



BIOSORPTION OF CHROMIUM VI BY UBIQUITOUS *DICTYOTA* BIOMASS

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ABSTRACT

The possibility of utilizing *Dictyota dichotoma* biomass for biosorption of toxic hexavalent Chromium VI was investigated at various pH ranges. The binding rate of Chromium metal at sequestering sites was very rapid at the initial stage of sorption process and reached equilibrium after 165 min in the agitation time experiment. The removal of Chromium was increased with the increasing dosage of adsorbing agent. The adsorption also increased at acidic pH ranges than at neutral or alkaline adsorbate. As the biomass concentration decreases, the percent biosorption also reduces over a period of contact time if the pH experiments.

KEY WORDS

Cyanobacteria, Tolypothrix nodosa, Tolypothrix tenuis, Organic solvent extracts, fungal strains, antifungal activity and zone of inhibition

1. INTRODUCTION

Hexavalent Chromium is extensively used in various industries like paint, pigment, leather tanning, electroplating, glass ceramic, textile dyeing and photography. These industrial effluents have concentrated chromium much more than biota required quantity. Therefore, removal of chromium ions is essential from such effluents before discharging into main stream of water. Conventional pollution treatment technologies like precipitation, coagulation, ion exchange, ultrafiltration, electrodialysis, reverse osmosis and adsorption etc. (Beszeditis, 1983; Dean *et.al.*, 1972) are less effective and require high capita cost and recurring expenses.

A search for effective, economic and environmental friendly adsorbent material has been started by biotechnologist. Several low-cost materials from biological and non- biological sources like seaweeds, fungi bacteria, tea bark, wood charcoal, peanut skin, onion skin and saw dust have been studied for

adsorption of chromium (Kapoor and Viraraghavan, 1995; Sujana *et.al.*, 1997). Seaweeds are the best material for biosorption because their macroscopic structures offer a convenient basis for the production of biosorbent particles suitable for sorption process. (Figueira *et.al.*, 2000; Volesky and Holan, 1995; Volesky *et.al.*, 1999 and Yang and Volesky, 1999). Brown marine kelp tends particularly to sequester heavy metals (Schiewer and Volesky, 2000; Volesky and Holan, 1995). Alginate in the cell wall of brown alga *Dictyota* is the main component responsible for the metal sorption (Fourest and Volesky, 1997). It is present in the gel form which appears very porous and easily permeable to small ionic species (Dodge, 1973; Percival and Mc Dowell, 1967). Apart from its abundance and metal sequestering capacity. *Dictyota* biomass is suitable for biosorption because its polysaccharide content is not easily leached out. (Vieira and Volesky, 2000). Hence, in the present study, we have investigated the possibility of utilization of *Dictyota dichotoma* biomass as the bio

sorbent under laboratory condition for removal of chromium.

2. MATERIALS AND METHODS:

The brown alga *Dictyota dichotoma*, the most common seaweed available abundantly at Valinokkam coast was collected from intertidal and subtidal region upto 100 m depth situated on the south east coast of Tamil Nadu (78°.08' E and 9° 17' N) in between Palk Bay and gulf of Mannar in the north and south side.

2.1. Preparation of different concentration of Chromium solution

From the Potassium chromate stock solution, different concentrations ranging from 10,20,30,40 and 50 ppm were prepared and stored in refrigerator for further experiments.

2.2. Analytical procedure

Quantitative analysis of Cr (VI): (Sheno Merrin *et al.* 1998). To a suitable aliquot of sample, 2 ml of 1 M Sulphuric acid, 1 drop of Phosphoric acid and 1 ml of Diphenyl carbozide solution (0.5 % in acetone) were added and made up to 10 ml with distilled water. After 5 minutes, the absorbance of test solution was measured at 540 nm against the reagent blank.

2.3. Effect of agitation time on removal of Cr (VI)

To determine the agitation time, various concentrations of metal ions were taken in conical flasks. To these solutions 1 g of freshly collected chopped *Dictyota dichotoma* (adsorbent) was added and agitated on a rotary shaker at 120 rpm at room temperature (27 ± 2°C). The flasks were withdrawn at predetermined time intervals for quantitative analysis of Cr(VI).

