Biosorption of chromium from aqueous solution by *Chaetomorpha antennina*

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Abstract

Aim: Aquatic system poses a serious threat from industrial effluents having heavy metals and chromium due to its wide use in industry. It becomes a prime responsibility for removal of chromium ions from effluents before discharged into the aquatic body. Biosorption comes as an effective technology in the removal of heavy metals from industrial effluents. This study deals with biosorption of chromium from aqueous solution by *Chaetomorpha antennina*.

Methodology: Biosorption of chromium was studied using microalgae *Chaetomorpha antennina*, as an adsorbent, which was characterized using Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM) to determine the functional groups and the structural characteristics, respectively. Equilibrium and optimization studies for various parameters like pH (1-11), adsorbent dosage (0.2 – 1 g l⁻¹), initial chromium concentration (10 µg – 100 µg ml⁻¹) and agitation time (0 – 50 mins) were examined using batch process.

Results: The maximum percent removal of chromium ions was found to be 83% at pH 1 at an adsorbent dosage of 1g at a contact time of 30 min, which showed maximum adsorption.

Interpretation: Biosorption of chromium ions onto the surface of *Chaetomorpha antennina*, showed that biosorption was dependent on the equilibrium pH of the solution, biosorbent and contact time.

Key words: Biosorption, *Chaetomorpha antennina*, Chromium, Industrial effluent.

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Introduction

Presence of heavy metals in the aquatic system has become the most pervasive threat to the environment. In the age of unplanned industrialization and urbanization, discharge of non-treated industrial effluent into the water bodies is impending dangerous towards human health and aquatic environment due to the presence of toxic heavy metals (Gupta *et al.*, 2001).

The concern regarding heavy metals is toxicity and their persistence in bioaccumulating in living organisms. Chromium is one of the widely used metal and finds its application in stainless steel production, chromate preparation and textile industries. Chromium is a potent water pollutant, which exists in two forms: hexavalent and trivalent. (Rezaei, 2016; Vijayaraghavan *et al.*, 2008). A trivalent form of chromium (Cr III ion) is an essential trace element found in insulin and lipid metabolism (Vincent, 2017), but still it is debated issue owing to its toxicity (Jaishankar *et al.*, 2014; Zhitkovich 2005). Another form is hexavalent, which is a potent causes pollutant than Cr III and causes cancer, diarrhea, hemorrhage (Gurkan *et al.*, 2017). It is considered as one of the hazardous substance as per Agency for Toxic Substance and Disease Registry (ATSDR)

There are various methods reported by Owlad *et al.* (2009) for removal of metal ions exchange, chemical precipitation, activated carbon (Kobya *et al.*, 2005), reverse osmosis and adsorption. Among the reported methods bio-adsorption comes as a versatile and efficient method in the removal of metal ions which overcomes the costly methods as chemical precipitation where a huge amount of chemical required to remove the metal ions and activated carbon which comes as a costly adsorbent.

Biosorption of heavy metals has gained interest as an alternative method for activated carbon. A wide range of studies done on biosorption (Veglio and Beolchini 1997) using *Spirulina* (Rezaei, 2016), *Saccharomyces cerevisiae* (Wang *et al.*, 2006), brown seed algae (Yun *et al.*, 2011), *Rhizopus nigricans* (Bai and Abraham 2001), Chitosan based biosorbent (Wang and Chan 2014), *Bacillus thuringiensis* (Oves *et al.*, 2013), *Chaetomorpha antennina* (Lahari *et al.*, 2011), *Aspergillus niger* (Khambhaty *et al.*, 2009) have been reported. The process of biosorption depends upon various parameters like pH, temperature, type of biosorbent material used, contact time and material dosage (Farooq *et al.*, 2010; Volesky and Holan, 1995).

There are very few reports available on biosorption properties of microalgae, *Chaetomorpha antennina* and this is the first report on biosorption of Cr VI using *Chaetomorpha antennina*. In view of the above, this study was conducted to evaluate properties of *Chaetomorpha antennina* as a potential adsorbent and optimization of various parameters in removal of Cr VI from an aqueous solution of industrial effluents.

Materials and Methods

***Chaetomorpha antennina* - Biosorbent:** *Chaetomorpha antennina* is a green algae belonging to family Cladophoraceae.

The seaweeds were collected from the Ennore Beach, Chennai. Identification of collected sample was done at Madras University. The sample was thoroughly washed with water for removing dirt and then sun dried for 3 days, and thoroughly grinded into powder the powder was stored in an air-tight container and no extra chemical treatment was required.

