

Removal of Cr(VI) from aqueous solutions using agricultural waste ‘maize bran’

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Abstract

Novel biosorbent ‘maize bran’ has been successfully utilized for 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 312.52 (mg g⁻¹) at pH 2.0, initial Cr(VI) concentration of 200 mg L⁻¹ and temperature of 40 °C. Effect of pH showed that maize bran was not only removing Cr(VI) from aqueous solution but also reducing toxic Cr(VI) into less toxic Cr(III). The sorption kinetics was tested with first order reversible, pseudo-first order and pseudo-second order reaction and it was found that Cr(VI) uptake process followed the pseudo-second order rate expression. Mass transfer of Cr(VI) from bulk to the solid phase (maize bran) was studied at different temperatures. Different thermodynamic parameters, viz., ΔG° , ΔH° and ΔS° have also been evaluated and it has been found that the sorption was feasible, spontaneous and endothermic in nature. The Langmuir and Freundlich equations for describing sorption equilibrium were applied and it was found that the process was well described by Langmuir isotherm. Desorption studies was also carried out and found that complete desorption of Cr(VI) took place at pH of 9.5. © 2007 Elsevier B.V. All rights reserved.

Keywords: Removal; Maize bran; Chromium(VI); Sorption isotherms; Sorption kinetics

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. Metal ions such as cadmium, chromium, copper, lead, zinc and iron are commonly detected in both natural and industrial effluents and therefore priority is given to regulate these pollutants at the discharge level. To minimize this problem, biosorption can be a part of the solution. Biosorption of heavy metals by bacterial fungal or algal biomass (live or dead cells) and agricultural waste biomass has been recognized as a potential alternative to existing technologies such as by precipitation, ion exchange, solvent extraction and liquid membrane for removal of heavy metals from industrial wastewater because these processes have technical and/or economical constraints [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 and 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 [7–12]. We therefore have chosen agricultural waste maize bran for the removal of chromium(VI) from wastewater, because maize bran 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

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Nomenclature

b	Langmuir constant related to the free sorption energy
C_e	equilibrium concentration of solute in bulk solution (mg L^{-1})
C_A	concentration of solute in the solution at any time (mg L^{-1})
C_B	concentration of solute on the sorbent at any time (mg g^{-1})
C_{Ae}	equilibrium concentration of solute on the sorbent (mg L^{-1})
C_{A0}	initial concentration of solute in the solution (mg L^{-1})
C_{B0}	initial concentration of solute on the sorbent (mg g^{-1})
d_p	diameter of the adsorbent particles (cm)
\bar{D}	pore diffusion coefficient (cm s^{-1})
ΔG°	Gibb's free energy change (K cal mol^{-1})
h	initial sorption rate of pseudo-second order sorption ($\text{mg g}^{-1} \text{min}^{-1}$)
ΔH°	enthalpy change (K cal mol^{-1})
k_{id}	rate constant of intraparticle pore diffusion ($\text{mg g}^{-1} \text{min}^{-1/2}$)
k_s	equilibrium rate constant of pseudo-first order sorption (min^{-1})
k''	overall rate constant of first order reversible reaction
k'_2	equilibrium rate constant of pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$)
K_c	equilibrium constant
K_F	Freundlich constant indicative of the relative sorption capacity of the sorbent (mg g^{-1})
m	mass of the adsorbent per unit volume (g L^{-1})
n	Freundlich constant indicative of the intensity of sorption
q_e	amount of solute sorbed per unit weight of sorbent at equilibrium (mg g^{-1})
q_t	amount of solute sorbed per unit weight of sorbent at any time (mg g^{-1})
Q^0	Langmuir constant related to the monolayer sorption capacity of (mg g^{-1})
r	average radius of the sorbent particle (cm)
R	universal gas constant ($\text{cal K}^{-1} \text{mol}^{-1}$)
R_L	equilibrium parameter
ΔS°	entropy change ($\text{cal mol}^{-1} \text{K}^{-1}$)
S_s	outer specific surface of the sorbent particle per unit volume of particle free slurry (cm^{-1})
t	time (min)
$t_{1/2}$	time for half of the sorption
T	absolute temperature (K)
$U_{(t)}$	fractional attainment of equilibrium
V	the volume of particle-free slurry solution (l)
W	is the weight of the sorbent (g)

Greek letters

β_1	mass transfer coefficient (cm s^{-1})
δ_ρ	density of the sorbent particles (g cm^{-3})
ε_p	are the porosity of the adsorbent particles

and Freundlich equations are being used for present work. The Langmuir 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 [13]. The linear form of the Langmuir isotherms may be represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (1)$$

