of the ΔH° (kcal mol^{-1}) and ΔS° (cal mol^{-1} K^{-1}) as a function of temperature;

$$\ln K_c = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5}$$

The values of ΔH° and ΔS° can be calculated from the slope and intercept of a plot of $\ln K_c$ versus $1/T$.

2.3. Sorption kinetics

The chemical kinetics describes reaction pathways along times to reach the equilibrium. Sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the sorbent material, which also influence the sorption mechanism. In order to investigate the mechanism of sorption, three different models have been used at different experimental conditions for sorption processes.

2.3.1. First-order reversible model

The sorption of chromium from liquid to solid phase may be considered as a reversible reaction with an equilibrium state being established between two phases. A simple first-order reaction model was, therefore, used to correlate the rates of reaction, which can be expressed as: [25].

$$\ln[1 - U_{(t)}] = -k'' t \tag{6}$$

where, k'' is the overall rate constant and calculate by following equation

$$k'' = k_1 \left(1 + \frac{1}{K_c}\right) = k_1 + k_2 \tag{7}$$

and k_1, k_2, and K_c can be obtained from

$$K_c = \frac{k_1}{k_2} = \frac{C_{A_e}}{C_e} \tag{8}$$

$$U_{(t)} = \frac{X}{X_e} \tag{9}$$

where, $U_{(t)}$ is called the fractional attainment of equilibrium. Therefore, a plot of $-\ln(1 - U_{(t)})$ versus time (min) will give a straight line. Constants k_1, k_2, k'' and K_c were calculated using Eqs. (7) and (8).

2.3.2. Pseudo-first-order model

This was the first equation (Lagergren [26]) for the sorption of liquid/solid system based on solid capacity. This model may be represented as:

$$\frac{dq_t}{dt} = k_s(q_e - q_t) \tag{10}$$

Eq. (10) can be integrated for the following boundary conditions to obtain Eq. (11).

$$t = 0, q_t = 0;$$

$$t = t, q_t = q_t$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_s}{2.303} t \tag{11}$$

where, q_t is amount of solute on the surface of the adsorbent at time 't' and k_s is the equilibrium rate constant of pseudo-first-order adsorption. k_s is calculated from the slope of $\log(q_e - q_t)$ against time (min) plots.

2.3.3. Pseudo-second-order model

This model is expressed as [27]:

$$\frac{dq}{dt} = k_2'(q_e - q_t)^2 \tag{12}$$

After integrating Eq. (12) for the following boundary conditions and rearranging it to obtain the linearized form is shown below;

$$t = 0, q_t = 0;$$

$$t = t, q_t = q_t$$

$$\frac{t}{q_t} = \frac{1}{k_2' q_e^2} + \frac{1}{q_e} t \tag{13}$$

$$h = k_2' q_e^2 \tag{14}$$

where, k_2' is the equilibrium rate constant and h is the initial sorption rate. The equation constants can be determined by plotting t/q_t against t.

3. Materials and method

3.1. Physico-chemical analysis of the biosorbent

Wheat bran is a byproduct of a flour milling plant. It was collected from M/s Shivangi (flourmill) Industries, Chunar, Mirzapur, and Uttar Pradesh. It was washed twice with double distilled water to remove soluble lighter materials. Thereafter, it was dried in an oven at 70 °C for an hour. After that, it was crushed by mortar and pistle and sieved to less than 178 μm size. The surface area of the wheat bran was determined by a three point N$_2$ gas adsorption method using a Quantasorb Surface Area Analyzer (model Q5-7, Quanta chrome Corporation, USA). The bulk density of the biosorbent was determined by densitometer. Porosity of the biosorbent

Table 1
Physical and chemical properties of biosorbent wheat bran.

Physical properties	Wheat bran
Surface area ($m^2 g^{-1}$)	441.00
Bulk density ($g cm^{-3}$)	0.2718
Particle size (μm)	<178
Porosity	0.33
Proximate analysis	
Volatile matter	40.92%
Ash	6.88%
Moisture	7.62%
Fixed carbon	31.78%
Oxides of Al, Mn, Mg, Si, Fe, Ca etc.	12.80%

was determined by porositometer (model H: M7 V, NGRI, Hyderabad, India). X-ray diffraction of the adsorbent was obtained using X-ray Diffractometer (model-ID-3000W, Rich Siefert and Company, Ahrensburg, Germany). Infrared spectra of the biosorbent were recorded using Infra Red Spectrophotometer (model FT/IR-5300, JASCO Corporation, Japan) in the range 4000–400 cm^{-1}. Percentage of volatile matter, ash, and moisture were determined as given in the "Vogel's Textbook of Quantitative Chemical Analysis", 5th Edition, Bath Press Ltd., U.K.

Various physico-chemical properties of wheat bran thus obtained are given in Table 1. X-ray diffraction and IR studies (values given in Table 2) of wheat bran show that apart from various organic functional groups wheat bran also contains metal oxides.

3.2. Reagents

The entire primary chemicals used were of analytical grade: Potassium dichromate, hydrochloric acid, sodium hydroxide, 1,5-diphenylcarbazide, potassium permanganate and purchased from E. Merck, India Ltd., Mumbai, India.

