

## Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis* hoffm.

Fatma Ekmekyapar<sup>a,\*</sup>, Ali Aslan<sup>b</sup>, Y. Kemal Bayhan<sup>a</sup>, Avni Cakici<sup>a</sup>

<sup>a</sup> Engineering Faculty, Department of Environmental Engineering, Atatürk University, Erzurum 25240, Turkey

<sup>b</sup> Education Faculty, Department of Biology, Atatürk University, Erzurum 25240, Turkey

Received 2 November 2005; received in revised form 5 January 2006; accepted 3 February 2006

Available online 13 March 2006

### Abstract

Biosorption of heavy metals can be an effective process for the removal of heavy metal ions from aqueous solutions. In this study, the adsorption properties of lichen biomass of *Cladonia rangiformis* hoffm. for copper(II) were investigated by using batch adsorption techniques. The effects of initial metal ion concentration, initial pH, biosorbent concentration, stirring speed and contact time on biosorption efficiency were studied. In the experiments the optimum pH value was found out 5.0 which was the native pH value of solution. The experimental adsorption data were fitted to the Langmuir adsorption model. The highest metal uptake was calculated from Langmuir isotherm and found to be 7.6923 mg Cu(II)/g inactivated lichen at 15 °C. The results indicated that the biomass of *C. rangiformis* is a suitable biosorbent for removing Cu(II) from aqueous solutions.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Biosorption; Copper; Heavy metal; Wastewater treatment; Lichen; *Cladonia rangiformis*

### 1. Introduction

Environmental contamination by toxic metals is a serious problem due to their incremental accumulation in the food chain and continued persistence in the ecosystem [1]. Heavy metals are discharged in small quantities into environment through numerous industrial activities. Heavy metals such as chromium, copper, lead, nickel in wastewater are hazardous to the environment and health [2].

Copper present in industrial wastes is primarily in the form of the bivalent Cu(II) as a hydrolysis product,  $\text{CuCO}_{3(\text{aq})}$  and/or organic complexes. The presence of copper(II) ions in water may cause toxic and harmful effects to the living organisms present and as well as to consumers. Several industries, for example, dyeing, paper, petroleum, copper/brass-plating and copper-ammonium rayon, release undesired amounts of Cu(II). In the copper-cleaning, copper plating and metal-processing industries, Cu(II) concentrations approach 100–120 mg/l; this value is very high in relation to water quality standards and

Cu(II) concentrations of wastewaters should be reduced to a value of 1.0–1.5 mg/l [3,4].

Mining and metallurgical wastewaters are considered to be the major sources of heavy metal contamination, and the need for economic and effective methods for the removal of metals has resulted in the development of new separation technologies. Precipitation, ion exchange, electrochemical processes and/or membrane processes are commonly applied to the treatment of industrial effluents. However, the application of such processes is sometimes restricted because of technical or economic constraints [5]. Biosorption of heavy metals from aqueous solution can be considered as an alternative technology in industrial wastewater treatment. Adsorbent materials (biosorbents) derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. Biosorption processes are particularly suitable for the treatment of wastewater streams containing dilute heavy metal ion concentrations or when very low concentrations of heavy metals are required [6].

The isotherm represents the equilibrium relationship between the metal uptake by the sorbent and the final metal concentra-

\* Corresponding author. Tel.: +90 4422314879; fax: +90 4422360957.  
E-mail address: fyapar@atauni.edu.tr (F. Ekmekyapar).

tion in the aqueous phase, showing the sorption capacity of the sorbent. There are two widely accepted and easily linearized adsorption isotherm models used in the literature which were proposed, respectively, by Langmuir and Freundlich.

