IJMEI

International Journal of Mining & Environmental Issues,
Vol. 1, No.1, 2010.

Biosorption of Lead (II) and Zinc (II) ions by pre-treated biomass of phanerochaete chrysosporium

R. Marandi[1]*, F. Doulati Ardejani[2], H. Amir Afshar[1]

1. Islamic Azad University –North Tehran Branch, Department of Environment
2. Faculty of Mining, Petroleum and Geophysics, Shahrood University of Technology; Shahrood, Iran

Received 10 February 2009; accepted 23 February 2010
*e-mail: r_marandi@iau-tnb.ac.ir

Abstract

The biosorption of heavy metals can be an effective process for the removal of such metal ions from aqueous solutions. In this study, the adsorption properties of nonliving biomass of phanerochaete chrysosporium for Pb (II) and Zn (II) were investigated by the use of batch adsorption techniques. The effects of initial metal ion concentration, initial pH, biosorbent concentration, stirring speed, temperature and contact time on the biosorption efficiency were studied. The experimental results indicated that the uptake capacity and adsorption yield of one the metal ion were reduced by the presence of the other one. The optimum pH was obtained as 6.0. The experimental adsorption data were fitted to both Langmuir and Frundlich adsorption models for Pb (II) and to the Langmuir model for Zn (II) ion. The highest metals uptake values of 57 and 87 mg/g were calculated for Zn (II) and Pb (II) respectively. Desorption of heavy metal ions was performed by 50 mM HNO_3 solution. The results indicated that the biomass of phanerochaete chrysosporium is a suitable biosorbent for the removal of heavy metal ions from the aqueous solutions.

Keywords: *Heavy metals, Biomass, Pb(II), Zn(II), Biosorption, Phanerochaete chrysosporium, Wastewater treatment.*

1. Introduction

There High concentration of heavy metals in the environment as a result of mining operations may cause the death of vegetation and having detrimental impacts on aquatic biota in receiving water ways. Heavy metals pose a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. In order to minimise the risk of environmental pollution from the waste effluents containing high concentrations of heavy metals, it is necessary to develop new techniques for metal removal from aqueous solutions. Attempts have been made to find appropriate treatment systems in order to remove heavy metals from the wastes discharged from different industries.

The use of conventional treatment technologies such as ion exchange, chemical precipitation, reverse osmosis and evaporative recovery is often inefficient or very expensive [1-5]. In recent years, the biosorption process has been extensively studied using microbial biomass as biosorbents for heavy metal removal. In these studies, metal removal abilities of various species of bacteria, algae, fungi and yeasts were investigated [6-8]. Biosorption consists of several mechanisms, mainly ion exchange, chelation, adsorption and diffusion through cell walls and membranes [9, 10], depending on the species used, the origin and processing of the biomass and solution chemistry.

The exact mechanism by which micro-organisms take up metals is not clear, but it has been demonstrated that both living and non-living fungal biomass may be utilised in biosorption processes, as they often exhibit remarkable tolerance towards metals and other adverse conditions such as low pH [11-13]. Although metal removal from industrial effluents using biosorption has been studied extensively [11, 14],

fewer studies have been carried out to examine the biosorbent characteristics of the white-rot fungi.
There are several factors affecting the biosorption process, such as temperature, pH, agitation rate, metal concentration, biomass concentration and stirring speed [6, 11, 15]. pH and metal concentration have greater influence on the metal removal by this process [8, 14, 15].
The purpose of this study is to investigate the use of nonliving biomass of Phanerochaete chrysosporium type white-rot funguse as a biosorbent, which was also employed for the treatment of industrial effluents containing chlorinated organics, such as the pulp and paper industries [16-18], and in heavy metal removal from wastewaters with more than one metal ion in their constituents. A biological process of wastewater treatment by white-rot fungi, such as Phanerochaete chrysosporium, continuously produces waste sludge of fungal mass, which needs to be appropriately disposed of. 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 Phanerochaete 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 Phanerochaete chrysosporiom [19].

