Biosorption of Lead and Zinc Ions by Phanerocheat Chrysasporium – Research on Fixed Bed Column

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Abstract
In this research the biosorption process of lead and zinc ions by Phanerocheat chrysasporium was investigated. The dried biomass of P. chrysasporium was used for the uptake of Pb (II) and Zn (II) ions from aqueous solution. The study was carried out in five main stages. The first stage involved the preparation of biomass under optimum conditions (pH=4.5 and T=35°C), making dried biomass, and investigation of methods for providing the active microorganisms. In this study, boiling in NaOH 0.1 N was selected as the best method that increases the biosorption process. In the second stage, the dried and active biomass were added to artificial wastewater containing heavy metal ions of single metals, in order to attain optimum conditions for biosorption of any individual metal. These conditions were pH=5, T=37 °C, V=150 rpm for lead and pH=5.5, T=30°C, V=150 rpm for zinc. The third stage deals with mixing wastewater containing metals in double and triple forms with the biosorbent. The biosorption process decreased relative to sorption obtained with a single metal. In the fourth stage, the column was designed as a stabilised ground for biosorption. The column was filled first by dried powder biomass and second by stabilised biomass with Ca-alginate which had been inactived by heat; the results of two methods were compared. Mathematical calculations for biosorption were also applied. The final stage of biosorption involves desorption by 50 mM HCl in which the biomass was washed out by HCl several times and heavy metals were then separated from it. The results show that the biosorption efficiency values of heavy metals without a stabilised bed were 86% and 64% for lead and zinc respectively, whereas with the stabilised bed, they were 98% and 85%. Compared to other metal removal methods, the desorption process with a stabilised bed resulted an efficiency more than 90%.

Key words: Biosorption, lead and zinc, fixed bed, Phanerocheat chrysasporium

Introduction
Heavy metal releases to the environment have been increasing continuously as a result of industrial activities and technological developments, posing a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. It is therefore important to develop new methods for metal removal from dilute solutions and for the reduction of heavy metal ions to very low concentrations. The use of conventional treatment technologies such as ion exchange, chemical precipitation, reverse osmosis and evaporative recovery is often inefficient and/or very expensive (Chong and Volesky 1995; Leusch et al. 1995). In recent years, the biosorption process has been extensively studied using microbial biomass as biosorbent for heavy metal removal. In these studies, the metal removal abilities of various species of bacteria, algae, fungi and yeasts were investigated (Chen and Yiacaumi 1997; Guibal et al.1992 Yetis et al. 2000). Biosorption consists of several mechanisms, mainly ion exchange, chelation, adsorption and diffusion through cell walls and membranes (Churchill et al. 1995), which differ depending on the species used, the origin and processing of the biomass and solution chemistry.
The purpose of this study is to investigate the use of nonliving biomass of *Phanerochaete chrysosporium* -type white-rot fungus as a biosorbent. This has been also employed for the treatment of industrial effluents containing chlorinated organics, such as in the pulp and paper industries (Kirby et al. 1995; Mittar et al. 1992), and heavy metal removal from wastewaters having more than one metal ion in their constituents. A biological process of wastewater treatment by white-rot fungi, such as *Phanerochaete chrysosporium,* continuously produces a waste sludge of fungal mass, which needs to be appropriately disposed. Thus, the main objective of selecting this type of fungus for biosorption study is to assess the possibility of utilising the waste sludge for removal of heavy metals from industrial effluents, before disposal. The effect of pretreatment of *p.chrysosporium* biomass on biosorption of lead and zinc was studied. Pretreatment of live biomass using sodium hydroxide resulted in significant improvements in biosorption of lead and zinc in comparison with live *p.chrysosporiom* (Kapoor and Viraraghavan 1997).

Materials and methods

Preparation of biosorbent

The nonliving biomass of *p.chrysosporium* was used as a biosorbent for the biosorption of lead and zinc ions from an aqueous solution. The fungus was cultivated in a liquid medium using the shake flask method. The growth medium consisted of (*g/L of distilled water*): D-glucose, 10.0; KH_2PO4, 20.0; $MgSO4.7H_2O$, 0.5; NH_4Cl, 0.1; $CaCl_2.H_2O$, 0.1; thiamine, 0.001. The pH of the medium was adjusted to 4.5 before autoclaving. Biomass pretreated with sodium hydroxide was ground and sieved through filtration using glass fiber filter papers (Whatman GF-C) and washed with deionised water until the pH of the wash solution was in near neutral range (pH 6.8-7.2).

