# EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES ON LEAD REMOVAL FROM AQUEOUS SOLUTION BY *TECTONA GRANDIS L.F*

## D. A. NAIDU[1], P. KING[2], NARAYANA SAIBABA K. V[3] & V. S. R. K. PRASAD[4]

[1,2]Environmental Pollution Control Engineering Laboratory, Department of Chemical Engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India

[3]Department of Biotechnology, GIT, GITAM University, Visakhapatnam, Andhra Pradesh, India

[4]ANITS, Sangivalasa, Visakhapatnam, Andhra Pradesh, India

## ABSTRACT

Biosorption of lead was investigated using a biomass obtained from *Tectona grandis L.f.* The effects of contact time, initial metal ion concentration, pH, adsorbent dosage, temperature, adsorbent size were investigated. Optimization studies were carried out using batch biosorption studies. Pseudo second order model adequately described the kinetics of lead sorption with high correlation coefficients. The equilibrium data were analyzed using Freundlich, Langmuir, Redlich-Peterson and Temkin adsorption isotherms. Freundlich adsorption isotherm model gave a good fit to the experimental data. The results proved that *Tectona grandis L.f.* has good adsorption capacity. The maximum lead sorption capacity by Langmuir adsorption isotherm was obtained as 32.363 mg/g for 20 mg/L of initial lead concentration at pH 5 and temperature $30^0$C. Thermodynamic parameters, such as free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) were calculated using Langmuir adsorption equilibrium constants. Evidences from the experimental results hinted that lead adsorption on *Tectona grandis L.f* was exothermic and spontaneous process.

**KEYWORDS:** *Tectona grandis L.f,* Biosorption, Isotherm, Kinetics, Lead

## INTRODUCTION

The usage of heavy metals has been increasing over the past few decades due to the advancement of technological development and rapid industrialization. This progress in industrialization resulted in the increasing concentration of metallic substances in the effluents which in turn reaches the aquatic environment. Industrial effluents originating from metal plating, mining, battery manufacture, tannery, petroleum refining, printing and photographic industries etc., contains considerable amounts of Cadmium, zinc, copper, nickel, lead, mercury and chromium (W.S. Wan Ngah , M.A.K.M. Hanafiah). These metals are highly susceptible and induce serious health hazards to human beingshence; safe disposal of these wastewaters is primary concern these days.

Treatment of heavy metals is highly difficult as metals are non-biodegradable. Generally industrial effluents containing heavy metals are treated by using the conventional methods such as chemical precipitation, ion exchange, filtration, electro deposition and membrane process. All these methods are generally expensive and difficult to apply because of technical and/or economic constraints [K.S. Low et al, A. Esposito et al]. Among the above said methods, Adsorption using activated carbon adsorbent has been accepted as a highly effective however its use is restricted due to its high cost [Jyotikusum Acharya et al, T.Viraraghavan et al].

Recently, the search is focused on the usage of waste biomaterials such as agricultural, bacterial and algal biomasses [P.King et al 2005] as alternative materials for activated carbon due to their high efficiency, low cost and

minimal disposal problems[P.King et al 2006, B. Volesky, and Z.R. Holan, E. Romera et al, B. Preetha et al]. These advantages are the primary motivators for developing full-scale biosorption processes to clean up the heavy metal pollution. Tectona grandis L.f (TGL)is widely available in almost all the forests on the earth. Lead is one of the most poisonous metallic contaminants present in industrial effluent streams. Hence in the present study, Biomass species known as TGL leaf was chosen for removal of Lead by biosorption technique.

The aim of the present study is to remove Lead from its aqueous solution using TGL, as adsorbent material. The effects of various parameters like contact time, pH, initial metal ion concentration, adsorbent dosage and adsorbent size on Lead removal efficiency were studied.

Equilibrium data waspresented in the form of adsorption isotherms such as Freundlich, Langmuir, Redlich-Peterson and Temkin. The kinetic experimental data for TGL as adsorbent was also correlated. The pseudo first and second order rate expressions were used to correlate the experimental data. The thermodynamic parameters such as free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$) were also calculated.

## MATERIALS AND METHODS

All the chemicals used in this study were of analytical reagent (AR) grade, obtained from Merck, India. Distilled water was used in preparing solutions throughout this study.

### Preparation of TGL Adsorbent

The green TGL leaveswere collected from the Teak garden of College of engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India. These leaves were washed several times with deionized water to remove dirt present on its surface.

These washed leaves were completely dried under sunlight for 20 days and were cut into small pieces and powdered using domestic mixer. This powdered material was subjected to sieve analysis and powder in the particle size range of 63-180 µm was used without any further pretreatment throughout all experiments in this study.

### Preparation of Metal Solutions

Stock solution of lead with a concentration of 1000 mg/L was prepared by dissolving 1.597 g of 100% $Pb(NO_3)_2$ in 1000 ml of distilled water. The lead solutions of different concentrations ranging from 20 to 100 mg/L were prepared by successive dilutions using the stock solution. The initial pHs of the solutions were adjusted with 0.1N NaOH and 0.1N HCl solutions before mixing the biosorbent.

### Batch Adsorption Studies

All the experiments in this study were conducted in 250 ml Erlenmeyer flasks containing 30 ml of lead solutions. After adding the predefined amounts of adsorbents of size 63 µm, flasks were agitated for optimum contact time at 180 rpm in orbital shaker maintained at predefined temperature.