The values of Q^0 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 [13]:

$$\log q_e = \log K_F + 1/n \log C_e \quad (2)$$

where n and K_F are the 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 [14,15]:

$$K_c = \frac{C_{Ae}}{C_e} \quad (3)$$

where K_c is the equilibrium constant and C_{Ae} 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° :

$$\Delta G^\circ = -RT \ln K_c \quad (4)$$

The K_c may be expressed in terms of the ΔH° (K cal mol^{-1}) and ΔS° ($\text{cal mol}^{-1} \text{K}^{-1}$) as a function of temperature:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

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 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 phase to solid 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 [16]:

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

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

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

and k_1 , k_2 , and K_c can be obtained from

$$K_c = \frac{k_1}{k_2} = \frac{C_{Ae}}{C_e} \quad (8)$$

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

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 (Lagergreen, 1898) for the sorption of liquid/solid system based on solid capacity [17]. This model may be represented as:

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

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

$$t = 0, \quad q_t = 0; \quad t = t, \quad q_t = q_t;$$

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

where q_t is the 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 [18]:

$$\frac{dq}{dt} = k'_2(q_e - q_t)^2 \quad (12)$$

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

shown below:

$$t = 0, \quad q_t = 0; \quad t = t, \quad q_t = q_t;$$

$$\frac{t}{q_t} = \frac{1}{k'_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

$$h = k'_2 q_e^2 \quad (14)$$

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 methods

3.1. Physico-chemical analysis of the biosorbent

Maize bran is a byproduct of a flour milling plant. It was collected from M/s Shivangi Industries (flourmill), Chunar, Mirzapur (UP) and was used in experiments with double washing with double distilled water to remove soluble lighter materials and drying at 60 °C in an oven and crushing and sieving to less than 178 μm. The surface area of the maize bran was determined by a three point N₂ 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 was determined by porosimeter (model H: M7V, 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 physicochemical properties of maize bran thus obtained are given in Table 1. X-ray diffraction and IR studies (values given in Table 2) of maize bran show that apart from various organic functional groups maize bran also contains metal oxides and carbon.

3.2. Reagents

All the primary chemical used were of analytical grade: potassium dichromate, hydrochloric acid, sodium hydroxide,

Table 1
Physical and chemical properties of biosorbent maize bran

Surface area (m ² g ⁻¹)	437.00
Bulk density (g cm ⁻³)	0.2432
Particle size (μm)	<178
Porosity	0.39
Proximate analysis (%)	
Volatile matter	42.34
Moisture	7.97
Fixed carbon	31.28
Ash (oxides of Al, Mn, Si, Fe and others)	18.41

Table 2
IR bands of maize bran along with their possible assignment

Band position (cm ⁻¹)		Assignment
3410	vw	–OH str.
2950	w	–C=C–H str.
1746	w	–C=O str.
1556–1518	s	Aromatic ring
1487	w	>N–H str.
945	vw	Fe–O
841	m	Mn–O
773	m	–C–H str.
746	m	Al–O
682, 550	vw	Si–O stretch
493	m	Fe–O
470	s	Si–O–Ca bond
450	s	Si–O bond

1,5-diphenylcarbazide, potassium permanganate, etc. were purchased from E Merck, India, Ltd., Mumbai, India.

The stock solution containing 1000 ppm of Cr(VI) was prepared by dissolving 1.4143 g of K₂Cr₂O₇ in 500 mL of deionized, double distilled water. Required initial concentration of Cr(VI) standard were prepared by appropriate dilution of the above stock Cr(VI) standard solution.

3.3. Batch sorption experiment

Using the different amount of biosorbent in a 250 mL stopper conical flask containing 50 mL of test solution, batch sorption studies were carried out at desired pH value, contact time, temperature and sorbate concentration. Different initial concentration of Cr(VI) solution was prepared by proper dilution from stock 1000 ppm Cr(VI) standard, 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 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 was analyzed for remaining Cr(VI) concentration in the sample. The amount of Cr(VI) sorbed per unit mass of the biosorbent was evaluated by using following equations:

$$q_{\max} = \frac{(C_i - C_e) \times V}{W} \quad (15)$$

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

$$\% \text{age removal of Cr(VI)} = \frac{C_i - C_e}{C_i} \times 100 \quad (16)$$

3.3.1. Effect of pH

Sorption experiments for the effect of pH were conducted by using 50 mL solution having 200 mg L⁻¹ Cr(VI) with 1 g of maize bran at 40 °C and the pH of the solution was adjusted from 1.4 to 8.0 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 5–180 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 1 g of biosorbent into 250 mL of conical flask containing 50 mL of 200 mg L⁻¹ of Cr(VI) solution.

