Adsorption 10: 317–326, 2004

# The Equilibrium and Kinetic Modelling of the Biosorption of Copper(II) Ions on *Cladophora crispata*

AYLA ÖZER*
*Department of Chemical Engineering, University of Mersin, 33343 Mersin, Turkey*
ayozer@mersin.edu.tr

DURSUN ÖZER
*Department of Chemical Engineering, Firat University, 23279 Elazığ, Turkey*

H. İBRAHIM EKİZ
*Department of Food Engineering, University of Mersin, 33343 Mersin, Turkey*

*Received February 14, 2003; Revised June 22, 2004; Accepted July 23, 2004*

**Abstract.** The biosorption of Cu(II) ions on *Cladophora crispata* was investigated as a function of the initial pH, temperature and initial Cu(II) ion concentration. Algal biomass exhibited the highest Cu(II) uptake capacity at 25°C and at the initial pH of 4.5. Equilibrium data fitted very well to both the Langmuir and Freundlich isotherm models. The pseudo second order kinetic model was applied to describe the kinetic data and the rate constants were evaluated in the studied concentration range of Cu(II) ions at all the temperatures studied. The experimental data fitted well to the pseudo second order kinetic model with a high correlation coefficient ($R^2 > 0.99$), which indicates that the external mass transfer limitations in the system can be neglected and the chemical sorption is the rate-limiting step. The pseudo second order kinetic constants were also used to calculate the activation energy of Cu(II) biosorption.

**Keywords:** adsorption, equilibrium, pseudo second order kinetics, activation energy

## Introduction

The sorption of heavy metal ions from aqueous solution plays an important role in water pollution control. Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for waste streams and natural waters. Many algae, yeasts, bacteria and other fungi are known to be capable of concentrating metal species from dilute aqueous solutions and accumulating them within their cell structure (Tsezos and Volesky, 1981; Darnall et al., 1986; Tsezos et al., 1988; Friis and Myers-Keith, 1989; Ting et al., 1989; Aksu et al., 1992; Holan and Volesky, 1994; Chen and Ting, 1995; Özer et al., 1999). Microorganisms are known to accumulate metals by two distinct processes; (i) bioaccumulation, an energy-dependent process, and (ii) biosorption, an energy independent physical adsorption (Akthar et al., 1995).

The term biosorption implies a direct interaction between the biosorbent and the metal sorbate. The diffusion of the metal ion from the bulk solution to the microorganism active sites, in non-living biomass, occurs predominantly by passive transport mechanisms. Initially, metal ions diffuse to the surface of the microbial cell where they bind to the active sites on the cell surface formed by the presence of various chemical groups such as carboxylate, hydroxyl, amino and phosphate

---

*To whom correspondence should be addressed.

which exhibit affinity for the metal ions (Palmieri et al., 2000). Generally, such adsorption is fast, reversible, and not a limiting factor in bioremoval kinetics when dealing with dispersed cells. Biosorption is often followed by a slower binding process in which additional component is bound, often irreversibly. Biosorption of heavy metal ions to microorganisms is affected by several factors including the specific surface properties of the microorganism and the physico-chemical properties of the solution. Although the effects of pH, initial metal ion concentration, biomass concentration on biosorption have been widely studied, processes which occur are not completely understood, for instance, the rate limiting step and the effect of temperature. Temperature changes will affect a number of factors which are important in heavy metal ion biosorption. Some of the factors include: (i) the stability of the metal ion species initially added to solution; (ii) the stability of the microorganism-metal complex depending on the biosorption sites; (iii) the effect of temperature on the cell wall configuration of the microorganism; (iv) the ionization of chemical moities on the cell wall (Bedell and Darnall, 1990; Sağ and Kutsal, 2000).

The magnitude of the heat effect on the biosorption process is the most important criterion to develop a thermodynamic and kinetic relationship for the metal-microorganism interaction process. The sorption kinetics describe the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid-solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants (Ho and McKay, 1999a).

In this study, the biosorption of Cu(II) ions to *Cladophora crispata* was investigated as a function of temperature and initial Cu(II) ion concentration and then the experimental data were analyzed using the pseudo second order adsorption kinetic model.

## Equilibrium Modelling

The physico-chemical phenomenon of metal biosorption, based on adsorption, ion exchange, complexation and/or micro precipitation, is relatively rapid and can be reversible. Inactivated and/or thermally killed cells have been shown to accumulate heavy metal ions to the same or greater extent than growing or resting cells. In this case metal ion binding to non-viable cells is presumed to occur exclusively through surface adsorption. Several isotherm models were used to describe the equilibrium between adsorbed metal ions on the algal cell ($q_{\mathrm{eq}}$) and metal ions in solution ($C_{\mathrm{eq}}$) at constant temperature. The Langmuir isotherm equation is given below:

$$q_{\mathrm{eq}} = [Q^o b\, C_{\mathrm{eq}}]/[1 + b\, C_{\mathrm{eq}}] \qquad (1)$$

where $q_{\mathrm{eq}}$ is the adsorbed amount (mg g$^{-1}$) at equilibrium, $C_{\mathrm{eq}}$ is the equilibrium concentration in the fluid (mg L$^{-1}$), $Q^o$ is the adsorption capacity (mg g$^{-1}$) and $b$ is a constant related to the energy or net enthalpy of adsorption (L mg$^{-1}$). $Q^o$ represents a practical limiting adsorption capacity when the surface is fully covered with heavy metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. $Q^o$ and $b$ can be determined from the linear plot of $1/q_{\mathrm{eq}}$ versus $1/C_{\mathrm{eq}}$.

The well-known Freundlich isotherm used for isothermal adsorption is a special case for heterogeneous surface energy in which the energy term in the Langmuir equation varies as a function of surface coverage strictly due to variation of the sorption. The Freundlich equation is given as:

$$q_{\mathrm{eq}} = K_F\, C_{\mathrm{eq}}^{1/\mathrm{n}} \qquad (2)$$

where $K_F$ is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. $K_F$ and $1/n$ can be determined from the linear plot of ln ($q_{\mathrm{eq}}$) versus ln ($C_{\mathrm{eq}}$).

