Performance and optimization of casia siamea pods powder for the removal of heavy metals(lead) by using bio sorption

Poba Venkata Rao[1],Chiranjeevi Kalesh[2]

Assistant Professor[1], M.Tech(student)[2], Department of Chemical Engineering,Andhra University,Visakhapatnam-530003,Andhrapradesh,INDIA.

Urbanization and industrialization leads to migration of heavy metals from industrial waste to underground water is deteriorating human beings life and sustainability. Perhaps the plant biomass is an economical and readily available as biosorbent for the biosorption of lead ions from aqueous solutions.Present experimental work comprising of the equilibrium, kinetics and thermodynamic study for biosorption of lead ions from aqueous solution using 'Cassia siamea pods powder' as a biosorbent in a batch process. The plant 'Cassia siamea' (common name: sima tangedu) is obtained from Andhra University campus, visakhapatnam, andhrapradesh, India. The biosorption process was carried out in batch process by varying six parameters: Agitation time, biosorbent size, biosorbent dosage, pH of the aqueous solution, Initial Pb ion concentration and temperature of the process.The results shows that biosorption of lead is augmented with an increase in biosorbent dosage(optimum dosage 35 g/L) , equilibrium agitation time(40 minutes) and at pH 6, the maximum biosorption of lead (83.5787 %) onto cassia siamea pods powder is observed. And present experimental data was well suited to Langmuir isotherm model(R^2=0.99889) over Freundlich and Temkin isotherm models. The thermodynamic data shows that % biosorption of lead is increased with an increase in temperature.

Keywords: Biosorption, heavy metals, concentration, PH, equilibrium time, isotherms.

Introduction: Water is no alien to all the living beings upon earth. It has no barrier or bars over constituencies or continents, as it leaves only 1/4th of the land of whole ecosystem. It's a gift if it's pure, but when it is impure even poison is of no match and has no discrimination over giving a life or taking it. Heavy metal pollution is of major threat to the environment and is persistent. Main sources of heavy metal contamination include urban industrial aerosols, mining activities, industrial and agricultural chemicals. Among these metals we found that lead has a wider range of danger, reach to the nature leaving all others back. It is poisonous, a characteristic that has led to a reduction in the use of lead compound as pigments for paints and inks.

The contamination of the aquatic systems with toxic heavy metal ions is a problem of global concern. In addition to their toxic effects even at low concentrations, heavy metals can accumulate along the food chain which leads to serious ecological and health hazards as a result of their solubility and mobility. Lead, for example, has both acute and chronic effects in humans. It may cause anemia, headache, chills, diarrhea and reduction in hemoglobin formation **[1]**.

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence poses environmental disposal problems due to their non-degradable and persistence nature. In addition mining, mineral processing and extractive metallurgical operations also generate toxic liquid wastes. Environmental engineers and scientists are faced with the challenging task to develop appropriate low cost technologies for effluent treatment **[2]**.Heavy metals are used in various industries due to their technological importance and wastewaters from these industries include metal ions having a permanent toxic effect. The disposal of industrial effluents containing heavy metals into natural water systems is a cause of serious environmental concern. Beyond certain limits, heavy metals are toxic to living organisms and may cause serious hazard to public health **[3]**.

A whole new family of suitably "formulated" biosorbents can be used in the process of metal removal and detoxification of industrial metal-bearing effluents. The sorption process is the most effective mode of application for the purpose. Recovery of the deposited metals from saturated biosorbent can be accomplished because they can often be easily released from the biosorbent in a concentrated wash solution which also regenerates the biosorbent for subsequent multiple reuse. This and extremely low cost of biosorbents makes the process highly economical and competitive particularly for environmental applications in detoxifying effluents of e.g.

- ➢ metal-plating and metal-finishing operations,
- ➢ mining and ore processing operations,
- ➢ metal processing, battery and accumulator manufacturing operations,
- ➢ Nuclear power generation, (etc.)

