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ORIGINAL PAPER

Modified biomass of *Phanerochaete chrysosporium* immobilized on luffa sponge for biosorption of hexavalent chromium

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Abstract *Phanerochaete chrysosporium,* a white rot basidiomycete, was immobilized over *Luffa cylindrica* sponge discs, treated with 0.1 N HCl and its potentiality for the removal of hexavalent chromium [Cr(VI)] from water was investigated in both batch and in up-flow fixed-bed bioreactor. The acid treatment of biomass increased the uptake capacity and percentage removal of Cr(VI) from 33.5 to 46.5 mg g^{-1} and 67 to 92 %, respectively. Maximum uptake of Cr(VI) was achieved at pH 2, temperature 40 °C after 100 min of contact time. The Cr(VI) sorption on the biomass was better explained by Langmuir isotherm. Thermodynamic studies indicated that the process was spontaneous and endothermic. Sorption kinetic study showed that pseudo-second-order model best correlates the Cr(VI) sorption on the biomass as compare to pseudo-first-order kinetic model. The performance of fixed-bed bioreactor was evaluated at different bed heights (5, 15 and 25 cm) and flow rates (1.66, 4.98 and 8.33 mL min^{-1}) by using bed depth service time model. Response surface methodology statistical method was applied for optimizing the process parameters. FTIR analysis showed that amino groups were mainly involved in adsorption of Cr(VI).

Keywords Immobilized *Phanerochaete chrysosporium* · Chromium biosorption · Up-flow fixed-bed bioreactor · Response surface methodology

Introduction

Heavy metals are among the most hazardous pollutants in source and treated water and are becoming a multiple problem causing agents. Chromium is the metal contaminant which exists as oxyanions in aqueous system like arsenic and selenium. Chromium is found in both trivalent and hexavalent form. Trivalent form of chromium is relatively innocuous, whereas hexavalent chromium [Cr(VI)] is toxic, carcinogenic, mutagenic and teratogenic in nature (Gupta et al. 2011a, b, c; Bai and Abraham 2002) Many industries like leather tanning, electroplating, dyeing, metal processing, paint, textile, steel fabrication and canning industry are the source of discharge containing high amount of chromium. The concentration of Cr(VI) in industrial effluent water ranges from 0.5 to 270.0 mg L^{-1}. However, United States Environmental Protection Agency (1990) has fixed the permissible limit of Cr(VI) for industrial discharge up to 0.1 mg L^{-1} for surface water and 0.05 mg L^{-1} in potable water (Demirbas et al. 2004). Therefore, the removal of Cr(VI) from industrial effluents is essential before discharging them into water bodies or on to land. Various treatment processes are available for removal of Cr(VI), some of them are in frequent use such as reduction and precipitation, lime coagulation, ion exchange, solvent extraction and reverse osmosis. Treatment cost, operational complexity, skill requirement and

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disposal protocol are the key factors which decides the suitability and utility of the treatment method and should be considered before selecting a treatment method. In the context of above factors, adsorption is a promising approach for the remediation of different contaminant such as dyes (Gupta et al. 2011c, Mittal et al. 2010a, b, c), fluorinated compounds (Gupta et al. 2007), phenolic contaminants (Mittal et al. 2009a, b) and more importantly hazardous metals (Gupta et al. 2001, 2011a, b; Fourest and Volesky 1997). Activated carbon-based adsorption systems are being widely used in industries (Gupta et al. 1997). Biosorption by inexpensive biomaterials can be an excellent cost effective, eco-friendly alternative for the removal of metal ions and other pollutants from water (Gupta et al. 2010; Mittal et al. 2010a, b, c).

Fungal biomasses have good capability to remove toxic heavy metals and other organic pollutants from aqueous solution (Perez et al. 1997). The biomass system becomes better in mechanical stability and easy to handle after immobilization. The ideal immobilization matrix should be highly porous, mechanically strong and sustainable at various pH and salt concentrations. The luffa sponge is a plant derived, inexpensive and easily available natural material which can be used as an immobilization matrix. The luffa sponge is an open interwoven network of cellulosic fibres. It provides support to fungal mycelium and allows rapid growth over it.

Phanerochaete chrysosporium is a known biosorbent tested for removal of various heavy metals from water chlorinated compounds and was found to be efficient in removing the contaminants from water (Reddy et al. 1998). In contrast, the negative charge of fungal cell wall reduces the efficiency of fungal biomass for the removal of metals which exist in oxyanionic form, such as arsenic, selenium and chromium. In the light of above fact, the alteration in the surface and surface charge through chemical treatment may be an alternative to enhance the affinity of biomass for metal oxyanions (Murugesan et al. 2006). In the present study, chemically treated immobilized biomass of *P. chrysosporium* on luffa sponge has been selected for the sorption of hexavalent chromium.

The objective of the study is to enhance Cr(VI) biosorption capacity of fungal biomass through chemical treatment and evaluation of its potentiality in batch and continuous adsorption process along with statistical optimization using response surface methodology (RSM). Response surface is the graphical representation of the multivariate regression equations, which represents the relationships between explanatory variables and response variables. Amongst the various designs available in RSM, the full-factorial central composite design (CCD) is the most commonly used (Tan et al. 2008).

Materials and methods

Micro-organism, culture medium, immobilization and pre-treatment

Phanerochate crysosporium MTCC 787, a member of class basidiomycetes commonly known as white rot fungus, was maintained by subculturing on slants containing malt extract agar (MEA) media incubated at 25 °C and stored at 4 °C. Constituents of the MEA were (g L^{-1}) as follows: malt extract 20.0; glucose 20.0; peptone 1.0 and agar 20.0 (pH 5.5). Growth and immobilization of fungus over luffa sponge were carried out in a synthetic media containing (g L^{-1}) as follows: D-glucose 10.0; KH_2PO_4 2.0; $MgSO_4{\cdot}7H_2O$ 0.5; NH_4Cl 0.1; $CaCl_2{\cdot}2H_2O$ 0.1; thiamine 0.001 and pH 4.5 (Iqbal et al. 2005). Immobilization of *P. chrysosporium* on luffa sponge discs was done using method described by M. Iqbal (Iqbal et al. 2005).

0.1 N H_2SO_4, 0.1 N HCl, 0.1 N NaOH, 0.1 N NH_4OH, formaldehyde (10 % v/v), $FeCl_3$ (15 mg L^{-1}) and polyethylenimine (PEI) (1 % w/v) were individually used for the chemical treatment of biomass. In the experiment, untreated immobilized biomass (IFB) was used as a control, and other process parameters were fixed at 100 mg L^{-1} initial Cr(VI) concentration, 2.0 g L^{-1} biomass dose, pH 2.0, 12 h of contact time and agitation speed 100 rpm. The resulted modified biomass was then separated from the solution and washed with deionised water before adsorption experiments.