## Kinetic Modelling

Several models can be used in order to investigate the mechanism of biosorption and potential rate controlling steps such as mass transport and chemical reaction processes. However, it is often incorrect to apply simple kinetic models such as first or second order rate equations to a sorption system with solid surfaces which are rarely homogeneous and because the effects of transport phenomena and chemical reactions are often experimentally inseparable. Numerious studies reported that the pseudo first-order Lagergren kinetics and the pseudo second order kinetics were avaliable for the sorption of metals (Ho and McKay, 1999a, 1999b, 2000; Aksu and Tezer, 2000; Aksu, 2001; Chiou and Li, 2002).

The Lagergren rate equation was the first rate equation for the sorption of liquid/solid system based on solid capacity. The Lagergren rate equation is one of the most widely used sorption rate equations for the sorption of a solute from a liquid solution (Ho and McKay, 1999a). Furthermore, in most cases the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20–30 min of the sorption process (Ho and McKay, 1999a). On the contrary, the pseudo second order equation predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step (Ho and McKay, 1999a, 1999b). Ho and McKay (1999a) have conducted a literature rewiev containing the use of sorbents and biosorbents to treat polluted aqueous effluents containing dyes/organics or metal ions and they noted that the highest correlation coefficients were obtained by using the pseudo second-order kinetic model for different metal ion-sorbent systems. The results of the biosorption of Remazol Black B on dried *R. arrhizus* and the biosorption of Cd(II) ion to *C. vulgaris* showed that the uptake processes followed the pseudo second order rate expression (Aksu and Tezer, 2000; Aksu, 2001). The similar phenomena was also observed in adsorption of reactive dye on cross-linked chitosan beats (Chiou and Li, 2002). Therefore, the biosorption of Cu(II) ions to *C. crispata* is modelled by using the pseudo second order kinetic model rather than the pseudo first-order kinetic model in this present study.

The two important aspects for parameter evaluation of the adsorption study are the kinetics and the equilibrium of adsorption. The mechanism involved in the metal removal is assumed basically, to be complexation and ion exchange. The simplest way to describe the kinetics of metal removal, in the absence of stoichiometric data, can be represented as (Anoop Krishnan and Anirudhan, 2002):

$$S + M \Leftrightarrow MS \tag{3}$$

where *M* represents the dissolved metal concentration, *S* is the available surface sites and *MS* is the concentration of metal bound to sorbent.

The reactions involving in pseudo second order are greatly influenced by the amount of metal on the surface of the adsorbent and the amount of metal adsorbed at equilibrium. It means that the rate of reaction is directly proportional to the number of active sites on the surface of the adsorbent. The rate expression for the pseudo second order reaction can be written as (Ho and McKay, 1999a; Anoop Krishnan and Anirudhan, 2002):

$$d(S)_t/\mathrm{d}t = k_{2\mathrm{ad}}[(S)_o - (S)_t]^2 \tag{4}$$

where $(S)_o$ and $(S)_t$ are the number of active sites occupied on the adsorbent at initial time ($t = 0$) and at any time t, respectively. In terms of adsorbed quantity, the Eq. (4) can be rewritten as (Scott and Karanjkar, 1995; Ho and McKay, 1999a, 1999b, 2000; Aksu and Tezer, 2000; Aksu, 2001; Anoop Krishnan and Anirudhan, 2002):

$$\mathrm{d}q/\mathrm{d}t = k_{2\mathrm{ad}}(q_{\mathrm{eq}} - q)^2 \tag{5}$$

where $k_{2\mathrm{ad}}$ is the rate constant of sorption (g mg$^{-1}$ min$^{-1}$), $q_{\mathrm{eq}}$ and $q$ are the metal uptake per unit mass of algae at equilibrium and at any time, respectively (mg g$^{-1}$). It is important to notice that for the application of this model the experimental estimation of $q_{\mathrm{eq}}$ is not necessary (Cruz et al., 2004).

Rearranging Eq. (5) gives:

$$\mathrm{d}q/[q_{\mathrm{eq}} - q]^2 = k_{2\mathrm{ad}}\,\mathrm{d}t \tag{6}$$

Integrating this for the boundary conditions; at $t = 0$, $q = 0$ and at $t = t$, $q = q$ gives:

$$1/[q_{\mathrm{eq}} - q] = 1/q_{\mathrm{eq}} + k_{2\mathrm{ad}}\,t \tag{7}$$

Equation (7) can be rearranged to obtain:

$$t/q = 1/k_{2\mathrm{ad}}\,q_{\mathrm{eq}}^2 + t/q_{\mathrm{eq}} \tag{8}$$

The plot of $t/q$ versus $t$ of Eq. (8) should give a linear relationship, from which $q_{\mathrm{eq}}$ and $k_{2\mathrm{ad}}$ can be determined from the slope and intercept of the plot.

## The Determination of Activation Energy

The pseudo second order rate constant is expressed as a function of temperature by the following Arrhenius type relationship:

$$k_{2\mathrm{ad}} = k_o \exp[-E/R\mathrm{T}] \tag{9}$$

where $k_o$ is the temperature independent factor (g mg$^{-1}$ min$^{-1}$), $E$ is the activation energy of sorption (kJ mol$^{-1}$), $R$ is universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature ($K$). The magnitude of activation energy may give an idea about the type of sorption. Two main types of adsorption may occur, physical and chemical. The activation energy for physical adsorption is usually no more than 1 kcal gmol$^{-1}$ (4.2 kJ mol$^{-1}$) since the forces involved in physical adsorption are weak (Treybal, 1980; Smith, 1981). Chemical adsorption is specific and involves forces much stronger than in physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions, 5 to 100 kcal mol$^{-1}$ (21–420 kJ mol$^{-1}$) (Treybal, 1980; Smith, 1981). Two kinds of chemisorption are encountered: activated and, less frequently, nonactivated. Activated chemisorption means that the rate varies with temperature according to a finite activation energy in the Arrhenius equation. However, in some systems chemisorption occurs very rapidly, suggesting an activation energy near zero. This is termed nonactivated chemisorption.

