KINETICS AND EQUILIBRIUM STUDIES ON THE BIOSORPTION OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS USING *BACILLUS SUBTILIS* BIOMASS

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Abstract. Heavy metal contamination of industrial effluents is one of the significant environmental problems due to their toxic nature and accumulation throughout the food chain as non-biodegradable pollutants. In this study, dead Bacillus subtilis biomass was assessed for its efficiency to remove chromium(VI) from aqueous solutions. Optimum pH and temperature for biosorption of Cr(VI) were found to be 2.0 and 30oC, respectively. The biomass has the maximum biosorption capacity of 14.54 mg/g of biomass at 100 ppm initial chromium concentration and 2 g/l biomass loading. The biosorption process followed pseudo first order kinetic model, implying that the initial rate of biosorption is totally independent of the initial concentration. The biosorption of Cr(VI) is well described by Langmuir isotherm, which express the existence of monolayer adsorption under the experimental conditions. The adsorption-desorption experiments performed inferred the reusability of the biomass. X-ray photoelectron spectroscopy studies revealed that chromium bound on to the B. subtilis biomass was in trivalent form.
Keywords: *Biosorption, Bacillus subtilis, hexavalent chromium, adsorption isotherms, biomass*

Introduction

Rapid industrialization has led to increased disposal of heavy metals and radionuclides into the environment. Current industrial metal effluent treatment methods posses various disadvantages such as lack of cost effectiveness, production of toxic chemical sludge, etc. Therefore the removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes greater importance. Biosorption, an environment friendly technology to clean up the environment based on the utilization of dead biomass can be an efficient and cost effective remedy.

Chromium is a toxic metal of widespread industrial use and exists in several oxidation states. The most stable and common forms are the trivalent Cr(III) and the hexavalent Cr(VI) species, which display quite different chemical properties. Chromium(VI) is designated and widely recognized to be a human inhalation carcinogen [1]. Chromium(III) is less toxic when compared to Chromium(VI) and it has low acute and chronic toxicity to humans at high doses. High doses of Chromium(VI) compounds are also associated with nephrotoxicity [2, 3]. Acute exposure to high levels of Chromium(VI) can produce nervous system damage and liver disorder [1, 3].

Extensive use of chromium in electroplating, tanning, textile dyeing results in the effluents containing Cr(VI) and Cr(III) at concentrations ranging from tenths to hundreds of milligrams/litre. Several procedures have been proposed for removal of chromium(VI) from industrial wastewaters. Conventional methods for removing chromium(VI) ions from wastewater include: chemical reduction, membrane separation, electrochemical

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treatment, ion exchange and evaporative recovery. Although the effectiveness of these methods has been proved, they suffer from a major disadvantage, namely lack of cost effectiveness. Other limitations include energy intensive processing and concentration dependence, low efficiency, not feasible to reduce the chromium concentration to levels as low as required by environmental legislation and production of toxic chemical sludge, which needs additional treatment. These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1–100 mg/l [4]. Hence many researchers worked on the biosorption of Cr(VI) using different biosorbents such as *Rhizopus*, dead fungal biomass of *Aspergillus niger, Rhizopus oryzae*, *Saccharomyces cerevisiae, Ecklonia* biomass, peat moss and modified saw [5-9].

Bacillus subtilis is a Gram-positive, aerobic, rod-shaped bacterium and ubiquitous in soils and waters. Its parietal structure is well known and is composed primarily of peptidoglycan and teichoic acid [10]. Peptidoglycan is a polymer of acetylglucosamine and acetylmuramic acid, which carry mainly carboxylic and hydroxyl functional groups. On the other hand, teichoic acid is a polymer of copyranosyl glycerol phosphate, which carries mostly phosphate and hydroxyl groups. *B. subtilis* is widely used in the commercial production of various enzymes. In this study, dead *B. subtilis* biomass has been used for the removal of hexavalent chromium. Advantages of using dead *B. subtilis* biomass mainly recline on the abundant availability of the source of biomass, which comes from the existing enzyme fermentation industries. Also, the use of dead cells in biosorption is most advantageous for wastewater treatment, in that, the dead organisms are not affected by toxic wastes; they do not require a continuous supply of nutrients and they can be regenerated and reused for many cycles [11]. Dead cells may also be stored or used for extended periods at room temperature without putrefaction.