2.4. Effect of adsorbent dosage on removal of Cr (VI)

The metal ion solutions were agitated with various concentrations of adsorbent dosage (0.5 - 2 g / 50 ml of *Dictyota dichotoma*) at 120 rpm at room temperature for the equilibrium period. After the equilibrium period, the adsorbent and adsorbent were separated, and the amount of metal ion adsorbed was determined as stated above. A graph was plotted with adsorbent dosage vs percent metal ion removal.

2.5. Effect of pH on removal of Cr (VI)

The metal ion solutions were adjusted to various pH levels (2.0, 4.0, 6.0, 8.0 and 10.0). After adjusting the pH, the adsorbate was agitated with optimum concentration of adsorbent (*Dictyota dichotoma*) for equilibrium period. The amount of metal ion adsorbed was calculated as stated above. The optimum pH was

determined from the plot drawn with pH against percent metal ion removal.

$$\% \text{ removal} = \frac{\text{O.D. of UT} - \text{O.D. of T}}{\text{O.D.}} \times 100$$

3. RESULTS AND DISCUSSION

Chromium exists in trivalent and hexavalent forms. Hexavalent Chromium is more toxic to animals and human beings (Verma and Rahal.1964). Biosorption of Chromium (VI) was studied by using *Dictyota dichotoma* at various pH ranges (0.5 to 2). A standard Chromium adsorption pattern was observed in all experiments. Similar biosorption work in other organisms was carried out by Garnham *et al.* (1993) in cyanobacteria and microalgae, Leusch *et. al.*, (1995) in marine algae and Tobin *et al.* (1994) in fungi. In the agitation time experiment, the rate of chromium sorption was very rapid during the initial stage of the sorption process (15-135 min). The adsorption of chromium starts at 15 minutes, then it gradually increases.

At 10 and 40 ppm levels, adsorption shows positive results, while in 20 ppm it is negative, but in 30 and 50 ppm levels, it is neutral. However, in 50 ppm concentration there was no further adsorption percentage. Uptake capacity was increased gradually with time and reached equilibrium after about 165 min. (Fig.1). Similar results were observed by Sheno Merrin *et al.* (1998). Maximum amount of chromium uptake was observed only at initial period of 6 hours contact time (9.02 mg/g). Increase in contact time beyond 6 to 24 hrs did not improve the uptake capacity of biomass and noticed a rapid adsorption phenomenon. Ariff *et al.* (1999) also showed that the rate of lead sorption was very rapid during the initial stages of the sorption process (0-20 min) in powdered *Rhizopus oligosporus* and reached equilibrium after 840 min.

In the adsorbent dosage experiment, the removal of chromium was increasing with the increasing dosage of adsorbing agent. The adsorbent dosage (*Dictyota dichotoma*) on removal of chromium was higher in 20 ppm when comparable with 10 ppm level. Similarly, the adsorbent dosage was also increased at 30 ppm level. However, in 40 & 50 ppm levels, a rapid increase was noted with 0.5 -1.0g of *Dictyota dichotoma*. Then a slight increase was observed at 50 ppm concentration and no further enhancement was noticed in any concentrations tested later. (Fig. 2) Similar result observed in *Phanerochaete — Chrysosporium* by Haluk

Ceribasi and Ulku Yetis (2001), showed that the initial sorption rate, increased with increasing metal concentrations. Generally, metal with a higher initial concentration have a higher sorption capacity (Gadd, 1990; Volesk *et al* 1993). Increase in bio-adsorbent in the present study did not show corresponding increase in chromium uptake from the adsorbate by biomass. These results are in accordance with the earlier observations with *Pseudomonas*, fungal mycelial waste, *Penicillium italicum*, *Cladosporium resinae* and *Rhizopus arrhizus*. (Kapoor and Viraraghavan (1995).