Stock solution: About 100 mg of potassium dichromate (Bio Rad) was dissolved in 100 ml of deionized water for preparation of the stock solution, which was further diluted for experiments as per required concentrations. Different pH values for the experiment were obtained by using 1 N HCl/ 1 N NaOH.

Batch process and optimization: Dilution of stock solution was done to obtain different concentrations (10-100 µg ml⁻¹) of standard test solution (Cr VI). Batch process was carried out using 250 ml of flask containing 50 ml of standard test solution at an agitation speed of 150 rpm in orbital shaker and biosorbent was added with desired quantity (0.2-1 g). To obtain the optimum parameters for biosorption process, an experimental study was done by varying one parameter at a time while keeping another parameter constant and this method was followed to obtain each optimum parameter.

Test solution was measured at different time interval to find the residual concentration of chromium ions until the reaction reached an equilibrium point. Using Whatmann filter paper, biosorbent was filtered after which it was centrifuged at 7000 rpm for 10 min and the filtrate was measured using atomic absorption spectroscopy to analyze the chromium concentration. Under similar conditions, blank studies were carried out.

Characterization studies : The adsorbent was characterized before and after treatment using FTIR and SEM to study the functional sites and surface topography.

Results and Discussion

Phytochemical Analysis: Phytochemical analysis of *Chaetomorpha antennina* showed the presence of carbohydrates, alkaloids, quinones, triterpenoids, coumarins and flavonoids (Thanigaivel *et al.*, 2014; Subathraa and Poonguzhali, 2013).

Biosorption is a surface phenomenon where pH acts an important parameter in binding of ionic form heavy metals onto the surface of adsorbent (Mishra *et al.*, 2015). The experimental study was carried out to find the optimal pH for removal of chromium VI (Cr (VI)) ions from aqueous solution. Mahajan *et al.* (2011) suggested that precipitation of Cr (VI) ions occur at higher pH due to negative charge on the overall surface of biosorbent decreases the biosorption of Cr ions.

The results depicted in Fig. 1A gives a clear information that Cr (VI) ions were adsorbed at lower pH 1-3 and adsorption decreased as the pH range increased. Optimum pH was found to

Fig. 1: Effect of (A) varying pH; (B) biosorbent dosage; (C) various concentration of metal ion and (D) different contact time on the percentage removal of chromium.

Fig. 2 : Equilibrium Modeling: (A) Langmuir isotherm; (B) Freundlich isotherm.

Fig. 3 : Kinetic models: (A) Pseudo-first order kinetics; (B) Pseudo-first order kinetics.

Fig. 4 : (A) FTIR analysis before treatment; (B) FTIR analysis after treatment.

Fig. 5 : (A) Scanning Electron Microscope image at 501x magnification before adsorption; (B) Scanning Electron Microscope image at 2.49x magnification before adsorption.

Fig. 6: (A) Scanning Electron Microscope result after adsorption at magnification level of 1 kx; (B) Scanning Electron Microscope result for after adsorption at magnification level of 5kx.

be at 1 and was used as the optimum value for further experimental studies. The chemistry behind the positively charged surface of biosorbent is due to protonation occurring at lower pH values, which makes easy binding of Cr (VI) anions to surface functional groups of biosorbent, and biosorption increases at lower pH due to higher protonation on the surface of biosorbent.

Biosorption of Cr (VI) decreases as pH value increases, due to decrease in the hydrogen ion concentration. As a result, chromium ions with a negative charge are prevented from binding to biosorbent having negatively charged surface, with that biosorption decreases (Pehlivan *et al.*, 2012).

Effect of biosorbent dosage experiment was carried out at varying dosages (0.2-1g) at optimum values which were already carried out with chromium concentration of $60 \mu\text{g ml}^{-1}$. Results shown in Fig. 1B indicate that biosorption of Cr (VI) increased at higher concentration and it was found out that 0.8 and 1 g values showed better biosorption rate upto 82 %.

The effect of different metal ion concentration was conducted at varying concentration from 20-100 $\mu\text{g ml}^{-1}$. As shown in figure (Fig. 1C) the biosorption increased at lower concentration like $20 \mu\text{g ml}^{-1}$, $40 \mu\text{g ml}^{-1}$ and $60 \mu\text{g ml}^{-1}$. Metal ions increased concentration have greater chances to collide with functional sites present on biosorbent giving the Cr (VI) required thrust to overcome the resistant between the aqueous phase and solid phase during the mass transfer (Baral *et al.*, 2006).

Effect of contact time (Fig. 1D) was carried out in the range of 10-100 min. Initially there was a rapid increase in adsorption which decreases after 60 minutes due to unavailability of active sites.