Materials and methods

Preparation of biomass

Bacillus subtilis strain was obtained from Tamil Nadu Agricultural University, Coimbatore. It was grown and maintained on both nutrient broth and nutrient agar. It was cultivated at room temperature in medium containing: soluble starch-20 g/l; beef extract-10 g/l; yeast extract -2 g/l; peptone -5 g/l; NaCl - 5 g/l. (pH adjusted to 7.2). After a week of incubation at 33±1°C, biomass was harvested by means of centrifugation at 10,000 rpm for 10 minutes, washed twice with distilled water and then dried for 6 hours at 80°C in an air oven. The dried biomass was then crushed with a mortar and pestle to a fine powder. The powdered biomass was stored in an air tight pack and used for biosorption.

Chemicals

$K_2Cr_2O_7$ used in the study was of analytical grade procured from Ranbaxy Chemicals. All other reagents used were of analytical grade, unless stated otherwise. Double distilled water has been used throughout the project work, unless stated otherwise. Chromium solution of different concentrations was prepared by suitably diluting the 1000 ppm stock solution to known volumes.

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Estimation of chromium

Amount of chromium in a given solution was determined spectrophotometrically at 540 nm using 1, 5-diphenyl carbazide as the complexing agent [12]. The sample containing Cr(VI) ions was mixed with 1 ml of 3 N H_2SO_4 and 1 ml of 0.25% 1, 5-diphenyl carbazide solution and made up to known volume. The absorbance at 540 nm was measured for the purple coloured solution after 10 minutes ageing. A calibration curve was drawn in the range of 5 to 50 ppm by plotting absorbance against concentration of chromium.

Biosorption experiments

Batch biosorption experiments were conducted in 100 ml Erlenmeyer flasks containing 50 ml chromium solution. Equilibrium studies were performed using 100 mg dried ground biomass per 50 ml of chromium solution. The test solutions were agitated on shaker with temperature controller at a constant speed of 75 strokes per minute. Samples were taken at definite intervals (0, 10, 20, 30, 45, 60, 120, 180, 240, 300, 360, 420 and 480 min), centrifuged at 10,000 rpm for 5 min to remove the biomass and analyzed for residual metal ion concentrations. Chromium ions adsorbed on to the biosorbent was calculated from the difference between the metal ion concentration in the solution before and after the biosorption process.

In order to find out the effect of pH on the biosorption process and to find the optimum pH, equilibrium batch experiments were carried out at various pH ranging from 2 to 8 by keeping all the other parameters constant. The batch biosorption experiments were also done at different temperatures (25, 30, 35 and 40 ^{o}C) to find the optimum temperature for biosorption. To study the effect of initial chromium concentration on the equilibrium uptake by the biomass, batch experiments were done at various initial metal ion concentrations (50, 75, 100, 125 and 150 mg/l). In order to find out the effect of the biomass loading on the uptake of chromium, batch experiments were done at various biomass concentrations (1, 1.5, 2, 2.5 and 3 g/l).

The Cr(VI) uptake by *B. subtilis* biomass was calculated from the difference between the initial and final chromium concentration as follows,

$$q = \frac{(C_o - C_e)}{S} V \qquad \text{(Eq.1)}$$

where, q is the Cr(VI) uptake by the biomass (mg/g), C_o is the initial Cr(VI) concentration (mg/l), C_e is the final Cr(VI) concentration (mg/l), S is the biosorbent dosage (g) and V is the solution volume (l).

Desorption experiments

In order to determine the reusability of biosorbent consecutive adsorption-desorption cycles were repeated three times by using the same biosorbent. Desorption of Cr(VI) ions was performed by 0.1 M NaOH solution. Biomass loaded with Cr(VI) ions was placed in the desorption medium and agitated for a period of 3 hours at a constant speed of 75 strokes per minute. The final Cr(VI) concentration in the aqueous phase was determined by using a spectrophotometer. After each cycle of adsorption–desorption, biosorbent was

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washed with distilled water and reconditioned for adsorption in the succeeding cycle. The desorption ratio was calculated from the amount of metal ions adsorbed on the *B. subtilis* biomass and the final Cr(VI) ion concentration in the adsorption medium.

XPS analysis

The X-ray photoelectron spectroscopy (XPS) studies were carried out by a VG Microtech Multilab ESCA 3000 spectrometer with non-monochromotized MgKα X-ray source (hν = 1253.6 eV). The samples were degassed for several hours in the chamber to minimize air contamination to sample surfaces.