In pH experiment, the effects of pH of the test solution on adsorption of chromium were plotted. The equilibrium time obtained from the agitation time experiment was utilized in pH experiments i.e. at 10 and 20 ppm the equilibrium time was 135 min, and at 30 ppm the equilibrium time was 150 min, at 40 and 50 ppm levels employed, the equilibrium time was 165 min. In 20, 30, 40 and 50 ppm levels, the adsorption was increased only at acidic pH ranges (pH 2.0 to 4.) when compared with the neutral as well as at the alkaline pH ranges (Fig. 3). Haluk Ceribasi and Liku Yetis (2001) also showed that the maximum initial sorption rates and capacity of Nickel and Lead were maximum at pH 4 in

Chrysosporium. Pairat Kaewsarn (2001) also pointed the sharpest increase between pH 3 and 4 in *Padina* sp. Sheno Merrin *et. al* (1998) also observed pH increase at acidic range and the adsorption capacity of biomass decreased gradually up to neutrality and then became constant suggesting that acidic pH ranges (2-4) are suitable for bio-adsorption of chromium ion in *Rhizopus arrhizus*. This result is in accordance with the present study. Prakasham *et. al* (1999) suggested that the first phase of chromium biosorption is attributed to the surface adsorption due to the action of ion exchange with the participation of the carboxyl groups of uronic acid present in cell structure which are known as metal sequestering sites (Fig. 4). Biomass concentration and biosorption percentage are directly proportional over a period of contact tie. It could be concluded that, this study provided basis for the biosorption studies with seaweed biomass, which will have an important contribution to the understanding of the biosorption mechanisms. In addition, information obtained would be useful to design economic bio sorption treatment process for effective practical application attempts to the seaweed industries.

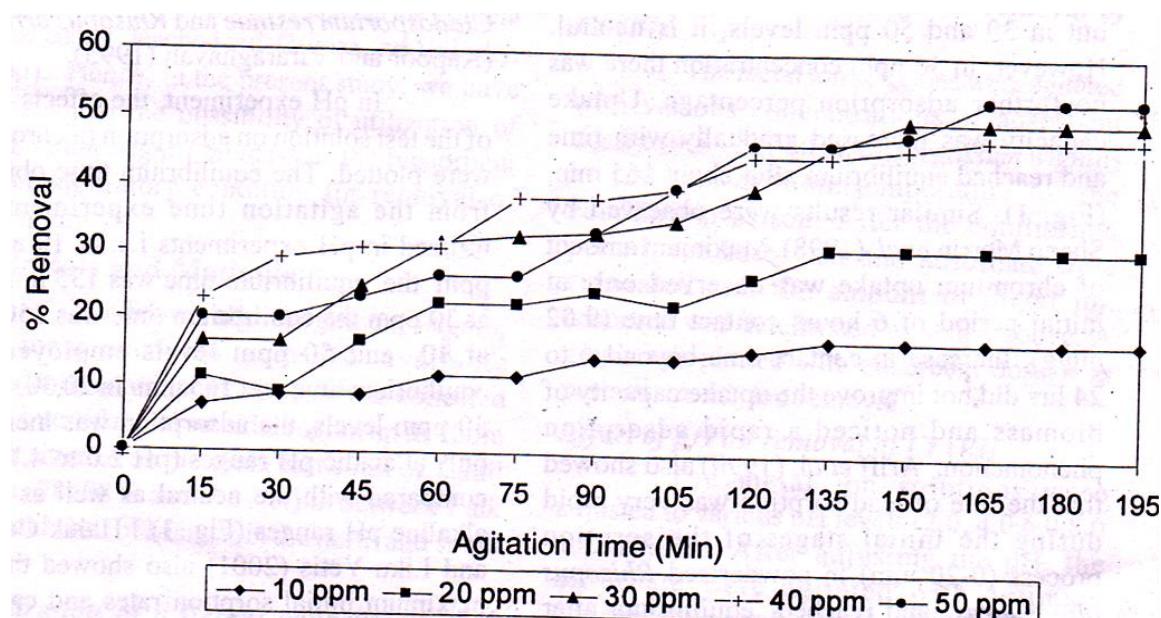


Fig 1. Effect of agitation time on adsorption of Chromium (VI) by *Dictyota dichotoma*

