

Removal of Cr (VI) From Aqueous Solution Using Dead Biomass of *Bacillus subtilis*

Kishor Kumar Singh

Head, Department of Chemistry, Govt. Post Graduate College, Obra, Sonebhadra, India

E-mail: singhanita36@gmail.com

Mobile: +91 9415388484

ABSTRACT

The dead biomass of *Bacillus subtilis* has been successfully utilised for the removal of Cr(VI) from aqueous solution. The effects of various parameters such as contact time, sorbate concentration, pH of the medium and temperature were investigated. The maximum removal of Cr(VI) was found to be 99.5 % at pH 2.0, with initial Cr(VI) concentration of 200 mg L^{-1} , and temperature 20°C . The sorption kinetics was tested with first order reversible, pseudo-first order and pseudo second order reaction and it was found that Cr(VI) uptake process followed the pseudo first order rate expression. Dynamics of the sorption process of Cr(VI) to *Bacillus subtilis* were investigated and the values of rate constant of adsorption and rate constant of intraparticle diffusion were calculated. Different thermodynamic parameters viz., changes in standard free energy, enthalpy and entropy have also been evaluated and it has been found that the reaction was feasible, spontaneous and endothermic in nature. The adsorption data fitted the Langmuir isotherm. Desorption studies was also carried out and found that complete desorption of Cr(VI) took place at pH of 9.5. The data were also subjected to multiple regression analysis and a model was developed to predict the removal of Cr(VI) from aqueous solution.

Keywords: Adsorption, Cr(VI), *Bacillus subtilis*, Endothermic, multiple regressions, isotherm.

1. Introduction

The presence of heavy and toxic metal ions such as chromium, cadmium, copper, lead, zinc, iron etc. in natural / industrial wastewater and their hazardous impact has been a subject of research in environmental science for a long time. Therefore, priority is given to regulate these pollutants at the discharge level. To solve this problem, biosorption can be part of the solution. Biosorption of heavy metals by bacterial fungal or algal biomass (live or dead cells) and agricultural waste biomass has been recognized as a potential alternative to existing

technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for the removal of heavy metals from industrial wastewater because all these processes have the limitations of technical and/or economical viability^[1-7].

The literature reveals two distinct approaches to use of living organisms and the use of a non-viable biomass^[8-9]. There are significant practical limitations to systems, which employ living microorganisms. The most significant limitation is that microbial growth is inhibited when the concentrations of metal ions are too high or when significant amount of metal ions are adsorbed by microorganisms^[8]. Dead cells or agricultural wastes accumulate heavy metal ions to the same or to a greater extent than living cells^[8-9]. For metal removal applications, the use of dead biomass may be preferable as large quantities are readily and cheaply available^[10]. Therefore, dead biomass of *Bacillus subtilis* was used for the removal of Cr(VI) from aqueous solution.

2. Materials and method

2.1 Media and Culture condition

The following medium and culture conditions were used for maintenance of cultures.

2.1.1. Maintenance of Culture

Bacillus subtilis strain was maintained on nutrient agar media. The medium had the composition: Beef Extract- 1.0 gL⁻¹, Yeast Extract- 2.0 gL⁻¹, Peptone- 5.0 gL⁻¹, Agar- 2.0 gL⁻¹, NaCl- 5.0 gL⁻¹, Distilled water- 1000 mL, pH- 7.0.

2.1.2 Growth Medium

Bacillus subtilis was grown on the broth medium having the composition: D-glucose- 10 gL⁻¹, KH₂PO₄- 2 gL⁻¹, MgSO₄.7H₂O- 0.5 gL⁻¹, NH₄Cl- 0.1 gL⁻¹, CaCl₂.2H₂O- 0.1 gL⁻¹, Thiamine- 0.001 gL⁻¹, Distilled water- 1000 mL, pH- 4.5.

2.1.3 Culture Condition

The culture condition of the *Bacillus subtilis* was given as: temperature- 37 °C, pH- 7.0, Aerobic, agitation rate- 200 rpm.

Initially, biomass of microorganisms was obtained through the cultivation in broth media followed by centrifugation, then autoclaved to obtain the dead biomass and sieved to less than 178 µm size.

2.2 Reagents

All the primary chemical used were of analytical grade: potassium dichromate, hydrochloric acid, sodium hydroxide, 1,5-diphenylcarbazide, potassium permanganate etc. were purchased from E Merck, India, Ltd., Mumbai, India.

The stock solution containing 1000 ppm of Cr(VI) was prepared by dissolving 1.4143 g

of $K_2Cr_2O_7$ in 500mL of deionised, double distilled water. Required initial concentration of Cr(VI) standard was prepared by appropriate dilution of the above stock Cr(VI) standard solution.

