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BIOSORPTION OF CHROMIUM (III) BY CHLOROPHYTE AND RHODOPHYTE

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ABSTRACT

Chromium, which promises to be an effective dye fastener in leather industries, poses serious ill effects on human health and on the environment. Studies reveal that compounds chromium (VI) is carcinogenic and chromium (III) is hazardous as well. Though many algae have been in use as biomass, not much focus has been made on the chlorophyte, Ulva fasciata and on the rohodophyte, Hypnea valentiae. Therefore the present study was designed on the chromium (III) biosorption ability of the above said algae. The parameters namely biomass size, metal concentration, pH, temperature and agitation conditions were optimized. The equilibrium data were fit using Langmuir and Freundlich isoltherm models. The results indicated the possibility of developing U. fasciate and H. valentiae as potential adsorbents of chromium ions in taniing and other industries.

KEY WORDS

Algae, biomass, biosorption, chromium, Langmuir isotherm

1.0 INTRODUCTION

Large amounts of chromium are introduced into the environment through various industries like dyeing and printing in textile industries, chemical manufacture, leather tannery, metal plating, and processing industrial effluents affected living cells. Chromium exists in two oxidation states, Cr (III) and Cr (VI). The hexavalent form is 500 times more toxic than the trivalent form[1]. Although Cr is an essential trace metal ion for living organisms, its elevated level is considered as mutagenic and carcinogenic[2]. Among the two forms, Cr (VI) is highly toxic and is high priority pollutant. Not only the toxicity of Cr but also its aqueous concentration and its mobility in different geologic environments are dependent on its oxidation state[3].

Cr (VI) may be converted to Cr (III) under reduced environment, which is much less toxic and less soluble by several microorganisms which possess chromate reductase and thus reduction by these enzymes affords a means of chromate bioremediation[4]. Chemical precipitation methods are commonly employed for the removal of chromium but this leads to formation of chrome-bearing solid wastes plus the fact that it is uneconomical when the concentration of the chromium in the effluent is low[5]. Studies of the biosorption of Cr by live and dead microorganisms have recently gained momentum[6]. Among the most promising types of biosorbents studied is the algal biomass. These algae possess a high metal-binding capacity because of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding sites for metals[7].

Aqueous batch experiments were carried out to optimize biosorption of Cr (III) onto *Hypnea valentiae* and *Ulva fasciata*. For a better understanding of the kinetics of biosorption for a preset concentration of Cr (VI), parameters namely sorbent dosages (w), pH, temperature (T) and agitation speed were varied. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm models.

2.0 MATERIALS AND METHODS

2.1. Preparation of biomass and Cr (III) Solution

The algae *Hypnea valentiae* and *Ulva fasciata* were collected from the coast of Kanyakumari, Tamil Nadu, India and beach dried. They were washed with 0.2 M H_2SO_4, rinsed with distilled water and dried in sunlight for 10 days, powdered in the range of 500–700 µm particle size and used as sorbents. Pretreatment of

the adsorbent was done by autoclaving the biomass for 15 min at 121˚C at 15 psi.

Basic chromium sulphate (BCS) solution of various concentrations namely 10, 50, 100, 250 and 500 ppm prepared from stock solution of 1000 ppm were used for the study. Desired pH was obtained using dilute HCl and NaOH.

2.3. Optimization of various parameters for chromium (III) absorption

Batch experiments using 100 ml Erlenmeyer flasks containing 50 ml of chromium solutions of varying concentration were used in the study. The parameters namely amount of biomass, pH, temperature and agitation rate were optimized. A control of 50 ml chromium solution was maintained in all the batch sorption studies. All the experiments were performed in triplicates.

To optimize the amount of biomass for chromium (III) sorption, various amount of biomass viz., 0.1, 0.25, 0.5, 0.75 and 1.0 g were added to the chromium solution of different concentrations (10, 20, 50, 100, 250 and 500 ppm) of neutral pH (7.0) maintained at room temperature (25^{o}C) under stationary condition.