2. Material and methods

2.1. Preparation of biosorbent

The nonliving biomass of Phanerochaete chrysosporiom was used as a biosorbent for sorption of lead and zinc ions from an aqueous solution. The fungus was cultivated in liquid medium using the shake flask method. The growth medium consisted of (g/L of distilled water): D-glucose, 10.0; KH_2PO_4, 20.0; $MgSO_4.7H_2O$, 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. Once inoculated, flasks were incubated on orbital shaker at 150 rpm for 72 h at 35 ˚C. After incubation, the biomass was collected from the medium and washed with distilled water. It was then boiled for 15 min in 500mL of 0.5N sodium hydroxide solution. Sodium hydroxide –pretreated biomass was ground and sieved through filtration using glass fiber filter papers (Whatman GF-C) and it was washed with deionised water until the pH of the wash solution was in near neutral range (pH 6.8-7.2). It was then dried at 60 ˚C in an oven for 12 h.

2.2. Preparation of stock solution

The stock solution of Pb (II) and Zn (II) (500 mg/L) was prepared by dissolving 42 grams of $Pb(NO_3)_2$ and $Zn(NO_3)_2.7H_2O$ in 1000mL of deionised water. The required concentrations were prepared from the stock solution by dilution. A known quantity of dried biomass (varied between 0.5 and 5gr) was added to various concentrations (10-100 mg/L) of 100mL metal solution in 250mL Erlen Meyer 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 HNO_3 0.1 N solutions. The observations showed that the ions settled and no concentration was remained in the solution phase for pH above 7. 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 360 min at the temperature range (20, 20.30,35 °C).
Samples were taken at various 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 flam atomic absorption spectrophotometer (Shimadzu AA-670).
The amount of adsorbed metal ions per gram of the biomass was obtained using the following equation:

$$q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where:
q: amount of metal adsorbed on the biomass (mg/g);
Co: initial metal ion concentration in solution (mg/L);
Ce: equilibrium metal ion concentration in solution (mg/L);
V: volume of the medium (L);
M: amount of the biomass used in the reaction mixture (g).

3. Results and discussion

There are several parameters that can affect the biosorption process. The major parameters that influence the rate of biosorption of metals are the structural properties of support and biosorbent (e.g. protein and carbohydrate composition and surface charge density, topography and surface area), the amount of biosorbent, initial concentration of metal ions and presence of other ions which may compete with the ions of interest for the active biosorption sites. Such studies can be found in the literature under different experimental conditions [20, 21].

Biosorption of heavy metal ions onto microbial biomass was studied through testing several factors including specific surface properties of the microbial cell wall, the physical and chemical properties of the adsorption medium such as metal ions concentration, temperature, pH, and the amount of biomass [22, 23].

3.1. Effect of contact time

The biosorption efficiency of metal ions was evaluated as a function of contact time. The initial concentration of metals was 100 mg/L. 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 was rapid for both ions at the beginning of the biosorption process and gradually decreased as time progressed to attain equilibrium after 60 minutes.

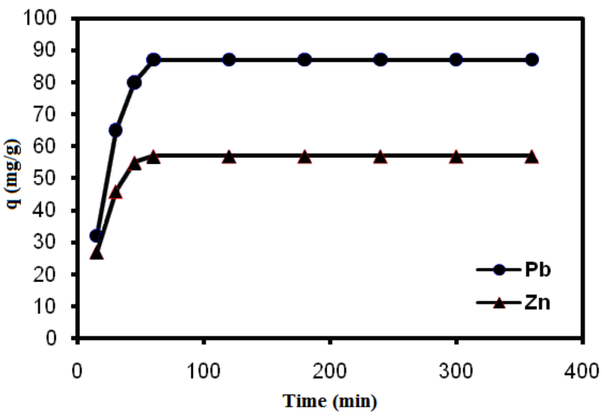

Figure 1. Effect of contact time on Pb (II) and Zn (II) adsorption by phanerochaete chrysosporium; 100 mL single metal solution: pH= 6; initial metal-ion concentration (C0)= 100 mg/L; biosorbent concentration (m)=5 g/L; temperature (T)= 35 ˚C; stirring speed=150 rpm.

The metal uptake capacity of biomass at 100 mg/L metal solution was different for two metals. The highest metal uptake values of 87.2 and 55.0 mg/g of dried biomass were obtained for Pb (II) and Zn (II) respectively.

3.2. Effect of pH

The pH of the metal solution is an important parameter in biosorption capacity. The pH of medium affects the solubility of metal ions and the ionization state of the functional groups (carboxylate, phosphate, and amino groups) on the microbial cell wall [22-25]. It should be noted that, the carboxylare and phosphate groups carry negative charges that allow the microbial cells to be strong scavengers of metal ions [26]. Figure 2 shows the effect of pH on Pb(II) and Zn(II) biosorption.