2.3 Batch sorption experiment

Using the different amount of sorbent in a 250 mL stopper conical flask containing 50 mL of test solution, batch sorption studies were carried out at desired pH value, contact time, temperature and sorbate concentration. Different initial concentration of Cr(VI) solution was prepared by proper dilution from stock 1000 ppm Cr(VI) standard. The pH of the solution was monitored by adding 0.1M HCl or 0.1M NaOH solution as required. Necessary amount of biosorbent was then added and content in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 125 rpm. The time required for reaching equilibrium condition estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of flask separated from sorbent by centrifuge at 15,000 rpm and was analysed for remaining Cr(VI) concentration in the sample. Blanks solutions were run under similar conditions of concentration, pH and temperature without the adsorbent in all the cases to correct for any adsorption on the internal surface of the bottles. The amount of Cr(VI) adsorbed per unit mass of the biosorbent was evaluated by using the following equation:

$$q_{\max} = \frac{C_i - C_e}{W} \times V \quad (1)$$

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

$$\text{percentage removal of Cr(VI)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

2.3.1 Effect of adsorbate concentration and contact time

It was studied using 50 mL Cr(VI) solution of concentration 200, 250 and 300 mgL^{-1} and contact time 5-180 minute with an interval of 10 minute, respectively at pH 2.0, temperature 40 °C and 1 g of sorbent in 50 mL of aqueous solution.

2.3.2 Effect of Temperature

The effect of temperature on the sorption of Cr(VI) was investigated at different temperature 20, 30 and 40 °C at pH 2.0 and 1 g of sorbent into 250 mL of conical flask containing 50 mL of 200 mgL^{-1} of Cr(VI) solution.

2.3.3 Effect of pH

Sorption experiment for the effect of pH were conducted by using 50 mL solution

having 200 mgL⁻¹ Cr(VI) with 1g of sorbent at 40 °C and the pH of the solution was monitored from 1.4 to 8.0 by adding 0.1 M HCl and 0.1 M NaOH.

2.4 Desorption

Desorption experiments were carried out using double distilled water and aqueous solution of different known pH solutions such as 2.5, 3.5, 4.5, 6.5 and 9.5 as eluant. For all desorption experiments chromium loaded dead biomass of *Bacillus subtilis* was shaken with 50 mL of eluant solution. Desorption efficiency was calculated by using following equation:

$$\text{Desorption efficiency} = \frac{\text{amount of Cr(VI) desorbed}}{\text{amount of Cr(VI) adsorbed}} \times 100 \quad (3)$$

2.5 Chromium analysis

2.5.1 Chromium (VI) analysis

The pink coloured complex was formed when 1,5-diphenylcarbazide was added into Cr(VI) in acidic solution and concentration was determined spectrophotometrically at 540 nm by Spectronic 20 (Bausch and Lomb, USA)^[11].

2.5.2 Chromium (III) analysis

For the determination of Cr(III) concentration, Cr(III) (formed due to the reduction of Cr(VI) into Cr(III) during the sorption process) was again converted to Cr(VI) by addition of excess KMnO₄ at high temperature (130-140 °C), thereafter 1,5-diphenylcarbazide was added. The pink coloured complex formed gives the concentration of Cr(VI) and Cr(III) which is total chromium. The Cr(III) concentration was calculated by the difference of the total chromium and Cr(VI) concentrations measured as above^[11].

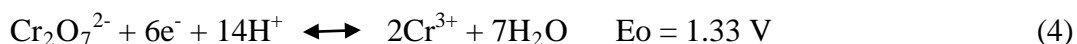
3. Results and Discussion

3.1 Effect of contact time and concentration

A series of experiments were performed at different adsorbate concentration viz., 200, 250 and 300 mg L⁻¹ and time interval of 10 minute at a temperature 40 °C and pH 2.0. The percentage removal of Cr(VI) was found to be 99.6, 94.35 and 88.25 % respectively (Figure 1). The extent of adsorption increased rapidly in the initial stages and became slower at later stages until the attainment of equilibrium. Equilibrium time for the adsorption of Cr(VI) on *Bacillus subtilis* at various adsorbate concentrations was found to be 110 minutes, which showed that equilibrium time was independent of the initial adsorbate concentration.

