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REGULAR ARTICLE

KINETICS AND EQUILIBRIUM PARAMETERS OF BIOSORPTION AND BIOACCUMULATION OF LEAD IONS FROM AQUEOUS SOLUTIONS BY *TRICHODERMA LONGIBRACHIATUM*

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ABSTRACT

Biosorption and bioaccumulation of Lead ions (Pb(II)) by *Trichoderma longibrachiatum* were investigated in a batch system. The effects of some important parameters such as pH, initial metal concentration, temperature and inoculum concerntration on biosorption capacity were also studied. The maximum biosorption capacity of *Trichoderma longibrachiatum* was at 25 ppm of lead, showed 100 % removal at pH 7 and 25 ^{o}C after fifteen days. Biosorption equilibrium was established in 150 minutes. The process fitted well into pseudo second order kinetic model and was best explained by Langmuir isotherm.

Keywords: Bioaccumulation, *Trichoderma longibrachiatum*, Equilibrium, Kinetic and Langmuir isotherm.

INTRODUCTION

Environmental contamination by toxic metals is a serious problem worldwide due to their incremental accumulation in the food chain and continued persistence in the ecosystem.

Convectional technologies, such as ion exchange or lime precipitation, are often ineffective and/or expensive, particularly for the removal of heavy metal ions at low concentrations (below 50 $mg.l^{-1}$). Furthermore, most of these techniques are based on physical displacement or chemical replacement, generating yet another problem in the form of toxic sludge, the disposal of which adds further burden on the techno-economic feasibility of the treatment process.

In naturally polluted environments, the microbe's response to heavy metals toxicity depends on the concentration and the availability of metals and on the action of factors such as the type of metal, the nature of medium and microbial species **(Hassen et al., 1998).** Fungi and yeast biomasses are known to tolerate heavy metals **(Gavrilesca, 2004; Baldrian, 2003)**. They are a versatile group, as they can adapt and grow under various extreme conditions of pH, temperature and nutrient availability, as well as high metal concentrations **(Anand et al., 2006).** They offer the advantage of having cell wall material which shows excellent metal-binding properties **(Gupta et al., 2000).** Generally, microbial biomasses have evolved various measures to respond to heavy metals stress via processes such as transport across the cell membrane, biosorption to cell walls, entrapment in extracellular capsules, as well as precipitation and transformation of metals **(Malik, 2004).** Studies have shown that strains isolated from contaminated sites have an excellent ability of removing significant quantities of metals both from aqueous solutions and electroplating effluents **(Malik, 2004).** Most of the studies dealing with biological removal of metals used dead biomass. However, it was reported that the live *Trichoderma longibrachiatum* cells exhibits higher *nickel* biosorption capacity than dead biomass, probably due to intracellular uptake **(Kapor et al., 1999)**.

In this study, we used *T. longibrachiatum* cells as a biosorbent for Pb (II) ions in aqueous solution. The effect of solution pH, biosorbent dose, initial metal concentration, temperature and inoculums concentration on biosorption capacity were also studied. The experimental results provide worthy information on application of this adsorbent in treatment of lead – contaminated wastewater.

MATERIAL AND METHODS

Equipment and chemicals

A Jenway 3015 precision pH meter, a Mettler MT5 electronic balance, a Clifton oscillator, with temperature control were used in the experiments. The concentration of the

residual Pb (II) in the solution was determined with AAS (Buck Scientific model 210 VGP). Aqueous solutions of lead ions of different concentration were prepared from lead nitrate $Pb(NO_3)_2$ obtained from BDH. These were used as adsorbate and was not purified prior to use. Double distilled water was employed for preparing all the solutions and reagents.