Optimization of pH was performed at various pH values such as 2, 3, 4, 5, 6 and 7 in different concentrations of chromium solution with optimized biomass at room temperature (25^{o}C) under stationary condition. The temperature of the biosorption study was optimized with the different concentrations of chromium solution of optimized pH value at 20, 30, 35, 40 and 45^{o}C under stationary condition. The agitation speed was optimized with different concentrations of chromium solution containing optimized biomass, of optimized pH and temperature values with different agitation conditions namely 0 (stationary), 50, 100, 150 and 250 rpm.

2.4 Chromium absorption and desorption study

Chromium absorption in different concentration of solution was studied for every parameter at 2nd, 22th, 24th and 30th hour. 10 ml of the sample was collected, centrifuged at 3000 rpm for 5 minutes. The supernatant was oxidized to yellow solution) by adding excess NaOH solution and warming with hydrogen peroxide. Chromium removal was determined by measuring the optical density of the chromate solution at 540 nm. The biomass collected was treated with small volume of 0.1 N HCl followed by excess addition of $CaCl_2$. This concentrated the adsorbed chromium thereby recovering the adsorbed chromium in to the solution.

2.5 Sorption efficiency study

The per cent of Cr sorption was calculated as follows:

C_f =Absorbance/Slope of calibration plot

Per cent sorption = $(C_0 – C_f) \times 100 / C_0$

Where, C_0 is the initial concentration of chromium (ppm)

C_f is the final concentration of chromium (ppm)

2.6 Data evaluation and kinetic studies

The chromium uptake capacity was evaluated using the Langmuir and Freundlich adsorption isotherms. The amount of metal adsorbed by biomass was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q= (C_i – C_f) \times V / M$$

Where Q is the metal uptake (mg / g)

C_i and C_f are the initial and final metal concentrations in the solution (g / ml) respectively

V is the solution volume (ml) and

M is the mass of biosorbent (g)

Langmuir isotherm model

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following linearized equation was used to model the adsorption isotherm:

$$1/Q = 1/Q_{max} + 1/b\ Q_{max}\ C_f$$

Where, Q = mg of metal uptake per gram of the biosorbent material (mg/g)

Q_{max} = mg of maximum metal uptake per gram of the biosorbent material (mg/g)

C_f = Equiblirium / residual metal concentration in solution (g/ml)

b = Langmuir equilibrium constant (L/mg) which is the ratio of adsorption and desorption rates

Freundlich Isotherm model

The Freundlish model was linearized as

$$\ln Q = \ln K + 1/n \ln C_f$$

Where, C_f = final concentration (mg/L)

Q = amount of metal ion adsorbed (mg/g) and

K and n = constants

A graph of ln C_f Vs lnQ was plotted and fron the solpe and intercept, the values of K and n were calculated.

3.0 RESULTS

Each of the microbial species has a tolerance of ecological minimums and maximums with regard to various conditions such as pH, temperature, dissolved oxygen levels and nutrient levels[8]. Hence the present study examined the impact of conditions such as pH, temperature, amount of mass and agitation rate on chromium absorption.

The kinetic study on chromium sorption by *H. valentiae* and *U. fasciata* at different time intervals showed linear increase in sorption with increase in time and the concentration (Figure 1 & 2). The difference in the sorption between 2 and 30 hrs were calculated to be on an average 95% and 91% for *H. valentiae* and *U. fasciata* respectively. The sorption was observed to be 15 folds more after 22 hrs than at 2 hrs. Both the algal biomass demonstrated maximal sorption after 30 hrs at 500 ppm of BCS. This ensures that the binding sites of the algae were saturated with the substrate at 500 rpm and could remove maximum metal from the solution.

The sorption when studied with varying amount of mass, *H. valentiae* showed more percent sorption than *U. fasciata*. With various pH values, the chromium absorption was more by *H. valentiae* than *U. fasciata.* Maximum removal was exhibited at pH 5 by both the algae.