3.2 Effect of pH

Experiments were performed by varying pH from 1.4 to 8.5 at temperature 40 °C and adsorbate concentration of 200 mgL⁻¹. Initially the uptake of Cr(VI) was increasing with increase of pH up to 2.0 and then decreased with the rise of pH from 2.0 to 8.5 (Figure 2). The optimum pH for maximum uptake of Cr(VI) was found at 2.0. This can be explained that since Cr(VI) exists in the form of oxyanions such as HCrO₄⁻, Cr₂O₇²⁻, CrO₄²⁻ etc. in acidic medium and lowering of pH caused the surface of the biosorbent to become protonated to a higher extent and as a result a strong attraction exists between these oxyanions of Cr(VI) and positively charged surface of the biosorbent. Hence, uptake increases with the decrease in the pH of the solution. Whereas at high pH biosorbent surface has been negatively charged and in addition to this there will be abundance of negatively charged hydroxyl ions in aqueous solution. Both of these factors can cause hindrance in the biosorption of negatively charged Cr₂O₇²⁻, CrO₄²⁻ etc. resulting in the decrease uptake of Cr(VI) at high pH value. Another change which was also observed at low pH (2.0) that the colour of the surface of biosorbent turned greenish during sorption. This was certainly due to the sorption of Cr(III) in a reduced form of chromium on the surface of the sorbent. Thus, during sorption of Cr(VI) on the surface of biosorbent, there was sorption of Cr(VI) as well as Cr(III). Reduction of Cr(VI) in to Cr(III) is also clear from the aqueous chemistry of Cr(VI) at low pH value. There, Cr₂O₇²⁻ acts as an oxidant, to oxidize the surface of the biosorbent, while it is reduced to Cr(III) [12-14].



3.3 Effect of temperature

Experiments were performed at different temperatures 20, 30 and 40 °C at concentration of 200 mg L⁻¹ and pH of 2.0. The percentage removal of Cr(VI) was increased from 92.10 to 99.50 with the rise in temperature from 20 to 40 °C (Figure 3). Equilibrium time for 20, 30 and 40 °C was found to be 110 minute indicating that the equilibrium time was independent of temperature. The above results showed the endothermic nature of the adsorption [14]. The increased adsorption with temperature is also attributed to the increase in the number of adsorption site generated due to breaking of some internal bonds near the edge of active surface sites of adsorbent [15-16].

3.4 Thermodynamic evaluation of the process

Thermodynamic parameters such as free energy (ΔG^0 , k cal mol⁻¹), enthalpy (ΔH^0 , k cal mol⁻¹) and entropy (ΔS^0 , cal mol⁻¹ k⁻¹) changes during the process were calculated using equations 5 to 7 on a temperature range of 20 - 40°C at 200 mgL⁻¹. The negative values of free energy change (ΔG^0) were an indication of the spontaneous nature of the adsorption process

and more negative value with increase of temperature (-1.28, -1.78 and -2.78 kcal mol⁻¹ respectively) shows that an increase in temperature favours the sorption process. The positive value of ΔH^0 (22.28 kcal mol⁻¹) indicate that the sorption process was endothermic in nature and the negative values of ΔS^0 (79.68 cal mol⁻¹ k⁻¹) suggest the probability of a favourable adsorption^[17].

$$K_c = \frac{C_{Ae}}{C_e} \quad (5)$$

Where K_c is the equilibrium constant and C_{Ae} and C_e (both in mgL⁻¹) are the equilibrium concentrations for the solute on sorbent and in the solution respectively.

$$\Delta G^0 = -RT \ln K_c \quad (6)$$

$$q_{\max} = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

The values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of a plot of $\ln K_c$ versus $1/T$ (Figure 4).

3.5 Sorption isotherms

The isotherm constants were calculated from the slope and intercept of figure 5a (Langmuir isotherm) and figure 5b (Freundlich isotherm) and presented in Table 1. The value of r^2 was higher for Langmuir isotherm^[18] than for the Freundlich isotherm^[19], this means the Langmuir equation represented the adsorption process very well. This may be due to the homogeneous distribution of active sites on biosorbent surface. Values of Q^0 , which is defined as the maximum capacity of sorbent was calculated from the Langmuir plots in the range of 282.74-310.62 mg g⁻¹ at different temperatures. This indicates the good sorbing capacity of dead biomass of *Bacillus subtilis*.

The equilibrium parameter R_L is defined as $R_L = 1/(1+bC_{A0})$. If R_L falls in the range $0 < R_L < 1$, it reflects the favourable adsorption process^[17]. In the present investigation, the equilibrium parameter was found to be in the range $0 < R_L < 1$ (Table 1). Hence the sorption process was very favourable and the adsorbent employed exhibited a good potential for the removal of Cr(VI) from aqueous solution^[20].

3.6 Sorption kinetics

In order to predict sorption kinetic models of Cr(VI), first order reversible^[21], pseudo-

first order^[22] and pseudo-second order^[23] kinetic models were applied to the data^[19-21]. The effect of the initial Cr(VI) concentrations and temperatures was investigated to find the best kinetic model. The straight line plots of $-\ln(1-U_t)$ vs t (min.) were tested to obtain the first order rate constant under different experimental conditions. For the pseudo-first order sorption rate constant, the straight plots of $\log(q_e - q_t)$ against t (min.) were analysed. The equilibrium rate constants of pseudo second order were determined by plotting t/q_t against t (min.). The kinetic constant and correlation coefficients of these models were calculated and are given in Table 2. Good correlation coefficients were obtained for the pseudo first order kinetic model, which showed that the Cr(VI) uptake process followed the pseudo first order rate expression, so only the pseudo first order plots are represented (figure 6a and 6b).