The Langmuir model assumes that the adsorption site is homogeneous, there is no interaction between the nearby adsorbed molecules on the adsorbent surface, adsorbed layer is monolayer, and all the adsorption sites have identical energy of adsorption. Theoretically, when a saturation value is reached, no further adsorption takes place. The Langmuir isotherm is generally applied when no strong adsorption is expected and the adsorption sites are uniform. The equilibrium occurring during physical adsorption at a certain concentration range could be represented by the Langmuir adsorption isotherm. A general form of the Langmuir model equation is [7]

$$q_e = \frac{bq_{\max}C_e}{1 + bC_e} \quad (1)$$

The linear form of this equation can be given as

$$\frac{1}{q_e} = \left( \frac{1}{bq_{\max}} \right) \left( \frac{1}{C_e} \right) + \left( \frac{1}{q_{\max}} \right) \quad (2)$$

where  $q_{\max}$  is the maximum metal uptake corresponding to the saturation capacity (amount of metal ions per unit weight of biosorbent to form a complete monolayer on the surface) and  $b$  is the energy of adsorption (the ratio of adsorption/desorption rates). The variables  $q_e$  and  $C_e$  also show the amount of metal adsorbed on the biomass and the equilibrium (residual) metal concentration in solution. The constants  $q_{\max}$  and  $b$  are the characteristics of the Langmuir isotherm can be determined from a linearised form of Eq. (1), represented by Eq. (2). Therefore, a plot of  $1/q_e$  versus  $1/C_e$  gives a straight line of slope  $(1/bq_{\max})$  and intercept  $(1/q_{\max})$ .

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The general Freundlich equation is as follows [8]:

$$q_e = K_f C_e^{1/n} \quad (3)$$

and linearized form of this model is

$$\log q_e = \log K_f + \left( \frac{1}{n} \right) \log C_e \quad (4)$$

where intercept,  $\log K_f$ , is a measure of adsorbent capacity, and the slope,  $1/n$ , is the intensity of adsorption.  $q_e$  and  $C_e$  are the amount of metal ion removed and the equilibrium concentration, respectively.

The amount of adsorbed metal ions per gram of biomass was obtained by using the general equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (5)$$

where  $q_e$  is the amount of metal adsorbed on the biomass (mg/g),  $C_0$  the initial metal ion concentration in solution (mg/l),  $C_e$  the equilibrium metal ion concentration in solution (mg/l),  $V$  the volume of the medium (l) and  $M$  is the amount of the biomass used in the reaction mixture (g).

Different types of biomass have been investigated for the biosorption properties of heavy metal ions. In these studies researchers used yeast [2], algae [6], fungi [9], bacteria [10,11] and inexpensive plant material such as dried leaves [12], cone [13], wheat shell [14], sawdust [15], rice husk [16].

Lichens are plants composed of an alga and a fungus in a symbiotic relationship that often attach to tree bark. Lichens have been widely used as air pollution monitors because of their ability to strongly bind and accumulate many metals. Lichens have also been found to bind metals in a strongly pH dependent manner. Generally optimum binding is observed at a pH of around 5.0. Little binding is seen below pH values of 2.0 for most metal ions, the metal ion-binding properties of lichens have been pointed out that nonliving lichen biomass is able to bond metal ions to a greater degree than living lichens. This strong metal binding ability of lichen biomass from aqueous solutions would seem to make lichen material an ideal biosorbent for removal of heavy metals [17,18].

Lichens are among the most widely used indicators of environmental quality because of their higher capacity for accumulation and retaining a variety of contaminants, particularly heavy metals and radionuclides [19]. Several studies have been carried out for biomonitoring metal pollution with lichens [17,20,21] but there is lack of information about the sorption ability of lichens. As far as the authors are aware, there is no investigation reported in the literature on the biosorption of Cu(II) by *Cladonia rangiformis*. The lichen biomass is natural, easily available and the use of this low-cost material as biosorbent for dissolved metal ions has been shown to provide economic solution to this global problem. Therefore, this new material was chosen as biosorbent in the study. The aim of the present study was to investigate the use of *C. rangiformis* biomass as a biosorbent for the removal of Cu(II) from an aqueous solution. The optimum biosorption conditions were determined as a function of contact time, pH, initial metal ion concentration, biosorbent concentration and stirring speed.

## 2. Materials and methods

### 2.1. Biosorbent preparation

The lichen biomass of *C. rangiformis* was used as a biosorbent for the biosorption of copper(II) ions. Samples of the lichen were collected from the east black sea region of Turkey in July and August of 2003. They were washed with deionized water and inactivated by heating in an oven at 80 °C for 48 h. The inactivated dried lichen biomass was ground and sieved through the following sizes: 75–180, 180–300, 300–425, 425–600 μm. Around 180–300 μm fraction was used in all experiments.

