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ORIGINAL PAPER

Adsorption, desorption, and kinetic study on Cr(III) removal from aqueous solution using *Bacillus subtilis* biomass

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Abstract Discharge of untreated industrial effluents containing heavy metals is hazardous to the environment as they are highly toxic and accumulates throughout the food chain. This study reports the removal of trivalent chromium from aqueous solution using *Bacillus subtilis* biomass, best suited for the treatment of real tannery effluents since Cr(III) salt is used for tanning. The optimum pH and temperature for biosorption was found to be 4.0 and 60°C, respectively. A biosorbent dosage of 1 g l^{-1} showed maximum metal uptake (q_e) of 23.9 mg g^{-1} for an initial metal concentration of 100 ppm. Pseudo-second-order kinetics best describes the adsorption process. Best fit for adsorption was obtained with Freundlich model. Desorption experiments with 5 M NaOH, inferred the reusability of the biomass. Fourier transform-infrared spectroscopy was used to study the mechanism of metal binding.

Keywords *Bacillus subtilis* biomass · Trivalent chromium · Adsorption · Desorption

Introduction

The application of chromium, a heavy metal in various industries (Bai and Abraham 2001), especially in leather tanning has gained a negative impact in the society with respect to its pollution potential. Chromium has several oxidation states ranging from Cr(II) to Cr(VI), but the trivalent and the hexavalent states are the most stable (Yadav et al. 2005). Although the oxidation state of chromium in tanning salt is only trivalent, discharge norms do not often specify the redox states, because of the concerns of possible conversion of trivalent state to the more toxic hexavalent state (Barrett and Yonge 1977). Cr(VI) is toxic, carcinogenic, and mutagenic to animals as well as humans and is associated with decreased plant growth and changes in plant morphology (James and Bartlett 1984; Costa 2003). In contrast, Cr(III) an essential trace element is relatively less toxic and less mobile (Shrivastava and Nair 2001). The untreated effluents emanating from chrome tanning contain 1,000–1,500 ppm of Cr(III), a major waste stream from tanning industry. However, the discharge limit of chromium in tannery wastewater is 2 ppm (Buljan 1996). The conventional methods for chromium removal include precipitation, lime coagulation, ion exchange, reverse osmosis, filtration, and solvent extraction (Aravindhan et al. 2004a). However, these methods are very expensive and end up with disadvantages such as incomplete metal removal, high reagent, and energy requirements especially when the metal ion concentration is in the range of 1–100 ppm (Abbas et al. 2008; Nourbakash et al. 1994). These challenges led to the development of new technologies for trivalent chromium removal from tannery effluent. Among these, bioremediation, a cost effective and safe method uses biological materials like plants and microorganisms to remove, convert or degrade highly toxic pollutants into less toxic innocuous substances (Machado et al. 2010; Kumari et al. 2005). Removal of heavy metals from aqueous solution using microorganisms takes place either by bioaccumulation or biosorption. In bioaccumulation,

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metals are transported from the outside of the microbial cell through the cellular membrane whereby the metal is sequestered (Wong and So 1993). For biosorption, chemical link formed between the functional group and the biomass is responsible for metal binding (Sivaprakash et al. 2009). The cell wall of *Bacillus subtilis*, a Gram-positive bacteria is mainly composed of peptidoglycan and teichoic acid. Peptidoglycan is a polymer of acetyl glucosamine and acetyl muramic acid, which displays mainly carboxyl and hydroxyl groups. On the other hand, teichoic acid is a polymer of copyranosyl glycerol phosphate, which displays mostly functional groups such as phosphate and hydroxyl groups thereby forming a chemical link between the metal ions and the biomass. The removal of heavy metals using *B. subtilis* biomass as a biosorbent has been studied only by few authors (Markai et al. 2003; Boyanov et al. 2003). In this study, dead *B. subtilis* biomass, a cost-effective biosorbent has been used for the removal of trivalent chromium. The use of dead cells for biosorption is most advantageous for wastewater treatment as the dead organism is not affected by toxic wastes, or they require continuous supply of nutrients. The dead cells may be stored or used for extended periods at room temperature without putrefaction. The experimental data obtained by batch assay have been analyzed using kinetics and adsorption isotherms. Desorption capacity of the biomass was also studied using 5 M NaOH. Fourier transform infrared (FT-IR) spectroscopy was done for the chromium-loaded and -unloaded biomass to identify the presence of functional groups responsible for metal binding.