3.7 Intraparticle diffusion study

The rate constants for intraparticle diffusion (k_{id}) at different temperatures were determined using following equation^[24]:

$$q = k_{id} t^{1/2} \quad (8)$$

Where, q is the amount sorbed at time t and $t^{1/2}$ is the square root of the time. The values of k_{id} (9.365×10^{-3} , 1.458×10^{-2} and $1.565 \times 10^{-2} \text{ mgg}^{-1} \text{ min}^{-1/2}$) at temperatures 20, 30 and 40°C respectively, were calculated from the slopes of respective plot q versus $t^{1/2}$ (Figure 7) at later stages. The dual nature of the curves was obtained due to the varying extent of sorption in the initial and final stages of the experiment. This can be attributed to the fact that in the initial stages, sorption was due to boundary layer diffusion effect whereas, in the later stages (linear portion of the curve) was due to the intraparticle diffusion effects. However, these plots indicated that the intraparticle diffusion was not the only rate controlling step because it didn't pass through the origin. This was further supported by calculating the intraparticle diffusion co-efficient (\bar{D} , $\text{cm}^2 \text{ sec}^{-1}$) using the following equation^[25]:

$$\bar{D} = 0.03r^2 / t_{1/2} \quad (9)$$

where r (cm) is the average radius of the sorbent particle and $t_{1/2}$ (min.) is the time for half of the sorption. According to the Michelsen et al.^[25] a \bar{D} value of the order of $10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ is indicative of intraparticle diffusion as rate determining step. In this investigation, the values of \bar{D} (5.846×10^{-9} , 7.512×10^{-9} and $8.545 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ at 20, 30 and 40°C respectively) obtained was in order of $10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ which was more than two order of magnitude higher, indicated that the intraparticle diffusion was not the only rate controlling step. It was concluded that both boundary layer and intraparticle diffusion might be involved in this removal process.

4. Multiple Regression Analysis

The effect of initial adsorbate concentration, contact time, temperature and pH of the system on Cr(VI) removal by dead biomass of *Bacillus subtilis* had been examined. The cumulative effect of all these independent variables (chromium removal) are given by the following relation:

$$Y = 0.9696 + 0.5141a_1 + 1.5168a_2 + 0.110a_3 + 1.8168a_4 - 0.5196a_5 \quad (10)$$

Where, Y is the predicted value of Cr(VI) removal, a_1 , concentration of adsorbate, a_2 , contact time; a_3 , temperature; a_4 , pH; a_5 , agitation rate of the system. The model values calculated with the help of equation (10) and the experimental values are given in Table 3. It may be seen that predicted values were pretty close to the experimental values. From these results it is concluded that all independent variables have cumulative effect on chromium removal by dead biomass of *Bacillus subtilis*.

5. Desorption Studies

Desorption results (Figure 8) indicated that 21.4, 44.2, 58.4, 74.5 and 100% of Cr(VI) were removed from the surface of the sorbent containing 9.95 mg g⁻¹ of Cr(VI) at pH of 2.5, 3.5, 4.5, 6.5 and 9.5 respectively and temperature of 40 °C. The rate of sorption was thus highly pH dependent. The sorbate ion which were bonded weakly to the sorbent surface started to remove on increasing of pH, while they were completely desorbed when pH reached to 9.5.

5.1 Infrared studies

The characteristics IR band of dichromate ion at 750 and 860 cm⁻¹ were shifted to 790 and 900 cm⁻¹ after the sorption of Cr(VI) on the sorbent. It showed the binding of surface sites with the sorbate ions^[26]. The disappearance of above bands after desorption at pH 9.5 supported the desorption result for complete Cr(VI) detachment from the sorbent surface.

6. Conclusion

The dead biomass of *Bacillus subtilis* was found to be a very effective biosorbent for the removal of Cr(VI) from aqueous solution. The study showed that the temperature and pH of the solution strongly influenced the adsorption process. Adsorption in the initial stages was due to the boundary layer diffusion whereas in the later stages adsorption was due to intraparticle diffusion. Thermodynamic studies confirmed that the process was spontaneous and endothermic. The fit of the adsorption data into the Langmuir isotherm confirmed monolayer adsorption. The best correlation coefficients were obtained using the pseudo first

order kinetic model, indicating that the chromium removal process followed the pseudo first order rate expression. Desorption studies were also carried out and found that the complete desorption of Cr(VI) took place at pH of 9.5. The data thus obtained from this investigation would be useful in designing and fabricating an efficient treatment plant for Cr(VI) rich effluents.