After the completion of predefined time; samples were subjected to centrifugation at 4000 rpm for 15 min and supernatant solution was filtered then it was analyzed for lead concentration in Atomic Absorption Spectrophotometer.

All the experiments were conducted in triplicate and average values were used in calculations.Preliminary experiments had shown that metal adsorption losses to the flask walls and filter paper were negligible. Hence, the lead uptake q (mg of lead adsorbed/ g of adsorbent) was calculated directly from the following equation

$$q = \frac{V(C_i - C_f)}{1000w} \tag{1}$$

Where $C_i$ and $C_f$ are the initial and final leadion concentrations (mg/L) respectively, V is the volume of the solution in mL and *w* is the mass of the adsorbent in g.

The influence of pH on lead removal was studied by adjusting 30 ml of 20 g/L lead concentration solutions to different pH values (2 to 10) and agitating with 0.1 g adsorbent at $30^0C$ for optimum time.

The effect of temperature on dye removal was carried out with 30 ml of 20 g/L lead concentration solutions to different temperatures (30, 40, 50, and $60^0C$) and agitating with 0.1 g adsorbent at $30^0C$ for optimum time.

**Adsorption Isotherms**

The adsorption data were analyzed and tested to fit different isotherms to develop the most suitable correlation for the equilibrium data in the design of adsorption system.

The Langmuir isotherm model [Z. Aksu and G. Donmez, McKay, G., and Ho, Y.s.] is valid for monolayer sorption onto surface and finite number of identical sites and is given by

$$q_e = \frac{Q_{max}bC_e}{1+bC_e} \tag{2}$$

where $Q_{max}$ is the maximum amount of the metal ion present per unit weight of cell to form a complete monolayer on the surface bound at high $C_e$(mg/g) and b the constant related to the affinity of the binding sites.

$Q_{max}$ and b values can be found from the slope and intercepts of a linear plot of $C_e/q_e$ versus $C_e$.

The empirical Freundlich isotherm model is based on a heterogeneous surface and is not restricted to the formation of a monolayer. It is expressed as$q_e = K_fC_e^{1/n}$-------- $\tag{3}$

Where $K_f$ and n are Freundlich constants characteristic of the system and they are indicators of adsorption capacity and intensity, respectively.

The values of $K_f$ and n are evaluated from the intercept and the slope respectively, of the linear plot of ln $q_e$ versus ln $C_e$ based on experimental data.

Jossens and co-workers modified the three parameter isotherm first proposed by Redlich and Peterson to incorporate features of both the Langmuir and Freundlich equations. It can be described as follows

$$q_e = \frac{AC_e}{1+BC_e^g} \tag{4}$$

Where A(L/g) and B(L/mg) are the Redlich – Peterson isotherm constants and g is the Redlich Peterson isotherm exponent, which lies between 0 and 1.

The Temkin isotherm has generally been applied in the following form

$$q_e = \frac{RT}{b_f}\ln(A_TC_e) \tag{5}$$

Where A(L/mg) and $b_f$ are Temkin isotherm constants. The derivation of Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation.

**Kinetic Studies**

**Pseudo First Order Model**

The Lagergren rate equation [S.Lagergren et al, C.Aharoni, and D.L.Sparks, M.Ungarish et al] was the first rate equation for the sorption of liquid/solid system based on solid capacity. This equation is one of the most widely used sorption rate equations for the sorption of solute from a liquid solution. It may be represented by the following equation.

$$\frac{dq}{dt} = k_1(q_e - q) \tag{6}$$

Where $q_e$ and q (mg/g) are the sorption capacities at equilibrium and at time t, respectively. $k_1$ is the rate constant of pseudo first order sorption, $(min^{-1})$. On integration and applying boundary conditions q=0 at t=0 to q=q at t=t, the equation (6) becomes

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303}t \tag{7}$$

**Pseudo Second Order Model**

If the rate of sorption follows a second order mechanism, the pseudo second order model proposed by the Ho and Mckay [Y.S. Ho and G. McKay] can be used to explain the adsorption kinetics. The pseudo second order model can be expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{8}$$

Where $q_e$ and q (mg/g) are the sorption capacities at equilibrium and at time t, respectively and $k_2$ is the rate constant of pseudo second order sorption(g/mg.min). After integration and applying boundary conditions q=0 at t=0 to q=q at t=t, the following form of equation can be obtained

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{9}$$

If the pseudo second order kinetics is applicable, the plot of t/q versus t of equation (9) should give a linear relationship, from which $q_e$ and $k_2$ can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

**Thermodynamic Studies**

Thermodynamic parameters such as enthalpy change $\Delta H^o$, free energy change $\Delta G^o$ and entropy change $\Delta S^o$ can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation

$$\Delta G^o = -RT \ln K_a \tag{10}$$

Where $\Delta G^o$ is the standard free energy change, J;

R is the universal gas constant, 8.314 kJmol$^{-1}$K$^{-1}$

T is the absolute temperature.

The free energy change indicates the degree of spontaneity of the adsorption process and the negative values reflects a more energetically favorable adsorption[M.Dikiky et al, Z.Aksu].The equilibrium constant may be expressed in terms of enthalpy change of adsorption as a function of temperature as follows

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^o}{RT^2} \tag{11}$$

The equation(11) gives the effect of temperature on the equilibrium constant $K_a$.  When $\Delta H^o$ is positive, the adsorption is endothermic, and an increase in T results in an increase in $K_a$. Conversely, when $\Delta H^o$ is negative, the adsorption is exothermic, and an increase in T causes a decrease in $K_a$, where $K_a$ is defined as the ratio of metal uptake and metal concentration in the aqueous solution at equilibrium i.e $\dfrac{q_e}{C_e}$ .