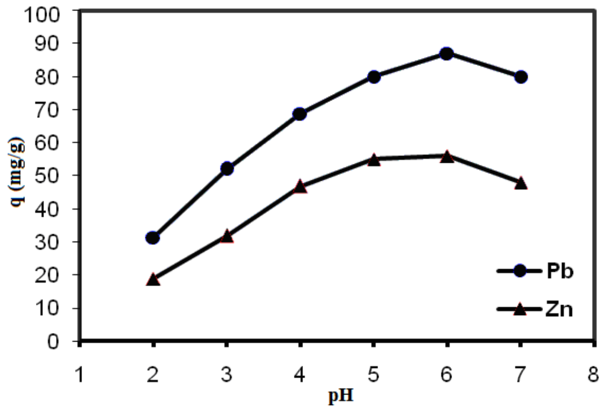

Figure 2. Effect of pH on Pb(II) and Zn(II) biosorption by phanerochaete chrysosporium; 100 mL single metal solution: contact time (t)=60 min; initial metal-ion concentration(C0)= 100 mg/L; biosorbent concentration (m)= 5 g/L; temperature (T)= 35 ˚C; stirring speed= 150 rpm.

The maximum biosorption of Pb(II) and Zn(II) occurred at pH 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. The adsorption of metal ions per unit weight of biosorbent increased gradually when pH increased from 2 to 6. The biosorption of Pb(II) and Zn(II) ions decreased above pH 6. This may be due to the hydrolysis of metals and complex formation [27]. The decrease can be also related to the micro-precipitation process of Pb(II) (at pH above 6.5) and Zn(II) (at pH above 7) as reported by Veglio and Beolchini [15] and Volesky and Holan [14].

The biosorption capacity of biomass is low at pH 2, because large quantities of proton compete with the metal cations for the adsorption sites. As the pH of the metal solution increases, the number of protons dissociated from functional groups of carboxylate on the cell wall increases and thus more negative groups for complexation of metal cations are provided [24, 28].

3.3. Effect of temperature

Temperature has a significant effect on the biosorption process. In this study, the removal of Pb(II) and Zn(II) ions from aqueous solution using the biomass of phanerochaete chrysosporium was investigated at four different temperatures ranged from 10 to 50˚C. Figure 3 shows the results of metal sorption experiments.

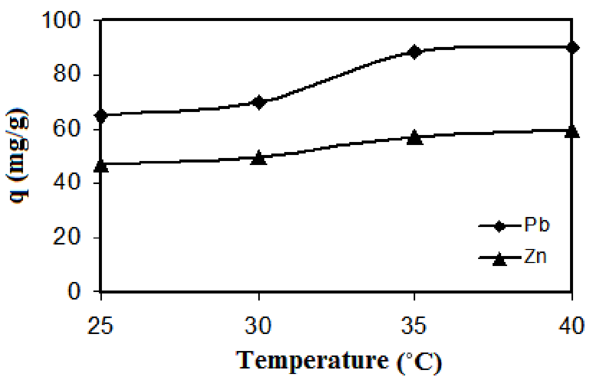

Figure 3. Effect of temperature on Pb(II) and Zn(II) adsorption by phanerochaete chrysosporium; 100 mL single metal solution: contact time (t)=60 min; initial metal-ion concentration (C0)= 100 mg/L; biosorbent concentration (m)=5 g/L ; pH=6; stirring speed=150 rpm.

The biosorption of Pb(II) and Zn(II) ions increased with an increase in the temperature.
Similar investigations were carried out by many researchers to consider the effect of temperature on the biosorption process [29]. Kapoor et al. [24] and Aksu et al. [30] observed that an increase in copper sorption by Aspergillus carbonarius when the temperature was increased from 4 to 25 ˚C. Further increase in temperature up to 50 ˚C decreased copper uptake. However, Iqbal and Edyvean [29] showed that Pb(II), Zn(II) and Cu(II) uptake by biosorbent were independent. It has been suggested that the increase in metal uptake at higher temperature is due to either higher affinity of sites for metal or an increase in binding sites on relevant biomass [31].

3.4. Effect of biosorbent concentration

An increase in biosorbent concentration generally increases the adsorbed metal ion concentration because of larger adsorption surface area. However, further increase in biomass concentration decreases the metal specific uptakes [32].
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 larger 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. This can be explained by forming aggregates during biosorption which takes place at high biomass concentrations causing a decrease of the effective adsorption area. It has been suggested that several factors including pH, ionic strength, temperature, metal ion in solution and biomass concentration explain the decreased adsorption capacity at increasing biomass [14].

