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Biosorption of copper by *Chaetomorpha Antennina* algae biomass – Thermodynamic studies

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ABSTRACT

A biosorbent prepared from marine algae was tested for its efficiency in removing metal ions of Copper from aqueous solutions. The sorption of these metals on *Chaetomorpha Antennina* sp. conformed to linear form of Langmuir adsorption equation. Langmuir C_m constants for each metal were found as 25.78 mg/g (Cu) at 30°C. Also, kinetic and thermodynamic parameters such as enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) were calculated and these values show that adsorption of heavy metal on *Chaetomorpha Antennina* sp.was an exothermic process and the process of adsorption was favoured at low temperatures.

KEYWORDS

Chaetomorpha Antennina sp.;
Metal ions;
Biosorption;
Thermodynamic parameters;
FTIR pattern.

INTRODUCTION

The world is running out of fresh water very fast due to water pollution. Water has become an essential commodity for the development of industries and agriculture. Its availability in abundance of right quality is necessary, for promoting better quality of life. Seas, rivers and lakes receive bulk of sewage, industrial effluents, domestic and agricultural wastes which consist of substances varying from simple nutrients to highly hazardous chemicals. Heavy metal pollution is one of the main problems. Copper is widely used in industrial metal plumbing, wiring, air-conditioning tubing, roofing etc. This metal arises from the industries of copper mining and smelting, brass and bronze manufacture, electro plating industries and excessive use of copper based agrichemicals[1]. Excessive exposure to copper and its compounds may cause health effects of digestive system, eye, kidney, liver, lung and nose[2-4]. So there is every need to treat waste water containing copper before discharging. For these reasons, removal of copper from effluent streams by indigenous biomaterials is chosen for the present study.

The major advantage of this process is very effective, simple and cheap. Biosorption rates were determined quantitatively and thermodynamic parameters like enthalpy, entropy and free energy change were evaluated to know the temperature feasibility. This information would be useful for further applications of system design in the treatment of practical waste effluents. The biosorbent characteristics, Fourier Transform Infra Red Spectroscopy is also described.

MATERIALS AND METHODS

Biosorbent material preparation

The *Chaetomorpha Antinnina* sp., used in the present study (10 kgs)was washed with deionized water ten times (20 liters at a time) to remove dirt particles. The washed *Chaetomorpha Antinnina* sp., was then completely dried in sunlight for 20 days. The resulting product was directly used as biosorbent. The dried *Chaetomorpha Antinnina* sp., was then cut into small pieces and powdered using domestic mixer. In the present study the powdered material with average particle size ranging from 75-283.5 μm were then directly used as biosorbent without any pretreatment.

RESULTS

Experiments have been done for biosorption of copper ions onto *Chaetomorpha Antennina* sp. surface, and from the studies we can achieve to the following results.

- The percentage biosorption of copper ions on *Chaetomorpha Antennina* sp decreased with in creasing temperature in the range 303-333 K.
- The thermodynamic parameters such as free energy change $\left(\Delta G^0\right)$, enthalpy change $\left(\Delta H^0\right)$ and entropy change $\left(\Delta S^0\right)$ indicated that the biosorption process is exothermic.
- The FTIR analysis of the biosorbents, *Chaetomorpha Antennina* sp and *Azadirachta Indica* bark, before and after biosorption of copper metal ions, clearly showed that the functional groups (OH, methyle and methylene, N-H bend etc.) are responsible for biosorption.

DISCUSSION

Effect of temperature

The rate of biosorption is a function of initial metal ion concentration as well as its temperature. The metal uptake of copper onto *Chaetomorpha Antennina* sp. is shown in Figure 2 as a function of the initial metal ion concentration at four different temperatures 303, 313, 323 and 333 K. The metal uptake of copper ion on *Chaetomorpha Antennina* sp. decreased from 5.4858 to 4.8927 mg/g as the temperature increased from 303 to 333K for 20 mg/L due to weakening of the binding of metal ions to the biosorbent sites favouring desorption, rather than adsorption. The convectional currents at high temperatures might lead to unstable metal ions thus affecting the binding characteristics of metal ions to the sorbent sites. Thus, the effluent streams can be effectively stripped off these metal ions at low temperatures.

