

BIOSORPTION OF COPPER FROM AQUEOUS SOLUTION BY *CHAETOMORPHA ANTENNINA* ALGAE BIOMASS

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Received 17 January 2011; revised 26 July 2011; accepted 20 December 2011

ABSTRACT

The adsorption study on removal of copper metal from aqueous solution using untreated marine green algae namely *Chaetomorpha Antennina* sp. was carried out under various experimental conditions. The effects of contact time, pH of the solution, average biosorbent particle size, biosorbent dosage and initial concentration of metal ion have been investigated by following the batch adsorption technique. 30 minutes of biosorption time was found to be sufficient to reach equilibrium rate of sorption for copper ion. The rate of copper removal was directly correlated to biomass amount and contact time. Biosorption of metal ion was pH dependent and the results indicated the optimum pH for the removal of copper as 6.0. The highest biosorption capacity was found to be 25.78 mg of metal ion per gram of biosorbent at initial concentration of 20 mg/L copper ion and increased for higher initial concentrations. The biosorption capacity increased with increase in the amount of biosorbent used for removal. Adsorption data was modeled with Freundlich, Langmuir, Redlich- Peterson and Dubinin-Radushkevich adsorption isotherms. Isotherm studies showed that the data best fitted with the Langmuir isotherm model. The kinetic data corresponded well with the pseudo-first order equation, suggesting that the biosorption process is presumably chemisorption.

Key words: Copper; Biosorption; *Chaetomorpha Antennina* sp.; Isotherm; Kinetics; Algae biomass

INTRODUCTION

The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life and environment. The release of large quantities of heavy metals into natural environment has not only intensified environmental pollution problems but also the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Some of the trace elements play essential roles in biological processes, but at higher concentration, they may be toxic to the biota, they disturb

the biochemical processes and cause hazards (Kazemipour *et al.*, 2008; Arivoli *et al.*, 2008) showing the necessity of their removal before effluents depositions entering into environment. Copper metal arises from the industries of copper mining and smelting, brass and bronze manufacturing, electroplating industries and excessive use of copper-based agrichemicals (Madhava Rao *et al.*, 2006). The presence of Cu(II) ions cause serious toxicological concerns; It is usually known to deposit in brain, skin, liver, pancreas and myocardium (Davis *et al.*, 2000) and is both vital and toxic for many biological systems.

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Several physico-chemical methods such as precipitation, ion exchange, membrane technologies, etc. have been widely used to remove heavy metal ions from wastewater, which may be ineffective or technically limited with economical viability (Viera and Volesky, 2000; Volesky, 2001; Ahalya *et al.*, 2003; Singh *et al.*, 2006). Biosorption process has proved its advantage over the other processes because of its cost effectiveness and high-quality of the treated effluent it produces. Activated carbon is widely used as an biosorbent due to its high biosorption capacity (Uzun and Guzel, 2000; Vasu, 2008).

The present study was undertaken to evaluate the efficiency of *Chaetomorpha Antennina* sp. powder for removal of copper ions in aqueous solution, in addition to estimating the optimum removal conditions and the suitable biosorption isotherms with their related constants.

MATERIALS AND METHODS

Biosorbent material preparation

The *Chaetomorpha Antennina* 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 Antennina* sp., was then completely dried in sunlight for 20 days and the resulting product was directly used as biosorbent. The dried *Chaetomorpha Antennina* sp., was then cut into small pieces and powdered using domestic mixer. The powdered

material with average particle size ranging from 75-283.5 μm was then directly used as biosorbent without any pretreatment.

Biosorption experiments

Batch biosorption experiments were conducted in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different copper concentrations (20-100 mg/L). All the experiments were carried out at room temperature ($30 \pm 1^\circ\text{C}$). Samples were taken at different time intervals upto 3 hours of contact time and the reaction mixture was centrifuged for 5 min and then filtered with Wattman filter paper (0.45 μm). After 30 min of contact (according to the preliminary sorption dynamics tests), with 0.1 g *Chaetomorpha Antennina* sp. Biomass, the equilibrium was reached. The copper metal concentration in the supernatant was determined using atomic absorption spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wavelength of 324.8 nm after filtering the biosorbent with Wattman filter paper. The amount of metal biosorbed by *Chaetomorpha Antennina* sp. was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation: Where Q is the metal uptake (mg/g); C_0 and C_f are the initial and equilibrium metal