Preparation of stock solution

The stock solution of Pb (II) and Zn (II) (500mg/L) was prepared by dissolving a weighed quantity of Pb $(NO3)_2$ and $Zn(NO3)_2.7H_2O$ in deionised water. The required concentrations were prepared from the stock solution by dilution. A known quantity of dried biomass was added to various concentrations (10-100 mg/L) of 100 mL metal solution in 250 mL Erlenmeyer flasks before pH adjustment of the metal solution. The pH of each solution was adjusted to the required value (1, 2, 3, 4, 5, 6, and 7) by using 0.1 $NHNO_3$ solutions. 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 6 h at the designated temperature range (20, 20.30, 35 °C).

Samples were taken at certain time intervals, filtered by using filter paper for removing the suspended biomass and analysed for residual metal concentration. The metal concentration in the supernatant solution was determined using a flame atomic absorption spectrophotometer (Shimadzu AA-670).

Results and discussion

Biosorption time

The kinetic profiles of Pb (II) and Zn (II) biosorption by powdered biomass at 100 mg/L metal concentrations are shown in Figure 1. The metal uptake is rapid for all concentrations in the first 30 minutes of contact, accounting for about 88% and 81% biosorption of Pb (II) and Zn (II) respectively.

Effect of pH on metal ion biosorption

The effect of pH on *Pb(II) and Zn(II)* biosorption is shown in Figure 2. The maximum adsorption of heavy metal species occurred between pH 5.0 and 6.0. The amounts of adsorbed heavy metal ions (Pb (II) and Zn (II) at 100 mg/L) on the biosorbent at pH 6 were found to be 87.32 and 57.21 mg/g for prepared biomass, respectively.

Figure 1 *Effect of contact time on Pb (II) and Zn (II) adsorption on p.chrysosporium; 100 mL single metal solution: pH= 6; initial metal-ion concentration (C_0)= 100 mg/L; biosorbent concentration (m)=5 g/L; temperature (T)= 35 °C; stirring speed=150 rpm*

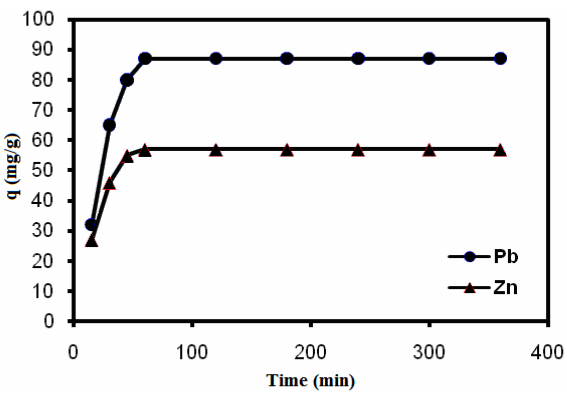
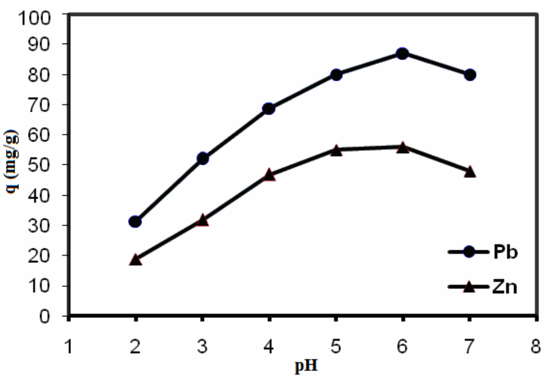


Figure 2 *Effect of pH on Pb(II) and Zn(II) adsorption on p.chrysosporium; 100 mL single metal solution: contact time (t)=60 min ; initial metal-ion concentration(C_0)= 100 mg/L; biosorbent concentration (m)= 5 g/L; temperature (T)= 35 °C; stirring speed= 150 rpm*



Effect of temperature
Results for metal sorption experiments carried out at different temperatures ranging from 10 to 50 ˚C are shown in Figure 3. Data show significant differences in specific metal uptake by the biomass.

Effect of biosorbent concentration
Pb (II) and Zn (II) biosorption on biomass were studied at various biosorbent concentrations ranging from 1 to 10 g/L. The percent removal of Pb (II) and Zn (II) increased with an increase in biosorbent concentration because of an increasing adsorption surface area. The maximum biosorption efficiency was obtained at 5 g/L of biosorbent for both metal species, but further increases in biosorbent concentration decreased the maximum removal of metal ions, as shown in Figure 4.