Media culture

The media used in this study are potato dextrose agar and potato dextrose broth. Potato Dextrose Agar was prepared by accurately weighing 10 g of potato dextrose agar powder and dissolved in 250 ml of sterile distilled water. The mixture was then melted in a water bath and sterilized in the autoclave at 121 ^{0}C for 15 minutes. The broth was prepared from 200 g of potato tuber, 20 g of dextrose and a drop of antibiotic. The potato was peeled, weighed and boil till soft (1 hour). It was marshed and sieved; the filtrate was kept in conical flask where distilled water was added. Dextrose agar and add lactic acid were added, the resulting solution was sealed with cotton wool and foil in a conical and sterilized in the autoclave at 121 ^{0}C for 15 minutes. *Trichoderma longibrachiatum,* was obtained from the Department of Microbiology laboratory of the University of Agriculture Abeokuta. The organism was picked with a sterile wire loop from the pure culture and sub cultured by streaking onto a freshly solidified media.

Equilibrium and Kinetic Experiment

Adsorption experiments were performed as earlier described **(Bello *et al.*, 2007 and Adeogun *et al.*, 2010)**. The amount of adsorption at equilibrium, q_e (mg.g^{-1}), was calculated by

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

where C_o and C_e (mg dm^{-3}) are the liquid-phase concentrations of lead ion at initial and equilibrium, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g). While the amount biosorbed at time t, (from the kinetic experiments) q_t (mg.g^{-1}), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \qquad (2)$$

where C_o and C_t (mg.dm^{-3}) are the liquid phase concentrations of lead ion at initial and any time t, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Effect of agitation time and concentration on biosorption of lead ion.

A series of contact time experiments for lead ion have been carried out at different initial concentration (25 – 100 mg.dm^{-3}) and at temperature of 25 ^{0}C. Figure 1 shows that the contact time necessary for lead ions with initial concentrations of 25 - 100 mg.dm^{-3} to reach equilibrium is about 20 minutes.

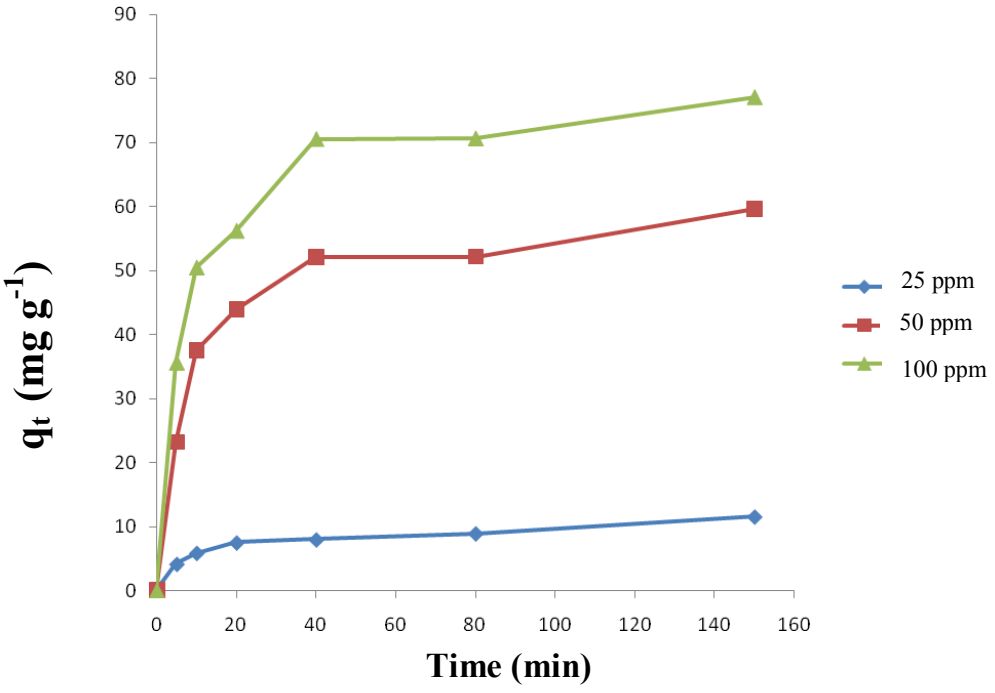

Figure 1 The variation of adsorption capacity with biosorption time at various concentration of lead ion (at 25 ^{0}C and pH 4,)

The amount of the lead ion biosorbed into the organism increases with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the lead ion desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the lead ion being biosorbed by the organism. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of lead ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. The adsorption capacity at equilibrium increases from 5.2 to 71.0 $mg.g^{-1}$ with an increase in the initial lead ion concentration from 20 to 100 $mg.l^{-1}$. It is evident that *T. longibrachiatum* is an efficient biosorbent for lead ion in aqueous solution as the process attains equilibrium gradually.