$$Q = (C_0 - C_f) \times \frac{V}{M} \quad (1)$$

Table 1: Different isotherm models used in this study

SNo	Isotherm	Formula	Parameters	Reference
1	Langmuir Isotherm	$Q = \frac{Q_{\max} b C_f}{1 + b C_f}$	Q_{\max} and b	Langmuir, 1916
2	Freundlich isotherm	$Q = K C_f^{1/n}$	K and n	Freundlich, 1906
3	Redlich-Peterson isotherm	$q_e = \frac{A C_e}{1 + B C_e^g}$	A, B and g	Jossens <i>et al.</i> , 1978 Redlich and Peterson, 1959
4	Dubinin - Radushkevich Isotherm	$q_e = q_D \exp \left(- B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right)$	B_D and q_D	Dubinin, 1960., Radushkevich, 1949., Dubinin, 1965

concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbent (g). In Table 1, different isotherm models used in this study are given.

Biosorption kinetics

The kinetic studies were carried out by conducting batch biosorption experiments with different initial copper concentrations. Samples were taken at different time periods and analyzed for their copper concentration.

Adsorption kinetics

Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full scale batch process. In order to clarify the adsorption kinetics of heavy metal ions, experimental data are mostly tested for the pseudo-first-order and pseudo-second-order.

Pseudo first-order kinetic model

The integrated form of pseudo first-order kinetic model as proposed by Lagergren (Lagergren *et al.*, 1898) generally expressed as:

$$\log (q_{eq} - q_t) = \log (q_{eq}) - \frac{k_1}{2.303} t \quad (2)$$

Where q_{eq} and q_t are the sorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo-first order sorption, (1/min). A straight line of $\log (q_{eq} - q_t)$ against t suggest the applicability of this kinetic model (Fig.7). Constants can be determined from the intercept and slope of the plot, respectively. The R^2 values for this model at studied concentration are 0.99 to 0.9934 as seen in Table 3. The low correlation coefficient values obtained from the pseudo first-order kinetic model indicates that sorption is not occurring exclusively onto one site per ion (Nuhoglu and Malkoc, 2009).

Pseudo second-order kinetic model

The pseudo second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where q_{eq} and q_t are the sorption capacity (mg/g) at equilibrium and at time t , respectively (mg/g) and k_2 is the rate constant of pseudo-second order sorption, (g/mg min).

RESULTS

Figs. 1 and 2 show the effect of concentration and pH of copper biosorption, respectively. Also, in Figs. 3 and 4 effects of metal ion concentration and adsorbent dosage are presented, respectively. Effects of *Chaetomorpha Antennina* sp. particle size on copper biosorption is shown in Fig. 5. Finally in Figs. 6, 7 and 8, the equilibrium pseudo-first and pseudo-second order kinetics are presented, respectively.

The Experimental data of biosorption of copper ions onto *Chaetomorpha Antennina* sp. surface, showed that:

- 1-The biosorption of metal ions onto *Chaetomorpha Antennina* sp. was dependent on the equilibrium pH of the solution and contact time.
- 2-The percent removal of copper ions by the new biosorbent was fairly high and range from

Table 2: Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich isotherm constants and correlation coefficients.

Langmuir	$Q(mg/g)$	25.78
	$b(L/mg)$	0.1413
	R^2	0.9979
Freundlich	$K_f(mg/g)$	4.5384
	n	2.0991
	R^2	0.9813
Redlich-Peterson	$A(L/g)$	1.07573
	$B(L/mg)$	4.0872
	g	0.745
	R^2	0.242
Dumbinin-Radushkevich	q_D	20.853
	E	0.912
	R^2	0.9638