Materials and methods

Chromium sulfate [$Cr_2(SO_4)_3 \cdot 15H_2O$] used in this study was of analytical grade, procured from SD-Fine chemicals Pvt. Ltd. Double-distilled water has been used throughout the study. All other reagents used were of analytical grade, unless stated otherwise. *B. subtilis* strain was obtained from Tamil Nadu Agricultural University, Coimbatore. Growth medium to maintain the bacterial strain was obtained from Hi-media, Mumbai, India.

Preparation of the biomass

Bacillus subtilis strain was grown and maintained using nutrient agar and nutrient broth. A loopful of culture from nutrient agar slant (3 g l^{-1} of meat extract, 5 g l^{-1} of peptic digest of animal tissue, and 15 g l^{-1} of agar, autoclaved at 121°C for 15 lbs pressure for 20 min) was transferred to a flask containing sterilized nutrient broth (5 g l^{-1} of peptone, 1.5 g l^{-1} of beef extract, 1.5 g l^{-1} of yeast extract, 5 g l^{-1} of NaCl, 2.5 g l^{-1} of glucose, and 1.25 g L^{-1} of $MgSO_4$ was sterilized at 121°C for 15 lbs pressure for 20 min) and incubated at 30°C in an incubator shaker for overnight incubation. The turbidity of the overnight culture was adjusted to 0.1 OD at 600 nm using sterilized nutrient broth. The turbidity-adjusted culture was used to inoculate fresh nutrient broth to obtain the biomass. The inoculated flask was incubated at 30°C in an incubator shaker, and the biomass was harvested after a week of incubation by centrifuging at 10,000 rpm for 10 min at 4°C. The harvested biomass was washed twice with double-distilled water and then dried for 6 h at 80°C in hot air oven. Dried biomass was then crushed with mortar and pestle and stored in an air-tight container.

Preparation of synthetic chromium solution

A stock solution containing 1,000 ppm of chromium was prepared by dissolving a known quantity of chromium sulfate in double-distilled water. The pH of the metal ion solution was adjusted to 3.0–3.5, aged for 12 h and stored in a refrigerator. For further experiments requisite amount was taken from the stock solution and made up to required volume in a standard flask. The pH of the synthetic chromium effluent was adjusted accordingly using 0.1 N H_2SO_4 and 0.1 N NaOH. The amount of chromium present in the synthetic chrome effluent was estimated according to the standard procedure using Perkin Elmer Lamda 35 UV–Vis spectrophotometer.

Biosorption experiments

Batch experiments were conducted in 100-ml Erlenmeyer flasks containing 50 ml of metal ion solution of different concentrations ranging from 25 to 100 ppm. In order to find out the equilibrium uptake time of chromium by *B. subtilis* biomass, biosorption studies were performed using 1 g l^{-1} of dried ground biomass. The test solutions were agitated at a constant speed of 75 strokes per min at room temperature using an incubator shaker. Samples were collected at definite time intervals (0, 10, 20, 30, 45, 60, 120, 180, 240, 300,360, 420, and 480 min), centrifuged at 10,000 rpm for 5 min. The residual chromium concentration was estimated as per standard procedure (Vogel 1989). In order to find out the optimum pH, equilibrium batch experiments were carried out at pH ranging from 3.0, 3.5, 4.0 and 4.5. The experiments were limited to pH 4.5, because Cr(III) starts precipitating at higher pH values (Mohan et al. 2006) The batch biosorption experiments were also done at different temperatures (30, 40, 50, and 60°C) to find out the optimum temperature for biosorption. To study the effect of initial chromium concentration on equilibrium uptake by the biomass, batch experiments were done at various initial metal ion concentrations (25, 50, 75,

and 100 ppm). The effect of biomass loading on the uptake of chromium was determined by conducting batch assays at different biomass concentrations (1, 1.5, 2, and 3 g l^{-1}).

Kinetics

Sorption kinetic studies are one of the important characteristics in defining the efficiency of adsorption process. The adsorption of chromium by *B. subtilis* biomass was carried out by the following kinetic studies. The adsorbent dosage was varied from 1, 1.5, 2, 3 g l^{-1} for an initial chromium concentration of 100 ppm for different time intervals. Several kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism of the adsorption process and to test the experimental data. The rate constant of adsorption was determined from the following first-order rate expression given by Lagergren (Namasivayam and Kanchana 1993).