Batch biosorption studies in shake flasks

All the standards and reagents were prepared in deionised double-distilled water using all analytical grade chemicals. Stock solution of Cr(VI) was prepared by dissolving the corresponding weight of potassium dichromate ($K_2Cr_2O_7$) to obtain a solution of 1,000 mg L^{-1}. Working solution of desired concentrations was obtained after further diluting the stock solution. Batch experiments were conducted using 100 mL of working solution in 250-mL Erlenmeyer flasks and agitating at 100 rpm with varying biomass dose, metal concentration, pH and temperature. Samples were taken out at regular time interval for the analysis of residual chromium in the solution. All the experiments were performed in triplicates, and the average value was taken.

Biosorption studies in up-flow fixed-bed bioreactor

Continuous mode biosorption experiments were conducted using bioreactor that is made up of borosilicate glass having internal diameter 2 cm and length 30 cm. Treated immobilized biomass discs (CIFB) were packed between two supporting layers of 1 cm of glass wool in bioreactor to attend different bed heights. Metal ion solution having the desired initial metal ion concentration was pumped in an up-flow mode through the bioreactor at the desired flow rate by a peristaltic pump (Miclins PP-10). Samples were collected at regular time intervals, and Cr(VI) concentration in the samples was analysed. After the exhaustion of bed, 100 mL of deionized double-distilled water was passed through bioreactor in an upward direction to wash out the bioreactor. Desorption was carried out by passing the eluting agent (10 % NaOH) through the bioreactor bed in an upward direction at a flow rate of 1.66 mL min^{-1}. The effluent metal solution was collected and analysed for elution efficiency and Cr(VI) content.

Analysis of Cr(VI) and Cr(III) in aqueous solution

Working solution initially contains only Cr(VI) species, but during the adsorption process, Cr(III) also appears in the solution due to the reduction of Cr(VI) through biomass. The determination of total chromium was done by atomic absorption spectrophotometer (AAS) (Shimadzu AA-6300) with hollow cathode lamp and using 12 mA lamp current, 0.7 nm slit width, light source set at 357.9 nm wavelength and deuterium lamp for background correction. The instrument was calibrated from 0.03 to 10.0 mg L^{-1} Cr(VI) using $Cr(NO_3)_3$ in 0.5 mol L^{-1} HNO_3 (Merck) standard solution samples. For determination of Cr(VI), the samples were again analysed by colorimetric method after complexation with 1-5 diphenylcabazide, and optical density was measured at 540 nm by UV spectrophotometer (Shimadzu UV mini 1240) (Yang and Chen 2008). The concentration of Cr(III) was then obtained by subtracting the concentration of Cr(VI) from the total chromium content of the corresponding sample.

Theory and equations

Equations used in present study for the calculations of different parameters along with brief theory are tabulated in Table 1.

Bed depth service time (BDST) model for evaluation of bioreactor performance

BDST model was used for predicting the relationship between bed height (Z) and service time (t) in terms of process concentrations and adsorption parameters, which is required for evaluating the performance of a fixed-bed bioreactor and designing the continuous bioreactor for the given process. The original BDST model was proposed by (Bohart and Adams 1920) and represented by the following Eq. (1):

$$\ln\left(\frac{C_o}{C_b}-1\right)=\ln\left(\exp\left(\frac{k_aN_oZ}{u}\right)-1\right)-k_aC_ot \quad (1)$$

Hutchins, correlated bed height (Z) and service time (t) in a linier manner as per given Eq. (2) (Hutchins 1973):

$$t=\frac{N_oZ}{C_ou}-\frac{1}{k_aC_o}\ln\left(\frac{C_o}{C_b}-1\right) \quad (2)$$

Results and discussion

Immobilization of *P. chrysosporium* on luffa sponge

The fungus was grown in luffa sponge–free media and in the media containing luffa sponge discs. Natural fibrous network of luffa sponge discs provided a supporting matrix for growth of the organism which lead to 20.4 % higher growth as compare to the growth of organism in the medium without luffa sponge. The growth of the fungus on luffa sponge disc reaches to maximum on 8th day of incubation. After full growth of micro-organism, the discs were taken out and oven dried at 70 °C overnight. The average yield of dry weight of immobilized biomass was 392 ± 16 mg g^{-1} of dry luffa sponge, and the amount of biomass immobilized on the fibrous luffa sponge disc was about threefold higher than the same organism immobilized within Ca-alginate beads (Kacar et al. 2002; Iqbal and Edyvean 2005).

Effect of immobilization on biosorption of Cr(VI)

Removal of Cr(VI) from water was studied using the immobilized biomass and pre-grown-free fungal pallets. Immobilized biomass shows 4.26 mg g^{-1} increase in uptake capacity as compared to free fungal biomass. The Immobilized biomass showed higher uptake capacity because after immobilization, fungal biomass becomes less compact as compare to free biomass pallets. Decrease in compactness increases the accessibility of fungal surface for the adsorption of metal ions; thus, the effective surface area for adsorption increases that leads to increase in the uptake capacity of biomass.

Effect of pre-treatment on biosorption of Cr(VI)

Treatment agent screening experiments were performed, and uptake capacities of CIFBs with the tested chemicals were found as follows: NaOH 14.5 mg g^{-1}, NH_4OH 23.8 mg g^{-1}, formaldehyde (HCHO) 19.5 mg g^{-1}, H_2SO_4

Table 1 List of equations along with brief theory for the calculations of different parameters