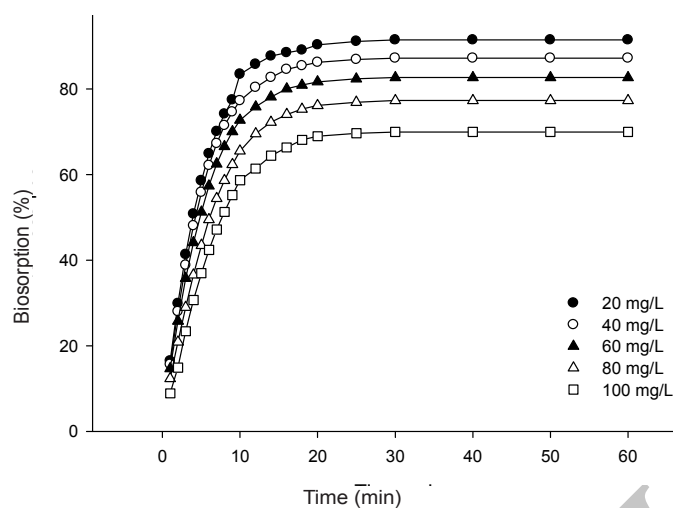


Fig. 1: Effect of contact time on biosorption of copper by *Chaetomorpha Antinninna* sp. for 0.1 g/30 mL of biosorbent concentration

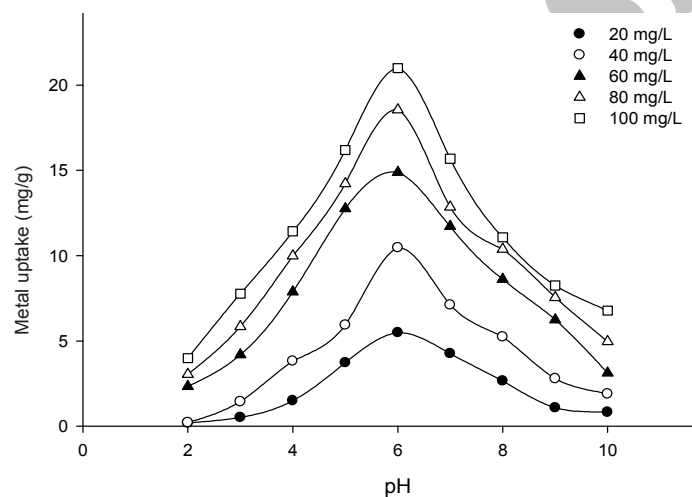


Fig. 2: Effect of pH on copper by *Chaetomorpha Antinninna* sp. for 0.1 g/30 mL of biosorbent concentration

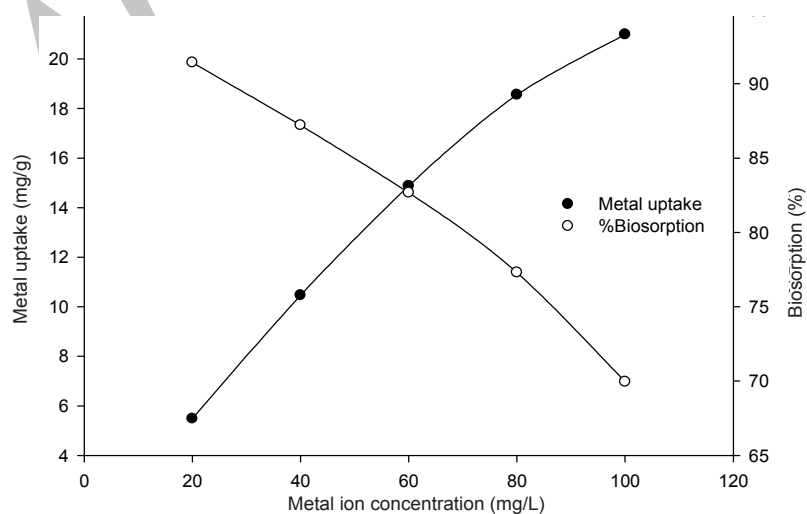


Fig. 3: Effect of metal ion on biosorption of copper by *Chaetomorpha Antinninna* sp. for 0.1 g/30 mL of biosorbent concentration