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Table 1

Values of Langmuir and Freundlich sorption constants and R_L values of Cr(VI) sorption on dead biomass of *Bacillus subtilis* at different temperatures

Temp. °C	Langmuir Constants			Freundlich constants			R_L
	Q^0 (mg g ⁻¹)	b (l mg ⁻¹)	r^2	n	k_F	r^2	
20	282.64	0.615	0.999	3.255	0.275	0.848	8.072×10^{-3}
30	296.55	0.175	0.993	4.496	0.325	0.889	2.975×10^{-3}
40	310.75	0.065	0.989	7.845	0.382	0.862	7.125×10^{-3}

Table 2

A comparison of first-order reversible, pseudo-first order and pseudo-second order kinetic model rate constants obtained under different experimental conditions

Parameters	First order reversible					Pseudo-first order		Pseudo-second order		
	k_c	k'	$k_1 \times 10^3$	$K_2 \times 10^3$	r^2	$k_s \times 10^{-2}$	r^2	h	q_e (cal)	r^2
C_0 (mg L⁻¹)										
200	15.25	0.075	66.25	4.35	0.585	6.635	0.998	0.470	12.775	0.942
250	34.75	0.065	60.20	1.75	0.655	5.945	0.997	0.515	15.625	0.658
300	157.35	0.050	48.95	0.35	0.499	4.910	0.998	0.545	18.215	0.836
Temperature (°C)										
20	34.75	0.065	61.85	1.80	0.655	5.896	0.998	0.355	13.285	0.864
30	15.25	0.075	66.25	4.35	0.585	6.635	0.998	0.470	12.775	0.942
40	7.85	0.085	74.50	9.55	0.835	7.625	0.999	0.539	12.655	0.836

Table 3

Percentage removal at different conditions (experimental and predicted values at equilibrium time, pH 2.0)

Initial adsorbate concentration (mg L ⁻¹)	Percentage removal at 30 °C		Temp. (°C)	Percentage removal	
	Exp. value	Predicted value		Exp. value	Predicted value
200	97.25	98.75	20	92.25	93.50
250	94.35	92.55	30	97.25	97.75
300	88.25	86.45	40	99.50	99.95

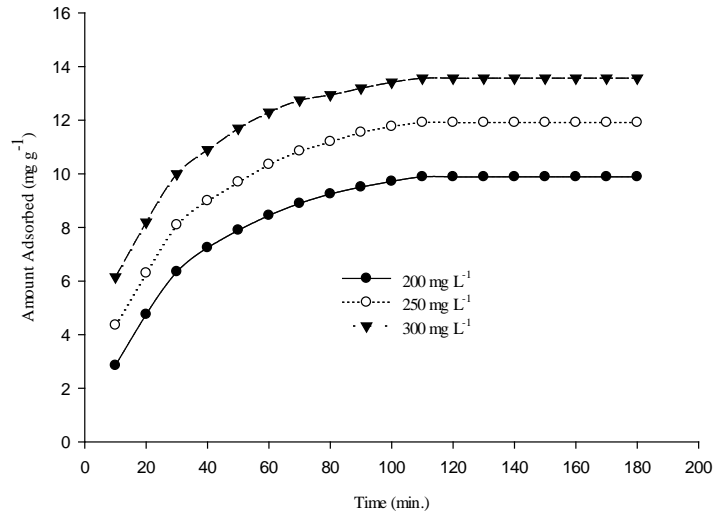


Fig. 1 Effect of contact time and initial adsorbate concentration on adsorption.

Conditions: pH 2.0, Temperature 40^oC, particle size <178 μ m,
initial Cr(VI) concentration 200 mg L⁻¹, 250 mg L⁻¹, 300 mg L⁻¹

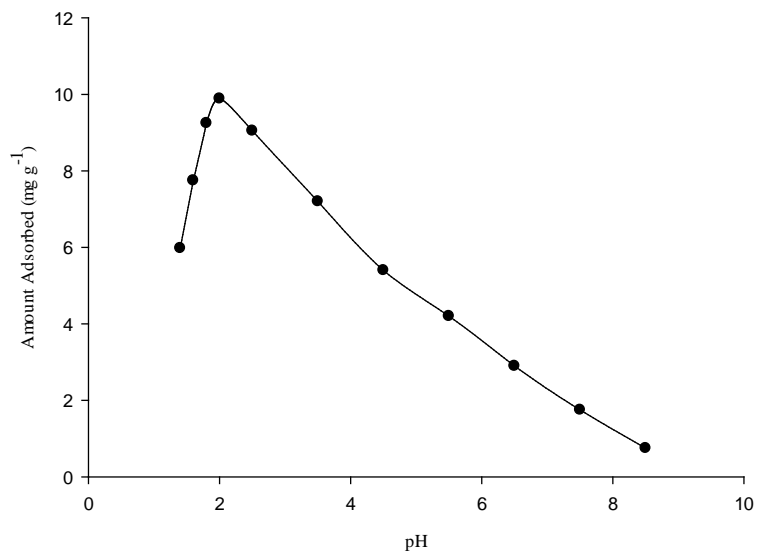


Fig. 2 Effect of pH on the adsorption by dead biomass of Bacillus subtilis

Conditions: initial Cr(VI) concentration 200 mg L⁻¹, pH 1.4-8.5,
Temperature 40^oC, particle size <178 μ m