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 maize bran was shaken with 50 mL of eluant solution. Desorption efficiency was calculated by using following equation:

$$\text{desorption efficiency} = \frac{\text{amount of Cr(VI) desorbed}}{\text{amount of Cr(VI) sorbed}} \times 100 \quad (17)$$

3.5. Chromium analysis

3.5.1. Chromium(VI) analysis

The pink colored 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, USA) [19].

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-diphenylcarbazide was added. The pink colored 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 [19].

4. Results and discussion

4.1. Effect of pH

Experiments were performed at 40 °C temperature and initial concentration of 200 mg L⁻¹ by varying pH from 1.4 to 8.5. It was observed that initial uptake of Cr(VI) increased with an increase of pH from 1.4 to 2.0 thereafter uptake started decreasing with the increase of pH from 2.0 to 8.5 (Fig. 1). The optimum pH for the maximum uptake of Cr(VI) was found at 2.0. This could be explained that since Cr(VI) exists in the form of oxyanions such as HCrO₄⁻, Cr₂O₇²⁻, CrO₄²⁻, etc. in acidic medium

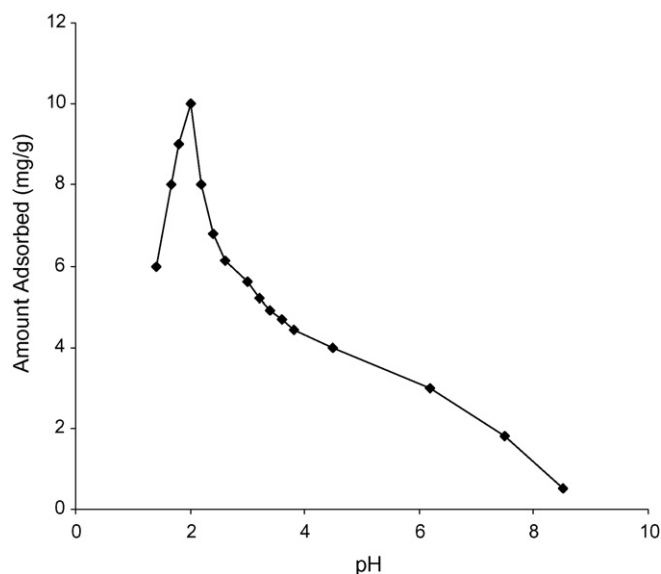
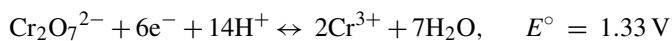


Fig. 1. Effect of pH on the adsorption by maize bran. Conditions pH 1.4–8.5; initial Cr(VI) concentration 200 mg L^{-1} ; temperature 40°C ; particle size $<178 \mu\text{m}$.

and the lowering of pH caused the surface of the biosorbent to be 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 these factors cause hindrance in the biosorption of negatively charge $\text{Cr}_2\text{O}_7^{2-}$, 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 color of the surface of biosorbent turn greenish during sorption. This was certainly due to the sorption of Cr(III) (greenish) a reduced form of chromium on the surface of sorbent. Thus during sorption of Cr(VI) on the surface maize 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:



there, $\text{Cr}_2\text{O}_7^{2-}$ act as an oxidant and it will oxidize the surface of the biosorbent and get reduced itself from Cr(VI) to Cr(III).

Another proof which is also supporting to the fact, that during the sorption of Cr(VI) there was sorption of Cr(VI) as well as Cr(III) on the surface of the biosorbent, was when equilibrium concentration (C_e) of Cr(VI) was analyzed. For this purpose supernatant after sorption was divided into two parts, in one sample Cr(VI) concentration (C_e) was measured by the prescribed method. Whereas another sample of Cr(VI) solution was heated upto $130\text{--}140^\circ\text{C}$ with KMnO_4 solution and then Cr(VI) concentration was analyzed. It was found that in second case concentration of Cr(VI) (C_e) was higher in comparison to the previous one. This can be explained that since KMnO_4 is a very powerful oxidant so it oxidized Cr(III) present in solution which was form at the surface of maize bran during the sorption process at low pH. Thus it can be concluded that during sorption