The thermodynamic criteria for the adsorption process were evaluated through computation of Gibb's free energy($\Delta G$), enthalpy of adsorption ($\Delta H$) and entropy of adsorption ($\Delta S$) by carrying out the adsorption experiments at four different temperatures and using the following equations.

$$\Delta G^o = \Delta H^o - T \, \Delta S^o \tag{12}$$

$$\log \left(\frac{q_e}{C_e}\right) = \frac{\Delta H^o}{2.303RT} + \frac{\Delta S^o}{2.303R} \tag{13}$$

Where $q_e/C_e$ is called adsorption affinity and $q_e$ is the amount adsorbed per unit mass at equilibrium and $C_e$, the equilibrium concentration of the adsorbate.

## RESULTS AND DISCUSSIONS

Experiments were conducted to establish the time of contact (t) at which maximum biosorption can be attained and also to study the effect of  initial metal ion concentration in the aqueous solution($C_i$), the adsorbent dosage(w), the particle size of the adsorbent($d_p$), initial pH of the aqueous solution and temperature(T).

The following discussion reveals the optimum conditions of various experimental variables for the removal of Lead from the effluents.

**Effect of Contact Time**

The effect of contact time on adsorption was studied by adding  0.1 g of 63µm size TGL powder adsorbent in 30 mL of aqueous solution of  initial metal concentration of 20 mg/L of Lead, at  pH 5.0 and the contents were agitated well in an orbital shaker for different time intervals (0.5, 1, 1.5, 2, 2.5 ..... up to 120 min) at a constant agitation speed of 180 rpm.

The experimental results reveal that the uptake of metal was faster at initial stages of contact and it became slower at equilibrium. This was due to the availability of a large number of vacant sites for adsorption during initial stages and

remaining vacant sites were difficult to be occupied at later stages of adsorption, and also most likely due to repulsive forces between the solute molecules on the adsorbent and aqueous solution.

It is evident from the figure-1& 2 that the adsorption equilibrium wasestablished very quickly as the percentage adsorption removal of 97.43% was achieved within 75 min.   This shows that the adsorption was quite fast.  Such rapid adsorption process was correlated with the characteristics of the biomass and its physico-chemical interactions with the metal ions [I.Ingelton and P.Simmons].  The rapid metal uptake is also desirable for the success of biosorbent for practical applications [B.Volesky].  Figure clarifies that the contact time of 35 min was sufficient for maximum lead uptake however, to ensure complete saturation of adsorption, the contact time was extended.  There was no significant change in the amount of adsorbed metal ion with further increase in contact time after attaining equilibrium at 75 min and therefore contact time of 75min was considered as the optimum contact time.Same optimum contact timeof 75 minutes as optimum time was obtained for different initial lead ion concentrated solutions also.
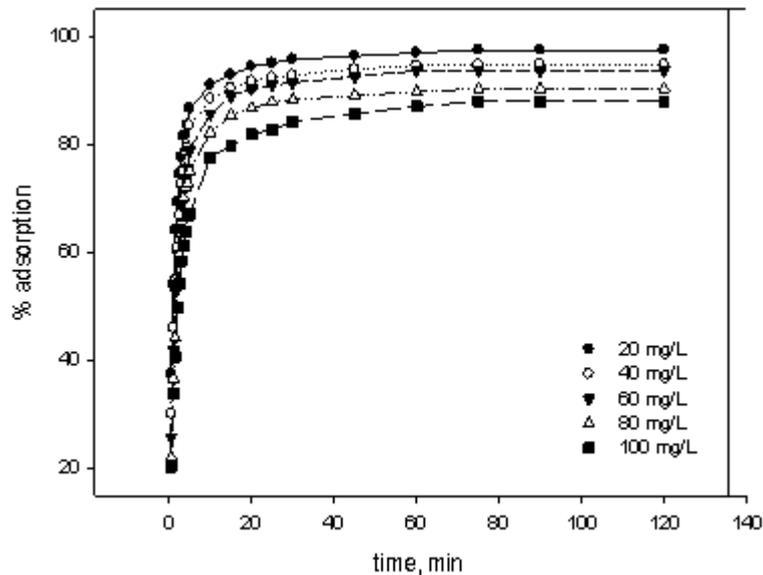


**Figure 1: Effect of Contact Time on % Adsorption of Lead for 0.1g of Adsorbent/30 ML Solution**
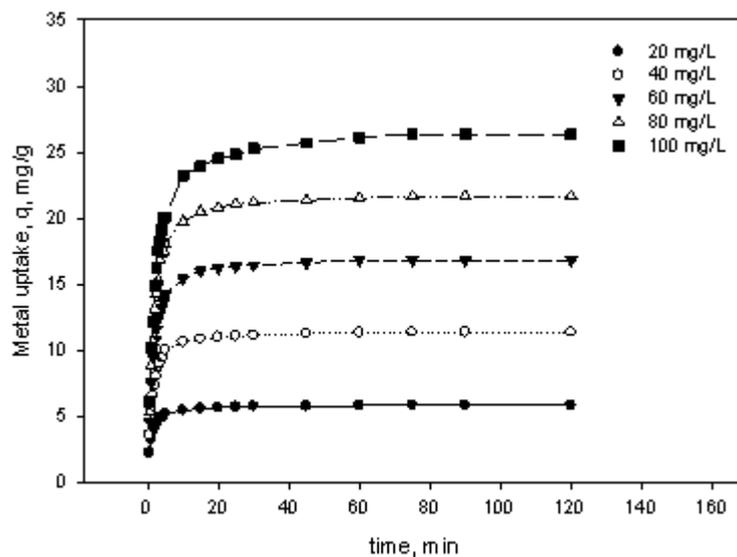