Bioaccumulation of lead ion by *T. longibrachiatum.*

Bioaccumulation of lead ion by *T. longibrachiatum* increases with the numbers of days (Figure 2), at the end of 15th days virtually all the metal ions in the aqueous solution had been accumulated by the organism when the initial concentration was 25 ppm. As the concentration of the metal ion increases from 25 - 75 ppm the amount accumulated decreases from 100% to 78.84%.

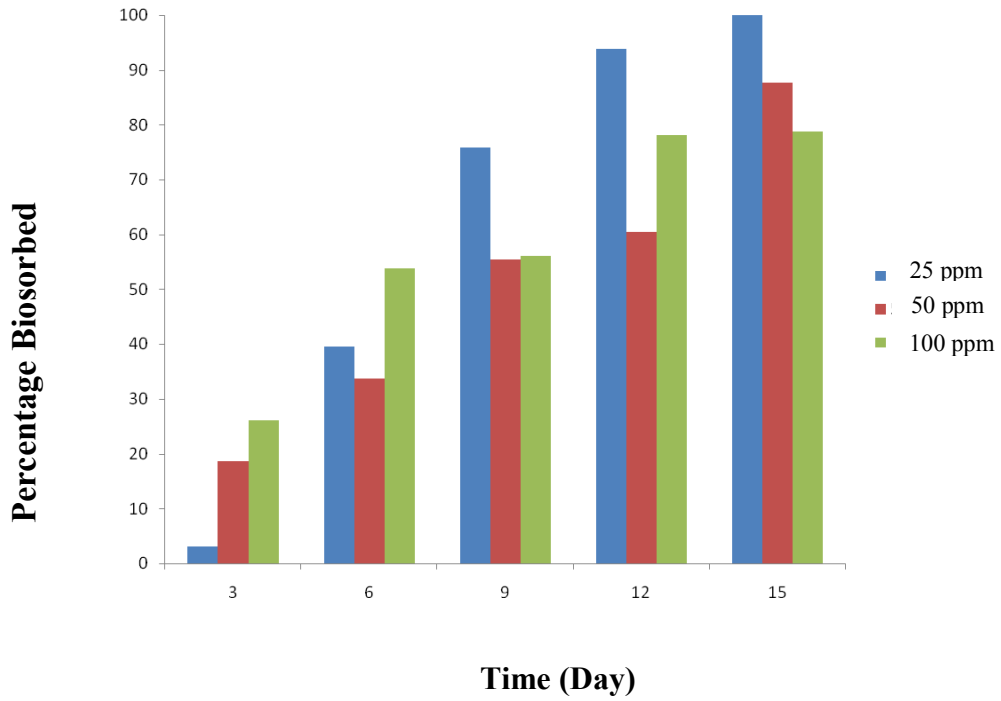

Figure 2 The variation in bioaccumulation capacity of *T. longibrachiatum* with time at various concentration of lead ion (at 25 ^{0}C and pH 4,)

This indicates the viability of the organism to remove the metal ions at a very low concentration. As earlier observed metals can be bio-accumulated by living organisms through complexation, coordination, ion exchange, chelation, and adsorption **(Volesky, 1990)**. Since the accumulation occurs gradually in the presence of living organism, adsorption on to the cellular structure is much more favoured than all other process.

Biosorption kinetics

The rate constant of adsorption is determined from the pseudo first-order equation given by **Langergren and Svenska (1998):**

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

where q_e and q_t are the amounts of lead ion biosorbed ($mg.g^{-1}$) at equilibrium and at time t (min), respectively, and k_1 the rate constant adsorption (h^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t for different concentrations of lead ion. The correlation coefficient values were less than 0.90, however, the experimental q_e values disagree slightly with the calculated ones, obtained from the linear plots (Table 1). This shows that the biosorption process is not fitted with first-order kinetics. On the other hand, a pseudo second-order equation based on equilibrium adsorption **(Malik, 2004)** is expressed as:

$$t/q_t = 1/k_2 q_e^2 + (1/q_t)t \qquad (4)$$

where k_2 (g/mg s) is the rates constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plots of t/q versus t (Figure 3) show a good agreement between experimental and calculated q_e values (Table 1). The correlation coefficients for the second-order kinetic model are about 0.99 indicating the applicability of this kinetic equation and the second-order nature of the biosorption process of lead ion on the adsorbent.