Parameters and brief theory	Equations
Uptake capacity or sorption capacity metal adsorbed per unit mass of the adsorbent	$q_t = \frac{(C_i - C_t) \times V}{W}$
	$\%\,\text{Removal} = \frac{(C_i - C_t)}{C_i} \times 100$
Langmuir sorption isotherm adsorption takes place on a homogeneous surface in a monolayer pattern without interaction between adsorbed neighbour molecules (Mittal et al. 2009a, b). For good sorbents, high values of Q^o and low values of b are desirable (Langmuir 1918)	$C_e/q_e = 1/Q^o b + C_e/Q^o$
Freundlich sorption isotherm assumption is that the binding sites with stronger affinity are occupied first and binding strength of later adsorbed solute molecules decreases with increase in extent of site occupation (Freundlich 1907)	$\log q_e = \log K_F + 1/n \log C_e$
Thermodynamic studies brief idea about thermodynamic parameters (ΔG, ΔH, ΔS and K_c) is required to understand the nature and changes of the sorption process reaction (Nouri et al. 2007). Parameters can be calculated with the help of Van't Hoff plot (ln Kc vs. 1/T) and given equations (Liu and Liu 2008)	$\Delta G = -\text{RT} \ln Kc$
	$K_c = C_{Ae}/C_e$
	$\ln K_c = -\Delta H/\text{RT} + \Delta S/R$
Sorption kinetics sorption kinetics study is necessary in order to design the sorption systems and to predict solute removal rate, which governs the residence time (Ho 2006). Several sorption kinetic models have been proposed and among these, two models, namely pseudo-first-order and pseudo-second-order model equations, are in widely use to describe sorption process (Erdem and Ozverdi 2006; Kiran et al. 2006)	Pseudo-first-order model (Pokhrel and Viraraghavan 2007; Singh et al. 2005)
	$\log(q_e - q_t) = \log(q_e) - \frac{k_s}{2.303} t$
	Pseudo-second-order model (Ho and McKay 1999):
	$\frac{t}{q_t} = \frac{1}{k_2' q_e^2} + \frac{1}{q_e} t$
	initial sorption rate (h): $h = k_2' q_e^2$
Calculation of fixed-bed bioreactor parameters (Vijayaraghavan et al. 2005)	
(a) *Breakthrough curve (C_t/C_o vs. time)* helps to analyse the dynamic sorbate removal in up-flow fixed-bed bioreactor. Effluent volume (V_{eff}) treated at any time (t) is represented by given equation. Effluent volume treated up to breakthrough time (t_b) and bed exhaustion time (t_e) is denoted as V_b and V_e, respectively	$V_{\text{eff}} = Q \times t$
b) *Total amount of metal ion fed to the bioreactor (X)*	$X = \frac{C_o Q t_e}{1{,}000}$
(c) *Uptake capacity of the biomass in bioreactor* (q_{tot}, calculated from the area above the breakthrough curve)	$q = \frac{q_{\text{tot}}}{M}$
(d) *Elution efficiency (E)* [metal mass desorbed (m_d) was calculated from the elution curve (C_t vs. t)].	$E\,(\%) = m_d/q\text{tot} \times 100$
(e) *Empty bed contact time (EBCT)* time required filling the empty bioreactor with the liquid at constant flow rate. It affects the shape of the breakthrough curve.	$\text{EBCT} = \frac{V_c}{Q} = \frac{A_c Z}{Q}$
(f) *Sorbent usage rate (U_r)* weight of sorbent saturated per litre of solution treated.	$U_r = \frac{M}{V_b} = \frac{V_c \rho}{V_c N_b} = \frac{\rho}{N_b}$
(g) *Critical bed height (Z_o)* theoretical height bed required to ensure *that* the outlet solute concentration does not exceed the breakthrough concentration C_b.	$Z_o = \frac{u}{k_a N_o} \ln\left(\frac{C_o}{C_b} - 1\right)$

37.6 mg g^{-1}, polyethylemine (PEI) 39.6 mg g^{-1}, $FeCl_3$ 43.6 mg g^{-1} and for HCl 46.5 mg g^{-1}, respectively. After comparing uptake capacities of pre-treated biomasses, 0.1 N HCl was selected for the pre-treatment of biomass in further experiments.

Effect of pH on reduction and biosorption of Cr(VI)

The effect of pH on the biosorption of Cr(VI) was investigated by performing the experiments at 40 °C temperature, 100 mg L^{-1} Cr(VI) initial metal concentration, biomass dose 2 g L^{-1} and varying pH from 1.0 to 12. The maximum uptake capacities of FFB, IFB and CIFB were found to be 29.25, 33.5 and 46.5 mg g^{-1}, respectively, at pH 2.0 (Fig. 1a). Cr(VI) in the solution exists mainly in three ionic states, $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} at acidic pH. Lowering of pH, results in the protonation of surface groups to a higher extent leading to greater electrostatic attraction between the chromium oxianions and positively charged surface groups. Consequently, the metal uptake increases with decrease in the pH of the solution. While at higher pH, the uptake of Cr(VI) lowers down due to increase in the number competitive hydroxyl anions along with unfavourable negative charge over the fungal cell wall. The Cr(VI) remediation takes place by reduction of Cr(VI) into Cr(III) followed by its adsorption over the biomass surface through complexation with the surface groups (Hasan et al. 2008). Moreover, results obtained as represented in Fig. 2a, b clearly illustrates the effect of pH on the Cr(VI) reduction and its biosorption for both untreated and treated biomass. At experimental pH (pH 2.0), $HCrO_4^-$ predominates (Kobya 2004) and the reduction of $HCrO_4^-$ is also clear from aqueous chemistry as represented by the given redox reaction:

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4\ H_2O \quad (3)$$

With the help of the Nernst equation, the redox potential of $HCrO_4^-$/Cr(III) can be calculated as follows:

$$E = E^\circ + 0.0197 \log \frac{[HCrO^{4-}]}{[Cr^{3+}]} - 0.138pH \quad (4)$$

As Eqs. 3 and 4 clearly indicate the involvement of both protons and electrons in the sorption process and strong effect of pH on the redox potential, respectively. The reason of favourable biosorption at lower pH might be associated with the protonation of surface functional groups, positive surface charge at low pH and increase in the redox potential at adsorption pH.

However, hike in the uptake capacity after acid treatment may be due to the fact that acid treatment further improves the reducing capability of the biomass as evident from Fig. 2a, b, where Cr(III) species was present in the