## Materials and Methods

### *Preparation of the Microorganism and Cu(II) Solutions for Biosorption*

*Cladophora crispata*, a species of green algae collected from the irrigation water channels near Firat University, Elaziğ, Turkey was used in this study. For the biosorption studies, the harvested fresh cells were rinsed with tap water, washed several times with distilled water and then inactivated in an oven at 90°C for 24 h. A 10 g L$^{-1}$ of inactivated dried *C. crispata* was suspended in double distilled water and homogenized for 45 min in a Waring mixer.

The stock solution of copper(II) was prepared in 1.0 g L$^{-1}$ concentration using $CuSO_4$ and then diluted to an appropiate amount. The pH of each solution was adjusted to the required value with diluted or concentrated $H_2SO_4$ and NaOH solutions before mixing with the algae solution.

## Experimental

The experiments were conducted in 250 ml Erlenmayer flasks containing 90 ml of Cu(II) solution and 10 ml homogenized algae solution at the desired temperature and pH. The flasks were agitated at 150 rev min$^{-1}$ on a shaker for 2 h, allowing ample time for adsorption equilibrium. Samples (3 ml) were taken before mixing the algae solution and metal-bearing solution and at predetermined time intervals (0, 5, 15, 30, 60, 120) for determining the residual metal ion concentration in the solution. The biomass was separated by centrifugation from the medium and the concentration of Cu(II) ions in the supernatant was measured by using an atomic absorption spectrophotometer, Perkin-Elmer 370 model. To determine the biosorption isotherms, the initial Cu(II) ion concentration was varied from 10 to 100 mg L$^{-1}$ while the dry cell weight in each experiment was held constant at 1.0 g L$^{-1}$. Each experiment was repeated three times and the results are given as avarage.

## Results and Discussion

The biosorption of Cu(II) ions to *Cladophora crispata* was investigated as a function of initial pH, temperature and initial Cu(II) ion concentration. The equilibrium and kinetic results are given as units of adsorbed Cu(II) quantity per gram of dried algae at any time ($q$, mg g$^{-1}$), equilibrium adsorbed Cu(II) quantity per gram of dried algae ($q_{eq}$, mg g$^{-1}$) and unadsorbed Cu(II) concentration in solution at equilibrium, ($C_{eq}$, mg L$^{-1}$).

## The Equilibrium Studies

### *The Effect of Initial pH*

pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other side, pH strongly influence the speciation and the biosorption availability of the heavy metals (Esposito et al., 2002). The variation of equilibrium uptake with the initial pH at 25°C was shown in Fig. 1. The pH of adsorption media affected the equilibrium uptake

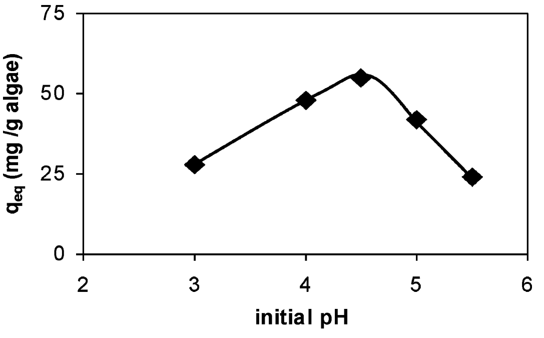

*Figure 1.* The effect of initial pH ($C_o = 200$ mg L$^{-1}$, temperature 25°C, $X_o$; 1.0 g L$^{-1}$).

of Cu(II) ions to *C. crispata* and the optimum initial pH was determined to be 4.5. The pH of adsorption media is related to the metal-adsorption mechanism onto microorganism surfaces from water and reflects the nature of the physicochemical interaction of both the ion in solution and the nature of the cell adsorption sites. At low pH values, the surface of adsorbent would also be surrounded by hydronium ions which decrease the copper interaction with binding sites of the *C. crispata* by greater repulsive forces. As the pH increased, the overall surface on the *C. crispata* became negative and adsorption increased. After pH 6.0, insoluble copper hydroxide starts precipitating from the solution, making true sorption studies impossible. Therefore, at these pH values, both adsorption and precipitation are the effective mechanisms to remove the copper(II) in aqueous solution. This type of behaviour had been observed for other hydrolyzable metals also (Mathialagon and Viraraghavan, 2002). The metal cations in aqua solution convert to different hydrolysis products. Elliot and Huang (1981) investigated the hydrolysis products of copper as a function pH (Elliott and Huang, 1981). Their results show that the dominant species of copper at the range 3–5 of pH are $Cu^{2+}$ and $CuOH^{+}$, while the copper at above 6.3 occurs as insoluble $Cu(OH)_2$ (s) (Elliott and Huang, 1981; Asmal et al., 1998). In our study, these copper cations at around pH 4.5 would be expected to interact more strongly with the negatively charged binding sites in *C. crispata*. As a result, the optimum pH for copper(II) adsorption was found as 4.5 and the other adsorption experiments were performed at this pH value.

### *The Effect of Temperature*

The equilibrium uptake of Cu(II) ions to *C. crispata* was also affected by the temperature (Fig. 2). The amount of the adsorbed metal ion per unit mass passes through a maximum at 25°C and then begins to decrease with increasing temperature from 25 to 50°C. An increase of the temperature in the interval 15–25°C deals with an increase in the adsorption capacity of *C. crispata* at equilibrium. The decrease of the equilibrium uptakes in the range of 25–50°C means that the biosorption process of Cu(II) ions is exothermic. Similar temperature effect on the adsorption trend has also been shown in the case of sorption of cadmium onto chitin (Benguella and Benaissa, 2002).