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where q_e is the amount of chromium adsorbed (mg g^{-1}) at equilibrium, q is the amount of chromium adsorbed (mg g^{-1}) at time t (min), k_1 is the rate constant of adsorption. The first-order rate constant (k_1) and q_e were determined from the slopes and intercepts of plots of $\log(q_e - q)$ versus t at different biomass dosages.

The kinetics of adsorption was also described by pseudo-second-order equation and it is given by (Ho and McKay 1999).

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (2)$$

The second-order rate constant (k_2) and q_e were determined from the intercept and the slope of the plot obtained by plotting t/q_t versus time t. Adsorption process incorporates the transport of adsorbate from bulk solution to the interior surface of the pores. There is a possibility that the transport of chromium from the solution into the pores of the adsorbent is rate controlling in batch experiments. So, the data was further processed for testing the role of diffusion (as the rate controlling step) in the adsorption process. The rate parameters for intraparticle diffusion (k_i) for the chromium were determined using the following equation:

$$q_t = k_i \sqrt{t} \quad (3)$$

where k_i is the rate constant of intraparticle transport (mg g^{-1} $min^{1/2}$). According to the Morris and Weber model, uptake is proportional to the square root of contact time during the course of adsorption. Sorption of chromium can be calculated from the slope of the plot of square root of time ($min^{1/2}$) versus amount of chromium adsorbed (mg g^{-1}).

Adsorption isotherm studies

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of adsorption. In this study, Langmuir and Freundlich adsorption isotherms were plotted to study the interaction between the biomass and the metal ion (Bishnoi et al. 2007).

FT-IR spectral studies

The FT-IR spectra of treated and untreated *B. subtilis* biomass were obtained using KBr disc technique, to analyze the functional groups present in the biomass (Silverstein et al. 1991). The biomass was ground using mortar and pestle, dried at 80°C for 2 h. Dilution and homogenization to 0.01% (W/W) with KBr (spectroscopic grade) were carried with additional grinding. The disc was pressed in a hydraulic KBr press. The transmission FT-IR spectra were then recorded using Perkin–Elmer Spectrum RX IFT-IR model between 400 and 4,000 cm^{-1}.

Desorption experiment

Desorption experiments were carried out with different concentrations of NaOH (1, 3, and 5 M). A known quantity of chromium-loaded biomass was agitated for a period of 4 h in a shaker. The amount of chromium desorbed from the chrome-loaded biomass was analyzed using UV–Vis spectrophotometer as per standard procedure (Vogel 1989).

Results and discussion

Effect of pH

The pH of the solution can significantly influence the removal of chromium by any adsorbent and there is an optimum pH for maximum uptake, below or above which a decrease in uptake generally occurs (Zhou and Kiff 1991). Hence, to study the effect of pH on the uptake of chromium by *B. subtilis* biomass, the pH was varied from 3.0 to 4.5. Trivalent chromium ions will precipitate as hydroxides at higher pH values (Mohan et al. 2006); hence in this study, the pH experiments were limited to 4.5. The solution pH affects the ionization state of the functional groups, such as carboxyl, amino, and phosphoric, the main groups responsible for the binding of metal ions. At low pH values, these groups retain their protons, which reduce the possibility of binding any positively charged ions. On the other hand, at high pH values the carboxyl groups become deprotonated and are negatively charged, which may attract the positively

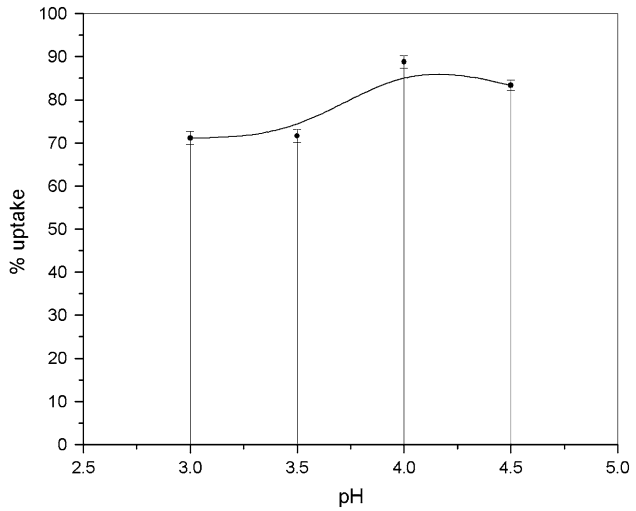

Fig. 1 Effect of pH on the metal uptake (q_e) for an initial concentration of 50 ppm