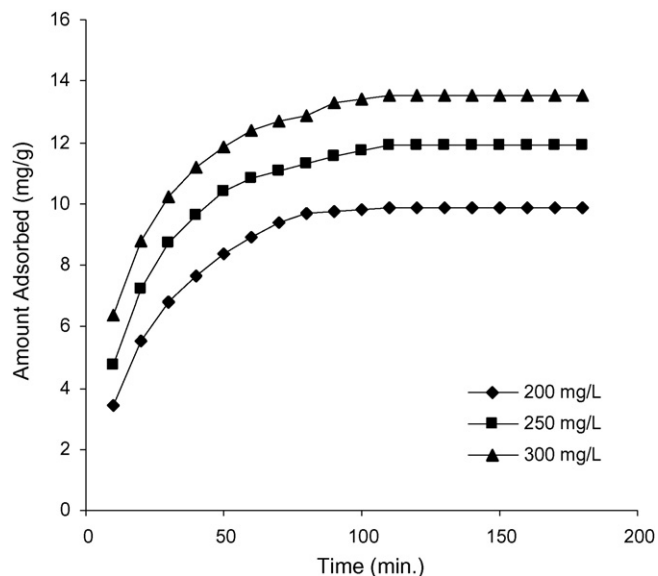


Fig. 2. Effect of contact time and initial metal ion concentration on adsorption. Conditions pH 2.0; temperature 40°C ; particle size $<178 \mu\text{m}$; initial Cr(VI) concentration (\blacklozenge) 200 mg L^{-1} , (\blacksquare) 250 mg L^{-1} , (\blacktriangle) 300 mg L^{-1} .

process at low pH there was not only the sorption of Cr(VI) but also reduction of Cr(VI) into a less toxic Cr(III) and sorption of Cr(III) also. Similar observations have also been reported by other workers [8,20,21].

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} and time interval of 10 min upto 3 h at a temperature of 40°C and pH 2.0. The uptake (mg g^{-1}) of Cr(VI) was found 9.88, 11.912 and 13.56, respectively (Fig. 2). 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 maize bran at various sorbate concentrations was found to be 110 min, which showed that equilibrium time was independent of initial sorbate concentration. The curves 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 (mg g^{-1}) increased from 9.0, 9.49 to 10.0 with the rise in temperature from 20 to 40°C (Fig. 3). Equilibrium time for 20, 30 and 40°C was found to be 110 min indicating that the equilibrium time was independent of temperature. The above results also showed that the sorption was endothermic in nature. Since sorbent is porous in nature and 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 favors the sorbate transport with in the pores of sorbent [21]. The increased

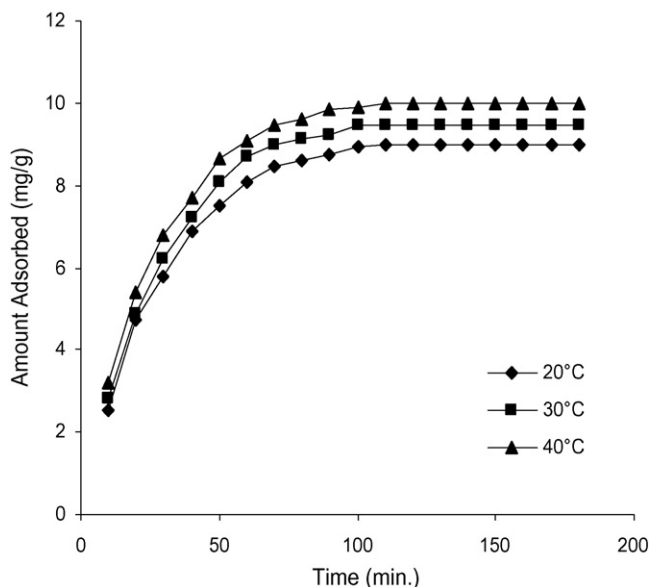


Fig. 3. Effect of temperature on the sorption by maize bran. Conditions initial Cr(VI) concentration 200 mg L^{-1} ; pH 2.0 temperature 20°C (◆), 30°C (■) and 40°C (▲); particle size $<178 \mu\text{m}$.

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 [22,23].