Results and discussion

Effect of pH

pH is a vital parameter affecting the biosorption process. The results obtained are shown in *(Fig. 1.)*

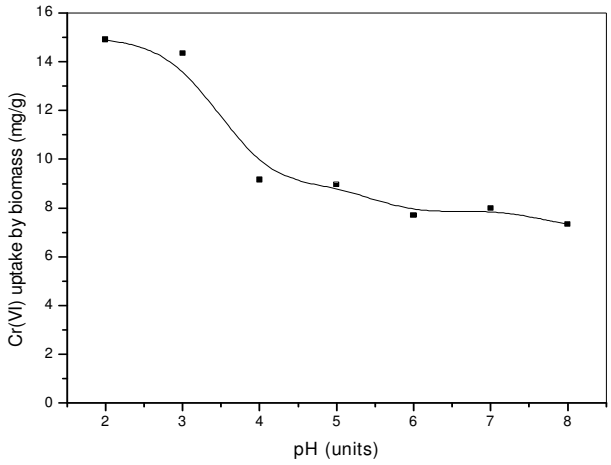

Figure 1. *Effect of pH on the Cr(VI) uptake by B. subtilis: Cr(VI) conc. 100ppm, biomass concentration=2g/l, Temperature=30^{o}C agitation=75 strokes per minute.*

From the figure, it is observed that the biosorption efficiency of Cr(VI) decreased as the pH increased. The maximum uptake capacity of the biomass was 14.9 mg/g for an initial Cr(VI) concentration of 100 ppm at pH of 2.0.

The increased binding of hexavalent chromium at low pH can be explained by two factors. First, adsorption of Cr(VI) at pH 2.0 suggests that the negatively charged chromium species (chromate/dichromate in the medium) bind through electrostatic attraction to positively charged functional groups on the surface of biosorbents. As the pH increased, the overall surface charge on the cells became negative and biosorption decreased. In alkali conditions, carboxylate group exists in deprotonated form and has net negative charge. As a result, the surface charge of the biosorbents become negative and biosorption of Cr(VI) decreases.

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Secondly, the solution chemistry of chromium(VI) ions can affect the biosorption process. Previous studies showed that chromium exhibits different types of pH dependent equilibria in solutions. Sorbate and chromium form stable complexes such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$, the fraction of any particular species is dependent on chromium concentration and pH. In low chromium concentration, the main fraction is $HCrO_4^-$ with pH below 5.0, whereas the CrO_4^{2-} increases with increase of pH value and becomes the main form with pH above 7.0 [13, 14].

Effect of temperature

In the present study, the temperature is varied from 25 to 40°C. With the increase of temperature from 30 to 40°C, the uptake decreases from 28.76 to 24.32%. The results obtained are illustrated in (*Fig. 2.*).

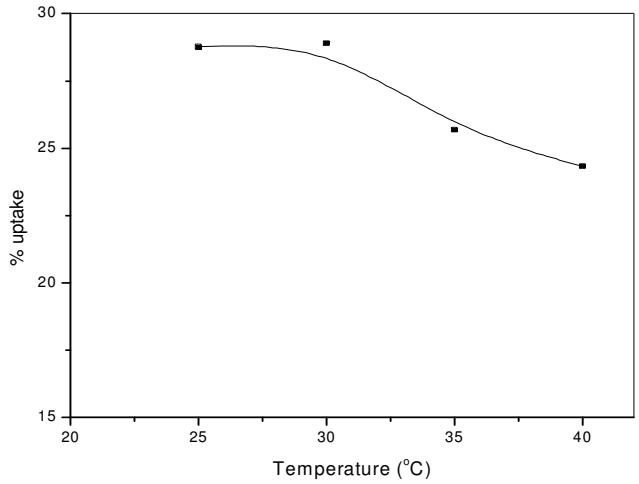

Figure 2. *Temperature versus % Cr(VI) uptake by B. subtilis: Cr(VI) conc. 100ppm, biomass concentration=2g/l, pH=2, agitation=75 strokes per minute.*

From the figure, it is observed that the uptake capacity is influenced by the experimental temperature conditions. The decrease of equilibrium uptake with the increase in temperature may be due to the exothermic nature of adsorption process.