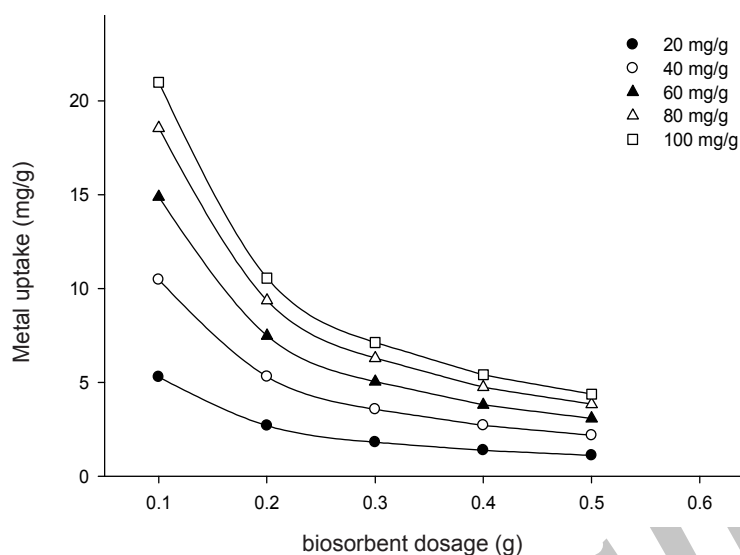


Fig. 4: Effect of *Chaetomorpha Antinninna* sp. dosage on metal uptake of copper for all metal concentrations

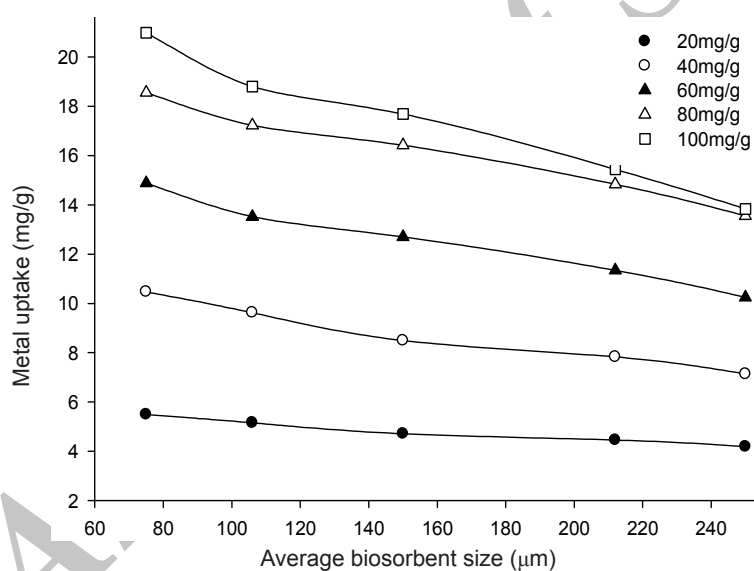


Fig. 4: Effect of *Chaetomorpha Antinninna* sp. average particle size on iosorption of copper for 0.1g/30 mL of biosorbent concentrations

16.44% to 91.43%, among the whole range of initial concentration used in the present study.

3-The amount of metal ions biosorbed increased with an increase in initial metal ion concentration.

4-The percentage biosorption of copper metal ions increased with an increase in biosorbent dosage.

5-The percentage biosorption of copper metal ions decreased with an increase in average biosorbent particle size.

6-From the experimental data it is clear that the biosorption process for copper is well described by Langmuir isotherm.

7-Kinetic of metal ions biosorption obeyed the pseudo second-order model, which suggest chemisorption as the rate-determining step in biosorption process.

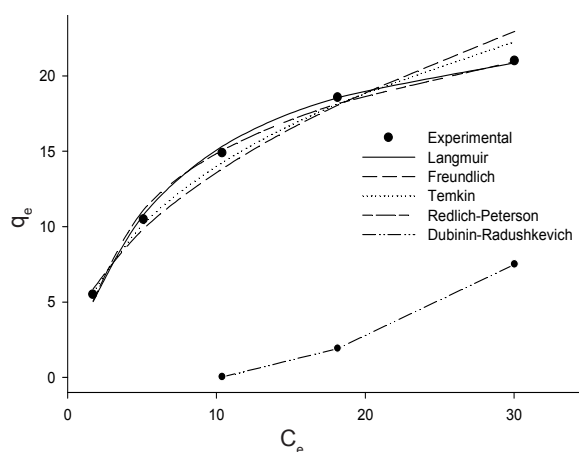


Fig. 6: Equilibrium curves for copper on to *Chaetomorpha Antinninna* sp.