### 2.2. Preparation of stock solution

The stock solution of Cu(II) (500 mg/l) was prepared by dissolving a weighed quantity of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in deionized water. The required concentrations were prepared from the stock solution by dilution.

### 2.3. Biosorption studies

A known quantity of dried lichen was added to various concentrations (10–100 mg/l) of 100 ml copper(II) solution in 250 ml Erlenmeyer flasks before the pH adjustment of the Cu(II) solutions. The pH of each solution was adjusted to the required value (2.0, 3.0, 4.0, 5.0) by using 0.1N HCl solution. The biosorbent concentrations varied from 1 to 10 g/l and the stirring speeds studied were 50, 100, 150 and 200 rpm. The mixture was stirred in a shaker at a constant speed for 60 min at the room temperature (15 °C). Samples were taken at certain time intervals, filtered by using filter paper (Whatman, 110 mm Ø and 11 µm pore size) for removing the suspended biomass and analyzed for residual copper(II) concentration. The Cu(II) concentration in the supernatant solution was determined using flame atomic absorption spectrophotometer (Shimadzu AA-670) at 324.8 nm [22]. Zeta potentials were measured with a zeta-meter (Zeta-Meter 3.0+542, USA). All experiments were carried out in a batch stirred system.

## 3. Results and discussion

### 3.1. Biosorption time

The mixture of the metal solution and dried lichen were continuously stirred in the shaker at 150 rpm for 4 h. The metal uptake by dried lichen was very rapid and the equilibrium was reached within 15 min. The biosorption continued until 60 min with a small increase in removal of metal ions after the equilibrium time as shown in Fig. 1. Thereafter an increase of residual concentration of metal ion in the solution was observed with time due to starting desorption in the system. This trend suggests that physical adsorption is effective in the bonding mechanism of Cu(II) ions on lichen biomass. Adsorption occurring as a result of van der Waals forces is generally termed “physical” adsorption. Physical adsorption is usually predominant at low temperature and characterized by a relatively low energy of adsorption, that is, the adsorbed molecule is not affixed to a specific site at the surface. This type of adsorption occurring a short time is a reversible reaction and the adsorbed molecule desorbs

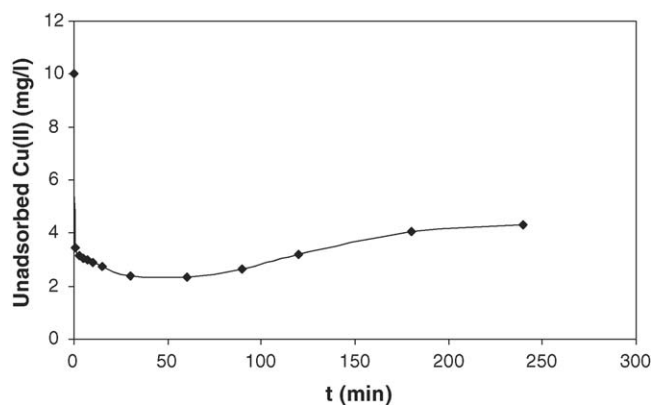


Fig. 1. Effect of contact time on biosorption (initial metal concentration ( $C_0$ ) = 10 mg/l, pH 5.0, temperature ( $T$ ) = 15 °C, biosorbent concentration ( $m$ ) = 5 g/l, stirring speed = 150 rpm).

with changing of adsorbate concentration in solution [23,24]. Thus the experimental period was determined as 60 min.

### 3.2. Effect of pH on copper(II) biosorption

pH seems to be the most important factor in the biosorptive process. It affects the solution chemistry of the metals, the activity of functional groups in the biomass and the competition of metallic ions [5,10,11,25,26]. The effect of initial pH on the biosorption of Cu(II) ions was studied by contacting 0.5 g dried lichen biomass with 100 ml Cu(II) solution. The pH values ranging from 2.0 to 5.0 were studied in the experimental run. Copper(II) removal sharply increased from 12.3% at pH 2.0 to 56.9% at pH 5.0 (Fig. 2). The increase in biosorption levels with an increase in pH can be explained by availability of negatively charged groups at the biosorbent surface which is necessary for the sorption of metals to proceed. At low pH values, the overall surface charge becomes positive and biosorption is interrupted due to competition between Cu(II) ions and  $H^+$  and  $H_3O^+$  ions for the same sites. All experiments were conducted at pH 5.0 because the highest biosorption efficiency was obtained in this pH value. At pH values higher than 5.5, Cu(II) ions precipitated and biosorption studies at these pH values could not be performed. Similar results were also found using *Sphaerotilus natans* [10], *Padina* sp. [27] and petiolar felt-sheath of palm [28].

