# Copper(II) and zinc(II) biosorption on *Pinus sylvestris* L.

Handan Ucun [a,*], Ozkan Aksakal [b], Ergun Yildiz [a]

[a] *Department of Environmental Engineering, Engineering Faculty, Atatürk University, Erzurum 25240, Turkey*
[b] *Department of Biology, Science and Letters Faculty, Atatürk University, Erzurum 25240, Turkey*

## ARTICLE INFO

## ABSTRACT

The biosorption properties of copper(II) and zinc(II) onto a cone biomass of *Pinus sylvestris* L. was investigated by using batch techniques. The biosorption studies carried out with single metal solutions. The removal of copper(II) and zinc(II) from aqueous solution increased with pH and sharply decreased when pH of the solution was decreased. The maximum biosorption efficiency of *P. sylvestris* was 67% and 30% for Cu(II) and Zn(II), respectively. Batch kinetic and isotherm of biosorption metal ions were investigated. The second-order kinetic model was used to correlate the experimental data. The Freundlich and Langmuir model can describe the adsorption equilibrium of metal(II) on cone biomass. The biosorption constants were found from the Freundlich and Langmuir isotherms at 25 °C. It is found that the biosorption data of metals on cone biomass fitted both the Freundlich and Langmuir adsorption models.

## 1. Introduction

Metals like Cd, Hg, Pb, Cr, Ni, Cu, Zn, and Co are, at elevated concentrations, detrimental to human health and ecosystem stability, and threshold values have been set for these metals for wastewater discharged into environment and for drinking water [1]. Copper present in industrial wastes is primarily in the form of the bivalent Cu(II) as a hydrolysis product, $CuCO_3$(aq) and/or organic complexes. Several industries, for example, dyeing, paper, petroleum, copper/brass plating and copper–ammonium rayon, release undesired amounts of Cu(II) ions. In the copper-cleaning, plating and metal-processing industries, Cu(II) concentrations approach 100–120 mg/L, respectively; 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 [2]. Zinc may be found in wastewater discharges from acid mine drainage, galvanising plants, as a leachate from galvanised structures and natural ores, and from municipal wastewater treatment plant discharges. Zinc is not biodegradable and travels through the food chain via bioaccumulation. Therefore, there is significant interest regarding zinc removal from wastewaters and its toxicity for humans at levels of 100–500 mg/day. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L [3].

Conventional wastewater treatments such as chemical precipitation as sulphides and hydroxides, chemical oxidation or reduction, ion exchange, lime coagulation, evaporative recovery have several disadvantages including high-energy requirements, incomplete metal removal, and high capital investment and running costs [4]. Hence, there is a crucial need for the development of a method that is not only cost effective, but can also be easily implemented. Biosorption by inexpensive biomaterials promises to be an excellent alternative [5,6]. This leads to a search for cheaper, easily obtainable materials for the adsorption of heavy metals [7–13]. Adsorption is defined as the taking up of molecules by the external or internal surface of solids or by the surface of liquids. Adsorption occurs on these surfaces because of attractive forces of the atoms and molecules that make up the surfaces. There are many application of adsorption in both industrial and pollution control processes and many solid adsorbents, including alumina, silica gel and activated carbon are used [14]. Biosorption is an emerging technology that uses biological materials to remove metals from solution through adsorption. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [15]. Biosorption is not restricted to one sorption mechanism only, but comprises several mechanisms such as ion exchange, chelation, precipitation, sorption by physical forces, and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural lignin and polysaccharide networks. Some types of biosorbents are broad spectrum with no specific selectivity for any particular metal ion, while others can be specific for certain types of metal ions [16,17].

* Corresponding author. Tel.: +90 442 231 48 29; fax: +90 442 236 09 57.
*E-mail address:* hanucun@atauni.edu.tr (H. Ucun).