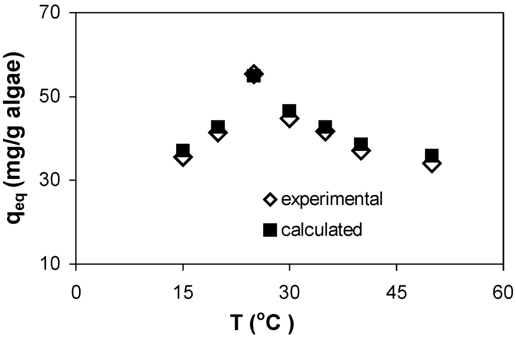

*Figure 2.* The effect of temperature ($C_o = 200$ mg $L^{-1}$, $X_o$; 1.0 g $L^{-1}$, initial pH 4.5).

### *The Effect of the Initial Copper(II) Ion Concentration*

The rate of adsorption is a function of initial metal ion concentration. The uptake values (mg Cu (g algae)$^{-1}$) for copper(II) adsorption onto *C. crispata* are given in Fig. 3 as a function of time at 50, 100 and 200 mg $L^{-1}$ of the initial copper(II) concentrations. It can be noticed that after an equilibrium time of 30 min, no more copper(II) was adsorbed for all the initial copper(II) ion concentrations. The uptake values were found as 26.7 mg/g for 50 mg/L and 55.4 mg/g for 200 mg $L^{-1}$ initial copper(II) ion concentrations. The uptake amounts increased with increasing initial metal ion concentrations as a result of the increase in the driving force ($\Delta C$). A plot of final versus initial copper(II) ion concentration in solution was also presented in Fig. 4. As seen from Fig. 4, the saturation plateau is reached at 200 mg/L and did not change with further increment in initial copper(II) ion concentration, suggesting that available sites on the biosorbent are the limiting factor for copper(II) biosorption.

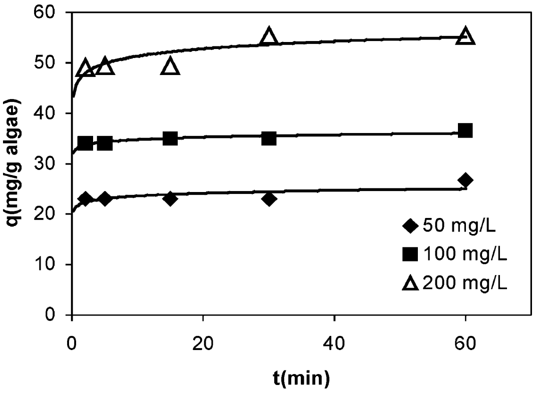

*Figure 3.* The effect of the initial copper(II) ion concentration ($T = 25$°C, $X_o$; 1.0 g $L^{-1}$, initial pH 4.5).

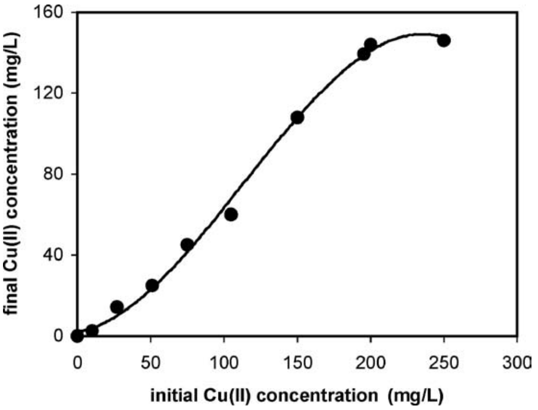

*Figure 4.* The variation of final concentration with initial copper(II) ion concentration.

The percent adsorption of copper(II) ions on *C. crispata* decreased from 50 to 28% as the initial copper(II) ion concentration was increased from 50 to 200 mg $L^{-1}$ at 25°C. The percent adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of copper(II) displays an opposite trend (Table 3). At lower concentrations, all copper(II) ions present in solution could interact with the binding sites and thus the percent adsorption were higher than those at higher initial copper(II) ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

*Equilibrium Isotherms*

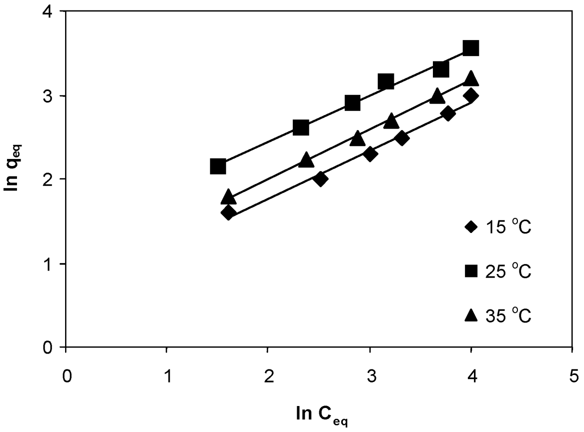

*Figure 5.* Freundlich isotherms at different temperatures ($X_o$; 1.0 g $L^{-1}$, initial pH 4.5).

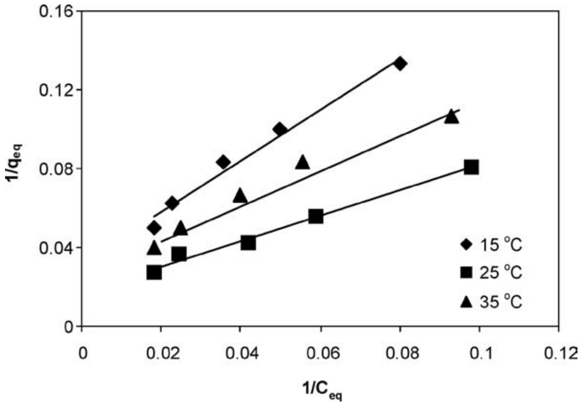

*Figure 6.* The Langmuir isotherms at different temperatures ($X_o$; 1.0 g $L^{-1}$, initial pH 4.5).