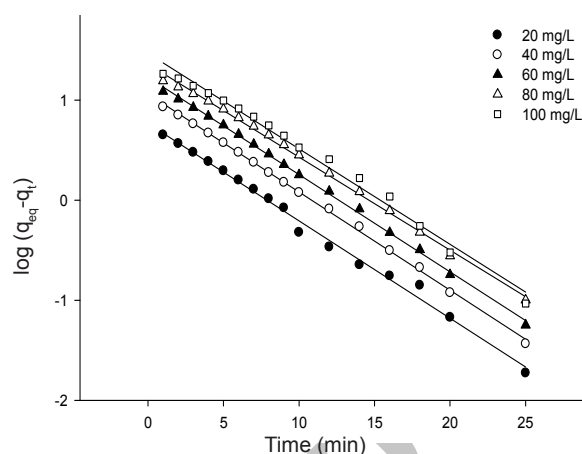


Fig. 7: Pseudo-first-order kinetics for on to *Chaetomorpha Antinninna* sp. (pH=5; adsorbent concentration=0.1 g/30mL; adsorbent size=75 μ m)

Table 3: Kinetic constants for copper onto *Chaetomorpha Antinninna* sp.

Initial concentration, mg/L	Pseudo-first order			Pseudo-second order		
	Rate constant, k_1	Amount of copper biosorbed on biosorbent, q_e , (mg/g)	Correlation coefficient, R_1^2	Rate constant, k_2	Amount of copper biosorbed on biosorbent, q_e , (mg/g)	Correlation coefficient, R_2^2
20	0.2243	5.8546	0.9934	0.0136	7.289	0.9989
40	0.226	11.562	0.9989	0.002	13.947	0.999
60	0.224	16.935	0.9986	0.0007	20.16	0.999
80	0.2144	22.977	0.9971	0.00038	27.322	0.9986
100	0.2197	29.41	0.99	0.00025	35.088	0.997

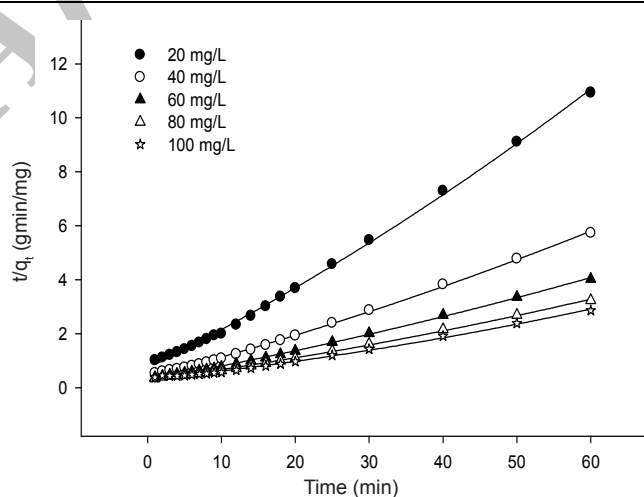


Fig. 8: Pseudo-second-order kinetics for on to *Chaetomorpha Antinninna* sp. (pH=6; adsorbent concentration=0.1 g/30mL; adsorbent size=75 μ m)

Table.4. The copper adsorption values using different adsorbents and with different experimental methods for comparison

Adsorbent material	Adsorption Capacity (mg/g)	pH	Reference
Thyme leaves	0.0464	-	Halawa <i>et al.</i> , 2003
<i>Ceratophyllum demersum</i>	6.17	-	Halawa <i>et al.</i> , 2003
Activated sawdust	13.495	4	Acar and Eren, 2006
Sawdust (bassia latifolia)	1.74	7.3	Vaishya and Prasad, 1991
Soybean hulls	24.78	-	Marshall <i>et al.</i> , 1999
Fly ash	7	5	Pehlivan <i>et al.</i> , 2006
Cotton ball	11.4	5	Ozsoy and Kumbur, 2006
<i>Tectona grandis</i> l.f	15.43	5	Kumar <i>et al.</i> , 2006
Sago waste	12.4	5	Quek <i>et al.</i> , 1998
Untreated wood	2.56	-	Low <i>et al.</i> , 2004
Chlorella fusca	3.2	6	Aksu <i>et al.</i> , 1998
Clay Soil sample	27.2	6	Tiwari <i>et al.</i> , 2007
Electrolysis method	97%	Current density of 20 mA/cm ² pH: 4 to 9	Konstantinos <i>et al.</i> , 2011
Ionexchange method using 1200H resin	26.73	5.8	Kyunghee <i>et al.</i> , 2004
Precipitation using 20%Na ₂ CO ₃	1.1mg/L	7	Negrea <i>et al.</i> , 2008
Membrane process (Reverse Osmosis)	98%	-	Hani and Hassan, 2004
<i>C. Antinninna</i> sp.	25.78	6	present study