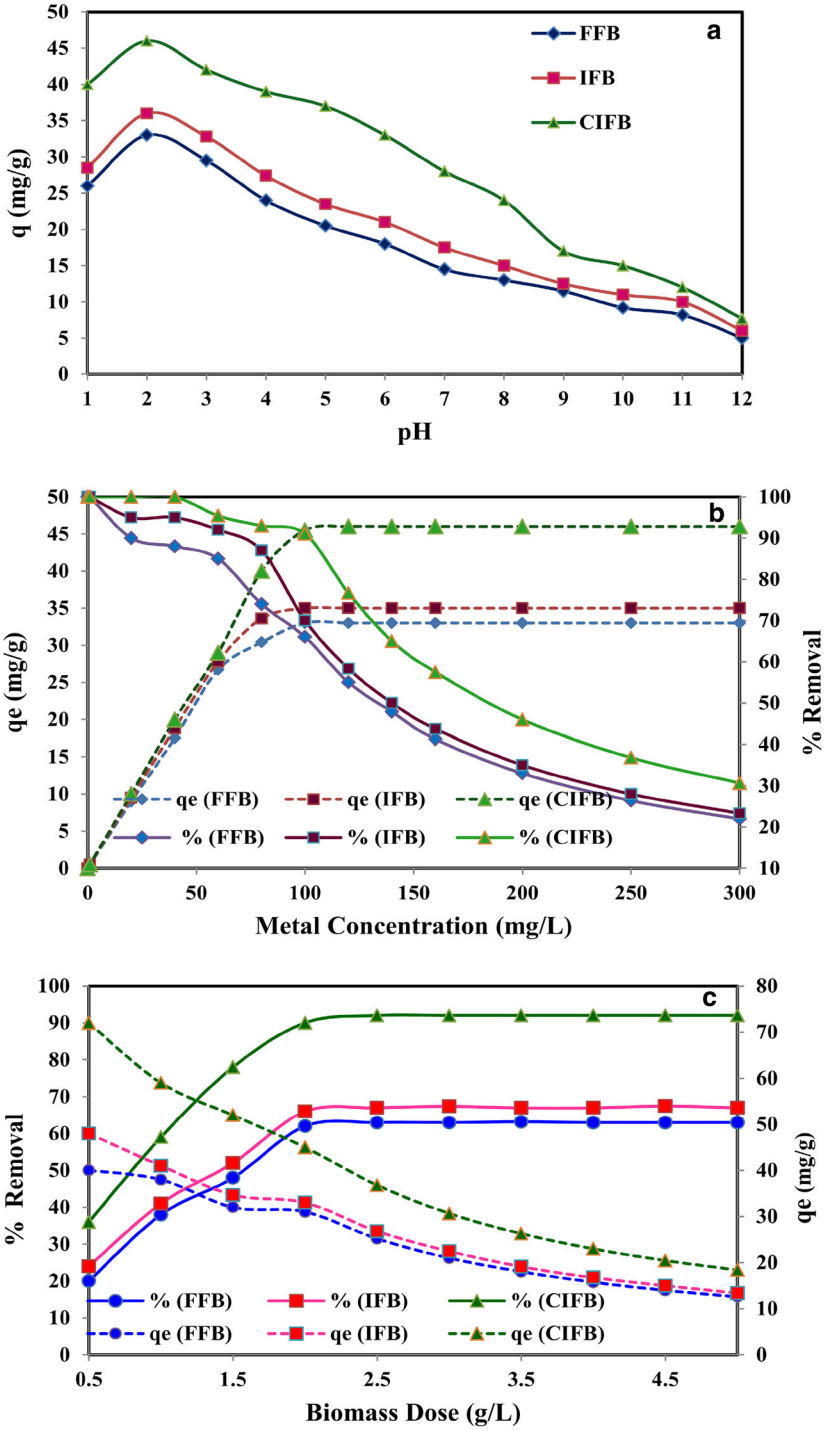

Fig. 1 **a** Effect of pH on Cr(VI) sorption capacity of biomasses. Conditions: initial metal concentration 100 mg L^{-1}; temperature 40 °C; biomass dose 2.0 g L^{-1} contact time 3 h at 100 rpm. **b** Effect of metal ion concentration on Cr(VI) sorption capacity and percentage removal. Conditions: pH 2.0; temperature 40 °C; contact time 3 h at 100 rpm. **c** Effect of biomass dose on Cr(VI) sorption capacity and percentage removal. Conditions: pH 2.0; temperature 40 °C; initial metal concentration 100 mg L^{-1} and contact time 3 h at 100 rpm. FFB—free fungal biomass, IFB—immobilized fungal biomass, CIFB—chemically treated immobilized fungal biomass

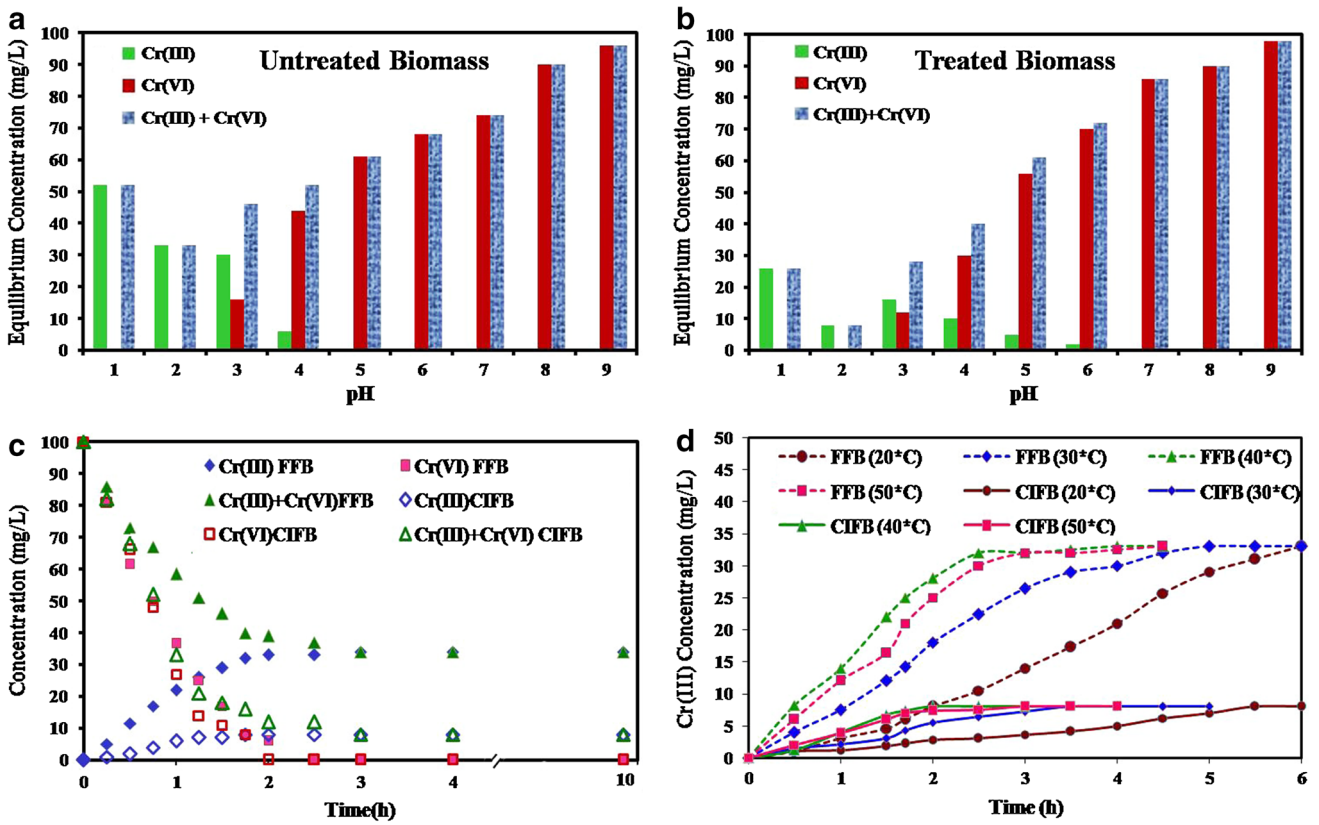

Fig. 2 **a** and **b** Distribution of chromium species [Cr(VI), Cr(III) and total chromium] in solution after adsorption. Conditions: initial metal concentration 100 mg L^{-1}; temperature 40 °C; biomass dose 2.0 g L^{-1} contact time 3 h at 100 rpm. **c** Distribution of chromium species in solution at different times. Conditions: initial metal concentration 100 mg L^{-1}; temperature 40 °C; biomass dose 2.0 g L^{-1}; pH 2.0 at 100 rpm. Solid symbols represent untreated free fungal biomass (FFB), and solid symbol represents chemically treated immobilized fungal biomass (CIFB). **d** Effect of temperature on chromium biosorption. Conditions: initial metal concentration 100 mg L^{-1}; biomass dose 2.0 g L^{-1}; pH 2.0 at 100 rpm. *Dotted lines* represent FFB, and *solid lines* denote CIFB

system up to the pH 6.0 in case of treated biomass while Cr(III) was present only up to pH 4.0 in case of untreated biomass. Furthermore, acid pre-treatment might expose more binding sites by cleanup the surface of biomass through replacing the already bound ionic species with the protons and sulphates over the biomass surface (Park et al. 2005). Bai and Abraham (2002) and Nair and Madhavan (1992) have also reported that acid treatment increases the number of surface groups due to the appearance of relatively pure amino sugars (D-glucosamines) which are more easily protonatated at biosorption pH (Bai and Abraham 2002; Nair and Madhavan 1992).

