

BIOSORPTION OF COPPER (II) BY BROWN SEAWEED *SARGASSUM ILICIFOLIUM* (TURNER) C. AGARDH

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ABSTRACT

The biosorption of copper (II) on *Sargassum ilicifolium* biomass was investigated. Batch biosorption experiments were conducted to determine the biosorption properties of the biomass and it was observed that the maximum capacity of copper uptake was around 47% at pH 4.5 during one hour with 1000 mg/L of initial concentration and 100mg algal material. Increased biomass 500 mg accelerated the rate of removal of metal to more than 90% at the similar pH value. Fourier transform infrared spectroscopy analysis of algal biomass revealed the presence of amino, carboxyl, hydroxyl and carbonyl group, which are responsible for biosorption of metal ions. SEM analysis revealed cross linkage between the copper ions and the organic functional groups of the biomass.

INTRODUCTION

Heavy metal pollution is one of the most important problems of this century (Park *et al.*, 2006). Conventional techniques for removing dissolved heavy metals include chemical precipitation, carbon adsorption, ion exchange, evaporation and membrane processes (Kojima and Lee, 2001). Low strength heavy metals present in waste water generally cannot be removed successfully with such methods. In recent years biosorption has emerged as a cost-effective and efficient alternative for the removal of heavy metals from low strength wastewater (Pavasant *et al.*, 2006). A number of biological materials can be used as biosorbents for effective removal and recovery of heavy metals.

Amongst various materials being used as biosorbents, "algae" is found to be the most promising one (Veglio and Beolchini, 1997). Esmaeili *et al.*, (2008) employed activated carbon prepared from *Gracilaria* and obtained more than 90% removal of Cu from waste water. Similarly use of brown seaweed *Cystoseira indica* for Cu (II) absorption from industrial effluents has been reported (Basha *et al.*, 2009). Kumar *et al.*, (2009) used green macroalgae as biosorbent for removal of cadmium, mercury and lead. Gold biosorption by brown alga *Fucus vesiculosus* has been reported (Mata *et al.*, 2009). The efficiency of *Sargassum ilicifolium* (Turner) C. Agardh which grows luxuriantly along the west coast of Maharashtra in biosorption of copper ions from aqueous solutions is reported in the present work.

MATERIALS AND METHODS

Algal collection and preparation

Fresh and mature thalli of *S. ilicifolium* were collected from

Malvan and Kunakeshwar located at latitude 16°4'59''N (16.083°) and longitude 73°30'E (73.500°) along the west coast of Maharashtra. The algal material was washed with tap water and thereafter with double distilled water thoroughly to remove epiphytes and adhering sand and dirt particles. It was then sundried for four days and then kept in oven to obtain constant weight. Dried biomass was milled and sieved through 0.212-0.025 mm and stored at room temperature in polyethylene bottles, protected from sunlight.

Metal biosorption

Experiments were performed at room temperature in 250 mL Erlenmeyer glass flask containing aqueous solution of copper sulphate (1000 mg/L). An accurately weighed 100 mg and 500 mg portion of biomass was added in different flasks maintained at different pH values using 0.1N HCl and NaOH. The samples were agitated on a rotary shaker at constant speed for 1 h, 2 h, 3 h, 4 h and 5 hrs. Controls for each concentration without the addition of heavy metal were also maintained. After the respective contact periods, the solutions were separated from the biomass by filtrations and subjected to further analysis on AAS.

Determination of copper (II)

The quantity of residual metal was determined by using atomic absorption spectrometer (Perkin Elmer analyst 300). The metal uptake was determined by using the following equation.

$$Q = V (C_i - C_f) / M$$

Where 'Q' represents the amount of metal taken per unit mass of the biomass (mg/mol g⁻¹), V is the volume of the solution (L), M the dry mass of the algae (g), C_i and C_f are the initial and final concentrations (mol m⁻³), respectively.

Ftir and sem analysis

In order to determine the probable functional groups involved in copper (II) sorption the chemical characteristics of dried *S. ilicifolium* biomass before and after copper sorption were analyzed and interpreted using FTIR Spectrometer (Perkin Elmer analyst 300). The spectra were recorded within the range of 400-4000cm⁻¹.

Surface morphology of the biosorbent was studied using scanning electron microscope (Jeol- Jsm 6360).