Cone biomass was a waste itself and a readily available biosorbent. The ovulate cone is the well-known cone of the *Pinus* and other conifers. Each cone is composed of an axis upon which are borne, in a spiral fashion, a large number of woody scales. Two megasporangia in ovules develop on the upper surface of each scale. Upon maturity they become seeds; the ovulate cone is, therefore, a seed-bearing cone. The scales of the mature cone are composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignin, rosin and tannins in their cell wall [18,19].

Previous studies have shown that cone has a high potential for the removal of lead, chromium and nickel from aqueous solution [8,20,21]. The present research described here was designed to test the characteristics of *Pinus sylvestris* L. biomass as biosorbent for removing Zn(II) and Cu(II) from aqueous solutions in batch system. The important factors affecting the biosorption efficiency such as solution pH, metal concentration and biosorbent dosage were investigated.

## 2. Materials and methods

### 2.1. Biosorbent preparation

*P. sylvestris* ovulate cones were used in this investigation. They were washed with deionized water and dried at 80 °C for 24 h. The dried biomass was ground in a mortar to a very fine powder and sieved through a 400-mesh copper sieve.

### 2.2. Solution preparation

The metal stock solutions of Cu(II) or Zn(II) were prepared by dissolving 3.803 g of $Cu(NO_3)_2 \cdot 3H_2O$ or 4.415 g of $ZnSO_4 \cdot 7H_2O$ in 1 L of deionized water. The metal solutions of different concentrations were prepared by adequate dilution of the stock solutions with deionized water. The test solutions containing single copper(II) or zinc(II) ions were prepared by diluting 1.0 g/L stock metal ion solution.

### 2.3. Batch biosorption studies

The range of concentrations of prepared Cu(II) and Zn(II) solutions varied from 10 to 100 mg/L. Biosorption of Cu(II) and Zn(II) from an aqueous solution containing a single metal ion was investigated. Biosorption experiments were carried out in 250-mL Erlenmeyer flasks using 100 mL metal-bearing solution with a known quantity of the dried biosorbent. Optimum conditions (pH, contact time and temperature) for biosorption of these metals were determined. Before mixing with the cone biomass for effect of pH, the pH of each solution was adjusted to desired values with $HNO_3$ (for Cu), and $H_2SO_4$ (for Zn). Biosorption at pH above 6.0 was not carried out to avoid any possible interference from metal precipitation. The biosorption medium was placed in a mechanical platform shaker (Thermolyne ROSİ 1000) and stirred for 1 h at the required temperature. The flasks were stirred at 150 rpm. Temperature was maintained at desired values using a temperature-controlled storage unit, where the experiments were conducted. The accuracy of temperature measurements was ±1 °C. The samples were taken at definite time and were filtered immediately to remove biomass by glass fiber filter paper (Whatman GF/A) and heavy metals in the remaining solution were analyzed. The metals biosorption equilibrium was modelled by using the Freundlich and Langmuir models at the optimum pH value of solution.

### 2.4. Analysis of Cu(II) and Zn(II) ions

The concentration of unadsorbed Cu(II) and Zn(II) ions in the effluent were determined using an atomic absorption spectrophotometer (PerkinElmer AAnalyst 700).

## 3. Result and discussion

### 3.1. Effect of solution pH

Biosorption of heavy metal ions (Cu(II) and Zn(II)) onto *P. sylvestris* L. biomass as a function of pH was studied and the results are shown in Fig. 1. The experiments were conducted at various initial metal solution pH values of 2.0–6.0. The metal solutions were contacted with the biosorbent (2.0 g/L) for 1 h at 25 °C. Both metal ions are best adsorbed on the biomass at higher pH values than 4.0. Similar findings were reported for other types of biosorbents [22,23]. The uptake of metal showed a sharp increase with an increase in pH from 2.0 to 4.0. In the experiments the optimum pH value for Cu(II) was obtained at pH 5.0 which was the native pH value of solution. Ekmekyapar et al. [12] reported that the native pH value of copper solution was found pH 5.0 value. Cu(II) and Zn(II) have different hydrolysis constants, and therefore different native pH values. No measurements were performed beyond pH 6 to avoid formation of hydrolysis products of Cu(II), such as $Cu(OH)_{aq}$, that may have different adsorption characteristics than Cu(II). The biosorption of Zn(II) was conducted at pH values of 3.0–6.0, since no significant adsorption was observed at pH 2.0. Zn ions also precipitated at pH values higher than 6.5. The optimum pH value for Zn(II) was obtained at pH 6.0 [24,25].