The linearized Freundlich and Langmuir adsorption isotherms of Cu(II) ions obtained at temperatures of 15, 25 and 35°C are given in Figs. 5 and 6, respectively. The $K_F$, $n$, $Q^o$ and $b$ values evaluated from the isotherms at different temperatures with the correlation coefficients are also presented in Table 1. The highest $K_F$ value was found as 3.78 at 25°C. The magnitude of $K_F$ and $n$ shows easy separation of metal ions from wastewater and also indicates favorable adsorption. If adsorption is favorable, then $1/n < 1.0$ or $n > 1.0$ (Treybal, 1980). For Cu(II) adsorption, the values of $1/n$ calculated from Freundlich isotherms at different temperatures were found to be very close to each other. The adsorption intensity was not affected by changing the temperature of adsorption medium.

*Table 1.* A comparison of constants obtained from the Freundlich and Langmuir adsorption isotherms of Cu(II) ions at different temperatures.

| Temperature (°C) | $K_F$ | $1/n$ | $n$ | $R^2$ | $Q^o$ (mg $g^{-1}$) | $b$ (L $mg^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|---|
| 15 | 1.859 | 0.57 | 1.754 | 0.992 | 31.0 | 0.0248 | 0.99 |
| 25 | 3.781 | 0.55 | 1.818 | 0.990 | 57.5 | 0.0270 | 0.99 |
| 35 | 2.293 | 0.58 | 1.724 | 0.998 | 35.2 | 0.0320 | 0.98 |

The highest $Q^o$ value was determined as 57.5 mg $g^{-1}$ (1.03 mmol $g^{-1}$) at optimum temperature. A comparison of the the maximum capacity, $Q^o$, of *C. crispata* with those of some other adsorbents reported in literature is given in Table 2. The adsorption capacity of *C. crispata* was relatively high when compared with other adsorbents. Differences of metal uptake are due to the properties of each biosorbent /adsorbent such as structure, functional groups and surface area. At 25°C

*Table 2.* Uptake capacities for copper(II) of various adsorbents.

| Adsorbent | $Q^o$ (mmol g$^{-1}$) |
|---|---|
| *Vaucheria sp.* (Christ et al., 1981) | 0.60 |
| *R. arrhizus* (Tobin et al., 1984) | 0.25 |
| *A. oryzae* (Huang et al., 1991) | 0.07 |
| *C. vulgaris* (Aksu et al., 1992) | 0.67 |
| *Z. ramigera* (Aksu et al., 1992) | 0.46 |
| *Lignite* (Allen and Brown, 1995) | 0.10 |
| *S. fuitans* (Kratochvil et al., 1995) | 0.96 |
| *P. aeruginosa* (Chang et al., 1997) | 0.30 |
| *S. cerevisiae* (Özer and Özer, 1998) | 1.26 |
| Peat (Ho and McKay, 1999) | 0.198 |
| *P. chrysosporium* (Say et al., 2001) | 0.47 |
| *Padina sp.* (Kaewsarn, 2002) | 0.80 |
| *C. crispata* (This study) | 1.03 |

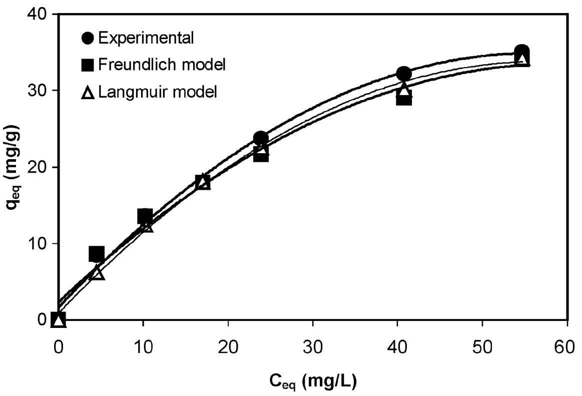

*Figure 7.* The graphically comparison of the experimental and calculated equilibrium data ($T = 25°C$, $X_o$; 1.0 g L$^{-1}$, initial pH 4.5).

and initial pH 4.5, the experimental and calculated $q_{eq}$ values by using Eqs. (1) and (2) (constants obtained from the linear form of the Langmuir and Freundlich isotherm models) versus experimental $C_{eq}$ were also plotted and the graphically compared in Fig. 7. The experimental data for copper(II) ions were in good agreement with those calculated by the Langmuir and Freundlich models. Figure 7 also indicated that the experimental and calculated values of $q_{eq}$ were closer to each other at low copper(II) ion concentrations than higher ones.

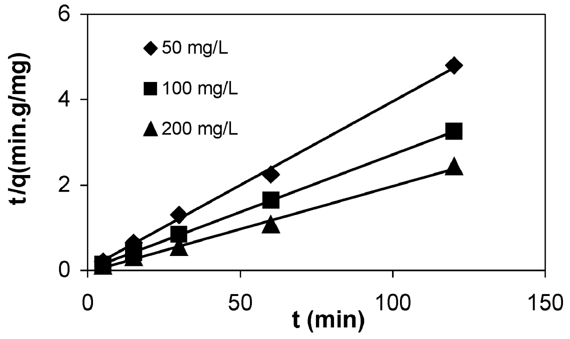

*Figure 8.* The variation of $t/q$ versus $t$ for different initial copper(II) concentrations.

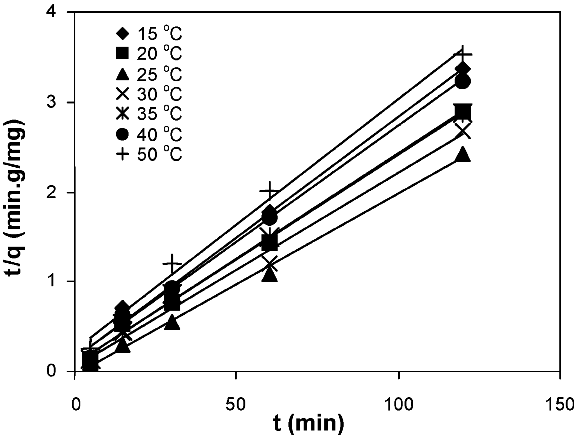

*Figure 9.* The variation of $t/q$ versus $t$ for copper(II) ions at different temperatures.