Further, the decrease in the percentage biosorption at high temperature is indicative that the biosorption of copper ions onto *Chaetomorpha Antennina* sp. is exothermic in nature which was further established through thermodynamic calculations.

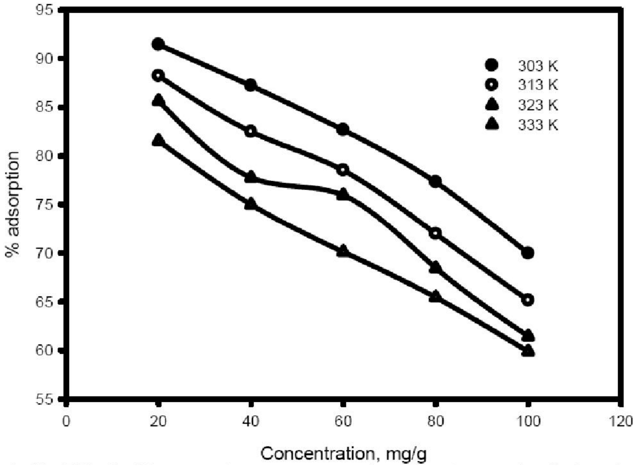

Figure 1: Effect of temperature on copper by *Chaetomorphe Antennina* sp. for 0.1g/30mL of adsorbent concentration.

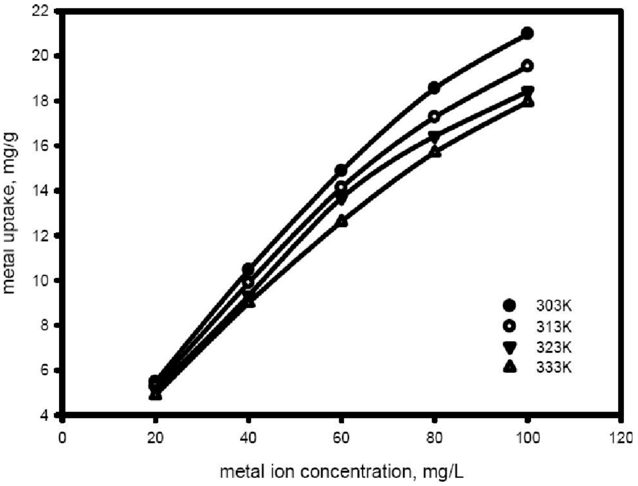

Figure 2 : Effect of temperature on biosorption of copper by *Chaetomorpha Antennina* sp. for 0.1g/30mL of biosorbent concentration.

Specific surface area

Coverage of the surface by a monolayer metal ions can be used for the calculation of the specific surface area, S according to the following equation[5,6].

$$S = \frac{Q_{max} NA}{M} \qquad (1)$$

Where S is the specific surface area, m^2/(g biosorbent); Q_{max} the monolayer sorption capacity, (g metal/g biosorbent); N the Avogadro number, 6.023x 10^{23}; A was the cross-sectional area of metal ion, m^2; M the molecular weight of metal. The molecular weight and the cross-sectional areas of copper ion was taken from the works of Ho et al[4] and Keskinkan et al[5] as 63.5, 64.5 and 1.58ú^2, 1.72 ú^2 in a closed packed monolayer respectively.

The maximum specific surface area of *Chaetomorpha Antennina* sp. towards Cu^{2+} binding was 3.863 m^2/(g biosorbent). The maximum specific surface area of tree fern and M.Spicatum for copper biosorption were reported as 1.59 and 1.56 m^2/(g biosorbent), respectively[5,6]. Comparison of the maximum specific surface area of the biosorbent for copper biosorption showed that the *Chaetomorpha Antennina* sp. has a larger surface area than that for the tree fern and M.Spicatum.