After biosorbent dosage, pH and initial concentration were optimized, a study was conducted to correlate the results observed in a forementioned parameters. About 83 % removal of Cr ions were removed at a pH of 1, concentration of $60 \mu\text{g ml}^{-1}$, bioadsorbent dosage of 0.8 g and contact time of 30 min.

The Langmuir isotherm can be represents as follows:

$$1/q_e = 1/Q_0 + 1/Q_0 K_L C_e \quad (1)$$

Where q_e is the amount of metal adsorbed per gram of the adsorbate at equilibrium (mg g^{-1}), Q_0 is the maximum monolayer coverage capacity (mg g^{-1}), K_L is the Langmuir isotherm constants (l mg^{-1}) and C_e is the equilibrium concentration of the adsorbate (mg l^{-1}). The values of Q_0 and K_L were computed from the slopes and intercepts of Langmuir plot of $1/q_e$ Vs $1/C_e$ as shown in Fig. 2A.

Freundlich adsorption isotherm is tested to check the affinity between adsorbate and adsorbent. The linearized equation of Freundlich isotherm is represented as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (2)$$

where, K_f is the Freundlich isotherm (mg g^{-1}), n is the adsorption intensity, C_e is the equilibrium concentration of the adsorbate (mg l^{-1}), q_e is the amount of metal adsorbed per gram of adsorbate at equilibrium (mg g^{-1}). The constant K_f is an indicator of adsorption capacity, while $1/n$ is a function of strength of adsorption in adsorption process which was found by linear plot as shown in (Fig. 2B)

The slightly higher in R_2 value for Langmuir compared with Freundlich isotherm models indicated the perfect fit of Langmuir isotherm model.

The kinetics mechanism involved in Cr (VI) ion adsorption was investigated using kinetic models such as first-order and pseudo second-order. The model with relatively higher R_2 values describes the kinetics of Cr(VI) ion adsorption successfully. Firstly, the simple first-order rate kinetics given as follows:

$$\log C_e = k_1 / 2.303 t + \log C_0 \quad (3)$$

where, C_0 and C_e are the concentration of metal ion at initial and at time t (mg l^{-1}) respectively, and k_1 is the first order rate constant ($1/\text{min}$). (Fig. 3A) depicts the plot of $\log C_e$ vs. t for constant initial concentration of metal ions from which the rate constant and correlation coefficient were obtained. The deviation in theoretical data indicates the failure in expressing the adsorption process by the simple first order kinetics. The pseudo-second order kinetics was determined as follows:

$$t/q_e = 1/k_2 q_0^2 + t/q_0 \quad (4)$$

Where, k_2 is the rate constant of second order adsorption (g/mg min). The plot of t/q_e against t (Fig. 3B) is a linear fit and also on comparison, highest R_2 value of 0.993 was observed which jointly suggests the applicability of this kinetic model for the system. It can be confirmed that the Cr (VI) ion adsorption process follows the pseudo-second order kinetics.

Fourier Transform Infrared spectroscopy revealed functional sites like hydroxyl, carbonyl, carboxyl, amine, amide and ether groups present on biosorbent before and after treatment. Presence of carboxylic group was confirmed by OH and carbonyl groups present at around 3400 cm^{-1} and 1600 cm^{-1} . Biosorption was assumed to take place due to smaller shift in the range of peak indicating the involvement of NH, OH, C=O groups towards the binding of metal ions in aqueous solution.

Biosorption process was found to be dependent on certain parameters like pH, adsorbent dosage, initial concentration and contact time. Maximum removal of chromium ions occurred at the pH 1 due to protonation of anionic Cr (VI) ions onto the surface functional sites of biosorbent resulted in better adsorption by *Chaetomorpha antennina* (Mishra *et al.*, 2015). Initial concentration was a factor for the time taken by biosorbent for adsorption of Cr (VI) ions. Similarly, the adsorption rate decreased as initial concentration increased. After optimal

parameters were found, 83% of chromium ions were removed at pH 1 with a contact time of 30 min having $60 \mu\text{g ml}^{-1}$ as the initial concentration. Characterization studies like FTIR revealed certain functional groups like hydroxyl, amine, amide, carboxyl and carbonyl groups present on biosorbent which were assumed to be responsible for biosorption. SEM images before and after biosorption showed the clear image of metal uptake by the *Chaetomorpha antennina*. The experimental results obtained from the batch process studies of green algae *Chaetomorpha antennina* provided fundamental information about the biosorption properties of *Chaetomorpha antennina* sp., and can be used as efficient and eco-friendly biosorbent.

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