Temperature affected the chromium sorption by both *H. valentiae* and *U. fasciata*. It was evident that chromium sorption ability of the algae increased linearly with increase in temperature. The sorption by *H. valentiae* was found to be maximum at both 30 and 35˚C. The sorption by *U. fasciata* displayed maximaum sorption at 35˚C with least sorption at 20˚C. The sorption was more by *H. valentiae* than by *U. fasciata*. *H. valentiae* exhibited more percent sorption than *U. fasciata*.

With different agitation conditions, both algal biomass displayed maximum sorption at 250 rpm. *H. valentiae* had 4% more sorption than the stationary condition while *U. fasciata* showed 14% more sorption at 250 rpm than at stationary condition. Agitation presumably ensures proper exposure of metal-sequestering sites and facilitates the interaction of these groups with the ions of chromium. The sorption by *H. valentiae* did not show any difference between stationary and agitation (50 rpm) condition while there was 9% increase in sorption by *U. fasciata.* Otomo et al., [3] indicated that the Cr concentration decreased with shaking time.

4.0 DISCUSSION

The percentage adsorption of Cr (III) increased as pH is increased from 2 to 5 with the maximum occurring at pH 5 and declined beyond that[9]. Parameswari et al[10]., studied the effect of pretreatment of Blue Green Algal (BGA) biomasses like *Anabaena variabilis, Aulosira sp, Nostoc muscorum, Oscillatoria* sp and *Westiellopsis sp*. on the Cr (VI) and Ni (II) biosorption capacity under single and binary metal conditions. The maximum metal removal efficiency was observed under autoclaved biomass followed by acetic acid treatment while the oven dried biomass and NaOH treated cells adsorbed least amount of metal.

Oninla[11] reported maximum adsorption of Cr (III) on *Basella alba* biomass within 6 minutes of agitation after which a decrease in metal uptake was noticed until equilibrium was reached after 10 minutes. Rajasimman and Murugaiyan[12] determined the optimum conditions for the maximum biosorption of chromium by *H. valentiae* to be pH – 2.8, temperature – 48.2^{o}C, sorbent dosage – 5.3 g/L, metal concentration – 103 mg/L and contact time – 27 min. At these optimized conditions the maximum removal was found to be 94.5%. Autoclaved biomass of *Spirlogyra* (89.91%) and *Nostoc* (91.73%) exhibhited the maximum absorption compared with acetic acid treated, NaOH treated and oven dried biomass[13].

Das[14] carried out the biosorption experiment using dried biomass powder of cyanobacteria *Oscillatoria laete-virens*. Adsorption of Cr (VI) was optimum at pH 5.0 within the first 60-75 min. Adsorption strongly supported to the pseudo second-order kinetics. Langmuir model gave a better fit with an R-Squared value of 0.967 (closer to unity than that of Freundlich), Langmuir constant, KL of 0.0188 and monolayer adsorption capacity, qm of 32.26 whereas the R-squared value for the Freundlich plot was 0.948 with adsorption capacity K_f and adsorption intensity, n of 1.156 and 1.146 respectively[9].

5.0 CONCLUSION

The present study could confirm the chromium removal ability of *H. valentiae* and *U. fasciata.* The chromium removal ability of *H. valentiae* edged over *U. fasciata* in all the conditions of reaction medium, indicating that it can be used as a better biosorbent for chromium removal in order to reduce the pollution load of the environment.