Earlier studies on heavy metal biosorption have shown that pH was the single most important parameter affecting the biosorption process [22–24]. The different pH biosorption profiles for various heavy metal ions could be related to the nature of chemical interactions of each metal with the biomass. Zeta potential values of cone biomass were determined at various pH values to deionized water from the previous study [8,20]. The negative charge on cone biomass increased with increasing pH and metal bound to the negatively charged sites. The pH dependence of the metal uptake could be largely related to the various functional groups on the cone cell surface and also on the metal solution chemistry. It has been well documented that several biomolecules, proteins, polysaccharides and extracellular polymers contain different surface functional groups, such as carboxyl, carbonyl, hydroxyl, amino, phosphoryl and sulfide groups. The different functional groups have a high affinity towards heavy metals so that they can complex the
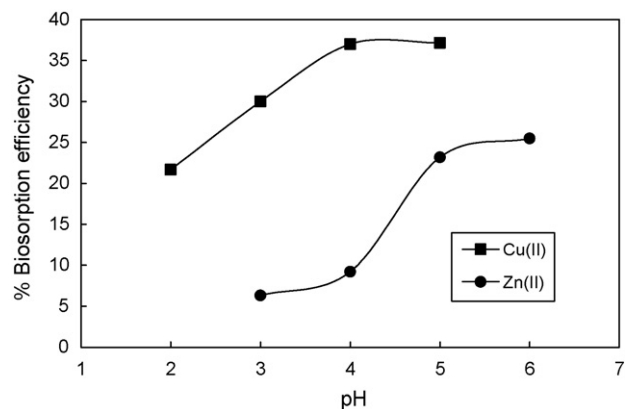


**Fig. 1.** Effect of pH on Cu(II) and Zn(II) biosorption efficiency (initial metal concentration, $C_o = 60$ mg/L; biosorbent dose, $m = 2.0$ g/L).
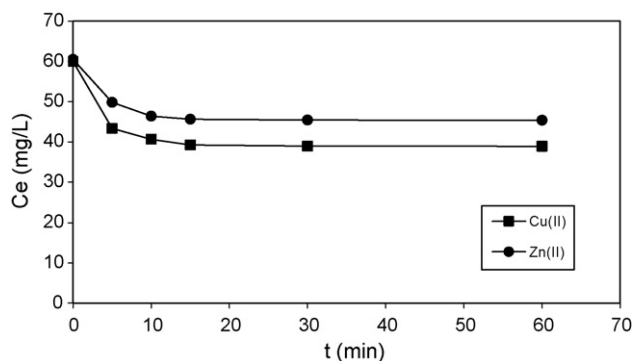
**Fig. 2.** The plot of residual metal ion concentration ($C_e$) with time for copper and zinc at optimum pH values ($m = 1.0$ g/L).

metal ions [13]. As the pH is lowered, however, the overall surface charge on the cells will become positive, which will inhibit the approach of positively charged metal(II) cations. It is likely that protons will then compete with metal ions for the ligands and thereby decreases the interaction of metal ions with the cells [20]. In addition, one can find that *P. sylvestris* biomass has better metal biosorptive capacity for Cu(II) than that for Zn(II), suggesting that the organic functional groups in the biomass have a higher affinity for Cu(II).

### 3.2. Biosorption kinetics

The time-course studies on the biosorption of copper and zinc ions were performed by contacting 60 mg/L of the metal solutions at optimum pH values with 1.0 g/L cone biomass. The experiments were carried out to determine the time of equilibrium for biosorption. The changes in residual metal concentration with time at optimum pH values are shown Fig. 2. Two metals showed a fast rate of sorption during the first 10 min of the metal–biosorbent contact. The equilibrium occurred within 60 min. After this equilibrium period, the amount of adsorbed metal ions did not significantly change with time.

