

Biosorption of Cr(III) from aqueous solution using algal biomass *spirogyra* spp.

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Abstract

In the present investigation, a fresh water green algae *spirogyra* spp. was used as an inexpensive and efficient biosorbent for Cr(III) removal from aqueous solution. The algal biomass was treated with 0.1 M NaOH, 0.2 M CaCl₂ and 5% HCHO. The biosorption efficiency was compared with untreated biomass. The effects of various physico-chemical parameters were studied, e.g. pH 3.0–6.0, initial metal ions concentration 20–150 mg L⁻¹, algal dose 1.0–3.0 g L⁻¹, and contact time 15–180 min, respectively. Biosorption of Cr(III) is highly pH dependent. Maximum 81.02% adsorption of Cr(III) was observed with 0.2 M CaCl₂ treated biomass at pH 5.0. Removal of Cr(III) was more than 70% in 45 min of contact time with different treated and untreated algal biomass at concentration 30 mg L⁻¹. Maximum metal uptake (Q_{\max}) was observed as 30.21 mg g⁻¹ with 0.2 M CaCl₂ treated algal biomass indicate good biosorbents than other treated and untreated biomass. The high values of correlation coefficient ($r^2 < 0.90$) indicate equilibrium data of treated and untreated form of algal biomass well fitted in Freundlich than Langmuir isotherms model equations.

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1. Introduction

The presence of toxic heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies, is one of the most important environmental issues [1]. Their presence in aquatic ecosystem poses human health risks and causes harmful effect to living organisms [2]. Chromium is released into the environment by a large number of industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservation [3]. These industries contain Cr(III) and Cr(VI) at concentration ranging from 10 to 100 mg L⁻¹ [4]. Chromium exists in several oxidation states (−2 to +6), the most stable and common forms are the hexavalent Cr(VI) and trivalent Cr(III) [5]. Cr(III) is selected instead of Cr(VI) because of following facts Cr(III) is toxic if excess quantity is taken and cause abnormalities in organisms. Chromium(III) sulphate salts are mainly used in tanning [6]. Several International Environmental Agencies have

introduced strict regulations with regard to metal discharge, especially from industrial activities. According to USEPA, the discharge of Cr(VI) into surface water is 0.5 mg L⁻¹, while total Cr including Cr(III), Cr(VI) and its other forms is regulated to below 2 mg L⁻¹ [5]. The conventional chemical processes are often restricted because of technical or economical constraints and generate large amount of toxic sludge. Thus the biosorption of heavy metals is relatively new technology. Several researchers found microorganisms, e.g. fungi [7,8], seaweed and seaweed derivatives [9,10] and fresh water algae [11,12] capable of efficiently accumulating heavy metals. Physical pretreatment methods such as heating, autoclaving, freeze-drying, boiling and chemical pretreatment such as using acids, alkali and organic chemical showed enhancement or reduction in metal biosorption depending upon the biomass and treatment procedures used [13–15]. Several studies has been reported for the removal of heavy metals by fresh water green algal biomass spp. *spirogyra* [11,12,16,17] but no work has been reported on removal of Cr(III) by algal biomass spp. *spirogyra* which is abundant in fresh water bodies. The main objectives of the present study are (i) to investigate the potential of Cr(III) biosorption with non living green algae treated and untreated *spirogyra* spp.

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and (ii) to optimize various parameters, i.e. pH, contact time, initial Cr(III) ion concentration and biosorbent dose.

2. Materials and methods

2.1. Biosorbents

Algal biomass of *spirogyra* species was collected from the Mansar Lake, Jammu and Kashmir, India. The biomass was thoroughly washed with distilled water to remove dirt and other unwanted material and was kept on a filter paper to reduce the water content. It was then dried at 50 °C overnight until a constant weight was obtained and recorded the final weight of biosorbents. After that the biosorbents was crushed and sieved through 300 µm sieve for uniform particle size and used for study.