Effect of contact time

Effect of contact time was studied at an initial solution pH 2.0, initial metal ion concentration of 100 mg L^{-1}, biomass dose 2.0 g L^{-1} and temperature 40 °C for FFB and CIFB to find out the time required for the establishment of equilibrium of adsorption process. Initially, Cr(III) species was absent, but due to reduction of the Cr(VI) species, it appears into the system, and Cr(III) concentration gradually increases in the system until equilibrium get established. At biosorption pH, the Cr(VI) concentration was decreased up to zero which indicates the complete reduction of hexavalent chromium into trivalent form at biosorption pH. Total chromium content also decreases up to equilibrium (Fig. 2c). Initially, rapid adsorption takes place and equilibrium was achieved in near about 120 min in case of FFB, while equilibrium was achieved in about 100 min in case of CIFB. This indicates the faster rate of adsorption over acid-treated biomass as compare to biomass without any chemical pre-treatment.

Effect of initial metal ion concentration

The effect of metal ion concentration on the Cr(VI) uptake of biomass was investigated using initial metal ion concentration range from 1 to 300 mg L^{-1} at pH 2.0, biomass dose 2.0 g L^{-1} and temperature 40 °C. As indicated by Fig. 1b, initially uptake capacity of biomass increases with increase in metal ion concentration, but at high metal

concentration, biomass becomes saturated and does not show further increase in adsorption capacity of biomass, while percentage removal decreases with increase in metal ion concentration. FFB gets saturated at lower metal ion concentration (at 70 mg L^{-1}) as compared to CIFB which saturates at 100 mg L^{-1}. The uptake capacity of biomass was found to be highest at initial metal ion concentration 100 mg L^{-1}, pH 2.0 and temperature 40 °C. Further increase in the metal ion concentration does not increase the uptake capacity of biomass.

Effect of biomass dose

The effect of biomass dose on the biosorption of Cr(VI) was investigated by performing the experiments at pH of 2.0, initial metal ion concentration 100 mg L^{-1}, temperature 40 °C and varying biomass dose from 1 to 5 gm L^{-1}. Results are represented in Fig. 1c. It was found that the uptake decreased with increase in biomass dose while percentage removal increases with increase in biomass dose. At high sorbent dose, the available solute is insufficient to completely cover the available exchangeable sites present over the biosorbent surface, which usually results the reduction in the uptake capacity of biosorbents while at high biomass dose, percentage removal increases due to excess availability of binding sites. In addition to this, further increased biosorbent dose also causes the interference between binding sites thus uptake capacity of biomass declines, also after some time, adsorption was governed by equilibrium and further increase in the biomass dose does not affect the adsorption and percentage chromium removal.

Sorption isotherms

Adsorption isotherms correlate the adsorbate concentration in aqueous phage with its concentration at adsorbate–adsorbent interface (Mittal et al. 2010a, b, c). The study of isotherms was carried out by varying initial metal ion concentration from 100 to 250 mg L^{-1} for FFB, IFB and CIFB and keeping other parameters constant at pH 2.0, biomass dose 2.0 g L^{-1} and temperature 40° C. Figure 3b represents Langmuir isotherms which better fits the current adsorption system as indicated by correlation coefficient, and values of isotherm constants of both Langmuir isotherms and Freundlich isotherms are presented in Table 2. The supportive Langmuir model indicates that the adsorption energy was uniformly distributed throughout the entire adsorption surface, and there was no interaction and transmigration of adsorbate on the biosorbents surface after monolayer adsorption (Mittal et al. 2008). Higher values of $Q°$ and lower values of b indicate that chemically treated biomass of *Phanerochaete chrysosporium* is a good sorbents for Cr(VI) adsorption.

Sorption kinetics study

Figure 2c represents the concentration variation profile of Cr(VI), Cr(III) and total chromium in the solution as a function of time, that is, kinetics of Cr(VI) biosorption on to FFB and CIFB at pH 2.0, biomass dose 2.0 g L^{-1}, initial metal concentration 100 mg L^{-1}, temperature 40 °C and agitation speed of 100 rpm. The Cr(VI) depletes while Cr(III) concentration increases during the sorption process, and at the end, Cr(VI) concentration becomes undetectable for all forms of taken biomasses. These results further supported to the fact that during the removal process reduction Cr(VI) into Cr(III) followed by the sorption of chromium on the biomass surface takes place. Time concentration profile indicates the high kinetic rate which might be due to the excellent reducing power of the biomass. Similar type of kinetic rate was also reported earlier in some sea weed biomasses where sorption completed within 1–3 h (Sheng et al. 2004; Chen and Yang 2005). Acid treatment further reduces the equilibrium time which may be due to the enhanced reducing power of biomass as evident from Fig. 2a, b.

The kinetic constant and correlation coefficients for the pseudo-first-order and pseudo-second-order model were calculated from the plots of log $(q_e - q_t)$ versus time for pseudo-first-order and t/q_t versus time for pseudo-second-order reaction kinetics (Fig. 3a), respectively. The values of different kinetic parameters are given in Table 3. Good correlation coefficients were observed for pseudo-second-order kinetic model as compare to pseudo-first-order model indicating that Cr(VI) uptake process can be explained with the pseudo-second-order kinetics model. This means that adsorption rate would be proportional to the metal ion concentration and the square of the number of free sites of the biosorbent, which corresponds to the term $(q_e - q_t)^2$ in the second-order model.

Thermodynamic study

The thermodynamic studies were performed for treated immobilized biomass at different temperatures (Fig. 2d), and Van't Hoff plot (Plot of ln Kc vs. $1/T$) was drown. Thermodynamic parameters were calculated using Van't Hoff plot and corresponding equations given in Table 1. Calculated values of thermodynamic parameters (ΔG, ΔH and ΔS) are given in Table 4. The negative values of ΔG indicate that the sorption process was spontaneous in nature and increase in negative value of ΔG with increase in temperature indicates that raise in temperature favours the sorption process. Positive value of ΔH shows the endothermic nature of this sorption process, and positive value of ΔS represents that during sorption process, the degree of freedom of metal ions get increased, and it is due to the disorderliness of the adsorption at solid–liquid interface (Barkat et al. 2009).