RESULTS AND DISCUSSION

Effect of pH on biosorption

The effect of pH is an important controlling parameter in the adsorption process (Asmal *et al.*, 1998). The effect of pH on copper biosorption by *S. ilicifolium* was studied at room temperature by varying the pH (Fig. 1). The uptake of copper (II) increased with pH from 3.5 to 4.5 and decreased thereafter. The maximum adsorption was found at pH 4.5 and during the first hour the percent uptake reached to 47% with this pH

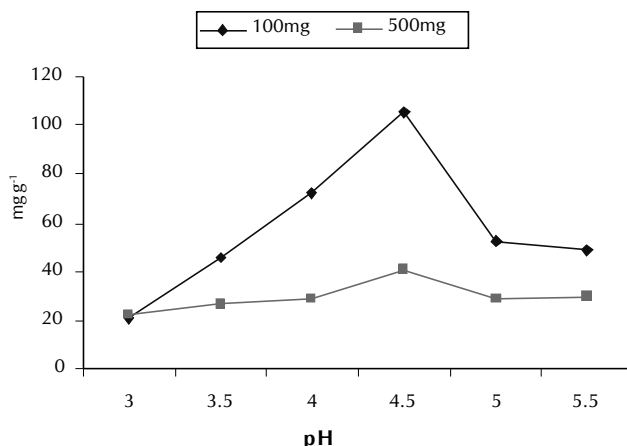


Figure 2: Effect of Biomass on the uptake of Copper (II) by *Sargassum ilicifolium*

Table 1: Effect of pH on biosorption of copper by *Sargassum ilicifolium*

pH	m mol g ⁻¹					% uptake				
	1 h	2 h	3 h	4 h	5h	1 h	2 h	3h	4h	5h
3	0.13	0.18	0.24	0.03	0.02	14.75	20.9	25.67	3.32	2.61
3.5	0.28	0.17	0.12	0.18	0.07	29.11	17.36	11.97	18	7.72
4	0.45	0.07	0.17	0.39	0.14	41.84	34.51	15.38	35.69	12.77
4.5	0.66	0.44	0.53	0.47	0.28	47.05	31.22	38.23	33.34	20.26
5	0.33	0.34	0.15	0.24	0.23	33.03	4.68	10.62	24.04	22.98
5.5	0.30	0.28	0.19	0.37	0.20	29.5	26.93	18.06	36.77	19.79

Wt of biosorbent-100 mg

Table 2: Effect of biomass dose on biosorption of copper by *Sargassum ilicifolium*

PH	100 mg		500 mg	
	m mol g ⁻¹	% uptake	m mol g ⁻¹	% uptake
j	0.13	14.75	0.14	78.55
3.5	0.28	29.11	0.16	83.81
4	0.45	41.84	0.18	83.25
4.5	0.66	47.05	0.25	90.45
5	0.33	33.03	0.18	91.38
5.5	0.30	29.5	0.18	89.01

Contact time-1 h

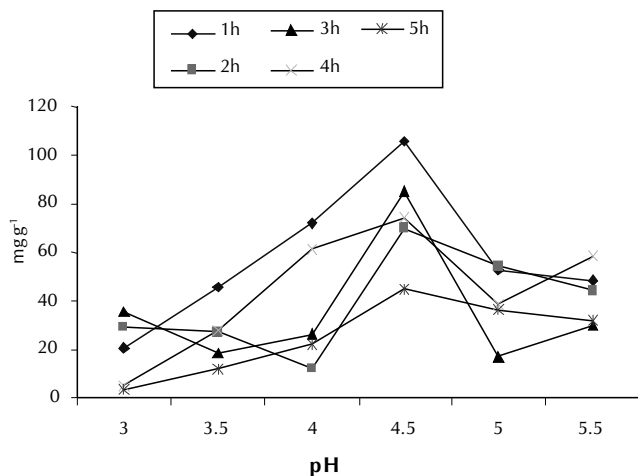


Figure 1: Effect of pH on the uptake of Copper (II) by *Sargassum ilicifolium*

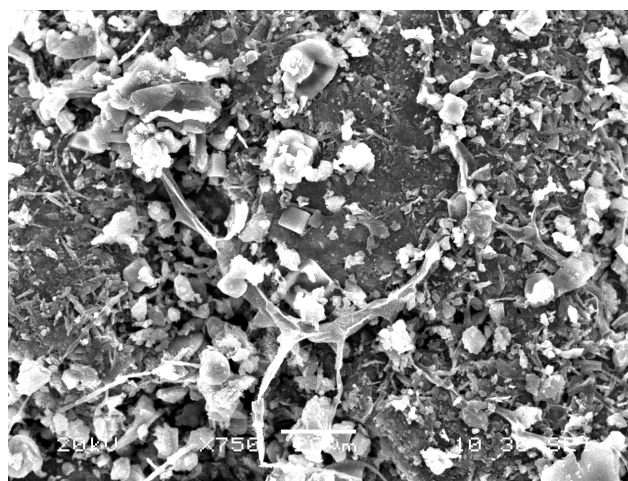


Figure 3: SEM micrograph of *Sargassum ilicifolium* biomass showing pores and irregular particles. (magnification X750)

(Table 1) and then shooted upto 90% when biomass was increased. No copper uptake was observed at pH less than 2.0 while the solutions over pH 6.0 were not used to prevent the possible precipitation of copper hydroxide as reported by Vijayaraghavan *et al.*, (2004). The lower uptake of copper at higher pH value was probably due to the formation of anionic hydroxide complexes. Because of this effect of higher pH values, legands such as carbohydrate and sulfonate group could take up fewer metal ions (Kalyani *et al.*, 2004).