Kinetic of heavy metal biosorption can be modelled by the pseudo-second-order equation shown as follows:

$$\frac{dq}{dt} = k(q_e - q_t)^2 \tag{1}$$

where $q_t$ (mg/g) is the amount of metal ion biosorbed at any given time $t$; $q_e$ the amount of metal ion biosorbed at equilibrium (mg/g) and $k$ (g/mg min) is the rate constant of second-order adsorption [26]. Eq. (2) can be rearranged and linearized to obtain

$$\frac{t}{q_t} = \frac{1}{k(q_e)^2} + \frac{1}{q_e} \tag{2}$$

The plot $t/q_t$ versus $t$ should give a straight line if second-order kinetics are applicable and $q_e$ and $k$ can be determined from the slope and intercept of the plot, respectively. For evaluating the biosorption kinetics of Cu(II) and Zn(II) ions, pseudo-second-order kinetic was used to fit the experimental data. Fig. 3 is shown these plots. The second-order rate constant ($k$) and $q_e$ values were determined from the plots (Table 1).

**Table 1**
Second-order kinetic model parameters for biosorption of copper and zinc on cone biomass

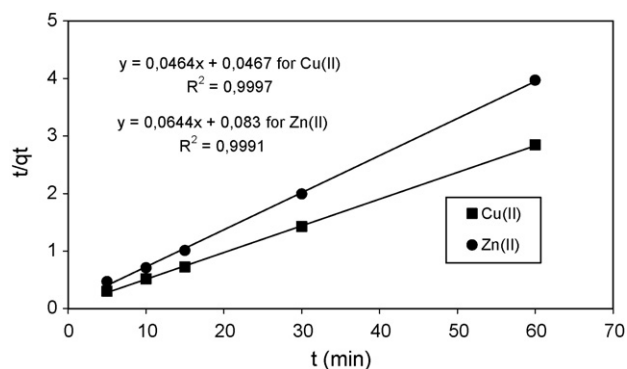|        | $q_{e,exp}$ | $k$   | $q_{e,cal}$ | $R^2$ | RMSE  |
|--------|-------------|-------|-------------|-------|-------|
| Cu(II) | 21.11       | 0.047 | 21.413      | 0.999 | 0.633 |
| Zn(II) | 15.12       | 0.107 | 12.048      | 0.999 | 2.889 |



**Fig. 3.** Second-order reaction kinetics plot for biosorption of Cu(II) and Zn(II) on cone biomass.

Standard statistics of root mean squared error (RMSE) is calculated with Eq. (3). Here, $q_p$ is the predicted biosorption capacity (mg/g), $q_o$ is the observed biosorption capacity (mg/g) and $n$ is the number of samples [27].

$$RMSE = \left[ \frac{1}{n} \sum_{i=1}^{n} (q_p - q_o)_i^2 \right]^{0.5} \tag{3}$$

In Table 1, $R^2$ denotes the correlation between the observed and predicted values, and RMSE speaks to the goodness of fit of the model to the data; the smaller the RMSE, the better the fit. It is found that the kinetic of heavy metal biosorption on the cone biomass was RMSE well for Cu(II) as compared to Zn(II). The values of correlation coefficient for Ho equation were very high ($R^2 > 0.999$) and the theoretical $q_{e,cal}$ values were closer to the experimental $q_{e,exp}$ values (Table 1). In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cu(II) and Zn(II) onto cone biomass.

### 3.3. Effect of temperature

The biosorption of Cu(II) and Zn(II) was studied between 15 and 35 °C. The results show that the sorption of Cu(II) and Zn(II) ions on the cone biomass did not change significantly in this temperature range (Fig. 4). Similar findings were reported for other type of biosorbent [28].