2.2. Preparation of synthetic Cr(III) solution

A stock solution of chromic chloride (CrCl₃) was prepared by dissolving 0.513 g of CrCl₃ (Hi-Media AR Grade) in 100 mL of double distilled water to make a concentration of 1000 mg L⁻¹ and working solution of 100 mg L⁻¹ was prepared by diluting the stock solution.

2.3. Pretreatments

Dried algal biomass was pretreated in three different ways: 25 g algal biomass was dipped into a 200 mL solution of 5% formaldehyde (HCHO) for overnight [15]; 25 g algal biomass was treated with a 200 mL solution of 0.1 M NaOH by suspending it for overnight [15]; 25 g algal biomass was dipped in 200 mL 0.2 M CaCl₂ solutions for 24 h under slow stirring to increase its efficiency [18]. After each pretreatment with chemicals, the biomass was washed with generous amount of deionized water and dried at 60 °C for 12 h. The sodium hydroxide pretreated biomass was washed with deionized water until the pH of the solution was near to natural range (pH 6.8–7.2).

2.4. Biosorption experiments

2.4.1. Effect of pH

The experiment was conducted for biosorption at concentration 30 mg L⁻¹ of Cr(III) ions, 0.5 g L⁻¹ of biosorbent dose in 50 mL metal solution for 90 min with varying pH from 3.0 to 6.0. The pH value of the solution was adjusted using 1N HCl or 1N NaOH.

2.4.2. Effect of contact time

Effect of contact time was studied at optimum pH 5.0; constant metal concentration 30 mg L⁻¹, biomass dose 0.5 g L⁻¹ in 50 mL of the solution. Samples were taken after 15, 30, 45, 60, 90, 120, 150 and 180 min.

2.4.3. Effect of initial metal ions concentration

Effect of initial metal ions concentration on biosorption of Cr(III) from 20 to 150 mg L⁻¹ was studied.

2.4.4. Effect of biosorbents dose

Different amount of biomass dose ranging from 1.0 to 3.0 g L⁻¹ for 50 mL of Cr(III) solution in 250 mL of Erlenmeyer flask was used, while keeping the pH 5.0, temperature 25 °C and concentration of the Cr(III) ions 50 mg L⁻¹.

2.5. Analysis of Cr(III)

The concentration of Cr(III) in the samples was determined by atomic absorption spectroscopy. The amount of Cr(III) adsorbed by the biomass was calculated using the following equation:

$$q = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where q is the amount of Cr(III) adsorbed by biomass (mg g⁻¹), C_0 is the initial concentration of Cr(III) ion (mg L⁻¹), C_e is the concentration of Cr(III) at equilibrium (mg L⁻¹), V is the volume of the metal solution (L) and W is the weight of adsorbent (g).

All the experiments were conducted at room temperature (25 °C) in triplicate.

2.6. Biosorption isotherm

Adsorption data for wide range of adsorbate concentrations are most conveniently described by various adsorption isotherms, such as Langmuir or Freundlich isotherms.

Langmuir model can be described as [19,20]:

$$q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (2)$$

The logarithmic equation:

$$\frac{1}{q_e} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max}} \times \frac{1}{C_e} \quad (3)$$

The constants, Q_{\max} and b is evaluated from the linear plot between $1/q_e$ and $1/C_e$, whereas Q_{\max} represent the maximum adsorption and b is affinity between the biosorbent and biosorbate.

Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecule is present on the adsorption surface, and the energy of adsorption is constant and there is no migration of adsorbate molecule in the surface plane.

Freundlich isotherm has the form [19,21]:

$$q_e = K C_e^{1/n} \quad (4)$$

The logarithmic form of the equation is given below as:

$$\log q_e = \log K + \frac{1}{n \log C_e} \quad (5)$$

The value of K and $1/n$ were found by plotting the graph between $\log q_e$ and $\log C_e$, which is the residual chromium concentration and is calculated from the laboratory data. The value of $\log K$ is the intercept and value of $1/n$ is the slope of the plot. After finding the $\log K$, its antilog is found out to calculate K and n is empirical parameters that vary with the degree of the heterogeneity. A high

'K' and 'n' value is indication of high adsorption through out the concentration range.