**Figure 2: Effect of Contact Time on Weight of Lead Removed Per Unit Mass of Adsorbent for 0.1g of Adsorbent/30 ML of Solution**

**Effect of pH**

It was observed that the adsorption was very less at the initial pH of 2.0(i.e., 10.43%) for 20mg/L of Lead ion concentration solution.  The low metal adsorption at pH below 3.0 may be supported on the basis of preference between $H^+$ and $M^{2+}$ to occupy the active binding sites [J.M.tobin et al]. A high proton concentration at lower pH exists and heavy metal uptake was decreased due to the positive charge density on metal binding sites, since hydrogen ions effectively compete with metal ions to rush towards the active binding sites.  A sharp increase in the biosorption occurred in the pH range 3-5 and it reached maximum at pH of 5.0 (97.43% removal).  This increase in metal removal can be explained on the basis of decrease in the predominance of $H^+$ ions for the same functional group and lowered electrostatic repulsion between surface and metal ions[Z.Reddad et al, P.Yin et al, A.Kapoor et al]as the pH increases.     Lead showed a trend of declining biosorption when the pH was increased from 5 to 10.   Above the pH value of 5.0, insoluble metal hydroxides starts precipitating and the precipitate was separated before analysis of the sample, reducing the amount adsorbed.  These results of the present study were in conformity with earlier studies [S.H. Hasana et al, Tamer Akar and Sibel Tunali, Dandan Lu et al, K. Jayaram et al].
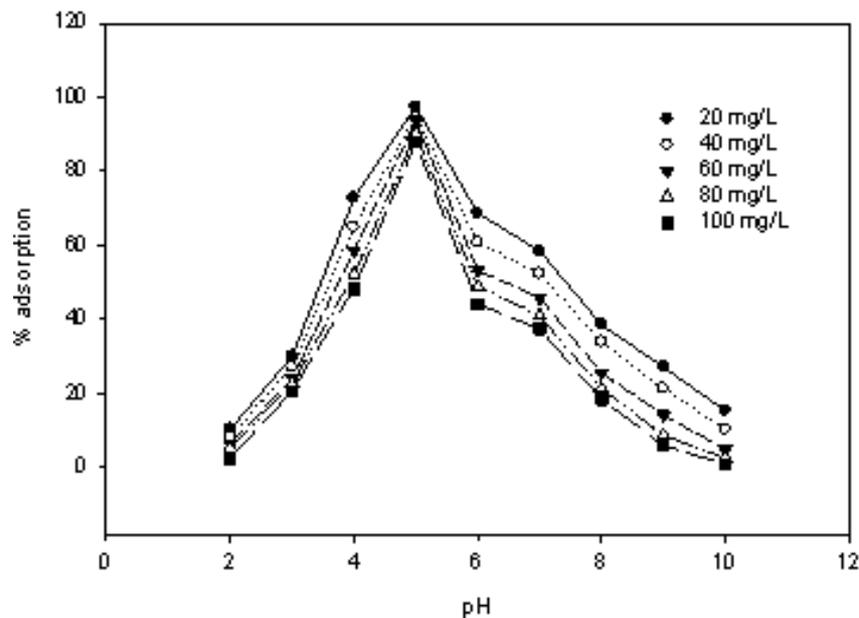


**Figure 3: Effect of PH on Lead Biosorption for 0.1g
of Adsorbent/30 ML of Solution**

**Effect of Metal Ion Concentration**

Experiments were conducted by adding 0.1 g of TGL powder into 30 ml of different initial leadion concentrated solutions (20,40,60,80 and100 mg/L) at pH 5 and 180 rpm for optimum contact time of 75 minto study the effect of initial Lead ion concentration on Lead removal from the solution.

It was evident from the results that the specific Lead uptake was increased and percentage adsorption of the metal was decreased with an increase in initial lead concentration in the solution. This increase in metal uptake may be attributed to an increase in the driving force i.e concentration gradient. At lower concentrations, most of the Lead ions present in solution could interact with the binding sites and thus the percentage of metal removal was higher.

At high concentrations, lower percentage ofremoval of metalwasmay be due to the lack of sufficient number of adsorption sites to accommodate metal ions available in the solution.
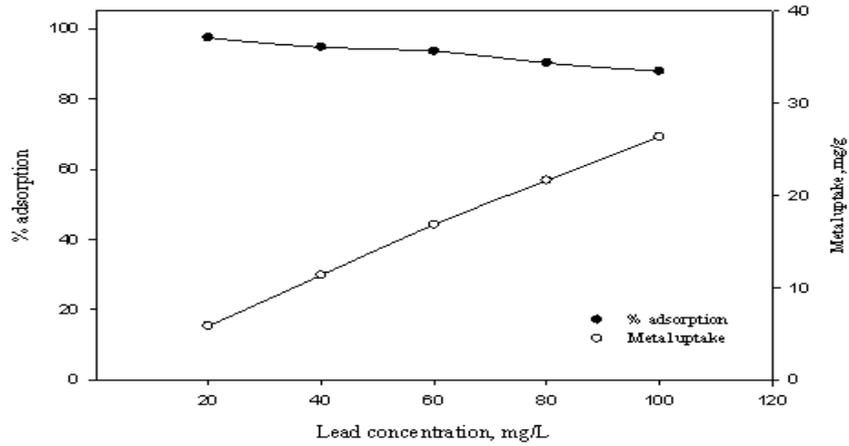
**Figure 4: Effect of Initial Lead Ion Concentraion on % Adsorption and Metal Uptake
of Lead for 0.1g of Adsorbent/30 ML of Solution**