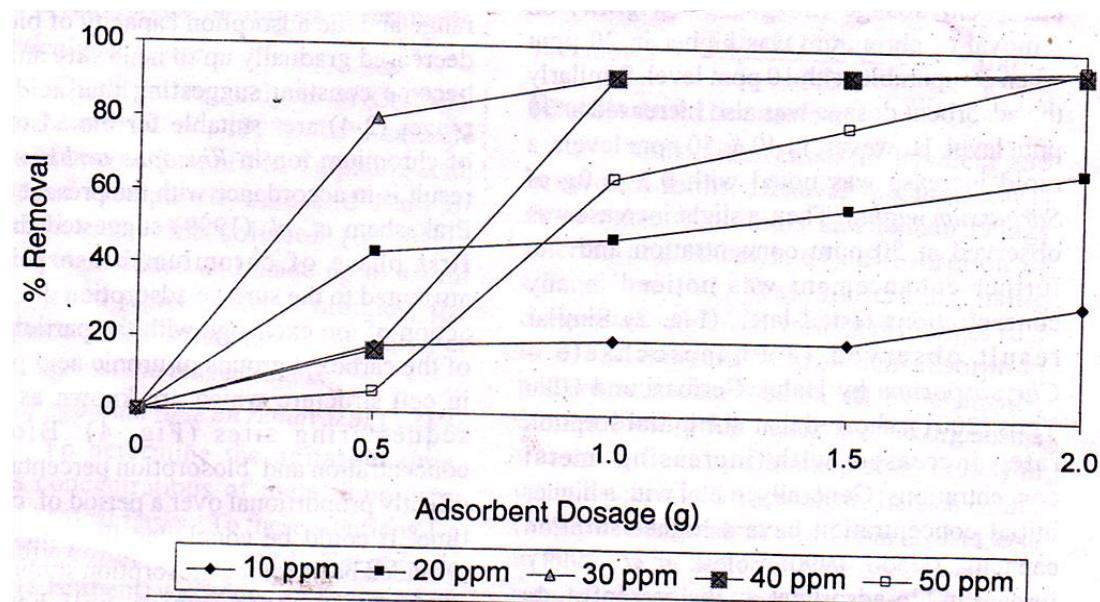
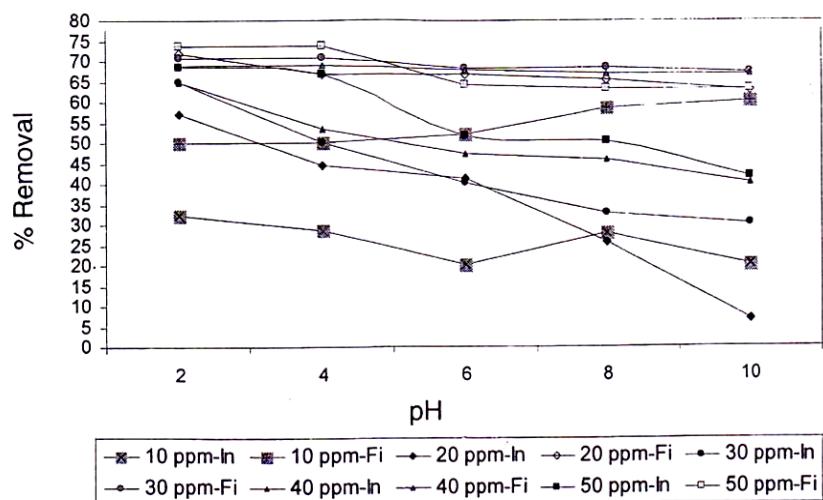
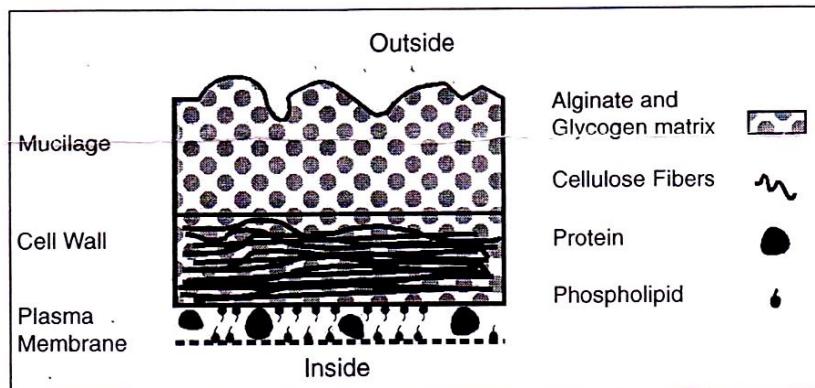


Fig 2:


 Fig 3. Effect of pH adsorption of Chromium(VI) (*Dictyota dichotoma*)

 Fig 4. Cell Wall of brown alga (*Dictyota dichotoma*)

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