charged metal ions (Comte et al. 2008; Krishnani et al. 2008). From Fig. 1 it is clear that the maximum uptake is obtained at pH 4.0 because, the carboxyl groups in the biomass attains its isoelectric point resulting in an increased uptake of chromium, above and below which the uptake remains minimum. A maximum uptake of about 88.78% was observed at pH 4 for 50 ppm of initial metal concentration. Thus, the optimum pH range for the removal of chromium was around pH 4.0, same as the pH of chrome liquor generated from the chrome tanning stream. In this study, as the biosorption was found to be more efficient at pH 4, further experiments were conducted at the same pH.

Effect of initial concentration of chromium

Biosorption of chromium by *B. subtilis* biomass was measured at four different initial metal ion concentrations (25, 50, 75, and 100 ppm) for a given contact time at an adsorbent dosage of 1 g l^{-1}. The effect of initial concentration of chromium on the removal percentage (R %) and metal uptake (q_e) by the biomass is shown Fig. 2a, b. It is clear from the figure that the dynamic equilibrium (C_e) was achieved after 6 h. The % removal decreased with an increasing concentration of chromium (Donmez and Aksu 2002), whereas the metal uptake (q_e) increases with an increasing concentration of chromium. This shows that the residual concentration of chromium is higher at higher initial concentration of chromium. For low concentrations, the ratio of initial number of chromium ions to the available sorption sites is lower and at higher concentrations the available sites of adsorption becomes fewer; hence, the chromium uptake depends on initial concentration.

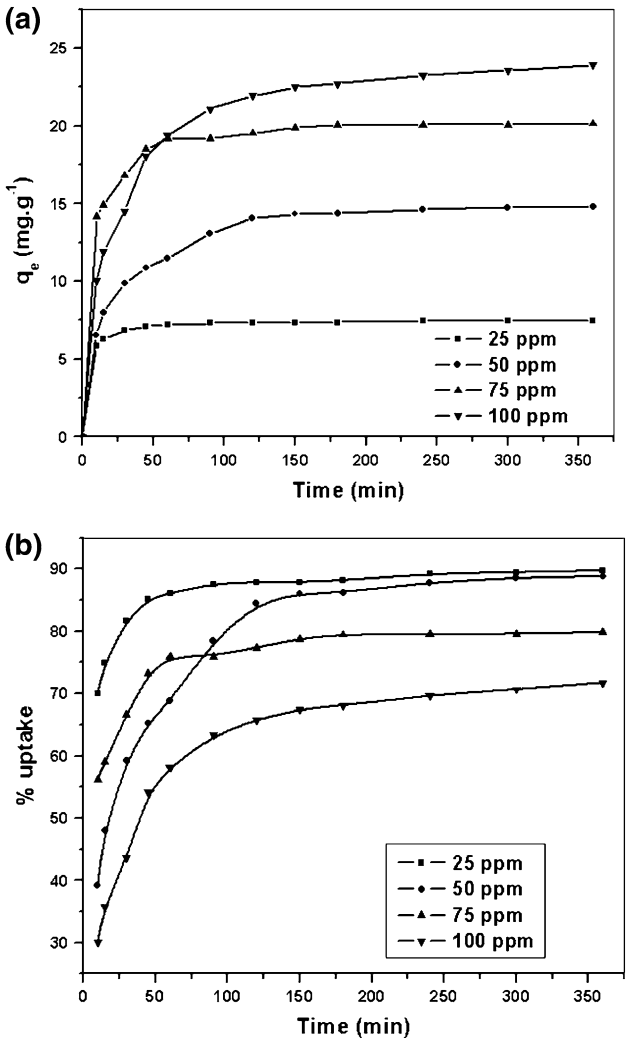

Fig. 2 Effect of time on **a** metal uptake (q_e) and **b** removal percentage (R %) for different initial concentrations