The stock solution containing 1000 mg L^{-1} of Cr (VI) was prepared by dissolving 1.4143 g of $K_2Cr_2O_7$ in 500 mL of deionized, double distilled water. Required initial concentration of Cr (VI) standard was prepared by appropriate dilution of the above stock Cr (VI) standard solution.

3.3. Batch sorption experiment

In the present investigation the batch mode of operation was selected in order to measure the progress of adsorption. It was carried out by shaking adsorbent with 50 mL aqueous solution of Cr (VI) of different concentrations at different temperatures, different pH, and at different contact time. Different initial concentration of Cr (VI) solution was prepared by proper dilution from stock 1000 mg L^{-1} Cr (VI) standard, and pH of the solution was monitored by adding 0.1 M HCl and 0.1 M NaOH solution as required. Necessary amount of biosorbent was then added and content in the flask were shaken for the desired contact time in an electrically

Table 2
IR bands of wheat bran along with their possible assignment.

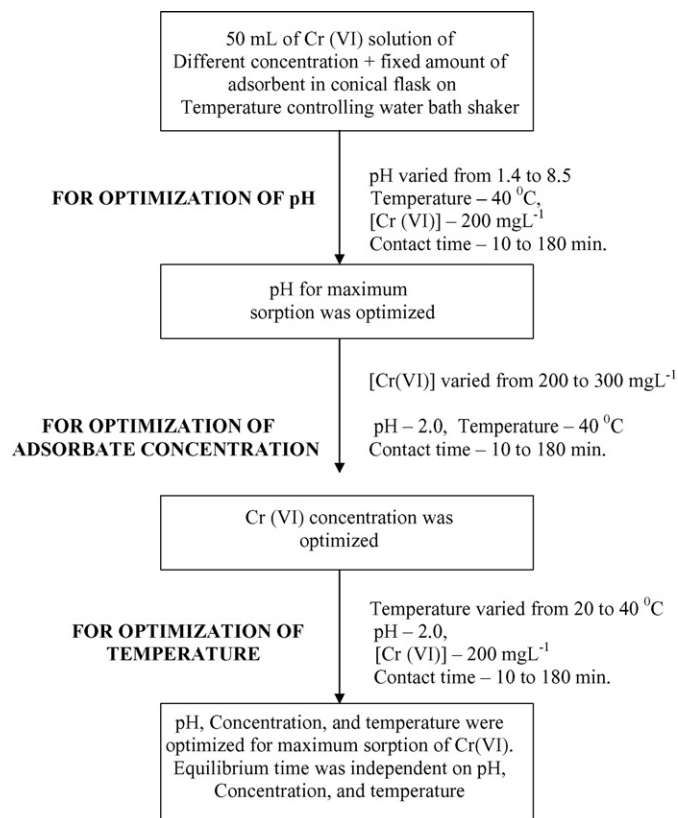| Band position (cm^{-1})		Assignment
3436	w	—OH str.
2910	w	—C=C—H str.
1748	w	—C=O str.
1552, 1520	s	Aromatic ring
1490	w	>N—H str.
775	m	—C—H Def.
750	m	Al—O
472	s	Si—O—Ca bend
448	s	Si—O bend
422	m	Fe—O

Fig. 1. A flow diagram to depict the full experimental scheme.

thermostated reciprocating shaker at 125 rpm. The time required for reaching equilibrium condition estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of flask separated from biosorbent by centrifuge at 15,000 rpm and supernatant liquid was analyzed for remaining Cr (VI) concentration in the sample. A flow diagram is also given to depict the full experimental scheme (Fig. 1).

The percentage removal of Cr (VI) was calculated as follows:

$$\text{Percentage removal of Cr (VI)} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (15)$$

3.3.1. Effect of pH
The effect of pH in sorption experiments was investigated by using 1 g of wheat bran for 50 mL solution with 200 mg L^{-1} Cr (VI) at 40 °C; the pH of the solution was adjusted from 1.4 to 8.5 by adding 0.1 M HCl and 0.1 M NaOH.

3.3.2. Effect of initial metal ion concentration and contact time
Effect of variation of initial metal ion concentration and contact time was studied using 50 mL Cr (VI) solution of concentration 200, 250, and 300 mg L^{-1} and contact time 10–180 min with an interval of 10 min, respectively, at pH 2.0 and 1 g of biosorbent in 50 mL of aqueous solution.

3.3.3. Effect of temperature
The effect of temperature on the sorption of Cr (VI) was investigated at different temperature 20, 30 and 40 °C at pH 2.0 and 50 mL Cr (VI) solution of concentration 200 mg L^{-1}, and 1 g of biosorbent.

3.4. Desorption

Desorption experiments were carried out using double distilled water and aqueous solution of different known pH solutions such as

2.5, 3.5, 4.5, 6.5 and 9.5 as eluant. For all the desorption experiments chromium loaded wheat bran was shaken with 50 mL of eluant solution. Desorption efficiency was calculated by using following equation:

$$\text{Desorption efficiency} = \frac{\text{Amount of Cr (VI) desorbed}}{\text{Amount of Cr (VI) sorbed}} \times 100 \qquad (16)$$

3.5. Chromium analysis

3.5.1. Chromium (VI) analysis

For the determination of Cr (VI) in the aqueous solution 0.25% solution of 1,5-diphenylcarbazide in 50% acetone was prepared as required. The standard solution for the calibration of spectrophotometer (Spectronic 20, Bausch and Lomb, U.S.A.) was in the range of 0.2–0.5 mg L^{-1} of dichromate. To about 15 mL of this solution added sufficient 3 M H_2SO_4 to make the concentration about 0.1 M, then to this solution added 1 mL of diphenylcarbazide reagent and was made up to 25 mL with water. The pink coloured complex was formed when 1,5-diphenylcarbazide was added into Cr (VI) in acidic solution and concentration was determined spectrophotometrically at 540 nm by Spectronic 20 (Bausch and Lomb, U.S.A.) [28].