Effect of initial metal concentration

Cr(VI) sorption was studied in batch experiments (pH 2.0) using different initial Cr(VI) concentrations of 50, 75, 100, 125, 150 ppm. The equilibrium uptake of the biomass was 12.03 mg/g (48.64%), 13.28 mg/g (35.57%), 14.34 mg/g (28.88%), and 14.73 mg/g (23.61%) and 15.02 mg/g (20.10%) at initial concentration 50, 75, 100, 125, and150 ppm chromium, respectively (*Fig. 3.*).

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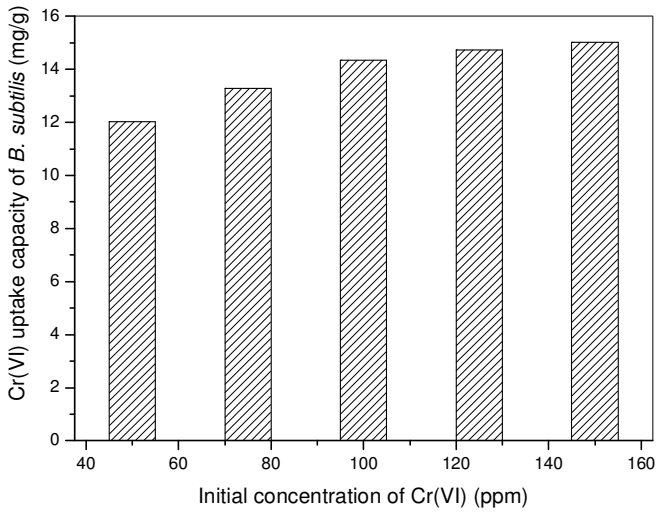

Figure 3. *Effect of initial concentration of Cr(VI) on uptake capacity: biomass concentration=2g/l, pH=2, Temperature=30°C,agitation=75 strokes per minute.*

It is evident that the amount of chromium adsorbed onto the biomass increases gradually with an increasing concentrations of Cr(VI). The increase of adsorption yield with the increase in metal ion concentration is probably due to higher interaction between the metal ions and metal sequestering sites of biosorbent.

Effect of biomass concentration

The Cr(VI) uptake by the biomass decreases with the increase in biomass concentration (*Fig. 4*).

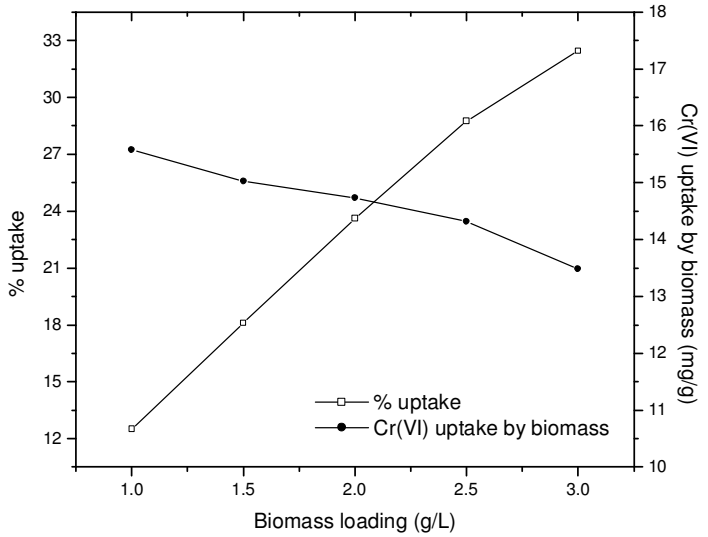

Figure 4. *Effect of biomass loading on % uptake and uptake capacity: Cr(VI) conc. 100ppm, pH=2, Temperature=30°C, agitation=75 strokes per minute.*

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When the biomass concentration increased from 1 to 3 g/l, the adsorption capacity of biomass decreased from 15.57 to 13.48 mg/g. The decrease in metal uptake by increasing the biosorbent dosage may be due to complex interactions of several factors. The important factor being at high sorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low metal uptake. In gold biosorption by dried biomass of *Azolla filiculoides*, 5% decrease in gold uptake efficiency was observed when the biomass concentration was increased from 1 mg/l to 9 mg/l [15].