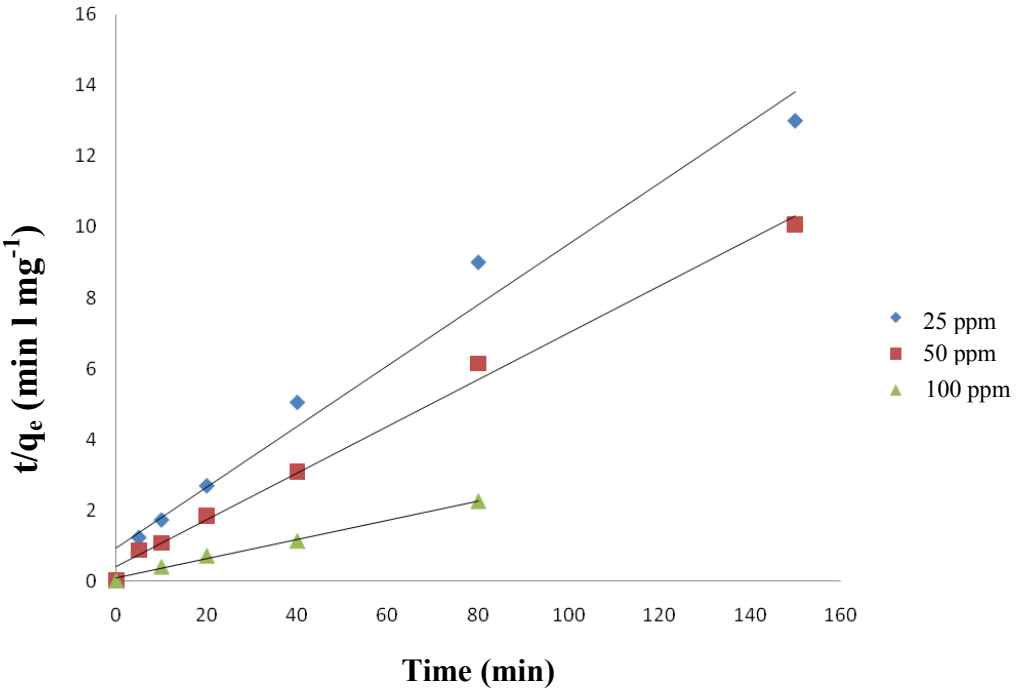

Figure 3 Pseudo-second order kinetics for the biosorption of lead ion by *T. longibrachiatum* at 25 ^{0}C

Test of kinetic models

Besides the value of R^2, the applicability of both kinetic models are verified through the sum of error squares (SSE, %). The biosorption kinetics of lead ion on adsorbent was tested at different initial concentrations. The validity of each model was determined by the sum or error squares (SSE, %) given by:

$$SSE(\%) = \sqrt{\frac{\sum (q_{e,\exp} - q_{e,cal})^2}{N}} \qquad (5)$$

where N is the number of data points. The higher is the value of R^2 and the lower is the value of SSE; the better will be the goodness of fit. Table 1 lists the calculated results. It is found that the biosorption kinetics of lead ion on *T. longibrachiatum* can be best described by the second-order kinetic model.