### 3.4. Effect of initial metal ions concentration on biosorption

Different initial metal ion concentrations were contacted with biomass and the biosorption capacity (mg metal
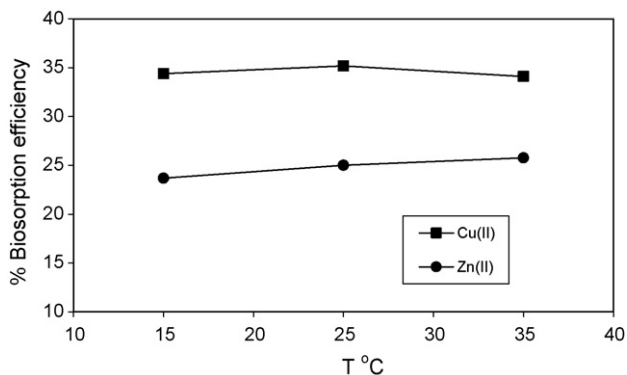


**Fig. 4.** The effect of temperature on the biosorption efficiency of copper and zinc ions to *P. sylvestris* ($C_o = 60$ mg/L, $m = 1.0$ g/L).
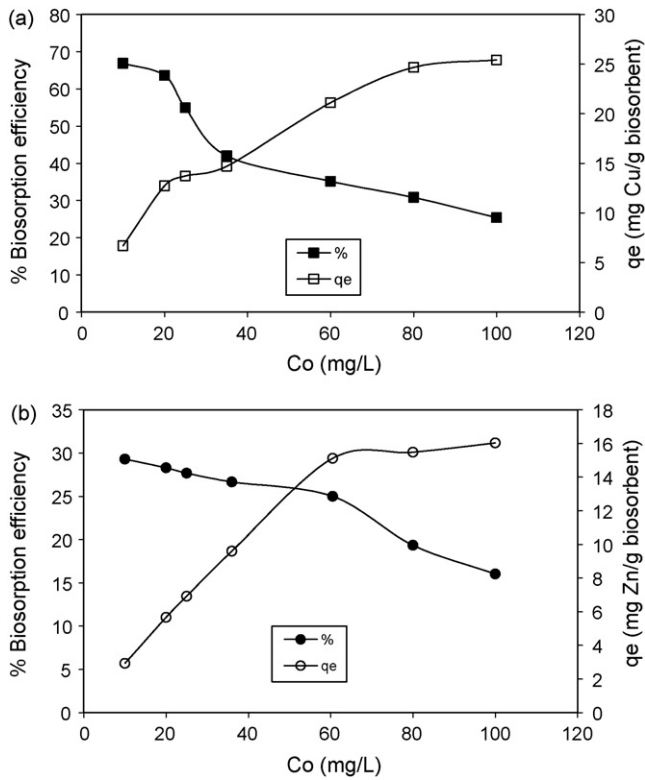
**Fig. 5.** Effect of initial metal concentration on biosorption capacity ($q_e$ mg/g biosorbent) and the biosorption efficiency of *P. sylvestris* for (a) Cu(II) and (b) Zn(II) ($m = 1.0$ g/L).

adsorbed/g biomass) and the biosorption efficiency (Fig. 5) was determined. For each flask, the initial Cu(II) and Zn(II) concentrations were varied from 10 to 100 mg/L. From 10 mg/L metal ion solution, the biosorption of 67% copper and 30% zinc were achieved with 1.0 g/L *P. sylvestris*. The rate of biosorption is a function of initial concentration of ions. The biosorption efficiency of metal ions to the cone biomass decreased as the initial concentration of metal ions was increased. This appears to be due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for complexation of Cu and Zn ions at higher concentration levels. The biosorption capacity, as it is a measure of the amount of metal ions bound by unit weight of biomass increased first with increasing of the initial concentration of metal ions and reached a saturation value. At higher concentrations, more metal ions are left unadsorbed in solution due to the saturation of adsorption site.