**Effect of Adsorbent Dosage**

The effect of adsorbent dosage on the amount of metal adsorbed was determined by agitating 30 ml of Lead solution of 20 mg/L separately with 0.1, 0.2, 0.3, 0.4 and 0.5 g of adsorbent at room temperature for optimum contact time at a constant agitation speed of 180 rpm, maintaining the pH at 5.  It is evident from the observations that the amount of Lead adsorbed was increased with an increase in adsorbent dosage from 0.1 to 0.5 g.  Few more experiments were conducted for dosages less than 0.1 g(0.05 and 0.075 g) to make sure that adsorption was less than that at 0.1 g.  Figure 5 revealed that change in % adsorption above 0.1 g was marginal hence optimum dosage was taken as 0.1g in all calculation in our study.  Even at high adsorbent dosage conditions also complete adsorptionwas not achieved due to the interference between binding sites and reduced mixing at high biomass densities. It may be suggested that a more economical design for the removal of heavy metal ions can be carried out using small batches of sorbent rather than in a single batch [F.A.Abu Al-Rub et al].
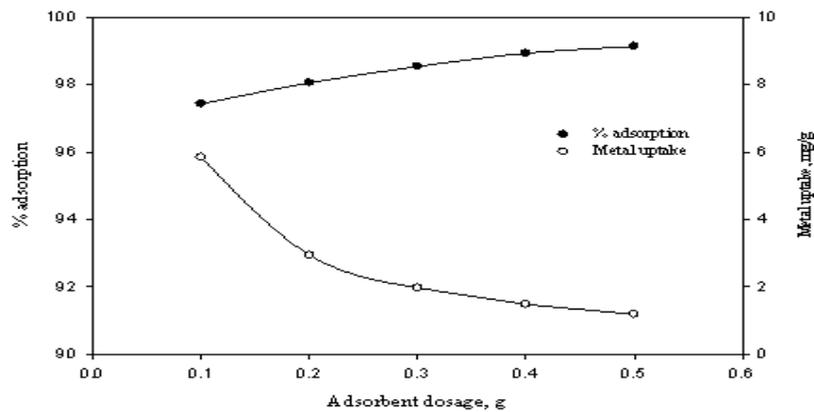


**Figure 5: Effect of Adsorbent Dosage on % Adsorption and Uptake of
Lead for 20mg/L Metal Ion Concentration**

**Effect of Adsorbent Size**

The effect of particle size on percentage adsorption of Lead was investigated by adding 0.1 g of adsorbent of various average particle sizes ranging from 63 – 180 µm to 30 ml of 20 mg/L Lead solution and biosorption studies were carried out.   It revealed that a 10% decrease in adsorption of Lead i.e from 97.43 to 86.76% was observed with a threefold increase in average particle size from 63 to 180 µm.  It is well known that decrease in the average particle size of the

adsorbent increases the surface area, thereby increases the adsorption capacity.  Drop in metal uptake was found to be, however marginal with an increase in the size of the adsorbent.
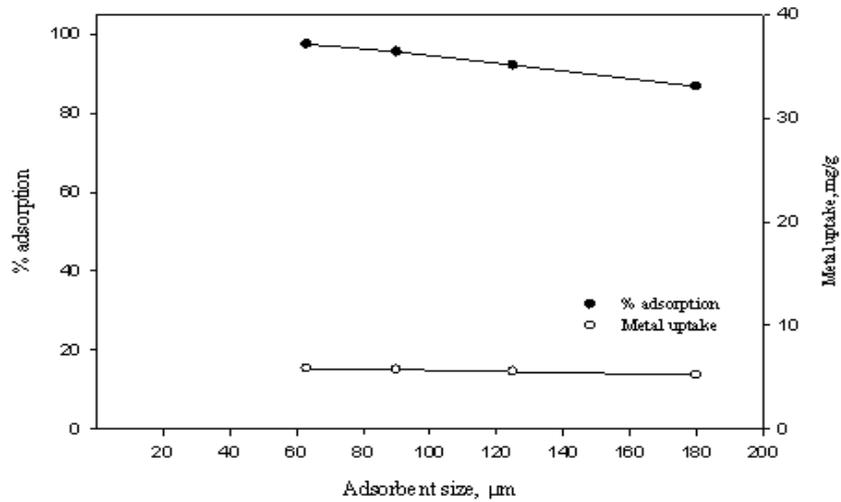


**Figure 6: Effect of Adsorbent Size on % Adsorption and Uptake of Lead
for 20mg/L of Metal Ion Concentration 0.1g of Adsorbent/30mL Solution**