4.4. Thermodynamic evaluation of the process

Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption (ΔH°) and standard entropy (ΔS°) changes during the sorption process were calculated using Eqs. (3)–(5) on a temperature range of $20\text{--}40^\circ\text{C}$ at 200 mg L^{-1} . (ΔH°) and (ΔS°) were obtained from the slope and intercept of a plot of $\ln K_c$ against $1/T$ (Fig. 4). The values of these parameters are recorded in Table 3. The negative values of ΔG° indicate the spontaneous nature of the process and more negative value with increase of temperature shows that an increase in temperature favors the sorption process. The positive values of ΔH°

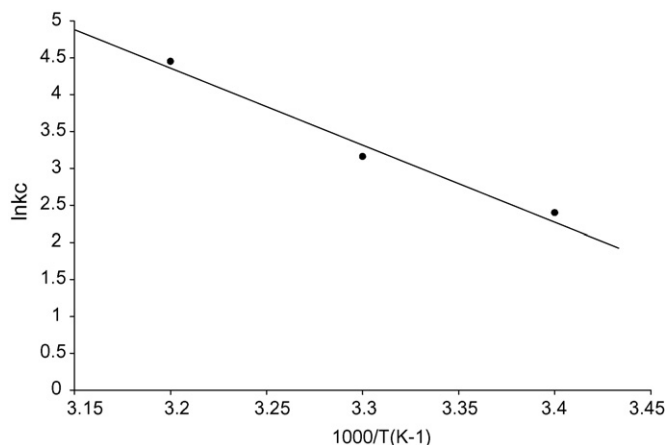


Fig. 4. A plot of $\ln K_c$ against $1/T$ for Cr(VI) sorption by maize bran at 200 mg L^{-1} .

Table 3

Thermodynamic parameters for sorption of Cr(VI) on maize bran at different temperature

Temperature ($^\circ\text{C}$)	$-\Delta G^\circ$ (K cal mol $^{-1}$)	ΔH° (K cal mol $^{-1}$)	$-\Delta S^\circ$ (cal mol $^{-1}$ K $^{-1}$)
20	1.26		
30	1.76	22.23	79.62
40	2.74		

indicate that the sorption process was endothermic in nature and the negative values of ΔS° suggest the probability of a favorable sorption.

4.5. Sorption isotherms

The isotherm constants were calculated from the slope and intercept of Fig. 5a (Langmuir isotherm) and Fig. 5b (Freundlich isotherm) and presented in Table 4. The value of r^2 was higher for Langmuir isotherm than the Freundlich isotherm; that means Langmuir equation represented the adsorption process very well. Value of Q^0 , which is defined as the maximum capacity of sorbent, was calculated from the Langmuir plots. The maximum

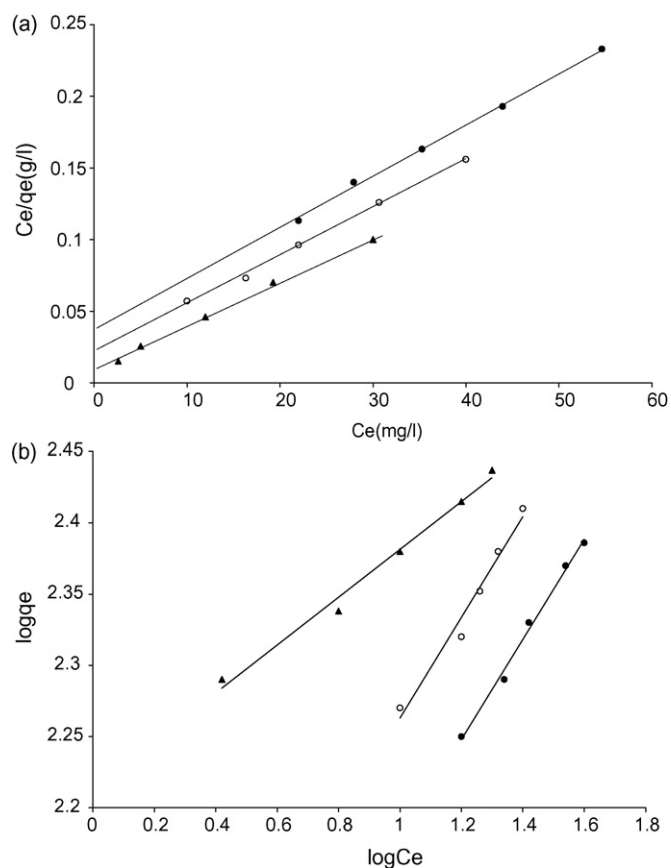


Fig. 5. (a) Langmuir isotherm plot for Cr(VI) removal using maize bran. Conditions: particle size: $<178 \mu\text{m}$, pH: 2.0; temperature: 20°C (●), 30°C (○) and 40°C (▲) and concentrations: 200, 225, 250, 275 and 300 mg L^{-1} . (b) Freundlich isotherm plot for Cr(VI) removal using maize bran. Conditions: particle size: $<178 \mu\text{m}$, pH: 2.0; temperature: 20°C (●), 30°C (○) and 40°C (▲) and concentrations: 200, 225, 250, 275 and 300 mg L^{-1} .

