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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.

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

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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°5S5′N 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 $K_2Cr_2O_7$ and that of mixed salts (10%, w/v) by dissolving NaCl, KCl and K_2SO_4 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_2HPO_4–NaH_2PO_4 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 μ 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 $HCrO_4^-$, $Cr_2O_7^{2-}$, etc., in solution at optimum sorption pH

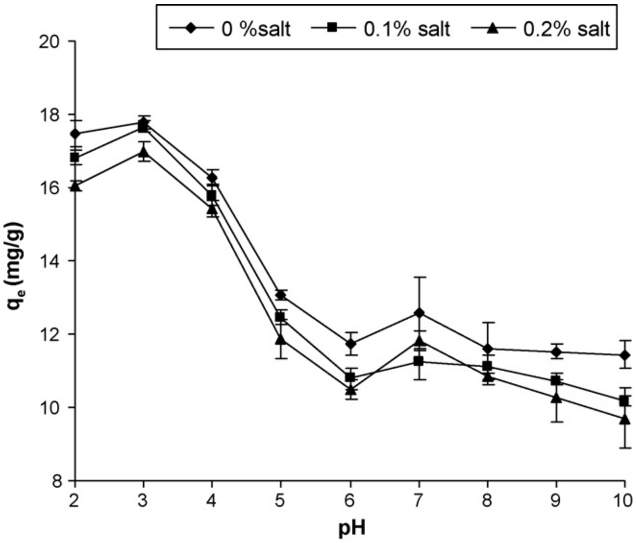

Fig. 1. Effect of pH on equilibrium Cr(VI) sorption capacity of *Lyngbya putealis* HH-15 in the absence and presence of salts (initial calculated Cr concentration, $C'_0 = 20$ mg/l; initial estimated Cr concentration, $C_0 = 19.1$ mg/l).