**Effect of Temperature**

The percentage adsorption of Lead as a function of the initial metal ion concentration at 303,313, 323 & 333 K is shown through plots of Figure7.  The percentage adsorption of Lead ion was decreased by 20% (from 97.43 to 78.33) as the temperature was varied from 303 to 333 K for the given Lead ion concentration in the solution. The percentage adsorption at higher temperatures showed a declining trend because the metal ions are highly energized and mobile overriding the attractive forces between adsorbent and adsorbate which escaped binding sites on the surface of the adsorbent.  At lower temperatures the Lead ions present in the solution could interact more with the binding sites and thus the percentage adsorption was found to be higher than those at higher temperatures. This decrease in the percentage adsorption at increased temperatures was indicative of exothermic behavior of adsorption process.  Similar results were reported byother authors for the removal of Lead [K. G. Bhattacharya and A. Sharma] using the Azadirachta indica as a biosorbent.
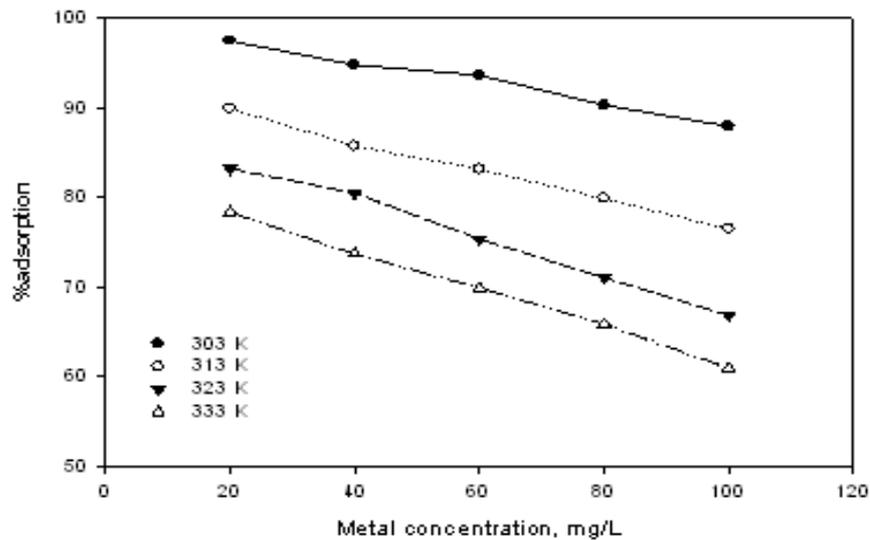


**Figure 7: Effect of Temperature on Adsorption of Lead
for 0.1g/30 ml of Metal Solution**

**Equilibrium Studies**

The equilibrium studies were carried out at room temperature $303 \pm 1$ K. The equilibrium data were analyzed using four of the most commonly used isotherm models, Freundlich, Langmuir, Redlich-Peterson and Temkin. The equilibrium data was well represented by all the four models. The calculated isotherm constants were presented in Table 1. The best fit equilibrium model was determined based on the linear regression correlation coefficient $R^2$. From the table it was observed that the adsorption data was best represented by Freundlich isotherm with an average higher correlation coefficient of 0.9973 followed by Langmuir, Redlich-Peterson and Temkin with a correlation coefficient of 0.9784, 0.9784 and 0.964 respectively.

**Table 1: Equilibrium Constants for Lead**

| Isotherm Name | Constants | Values |
|---|---|---|
| Langmuir | $Q_{max}$(mg/g) | 32.363 |
| | b(L/mg) | 0.3056 |
| | $R^2$ | 0.9784 |
| Freundlich | $K_f$ (mg/g) | 8.147 |
| | n(g/I) | 0.4819 |
| | $R^2$ | 0.9973 |
| Redlich-Peterson | A(L/g) | 15.089 |
| | B(L/g) | 0.702 |
| | g | 0.905 |
| | $R^2$ | 0.9784 |
| Temkin | $A_T$ (L/mg) | 3.850 |
| | $b_T$ | 390.25 |
| | $R^2$ | 0.964 |

**Specific Surface Area**

Mono layer coverage of the surface by the metal ions can be used for the calculation of the specific surface area S according to the following equation

$$S = \frac{Q_{max} NA}{M} \tag{14}$$

Where S is the specific surface area, m$^2$/(g of adsorbent); $Q_{max}$ the mono layer sorption capacity, g of metal/(g of adsorbent); N the Avogadro number, $6.02 \times 10^{23}$; A, the cross sectional area of metal ion, m$^2$; M the molecular weight of the metal. The molecular weight, cross-sectional area and radius of Lead are 207, 5.56 $A^{o^2}$ and 1.33 $A^o$ respectively in a close packed monolayer [Raziya Nadeem et al, Y.S.Ho et al]. The maximum specific surface area calculated from equation (14) for Lead was 5.233 m$^2$/(g of adsorbent).

**Kinetic Studies**

The prediction of rate of adsorption gives significant information for designing batch adsorption systems. Information on the kinetics of the solute uptake is required for selecting optimum operating conditions for full-scale batch process. Hence, the kinetics of the adsorption data was analyzed using pseudo first order and pseudo second order models. The values of rate constants, $q_e$ and their corresponding linear regression correlation coefficients for both pseudo first and second order kinetics were presented in Table 2. Figure 8 shows that the Lagergren pseudo-first order kinetic plot did not fit wellfor the adsorption of Lead onto TGL. The linear regression correlation coefficients( $R_1^2$ ) were found for the first order were in the range of 0.8749 to 0.9142, which were very less comparative to second order kinetics.Where as the