3.5.2. Chromium (III) analysis

For the determination of Cr (III) concentration, Cr (III) (formed due to the reduction of Cr (VI) into Cr (III) during the sorption process) was again converted to Cr (VI) by the addition of excess potassium permanganate at high temperature (130–140 °C) thereafter the 1,5-diphenycarbazide was added. The pink coloured complex formed gives the concentration of Cr (VI) and Cr (III) which is total chromium. The Cr (III) concentration was then calculated by the difference of the total chromium and Cr (VI) concentrations measured above [28].

4. Results and discussion

4.1. Effect of pH

Experiments were performed by varying pH from 1.4 to 8.5 at 40 °C temperature and initial concentration of 200 mg L^{-1}. Initially, the uptake of Cr (VI) was increasing with increase of pH up to 2.0 and then decreased with the rise of pH from 2.0 to 8.5 (Fig. 2). The optimum pH for the maximum uptake of Cr (VI) was found at 2.0. This can be explained that since Cr (VI) exists in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, etc. in acidic medium and the lowering of pH caused the surface of the biosorbent to become protonated to a higher extent and as a result a strong attraction exists between these oxyanions of Cr (VI) and positively charged surface of the biosorbent. Hence, the uptake increases with the decrease in the pH of the solution. Whereas at high pH, biosorbent surface will be negatively charged and in addition to this there will be abundance of negatively charged hydroxyl ions in aqueous solution. Both of these factors can cause hindrance in the biosorption of negatively charge $Cr_2O_7^{2-}$, CrO_4^{2-} etc. resulting in the decrease uptake of Cr (VI) at high pH value. Another change which was also observed at low pH (2.0) that the colour of the surface of biosorbent turned greenish during sorption. This was certainly due to the sorption of Cr (III) (greenish) in a reduced form of chromium on the surface of sorbent. Thus, during sorption of Cr (VI) on the surface wheat bran, there was sorption of Cr (VI) as well as Cr (III). Reduction of Cr (VI) into Cr (III) is also clear from the aqueous chemistry of Cr (VI) at low pH value;
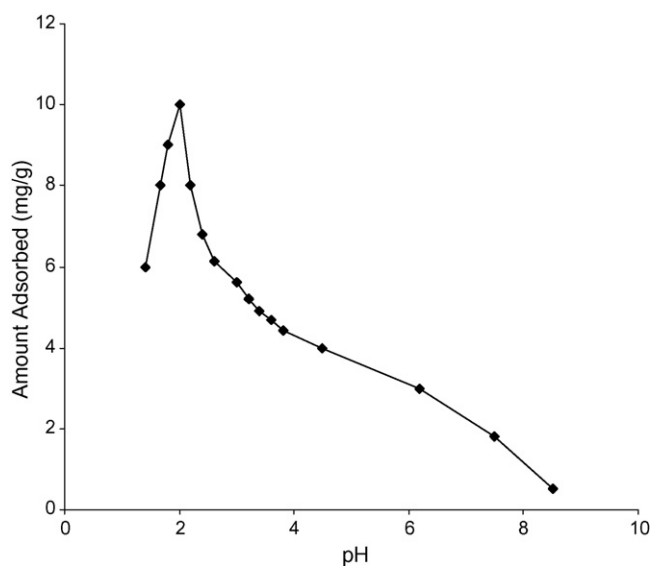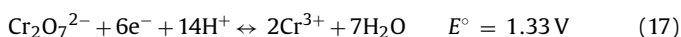
$$Cr_2O_7^{2-} + 6e^- + 14H^+ \leftrightarrow 2Cr^{3+} + 7H_2O \qquad E^\circ = 1.33\,\text{V} \qquad (17)$$

Fig. 2. Effect of pH on the adsorption by wheat bran. Conditions: pH 1.4–8.5; initial Cr (VI) concentration 200 mg L^{-1}; temperature 40 °C; particle size <178 μm.

There, $Cr_2O_7^{2-}$ acts as an oxidant, to oxidize the surface of the biosorbent, while it is reduced to Cr (III).

Another proof which is also supporting this fact is that, there was sorption of Cr (VI) as well as Cr (III) on the surface of the biosorbent during the sorption process. It was observed when concentration of Cr (VI) was analyzed at equilibrium (C_e). For this purpose, supernatant liquid after sorption was divided into two parts. In one sample, Cr (VI) concentration (C_e) was measured by the prescribed method. In contrast, another sample of Cr (VI) was determined after heating up solution up to 130–140 °C with $KMnO_4$ solution. It was found that in the second case, concentration of Cr (VI) was higher than the previous one. This may be explained because $KMnO_4$ (as a very powerful oxidizing agent) oxidized Cr (III) to Cr (VI) during the sorption process at low pH. Thus, it is expected that the sorption of Cr (VI) and Cr (III) can proceed simultaneously during sorption process at low pH. Similar observations have also been reported by other workers [16,29,30].