Water is used for several purposes but each and every ounce of it needs to be up to the mark as per environmental protection laws depending upon its use. When it comes to the industrial purposes they need to purify the water and they do need to remove heavy metal constraints present in their effluents, harmoniously. Many methods are applied for the removal of heavy metals from water. These methods may be used in a combination or alone. Reverse Osmosis, Electro dialysis, Evaporation, Ion Exchange, Chemical

Precipitation, Solvent Extraction, Adsorption/Biosorption. The methods, advantages and percentage removal efficiencies demands the application of these methods depending on the requirement.

Sorption refers to the removal of solute components from the aqueous phase of an environmental system by the solid phase, at the surface of the solid phase **[4].** This issue has been resolved in favour of adsorption being a chemical reaction. However the generally used term 'adsorption' is somewhat of a misnomer in that it conveys the impression of a one-way process to some investigators **[9].** Adsorption was defined as 'the enrichment of one or more of the components (of a liquid or gas) in the region between two bulk phases (i.e. in the interfacial area) **[6],** while the Soil Science Society of America took a more pragmatic approach by defining it as 'the process by which atoms, molecules, or ions are taken up from the aqueous or gaseous phase and are retained on the surfaces of solids by chemical or physical binding **[7].**

In this thesis the term 'sorption' has been used extensively. Mechanisms of Sorption: Definition of the mechanisms of sorption in the literature can be confusing at times due to differences accorded by various researchers. The main processes are agreed upon but are perhaps referred to by differing names, especially under the terms complexation and chemisorption. The mechanisms detailed in this thesis **[7]** may not contain additional segregation of the mechanisms. As such what may be detailed here may vary slightly from other definitions and so are specific to the sorption of metals by plant biomass.Under the term chemical adsorption there are two main mechanisms of adsorption. In the literature the distinction between them (as mentioned) is somewhat murky and at times confusing. This is mainly due to the difficulties involved in physically 'measuring' the different mechanisms. The most important chemical process responsible for the sorption of ionic species is ion exchange **[5].**

Complexation between dissolved and surface materials is another important adsorption mechanism. Surface complexation reactions generally involve the loss of one or more water molecules from the inner-coordination sphere of the metal ion for one or more ligand coordinating atoms on the surface of the particle in a ligand-exchange reaction leading to the formation of an inner sphere complex. Ionic and covalent bonding are likely to be involved and this is defined as specific sorption. An outer-sphere complex does not involve the loss of water molecules and is termed non-specific due to the weak dependence on the electron configuration of the surface group and adsorbed ion. Precipitation and co-precipitation are sorption mechanisms, but are not adsorption processes. They can be important processes for removing inorganic heavy metals from solution. Precipitation is the separation of the solute as a solid from the aqueous phase under conditions of saturation and is a three-dimensional process, unlike adsorption processes **[8].** Co-precipitation is the removal of a solute from solution by a dissolution / precipitation two stage process with the sorbent partially dissolving and reprecipitating with the heavy metal incorporated in a new phase. Isomorphous substitution is likely to have minimal influence in the sorption mechanisms occurring for the sorption of metals onto bone charcoal yet is worthy of mention. It involves the substitution of similar sized ions and different charge in the sorbent structure. It leads to the creation of a surface charge **[9].**

Table - 1
Standard AAS conditions for lead

Condition	Lead
Wavelength, nm	283.31
Slit, nm	2.7
Relative noise, mg/L	0.43
Sensitivity, mg/L	10
Sensitivity check, mg/L	8

EXPERIMENTAL PROCEDURE:

The present experimentation is carried out batch wise by using Atomic absorption spectrophotometer(AAS): (Perkin Elmer A Analyst 200 model), on biosorption of lead metal from aqueous solution by a biosorbent – *Cassia siamea* pod*s* powder.

The experimental procedure consists of the following steps.

1. Preparation of the biosorbent,
2. Preparation of the 1000 mg/L of lead stock solution,
3. Studies on equilibrium biosorption,
4. Kinetic studies and
5. **Thermodynamics.**

Preparation of the biosorbent

Cassia siamea pods collected were firstly washed cleanly with water and then with deionised water so as to remove dust and soluble impurities then dried at room temperature. Moisture free pods, having less strength will be obtained after drying, being easier to grind. These pods are finely powdered and varied through sizing, by passing the powder through a set of sieves ranging from 152 μm to 53 μm sizes.