pseudo-second order kinetic plot fits wellthe adsorption data of Lead onto TGL (Figure 9). Hence this model could be applied to predict the adsorption kinetics of Lead onto TGL very well.
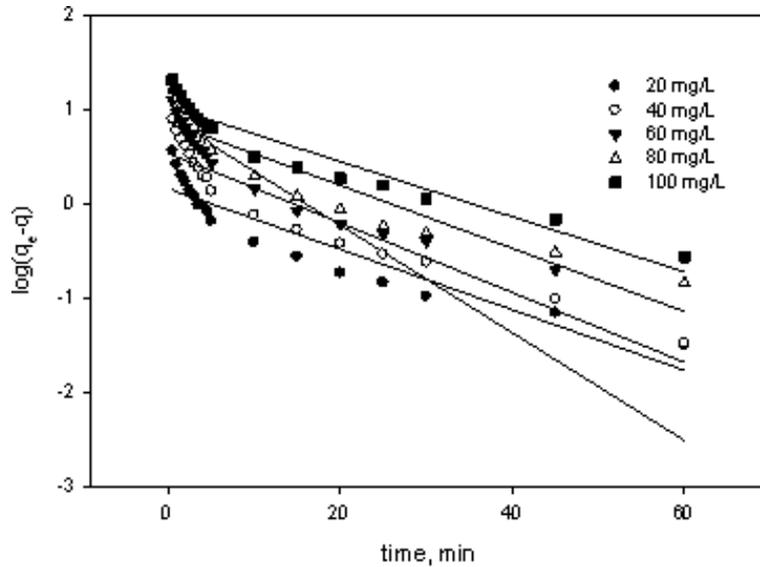


**Figure 8: Pseudo First Order Kinetics for Lead at pH=5, Adsorbent Dosage=0.1g/30mL Solution, Adsorbent Si8ze=63μm**



**Figure 9: Pseudo Second Order Kinetics for Lead at pH=5 Adsorbent Dosage=0.1g/30 ML Solution, Adsorbent Size=63μm**

**Table 2: Pseudo First and Second Order Kinetic Constants for Lead**

| $C_i$ (mg/L) | Pseudo First Order Kinetics | | | Pseudo Second Order Kinetics | | |
|---|---|---|---|---|---|---|
| | Rate Constant, $k_1$(1/min) | $q_e$ | Correlation Coefficient $R_1^2$ | Rate Constant, $k_2$(1/min) | $q_e$ (mg/g) | Correlation Coefficient $R_2^2$ |
| 20 | 0.0742 | 1.4378 | 0.8749 | 0.2139 | 5.8928 | 0.9998 |
| 40 | 0.0849 | 3.4095 | 0.9122 | 0.0914 | 11.4811 | 0.9995 |
| 60 | 0.1310 | 7.264 | 0.8806 | 0.0525 | 17.0648 | 0.9991 |
| 80 | 0.0884 | 8.1096 | 0.8781 | 0.0369 | 21.9298 | 0.9993 |
| 100 | 0.0672 | 10.6905 | 0.9142 | 0.0223 | 26.8097 | 0.9983 |

**Thermodynamic Studies**

The free energy changes for Lead adsorption onto TGL were determined by using the equilibrium constants obtained from Langmuir isotherm model. The $\Delta G^o$ and $\Delta S^o$ values of Lead at different temperatures(303,313,323,333 K) at pH=5 were given in Table3. The negative values of $\Delta G^o$ confirmed the feasibility of the process and the high spontaneity at lower temperatures.From the Figure10, the standard enthalpy change, $\Delta H^o$ and the standard entropy change, $\Delta S^o$ were determined using the slope and intercept of the plot between ln $K_a$ versus 1/T. The values of $\Delta H^o$ and $\Delta S^o$ were –67.6 kJ/mol and -0.195 kJ/mol.K , respectively. On the other hand enthalpy change for lead was negative and a decrease in the removal capacity was observed with an increase in temperature from 303K to 333K. This shows that biosorption of lead was exothermic.
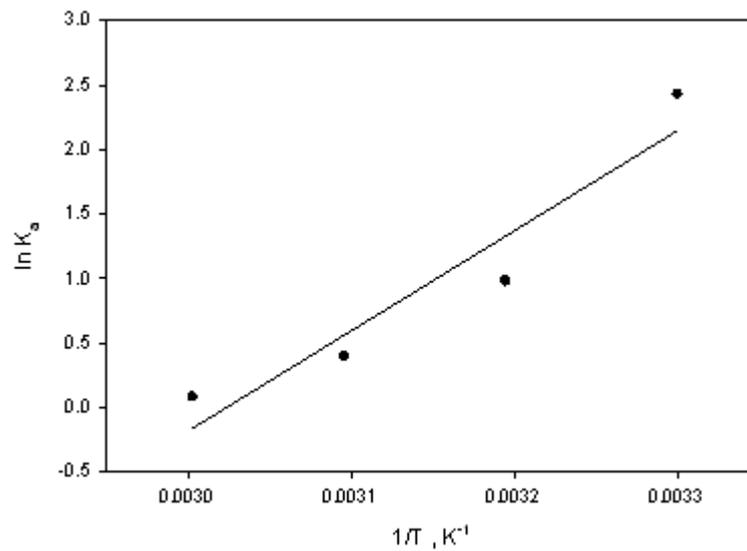


**Figure 10: Variation of in $K_a$ with 1/T**

**Table 3: $\Delta G^o$ And $T\Delta S^o$ Values for Adsorption of Lead at Different Temperatures at pH=5**

| Temperature(K) | $K_a$(L/mg) | $\Delta G^o$ (kJ/mol) | $-T\Delta S^o$ (kJ/mol) |
|---|---|---|---|
| 303 | 11.3505 | -8.515 | 59.085 |
| 313 | 2.6640 | -6.565 | 61.035 |
| 323 | 1.4834 | -4.615 | 62.985 |
| 333 | 1.0841 | -2.565 | 64.935 |