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

Temperature (°C)	Langmuir constants		Freundlich constants				
	Q^0 (mg g ⁻¹)	b (L mg ⁻¹)	R_L	r^2	n	K_F	r^2
20	285.71	0.614	8.078×10^{-3}	0.998	3.200	0.267	0.854
30	294.13	0.163	2.976×10^{-2}	0.992	4.470	0.313	0.891
40	312.52	0.066	7.042×10^{-2}	0.992	7.818	0.351	0.864

capacity of maize bran for Cr(VI) was calculated in the range of 285.71–312.52 mg g⁻¹ at different temperatures that indicated the good sorbing capacity of the maize bran.

The equilibrium parameter R_L , which is defined as $R_L = 1/(1 + bC_{A0})$ in the range $0 < R_L < 1$ reflects the favorable adsorption process [24]. In the present investigation the equilibrium parameter was found to be in the range $0 < R_L < 1$ which is shown in Table 5. This indicated to the fact that the sorption process was very favorable and the adsorbent employed exhibited a good potential [24].

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 were investigated to find 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 for all concentrations and temperatures, indicating that sorption reaction can be approximated to be of the first-order reversible kinetics. Correlation coefficients were found to be between 0.803 and 0.932 (Table 5), which means that there is a good agreement but not a perfect one. For the pseudo-first order adsorption rate constant, the straight-line plots of $\log(q_e - q_t)$ against time were analyzed. Approximately, linear fits were observed for all concentrations and temperatures indicating that sorption reaction can be approximated to first-order kinetics. The smallest correlation coefficient in this case was 0.868, which is still better than the first-order reversible reaction model. Constant k_s for all situations tested have been calculated and summarized in Table 5. The equilibrium rate con-

Table 6
Comparison of sorption capacities of the maize bran for the removal of Cr(VI) with those of other biosorbents

Sl. no.	Biosorbent	Sorption capacities (mg g ⁻¹)
1	Maize bran	312.52
2	Sphagnum moss peat	119.0
3	Coconut husk fibre	29.0
4	Sugar cane bagasse	13.4
5	Wood activated carbon	87.6
6	Chitosan-cross linked and non-cross linked	78.5
7	Saw dust	15.82
8	Pine needles almond	21.50
9	Cactus	7.08
10	Coniferous leaves	83.3
11	Eucalyptus bark	45.0
12	Neem bark	23.58

stants of pseudo-second order were determined by plotting t/q_t against t (min) (Fig. 6a and b). The kinetic constant and correlation coefficients of these models were calculated and given in Table 6. Good correlation coefficients were observed 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 in this case was 0.995, which is even better than the first-order reaction model. Thus the pseudo-second order kinetics was pathway to reach the equilibrium.

4.7. Intraparticle diffusion study

During the batch mode of operation, there was a possibility of transport of sorbate species into the pores of sorbent, which is often the rate controlling step. The rate constants of intraparticle diffusion (k_{id}) at different temperatures were determined using

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_0 (mg L ⁻¹) at 40 °C										
200	7.82	0.084	74.41	9.51	0.932	5.358	0.927	0.509	12.33	0.996
250	14.95	0.072	67.43	4.65	0.865	4.225	0.903	0.756	13.83	0.998
300	33.26	0.062	62.24	1.86	0.812	3.354	0.899	1.179	15.22	0.997
Temperature (°C) at Cr(VII) 200 mg L ⁻¹										
20	34.71	0.064	61.82	1.78	0.803	4.321	0.868	0.385	11.79	0.997
30	15.23	0.071	66.21	4.35	0.843	4.982	0.901	0.419	12.39	0.995
40	7.82	0.084	74.41	9.51	0.932	5.358	0.927	0.509	12.72	0.996