Thermodynamic studies

Thermodynamic parameters such as enthalpy change (ΔH^0), free energy change (ΔG^0) and entropy change (ΔS^0) can be estimated using equilibrium constants at varying temperatures. The free energy change of the sorption reaction is given by the following equation:

$$\Delta G^0 = -RT \ln K_a \qquad (2)$$

Where ΔG^0 is standard free energy change, J/mol; K_a is the equilibrium constant; R the universal gas constant, 8.314 J/mol K and T the absolute temperature, K. The free energy change indicates the degree of spontaneity of the biosorption process and the negative value reflects a more energetically favourable biosorption[7,8]. The equilibrium constant may be expressed in terms of enthalpy change of biosorption as a function of temperature as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^0}{RT^2} \qquad (3)$$

According to Eq.(3), the effect of temperature on the equilibrium constant is determined by the sign of . Thus when is positive, i.e., when the biosorption is endothermic, an increase in results in an increase in . Conversely, when is negative, i.e., when the biosorption is exothermic, an increase in causes a decrease in . This implies a shift of the biosorption equilibrium[9].

The integrated form of Eq.(3) becomes

$$-RT \ln K_a = \Delta H^0 - TRY \qquad (4)$$

Where is *RY*, the change with temperature of the free energy change and the equilibrium constant can be represented as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (5)$$

Eq (5) shows clearly enthalpy and entropy characterise the spontaneity of a biosorption process[10]. The free energy changes for copper biosorption onto *Chaetomorpha Antennina* sp. was determined by using the equilibrium constants obtained from Langmuir isotherm model. The and values of copper at different temperatures (303, 313, 323, 333 K) and pH (6.0) are given in TABLE 1. As seen from TABLE 1, the negative values of confirm the feasibility of the process and the spontaneous nature of sorption with a high preference of copper on the *Chaetomorpha Antennina* sp. at lower temperatures. However, the contribution of entropy was found to be even larger than the free energy of biosorption . Therefore, it can be concluded that the biosorption of copper onto *Chaetomorpha Antennina* sp. is essentially governed by entropy.

The standard enthalpy change were obtained from the plots of Figure 3 (ln K_a plotted against 1/T) as -23.544 kJ/mol for copper while the standard entropy change was determined as -93.943 kJ/mol K for copper at pH 6.0. The values of is negative, indicating that the sorption process is exothermic.

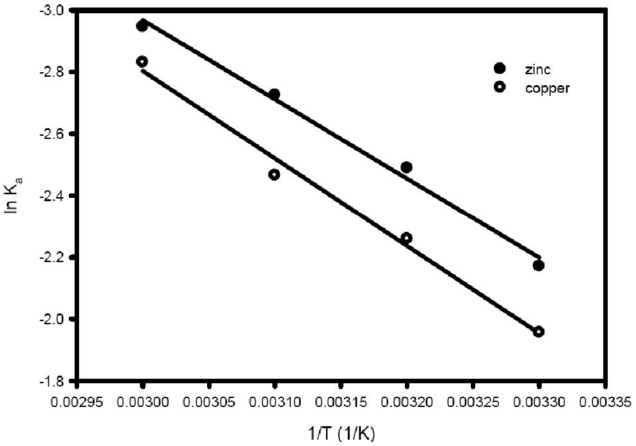

Figure 3 : ln K_a Vs 1/T plot

TABLE 1 : -ΔG° and TΔS° values for the biosorption of copper ions at different temperatures at pH 6.0

Temperature (K)	K_a (L/mg)	$-\Delta G^0$ (kJ/mol)	$T\Delta S^0$ (kJ/mol)
303	0.1413	-4.92	-28.465
313	0.1043	-5.859	-29.404
323	0.0849	-6.799	-30.343
333	0.0589	-7.738	-31.283

FIIR analysis of chatomorpha Antennina sp

A perkin-Elmer spectrum 100 FTIR spectrometer adapted with perkin-Elmer Auto image Microscope system was used in the identification of the functional groups that may be responsible for absorption of metal ions on the adsorbent surface. The pure adsorbent and metal ions bearing adsorbent samples were first dried at 105-248^0 C for 16 hour and then stored in a desiccator. The dry samples were then diluted to 5 % in KBR and cast into thin semitransparent disks before FTIR analysis. The wavelength is studied in the range 4000 cm^{-1} into 450 cm^{-1} taking air as reference.