## CONCLUSIONS

The biomass of TGLused in this study is freely and abundantly available in almost all places. The results obtained demonstrate a good adsorption capacity of Lead, and highlighting its potential as an effective adsorbent in the industrial effluent treatment.The data obtained from the adsorption of Lead on the TGL showed a contact time of 75 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time.It was observed that the maximum adsorption was at the pH of 5. Further increase in pH showed a declining trend of adsorption. It was noticed that the metal uptake was increased and percentage adsorption of the metals was decreased with an increase in the initial lead ion concentration. The effect of different adsorbent particle sizes on the adsorption of Lead was quite significant. The extent of adsorption of all the three metals was decreased with an increase in particle size. The amount of Lead adsorbed was increased considerably with an increase in adsorbent dosage. The percentage adsorption of

Lead was decreased as temperature increases. The experimental data was fitted well with Freundlich isotherm and the adsorption coefficients agreed well with the conditions of favorable adsorption. Kinetic studies indicated that the adsorption tends to follow pseudo second order for the range of concentrations studied for the entire adsorption period. The kinetic studies show that lead adsorption by TGL was fast, the maximum extent of adsorption reaching 85percent of total adsorption capacity of metal in the initial stages of contact period within five minutes. The calculated thermodynamic quantities such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) indicated that the adsorption process is spontaneous and exothermic. The present study shows that the Tectona grandis L.f is an effective adsorbent to remove Lead from the aqueous solutions.

## REFERENCES

1. Esposito , F. Pagnanelli , A. Lodi , C. Solisio , F. Veglio, Hydrometallurgy. 60 (2001) 129 –141.

2. A.Kapoor, T.Viraraghavan, D.R.cullimore, Bioresour.Technol.70 (1999) 95-104.

3. Preetha, T. Virithagiri, Afr. J. Biotechnol. 6 (2005) 506–508

4. Volesky, Z.R. Holan,Biotechnol. Prog. 11(1995) 235–250.

5. B.Volesky, Biosorption of Heavy metals, CRC Press, BocaRaton, FL, 1990.

6. C.Aharoni, D.L.Sparks, Soil Science society of America, Madison, WI, (1991)1-18.

7. Dandan Lu, Qilin Cao, Xiuju Cao, Fang Luo, Journal of Hazardous Materials 166 (2009) 239–247.

8. Romera, F. Gonzalez, A. Ballester, M.L. Blázquez, J.A. Munoz, Bioresour. Technol. 98 (2007) 3344 – 3353.

9. F.A.Abu Al-Rub, M.H.El-Naas, F.Benyahia, I.Ashour, Process Biochem. 39 (2004) 1767-1773.

10. I.Ingelton, P.Simmons, J.Chem.Technol.Biotechnol, 65(1996) 21.

11. J.M.tobin, D.G.Cooper, R.J.Neufeld, Appl.Environ.Microbiol, 47 (1984) 821.

12. K. Jayaram, I.Y.L.N. Murthy, H. Lalhruaitluanga, M.N.V. Prasad, Colloids and Surfaces B: Biointerfaces 71 (2009) 248–254.

13. K.G.Bhattacharya, A.Sharma, Journal of Hazardous materials, B113 (2004) 97-109.

14. K.S. Low , C.K. Lee, S.C. Liew, Process Biochemistry. 36 (2000) 59–64.

15. M.Dikiky, M.Khamis, A.Manasra, Adv Environ Res.6 (2002) 533-540.

16. M.Ungarish, C.Aharoni, J.C.s.Faraday Trans.77 (1981) 975.

17. McKay, G., Ho, Y.s., 1999. Pseudo second order model for sorption processes. Process Biochem. 34, 451-465.

18. P.King, Y.Prasanna Kumar, V.S.R.K.Prasad, J of Industrial pollution control. 21(1), (2005) 155-162.

19. P.King, Y.Prasanna Kumar, V.S.R.K.Prasad, J of Industrial pollution control. 22(1), (2006) 25-32.

20. P.Yin, Q.Yu, B.Jin, Z.Ling, Water Res. 33(1999) 1960-1963.

21. Raziya Nadeem, Tariq Mahmood Ansari , Ahmad Mukhtar Khalid , Journal of Hazardous Materials 156 (2008) 64–73.

22. S.H. Hasana, P. Srivastava, M. Talat , Journal of Hazardous Materials 168 (2009) 1155–1162.

23.  S.Lagergren, S.Kungliga, Band.24(4) (1898)1-39.

24.  Tamer Akar , Sibel Tunali, Bioresource Technolagy 97 (2006) 1780–1787.

25.  W.S. Wan Ngah , M.A.K.M. Hanafiah, Bioresource Technology. 99 (2008) 3935–3948.

26.  Y.S.Ho, C.T.Huang, H.W.Huang, Process Biochem.39(2)(2003)179-183.

27.  Y.S.Ho, G.McKay, Can J Chem Eng. 76(1998d) 822-827.

28.  Z. Aksu and G. Donmez, A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye, Chemosphere 50 (2003) 1075-1083.

29.  Z.Aksu, Process Biochem.38 (2002) 89-99.

30.  Z.Reddad,C.Gerente, Y.Andres, P.LeCloiree, Environ.Sci.Technol.36(2002)2067.