For the low solution concentrations, which are typically encountered in process chemistry, negative deviations from ideal behavior are experienced, and activity coefficient has a value less than unity. However, the value of the activity coefficient approaches unity as the solution approaches infinite dilution because the magnitude of the chemical and physical interactions, which occur due to the presence of the ionic species, becomes insignificant. The ionic strength of a solution, $I$, is a value obtained by integrating the effect of these two parameters into a single expression suitable for use in the theoretical equations which have been derived for the calculation of activity coefficients. Ionic strength is determined by following relationship [14]:

$$I = \frac{1}{2}\sum_{i=1}^{i=i} C_i Z_i^2 \tag{4}$$

where $I$ is ionic strength, $C_i$, analytical concentration (M) of $i$th species and $Z_i$, oxidation number of $i$th species.

The activity coefficient $\gamma$ for ionic chemical species can be estimated from the extended Debye–Hückel relationship for solutions whose ionic strength is not 0.1 M [14]:

$$\log \gamma = -AZ^2 \left( \frac{\sqrt{I}}{1 + Bb\sqrt{I}} \right) \tag{5}$$

where $A$ and $B$ are constants and $b$ the hydrated-ion diameter of ions. When the ion concentration is low ($I \sim 0$), these ions behave independently and the ion activity is equal to the ion concentration, i.e., $\gamma = 1.0$. However, with increasing ionic strength $I$, there is electrostatic attraction between ions with opposite charges, then the ion activity becomes smaller than the concentration, and as a result $\gamma$ becomes smaller than 1.0. The interaction between ions with charges of the same sign is not considered, because these ions repel each other and migrate to areas where there is no interaction. The activity coefficient of neutral species in solution is taken as 1.0 because of the absence of electrostatic interaction with other ions [29].

A 10 mg/L solution of Zn(II) is equivalent to 0.15 mM Zn(II), and a 10 mg/L solution of Cu(II) is equivalent to 0.16 mM Cu(II). Hence the Zn(II) solution have an ionic strength of 0.0006 M, and the Cu(II) solution have an ionic strength of 0.0005 M. The individual activity coefficient for Cu(II) and Zn(II) ions can be calculated as $\gamma_{Cu} = 0.9$ M $\gamma_{Zn} = 0.9$ M by taking; $A = 0.5106$, $B = 0.3293$, $b = 6$ for 25 °C. According to the Debye–Hückel equation for solutions with ion concentration <0.1 M, the activities for both Cu(II) and Zn(II) were calculated to be 1.0, and therefore equivalent.

### 3.5. Equilibrium adsorption models

Cu(II) and Zn(II) biosorption isotherms were obtained at constant pH, temperature and biosorbent dosage. For each metal, the pH value was chosen at its optimum value. To test the fit of data, the Langmuir and Freundlich isotherm models were applied to this study. The Langmuir and Freundlich isotherms are the most widely used models for studying the biosorption equilibrium between the metal solution and the solid biomass phase [1,22–25]. The empirical Freundlich isotherm model based on a heterogeneous surface is given below:

$$q_e = K_f C_e^{1/n} \tag{6}$$

where $K_f$ and $n$ are Freundlich constants characteristic of the system. $K_f$ and $n$ are indicators of adsorption capacity and intensity, respectively [30].

The Langmuir isotherm model is valid for monolayer biosorption onto surface and finite number of identical sites and given by the following equation:

$$q_e = \frac{(Q_{max}bC_e)}{(1 + bC_e)} \tag{7}$$

where $Q_{max}$ and $b$ are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively [31].