3. Results and discussion

3.1. Effect of pH

The maximum biosorption of Cr(III) was obtained at pH 5.0 with untreated and treated biosorbents (Fig. 1). Removal of Cr(III) was obtained 81.02% with 0.2 M CaCl_2 , 75.30% with 0.1 M NaOH, 73.0% with 5% HCHO and 62.01% with untreated biosorbents, respectively. When pH was further increased up to 6.0, the percentage adsorption is decreased. Because OH^- ions increased the hindrance of diffusion as well as some of the divalent cations may react with OH^- ion and precipitated and there by decreased the free metal ions available in the solution [19]. At lower pH, there may be competition between H^+ and Cr^{3+} (III) ions and thus decreased the adsorption capacity of algae [22]. Uptake capacity of Cr(III) with seaweed biosorbent was reported negligible at lower pH range 1.0 and 2.0 and $\text{Cr}(\text{OH})^{2+}$ cations exist in solutions at $\text{pH} < 2.5$, and Cr(III) starts precipitating as $\text{Cr}(\text{OH})_3$ at $\text{pH} > 5.0$ [23,24]. Adsorption efficiency of Cr(VI) was observed maximum at pH 2.0 with activated rice husk and at pH 4.0 with activated alumina [25]. Because at lower pH, functional groups like hydroxyl, carboxyl, sulfonate, amine, and phosphate, etc. are present on algal surface spp. *spirogyra* become positively charged due to increase in hydrogen ion concentration responsible for reduction in biosorption capacity [12,26].

3.2. Effect of contact time

The experiment was conducted in 30 mg L^{-1} initial Cr(III) concentration, 0.5 g L^{-1} algal dose, optimum pH 5.0 and the contact time was varied from 15 to 180 min at 25°C temperature. It was observed from the results that Cr(III) removal was 78.48% with 0.2 M CaCl_2 , 75.18% with 0.1 M NaOH, 72.14% with 5%

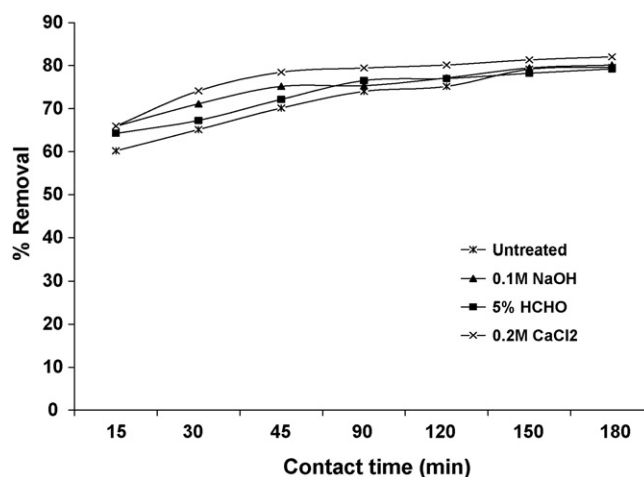


Fig. 2. Effect of contact time on biosorption of Cr(III) using pretreated and untreated algal biomass at concentration 30 mg L^{-1} , temperature 25°C , algal dose 0.5 g L^{-1} , pH 5.0.

HCHO treated biosorbents and 70.15% with untreated biosorbents after 45 min at 25°C temperature (Fig. 2). There was no appreciable increase in percent removal of Cr(VI) after 45 min and only further 3–6% removal was observed up to 180 min (Fig. 2). Adsorption got slow down in later stages because initially a large number of vacant surface sites may be available for adsorption and after some time, the remaining vacant surface sites may be difficult to occupy due to forces between the solute molecules of the solid and bulk phase [26–28]. The diminishing removal with increasing time may also be due to intraparticle diffusion process dominating over adsorption [29,30].