## Kinetic Model Studies

In this part, the pseudo second order kinetic equation was applied to the experimental data in order to investigate the biosorption mechanism of Cu(II) ions and potential rate controlling steps such as mass transport and chemical reaction processes. Figures 8 and 9 show the plots of the linearized form of the pseudo second order model for the biosorption of Cu(II) ions onto *C. crispata* at various temperatures and initial Cu(II) ion concentrations, respectively. The values of the $k_{2ad}$, experimental and calculated $q_{eq}$, and correlation coefficients are presented in Table 3. $q_{eq}$ and $k_{2ad}$ values increased up to 25°C and then decreased with further increase in temperature.The temperature optima obtained from the pseudo second order kinetic model confirmed the experimental optimum temperature (Fig. 2). As seen from Table 3, the values of rate constant were found to increase from $9.3 \times 10^{-3}$ to $6.1 \times 10^{-2}$ g mg$^{-1}$ min$^{-1}$, for a decrease in the initial Cu(II) ion concentration from 200 mg L$^{-1}$ to 50 mg L$^{-1}$. The decrease in $k_{2ad}$ values with an increase in metal concentration is a common phenomena observed with variety of adsorbents such as chitosan and 2-mercaptobenzimidazole-clay, moss peat, activated carbon and cross-linked

*Table 3.* A comparison of the pseudo second order rate constants, experimental $q_{eq}$ values and correlation coefficients for the various initial copper(II) concentrations and temperatures.

| Temperature (°C) | $C_o$ (mg $L^{-1}$) | $q_{eq,exp}$ (mg $g^{-1}$) | $q_{eq,cal}$ (mg $g^{-1}$) | $k_{2ad} \times 10^3$ (g $mg^{-1}$ $min^{-1}$) | $R^2$ |
|---|---|---|---|---|---|
| 20 | 200 | 41.38 | 42.73 | 6.8 | 0.9967 |
| 25 | 50 | 25.00 | 25.36 | 61 | 0.9989 |
|  | 100 | 36.81 | 36.76 | 35 | 0.9997 |
|  | 200* | 55.42* | 54.95* | 9.3* | 0.9960* |
| 30 | 200 | 44.77 | 46.51 | 8.6 | 0.9921 |
| 35 | 200 | 41.67 | 42.74 | 6.2 | 0.9975 |
| 40 | 200 | 37.15 | 38.61 | 4.7 | 0.9957 |
| 50 | 200 | 34.09 | 35.84 | 3.2 | 0.9931 |

*The results of the variation with temperature.

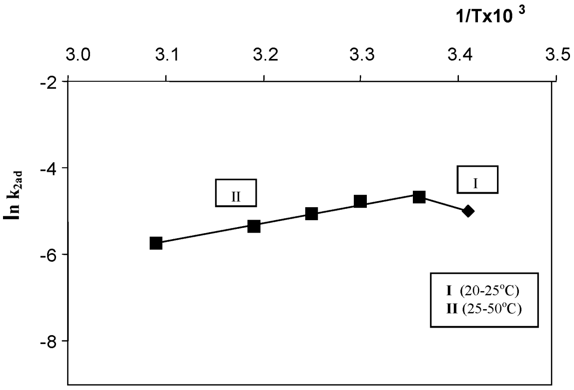

*Figure 10.* Determination of the activation energy.

chitosan bead used for the adsorption of Hg(II), Ni(II), Cr(VI) and reactive dye, respectively (Anoop Krishnan and Anirudhan, 2002; Manohar et al., 2002; Chiou and Li, 2002). There are many factors which can contribute to this sorbate concentration effect on rate of adsorption. Increasing the metal concentration in solution seems to reduce the diffusion of metal ions in the boundary layer and to enhance the diffusion in the solid (Anoop Krishnan and Anirudhan, 2002). It was observed that the pseudo second-order rate constants increased up to 25°C and then decreased with further increase in temperature. Also, the experimental equilibrium data for Cu(II) ions are in good agreement with those calculated using the pseudo second order kinetics (Table 3). In accordance, it has also been reported that, in the study of biosorption of Cd(II) ions to *C. vulgaris*, the experimental equilibrium Cd(II) uptake values agreed very well with the theoritical values in the case of pseudo second order kinetics (Aksu, 2001).

The correlation coefficients for the pseudo second order rate law were obtained greater than 0.99 for all the initial concentrations and temperatures for contact times of 120 min. These results suggest that the Cu(II)-*C. crispata* biosorption system is well described by the pseudo second order model, based on the assumption that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate.

## The Activation Energy for Cu(II) Biosorption

The activation energy of Cu(II) ions onto *C. crispata* were calculated by using pseudo second order kinetic constants. The activation energy was obtained by calculating the slope of the plot of ln $k_{2ad}$ versus $1/T$. The activation energy for the biosorption of Cu(II) ions onto *C. crispata* were calculated for two regions (Fig. 10). In the first region, the straight line with negative slope was obtained up to 25°C for which the activation energy was determined as 51.5 kJ $mol^{-1}$ ($R^2 = 1$). In the second region, the activation energy for the temperature range of 25–50°C was found to be $-35$ kJ $mol^{-1}$ ($R^2 = 0.9787$). The observed activation energy values for the biosorption of copper(II) ions were of the same magnitude as the heat of chemisorption. An increase in the adsorption of Cu(II) ions by *C. crispata* deals with an increase in the uptake capacity of *C. crispata* up to 25°C and then followed by an exothermic uptake process with further increase in temperature.

## Conclusion

The biosorption of Cu(II) ions to *Cladophora crispata* was studied in a batch system with respect to the initial pH, temperature and the initial Cu(II) ion concentration. The pH, the initial metal ion concentration and temperature affected the equilibrium uptake of Cu(II) ions to *C. crispata* and the optimum initial pH, the initial copper(II) ion concentration and temperature were determined as 4.5, 200 mg $L^{-1}$ and 25°C, respectively. The Langmuir and Freundlich adsorption models were applied to describe the experimental isotherms and isotherm constants. Equilibrium data fitted very well to both the Langmuir and Freundlich isotherm models. The maximum biosorption capacity of algal biomass was determined as 1.03 mmol $g^{-1}$. A comparison of sorption capacity of *C. crispata* with those obtained in the literature for the adsorption of Cu(II) ions on some other biosorbents and adsorbents also showed that *C. crispata* is more effective for this purpose.