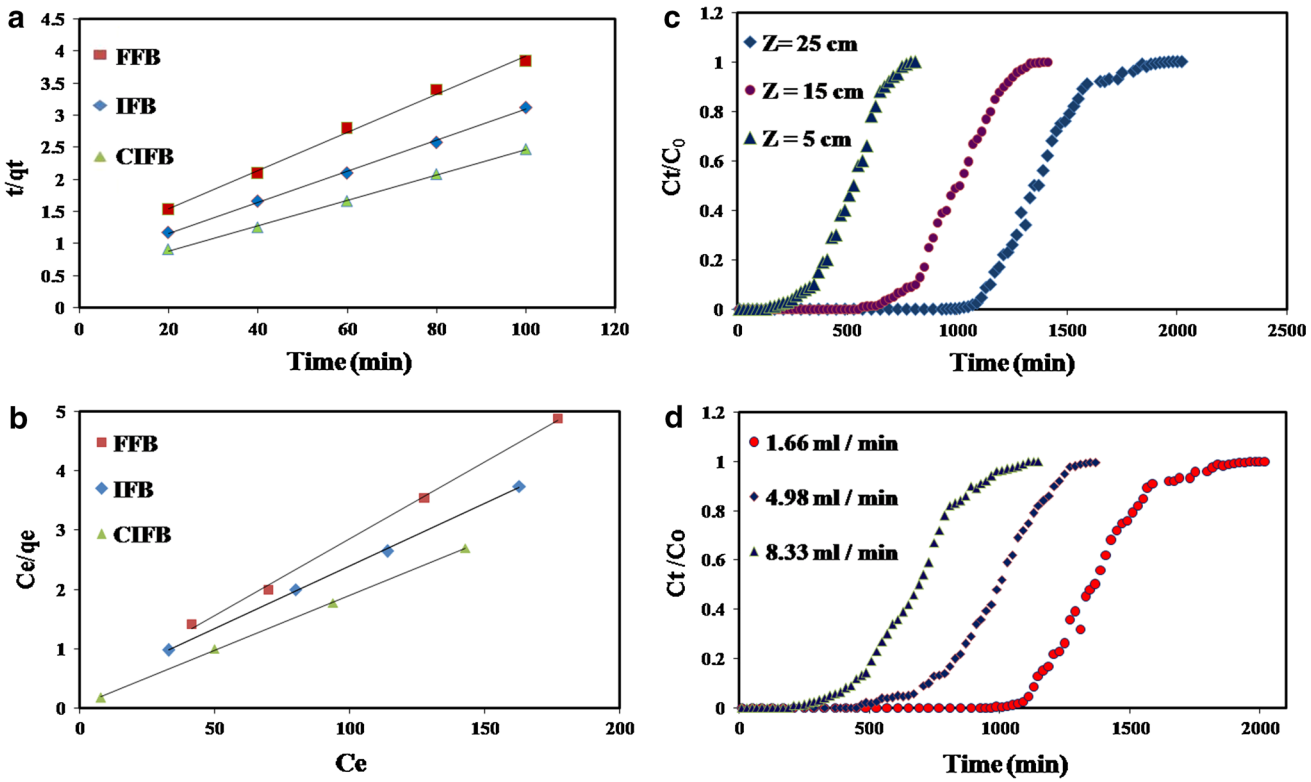

Fig. 3 **a** Pseudo-second-order plot for Cr(VI) removal. Conditions: pH 2.0, initial metal concentration 100 mg L^{-1}, biosorbent dose 2.0 g L^{-1}, temperature 40 °C. **b** Langmuir isotherm plot for Cr(VI) removal. Conditions: pH 2.0, biosorbent dose 2.0 g L^{-1}, temperature 40 °C at 100 rpm. **c** *Breakthrough curves* for Cr(VI) removal in continuous up-flow fixed-bed bioreactor at different bed heights (5, 15, 25 cm) and constant flow rate 1.66 mL min^{-1} and solution pH 2.0. **d** *Breakthrough curves* for the removal of Cr(VI) in continuous up-flow fixed-bed bioreactor of bed height 25 cm and different flow rates (1.66, 4.98 and 8.33 mL min^{-1}) at pH 2.0

Table 2 Langmuir and Freundlich isotherm model constants for biosorption of Cr(VI) on FFB, IFB and CIFB of *P. chrysosporium*

Biosorbent *P. chrysosporium*	Langmuir constants			Freundlich constants		
	$Q°$ (mg g^{-1})	b (L mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2
FFB	38.46	0.095	0.999	13.51	5.20	0.878
IFB	45.45	0.102	0.997	15.39	4.95	0.911
CIFB	55.55	0.486	0.993	17.63	4.73	0.900

FFB free fungal biomass, *IFB* immobilized fungal biomass, *CIFB* chemically treated immobilized fungal biomass

Table 3 Kinetic parameters for the sorption of Cr(VI) on FFB, IFB and CIFB of *P. chrysosporium*

Type of Biomass	Pseudo-first order				Pseudo-second order		
	k_s (L min^{-1})	q_e (mg g^{-1})	R^2	k'_2 (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	q_e (mg g^{-1})	R^2
FFB	0.0229	28.57	0.913	0.00114	1.0482	30.20	0.995
IFB	0.0207	32.73	0.858	0.00123	1.4742	34.48	0.998
CIFB	0.0299	46.34	0.921	0.00904	2.0490	47.61	0.999

FFB free fungal biomass, *IFB* immobilized fungal biomass, *CIFB* chemically treated immobilized fungal biomass

Fixed-bed bioreactor studies for Cr(VI) removal

Removal of Cr(VI) in continuous up-flow fixed-bed bioreactor was studied at different flow rates (1.66, 4.98 and 8.33 mL min^{-1}) and different bed heights (5, 15 and 25 cm). The effect of these two variables on the different parameters such as break through time (t_b), bed exhaustion time (t_e), volume treated up to break through point (V_b),

volume treated up to exhaustion point (V_e), metal uptake capacity (q mg g^{-1}), percentage removal of metal, empty bed contact time (EBCT) and sorbent usage rate (Ur, that is, weight of sorbent saturated per litre of solution treated) was determined. The results are shown in Table 5, which indicate that breakthrough time increase with increase in bed height and decrease with increase in flow rate. Maximum 1,610 and 3,120.8 mL volumes were treated by 25 cm bed height bioreactor at 1.66 mL min^{-1} flow rate, before breakthrough time (t_b 970 min) and exhaustion time (t_e 1,880 min), respectively. Figure 3c, d represents the breakthrough curves (Ct/C_0 vs. time) at different bed heights and at different flow rates. Maximum uptake capacity achieved was 68.87 mg g^{-1} for bed height 25 cm and at 1.66 mL min^{-1} flow rate. Regeneration of biomass or desorption was done by 10 % NaOH solution. Desorption of 25 cm bed height bioreactor at flow rate 4.98 mL min^{-1} was completed in 320 min, with 98 % elution efficiency. After desorption, 0.1 M HCl was passed through the bioreactor up to 1 h to reprotonate the surface groups followed by the washing through deionized water up to 1 h.