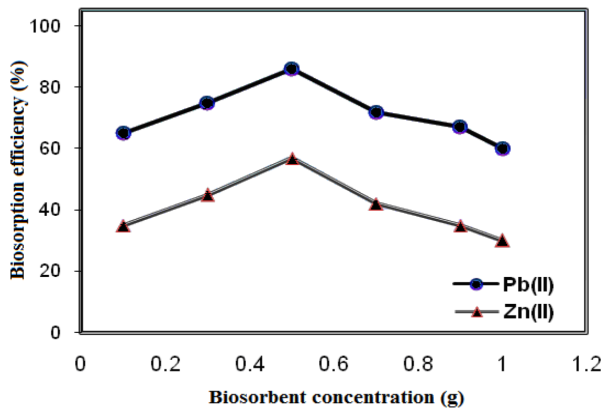

Figure 4. Effect of biosorbent concentration on Pb(II) and Zn(II) adsorption by phanerochaete chrysosporium; 100 mL single metal solution: contact time (t)= 60 min; initial metal-ion concentration (C0)= 100 mg/L; temperature (T)= 35˚C; pH=6; stirring speed=150 rpm.

3.5. Effect of stirring speed

Biosorption studies were carried out in a shaker at pH 6 and for initial metals concentrations of 100 mg/L. The stirring speed varied from 50 to 200 rpm. Samples were taken at certain time intervals and analysed for metal ions concentrations in solution. Figure 5 illustrates the effect of stirring speed on the biosorption process.

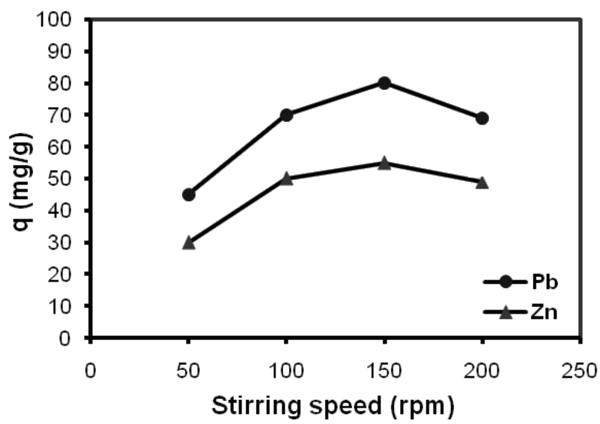

Figure 5. Effect of stirring speed on Pb(II) and Zn(II) biosorption by phanerochaete chrysosporium; 100 mL single metal solution: contact time (t) =60 min; initial metal-ion concentration (C0)= 100 mg/L; biosorbent concentration (m)=5 g/L; temperature (T)=35 ˚C; pH =6.

The maximum removal efficiency of Pb (II) and Zn (II) was obtained at 150 rpm. The increase in stirring speed from 50 to 150 rpm resulted in an increase in metal ions removal efficiency. It has been investigated that the mass transfer rate increases with the increase in stirring speed. According to Ekmekyapar et al. [32], the boundary layer thickness decreases with increased stirring speed which results in a reduction in surface film resistance. Therefore, the metal ions are adsorbed to the biosorbent surface more easily. However, further increase in stirring speed decreased the biosorption efficiency. As Figure 5 shows, the biosorption of Pb (II) and Zn (II) decreased steadily when stirring speed increased from 150 rpm to 200 rpm. The suspension was not homogenous due to the high stirring speed which made the biosorption of Pb (II) and Zn (II) difficult. The results indicate that the contact between solid and liquid was more effective at moderate speed (150rpm).

3.6. Effect of initial metal ion concentration

Figure 6 shows the heavy metal ion biosorption capacities of phanerochaete chrysosporium as a function of the initial concentration of Pb (II) and Zn (II) ions within the aqueous solution. The experiments were performed using single solutions (10- 450 mg/L) of the metal ions at pH 6.0.