Biosorption kinetics

The initial adsorption rate was rapid and thereafter adsorption was gradual and equilibrium was reached after 8 hours. Kinetic models such as pseudo first order and pseudo second order have been used to describe the kinetics of adsorption. The rate constants of chromium adsorption on biomass were determined using the pseudo first order (Lagergren rate equation) expression shown below, [16]

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad \text{(Eq.2)}$$

where, k_1 is the Lagergren rate constant and q_e and q_t are the amounts of chromium adsorbed (mg/g) at equilibrium and at time t, respectively. The straight-line plots of $\log(q_e-q_t)$ versus t for different chromium concentrations indicate the applicability of the above equation to chromium biosorption on the biomass. The values of k_1 and R^2 along with the calculated uptake capacity at particular initial concentration are provided in (*Table 1.*)

Table 1. *Rate constants of Cr(VI) biosorption by dead B. subtilis*

		First order rate constants			Pseudo second order rate constants			Intraparticle diffusion rate constants	
Initial conc. (m g/g)	**$q_{e\ (exp)}$ (mg/g)**	**k_1 (min^{-1})**	**$q_{e\ (cal)}$ (mg/g)**	**R^2**	**k_2, ($gmg^{-1}\ min^{-1}$)**	**$q_{e\ (cal)}$ (mg/g)**	**R^2**	**k_p ($mgg^{-1}min^{-1/2}$)**	**R^2**
50	12.04	4.61×10^{-03}	12.47	0.971	1.17×10^{-04}	21.42	0.831	0.64	0.984
75	13.30	4.25×10^{-03}	13.55	0.982	1.01×10^{-04}	23.66	0.823	0.69	0.984
100	14.40	4.12×10^{-03}	14.69	0.976	8.79×10^{-05}	26.04	0.796	0.75	0.982
125	14.80	4.27×10^{-03}	15.42	0.973	7.22×10^{-05}	28.51	0.79	0.78	0.981
150	15.20	4.28×10^{-03}	15.67	0.971	8.35×10^{-05}	27.56	0.784	0.80	0.981

Cr(VI) conc. range 50-150 ppm, pH=2, Temperature=30°C

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The kinetics of adsorption can also be described by pseudo second order equation and it is given by [17]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \text{(Eq.3)}$$

where k_2 (g/mg min) is the second order rate constant. The straight line plots of t/q_t versus t for different chromium concentrations indicate the applicability of the above equation to chromium biosorption on the biomass. The second order rate constant, R^2 along with the calculated uptake capacity at particular initial concentration are provided in (*Table 1*). From the table, it is very clear that the sorption of Cr(VI) by *B. subtilis* biomass follows pseudo first order kinetic model, implying that this system is totally independent of initial concentration.

Adsorption process incorporates the transport of adsorbate from bulk solution to the interior surface of the pores. In some adsorption processes this step becomes the rate-controlling factor. Hence, the data obtained were further processed for testing the role of diffusion (as the rate controlling step) in the adsorption process. The rate parameters for intraparticle diffusion (k_d) for Cr(VI) were determined by using the following equation,

$$q_t = k_d \sqrt{t} \qquad \text{(Eq.4)}$$

where, k_d is the rate constant of intraparticle diffusion parameter ($mgg^{-1}min^{-1/2}$).

According to the Weber and Moris model [18], uptake is proportional to the square root of contact time during the course of adsorption. (*Fig. 5.*) shows a plot of q_t versus $\sqrt{t}$ for the present system. It is known that if the intraparticle diffusion is the rate limiting step then the lines should pass through the origin. It can be seen from the figure that the lines didn't pass through the origin. Hence, in this case, intraparticle diffusion is not the rate-limiting step.

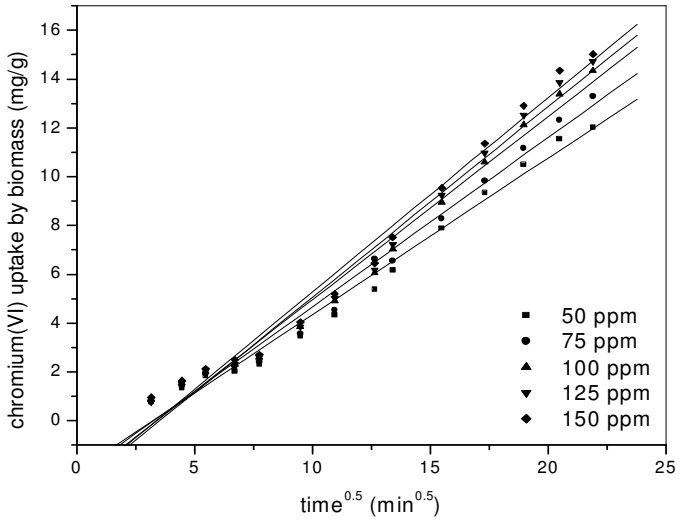

Figure 5. *Intraparticle diffusion model of Cr(VI) biosorption by dead B. subtilis*: *pH=2, Temperature=30^{o}C, adsorption period =8 hours.*