The electrical potential at the surface of a particle is zeta potential. Zeta potential measurements have been used experimentally to predict optimum pH levels. It can be determined by the measurement of the velocity of particles in the electric field. By measuring how fast particles move across a microscopic grid toward an anode or cathode (positive or negative poles), zeta potential defines the charge on particles in water. The effect of pH on the zeta potential of lichen biomass is illustrated in Fig. 3. Zeta potential values were determined at various pH for deionized water and copper(II) solution. The zeta potential values were measured as 0 mV which is the isoelectric pH point at pH 2.0 for the deionized water and copper(II) solution. As the pH increased the negative charge on lichen biomass increased and copper(II) adsorbed to the negatively charged sites. The

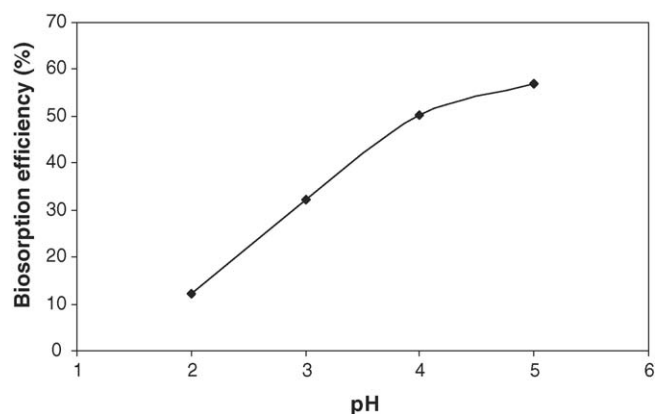


Fig. 2. Effect of pH on biosorption efficiency ( $C_0$  = 50 mg/l,  $T$  = 15 °C,  $m$  = 5 g/l, stirring speed = 150 rpm, contact time ( $t$ ) = 60 min).

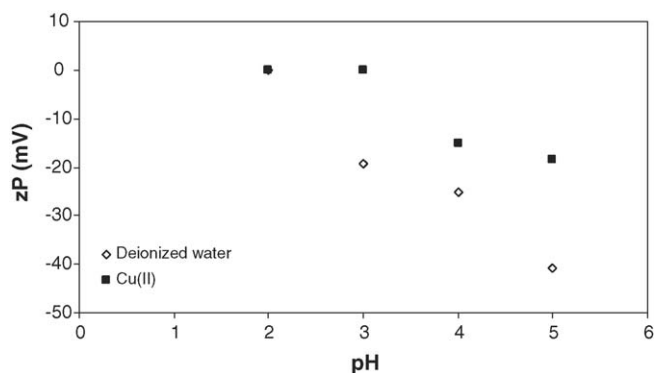


Fig. 3. Relationship between zeta potential and pH ( $C_0 = 50 \text{ mg/l}$ ,  $T = 15^\circ\text{C}$ ,  $m = 5 \text{ g/l}$ , stirring speed = 150 rpm,  $t = 60 \text{ min}$ ).

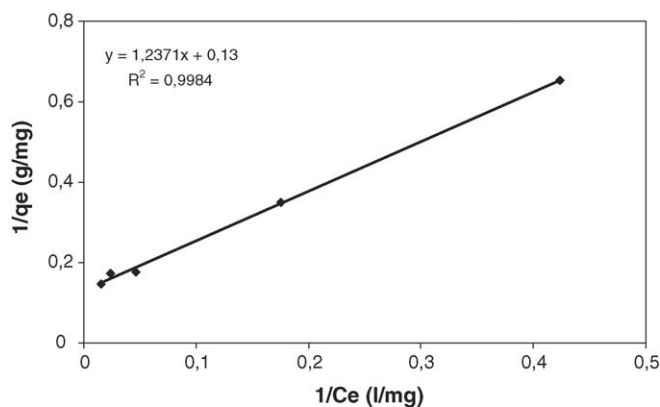


Fig. 5. Langmuir adsorption isotherm for Cu(II) by lichen biomass (pH 5.0,  $T = 15^\circ\text{C}$ ,  $m = 5 \text{ g/l}$ , stirring speed = 150 rpm,  $t = 60 \text{ min}$ ).