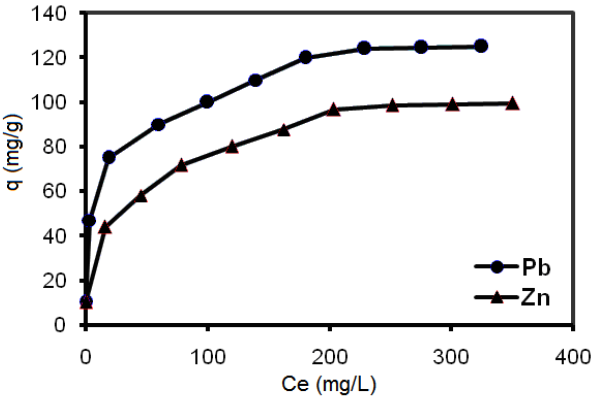

Figure 6. Effect of initial metal-ion concentration on Pb(II) and Zn(II) biosorption by phanerochaete chrysosporium; 100 mL single metal solution: contact time (t)=60 min; biosorbent concentration (m)=5 g/L; temperature (T)=35 ˚C; stirring speed=150 rpm; pH=6.

The amount of metal ions adsorbed per unit mass of phanerochaete chrysosporium increases with an increase in initial metal ion concentration. This increase could be due to the increase in electrostatic interactions (related to covalent interactions), involving sites of progressively lower affinity for metal ions. Therefore, more metals ions were left un-adsorbed in solution at higher concentration levels [29].

3.7. Adsorption isotherms

Adsorption isotherms demonstrate the relationships between equilibrium concentrations of adsorbate in the solid phase q, and in the liquid phase C at constant temperature. Adsorption isotherms are often obtained in the laboratory using batch tests in which the equilibrium data are attempted by various isotherm models. In this study, the experimental data were fitted to the two most commonly used adsorption isotherms (Langmuir and Freundlich models) for biosorption studies [30, 31]

The Langmuir equation is applicable for monolayer adsorption onto a surface containing a finite number of identical adsorption sites [33]. The Langmuir model is described by the following equation:

$$q=\frac{bq_{\max}C_e}{1+bC_e} \tag{2}$$

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

$$\frac{1}{q}=\left(\frac{1}{bq_{\max}}\right)\left(\frac{1}{C_e}\right)+\left(\frac{1}{q_{\max}}\right) \tag{3}$$

where;

$q_{\max}$ = 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) (mg/g);

b= energy of adsorption (the ratio of adsorption / desorption rates) (L/mg);

q = amount of metal adsorbed on the biomass (mg/g);

C_e = equilibrium metal concentration in solution (mg/L).

The constants $q_{\max}$ and b are the characteristics of the Langmuir isotherm and can be determined from Equation 3. A plot of 1/q versus 1/Ce gives a straight line with a slope of $(1/bq_{\max})$ and an intercept of $(1/q_{\max})$ as shown in Figure 7.

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The general Freundlich equation is given as:

$$q=K_f\,C_e^{\frac{1}{n}} \tag{4}$$

The linearised form of this model is:

$$Ln\,q=Ln\,K_f+\left(\frac{1}{n}\right)Ln\,C_e \tag{5}$$

where, the slope (1/n) and intercept (LnK_f) of the linear plot of Freundlich equation are the intensity of adsorption and a measure of adsorbent capacity respectively. Figure 8 shows the linear plot of the Freundlich equation.

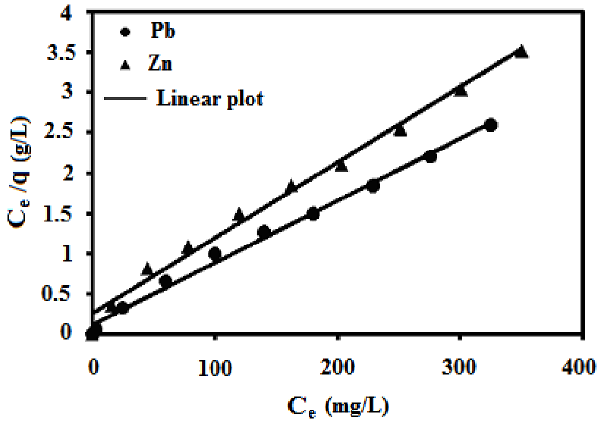

Figure 7. Langmuir adsorption isotherm for Pb (II) and Zn (II) biosorption by phanerochaete chrysosporium.