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Analysis of adsorption isotherms

Adsorption isotherms were used to characterize the interaction of each chromium species with the adsorbent. This provides a relationship between the concentration of Cr(VI) in the adsorption medium and the amount of Cr(VI) adsorbed on the solid phase when the two phases are at equilibrium.

Langmuir and Freundlich adsorption isotherms are the two widely used isotherms. The Langmuir model is based on the assumption of surface homogeneity such as equally available adsorption sites, monolayer surface coverage, and no interaction between adsorbed species. This model assumes: (i) reversible adsorption (ii) no change in the properties of the adsorbed molecules (iii) no lateral interaction between adsorbed molecules (iv) one adsorption site per molecule and (v) that all adsorption sites have the same affinity for the sorbate [19]. The following represents the Langmuir isotherm equation,

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad \text{(Eq.5)}$$

The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. One limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. The empirical equation takes the form [20]

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad \text{(Eq.6)}$$

where q_e and C_e are the equilibrium adsorption capacity of the biosorbent and the equilibrium concentration in the aqueous solution, respectively. K and n are Freundlich constants related to sorption capacity and sorption intensity of adsorbents, Q_o is the maximum sorption capacity of biomass to uptake Cr(VI) (mg/g) and b is the Langmuir constant related to the energy of adsorption (l/g). The value of n falling in the range of 1–10 indicates favorable sorption. The adsorption constants and correlation coefficients obtained from the Langmuir and Freundlich isotherms are provided in (*Table 2.*).

Table 2. *Equilibrium isotherm constants of Cr(VI) biosorption by by dead B. subtilis*

Quantity of biomass used (mg)	Langmuir constants			Freundlich constants		
	Q_o (mg/g)	b (Lmg^{-1})	R^2	K	1/n	R^2
500	14.73	0.095	0.998	7.74	0.117	0.941
750	16.26	0.075	0.990	7.08	0.151	0.844
1000	16.37	0.103	0.999	7.52	0.149	0.976
1250	15.97	0.102	0.999	6.84	0.165	0.976

Cr(VI) conc. range 50-150 ppm, biomass loading range 1 - 3g/l, pH=2, Temperature=30°C.

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It is observed from (*Table 2*) that the equilibrium data are well represented by Langmuir isotherm equation when compared to Freundlich equation. The sorption equilibrium data fit Langmuir and Freundlich equation with an average R^2 value of 0.997 and 0.934, respectively. The best fit of equilibrium data for Langmuir expression confirms the monolayer coverage of Cr(VI) onto *B. subtilis* biomass

Separation factor, R_L

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as:

$$R_L = \frac{1}{1 + bC_o} \qquad \text{(Eq.7)}$$

Where b is the Langmuir constant and C_o is the initial concentration of Cr(VI).

It is known that R_L values between 0 and 1 indicate favourable adsorption [21]. The calculated R_L values are represented in (*Table 3*).

Table 3. *R_L Values for the Adsorption of Cr(VI) onto B. subtilis biomass*

Amount of biomass (g/l)	Initial Concentration of Cr(VI) (mg/l)				
	50	**75**	**100**	**125**	**150**
1.00	0.17	0.12	0.10	0.08	0.07
1.50	0.21	0.15	0.12	0.10	0.08
2.00	0.16	0.11	0.09	0.07	0.06
2.50	0.16	0.12	0.09	0.07	0.06

Cr(VI) conc. range 50-150 ppm, biomass loading range 1 - 3 g/l, pH=2, Temperature=30°C.