BDST model

Bed depth service time plot, service time (t) versus bed height (Z) at different flow rates, is given in supplementary data S. Fig. 2. With the help of this plot, the bed sorption capacity (N_o) and sorption rate constant (k_a) were determined from the slope and intercept. Critical bed depth (Z_o) was calculated with the help of the equation in Table 1, given in theory section. Values of N_o, k_a, Z_o and R^2 are summarized in Table 6. The linear nature and high correlation coefficients of BDST plot indicate the validity of the BDST model for the present system. It has been found that the rate constant (ka) decreased from 0.00456 to 0.000549 L/(mg min^{-1}) with increase of flow rate from 1.66 to 8.33 mL min^{-1}. For larger k_a, a short bed is required to avoid breakthrough, but as k_a decreases, a progressively longer bed is required to avoid breakthrough for immediate effluent.

Table 4 Thermodynamic parameters for sorption of Cr(VI) on HCl pre-treated fungal biosorbent (CIFB) at different temperatures

Temperature (K)	$-\Delta G$ (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
293	0.286	17.736	61.4
303	0.8401		
313	1.5274		

Optimization of process using RSM

Two-level four-factor full-factorial CCD and two-level two-factor full-factorial CCD of RSM technique were applied for the optimization of batch (pH, temperature, biomass dose and metal ion concentration) and continuous mode operation parameters (flow rate and bed height), respectively, for adsorption of Cr(VI) using software MINITAB® Release 15. Regression analysis was performed for both batch and continuous bioreactor study, and regression equations were obtained using the coefficients, which are given below:Regression equation for the batch mode operation:

$$\begin{aligned} Y = {} & 25.2400 - 10.4667\ \text{pH} - 20.3783\ \text{biomass dose} \\ & + 3.3300\ \text{metal concentration} + 4.4350\ \text{temperature} \\ & + 1.1892\ \text{pH} \times \text{pH} + 18.6292\ \text{biomass dose} \\ & \times \text{biomass dose} + 0.2392\ \text{metal concentration} \\ & \times \text{metal concentration} + 0.3792\ \text{temperature} \\ & \times \text{temperature} + 8.7100\ \text{pH} \times \text{biomass dose} \\ & - 0.9250\ \text{pH} \times \text{metal concentration} + 1.9800\ \text{pH} \\ & \times \text{temperature} + 1.2100\ \text{biomass dose} \\ & \times \text{metal concentration} - 2.1350\ \text{biomass dose} \\ & \times \text{temperature} + 0.0300\ \text{metal concentration} \\ & \times \text{temperature}. \end{aligned}$$

where Y is the response variable, predicted chromium uptake capacity (mg g^{-1}). The values of standard deviation R^2 and R^2 (adjusted) were found to be-1.59144; 99.01 and 98.14 %, respectively.

Regression equation for the bioreactor study is as follows:

Table 5 Sorption data for up-flow fixed-bed bioreactor packed with immobilized acid-treated biomass containing luffa sponge discs (CIFB discs), for Cr(VI) sorption at different bed heights and constant flow rate (1.66 ml min^{-1}) and at different flow rates and constant bed height 25 cm

Flow rate (mL min^{-1})	Bed height (cm)	t_b (min)	t_e (min)	V_b (mL)	V_e (mL)	q (mg g^{-1})	M (gm)	% Cr(VI) removal	EBCT (min)	U_r (g L^{-1})
1.66	5	250	730	415	1,211.8	41.76	0.87	30.00	9.45	2.096
1.66	15	590	1,310	797.4	2,174.6	52.1	2.47	59.17	28.37	2.521
1.66	25	970	1,880	1,610	3,120.8	68.87	4.36	96.21	47.28	2.708
4.98	25	470	1,390	2,340.6	6,922.2	59.24	4.36	37.30	15.76	1.863
8.33	25	230	1,010	2,665.6	8,413.3	51.76	4.36	26.82	9.42	1.636

Table 6 BDST model parameters for the sorption of chromium (VI) in fixed-bed bioreactor

Flow rate (mL min^{-1})	N_0 (mg L^{-1})	k_a (L mg^{-1} min^{-1})	Z_0 (cm)	R^2
1.66	3,914.6	0.00456	0.225	0.998
4.98	3,015.3	0.00106	1.252	0.987
8.33	2,380.5	0.000549	5.819	0.992

$$Y = 42.130 - 9.60 \text{ flow rate} + 12.166 \text{ bed height} + 1.672 \text{ flow rate} \times \text{flow rate} + 6.622 \text{ bed height} \times \text{bed height} - 2.560 \text{ bed height} \times \text{flow rate}.$$

The values of R^2 and R^2 (adj.) were found to be 97.62 and 95.92 %, respectively.

FTIR analysis

FTIR analysis of biomass was done, before and after acid treatment and after Cr(VI) adsorption, in order to analyse the nature and groups present over the surface of biomass and groups involve in metal ions binding. Translucent sample discs were prepared by biomass pellets, and KBr in the ratio 1:10 and infrared spectra were obtained in the range of 4,000–400 cm^{-1}, with the help of Perkin Elmer FTIR-1600 spectrophotometer, USA. FTIR spectra are shown in Fig. 4, which represents various absorption bands. The broad band around 3,200–3,400 cm^{-1} represents groups of the glucose and the stretching of the protein and the acetamido group of chitin fraction (Bai and Abraham 2002; Chhikara et al. 2010). Acid treatment sharpens the −NH stretching and polymeric association band (3,200–3,400 cm^{-1}), which might be due to appearance of relatively pure amino sugars (D-glucosamines), resulting from partial hydrolysis of chitin (Bai and Abraham 2002; Nair and Madhavan 1992). A new peak appears at 2,300 cm^{-1} after acid treatment. This peak was due to $-NH^{2+}$ and $-NH^{3+}$ stretching vibration (Chhikara et al. 2010). Absorption peak at 2,924 and 2,856 cm^{-1} indicates the −CH stretching, and peak at 2,360 cm^{-1} is the assignment of P–H groups. The absorption at 1,651 cm^{-1} can be attributed to the amide I band of amide bond in N−acetyl glucosamine polymer or of the protein peptide bond (Bai and Abraham 2002). The peak at 1,550 cm^{-1} is the assignment of primary and secondary amines and amides (N–H bending). Peak at 1,371 cm^{-1} represents sulfamide bonds (S=O). Peaks at 1,035, 1,080 and 1,149 cm^{-1} assign to −CN stretching vibration of chitin–chitosan and protein fraction. Peeks ranging from 690 to 990 cm^{-1} represent C–H bending. After Cr(VI) adsorption, decrease in the absorption intensity of −NH stretching (3,388 cm^{-1}) and sifting the peak of −NH bending (1,539–1,651 cm^{-1}) from 1,651.12 to 1,643.41 cm^{-1} shows that of amino groups are involve in Cr(VI) binding. The major cell wall constituents like hexosamines and proteins are the providers of major portion of amino groups. These amino groups are protonated at the adsorption pH (pH 2.0) and during acid treatment. Chromate ions which are negatively charged become electrostatically attracted towards the positively charged amines of the biomass cell wall (Bai and Abraham 2002), and these findings are in agreement with the results of many researchers (Gupta and Rastogi 2009).