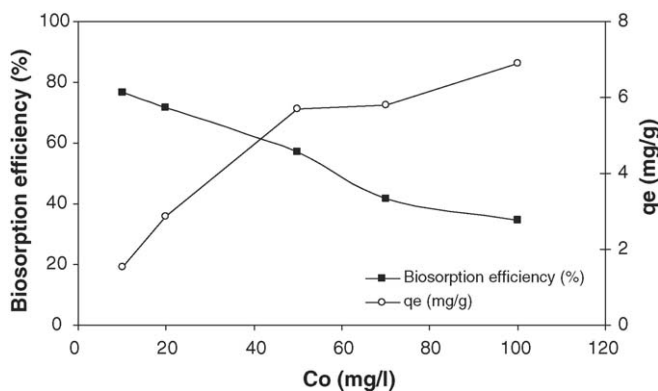


Fig. 4. Effect of initial Cu(II) concentration on Cu(II) uptake ( $q_e = \text{mg Cu(II)/g}$  biomass) and biosorption efficiency (pH 5.0,  $T = 15^\circ\text{C}$ ,  $m = 5 \text{ g/l}$ , stirring speed = 150 rpm,  $t = 60 \text{ min}$ ).

maximum zeta potential value ( $zP = -40.7$ ) was obtained at pH 5.0, which corresponded to the maximum sorption efficiency of Cu(II). Therefore, the sorption of Cu(II) to lichen biomass occurred through electrostatic interaction.

### 3.3. Effect of initial Cu(II) concentration on biosorption

The effect of initial metal concentration on the biosorption capacity of lichen biomass is shown in Fig. 4. Biosorption experiments were carried out at different initial copper(II) concentrations ranging from 10 to 100 mg/l. The biosorption efficiency decreased with the increasing of the initial concentration of the metal ions. As shown in Table 1, the amount of Cu(II) adsorbed on the biomass (mg Cu(II)/g biomass) increased with increasing of initial concentration of Cu(II). These results may be explained

Table 1  
Effect of initial Cu(II) concentration on biosorption (pH 5.0,  $T = 15^\circ\text{C}$ ,  $m = 5 \text{ g/l}$ , stirring speed = 150 rpm,  $t = 60 \text{ min}$ )

$C_0$ (mg/l)	$C_e$ (mg/l)	Adsorbed Cu(II) (mg/l)	$q_e$ (mg/g)
10	2.354	7.646	1.5292
20	5.697	14.303	2.8606
50	21.545	28.455	5.691
70	40.940	29.060	5.812
100	65.570	34.430	6.886

to be due to the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the biomass at higher concentrations. Therefore, more Cu(II) ions were left unadsorbed in solution at higher concentration levels.

The study of the isotherms indicates the adsorption capacity of biomass for removal of copper(II) from the solution at constant conditions. The Langmuir model was widely adopted to characterize the biosorption experimental data of Cu(II) with a correlation coefficient of ( $R^2$ ) 0.9984 (Fig. 5). The adsorption constants of the Langmuir isotherm  $q_{\text{max}}$  and  $b$  were estimated from the intercept and slope of  $1/q_e$  versus  $1/C_e$  graph, respectively and determined as 7.6923 mg/g (0.12 mmol/g) and 0.1051 l/mg (6.68 l/mmol), respectively. The uptake capacities ( $q_{\text{max}}$ ) for Cu(II) of lichen biomass and other adsorbents reported in the literature are given in Table 2. The uptake values obtained in this study are comparable with those values. Some species of algae and bacteria given in the table have higher values for  $q_{\text{max}}$ , however, the lichen biomass presents a higher or approximately the same value for fungi biomass of *Aspergillus oryzae*, lignite and various plant materials.