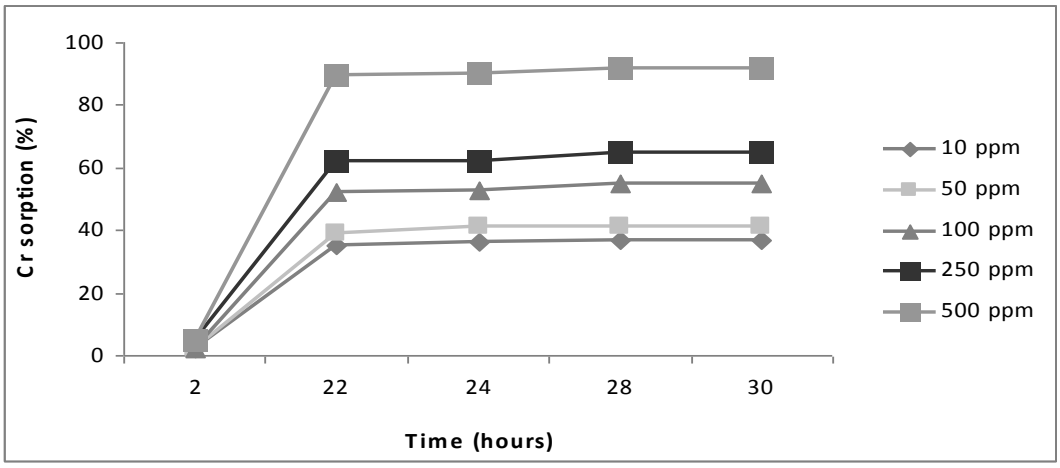

Figure 1. Kinetic chart for *H.valentiae*

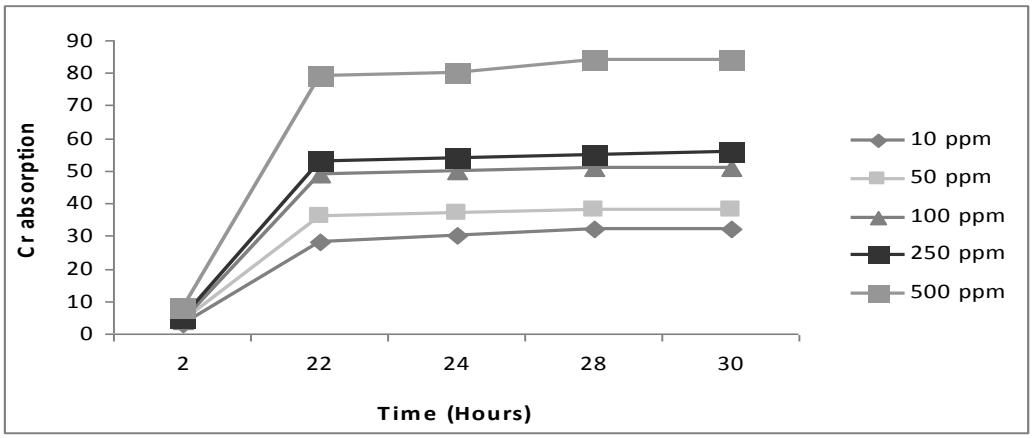

Figure 2. Kinetic chart for *U. fasciata*

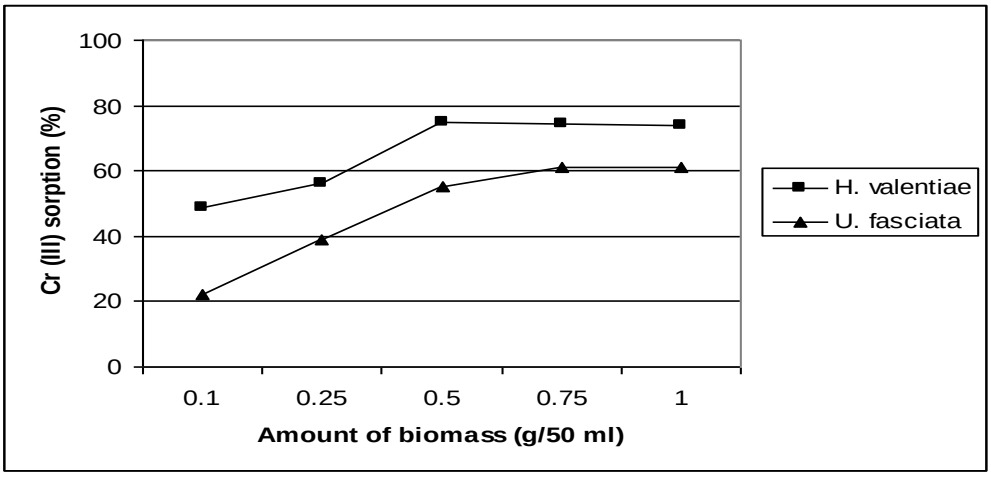

Figure 3. Mass optimization for (a) *H.valentiae* and (b) *U. fasciata*

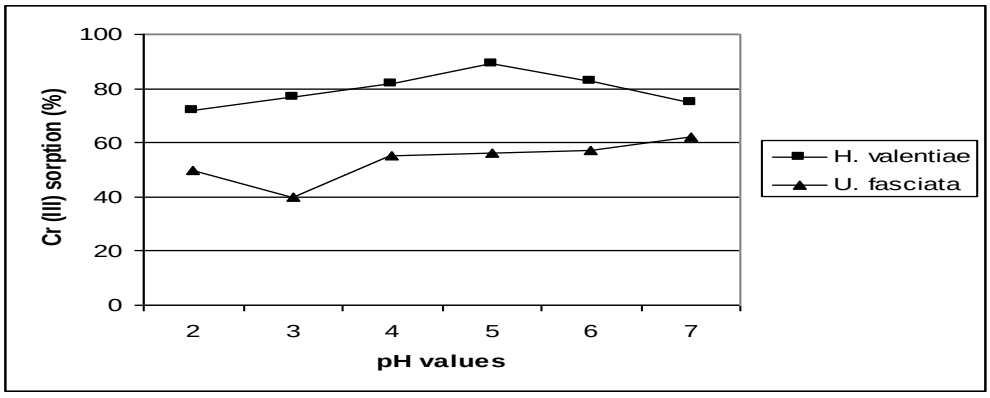