4.2. Effect of contact time and concentration

A series of experiments were performed at different initial sorbate concentration viz., 200, 250 and 300 mg L^{-1} at time interval of 10 min up to 3 h at a temperature of 40 °C and pH 2.0. The uptake of Cr (VI) was found 9.92, 11.96 and 13.64 mg g^{-1}, respectively (Fig. 3). The extent of sorption increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium. Equilibrium time for the sorption of Cr (VI) on wheat bran at various sorbate concentrations was found to be 110 min, which showed that equilibrium time was independent of initial sorbate concentration. The removal curves thus obtained are single smooth and continuous, suggesting the formation of monolayer of sorbate on the surface of the sorbent.

4.3. Effect of temperature

Experiments were performed at different temperatures 20, 30 and 40 °C at a concentration of 200 mg L^{-1} and pH of 2.0. The uptake of Cr (VI) was increased from 9.1, 9.49, and 9.92 mg g^{-1} with the rise in temperature from 20 to 40 °C (Fig. 4). Equilibrium time for all three temperatures (20, 30 and 40 °C) was approximately 110 min, being independent of temperature. The above results also showed that the sorption was endothermic in nature. Since sorbent
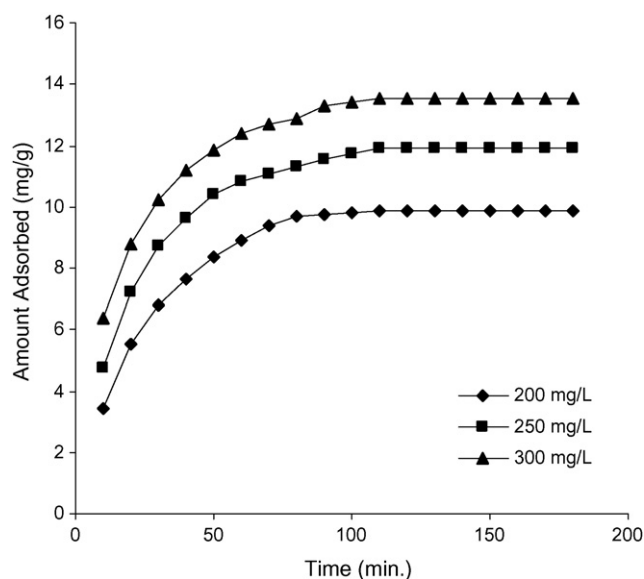
Fig. 3. Effect of contact time and initial metal ion concentration on adsorption by wheat bran. Conditions: pH 2.0; temperature 40 °C; particle size <178 μm; initial Cr (VI) concentration (◆) 200, (■) 250, (▲) 300 mg L^{-1}.

is porous in nature, possibilities of diffusion of sorbate cannot be ruled out. Therefore, increase in the sorption with the rise of temperature may be diffusion controlled which is endothermic process, i.e., the rise of temperatures favours the sorbate transport with in the pores of sorbent [30]. The increased sorption with the rise of temperature is also due to the increase in the number of the sorption sites generated because of breaking of some internal bonds near the edge of active surface sites of sorbent [31,32].

4.4. Thermodynamic evaluation of the process

Thermodynamic parameters such as free energy of sorption ($\Delta G°$), the heat of sorption ($\Delta H°$), and standard entropy ($\Delta S°$) changes during the adsorption process were calculated using Eqs. (3)–(5) at different temperatures (20, 30 and 40 °C) at 200 mg L^{-1}.
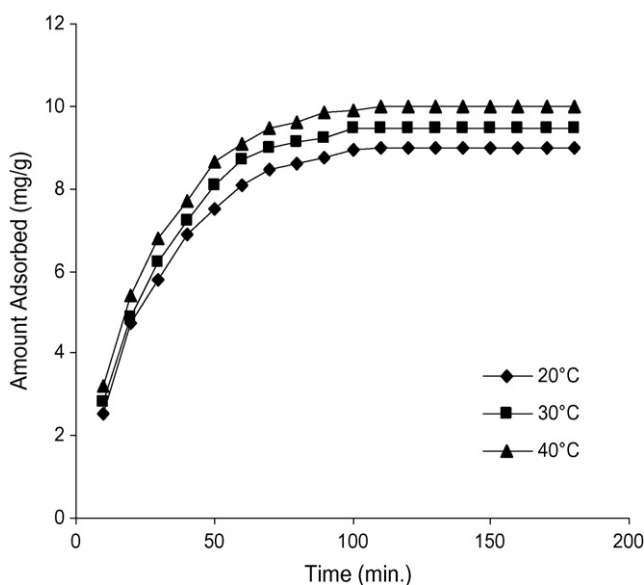

Fig. 4. Effect of temperature on the sorption by wheat bran. Conditions: initial Cr (VI) concentration 200 mg L^{-1}; pH 2.0; temperature 20 °C (◆), 30 (■) and 40 °C (▲); particle size <178 μm.
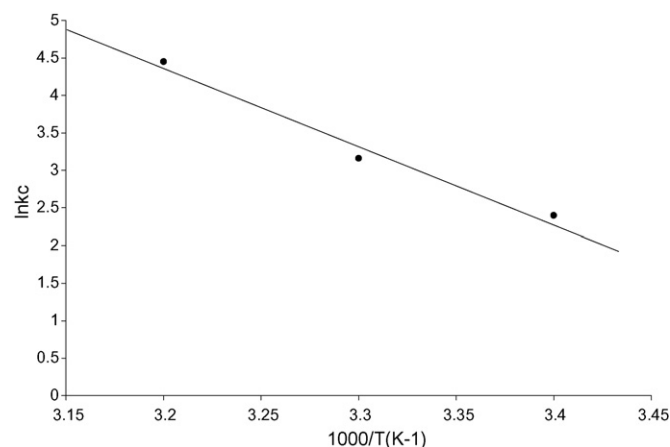

Fig. 5. A plot of ln K_c versus $1/T$ for Cr (VI) sorption by wheat bran at 200 mg L^{-1}.