From the table, it is observed that sorption is more favorable. Also the value of R_L in the range of 0–1 at all initial chromium concentrations confirms the favorable uptake of Cr(VI) by *B. subtilis* biomass

Desorption and reuse

Desorption is a phenomenon or a process wherein some of a sorbed substance is released. The desorption of the adsorbed Cr(VI) ions from the biosorbents were studied in a batch system. The Cr(VI) ions adsorbed onto biosorbents were eluted with 0.1 M NaOH. More than 85% of the adsorbed Cr(VI) ions were desorbed from the biosorbents. In order to show the reusability of the biosorbent, adsorption-desorption experiments of Cr(VI) ions was repeated three times by using the same experimental conditions. The adsorption capacities for the biosorbent did not noticeably change during the repeated adsorption-desorption experiments. Hence this study confirms the reusable potential of the *B. subtilis* biomass.

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Mechanism of chromium removal

From the present study, it is clear that, bisorption is the mechanism of Cr(VI) removal from aqueous solution, where the anionic chromium species binds to positively charged groups of dead bacterial biomass. However, from literatures it is observed that both biosorption and bioreduction are involved in the removal of Cr(VI) from aqueous solution [22]. In order to determine the valance state of the bound chromium on the biomass, X-ray photoelectron spectroscopy was employed. The narrow scan of the $Cr^2p_{3/2}$ for Cr(VI) loaded biomass is shown in the (*Fig. 6.*).

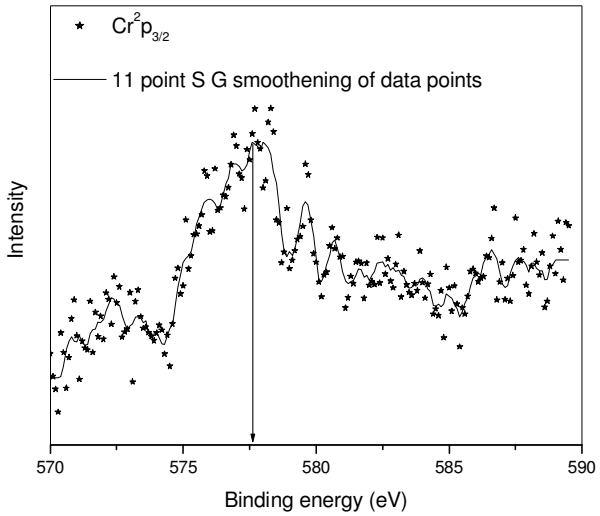

Figure 6. *$Cr^2p_{3/2}$ spectra of the chromium bound B. subtilis biomass after Cr(VI) biosorption*

There were significant amount of chromium bound on the biomass. The bands appeared at binding energies of around 577-578 eV, which corresponds to the $Cr^2P_{3/2}$ orbital of Cr(III). Based on the XPS data the existence of Cr(III) on the biomass could be inferred. The presence of Cr(VI) is also possible, however, the quantifications was not possible due to the existence of noise peaks. Park et al., [7, 23] has established two possible mechanism for the removal of Cr(VI) from aqueous solution by dead fungal biomass. According to which, the first mechanism involves direct reduction of Cr(VI) to Cr(III) in the aqueous solution by contact with the biomass. The second mechanism consists of two steps: 1) the binding of Cr(VI) to positively charged groups of the biomass and 2) the reduction of Cr(VI) to Cr(III) by adjacent functional groups having lower reduction potential value than that of Cr(VI). Thus, the present study also reports the same conclusion as the earlier studies, i.e. the most of the chromium bound on the dead bacillus biomass was in Cr(III) state.

Conclusions

Biosorption of heavy metals is one of the most promising technologies involved in the removal of toxic materials from the industrials wastewater and natural waters. The biosorption process depends significantly on the pH of the solution and is favoured at around pH value of 2.0. The biosorption process is found to be exothermic in nature. The

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maximum uptake capacity of biomass for Cr(VI) increased with the increase in initial metal ion concentration and decreased with increase in biomass concentration. Biosorption obeys the pseudo first order kinetics, which implies that the rate of biosorption process is independent of initial concentration. Intraparticle diffusion is not the rate limiting step in the biosorption process. The adsorption is well described by Langmuir isotherms that expresses that monolayer adsorption exist under the experimental conditions. The adsorption-desorption experiments were successfully carried out three times. The mechanism of Cr(VI) removal by the B. subtilis biomass was found to be adsorption-coupled reduction by employing XPS analysis. Hence, Bacillus subtilis biomass, a fermentation by-product can be used as an effective, inexpensive and alternative biosorbent for the removal of Cr(VI) from the industrial wastewaters.

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