Effect of biosorption time

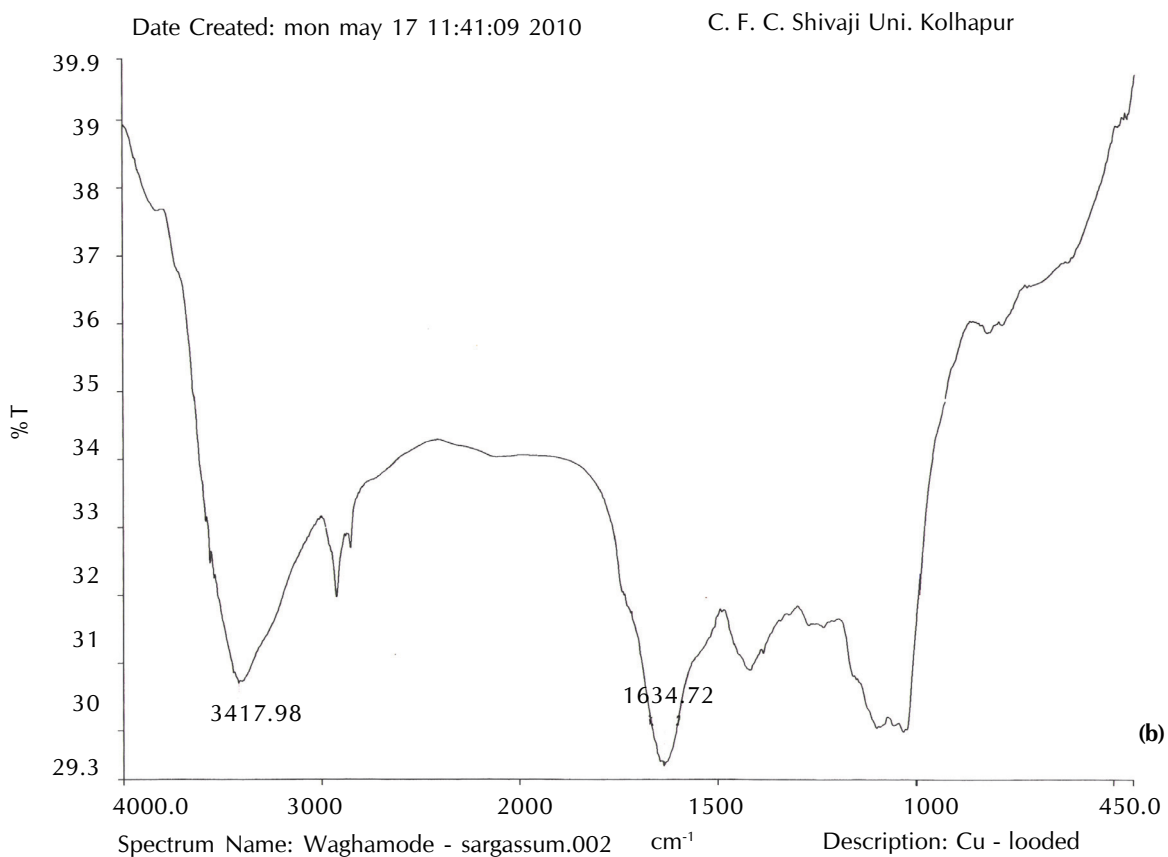
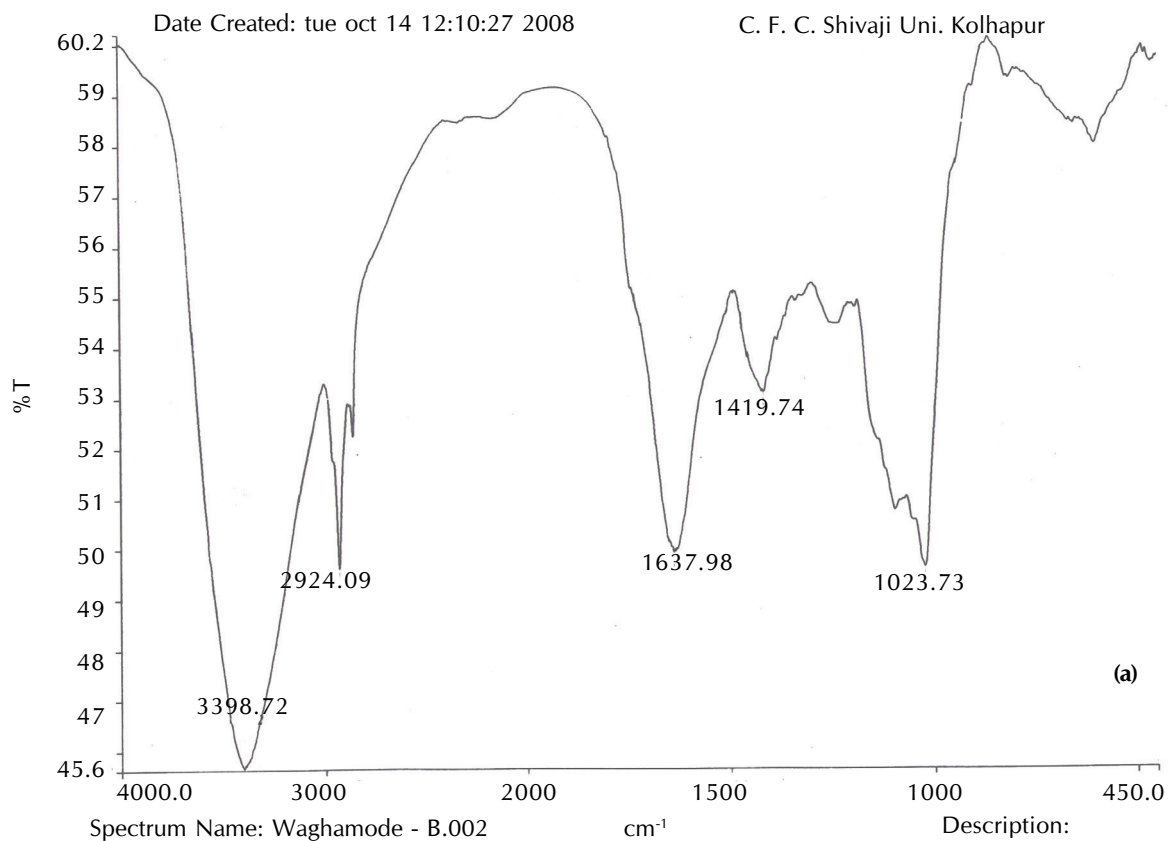


