

## Biosorption of Cr(VI) by native isolate of *Lyngbya putealis* (HH-15) in the presence of salts

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### Abstract

Industrial wastewaters containing heavy metals along with high concentration of soluble salts pose a major environmental problem that needs to be remedied. The present study reports on biosorption of Cr(VI) by native isolate of *Lyngbya putealis* HH-15 in batch system under varying range of pH (2.0–10.0), initial metal ion concentration (10–100 mg/l) and salt concentration (0–0.2%). Maximum metal removal (94.8%) took place at pH 3.0 with initial Cr concentration of 50 mg/l, which got reduced (90.1%) in the presence of 0.2% salts. Adsorption equilibrium and kinetic behavior of Cr(VI) in solution was also examined. Both Langmuir and Freundlich models fitted well to explain the adsorption data ( $R^2 = 0.90$  and  $0.87$ , respectively) at 0.2% salt concentration. Pseudo-second order kinetic model also fitted well to both the systems, viz. Cr(VI) and Cr(VI) + salt. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Biosorption; Hexavalent chromium; *Lyngbya putealis*; Adsorption isotherms

### 1. Introduction

Widespread contamination of wastewaters with various toxic and non-biodegradable heavy metals pose several health problems and consequently need to be decontaminated to standard permissible levels. Chromium (Cr), which is present in the effluent of industries like leather tanning, electroplating, textile dyeing and metal finishing [1] exists in hexavalent and trivalent forms and it is the hexavalent form that is more toxic and is reported to cause cancer in the digestive tract and lungs of human beings [2]. Wastewaters from tanning and textile industries not only have high chromium concentrations but also contain significant quantities of soluble salts. Several conventional methods like precipitation, reduction of hexavalent chromium [Cr(VI)] to trivalent form and ion-exchange technique are in practice to deal with the metal contamination problem but these methods are not considered to be ecologically sound. Use of microorganisms for metal removal has been reported in the recent years to provide a better alternative to these conventional methods [3,4]. Use of algal biomass as a biosorbent is emerging as an attractive, economic and effective proposition because of certain added

advantages of algae giving them an edge over others [5–7]. Algae have low nutrient requirements, being autotrophic they produce a large biomass, and unlike other microbes, such as, bacteria and fungi they generally do not produce toxic substances. There are several reports on accumulation of heavy metal ions by algal biomass from aqueous solutions [8–12]. Binding of metal ions on algal surface depends on different conditions like ionic charge of the metal ion, algal species and chemical composition of the metal ion solution [13–15].

The present study was undertaken with an objective to assess and optimize the Cr(VI) sorption ability of a hitherto unexplored algal strain *Lyngbya putealis* HH-15 (Synonym: *Phormidium putealis*; [16]), isolated from a metal-contaminated industrial site. Although different algal systems have been tried to remove heavy metals from wastewaters, but there is lack of information on biosorption of algae in the presence of salts. Effect of different concentrations of salts on biosorption of Cr(VI) was therefore studied, as high concentration of total dissolved solids (TDS) associated with metals generally aggravate the pollution load of several industrial effluents. Suitability of Freundlich and Langmuir adsorption isotherms was studied for modelling equilibrium between adsorbed and unadsorbed metal ions. Kinetic model was also applied to the individual metal and metal–salt mixture biosorption data. The findings of the study would be useful in designing wastewater treatment systems containing Cr(VI)

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as well as soluble salts, particularly for electroplating and textile industries.

## 2. Materials and methods

### 2.1. Isolation of algal strain

*L. putealis* HH-15 used in the present study was isolated from soil samples collected from within the premises of an electroplating industry, Haryana, India (28°55'S 76°43'E), which is a semi-arid sub-tropical region. The soil in the region is rich in soluble salts that tend to accumulate in the upper profile due to high solar intensity, high evaporation rates and low annual rainfall (475 mm). Average maximum temperature is 45 °C and minimum temperature is 4 °C. Pure culture of the cyanobacterium was obtained by streaking on basal agar medium at pH 8.5 by using standard isolation and culturing techniques on nitrogen supplemented BG-11 medium [17]. The algal cultures were maintained at a light intensity of 3000 lx at 28 ± 3 °C.

### 2.2. Preparation of adsorbent and synthetic solution

Fourteen-day-old algal cultures were harvested and the algal biomass was washed with distilled water and dried at 70 °C in oven for 24 h. The dry biomass was sieved to select particles of 0.3 mm size for use as a biosorbent.