The values of ($\Delta H°$) and ($\Delta S°$) were obtained from the slope and intercept of a plot of ln K_c against $1/T$ (Fig. 5). The values of these parameters are recorded in Table 3. The negative values of $\Delta G°$ indicate the spontaneous nature of the process. In addition, more negative value with the increase of temperature shows that the sorption process is promoted with an increase in temperature. The positive values of $\Delta H°$ indicate that the sorption process was endothermic in nature and the negative values of $\Delta S°$ suggest the probability of a favorable sorption.

4.5. Sorption isotherms

The isotherm constants were calculated from the slope and intercept of the Fig. 6a (Langmuir isotherm) and Fig. 6b (Freundlich isotherm) and presented in Table 4. The value of r^2 was higher for Langmuir isotherm than the Freundlich isotherm; this implies that Langmuir equation represented the adsorption process more ideally. $Q°$ value defined as the maximum capacity of sorbent was calculated from the Langmuir plots in the range of 282.54–310.58 mg g^{-1} at different temperatures. This indicates the good sorbing capacity of the wheat bran.

The equilibrium parameter R_L is defined as $R_L = 1/(1 + bC_{A_0})$. If R_L falls in the range $0 < R_L < 1$, it reflects the favorable adsorption process [33]. In the present investigation, the equilibrium parameter was found to be in the range $0 < R_L < 1$, as shown in Table 4. Hence the sorption process was very favorable and the adsorbent employed exhibited a good potential for the removal of Cr (VI) from aqueous solution [33].

4.6. Sorption kinetics

In order to predict the sorption kinetic models of Cr (VI), first-order reversible, pseudo-first-order, and pseudo-second-order kinetic models were applied to the data. The effect of the initial Cr (VI) concentrations and temperatures exhibited the best kinetic model. The straight-line plots of $-\ln(1 - U_{(t)})$ versus t (min) were tested to obtain the first-order rate constant at the different experimental conditions. Approximate linear fits were generally observed

Table 3
Thermodynamic parameters for sorption of Cr (VI) on wheat bran at different temperature.

Temperature (°C)	$-\Delta G°$ (kcal mol^{-1})	$\Delta H°$ (kcal mol^{-1})	$-\Delta S°$ (cal mol^{-1} K^{-1})
20	1.265		
30	1.745	22.514	79.452
40	2.783		

Table 4
Values of Langmuir and Freundlich sorption constants and R_L values for sorption of Cr (VI) on wheat bran at different temperatures.

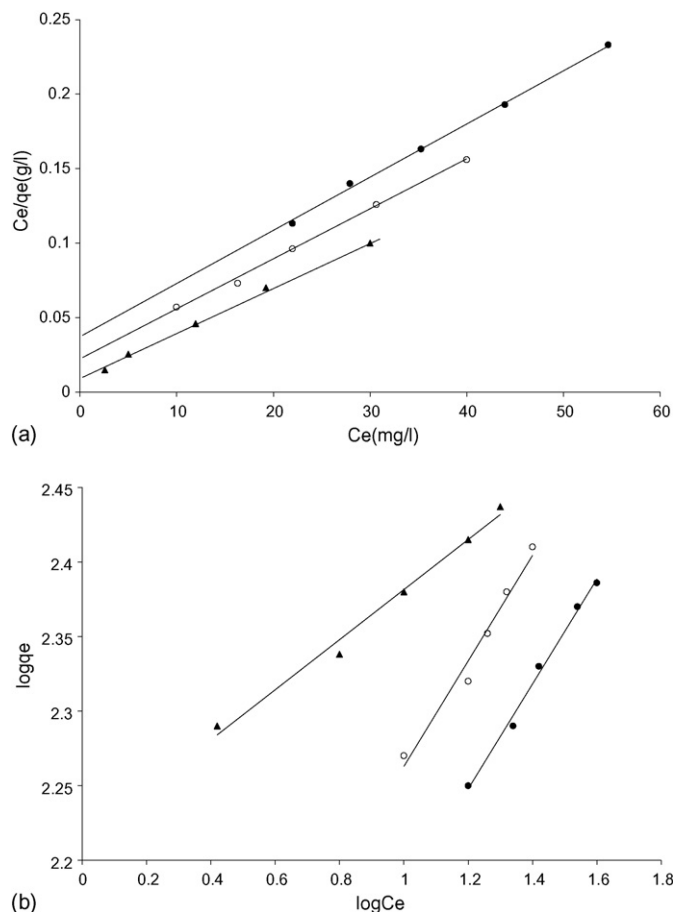| Langmuir constants					Freundlich constants			
Temperature (°C)	$Q°$ (mg g^{-1})	b (L mg^{-1})	R_L	r^2	n	K_F	r^2
20	282.54	0.604	8.070×10^{-3}	0.999	3.246	0.272	0.848
30	296.43	0.158	2.968×10^{-2}	0.993	4.485	0.318	0.889
40	310.58	0.062	7.025×10^{-2}	0.989	7.828	0.362	0.862