Effect of adsorbent dosage

In order to study the effect of adsorbent dosage on chromium removal from the metal ion solution of 100 ppm, experiments were conducted by varying the adsorbent dosage (1, 1.5, 2, and 3 g l^{-1}). The % uptake and q_e (mg g^{-1}) values, obtained after agitation for a period of 6 h, were plotted against the quantity of biomass used. The adsorption increases with an increase in the biomass dose. From Fig. 3 it could be seen that the % uptake increased from 71 to 75% when biomass dose was increased from 1.0 to 3.0 g l^{-1}, respectively. This could be attributed to the fact that as the adsorbent dosage increases, more adsorption sites are available for chromium, thus enhancing the uptake (Hanif et al. 2007). However, with increasing biomass dose, the quantity of chromium adsorbed on to the unit weight of biomass gets reduced, thus causing a decrease in metal uptake (q_e) value. This may be due to complex

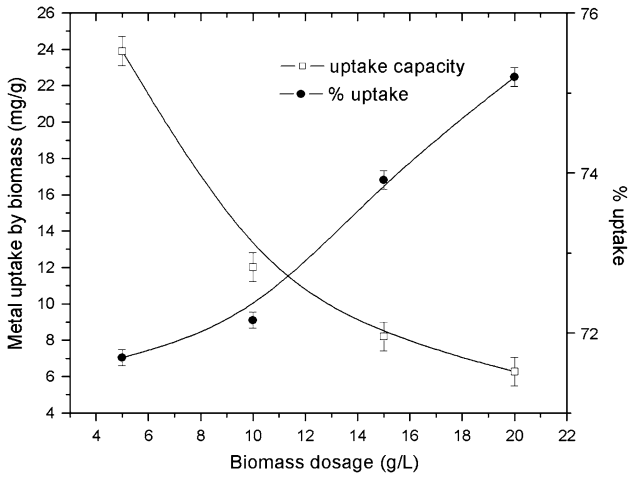

Fig. 3 Effect of adsorbent dosage on the metal uptake (q_e) and removal percentage (R %)

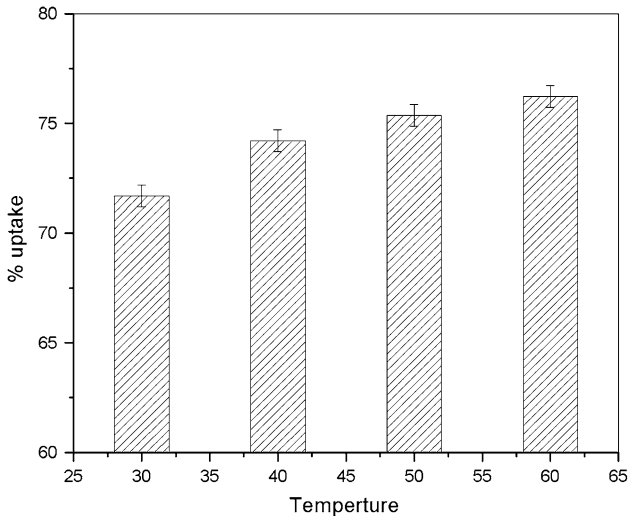

Fig. 4 Effect of temperature on the metal uptake (q_e) for an initial concentration of 100 ppm

interactions of several factors including availability of solute, electrostatic interactions, interference between binding sites, etc. The important factors being at high sorbent dosages the available chromium are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low metal uptake.

Effect of temperature

In order to study the effect of temperature on adsorption of chromium by *B. subtilis* biomass, experiments with varying temperature was carried out and the results of the same are given in Fig. 4. It can be seen from the figure that there is an increase in the % uptake as the temperature is increased from 30 to 60°C. At 60°C for 100 ppm initial concentration of chromium, the % uptake was found to be 76.22%. For the same concentration at 30°C, the % uptake was found to be 71.69%. This shows that the adsorption is determined by the reaction temperature. An increase in the amount of adsorption, with a rise in the temperature may be due to higher adsorption caused by an increase in the thermal energy of the adsorbate. This indicates that the adsorption process is endothermic in nature (Turan et al. 2007).