Synthetic stock solution of chromium (1000 mg/l) was prepared by dissolving calculated quantities of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and that of mixed salts (10%, w/v) by dissolving NaCl, KCl and K<sub>2</sub>SO<sub>4</sub> in a ratio of 9:0.5:0.5 using double distilled water. Working solutions of varying concentrations were obtained by diluting the stock solutions. All the experiments were conducted at desired pH using buffer solutions (KCl–HCl buffer for pH 2, citric acid–sodium citrate buffer for pH 3.5, Na<sub>2</sub>HPO<sub>4</sub>–NaH<sub>2</sub>PO<sub>4</sub> buffer for pH 6–8 and glycine–NaOH buffer for pH 9). The range of initial concentration of Cr(VI) and salt prepared from the stock solutions varied from 10 to 100 mg/l and 0% to 0.2%, respectively.

### 2.3. Metal analysis

Concentration of Cr(VI) ions in the synthetic solution were analyzed using a Systronics Spectrophotometer-106 at 540 nm using 1,5-diphenyl carbazide reagent in acid solution as complexing agent for Cr(VI) [18].

### 2.4. Batch mode studies

The experiments were carried out in 250 ml Erlenmeyer flasks with dry algal mass of 0.1 g/100 ml aqueous solution. The flasks were kept at 25 °C on a rotary shaker at 120 rpm with initial Cr(VI) concentration ranging from 10 to 100 mg/l. Additional treatment of 0%, 0.1% and 0.2% salt was also given to each flask. For each treatment blanks were also taken without alga. The flasks were shaken for 2 h (120 rpm) at pH 3. Optimization of pH was done for maximum metal biosorption by the alga using buffer solutions of varying pH (2.0–10.0) using 100 ml of

20 mg/l Cr(VI) solution with an algal dose of 0.1 g (dry weight) per flask. In order to check the maintenance of pH, measurement was done at intervals with Systronics  $\mu$  pH system-361.

## 3. Results and discussion

Biosorption of Cr(VI) was studied as a function of pH, initial concentration of Cr(VI) and salt concentration. The biosorption data were fitted to different isotherms.

### 3.1. Effect of pH on Cr(VI) biosorption

Hexavalent chromium removal by the alga at an initial calculated metal ion concentration of 20 mg/l was found to be pH-dependent as shown in Fig. 1. Equilibrium Cr sorption was favoured by acidic pH range of 2–3 and maximum biosorption by the alga (93.02%) was observed at pH 3.0. Increase in pH decreased the biosorption of chromium by the alga. However, no significant variations in Cr(VI) concentrations were observed due to varying pH based on blank readings (without alga). Distinct pH dependence was also observed for Cr removal from the metal containing saline solutions. pH 3.0 was found to be optimum for biosorption of Cr from the solution both in the presence and absence of salts. The presence of salts, however, decreased the metal biosorption from 93% to 89%. This may be due to competition of chloride and sulphate ions with the chromate anions [19]. Several other studies have also shown dependence of biosorption of metal ions on pH of the solution [20,21]. Maximum metal adsorption at pH 2–3 seems to be due to a net positive charge on algal surface at low pH. Due to isoelectric point at pH 3.0 for algal biomass [22], protonation of certain functional groups and presence of hydronium ions around the binding sites at low pH there is greater attraction of Cr(VI) to the algal surface [23]. Cr(VI), which may exist as HCrO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, etc., in solution at optimum sorption pH

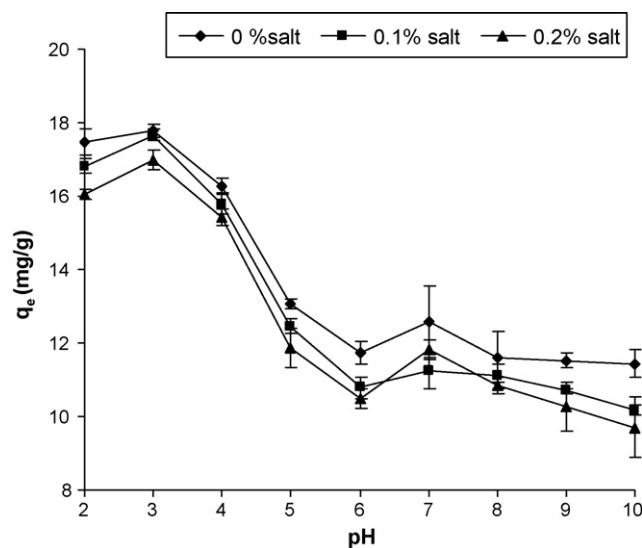


Fig. 1. Effect of pH on equilibrium Cr(VI) sorption capacity of *Lyngbya putealis* HH-15 in the absence and presence of salts (initial calculated Cr concentration,  $C'_0 = 20$  mg/l; initial estimated Cr concentration,  $C_0 = 19.1$  mg/l).