Figure 4: IR Spectra of *Sargassum ilicifolium* (a) before and (b) after Copper biosorption

The uptake of copper (II) in 1, 2, 3, 4 and 5h was recorded and found maximum in the first hr (105mg g⁻¹) and decreased thereafter (Fig. 2). A high rate of copper uptake was noticed by Hamdy (2000) in first two hours using different brown and red algae. The rate of copper uptake was 6.65 mg g⁻¹ when red algae *Palamaria palmata* was used as the adsorbent (Prasher *et al.*, 2010).

Effect of adsorbent dose on biosorption

The weight or mass of the biosorbent had a positive effect on the biosorption of copper and the use of 500 mg biosorbent showed higher uptake than 100 mg (Fig. 2). A Linear increase in metal uptake with increasing algal biomass has been reported by Hamdy (2000). Thus the biosorption capacity may depend upon the dose of the biomass due to the availability of sufficient number of binding sites.

Characterization of biosorbent

The SEM analysis of *S. ilicifolium* (Fig. 3) revealed important information on surface morphology. In these micrographs structures with large surface area were evident.

The FTIR spectrum of *S. ilicifolium* (Fig. 4) revealed the presence of amino, carboxylic, hydroxyl and carbonyl groups. In pure form of algae carboxylic bonds were present in the region 3398.72 cm⁻¹. Carboxylic/ Phenolic stretching bonds occurred in the region 2924.09 cm⁻¹. The peaks appearing in the region 1637.98 cm⁻¹ might be attributed to >c = c, > c = 0 and are characteristic of carbonyl group stretching from aldehyde and ketones. The presence of OH group along with carbonyl group confirmed the presence of carboxylic acid groups in the biosorbent. The broadening of OH peak at 3398.72 cm⁻¹ to 3417.98 cm⁻¹ and the carbonyl group peak at 1637.98 cm⁻¹ to 1634.72 cm⁻¹ was observed in the material analysed after biosorption. This indicated the involvement of hydroxyl and carbonyl groups in the biosorption of copper.

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