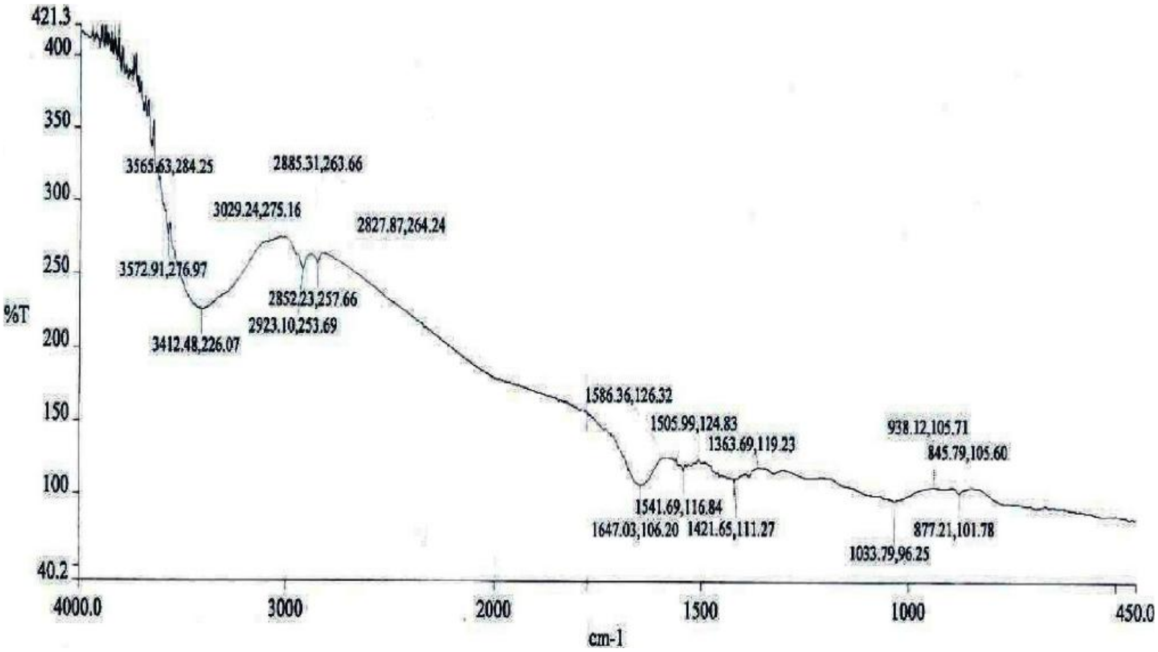

Figure 4 : FTIR analysis graph of *Cheatomorpha Antennina* sp. before biosorption

This method is used as a finger print for identification by the comparison of the spectrum from an "unknown" with previously recorded reference spectra. Infrared spectral interpretation may be applied to both organic and inorganic compounds, LinVien[11] being recommended for general organics, and by Nakamoto[12] and Nyquist et.al[13] for inorganics (salt and coordination compounds). The infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. It is defined as the sum of the contributing energy terms[14].

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}$$

Vinowanda et.al[15] reported that the involvement – H, -NH$_2$, -C=O and – COOH which are polar legends are capable of binding heavy metals. Amide1 ~ 3 were observed by Guibal et. al for fungi Aspergillus, Pencillium and Mucor[16], Ashkenazy et. al[17] reported the presence of negativity charged – COOH groups of yeast biomass in Pb biosorption through FTIR spectroscopic analysis. The role of carboxyl groups of cell wall of alginate in Sargassum fluitans and involvement of complexation mechanism were reported for the biosorption of heavy metal[17]. N.Kannan and T.Veemaraj[18] confirmed the presence of functional groups like OH, C-H, C=O CH$_2$, C-S and C-O-C are responsible for adsorption to be took place. S.S.Ahluwalia & D.Goyal[19] informed that the carboxyl group was involved in the binding of lead and iron, where as the amine group was involved in the binding of Nickle and Zinc.