Table 1 Comparison of the pseudo first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial concentrations of lead ions

		First order kinetic model				Second order kinetic model			
Initial **Concentration** ($mg.dm^{-3}$)	$Q_{e\,exp}$ ($mg.g^{-1}$)	k_1(min)	$q_{e\,cal}$ ($mg.g^{-1}$)	R^2	SSE (%)	k_2 g($mg.min^{-1}$)	$q_{e\,cal}$ ($mg.g^{-1}$)	R^2	SSE (%)
25	11.54	0.015	8.04	0.82	0.60	0.0053	11.74	0.99	0.48
50	16.57	0.017	10.72	0.72	0.75	0.0026	16.98	0.99	0.35
100	46.35	0.006	43.08	0.88	0.37	0.0017	45.49	0.99	0.42

Adsorption isotherms

The adsorption isotherm indicates how the biosorbed molecules distribute between the liquid phase and the biosorbent phase when the biosorption process reaches an equilibrium state. The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose **(Haghseresht, and Lu, 1998).** Biosorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface **(Fytianos *et al.*, 2003).** While, Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage **(Fytianos *et al.*, 2003)**. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Langmuir isotherm

The linear form of Langmuir's isotherm model is given by the following equation:

$$C_e/q_e = 1/Q_o b + (1/Q_o)C_e \qquad (6)$$

where C_e is the equilibrium concentration of the adsorbate (lead ion) ($mg.l^{-1}$), q_e, the amount of adsorbate adsorbed per unit mass of adsorbate ($mg.g^{-1}$), and Q_o and b are Langmuir

constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively. When C_e/q_e was plotted against C_e, straight line with slope $1/Q_o$ was obtained (Figure 4), indicating that the biosorption of the lead ion by *T. longibrachiatum* follows the Langmuir isotherm. The Langmuir constants '*b*' and 'Q_o' were calculated from this isotherm and their values are given in Table 2.

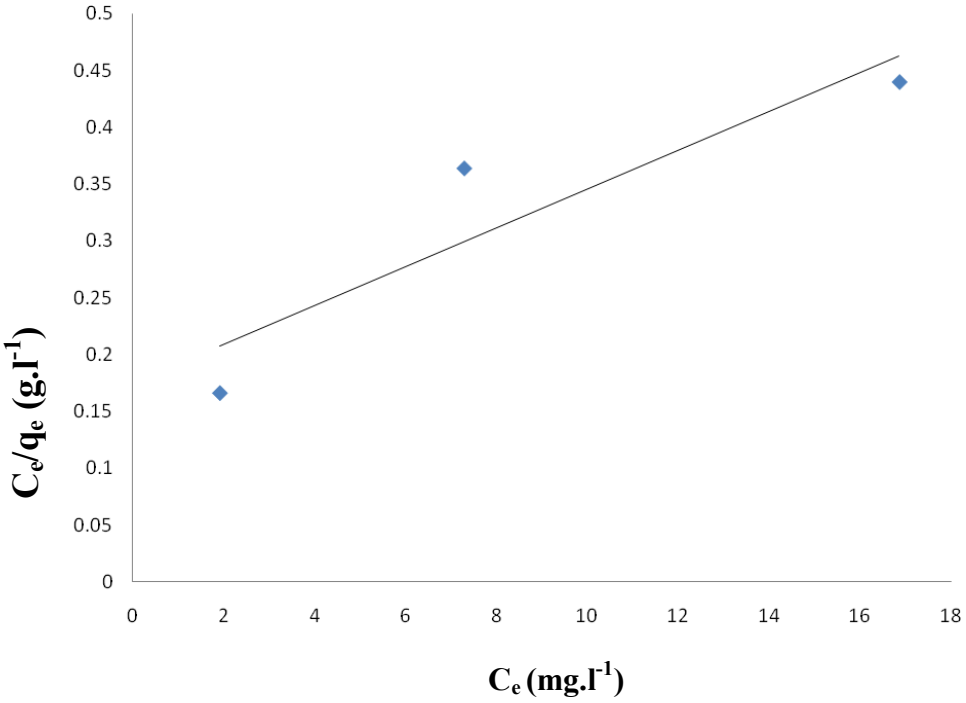

Figure 4 Langmuir adsorption isotherm for the biosorption of lead ion on *T. longibrachiatum* at 25 ^{0}C

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of *T. longibrachiatum* surface, i.e. each lead ion molecule/ *T. longibrachiatum* biosorption has equal adsorption activation energy.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) (**Weber and Chakkravorti, 1974**), which is defined by:

$$R_L = 1/(1 + bC_o) \qquad (7)$$

where b is the Langmuir constant and C_0 the highest metal concentration (mg.l^{-1}). The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found to be 0.092 and confirmed that the biosorbent prepared from *T. longibrachiatum* is favorable for biosorption of lead ion under conditions used in this study.