### 3.4. Effect of biosorbent concentration

Cu(II) biosorption on lichen biomass was studied at various biosorbent concentrations ranging from 1 to 10 g/l. The

Table 2  
Uptake capacities for Cu(II) of various adsorbents reported in the literature

Adsorbent	$q_{\text{max}}$ (mmol/g)
<i>A. oryzae</i> [27]	0.07
Groundnut shell [29]	0.07
Sawdust [29]	0.08
Lignite [27]	0.10
<i>C. rangiformis</i> (this study)	0.12
Wheat shell [14]	0.13
<i>R. arrhizus</i> [27]	0.25
<i>Pseudomonas aeruginosa</i> [27]	0.30
<i>Z. ramigera</i> [27]	0.46
<i>Padina</i> sp. [27]	0.80
<i>E. radiate</i> [27]	1.11

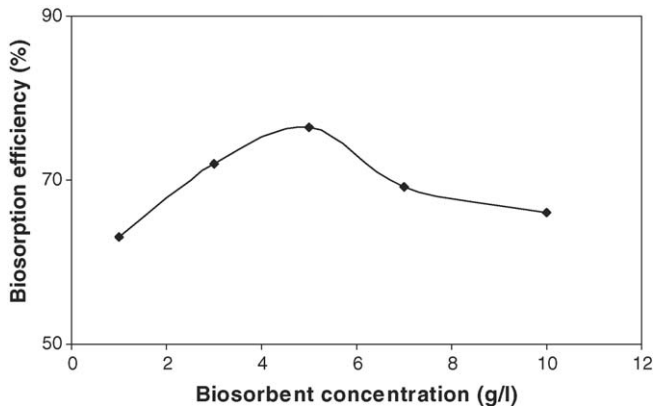


Fig. 6. Effect of biosorbent concentration ( $C_0 = 10$  mg/l, pH 5.0,  $T = 15$  °C, stirring speed = 150 rpm,  $t = 60$  min).

percent removal of Cu(II) increased with an increase in biosorbent concentration because of an increasing adsorption surface area. Copper(II) removal efficiency was the maximum at 5 g/l of biosorbent. But further increases in biosorbent concentration decreased the maximum removal of Cu(II) ions (Fig. 6). This can be explained by forming aggregates during biosorption which takes place at high biomass concentrations causing a decrease of the effective adsorption area. An increase in biosorbent concentration generally increases the adsorbed metal ion concentration because of an increasing adsorption surface area. But in several studies reported in the literature a decrease was found in the metal specific uptakes when the biomass concentrations were increased [30–32]. The researchers implied that a partial cell aggregation taking place at high biomass concentrations caused a decrease of active sites. Various reasons including pH, ionic strength, temperature, metal ion in solution and biomass concentration have been suggested to explain the decreased adsorption capacity at increasing biomass [32].

### 3.5. Effect of stirring speed

Biosorption studies were carried out in a shaker at pH 5.0 and 10 mg/l initial Cu(II) ion concentrations. The stirring speed varied from 50 to 200 rpm. Samples were taken at certain time intervals and analysed for copper(II) ion concentration in solution; the results are presented in Fig. 7. The maximum copper(II) removal efficiency was obtained at 150 rpm. The increase in stirring speed from 50 to 150 rpm resulted in an increase in copper(II) ion removal efficiency. It is known that the mass transfer rate increases with the increase in stirring speed. The boundary layer thickness decreases with increased stirring speed which results in a reduction in surface film resistance [33]. Therefore, the metal ions adsorbed to the biosorbent surface more easily. Further increase in stirring speed did not show an increase in the biosorption efficiency (Fig. 8). At 200 rpm, the biosorption efficiency was found to be slightly lower than that at 150 rpm. The suspension was not homogenous due to the high stirring speed which made the biosorption of Cu(II) difficult. This result indicated that the contact between solid and liquid was more effective at moderate speed (150 rpm).

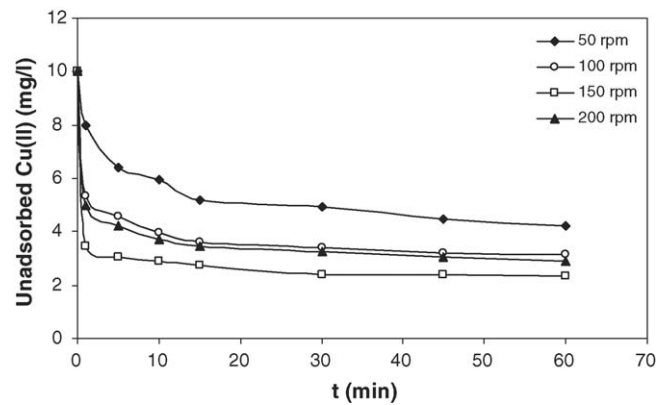


Fig. 7. Effect of stirring speed on biosorption ( $C_0 = 10$  mg/l, pH 5.0,  $T = 15$  °C,  $m = 5$  g/l,  $t = 60$  min).