Both isotherms consider $q_e$ as a function of the $C_e$, corresponding to the equilibrium distribution of ions between aqueous and solid phases as the $C_o$ increases. The batch biosorption data were fitted to the above two models by non-linear regression analysis using the software package STATISTICA 6.0 for WINDOWS. The Freundlich and Langmuir equations for isotherm data were modelled using Simplex and Quasi-Newton algorithms. The curves in Fig. 6 were generated from Freundlich and Langmuir model equations, respectively. As seen from Fig. 6, both the Freundlich and Lang-
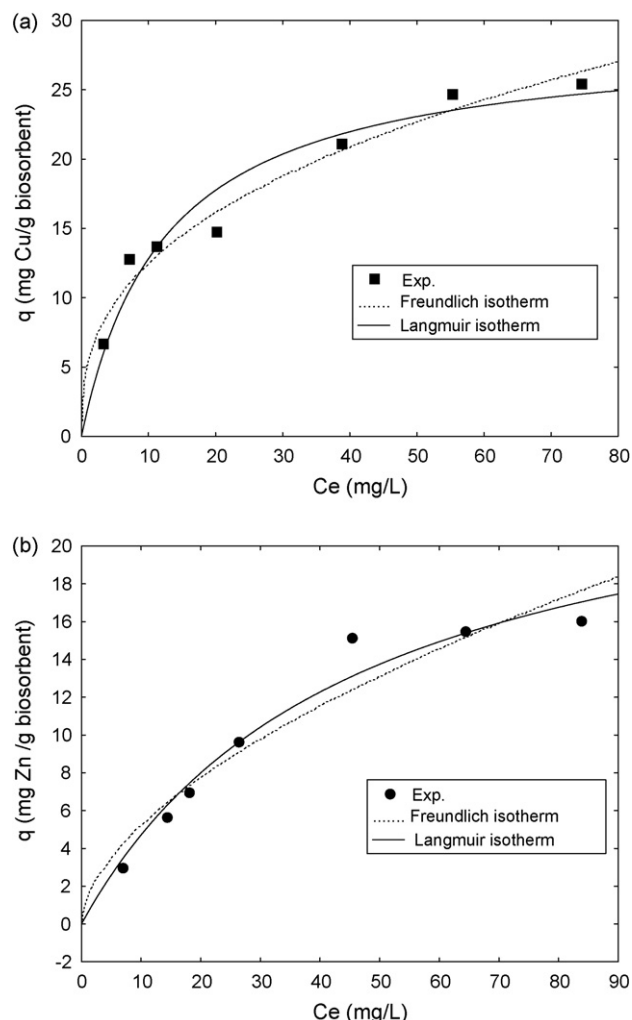
**Fig. 6.** Application of equilibrium adsorption models by *P. sylvestris* for (a) Cu(II) and (b) Zn(II).

muir adsorption models were suitable for describing the short-term biosorption of copper(II) and zinc(II) by *P. sylvestris* L. Table 2 shows the model constants along with correlation coefficients and RMSE for biosorption of copper and zinc on cone biomass. Standard statistics of RMSE is calculated with Eq. (3).

The $K_f$ values obtained from the Freundlich model, suggest that the metal binding affinity was in the order Cu > Zn. The organic functional groups in the biomass have a higher affinity for Cu(II). A large value of $b$ implies strong bonding. The larger the value of $b$, the greater is the fractional surface coverage at a fixed temperature and at a fixed value of $C_e$, or the higher is the temperature required for a specified fractional surface coverage at fixed $C_{eq}$ [24]. The experimental values of the maximal biosorption capacities ($Q_{max}$) of cone biomass were 28.83 and 26.39 mg/g for Cu and Zn, respectively. It was hard to compare the maximum capacity with many reported
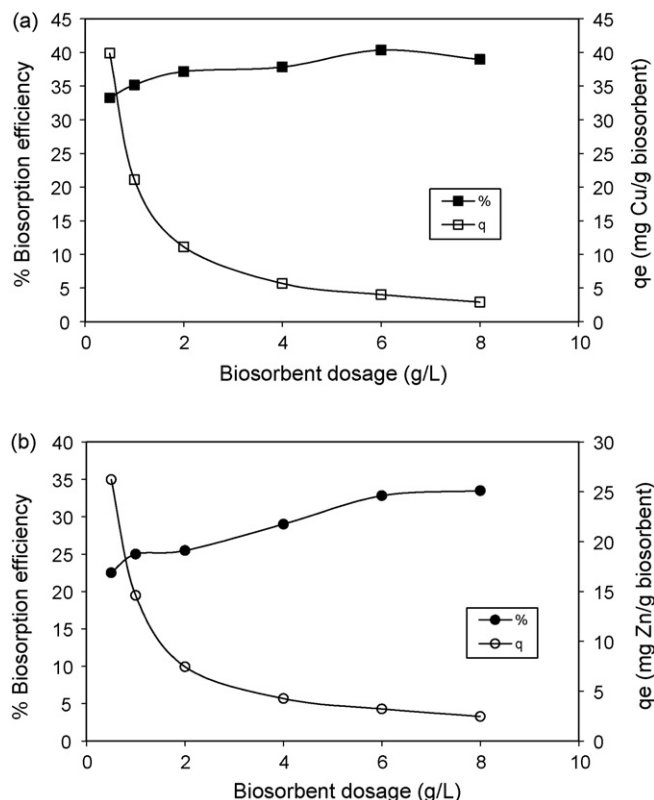