Freundlich isotherm

The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (8)$$

where q_e is the amount adsorbed at equilibrium (mg.g^{-1}), C_e the equilibrium concentration of the adsorbate (lead ion) and K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process and K_F (mg.g^{-1}(l.mg^{-1})^n) is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of lead ion adsorbed onto biosorbent (*T. longibrachiatum*) for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero **(Haghseresht and Lu, 1998).** A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption **(Fytianos *et al.*, 2003)**. The plot of log q_e versus log C_e gives straight lines with slope '$1/n$' (Figure 5), which shows that the biosorption of lead ion does not fitted well with the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 2.

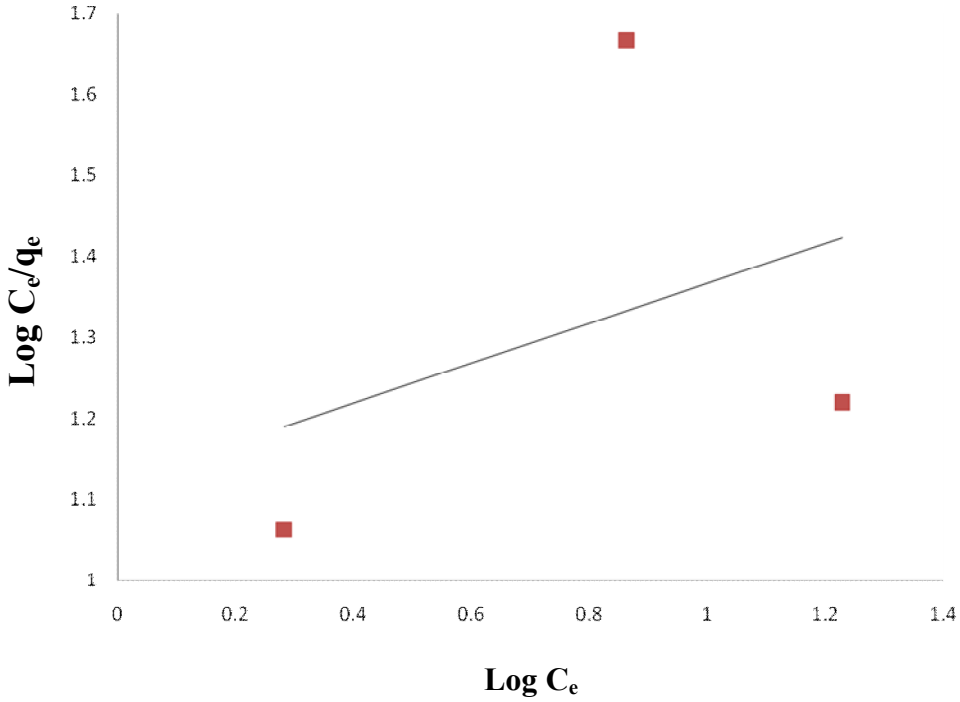

Figure 5 Freundlich adsorption isotherm for the biosorption of lead ion on plumb shell at 25^0C

Table 2 Langmuir and Freundlich isotherm constants for lead ions at 25^oC

Langmuir isotherm				Freundlich isotherm		
Qo ($mg.g^{-1}$)	**b ($dm^3.mg^{-1}$)**	**R^2**	**R_L**	**1/n**	**$K_F[(mg.g^{-1})(m.g^{-1})^{1/n}]$**	**R^2**
58.82	0.098	0.84	0.092	0.25	13.18	0.14

Table 2 shows the values of the parameters of the two isotherms and the related correlation coefficients. As seen from Table 2, the Langmuir model yields a somewhat better fit (R^2 = 0.14) than the Freundlich model (R^2 = 0.84). As also illustrated in Table 2, the value of 1/*n* is 0.25, which indicates favorable adsorption **(Adamson, 2001)**.