Figure 3 *Effect of temperature on Pb(II) and Zn(II) adsorption on p.chrysosporium; 100 mL single metal solution: contact time (t)=60 min ; initial metal-ion concentration (C_0)= 100 mg/L; biosorbent concentration (m)=5 g/L ; pH=6; stirring speed=150 rpm*

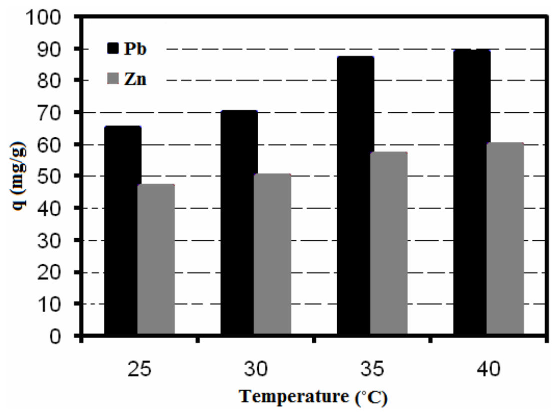
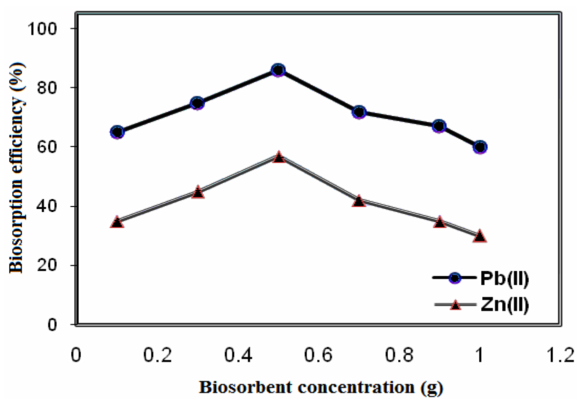


Figure 4 *Effect of biosorbent concentration on Pb(II) and Zn(II) adsorption on p.chrysosporium; 100 mL single metal solution: contact time (t)= 60 min ; initial metal-ion concentration (C0)= 100 mg/L; temperature (T)= 35˚C; pH=6; stirring speed=150 rpm*



Adsorption isotherms
In this study, the experimental data were fitted to the two most commonly used adsorption isotherms for biosorption studies incorporating Langmuir and Freundlich models. The Langmuir equation is applicable for monolayer adsorption on a surface containing a finite number of identical adsorption sites (Namasivayam and Arasi 1997). The Langmuir model is described by the following equation:

$$q = \frac{b q_{\max} C_e}{1 + b C_e} \tag{1}$$

A linear expression for the Langmuir isotherm can be expressed as:

$$\frac{1}{q} = \left(\frac{1}{b q_{\max}}\right)\left(\frac{1}{C_e}\right) + \left(\frac{1}{q_{\max}}\right) \tag{2}$$

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 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 that can be determined from a linearised form of Equation 1, represented by Equation 2. Therefore, a plot of 1/q versus $1/C_e$ gives a straight line with slope of $1/bq_{max}$ and intercept of $(1/q_{max})$. The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The general Freundlich equation is as follows:

$$q = K_f C_e^{\frac{1}{n}} \tag{3}$$

The linearised form of this model is:

$$Ln\,q = Ln\,K_f + \left(\frac{1}{n}\right) Ln\,C_e \qquad (4)$$

where q and C_e are the amount of metal ion removed and the equilibrium concentration respectively. K_f and n are Freundlich isotherm constants depending on temperature and adsorbent-adsorbate system. A linear plot of $Ln\,q$ versus $Ln\,C_e$ gives the values of K_f and n.

The determined constants and the correlation coefficients of the Langmuir and Freundlich isotherms are shown in Table 1.

Table 1 *Parameters of Langmuir and Freundlich isotherms for Pb(II) and Zn(II) adsorption on P.chrysosporium in single-ion situation*

	Langmuir isotherm constants			Freundlich isotherm constant		
Metal ion	q_{max}	b	R^2	K_f	n	R^2
Pb(II)	129.87	0.067	0.9935	33.11	4.149	0.9909
Zn(II)	106.383	0.0376	0.99094	13.46	2.755	0.9849

Conclusions

In this study, nonliving biomass of *phanerochaete chrysosporium* was used as a biosorbent for lead (II) and zinc (II) removal from aqueous solution. The experimental run was observed for 6 h and the contact time was determined as 60 min. The biosorption was rapid and the equilibrium was reached within 15 min. 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 use 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 57% for Zn (II) and 87% for Pb (II) at Co=100 mg/L, pH=6 and 150 rpm for a 5 g/L biomass concentration. The adsorption equilibrium data fitted well to the Langmuir and Freundlich isotherms. *P.chrysosporium* can be used as a potential biosorbent in removal of Pb (II) and Zn (II) ions from aqueous solution. The biosorbent can be regenerated and reused by HNO_3 (50 Mm). The affinity order of heavy metal ions was Pb (II) > Zn (II). The presence of other ions (as the competitive ions) decreases experimental ion uptake. This natural material is easily available and economic for treatment of industrial wastewater.

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