Kinetics of adsorption process

The correlation co-efficient values at various adsorbent dosages for the first-order kinetic model was determined and were compared with the correlation co-efficient values obtained for second-order kinetic model (Table 1). It is seen that the correlation coefficient of first-order kinetic is lower than in the case of second-order kinetic model. This shows that kinetics of chromium adsorption by *B. subtilis* biomass is better described by pseudo-second-order kinetic model rather than pseudo-first-order. The linearity of the plot (Fig. 5) also shows the applicability of the pseudo-second-order kinetic model with regression coefficient, $R^2 = 0.999$. Also, $q_{e(\mathrm{cal})}$ using pseudo-second-order model is equal to the that obtained experimentally. The reaction rate constants increase with increase in the adsorbent dosage. The k_2 values vary from 0.0023 to 0.0152 g mg^{-1} min^{-1} as adsorbent dosage varies from 1 to 3 g l^{-1}. This shows that the adsorption rate of higher biomass dosage is better than that of lower dosage. The intraparticle diffusion controls the sorption process for a system with good mixing, large particle size of the biosorbent, high concentration of adsorbate, and low affinity of adsorbate for the biosorbent. The calculated intraparticle diffusion coefficient k_{i} values for varying biosorbent dosage are given in Table 1. Figure 6 shows a plot of q_t versus $\sqrt{t}$ for the present systems. In the plot, as the lines do not pass through the origin the intraparticle diffusion is not the rate-limiting mechanism. From the plot it becomes clear that at all the biosorbent dosages the biosorption process follows two phases, which suggests the process proceeds by surface biosorption and intraparticle diffusion.

Theory on adsorption isotherm

The successful representation of the dynamic adsorptive separation of solute from solution on to an adsorbent depends upon a good description of the equilibrium separation between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed on to the adsorbent is equal to the amount being desorbed. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration graphically, it is possible to depict the equilibrium adsorption isotherm. There are many

Table 1 Rate constants for kinetic models

Biomass quantity (g l^{-1})	q_e, exp (mg g^{-1})	Pseudo-first-order rate constants			Pseudo-second-order rate constants					Intra particle diffusion	
		K_1 (min^{-1})	q_e, cal (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e, cal (mg g^{-1})	R^2	K_d (mg g^{-1} $min^{1/2}$)	R^2	K_d (mg g^{-1} $min^{1/2}$)	R^2
1	23.9	0.0159	15.1	0.913	0.0023	24.9	0.999	0.83	0.814	0.83	0.814
1.5	12.03	0.0197	7.27	0.970	0.0053	12.9	0.999	0.34	0.787	0.34	0.787
2	8.21	0.0151	2.69	0.992	0.0079	8.6	0.999	0.12	0.834	0.12	0.834
3	6.27	0.0163	4.01	0.977	0.0152	6.9	0.998	0.19	0.845	0.19	0.845

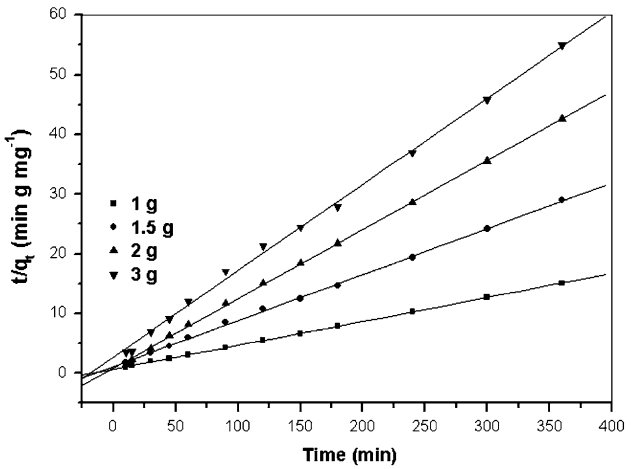

Fig. 5 Pseudo-second-order kinetic model

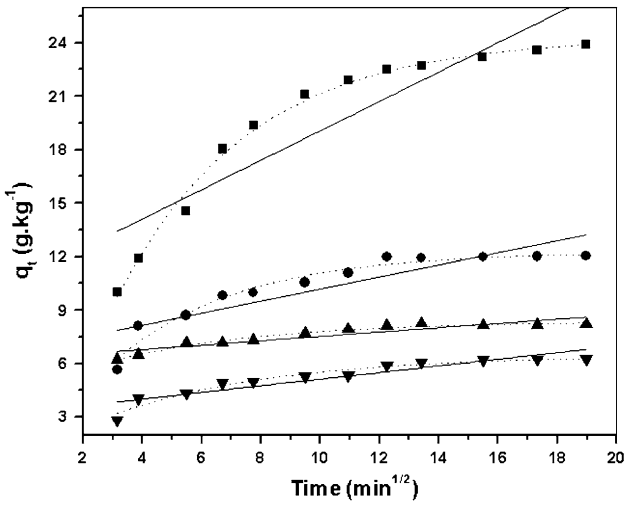

Fig. 6 Intraparticle diffusion model

theories relating to adsorption equilibrium. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. Sorption is assumed to take place at specific homogeneous sites on the adsorbent; once a chromium ion occupies a site, no further adsorption can take place at the site. Langmuir constants q_0 and b can be determined from the linear plot of C_e/q_e versus C_e, which has a slope of $1/q_0$ and an intercept of $1/q_0\ b$. The linear form of Langmuir (1918) plot is given by.