Effect of pH on the biosorption of lead ion

Ambient pH was likely to be a major factor in the quantity of metal ion bio-adsorption owing to cation competition effects with hydrogen ions. The result of effect of pH on cadmium adsorption is presented in Figure 6. Interactions between metal cations and electron- rich functional groups on the biomass may be strongly sensitive to the pH value of

environment. The way in which pH changes the adsorption of metal ions to biomass varies with the types of adsorbents (biomass) and adsorbates (metal ions). The optimal pH for adsorption of Pb by mycelia by-products of *Rhizopus arrhizus* is 5.0 **(Fourest and Roux, 1992),** and the optimal pH for adsorption of the same metal ion is around 4.5 for biomass of *Penicilluium chrysogenum* **(Niu *et al.*, 1993)**.

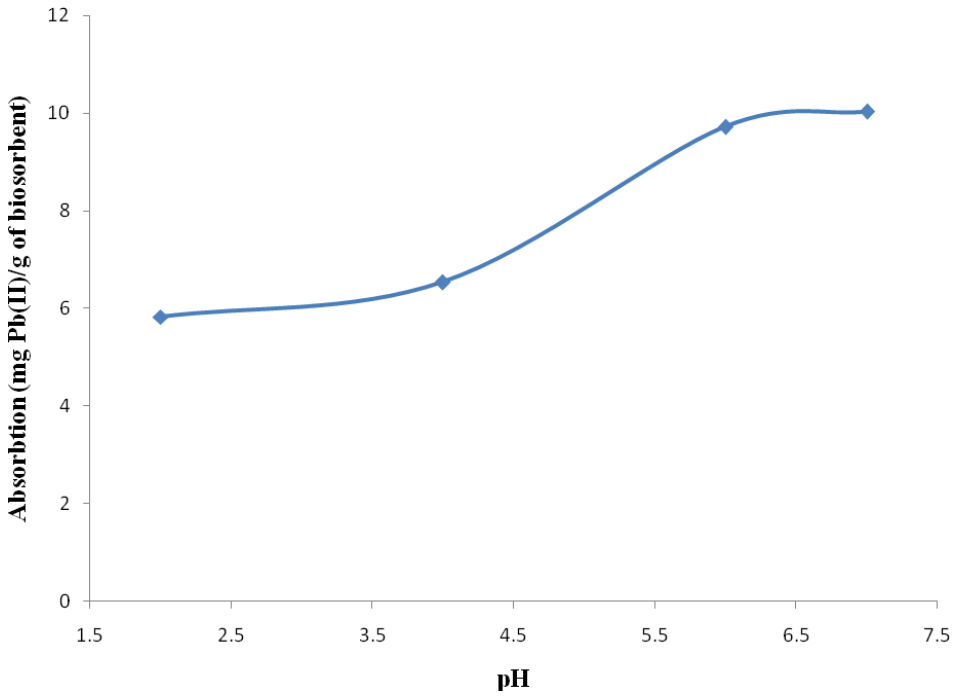

Figure 6 Effect of pH on the biosorption of lead ion by *T. longibrachiatum*

While an optimal pH of 6.5 for the adsorption of Cu was found using *Saccharomyces cerevisiae* as the bioabsorbent **(Brady and Ducan, 1994), Kiff and Little (1986)** reported that the maximal capacity occurs at a value of pH 8.0 for the bio-adsorption of Cd by fungal biomass and the Hg^{2+} uptake by *Pseudomonas aeruginosa* PU21 reaches maximum at pH 7 – 8 **(Chang, *et al,* 1997)**. The current study shows that the maximum biosorption capacity of Pb^{2+} occurs as the pH > 4 suggesting that the binding sites must be located peripherally, under the influence of extracellular pH rather than sites exposed to the constancy of intracellular pH.

CONCLUSION

The present investigation showed that *T. longibrachiatum* can be effectively used as a material for biological removal of lead ion from aqueous solution over a wide range of concentration and pH. Biosorption behaviour is described by a monolayer Langmuir type isotherm. Kinetic data follows pseudo second-order kinetic model. The value of the maximum adsorption capacity, Q_o, (58.82 $mg.g^{-1}$) is comparable with the values observed for other biosorbent reported in earlier studies.

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