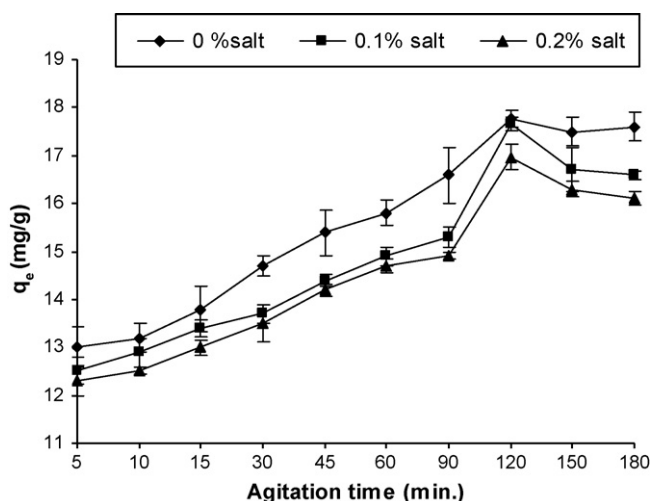


Fig. 2. Effect of agitation time on equilibrium Cr(VI) sorption capacity of *Lymnobia putealis* HH-15 in the absence and presence of salts (initial calculated Cr concentration,  $C_0 = 20$  mg/l).

[3,24] has a tendency to bind to the protonated active sites of the biosorbent. But as pH of the solution increases, algal cell wall becomes more and more negatively charged due to functional groups, which repulse the negatively charged chromate ions thereby affecting Cr(VI) biosorption on the algal surface. However, 85–60% removal of Cr(VI) takes place even above pH 3.0, which indicates involvement of some other metal binding mechanism such as physical adsorption or ion-exchange mechanism at higher pH [25].

### 3.2. Biosorption kinetics

Kinetics of biosorption was studied to describe the rate of metal uptake in the absence and presence of salts and the data of metal removal at different salt concentrations with initial Cr(VI) concentration of about 20 mg/l were plotted as a function of time (Fig. 2). Metal adsorption increased with increasing agitation time and equilibrium was attained at 120 min. Beyond this no significant increase in adsorption was observed with increasing contact time. In the presence of salts, metal adsorption was slightly less as compared to salt-free solution and biosorption of Cr declined as the contact time exceeded 120 min, indicating

onset of desorption. Algal biosorption of Cr(VI) decreased from 93% in salt-free solution to 88.9% at 0.2% salt concentration. Equilibrium was, however, found to be independent of initial salt concentration.

Rate constants for adsorption of Cr(VI) were determined using pseudo-second order equation [26]:

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (1)$$

where  $K_2$  is pseudo-second order rate constant (g/mg min),  $q_e$  and  $q_t$  are amounts of metal ion sorbed (mg/g) at equilibrium and at any time ( $t$ ), respectively.

Linear form of Eq. (1) is

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Linear plot of  $t/q$  versus  $t$  shows fitness of the data to pseudo-second order kinetic model at 20 mg/l initial Cr(VI) concentration plus salts. The values of  $K_2$ ,  $q_e$  and  $R^2$  calculated from the plot are given in Table 1 for all Cr(VI) and salt combinations. These theoretical values of  $q_e$  obtained from the graph have been compared with the experimental values of  $q_e$  in Table 1 and good agreement between calculated value of  $q_e$  from second order kinetic model and experimental value of  $q_e$  was observed, as indicated by very high values of coefficients of correlation ( $R^2$ ) exceeding 0.978. This proves the validity of this model to explain biosorption of Cr(VI) by the alga.