$$C_e/q_e = 1/q_0 b + 1/q_0 C_e \quad (4)$$

The experimental chromium uptake values obtained have also been analyzed using Freundlich equation. In Freundlich adsorption isotherm, the model assumes that the adsorbent consists of a heterogeneous surface composed of different classes of adsorption sites. The Freundlich (1906) constants n and k were obtained from the linear regression analysis of the equation.

$$\log q_e = \log k + (1/n)\log C_e \quad (5)$$

where q is the maximum uptake capacity and C_e is the equilibrium concentration. Plot of log q_e versus log C_e should give a straight line with a slope of $1/n$ and intercept of log k. A linear relation was observed among the plotted parameters at different temperatures, which indicates the applicability of the Freundlich equation. A comparison of the isotherm constants along with regression coefficients is presented in Table 2. The shape of the isotherm, R^2, values and the heterogeneity factor ($1/n$) seem to support a Freundlich model for adsorption. Thus, it has been inferred that the biosorption of chromium on to *B. subtilis* biomass is a heterogeneous process.

FT-IR spectral analysis

The spectrum of the untreated biomass (Fig. 7a) shows a broad and strong absorption peak around 3,418 cm^{-1} indicative of bonded hydroxyl groups. The peak at 2,927 cm^{-1} region, which is in the range of 2,930–2,925 cm^{-1}, was due to the stretching of C–H group. The strong peak near 1,647 cm^{-1} suggests the presence of amino group and peaks around 1,404, 1,245, and 1,034 cm^{-1} region can be attributed to C–C and C–O band, which indicates the presence of functional groups

Table 2 Langmuir and Freundlich constants

Langmuir constants			Freundlich constants		
q_0 (mg g^{-1})	b (L mg^{-1})	R^2	K	n	R^2
29.64	0.059	0.995	3.451	2.137	0.923
17.60	0.075	0.913	1.298	1.841	0.984
11.10	0.103	0.932	1.566	1.658	0.994
7.50	0.148	0.919	1.087	1.915	0.973

like carboxyl and hydroxyl (Yun et al. 2001). At 603 cm^{-1} region, the peak observed might be due to the C–H bend, in the untreated biomass. The spectrum of the chromium-treated biomass (Fig. 7b) after contact with the metal ion solution exhibited clear shifts in the carboxyl stretching band to lower frequencies. These kinds of shifts are typical for the complexation of the carbonyl group by coordination with metal ions (Nakamoto 1986).