3.3. Effect of initial concentration of Cr(III) ions

The biosorption of Cr(III) as a function of the initial concentration of Cr(III) in solution with untreated and different treated biosorbents (Fig. 3). The initial concentration of Cr(III) was varied from 20 to 150 mg L^{-1} at temperature 25°C , dose

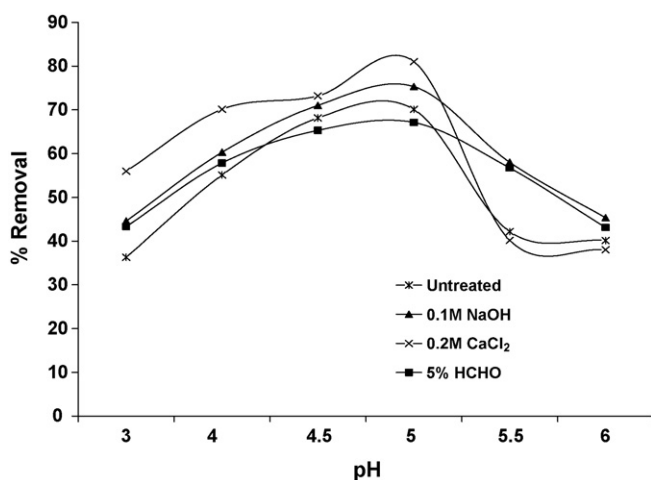


Fig. 1. Effect of pH on biosorption of Cr(III) using treated and untreated algal biomass at concentration 30 mg L^{-1} , temperature 25°C , algal dose 0.5 g L^{-1} , contact time 90 min.

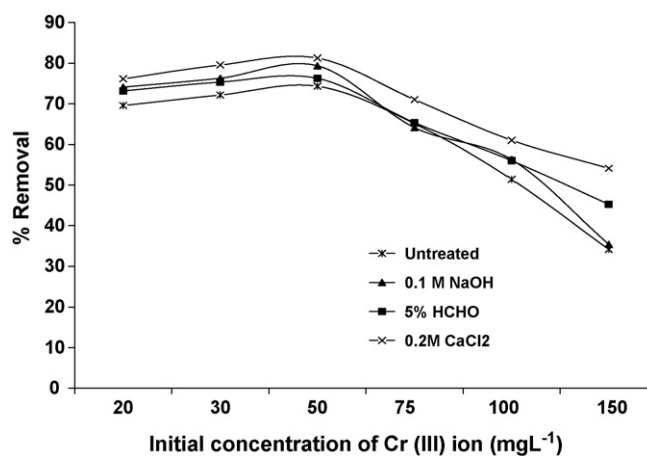


Fig. 3. Effect of initial ion concentration on biosorption of Cr(III) using treated and untreated algal biomass at contact time 45 min, temperature 25°C , algal dose 0.5 g L^{-1} , pH 5.0.

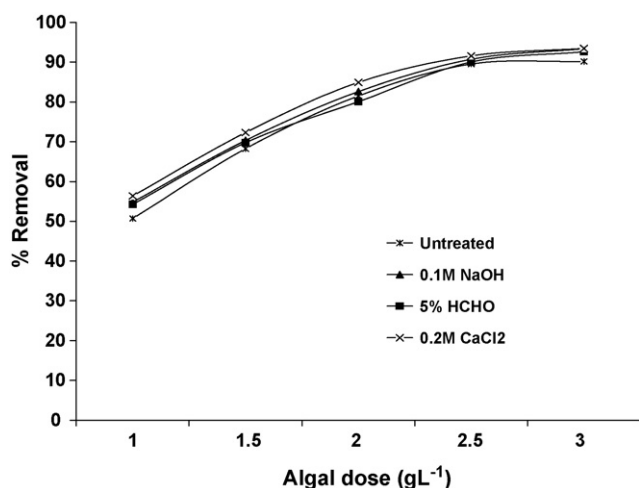


Fig. 4. Effect of algal dose on biosorption of Cr(III) using treated and untreated algal biomass at concentration 50 mg L^{-1} , contact time 90 min, temperature 25°C , pH 5.0.