DISCUSSION

Effect of contact time

Contact time profile for all concentrations is given in Fig.1. The plot reveals that the curves are smooth and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal ions on *Chaetomorpha Antennina* sp. powder surface (Sudha *et al.*, 2007). A time of 30min is sufficient to attain maximum copper metal uptake. Same was

found for chromium adsorption on *Ulmus Leaves*(Gholami *et al.*, 2006). Therefore, 30 min was considered to be the equilibrium time for further studies of biosorption.

Effect of pH

The experiments carried out at different pH values showed that there was a change in the quantity of adsorbed copper ions on the solid phase of

biosorbent powder over the entire pH range of 2 to 10, as shown in Fig. 1. This indicates the strong force of interaction between the copper ions and the biosorbent powder that, H^+ ion could influence the biosorption capacity. Electrostatic repulsion decreases with the increasing in pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal biosorption (Sari *et al.*, 2009). Here the interaction is more at pH=6 due to the competence of acidic H^+ ion with metal cation for the sorption sites.

Effect of initial concentration

The equilibrium data of biosorption of copper metal ions on biosorbent at various initial concentrations (20, 40, 60, 80 and 100 mg/L) is given in Table 2. From Fig. 3 it was found that the copper metal uptake increased and percentage biosorption of the copper decreased with increase in the initial metal ion concentration. It means that the biosorption is highly dependent on initial concentration of metal ion. This increase could be a result of increase in the driving forces i.e. concentration gradient.

Effect of biosorbent dosage

The number of available sites and exchanging ions for biosorption depends upon the amount of biosorbent used in the biosorption process. It can be observed from Fig. 4 that the metal uptake was found to decrease with increasing dosage of biosorbent by keeping other parameters constant. At very low biosorbent dosage, the biosorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution is large. This is because of the availability of more binding sites for complexation of copper ions. This can be attributed to (i) availability of solute, (ii) electrostatic interactions, (iii) interference between binding sites and (iv) reduced mixing at high biomass densities.

Effect of biosorbent size

The effect of different biosorbent particle sizes on percentage removal of copper is investigated and showed in Fig.5. It reveals that the adsorption of copper on *Chaetomorpha Antennina*

sp. decreased with the increased particle size from 75 to 283.5 μm at an initial concentration of 20 mg/L. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity. The increase in metal uptake with increase in biosorbent size can be attributed to increase in binding sites (Riaz *et al.*, 2009).

Biosorption isotherm

The equilibrium biosorption of copper onto *Chaetomorpha Antennina* sp. as a function of the initial concentration of copper is shown in Fig.2. There was a gradual increase of biosorption for copper ions until equilibrium was attained. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms and Redlich-Peterson and Dubinin-Radushkevich models are also applied to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, Redlich-Peterson and Dubinin-Radushkevich isotherm constants are given in Table.2

It is found that the adsorption of copper onto *Chaetomorpha Antennina* sp. was correlated well with the Langmuir equation and followed by Freundlich, Dubinin-Radushkevich and Redlich-Peterson equations under the concentration range studied(Fig 6).

The best fit for the experimental data of this study was achieved by the application of pseudo second-order kinetic equation (Fig 8). The coefficient of correlation for pseudo second order kinetic model was equal to 0.997 to 0.9989 for copper. Both factors suggest that the biosorption of Copper ions followed the pseudo second-order kinetic model, indicating that the rate limiting step was a chemical biosorption process between metal ions and clove biosorbent through the exchange of electrons between the particles involves (Ho and McKay, 2000; Dundar *et al.*, 2008;). Similar conclusions were found by Ho and McKay as a result of an analysis of data from literature. They reported that most of the sorption systems follow a pseudo second-order kinetic (Ho and McKay, 1999).

ACKNOWLEDGEMENTS

The authors are most grateful to the laboratory staff of the Environmental pollution Control Engineering Laboratory, Department of Chemical Engineering, A.U. College of Engineering, Andhra University, Visakhapatnam, India for financial support and their collaboration in this research.

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