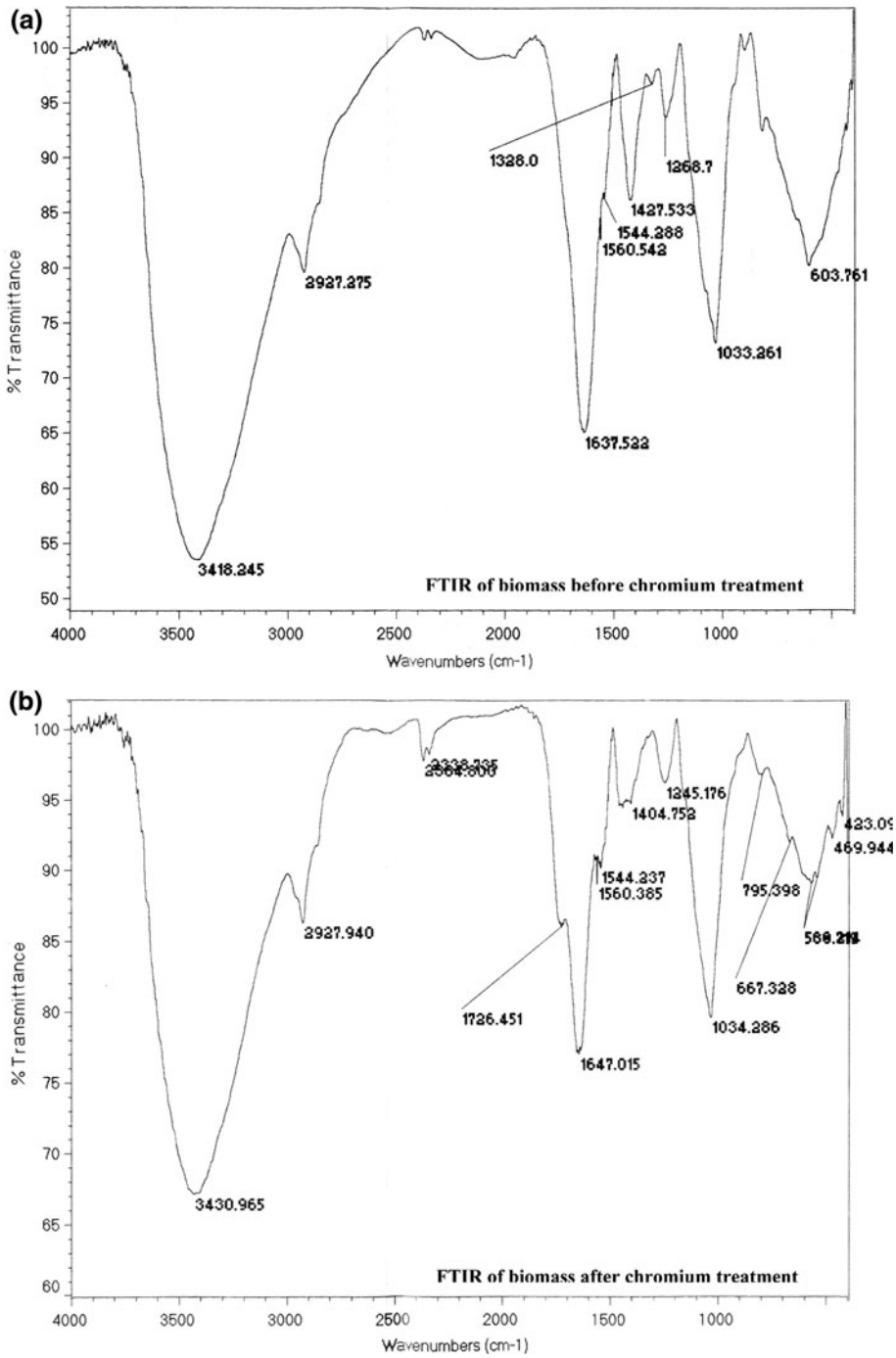

Fig. 7 FT-IR spectra of **a** bacterial biomass and **b** bacterial biomass treated with chromium

Table 3 Percentage removal of chromium after desorption

Stages of treatment (h)	Chromium in biomass before desorption (mg)	Chromium in biomass after desorption (mg)	Desorption (%)
4	9.5	4.25	55
8	4.25	1.75	81

Desorption studies

In order to assess the reusability of chromium-loaded *B. subtilis* biomass, desorption studies were carried out. The percentage desorption of chromium was higher at higher concentration of NaOH, hence 5 M NaOH was employed for desorption. The percentage removal of chromium from the chromium-loaded biomass shown in Table 3 was found to be 81% with 5 M NaOH. Thus, a significant amount of chromium is being desorbed, which shows that the *B. subtilis* biomass can be reused effectively after desorption (Xu et al. 2006).

Conclusion

The dead biomass of *B. subtilis* proves to be highly efficient for the removal of Cr(III) from aqueous solution because of its cheap source and reusability. Optimization of the batch experiments at pH 4 and temperature 60°C using 1 g l^{-1} of biomass for an initial metal ion concentration of 100 ppm, showed the maximum uptake (q_e) of 23.9 mg g^{-1} and metal removal (%) of 71.7. Desorption of chrome-bearing biomass with 5 M NaOH resulted in metal recovery of about 81%. The chromium-loaded biomass can either be desorbed and reused as in this case or used as a reductant in the manufacture of basic chromium sulfate, a tanning agent (Aravindhan et al. 2004b), thereby recycling the sorbed chromium and preventing its leaching into the environment. Therefore, this technology provides a viable sorption, especially when the metal concentration in the solution is low, for which the conventional removal methods are not suitable.

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