The pseudo second order model was used to describe the kinetic data and the rate constants were evaluated. The results indicated that the experimental data fitted very well to this kinetic model. This suggests that the rate-limiting step may be the chemical adsorption but not the mass transport. The pseudo second kinetic parameters obtained can be used to determine equilibrium sorption capacity, percent metal ion removal, rate constants and initial sorption rate for bioreactor design. It may be useful to apply such simple kinetic models to a well agitated batch biosorption system consisting of free cell suspension neclecting external film diffusion. The results show that an increase in the adsorption of Cu(II) ions deals with an increase in the uptake capacity of *C. crispata* with increasing temperature up to 25°C and then followed by an exothermic uptake process at higher temperatures.

Consequently, the dried *C. crispata* is succesfully used as adsorbing agent and especially has a high adsorption capacity for Cu(II) ions.

## Nomenclature

| | |
|---|---|
| $b$ | Constant related to the energy or net enthalpy of adsorption (L mg$^{-1}$) |
| $C_{\mathrm{eq}}$ | The concentration in the solution (mg L$^{-1}$) |
| $C_o$ | The initial metal ion concentration in the solution (mg L$^{-1}$) |
| $E$ | The activation energy of sorption (kJ mol$^{-1}$) |
| $K_F$ | Freundlich adsorption constant (indicator of adsorption capacity) |
| $k_o$ | The temperature independent factor (g mg$^{-1}$ min$^{-1}$) |
| $k_{2\mathrm{ad}}$ | The rate constant of sorption (g mg$^{-1}$ min$^{-1}$) |
| $M$ | The dissolved metal concentration (mg L$^{-1}$) |
| $MS$ | The concentration of metal bound to sorbent (mg L$^{-1}$) |
| $n$ | Freundlich adsorption constant (adsorption intensity) |
| $q_{\mathrm{eq}}$ | The metal uptake per unit mass of algae at equilibrium (mg g$^{-1}$) |
| $q$ | The metal uptake per unit mass of algae at any time (mg g$^{-1}$) |
| $Q^o$ | The adsorption capacity (mg g$^{-1}$) |
| $R$ | Universal gas constant (8.314 kJ mol$^{-1}$ K$^{-1}$) |
| $R^2$ | Correlation coefficient |
| $S$ | The available surface sites |
| $(S)_o$ | The number of active sites occupied on the adsorbent at initial time ($t = 0$) |
| $(S)_t$ | The number of active sites occupied on the adsorbent at any time t |
| $t$ | Time (min) |
| $T$ | Solution temperature (°C, K) |
| $X_o$ | The initial biomass concentration in the solution (g L$^{-1}$) |

## References

Aksu, Z., Y. Sağ, and T. Kutsal, "The Biosorption of Copper(II) by *C. vulgaris* and *Z. ramigera*," *Environ. Technol.*, **13**, 579–586 (1992).

Aksu, Z. and S. Tezer, "Equilibrium and Kinetic Modelling of Biosorption of Remazol Black B by *R. arrhizus* in a Batch System: Effect of Temperature," *Process Biochemistry*, **36**, 431–439 (2000).

Aksu, Z., "Equilibrium and Kinetic Modelling of Cadmium(II) Biosorption by *C. vulgaris* in a Batch System: Effect of Temperature," *Separation and Purification Technology*, **21**, 285–294 (2001).

Akthar, N., S. Sastry, and M. Mohan, "Biosorption of Silver Ions by Processed *Aspergillus niger* Biomass," *Biotech. Letters*, **17**, 551–556 (1995).

Allen, S.J. and P.A. Brown, "Isotherm Analysis for Single Component and Multi-Component Metal Sorption onto Lignite," *J. Chem. Technol. Biotechnol.*, **62**, 17–24 (1995).

Anoop Krishnan, K. and T.S. Anirudhan, "Removal of Mercury(II) from Aqueous Solutions and Chlor-Alkali Industry Effluent by Steam Activated and Sulphurised Activated Carbons Prepared from Bagasse Pith: Kinetics and Equilibrium Studiees," *Journal of Hazardous Materials*, **B92**, 161–183 (2002).

Asmal, M, A.H. Khan, S. Ahmad, and A. Ahmad, "Cole of Sawdust in the Removal of Copper(II) from Industrial Wastes," *Water Research*, **32**, 3085–3091 (1998).

Bedell, G.W. and D.W. Darnall, "Immobilization of Nonviable, Biosorbent, Algal Biomass for the Recovery of Metal Ions," *Biosorption of Heavy Metals*, B. Volesky (Ed.), pp. 314–326, CRC Press, Boca Raton, 1990.

Benguella, B. and H. Benaissa, "Cadmium Removal from Aqueous Solutions by Chitin: Kinetic and Equilibrium Studies," *Water Research*, **36**, 2463–2474 (2002).

Chang, J.S., R. Law, and C.C. Chang,"Biosorption of Lead, Copper and Cadmium by Biomass of *Pseudomonas aeruginosa* PU21," *Water Research*, **31**, 1651–1658 (1997).

Chen, P. and Y.P. Ting, "Effect of Heavy Metal Uptake on the Electrokinetic Properties of *Saccharomyces cerevisiae*," *Biotechnology Letters*, **17**, 107–112 (1995).

Chiou, M.S. and H.Y. Li, "Equilibrium and Kinetic Modeling of Adsorption of Reactive Dye on Cross-Linked Chitosan Beads," *J of Hazardous Materials*, **B93**, 233–248 (2002).