The FTIR spectra were obtained for the biomass particles of this study before and after adsorption ex-

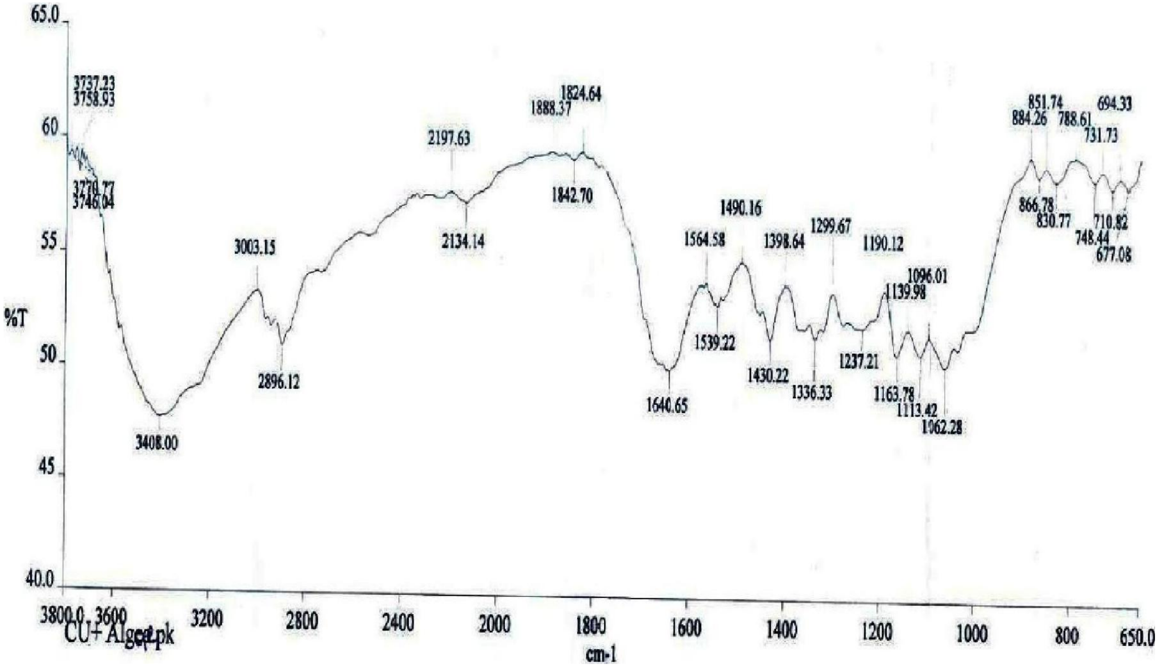

Figure 5 : FTIR analysis graph of *Cheatomorpha Antennina* sp. after copper metal biosorption

periments. As shown in Figure 1 and 2 the peak observed at 3412 cm^{-1} (before) and 3408 cm^{-1} (with copper) result form NH_2 arsymmetric stretch mode of amines. The peak observed at 3412 cm^{-1} is broad and seems to be indicative of both amine and bonded OH groups.

The peak observed at 2852 cm^{-1} (before) and 2896 cm^{-1} (with copper) is indicative of the C-H groups.

The peak present at 1647 cm^{-1} (before) and 1640 CM^{-1} (with copper) is from CO stretching mode conjugated to a N – H deformation mode and is indicative of amine 1 band.

The peaks at 1541 cm^{-1} (before) and 1539 cm^{-1} (with copper) confirms the presence of Aromatic Nitro Compound.

The peaks at 1421 cm^{-1} (before) and 1430 cm^{-1} (with copper) indicates the involvement of carbonate ion in the adsorption process.

The change of peaks can be interpreted as the result of weakened bond structure of biomass due to the reaction between the functional groups and metal ions. The elements which are in high quantities in the powder are easily exchangeable by heavy metals which have low lying d and f orbitats. The sites on the biosorbent holding up these exchangeable metal ions can then act as active sites for the exchange of heavy metals.

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