Fig. 6. (a) Langmuir isotherm plot for Cr (VI) removal using wheat bran. Conditions: Particle size <178 μm; pH 2.0; temperature 20 °C (●), 30 (○) and 40 °C (▲) and concentrations 200, 225, 250, 275 and 300 mg L^{-1}. (b) Freundlich isotherm plot for Cr (VI) removal using wheat bran. Conditions: Particle size <178 μm; pH 2.0; temperature: 20 °C (●), 30 (○) and 40 °C (▲) and concentrations 200, 225, 250, 275 and 300 mg L^{-1}.

for all concentrations and temperatures, indicating that sorption reaction can be approximated to be of the first-order reversible kinetics. The computed correlation coefficients 0.808 and 0.922 (Table 5) suggest a good agreement with first-order reversible

kinetic model. For the pseudo-first-order adsorption rate constant, the straight-line plots of log $(q_e - q_t)$ against time were analyzed. As linear fits were observed for all concentrations and temperatures, sorption reaction can be approximated to first-order kinetics. The smallest correlation coefficient in this case was 0.862, which is still better than the first-order reversible reaction model. Constant k_s for all tested situations have been calculated and summarized in Table 5. The equilibrium rate constants of pseudo-second-order were determined (Fig. 7a and b) by plotting t/q_t against time t (min). The kinetic constant and correlation coefficients of these models were calculated and given in Table 5. Good correlation coefficients for all the concentrations and temperatures indicating that chromium uptake process can be approximated with the pseudo-second-order kinetics model. The smallest correlation coefficient of 0.996 suggests its superiority to the first-order reaction model. Thus, the pseudo-second-order kinetics was determined as a pathway to reach the equilibrium.

4.7. Intraparticle diffusion study

During the batch mode of operation, there was a possibility for transport of sorbate species into the pores of sorbent, which often acts as the rate controlling step. The rate constants of intraparticle diffusion (k_{id}) at different temperatures were hence determined using the following equation [34]:

$$q = k_{id}\, t^{1/2} \tag{17'}$$

where, q is the amount sorbed at time t and $t^{1/2}$ is the square root of the time. The values of k_{id} (9.348×10^{-3}, 1.332×10^{-2}, and 1.528×10^{-2} mg g^{-1} min$^{-1/2}$) at temperatures 20, 30 and 40 °C respectively were calculated from the slopes of respective plot q versus $t^{1/2}$ (Fig. 8) at later stages. The dual nature of the curves was obtained due to the varying extent of sorption in the initial and final stages of the experiment. This can be attributed to the fact that in the initial stages, sorption was due to boundary layer diffusion effect, whereas in the later stages (linear portion of the curve) due to the intraparticle diffusion effects. However, these plots indicated that the intraparticle diffusion was not the only rate controlling step because it did not pass through the origin. This was further supported by calculating the intraparticle diffusion coefficient ($\bar{D}$) using the following equation [35].

$$\bar{D} = \frac{0.03 r^2}{t_{1/2}} \tag{18}$$

Table 5
A comparison of first-order reversible, pseudo-first-order and pseudo-second-order kinetic models rate constants obtained at different experimental conditions.