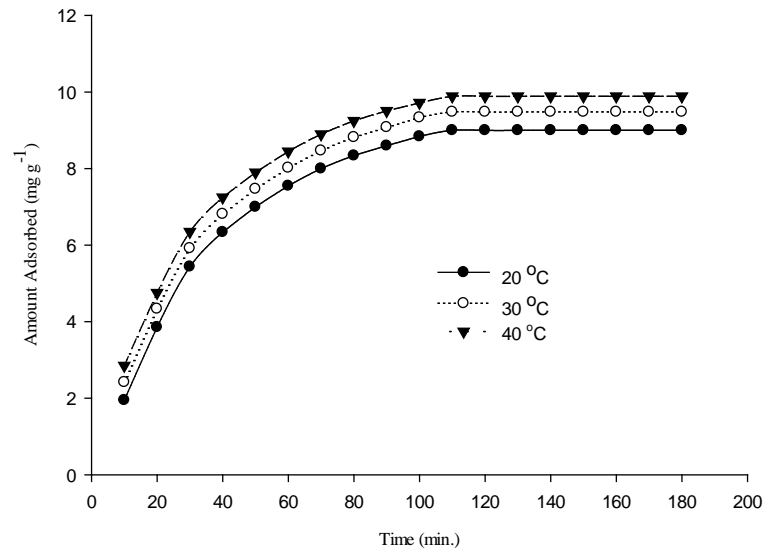


Fig. 3 Effect of temperature on the sorption by dead biomass of *Bacillus subtilis*
 Conditions: initial Cr(VI) concentration 200 mg L⁻¹, pH 2.0, particle size <178 μm
 temperature 20 °C, 30 °C and 40 °C

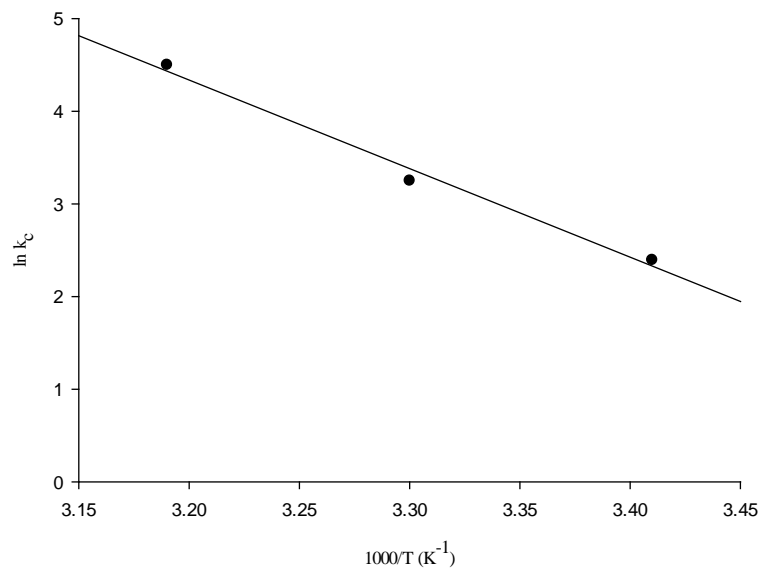


Fig. 4 A plot of ln kc against 1/T for Cr(VI) sorption by dead biomass of *Bacillus subtilis*
 Conditions: initial Cr(VI) concentration 200 mgL⁻¹, temperature 20, 30 and 40 °C

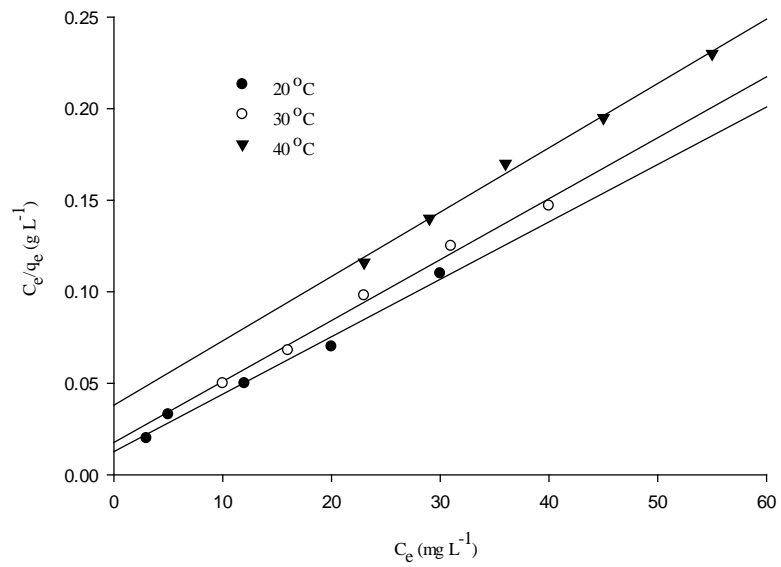


Fig. 5a Langmuir isotherm plot for Cr(VI) removal using dead biomass of *Bacillus subtilis*
 Conditions: pH 2.0, particle size <178 μm, concentrations 200, 225, 250, 275 and 300 mg L⁻¹