Figure 4. pH value optimization for Cr (III) absorption by (a) *H.valentiae* and (b) *U. fasciata*

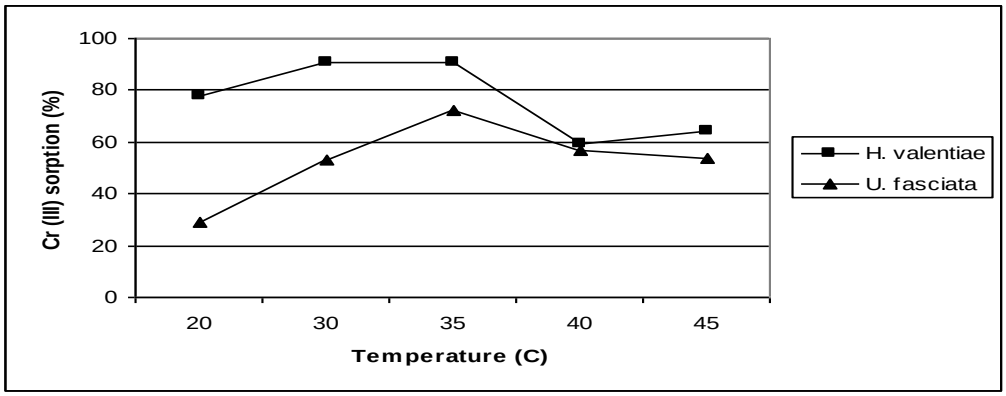

Figure 5. Temperature optimization for Cr (III) absorption by *H.valentiae* and *U. fasciata*

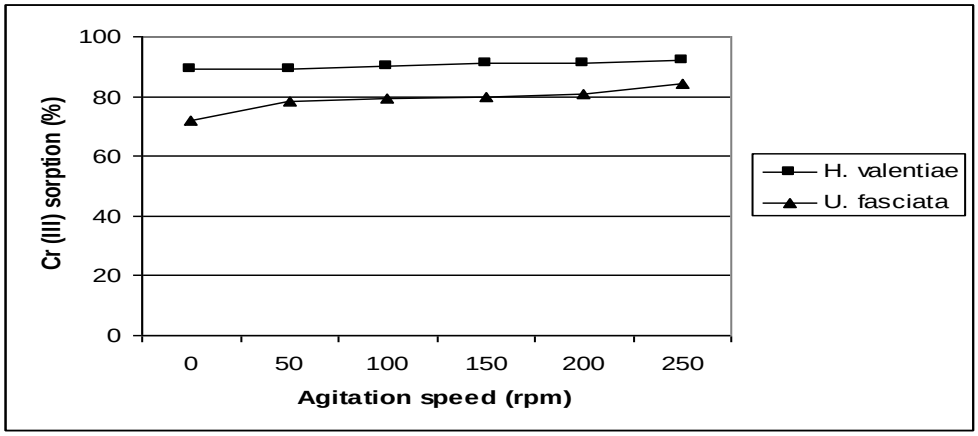

Figure 6. Effect of agitation for Cr (III) absorption by *H.valentiae* and *U. fasciata*