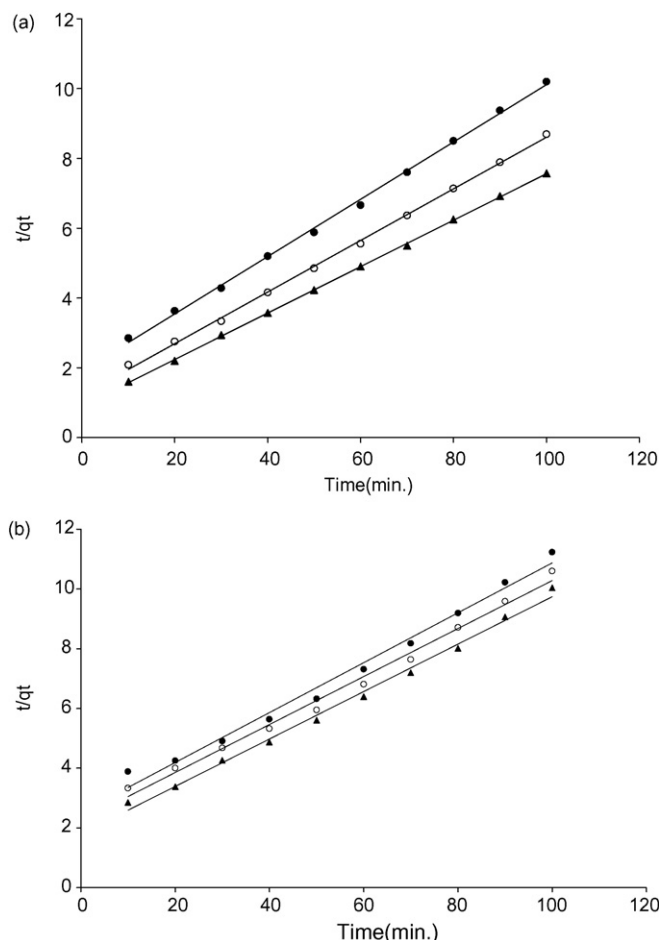


Fig. 6. (a) Pseudo-second order plot for Cr(VI) removal using maize bran at 200 mg L^{-1} (●), 250 mg L^{-1} (○) and 300 mg L^{-1} (▲). Conditions: temperature: 30°C ; particle size $<178 \mu\text{m}$, pH: 2.0 and agitation rate 125 rpm. (b) Pseudo-second order plot for Cr(VI) removal using maize bran at 20°C (●), 30°C (○) and 40°C (▲). Conditions: concentration: 200 mg L^{-1} ; particle size: $<178 \mu\text{m}$, pH: 2.0 and agitation rate 125 rpm.

the following equation [25]:

$$q = k_{id}t^{1/2} \quad (18)$$

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} (9.342×10^{-3} , 1.316×10^{-2} and $1.524 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-1/2}$) at temperatures 20, 30 and 40°C , respectively, were calculated from the slopes of respective plot (q versus $t^{1/2}$ —Fig. 7) 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) was 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 [26]:

$$\bar{D} = \frac{0.03r^2}{t_{1/2}} \quad (19)$$

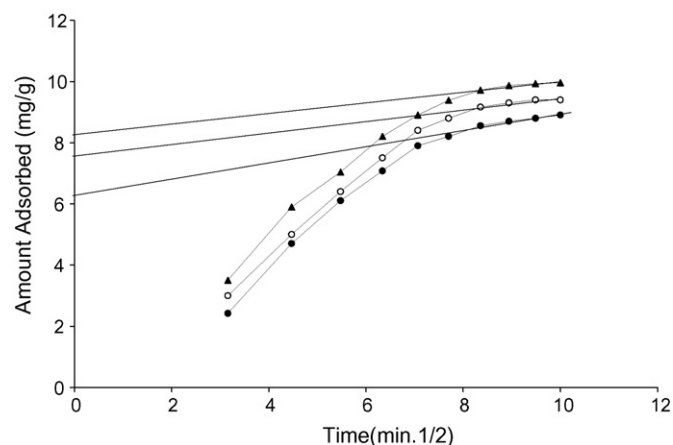


Fig. 7. Intraparticle diffusion plot for adsorption of Cr(VI) on maize bran at 20°C (●), 30°C (○) and 40°C (▲). Conditions: concentration: 200 mg L^{-1} ; pH: 2.0; particle size: $<178 \mu\text{m}$ and agitation rate: 125 rpm.

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 Michelson [26] a \bar{D} value of the order of $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ is indicative of intraparticle diffusion as rate determining step. In this investigation, the values of \bar{D} (5.814×10^{-9} , 7.452×10^{-9} and $8.435 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 20, 30 and 40°C , respectively) obtained was in order of $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ which was more than two order of magnitude higher, indicated that the intraparticle diffusion was not the only rate controlling step. It was concluded that both boundary layer and intraparticle diffusion might 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 can be considered participating in the process and out of various models tried for the present studies, overall sorption process is assumed to occur using a three-step McKay et al. model [27]:

1. Mass transfer of sorbate from the aqueous phase on to the solid surface.
2. Sorption of solute on to the surface sites.
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 and therefore it is not rate limiting in any kinetic study. Taking in to account these probable steps, McKay et al. model [27] has been used for the present investigation:

$$\ln \left(\frac{C_A}{C_{A0}} - \frac{1}{1+mK} \right) = \ln \left(\frac{mK}{1+mK} \right) - \left(\frac{1+mK}{mK} \right) \beta_1 S_s t \quad (20)$$

where m is the mass of the biosorbent per unit volume, K the constant obtained by multiplying Q^0 and b (Langmuir's constants),