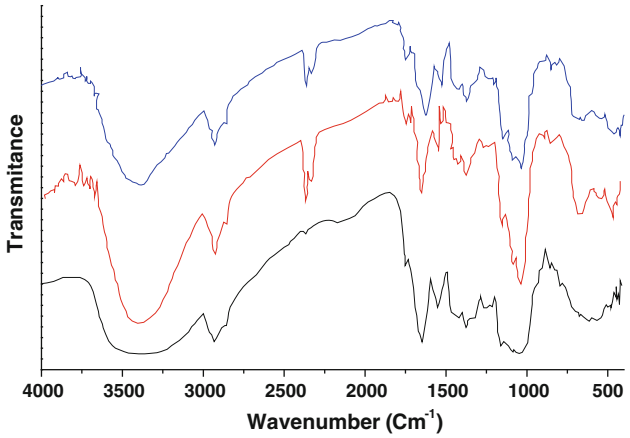

Fig. 4 FTIR spectra for *P. chrysosporium* before treatment (*Lower*, *Black line*), after HCl treatment (*Middle*, *Red line*) and after Cr(VI) adsorption over treated biomass (*Upper*, *Blue line*)

Conclusion

Phanerochaete chrysosporium was successfully immobilized over luffa sponge and was used for removal of Cr(VI) from water. The immobilized biomass (IFB) showed better uptake capacity of Cr(VI) as compared to free fungal biomass (FFB) due to more surface area and less compactness. Acid treatment of the immobilized biomass showed increase in chromium uptake capacity of fungal biomass due to generation of relatively pure amino sugars as the result of acid hydrolysis followed by the protonation of the functional groups present on the surface of the biomass. During adsorption process, both the reduction of Cr(VI) into Cr(III) and its adsorption over biomass surface take place simultaneously. At optimum conditions, 92 % Cr(VI) was removed from the water, and remaining was reduced into lesser toxic form of chromium, that is, in Cr(III). FTIR analysis showed that amino groups ($-NH_2$) and hydroxyl groups are mainly involved in Cr(VI) adsorption. Thermodynamic studies indicate that the biosorption of Cr(VI) was endothermic and spontaneous process. Various parameters such as temperature, pH, biomass dose and Cr(VI) concentration in solution govern the biosorption of Cr(VI) over the immobilized fungal biomass on luffa sponge in batch mode operation. In batch studies, the maximum uptake capacity of *P. chrysosporium* biomass (46.5 mg g^{-1}) was achieved at pH 2.0; biomass dose 2.0 g L^{-1}; metal ion concentration 100 mg L^{-1} and temperature 40° C. The flow

rate and bed height are main influencing factors for the adsorption process in continuous up-flow fixed-bed bioreactor. In continuous up-flow mode of operation, the maximum uptake capacity (68.87 mg g^{-1}) was achieved at bed height 25 cm and flow rate 1.66 mL min^{-1}. Under the above-mentioned conditions, the treated volume up to breakthrough time (t_b 970 min.) and treated volume up to bed exhaustion time (t_e 1,880 min.) were 1,610, 3,120.80 mL, respectively. Overall, *P. chrysosporium* was immobilized over luffa sponge and its acid treatment improved the uptake capacity of biomass. This immobilized and acid-treated biomass system can be used very efficiently for the removal of Cr(VI) from the water.

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Nomenclature

A_c	Bioreactor cross-sectional area (cm^2)
b	Langmuir constant related to free sorption energy (L mg^{-1})
C_{Ae}	Concentrations of adsorbed molecules over sorbent surface (mg L^{-1})
C_b	Breakthrough concentration of metal ions (mg L^{-1})
C_e	Equilibrium concentration of solute in solution (mg L^{-1})
C_i	Initial metal ion concentration in solution (mg L^{-1})
C_t	Remaining metal ion concentration in solution at any time (mg L^{-1})
C_0	Metal ion concentration in the inlet solution (mg L^{-1})
E	Elution efficiency
ΔG	Gibbs free energy change (kcal mol^{-1})
h	Initial sorption rate (mg $g^{-1}min^{-1}$)
ΔH	Enthalpy change (kcal mol^{-1})
k_a	Rate constant in BDST model (L mg^{-1} min^{-1})
K_c	Equilibrium constant
K_F	Freundlich constant indicative of sorption (uptake) capacity (mg g^{-1})
k_s	Equilibrium rate constant of pseudo-first-order sorption (min^{-1})
k_2'	Equilibrium rate constant (g mg^{-1} min^{-1})
M	Weight of biosorbent in bioreactor (gm)
m_d	Metal mass desorbed
n	Freundlich constant indicates the intensity of sorption
N_b	Bed volumes treated up to breakthrough
N_o	Sorption or uptake capacity of bed (mg L^{-1})
Q	Volumetric flow rate of solution (mL min^{-1})
Q^o	Sorption capacity of biosorbent under experimental conditions (mg g^{-1})
q_e	Uptake capacity of sorbent at equilibrium (mg g^{-1})
q_t	Uptake capacity of sorbent at any time (mg g^{-1})
q_{tot}	Total quantity of metal adsorbed in the bioreactor
R	Universal gas constant (8.314 J/(mol K))
ΔS	Change in the entropy (cal mol^{-1} K^{-1})
t	Time
t_b	Breakthrough (min)
t_e	Bed exhaustion time (min)
u	Linear velocity of solution in bioreactor (cm min^{-1})
U_r	Sorbent usage rate (g L^{-1})
V	Volume of solution (L)
V_b	Volume of the effluent treated up to breakthrough time (mL)
V_c	Sorbent volume in the bed (mL)
V_e	Volume of the effluent treated up to exhaustion time (mL)
V_{eff}	Volume of effluent (mL)
W	Weight of biosorbent (g)
X	The total amount of metal ion fed to the bioreactor (mg)
Z	Bed height (cm)
Z_o	Critical bed height (cm)
ρ	Sorbent density in the bioreactor (g cm^{-3})
CCD	Central composite design
MEA	Malt extract agar
FFB	Free fungal biomass
IFB	Immobilized fungal biomass (untreated)
CIFB	Chemically treated biomass (acid treated)

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