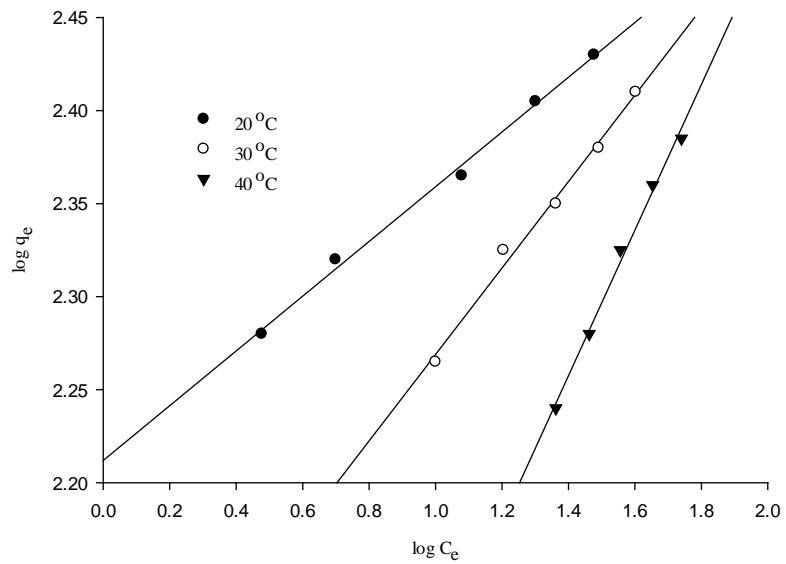


Fig. 5b Freundlich isotherm plot for Cr(VI) removal using dead biomass of *Bacillus subtilis*
 Conditions: pH 2.0, particle size <178 μm, Concentrations 200, 225, 250, 275 and 300 mg L⁻¹

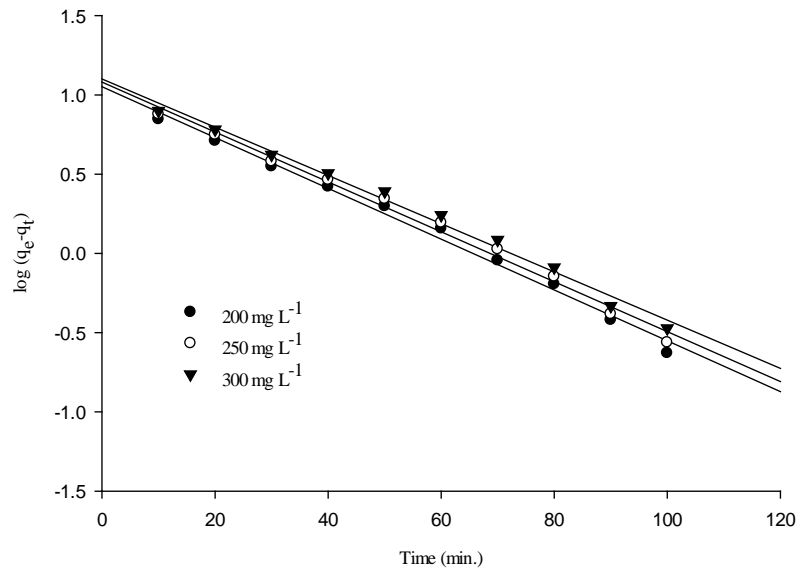


Fig. 6a Pseudo-first order plot for Cr(VI) removal at different concentrations
 Conditions: temperature 30 °C, particle size <178 μm, pH 2.0

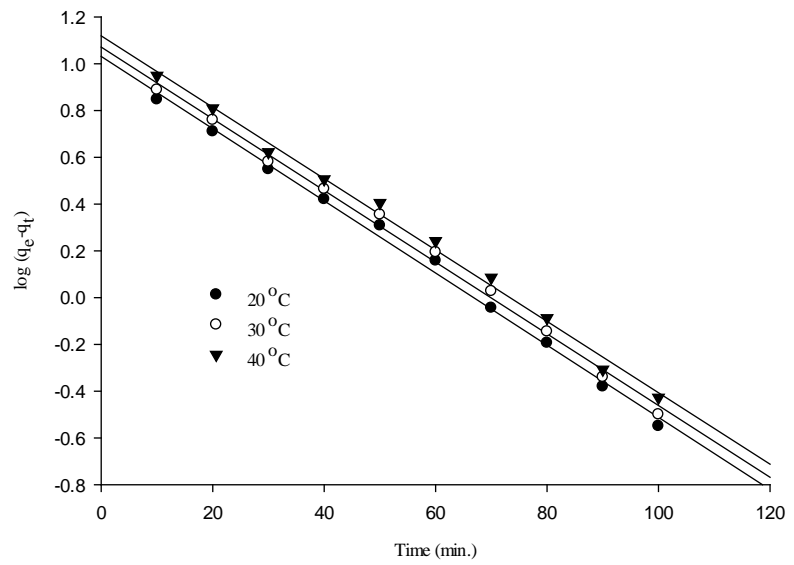


Fig. 6b Pseudo-first order plots for Cr(VI) removal at different temperatures
 Conditions: initial concentration 200 mg L⁻¹, pH 2.0, particle size < 178 μm