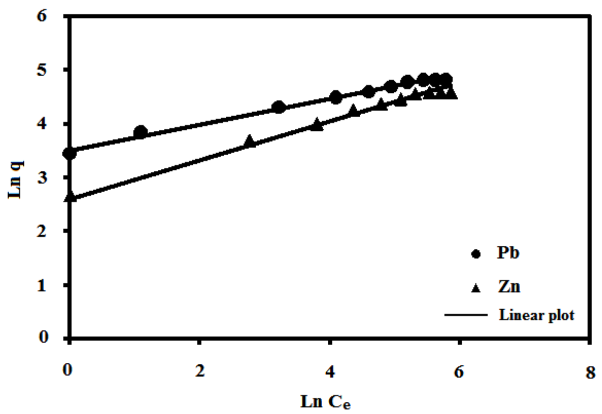

Figure 8. Freundlich adsorption isotherm for Pb (II) and Zn (II) biosorption by phanerochaete chrysosporium.

The empirical parameters of the Langmuir and Freundlich isotherms along with the correlation coefficients (R^2) are given in Table 1.

4. Biosorption in mixed-metals system

4.1. The competitive biosorption of Pb (II) ions from binary metal solutions

Effects of the presence of Zn (II) ions on the biosorption of Pb (II) ions were also investigated in terms of equilibrium isotherm and adsorption yield (Figure 9). The results indicated that the equilibrium uptake of Pb (II) ions decreased with increasing concentration of Zn (II) ions. When the initial concentration of Zn(II) ions increased from 0 to 25 mg/L, there was a sharp drop in the adsorbed quantity of Pb(II) ions, and q (Pb(II)) decreased by about 80 % as Ce (Pb(II)) reached 150 mg/L. A certain quantity of biomass produces a finite number of surface binding sites, some of which would be expected to be saturated by the competing metal ions, especially at relatively high concentration [21]. When the initial concentration of Zn (II) ions increased from 25 to 50 mg/L, there was only a steady and slow fall in the Pb (II) ions uptake. In addition, it is important to note that the phenomenon might not only result from the saturation of the biomass, but also be partly related to the ability of these two metal ions to compete for the adsorption sites. Hence, with increase in the initial concentration of Zn (II) ions, the surface binding sites available for Pb (II) ions drops rapidly [34].

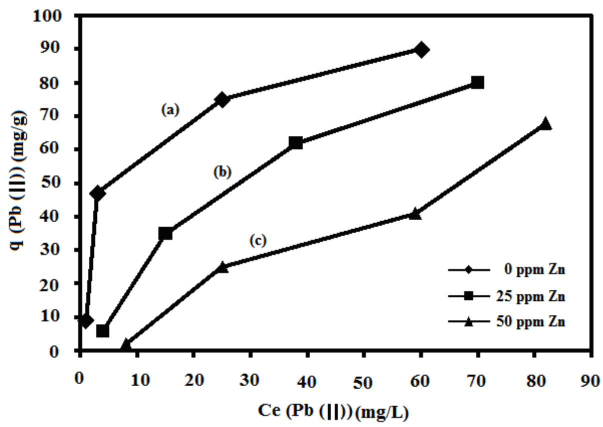

Figure 9. Adsorption isotherms for Pb (II) biosorption by phanerochaete chrysosporium determined for (a): Pb(II) single metal solution, (b): Pb(II) solution with 25 ppm Zn (II) ions, (c): Pb(II) solution with 50 ppm Zn (II) ions (Contact time (t) = 60 min; biosorbent concentration (m) = 5 g/L ; temperature (T) =35 ˚C; stirring speed = 150 rpm; pH=6).

4.2. Competitive biosorption of Zn (II) ions from binary metal solutions

Figure 10 compares the equilibrium uptake of Zn (II) ions by phanerochaete chrysosporium in the presence of Pb (II) ions with concentrations ranged from 0 to 50 mg/L.

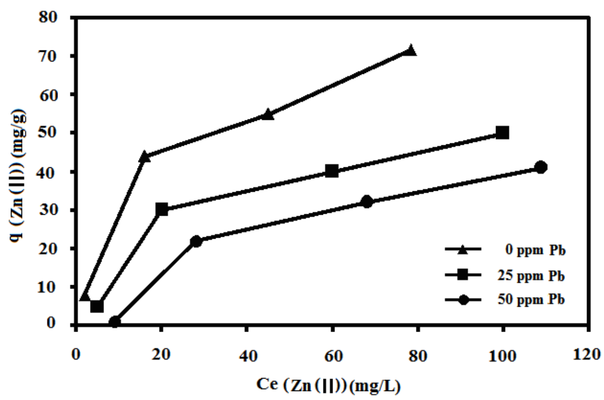

Figure 10. Adsorption isotherms for Zn (II) biosorption by phanerochaete chrysosporium determined for (a): Zn (II) single metal solution, (b): Zn (II) solution with 25 ppm Pb (II) ions, (c): Zn (II) solution with 50 ppm Pb (II) ions (Contact time (t) = 60 min; biosorbent concentration (m) = 5 g/L ; temperature (T) =35 ˚C; stirring speed = 150 rpm; pH=6).