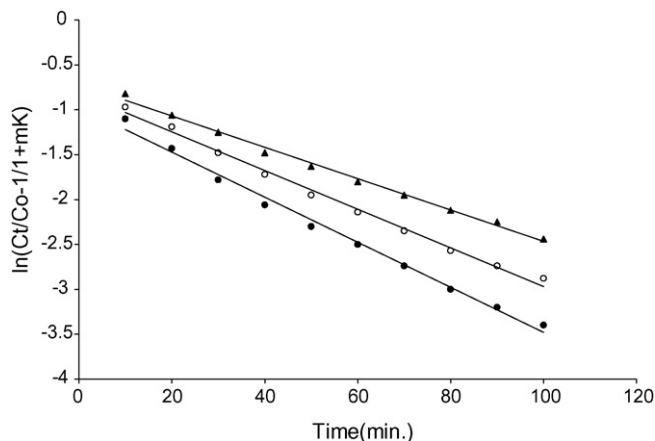


Fig. 8. Mass transfer plot for the adsorption of Cr(VI) on maize bran at 20 °C (●), 30 °C (○) and 40 °C (▲). Conditions: concentration: 200 mg L⁻¹; particle size: <178 μm, pH: 2.0 and agitation rate: 125 rpm.

β_1 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:

$$m = \frac{W}{V} \quad (21)$$

$$S_s = \frac{6m}{d_p \delta_p (1 - \varepsilon_p)} \quad (22)$$

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

The values of β_1 (6.832×10^{-5} , 6.422×10^{-5} and 5.842×10^{-5} cm s⁻¹) calculated from the slopes and intercepts of the plots (Fig. 8) of $\ln(C_t/C_0 - 1/1 + mK)$ versus t (min) at different temperatures (20, 30 and 40 °C). The values of β_1 obtained show that the rate of transfer of mass from bulk solution to the biosorbent surface was rapid enough so it cannot be rate controlling step [28]. 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.

5. Desorption studies

Desorption results (Fig. 9) indicated that 21.2, 44.0, 58.1, 74.2 and 100% of Cr(VI) were removed from the surface of the biosorbent containing 9.88 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 weakly bonded adsorbate ions were removed at acidic or neutral pH, while they were completely desorbs in alkaline solution owing to the formation of soluble sodium chromate.

5.1. 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

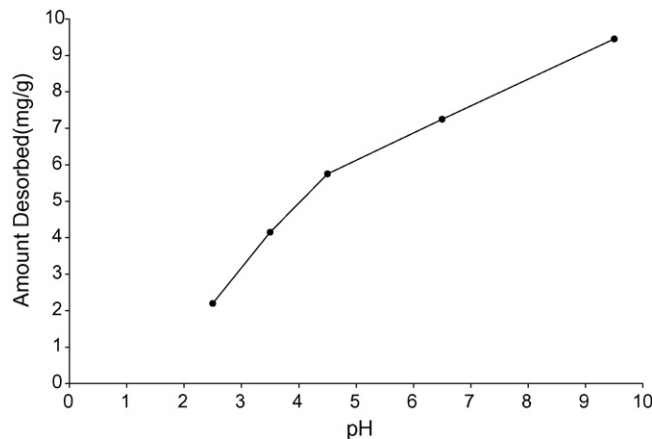


Fig. 9. Effect of pH on the desorption of Cr(VI) from maize bran.

of Cr(VI) on the adsorbent. It showed the binding of surface sites with the sorbate ions [29]. The disappearance of above bands after desorption at pH 9.5 supported the desorption result for complete Cr(VI) detachment from the biosorbent surface.

6. Conclusion

Maize bran has been found to be a economically viable and potential biosorbent for the removal of Cr(VI) (Table 6). Sorption of Cr(VI) was found to be effective in the lower pH range and at higher temperature. Effect of pH showed that maize bran was not only removing Cr(VI) from aqueous solution but also reducing toxic Cr(VI) into less toxic Cr(III). Thermodynamic studies confirmed that the process was favorable, spontaneous and endothermic. The fitness of the sorption data into 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. Mass transfer studies confirmed that the rate of mass transfer from sorbate to adsorbent was rapid enough. 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 designing and fabricating an efficient treatment plant for Cr(VI) rich effluents.

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