| Parameters	First-order reversible					Pseudo-first-order		Pseudo-second-order		
	K_c	k''	k_1 ($\times 10^{-3}$)	k_2 ($\times 10^{-3}$)	r^2	k_s ($\times 10^{-2}$)	r^2	h	q_e (cal)	r^2
C_o (mg L^{-1}) at 40 °C										
200	7.84	0.088	73.98	9.66	0.922	5.365	0.917	0.516	12.84	0.998
250	14.98	0.075	66.85	4.85	0.862	4.198	0.896	0.764	13.95	0.998
300	33.34	0.065	61.82	1.96	0.818	3.328	0.886	1.195	15.34	0.997
Temperature (°C) at Cr (VI) 200 mg L^{-1}										
20	34.72	0.068	61.25	1.84	0.808	4.305	0.862	0.398	11.75	0.997
30	15.25	0.074	65.78	4.65	0.838	4.976	0.887	0.436	12.48	0.996
40	7.84	0.088	73.98	9.66	0.922	5.365	0.917	0.516	12.84	0.998
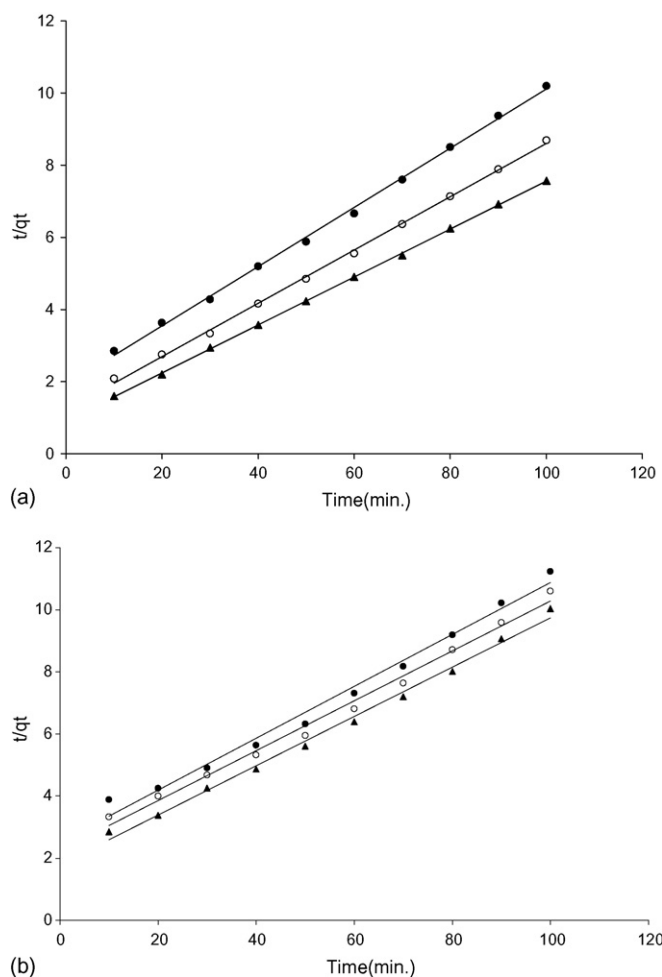
Fig. 7. (a) Pseudo-second-order plot for Cr (VI) removal using wheat bran at 200 (●), 250 (○) and 300 mg L^{-1} (▲). Conditions: Temperature 30 °C; particle size <178 μm, pH 2.0 and agitation rate 125 rpm. (b) Pseudo-second-order plot for Cr (VI) removal using wheat bran at 20 (●), 30 (○) and 40 °C (▲). Conditions: Concentration 200 mg L^{-1}; particle size <178 μm, pH 2.0 and agitation rate 125 rpm.

where r (cm) is the average radius of the sorbent particle, and $t_{1/2}$ (min) is the time for half of the sorption. According to the Michelsen et al. [35], a $\bar{D}$ value of the order of 10^{-11} cm^2 s^{-1} is indicative of intraparticle diffusion as rate determining step. In this inves-
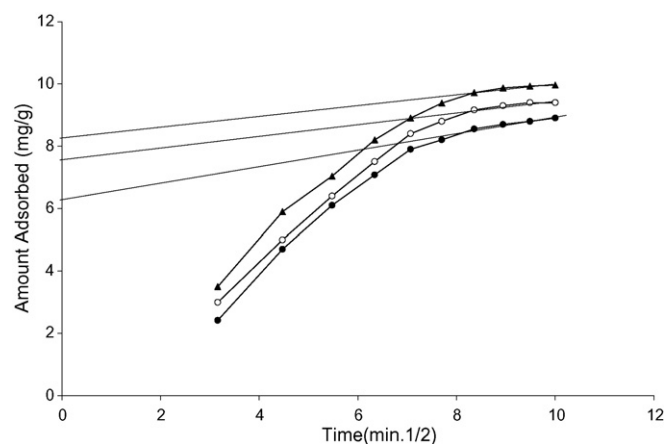

Fig. 8. Intraparticle diffusion plot for adsorption of Cr (VI) on wheat bran at 20 (●), 30 (○) and 40 °C (▲). Conditions: Concentration 200 mg L^{-1}; pH 2.0; particle size <178 μm and agitation rate 125 rpm.

tigation, the computed values of $\bar{D}$ (5.816×10^{-9}, 7.482×10^{-9}, and 8.316×10^{-9} cm^2 s^{-1} at 20, 30 and 40 °C, respectively) was in order of 10^{-9} cm^2 s^{-1}, this was more than two order of magnitude higher than 10^{-11} cm^2 s^{-1}. It thus suggests that the intraparticle diffusion was not the only rate controlling step. Thus, both boundary layer and intraparticle diffusion are suspected to be involved in this removal process.

4.8. Mass transfer study

The uptake of pollutant species from liquid phase (sorbate) to solid surface (sorbent) is carried out by transfer of mass from the former to the latter. A number of steps have been considered which are taking part in the sorption process. For this purpose, various models were tried and discussed to explain the sorption process. However, a three step McKay et al. model [36] was considered to be the best to explain the process:

1. Mass transfer of sorbate from the aqueous phase on to the solid surface.
2. Sorption of solute on to the surface sites, and
3. Internal diffusion of solute via either a pore diffusion model or homogeneous solid phase diffusion model.

During the present investigation, step (2) has been assumed rapid enough with respect to the other steps. Therefore, it is unlikely rate limiting in any kinetic study. Taking in to account these probable steps, McKay et al. model [36] has been used for the present investigation:

$$\ln \left(\frac{C_A}{C_{A0}} - \frac{1}{1+mK} \right) = \ln \left(\frac{mK}{1+mK} \right) - \left(\frac{1+mK}{mK} \right) \cdot \beta_1 \cdot S_s \cdot t \quad (19)$$

where m is the mass of the biosorbent per unit volume, K is the constant obtained by multiplying Q° and b (Langmuir's constants), β_1 is the mass transfer coefficient, and S_s is the outer specific surface of the biosorbent particles per unit volume of particle-free slurry. The values of m and S_s were calculated using the following relations:

$$m = \frac{W}{V}, \quad (20)$$

$$S_s = \frac{6m}{d_p \delta \rho (1 - \varepsilon_p)}, \quad (21)$$

where W is the weight of the adsorbent, V the volume of particle-free slurry solution, and d_p, $\delta \rho$ and ε_p are the diameter, density and porosity of the adsorbent particles, respectively.