**Fig. 7.** Effect of initial biosorbent concentration on biosorption capacity and the biosorption efficiency of *P. sylvestris* for (a) Cu(II) and (b) Zn(II) ($C_o = 60$ mg/L).

studies due to differences in experimental conditions and models used to fit the data in each study. However, under similar conditions, the isotherm parameters of fungus biomass were reported to be $K_f = 1.47$, $n = 2.89$, $b = 0.19$ and $Q_{max} = 6.35$ for Cu(II) [22]. The results from the present study clearly showed that the Cu(II) binding capacity of cone biomass was higher than the reported capacity for fungus biomass.

### 3.6. Effects of initial biosorbent concentrations

The influence of initial biosorbent concentration on the biosorption capacity of cone biomass was studied for metals concentration of 60 mg/L and a content of 0.5–8.0 g/L of biomass. The experimental results are presented in Fig. 7. The increase in biomass dose resulted in increase in biosorption efficiency. This is because of the availability of more and more binding sites for complexation of metal ions. Further, increment in cone biomass dose did not cause significant improvement in biosorption. It may be that further increase in dose results in clumping of the sorbent particles, which can result in loss of available surface area for metal ion uptake. However, Cu(II) and Zn(II) binding capacity values showed a reverse trend and therefore, its magnitude decrease with increment in biomass dosage. Its maximum values were, therefore,

**Table 2**
Freundlich and Langmuir model parameters for biosorption of metal ions by cone biomass ($m = 1.0$ g/L; $T = 25$ °C)

| Metal ion | pH | Freundlich isotherm | | | | Langmuir isotherm | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $K_f$ | $n$ | $R$ | RMSE | $Q_{max}$ (mg/g) | $b$ (L/g) | $R$ | RMSE |
| Cu | 5 | 5.30 | 2.69 | 0.98 | 1.21 | 28.83 | 0.08 | 0.97 | 1.56 |
| Zn | 6 | 1.39 | 1.74 | 0.96 | 1.35 | 26.39 | 0.02 | 0.98 | 1.04 |

obtained for the lowest biosorbent dosage (0.5 g/L). An increase in metal/biosorbent ratio caused a decrease in biosorption efficiency.

## 4. Conclusions

The biosorption of Cu(II) and Zn(II) on cone biomass of *P. sylvestris* was studied. It has been considered that this biosorbent has acceptable biosorption capacity towards the investigated metal ions. The pH of the aqueous phase strongly affects the biosorption capacity. It was concluded that the adsorption is favoured by an increase of pH. The maximum biosorption efficiency of *P. sylvestris* was 67% and 30% for Cu(II) and Zn(II) at $C_o = 10$ mg/L, respectively. The extent of the removal of the heavy metals is directly related with the concentration of cone biomass in the suspension. The biomass exhibited high biosorption capacity in 1 h at $C_o = 60$ mg/L and $m = 0.5$ g/L. The adsorption isotherms were used for a mathematical description of biosorption of metal ions onto cone biomass. It was seen that the adsorption equilibrium data fitted well to the adsorption models. The results of this study indicate the possibilities that exist in the clean-up of the environment with the use of natural resources.

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