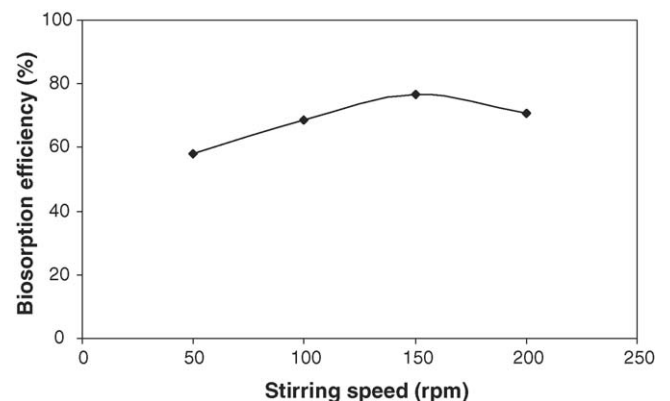


Fig. 8. Effect of stirring speed on biosorption efficiency ( $C_0 = 10$  mg/l, pH 5.0,  $T = 15$  °C,  $m = 5$  g/l,  $t = 60$  min).

## 4. Conclusions

In this study lichen biomass of *C. rangiformis* was used as a biosorbent for copper(II) removal from aqueous solution. The experimental run was observed during 4 h and the contact time was determined as 60 min. The biosorption was rapid and the equilibrium was reached within 15 min. The metal biosorption, which depends on the physical adsorption on the cell surface, is usually rapid during the early period of contact between the adsorbent and the adsorbate. This rapid metal sorption is highly desirable for successful deployment of the biosorbent for a practical application in industrial wastewater treatment. The results showed that pH and initial metal concentration significantly affected the biosorption performance. The maximum biosorption efficiency was 76.5% at  $C_0 = 10$  mg/l, pH 5.0 and 150 rpm for a 5 g/l lichen biomass concentration. The adsorption equilibrium data fitted well to the Langmuir isotherm. *C. rangiformis* can be used as a potential biosorbent in removal of Cu(II) ions from aqueous solution. This natural material is easily available and economic for treatment of industrial wastewater.

## References

- [1] A. Saeed, M. Iqbal, Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arietinum*), Water Res. 37 (2003) 3472–3480.