The values of β_1 (6.836×10^{-5}, 6.415×10^{-5} and 5.848×10^{-5} cm s^{-1}) were calculated from the slopes and intercepts of the plots (Fig. 9) of $\ln(Ct/C0 - 1/1 + mK)$ versus t (min) at different temperatures (20, 30 and 40 °C). The values of β_1 obtained show that the rate of mass transfer from bulk solution to the biosorbent surface was rapid enough so that it cannot be a rate controlling step [37]. It can also be mentioned that the deviation of some of the points from the linearity of the plots indicated the varying extent of mass transfer at the initial and final stages of the sorption.

4.9. Desorption studies

Desorption results (Fig. 10) indicated that 21.2, 44.0, 58.1, 74.2 and 100% of Cr (VI) were removed from the surface of the biosorbent containing 9.92 mg g^{-1} of Cr (VI) at pH of 2.5, 3.5, 4.5, 6.5 and 9.5 respectively and temperature of 20 °C. The rate of sorption was thus highly pH dependent. The adsorbate ions which were bonded weakly to the adsorbent surface started to remove on increasing of pH, while they were completely desorbed when pH reached to 9.5.
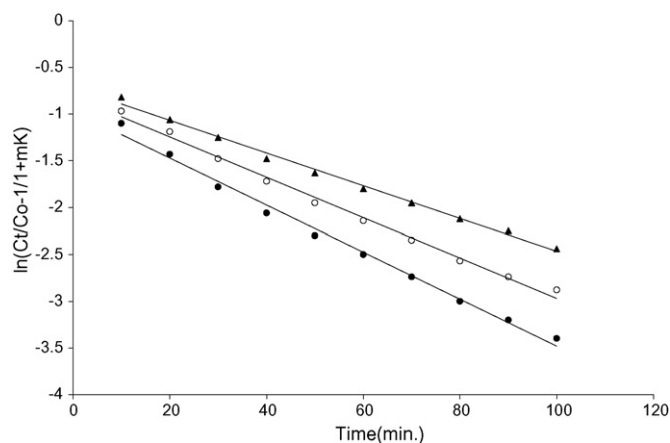
Fig. 9. Mass transfer plot for the adsorption of Cr (VI) on wheat bran at 20 (●), 30 (○) and 40 °C (▲). Conditions: Concentration 200 mg L^{-1}; particle size <178 μm; pH 2.0 and agitation rate 125 rpm.
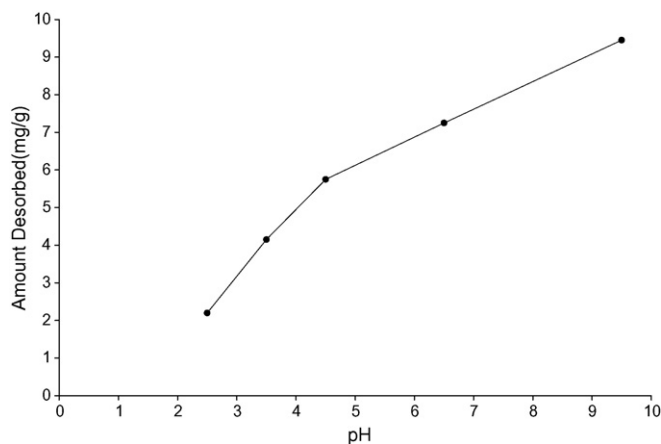

Fig. 10. Effect of pH on the desorption of Cr (VI) from wheat bran.

4.9.1. Infrared studies

The characteristics IR band of dichromate ion at 750 and 860 cm^{-1} were shifted to 790 and 900 cm^{-1} after the biosorption of Cr (VI) on the adsorbent. It showed the binding of surface sites with the sorbate ions [38]. The disappearance of above bands after desorption at pH 9.5 supported the desorption result for complete Cr (VI) detachment from the biosorbent surface.

5. Conclusions

Wheat bran has been found to be a very economically viable and effective biosorbent for the removal of Cr (VI). The maximum removal of Cr (VI) was found to be 310.58 mg g^{-1} at pH 2.0, initial Cr (VI) concentration of 200 mg L^{-1} and temperature of 40 °C. The removal of Cr (VI) was rapid in the initial stages and became slower afterwards; it was also confirmed by the mass transfer studies. The double nature of the curves attributed to the fact that the adsorption in the initial stages was due to the boundary layer diffusion whereas in the later stages sorption was due to the intra particle diffusion. Thermodynamic studies confirm that the process was spontaneous and endothermic. The fit of the adsorption data in to Langmuir isotherm confirmed the monolayer adsorption. The best correlation coefficient was obtained using the pseudo-second-order kinetic model indicated that chromium removal process followed the pseudo-second-order rate expression. Desorption studies was also carried out and found that complete desorption of Cr (VI) took place at pH of 9.5. The data thus obtained would be useful in design-ing and fabricating an efficient treatment plant for Cr (VI) rich effluents.

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