### 3.3. Effect of initial metal concentration

The initial metal concentration plays an important role in the process of biosorption. With increase in initial Cr concentration there is an increase in biosorption of Cr(VI) both individually and in combination with different concentrations of salts as shown in Table 2. When Cr(VI) concentration was increased from 10 to 50 mg/l approximately in the absence of salts, the adsorption capacity increased from 8.0 to 48.0 mg/g of algae. The reason for this seems to be increase in the number of ions available for competing at the binding sites. But Cr concentration above 50 mg/l did not increase the biosorption significantly and percent metal removal remained almost constant or showed even a decrease indicating saturation of all the binding sites on algal surface beyond a particular concentration. Same pattern

Table 1  
Pseudo-second order kinetic model parameters for metal adsorption on algal surface at different initial chromium(VI) concentration in the absence and presence of salts

Salt concentration (%)	Initial metal ion concentration (mg/l)	$q_e$ (mg/g)		$K_2$ (g/mg min)	$R^2$
		Experimental	Calculated		
0	19.1	17.77	18.08	0.01035	0.9985
	50.6	47.95	51.28	0.00157	0.9927
0.1	19.1	17.66	17.24	0.01045	0.9955
	50.6	46.88	50.76	0.00129	0.9846
0.2	19.1	16.97	16.69	0.01159	0.9965
	50.6	45.57	48.78	0.00125	0.9785

Table 2

Equilibrium adsorption quantities and % removal of Cr(VI) ions at different initial Cr concentrations in the absence and presence of salts<sup>a</sup>

$C'_0$ (mg/l)	$C_0$ (mg/l)	0% salt		0.1% salt		0.2% salt	
		$q_e$ (mg/g)	% removal	$q_e$ (mg/g)	% removal	$q_e$ (mg/g)	% removal
10	9.05	8.00	88.40	7.93	87.63	7.78	85.97
20	19.1	17.77	93.04	17.66	92.46	16.97	88.85
30	29.4	27.47	93.44	27.19	92.48	26.22	89.18
40	39.5	37.30	94.43	36.56	92.56	35.53	89.95
50	50.6	47.95	94.76	46.88	92.65	45.57	90.06
60	62.0	57.30	92.42	56.04	90.39	54.17	87.37
70	69.6	64.01	91.97	61.77	88.75	58.87	84.59
80	78.4	70.16	89.49	68.78	87.73	64.98	82.89
90	89.2	76.38	85.62	75.68	84.84	71.40	80.04
100	101.0	81.02	80.22	77.49	76.72	72.97	72.24

<sup>a</sup>  $C'_0$ : initial calculated Cr;  $C_0$ : initial estimated Cr.

was observed for Cr(VI)–salt combinations, indicating suitability of the present strain for treating wastewaters containing up to 50 mg/l chromium.

### 3.4. Effect of salt concentration on Cr(VI) biosorption

When salt concentration was increased up to 0.2% there was a slight decrease in biosorption of Cr(VI) indicating a little antagonistic effect of salts on Cr biosorption. As salt concentration increased from 0% to 0.2% at initial Cr concentration of 20 mg/l, Cr uptake decreased slightly from 18.0 to 17.0 mg/g of algae. The reducing effect may be due to reasons related to biosorption mechanisms, such as, competition between chloride, sulphate and chromate ions for binding sites reducing the adsorption of Cr or reduction in permeability of cell by the salt ions with respect to Cr(VI).

### 3.5. Adsorption isotherms

Fig. 3 shows the adsorption isotherms for Cr(VI) removal by *L. putealis*. To understand the biosorption mechanism and surface characteristics of the alga, the mathematical models developed by Langmuir and Freundlich have been applied to the data.

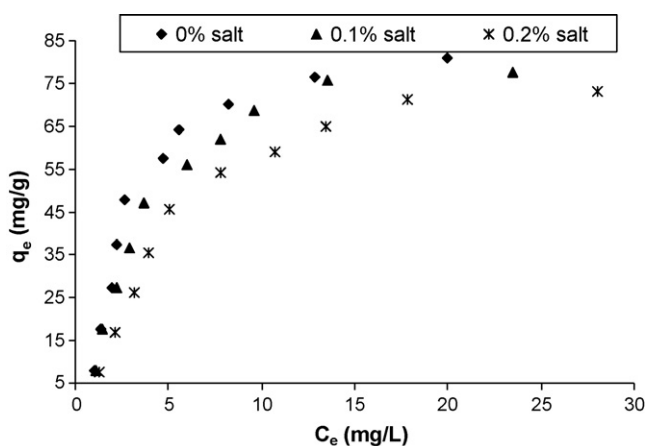


Fig. 3. Isothermal curve for Cr(VI) adsorption by *Lyngbya putealis* HH-15 in the absence and presence of salts.