0.5 g L^{-1} , and contact time 45 min and at optimum pH. The percentage removal was increased as the initial Cr(III) concentration increased up to 50 mg L^{-1} but further increase in concentration removal was decreased. The removal of Cr(III) was 81.25% with 0.2 M CaCl_2 , 79.26% with 0.1 M NaOH, 76.28% with HCHO and 74.32% with untreated algal biomass at concentration 50 mg L^{-1} . The maximum percentage removal was observed 81.25% with 0.2 M CaCl_2 treated biosorbents at 50 mg L^{-1} concentration (Fig. 3). This may be due to the fact that the available sites on surfaces of algal cell get saturated, thereby further adsorption of metal ions is prevented [29,31].

3.4. Effect of algal dose

The dependence of Cr(III) adsorption on the amount of algae was studied at 25°C temperature at pH 5.0 by varying the adsorbent amount from 1.0 to 3.0 g L^{-1} , while keeping the volume of Cr(III) ion solution 50 mL in 250 mL of Erlenmeyer flask and concentration of the metal solution 50 mg L^{-1} (Fig. 4). It was apparent that the percent removal of Cr(III) increased rapidly with increase in the dose of algal biomass due to the greater availability of the biosorbents. The maximum percent removal of Cr(III) was 90.16% with untreated biomass, 93.46% using 0.2 M CaCl_2 , 92.60% with 5% HCHO and 93.38% treated with 0.1 M NaOH biomass at 3.0 g L^{-1} of algal dose. There was slow increase in Cr(III) removal after biomass dose of 2.5 g L^{-1} .

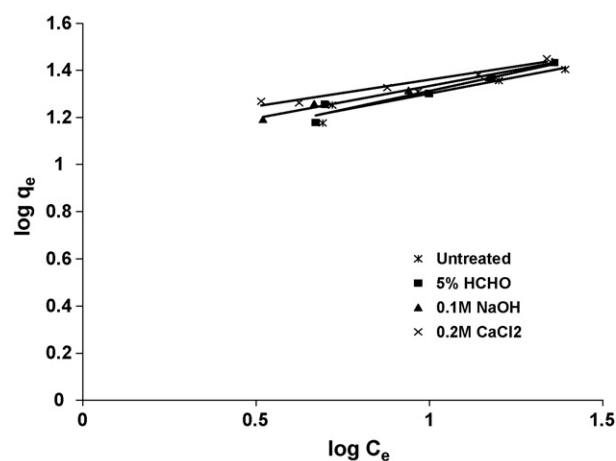


Fig. 5. Freundlich adsorption isotherm for Cr(III) using treated and untreated algal biomass Cr(III) concentration 50 mg L^{-1} , algal dose $1.0\text{--}3.0 \text{ g L}^{-1}$, pH 5.0.

However, a possible reason is that removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbent and adsorbate at the operating condition. It is suggested that a 0.2 M CaCl_2 treated biosorbents is capable of removing higher percentage of Cr(III) compared to other treated and untreated biomass. The increases in biosorption capacity with alkali pretreatment may be due to the release of certain biopolymers having high affinities towards heavy metal ions from the cell wall by autolytic enzymes released as a result of alkali pre-treatment [32,33]. The acid treatment decreased the adsorption capacity of *A. niger* [34].

3.5. Adsorption isotherms

The Freundlich and Langmuir isotherms constants have a high value of the correlation coefficient (r^2) (Table 1). In view of high value of correlation coefficients, adsorption data are best fitted in Freundlich model than Langmuir (Figs. 5 and 6). These values indicate that there is a strong positive relationship in the data. Higher the value of k and n , i.e. 13.64 mg g^{-1} and 4.42, respectively, for 0.2 M CaCl_2 treated biosorbents correlated the higher the adsorption capacity than other treated and untreated biosorbents. The high value of K indicates a high adsorption. This is defined as the adsorbate adsorbed per unit weight of adsorbent. Higher the n ($n > 1$) value, higher is the intensity of adsorption [29]. The sorption performances of the different treated and untreated biosorbents were compared by their