Table 1. Linearised parameters of Langmuir and Freundlich isotherms for Pb(II) and Zn(II) adsorption on phanerochaete 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

The results showed that the equilibrium uptake of Zn(II) decreased with increasing concentration of the competing metal ions (Pb (II)).

5. Desorption and regeneration

The regeneration of the biosorbent is expected to be a key factor in accessing the potential of the biosorbent for commercial application. The capacity of the biomass to adsorb metal ions was determined by repeating the adsorption experiments in five successive cycles. HNO_3 (10 mM) solution was used as a desorption agent. The observations showed that more than 97% desorption was obtained after five adsorption-desorption cycles and the biomass conserved metal adsorption capacity even after five cycles. Desorption ratio can be expressed as:

$$\text{Desorption ratio}=\frac{\text{Amount of metal ions desorbed to the elution medium}}{\text{Amount of metal ions adsorbed on to the beads}}\times 100 \quad (6)$$

6. Conclusions

This paper presents an investigation on the biosorption of lead (II) and zinc (II) from aqueous solutions on nonliving biomass of phanerochaete chrysosporium as a biosorbent. The experimental run was observed during 6 h and the contact time was determined as 60 min. The biosorption was rapid and the equilibrium was reached within 15min. The metal biosorption, which depends on the physical adsorption on the cell surface, is generally 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 both Langmuir and Freundlich isotherms for Pb (II) and to the Langmuir model for Zn (II) ion. Phanerochaete 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 the heavy metal ions was Pb (II) > Zn (II). This natural material is easily available and economic for treatment of the industrial wastewater.

References

[1]. Chong, K.H. and Volesky, B. (1995). Description of two-metal biosorption equilibria by Langmuir-type models. Biotechnol. Bioeng 47(0): 1-10.

[2]. Leusch, L., Holan, Z.R. and Volesky, B. (1995). Biosorption of heavy metals (Cd,Cu,Ni,Pb,Zn) by chemically reinforced biomass of marine algae. J Chem Technol Biotechnol 62(3): 279-288.

[3]. Wilde, E.W., and Benemann, J.R. (1993). Bioremoval of heavy metals by the use of micro algae. Biotechnol. Adv. 11 781-812.

[4]. Yu, Q. and Kaewsarn, P. (1999). Binary adsorption of copper(II) and cadmium(II) from aqueous solutions by biomass of marine alga Durvillaea potatorum. Sep. Sei. Technol. 34(8) 1595-1605.

[5]. Zhao, M., Duncan, J.R., and Van Hille, R.P. (1999). Removal and recovery of zinc from solution and electroplating effluent using Azolla filiculoides. Water Res. 33(6) 1516-1522.

[6]. Chen, J.P. and Yiacaumi, S. (1997). Biosorption of metal ions from aqueous solutions. Sep Sci Technol 32 (1-4): 51-69.

[7]. Guibal, E., Roulph, C. and Lecloure, C.P. (1992). Uranium biosorption by the filamentous fungus Mucor miehei, pH effect on mechanisms and performance of uptake. Water Res 26 (8): 1139-1145.

[8]. Yetis, U., Dolek, A., Dilek, F.B., Ozcengiz, G. (2000). The removal of Pb(II) by Phanerochaete chrysosporium. Water Res 34 (16): 4090-4100.

[9]. Churchill, S.A., Walters, J.V. and Churchill, P.F. (1995). Sorption of heavy metals by prepared bacterial cell surfaces. J Environ Eng 121(10): 706-711.

[10]. Kuyucak, N. and Volesky, B. (1988). Biosorbents for recovery of metals from industrial solution. Biotechnol. Lett. 10(2) 137-142.

[11]. Gadd, G.M. (1990). Heavy metal accumulation by bacteria and other micro-organisms. Experientia 46 834-839.

[12]. Standberg, G.W., Schumate, S.E., and Parrot, J.R., (1981). Microbial cells as biosorbents for heavy metals : Accumulation of uranium by Saccharomyces cerevisiae and Pseudomona aeruginosa. Appl. Environ. Microbiol. 41(1) 237-245.

[13]. Volesky, B., May, H. and Holan, Z.R., (1993). Cd(II) biosorption by Saccharomyces cerevisiae. Biotrchnol. Bioeng. 41 (8) 826-829.