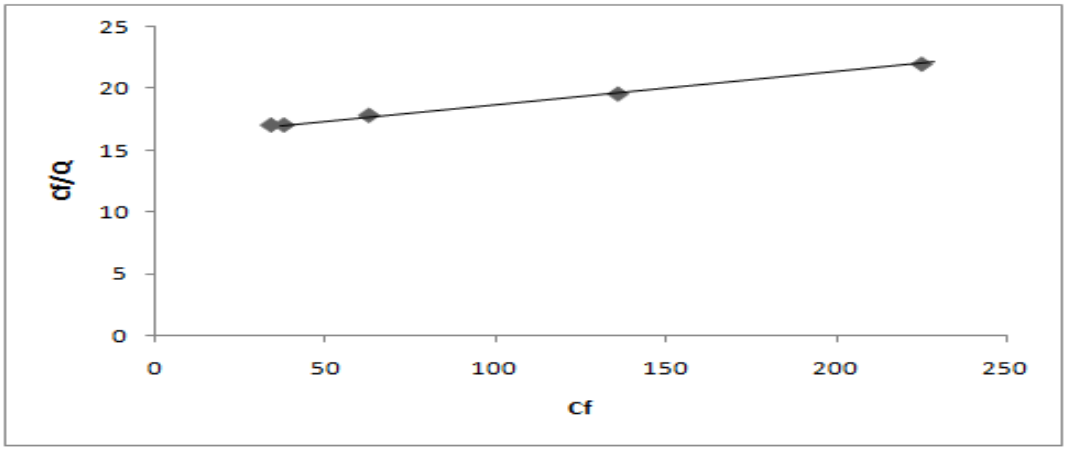

Figure 7. Langmuir model for Cr (III) absorption by *H. valentiae*

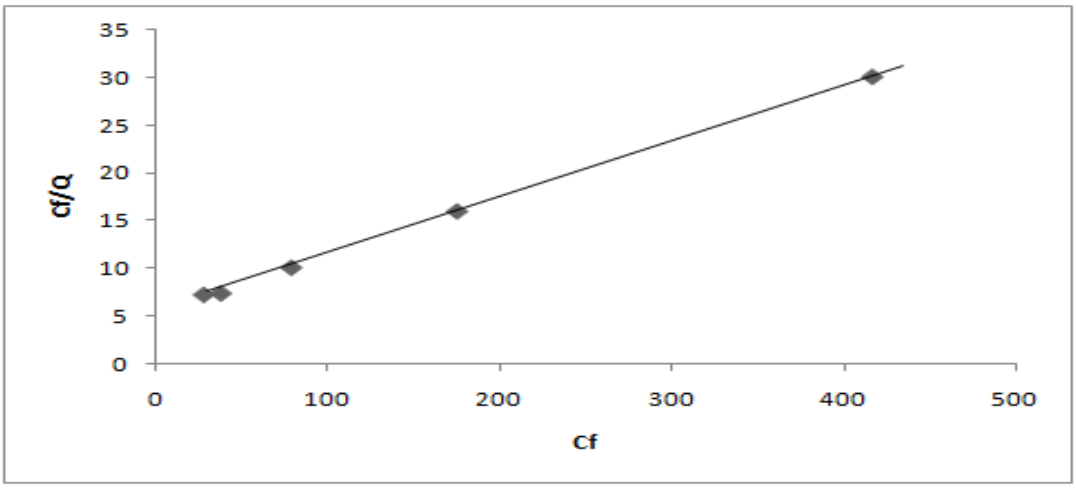

Figure 8. Langmuir model for Cr (III) absorption by *U. fasciata*

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