Table 1
Freundlich and Langmuir constants for Cr(III) with pretreated and untreated algal biomass

Biosorbents	Freundlich constants			Langmuir constants		
	r^2	k (mg g^{-1})	n	r^2	b (L mg^{-1})	Q_{max} (mg g^{-1})
Untreated	0.91	10.51	3.57	0.91	0.034	28.16
0.1 M NaOH	0.99	11.45	3.63	0.91	0.035	29.15
5% HCHO	0.93	9.873	3.14	0.89	0.033	28.81
0.2 M CaCl_2	0.97	13.64	4.42	0.908	0.035	30.21

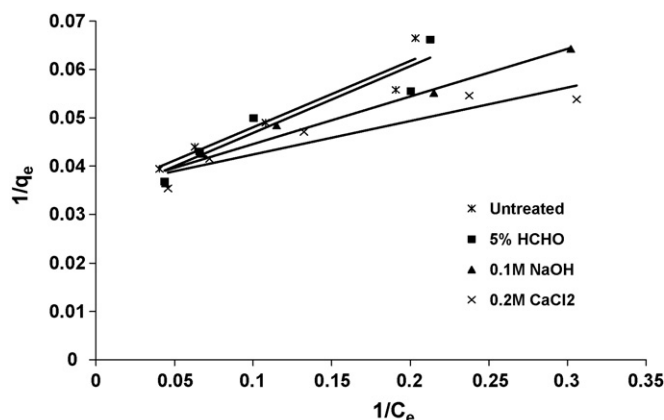


Fig. 6. Langmuir adsorption isotherm for Cr(III) using treated and untreated algal biomass Cr(III) concentration 50 mg L^{-1} , algal dose $1.0\text{--}3.0 \text{ g L}^{-1}$, pH 5.0.

respective Langmuir constant Q_{max} and b values. The value of constant Q_{max} and b was obtained from fitting the experimental data into Langmuir isotherms (Table 1). This data shows maximum metal uptake Q_{max} is 30.21 mg g^{-1} with 0.2 M CaCl_2 , 29.15 mg g^{-1} with 0.1 M NaOH , 28.81 mg g^{-1} with $5\% \text{ HCHO}$ treated and 28.16 mg g^{-1} untreated biosorbents and lower value of constant b indicate the high affinity of the biosorbents. It indicates that 0.2 M CaCl_2 treated biosorbent is better than other treated and untreated biosorbents. The obtained value of Q_{max} is much higher than the other biosorbents, i.e. *P. palmate* (6.65 mg g^{-1}), *P. aruginosa* (23.00 mg g^{-1}), *C. cryptica* (26.28 mg g^{-1}) [17,35].

4. Conclusions

In this study biosorption of Cr(III) on algal biomass (*spirogyra* spp.) in treated and untreated forms has been investigated. The biosorption capacity of Cr(III) is influenced by pH of the solution, concentration of ions, contact time and biosorbents dose. Maximum removal of Cr(III) on 0.2 M CaCl_2 treated algal biomass is at pH 5.0. The biosorption equilibrium data were correlated by Freundlich and Langmuir isotherms. It is found that the experimental data is well fitted in Freundlich isotherms. The adsorption capacity of the treated algal biomass is increased more than its natural form. The high value adsorption capacity (13.64 mg g^{-1}) with 0.2 M CaCl_2 , (11.45 mg g^{-1}) with 0.1 M NaOH , (9.873 mg g^{-1}) with $5\% \text{ HCHO}$ and (10.51 mg g^{-1}) with untreated indicate 0.2 M CaCl_2 treated algal biomass is better performed than other treated and untreated. High value of Q_{max} 30.21 mg g^{-1} with 0.2 M CaCl_2 treated algal biomass is also indicated its better biosorbents than other treated and untreated. The results obtained through this study support that the algae is an effective and low cost adsorbent for removal of Cr(III).

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