- [2] Y.K. Bayhan, B. Keskinler, A. Cakici, M. Levent, G. Akay, Removal of divalent heavy metal mixtures from water by *Saccharomyces cerevisiae* using crossflow microfiltration, *Water Res.* 35 (2001) 2191–2200.
- [3] Z. Aksu, Y. Sag, T. Kutsal, The biosorption of copper(II) by *C. vulgaris* and *Z. ramigera*, *Environ. Technol.* 13 (1992) 579–586.
- [4] Y. Sag, M. Nourbakhsh, Z. Aksu, T. Kutsal, Comparison of Ca-alginat and immobilized *Z. ramigera* as sorbents for copper(II) removal, *Process Biochem.* 30 (1995) 175–181.
- [5] F. Veglio, F. Beolchini, Removal of metals by biosorption: a review, *Hydrometallurgy* 44 (1997) 301–316.
- [6] D. Feng, C. Aldrich, Adsorption of heavy metals by biomaterials derived from the marine alga *Ecklonia maxima*, *Hydrometallurgy* 73 (2004) 1–10.
- [7] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [8] H.M.F. Freundlich, Ueber die adsorption in loesungen, *Zeitschrift fr Physikalische Chemie* 57 (1907) 385–470.
- [9] Y. Sag, A. Kaya, T. Kutsal, The simultaneous biosorption of Cu(II) and Zn(II) on *Rhizopus arrhizus*: application of the adsorption models, *Hydrometallurgy* 50 (1998) 297–314.
- [10] F. Pagnanelli, A. Esposito, L. Toro, F. Veglio, Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto *Sphaerotilus natans*: Langmuir-type empirical model, *Water Res.* 37 (2003) 627–633.
- [11] N. Rangsayatorn, P. Pokethitiyook, E.S. Upatham, G.R. Lanza, Cadmium biosorption by cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel, *Environ. Int.* 30 (2004) 57–63.
- [12] M.M. Al-Subu, The interaction effects of cypress (*Cupressus sempervirens*), cinchona (*Eucalyptus longifolia*), and pine (*Pinus halepensis*) leaves on their efficiencies for lead removal from aqueous solutions, *Adv. Environ. Res.* 6 (2002) 569–576.
- [13] H. Uzun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of lead(II) from aqueous solution by cone biomass of *Pinus sylvestris*, *Desalination* 154 (2003) 233–238.
- [14] N. Basci, E. Kocadagistan, B. Kocadagistan, Biosorption of copper(II) from aqueous solutions by wheat shell, *Desalination* 164 (2004) 135–140.
- [15] V.C. Taty-Costodes, H. Fauduet, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*, *J. Hazard. Mater.* 105 (2003) 121–142.
- [16] M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater, *Bioresource Technol.* 86 (2003) 147–149.
- [17] J.N. Beck, G.J. Ramelow, Use of lichen biomass to monitor dissolved metals in natural waters, *Bull. Environ. Contamin. Toxicol.* 44 (1990) 302–308.
- [18] G. Akcin, O. Saltabas, F. Yesilcimen, A. Aslan, Biosorption of heavy metal from aqueous solution by dried lichens, *Int. J. Chem.* 11 (2001) 141–146.
- [19] T.H. Nash, V. Wirth, Lichens, bryophytes and air quality, *Bibliotheca Lichenologica* 30 (1988) 1–298.
- [20] M.A. Reis, L.C. Alves, H.Th. Wolterbeek, T. Verburg, M.C. Freitas, A. Gouveia, Main atmospheric heavy metal sources in Portugal by biomonitor analysis, *Nucl. Instrum. Methods Phys. Res. B* 109/110 (1996) 493–497.
- [21] S.M. Al-Shayeb, M.A. Al-Rajhi, M.R.D. Seaward, The date palm (*Phoenix dactylifera* L.) as a biomonitor of lead and other elements in arid environments, *Sci. Total Environ.* 168 (1995) 1–10.
- [22] American Public Health Association, Standard Methods for Examination of Water and Wastewater, 16th ed., American Public Health Association, Washington, DC, 1986.
- [23] L. Metcalf, H.P. Eddy, Waste Water Engineering, MacGraw-Hill Inc., USA, 1972.
- [24] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, *Biotechnol. Bioeng.* 23 (1981) 583–604.
- [25] A. Lopez, N. Lazaro, J.M. Priego, A.M. Marques, Effect of pH on the biosorption of nickel and other heavy metals by *Pseudomonas fluorescens* 4F39, *J. Ind. Microbiol. Biotechnol.* 24 (2000) 146–151.
- [26] J. Yang, B. Volesky, Biosorption of uranium on *Sargassum* biomass, *Water Res.* 33 (1999) 3357–3363.
- [27] P. Kaewsarn, Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina* sp., *Chemosphere* 47 (2002) 1081–1085.
- [28] M. Iqbal, A. Saeed, N. Akhtar, Petiolar felt-sheath of palm: a new biosorbent for the removal of heavy metals from contaminated water, *Bioresource Technol.* 81 (2002) 151–153.
- [29] S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust, *Sep. Purif. Technol.* 43 (2005) 1–8.
- [30] Z. Aksu, Y. Sag, T. Kutsal, A comparative study of the adsorption of chromium(VI) ions to *C. vulgaris* and *Z. Ramigera*, *Environ. Technol.* 11 (1990) 33–40.
- [31] A. Selatnia, M.Z. Bakhti, A. Madani, L. Kertous, Y. Mansouri, Biosorption of Cd(II) from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass, *Hydrometallurgy* 75 (2004) 11–24.
- [32] A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veglio, Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations, *Hydrometallurgy* 60 (2001) 129–141.
- [33] L.D. Benefield, J.F. Judkins Jr., B.L. Weand, Process Chemistry for Water and Wastewater Treatment, Englewood Cliffs, New Jersey, 1982.