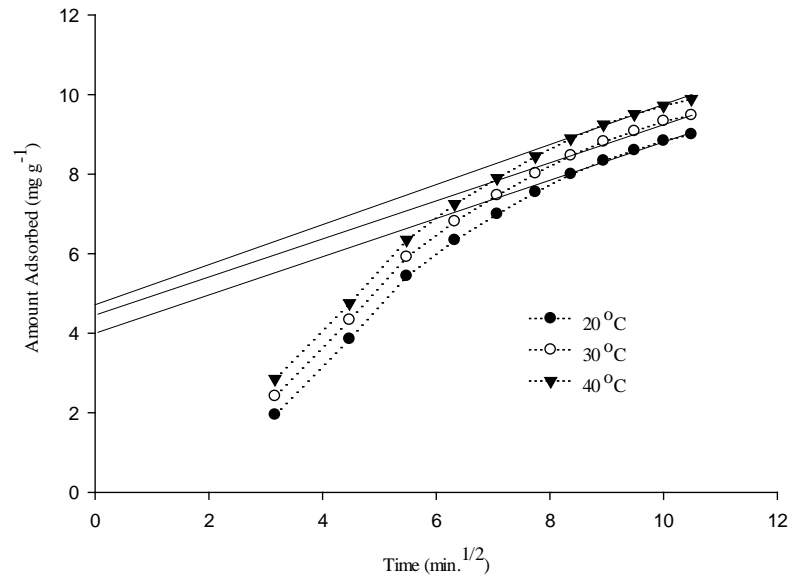


Fig. 7 Intraparticle diffusion plot for sorption of Cr(VI) on dead biomass of *Bacillus subtilis* at 20 °C, 30 °C and 40 °C

Conditions: concentration 200 mg L⁻¹, pH 2.0, particle size <178 μm

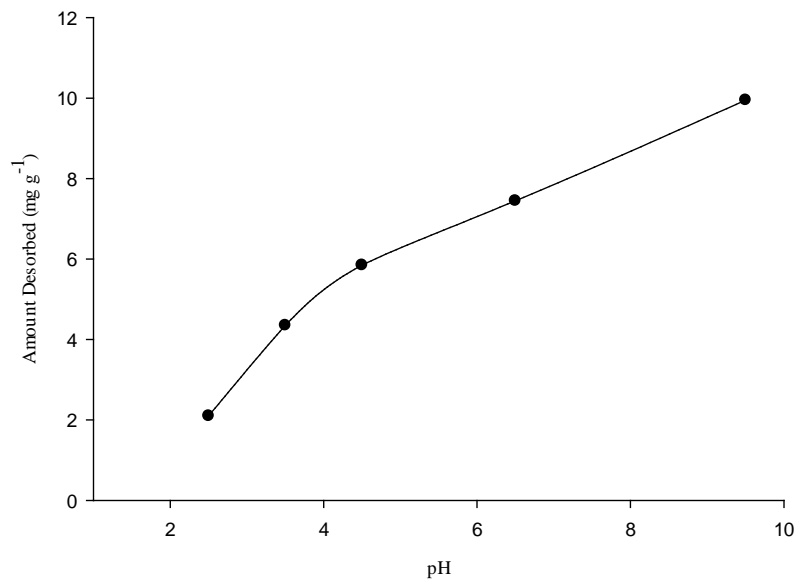


Fig. 8 Effect of pH on the desorption of Cr(VI) from dead biomass of *Bacillus subtilis*

Author – Dr. Kishor Kumar Singh, M.Sc – Inorganic chemistry, Ph.D – Applied Chemistry, Dept. of Applied Chemistry, IIT, BHU, Varanasi. Ph.D topic – Studies on the removal of heavy metal pollutants from water/ wastewater. I am also qualified CSIR-UGC NET in Chemical Sciences. Presently I am head, Department of chemistry, Govt. Post Graduate College, Obra, Sonbhadra, Uttar Pradesh, India. I have published 33 research papers in various International/ National journals such as Bioresource Technology, Hazardous Material, Chemical Engineering journal, Colloid and interface Science, Journal of Indian Chemical Society, Chemical and Environmental Research, Indian Journal of Environmental protection, JIST, AJBPR, JOCP, IJGHC, JECET, IJSET etc.