Langmuir isotherm, which assumes that there are finite numbers of binding sites distributed homogeneously over the surface of the adsorbent, can be represented as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where  $C_e$  is equilibrium concentration (mg/l),  $q_e$  is amount of Cr(VI) adsorbed at equilibrium (mg/g),  $Q_0$  (mg/g) and  $b$  (l/mg) are Langmuir constants showing the adsorption capacity and energy of adsorption, respectively [27].

Langmuir isotherm showed linear plots ( $C_e/q_e$  versus  $C_e$ ) for all salt concentrations. Values of Langmuir constants ( $Q_0$  and  $b$ ) were calculated from the slope and intercept of the plots. Adsorption capacity was very high ( $Q_0 = 113.6$  mg/g) in the absence of salts (Table 3).

Freundlich isotherm was also applied to study the adsorption behavior as it is widely used in environmental engineering practice. This assumes heterogeneous surface of the adsorbent and linearized form of the model is as follows:

$$\log_{10} q_e = \log_{10} K_f + \frac{1}{n(\log_{10} C_e)} \quad (4)$$

where  $K_f$  is Freundlich constant indicating adsorbent capacity (mg/g dry weight),  $n$  is Freundlich exponent known as adsorbent intensity [28].

Linear plot of  $\log q_e$  versus  $\log C_e$  shows the applicability of this isotherm for both the systems, i.e. Cr(VI) and salt containing Cr(VI). The values of  $K_f$  and  $n$  along with  $R^2$  calculated from the plots are given in Table 3. The high values of  $K_f$  and  $n$  show high feasibility of Cr(VI) adsorption on the algal surface from metal containing waste water. But both the Freundlich constants show a little decrease in the presence of high salt concentration (Table 3).

High values of regression coefficients between the sorbate and sorbent systems for both Langmuir and Freundlich models indicated the applicability of this algal system for Cr(VI) removal in both monolayer biosorption and heterogeneous surface conditions even in the presence of salts.

When compared with several other algal systems the present cyanobacterial strain was found to show better hexavalent chromium biosorption (48.0 mg/g). Green algae like *Chlamy-*

Table 3  
Langmuir and Freundlich adsorption constants for Cr(VI) biosorption in the absence and presence of salts

Salt concentration (%)	Langmuir parameters			Freundlich parameters		
	$Q_0$ (mg/g)	$b$ (l/mg)	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
0	113.6	0.157	0.809	16.11	1.49	0.775
0.1	108.7	0.140	0.861	13.71	1.47	0.834
0.2	105.3	0.104	0.900	10.63	1.45	0.870

*domonas reinhardtii*, *Chlorella vulgaris*, *Synechocystis* sp., *Spirogyra* sp. and *C. crispata* have been reported to show maximum Cr (VI) uptake of 18.0, 34.0, 39.0, 15.0 and 40.0 mg/g, respectively [10,13,29,30]. Further, industrial wastewaters from textile and electroplating industries that are usually not only contaminated with Cr (5–50 mg/l) but also have a high TDS (500–2000 mg/l), the present algal biosorbent holds promise for effective removal of the metal even in the presence of salts.

#### 4. Conclusions

The purpose of the present study was to find out the adsorption capacity of natively isolated *L. putealis* HH-15 for Cr(VI) in the presence of mixed salts keeping in view the dual problems encountered in industrial effluent treatment. Different experiments performed with varying initial pH, initial Cr concentration and salt concentration revealed that pH 3, contact time 120 min and initial metal concentration of 50 mg/l were optimum for biosorption of Cr(VI). Pseudo-second order equation, which fits the data well showed that there is good correlation between experimental and calculated value of  $q_e$  explaining the biosorption kinetics based on the assumption that algal biosorption of the metal is the rate limiting step.

Langmuir and Freundlich isotherms applied to the sorption data were compared to observe the Cr(VI) biosorptive capacity of the alga in the presence and absence of salts. It was found that Cr uptake capacity of this alga is higher in the absence of salt ( $K_f = 16.1$ ;  $Q_0 = 113.6$  mg/g) than in the presence of 2000 ppm salts ( $K_f = 10.63$ ;  $Q_0 = 105.3$  mg/g). Thus, presence of salts slightly reduced the uptake of Cr(VI) yet, under optimized conditions it was found to remove 94.8%, 92.7% and 90.1% Cr(VI) when salt concentration was 0, 1000 and 2000 ppm, respectively. Thus, this algal system has the potential for effective use in treatment of metal-contaminated saline wastewaters.

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