Crist, R.H., K. Oberholser, N. Shank, and M. Nguyen, "Nature of Bonding Between Metallic Ionc and Algal Cell Walls," *Environ. Sci. Technol.*, **15**, 1212–1217 (1981).

Cruz, C.C.V., A.C. A.da Costa, and A.S. Henriques Cai Luna, "Kinetic Modeling and Equilibrium Studies During Cadmium

Biosorption by Dead Sargassum sp. Biomass," *Bioresource Technology*, **91**, 249–257 (2004).

Darnall D.W., B. Greene, M. Hosea, R.A. McPherson, M. Henzl, and M.D. Alexander, "Recovery of Heavy Metals by Immobilized Algae: In Trace Metal Removal from Aqueous Solutions," in *Industrial Division of the Royal Society of Chemistry Annual Chemical Congress,* R. Thomson (Ed.), pp. 1–24, UK, 1986.

Elliott, H.A. and C.P. Huang, "Adsorption Characteristic of Some Cu(II) Complexes on Alumino Silicates," *Water Research*, **15**, 849–855 (1981).

Esposito, A., F. Pagnelli, and F. Veglio, "pH-Related Equilibria Models for Biosorption in Single Metal Systems," *Chemical Engineering Science*, **57**, 307–313 (2002).

Friis, N. and P. Myers-Keith, "Biosorption of Uranium and Lead by *Streptomyces longwoodensis,*" *Biotech. and Bioeng*., **28**, 21–28 (1989).

Holan, Z.R. and B. Volesky, "Biosorption of Lead and Nickel by Biomass of Marine Algae," *Biotech. and Bioeng*, **43**, 1001–1009 (1994).

Ho, Y.S. and G. McKay, "Pseudo-Second Order Model for Sorption Processes," *Process Biochemistry*, **34**, 451–465 (1999a).

Ho, Y.S. and G. McKay, "The Sorption of Lead(II) Ions on Peat," *Water Research*, **33**, 578–584 (1999b).

Ho, Y.S. and G. McKay, "Competitive Sorption of Copper and Nickel Ions from Aqueous Solution Using Peat," *Adsorption*, **5**, 409–417 (1999c).

Ho, Y.S. and G. McKay, "The Kinetics Sorption of Divalent Metal Ions Onto *Sphagnum* Moss Peat," *Water Research*, **34**, 735–742 (2000).

Huang, J.P., C.P. Huang, and A.L, Morehart, "Removal of Heavy Metals by Fungal (*Aspergillus oryzae*) Adsorption," *Heavy Metals in the Environment*, J.P. Vernet (Ed.), pp. 329–349, Elsevier, London, 1991.

Kaewsarn, P., "Biosorption of Copper(II) from Aqueous Solutions by Pre-Treated Biomass of Marine Algae *Padina sp.*," *Chemosphere*, **47**, 1081–1085 (2002).

Kratochvil D., E. Fourest and B. Volesky, "Biosorption of Copper by *Sargassum fluitans* Biomass in a Fixed Bed Column," *Biotechnology Letters*, **17**, 777–782 (1995).

Manohar, D.M., K. Anoop Krishnan, and T.S. Anirudhan, "Removal of Mercury(II) from Aqueous Solutions and Chlor-Alkali Industry Wastewater Using 2-mercaptobenzimidazole-Clay," *Water Research*, **36**, 1609–1619 (2002).

Mathialagon, T. and T. Viraraghavan. "Adsorption of Cadmium from Aqueous Solutions by Perlite," *J. Hazardous Material*, **B94**, 291–303 (2002).

Özer, A. and D. Özer, "Modelling of Copper(II) Adsorption by Using *Saccharomyces cerevisiae* in Batch Stirred Reactors in Series," *Chimica Acta Turcica*, **26**, 75–80 (1998).

Özer, A., D. Özer, and H.İ. Ekiz, "Application of Freundlich and Langmuir Models to Multistage Purification Process to Remove Heavy Metal Ions by Using *Schizomeris leibleinii,*" *Process Biochemistry*, **34**, 919–927 (1999).

Palmieri, M.C., O. Jr. Garcia, and P. Melnikov, "Neodymium Biosorption from Acidic Solutions in Batch System," *Process Biochemistry*, **36**, 441–444 (2000).

Sağ, Y. and T. Kutsal, "Determination of the Biosorption Heats of Heavy Metal Ions on *Zooglea ramigera* and *Rhizopus arrhizus*," *Biochem. Eng. J.*, **6**, 145–151 (2000).

Say, R., A. Denizli, and M.Y. Arıca,"Biosorption of Cadmium(II), Lead(II) and Copper(II) with the Filamentous Fungus *P. Chrysosporium*," *Bioresource Technology*, **76**, 67–70 (2001).

Scott, J.A. and A.M. Karanjkar, "Adsorption Isotherms and Diffusion Coefficients for Metals Biosorbed by Biofilm Coated Granular Activated Carbon," *Biotechnology Letters*, **17**, 1267–1270 (1995).

Smith, J.M., *Chemical Engineering Kinetics*, pp. 314–320, McGraw-Hill, Chemical Engineering Series, Singapore, 1981.

Ting, Y.P., F. Lawson, and I.G. Prince, "Uptake of Cadmium and Zinc by the Alga *Chlorella vulgaris* Part I: Individual Ion Species," *Biotech. and Bioeng*., **34**, 990–999 (1989).

Tobin, J.M., D.G. Copper, and R.J. Neufeld, "Uptake of Metal Ions by *Rhizopus arrhizus* Biomass," *Appl. Environ. Microbiol.,* **47**, 821–824 (1984).

Treybal, R.E., *Mass-Transfer Operations,* pp. 566–575, McGraw-Hill, Singapore, 1980.

Tsezos, M., S.H. Noh, and M.A. Baird, "Batch Reactor Mass Transfer Kinetic Model for Immobilized Biomass Biosorption," *Biotech. and Bioeng*., **32**, 545–553 (1988).

Tsezos, M. and B. Volesky, "Biosorption of Uranium and Thorium," *Biotech. and Bioeng*., **25**, 583–604 (1981).