[14]. Volesky, B., and Holan, Z.R. (1995). Biosorption of heavy metals. Biotechnol. Prog. 11(3) 235-250.

[15]. Veglio, F., and Beolchini, F., (1997). Removal of metals by biosorption: A review. Hydrometall. 44 (3) 301-316.

[16]. Barr, D.P., and Aust, S.D. (1994). Mechanisms white rot fungi use to degrade pollutants. Environ. Sci. Technol. 28(2) 78A-87A.

[17]. Kirby, N., Mcmullan, G. and Marchant, R. (1995). Decolorization of an artificial textile effluent by Phanerochaete chrysosporium. Biotechnol. Lett 17: 761-764.

[18]. Mittar, D., Khanna, P.K., Marwaha, S.S. and Kennedy, J.F. (1992). Bioleaching of pulp and paper mill effluents by P.chrysosporium. J Chem Technol Biotechnol 53: 81-92.

[19]. Kapoor, A. and Viraraghavan, T. (1997). Heavy metal biosorption sites in Aspergillus niger. Bioresource Technol., 61, 221-227.

[20]. Kaewsarn P and Yu Q (2001) Cadmium (II) removal from aqueous solution by pre-treated biomass of marine alga Padina sp. Environmental pollution, 112,209-213.

[21]. Say, R., Denizli, A. and Arica, M.Y. (2001). Biosorption of cadmium(II), lead(II) and copper(II) with the filamentous fungus Phanerochaete chrysosporium. Bioresource Technol., 76, 67-70.

[22]. Saglam, N., Say, R., Denizli, A., Patir, S. and Arica, M.Y. (1999). Biosorption of inorganic mercury and alkylmercury species on to by Phanrochaete chrysosporium mycelium. Process Biochemistry, 34, 725-730.

[23]. Gadd, G.M. (1993). Interaction of fungi with toxic metals. New Phytology, 124, 25-60.

[24]. Kapoor, A., Viraraghavan, T., and Cullimore, D.R., (1999). Removal of heavy metals using the fungus Aspergillus niger. Bioresource Technol., 70, 95-104.

[25]. Tobin, J.M., White, C. and Gadd, G.M. (1994). Metal accumulation by fungi: Application in environmental biotechnology. J Industrial Microbiol., 13, 126-130.

[26]. Kapoor, A. and Viraraghavan, T. (1998). Biosorption of heavy metals on Aspergillus niger: effect of pretreatment. Bioresource Technol., 63 109-113.

[27]. Fourest, E. and Roux, J.C. (1992). Heavy metal biosorption by fungal mycelia by-products: Mechanisms and influence of ph. Appl. Microbiol. Biotechnol. 37: 399-403.

[28]. Saglam, A., Yacinkaya, Y., Denizli, A., Arica, M.Y., Genc, O. and Bektas, S. (2002). Biosorption of mercury by carboxycellulose and immobilized Phanerochaete chrysosporium. Microchem. J., 71, 73-81.

[29]. Iqbal, M. and Edyvean, R.G.J. (2004). Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of Phanerochaete chrysosporium. Minerals Eng., 17. 217-223.

[30]. Aksu, Z. (1999). Biosorption of heavy metals by microalgae in batch and continuous systems, in: YS Wong, NFY Tam (Eds.), Algae for Waste water Treatment, Springer-Verlag and Landes Bioscience, Germany.

[31]. Aksu, Z., Ozer, D., Ekiz, H.I., Kutsai, T. and Cag Brevelar, A. (1996). Biosorption of Copper ion’s by Aspergillus niger biomass” Environ.Technol. 17 (6), 215-224.

[32]. Ekmekyapar, F., Aslan, A. and Bayhan, Y.K. (2006). Biosorption of copper (II) by nonliving lichen biomass of Cladonia rangiformis hoffm. Haz. Mat., B137 293-298.

[33]. Namasivayam, C. and Arasi, D.J.S.E. (1997). Removal of congo red from wastewater by adsorption onto waste red mud. Chemosphere 34 (2): 401-417

[34]. Qingbiao, L., Songtao, W., Gang, L., Xinkai, L., Xu, D., Daohua, S., Yuelin, H. and Yili, H. (2004). Simultaneous biosorption of cadmium(II) and lead(II) ions by pretreated biomass of Phanerochaete chrysosporium. Separation and Purification Technol., 34 135-142.