Preparation of lead stock solution

$Pb(NO_3)_2$ is used as the source for lead stock solution. All the required solutions are prepared with analytical reagents and double-distilled water. 1.615 g of 99% $Pb(NO_3)_2$ is dissolved in distilled water of 1.0 L volumetric flask up to the mark to obtain 1000 mg/L of lead stock solution. Synthetic samples of lead of different concentrations are prepared from this stock solution by appropriate dilutions. 100 mg/L lead stock solution is prepared by diluting 100 mL of 1000 mg/L lead stock solution with distilled water in 1000 mL volumetric flask up to the mark. Similarly solutions with different metal concentrations such as (20, 50, 100, 150 and 200 mg/L) are prepared. The pH of aqueous solution is adjusted to the desired value by addition of 0.1 N H_2SO_4 or 0.1N NaOH solution.

Lead equivalent to 1 g is given by =

$$\frac{\text{Molecular weight of } Pb(NO_3)_2 \quad \mathbf{X} \quad 100}{\text{Atomic weight of Lead} \quad \mathbf{X} \quad \text{purity}}$$

Studies on equilibrium biosorption

The initial concentration of lead in the aqueous solution is analyzed in an Atomic Absorption Spectrophotometer (**Perkin Elmer A Analyst 200 model**). Wave length is 283.31 nm and sensitivity check is 2.7 mg/L.

Effect of agitation time, biosorbent dosage and biosorbent size

Adding 10 g/L of biosorbent having a 53 μm size to 50 mL of aqueous solution is taken in a 250 mL conical flask. At room temperature (303 K) orbital shaker is set to rotate with a speed of 180 rpm for 1 min. Similarly 10 g/L of biosorbent is added to 14 more flasks and exposed to respective agitation times (3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 min). These samples are filtered separately with whatman filter papers and the filtrates are analyzed in AAS to obtain final concentrations of lead. Eight more dosages undergo similar experiments (20, 25, 30, 35, 40, 45, 50 and 60 g/L). The percentage biosorption of lead is calculated as (C_0-C_e) x $100/C_0$. Graphs are plotted between the agitation time and % biosorption of lead to identify the equilibrium agitation time and optimum dosage. Similarly biosorbent size is varied from 152 μm to 53 μm.

Effect of initial concentration of the lead in aqueous solution:

Initial concentration of lead can be determined by taking 50 mL of aqueous solution containing 20 mg/L of lead in a 250 mL conical flask, biosorbent size of 53 μm and adding 10 g/L. A continuous contact was maintained for equilibrium agitation time by shaking in an orbital shaker at room temperature. The settled samples were filtered leaving no traces of particles in it. Final lead concentrations of the filtrate were found out by the help of AAS. Rest of concentrations of lead in aqueous solution go through the same process to obtain respective values (20, 50, 100, 150 and 200 mg/L).

Effect of pH of the solution:

50 mL of aqueous solution is taken in each of seven conical flasks. The pH values of the solutions are adjusted to 2, 3, 4, 5, 6, 7 and 8 in separate flasks by adding required amounts of 0.1 N H_2SO_4 or 0.1N NaOH respectively. 10 g/L of 53 μm size biosorbent is added separately to these flasks. The samples are shaken on an orbital shaker at room temperature for equilibrium agitation time. Samples are filtered and analyzed using AAS and lead concentrations were determined.

Kinetic studies:

In order to examine the biosorption or chemisorption and to determine the order of the rate of biosorption, 50 mL of aqueous solution containing 20 mg/L of lead is taken in each of twelve conical flasks. 10 g/L of biosorbent having 53 μm size is added in each of the flasks. The conical flasks are shaken on an orbital shaker for different time intervals at room temperature. They are then settled, filtered and the filtrates are analyzed to find the concentrations of lead. Similar procedure is adopted for other biosorbent dosages of 10, 20, 25, 30, 35, 40, 45, 50 & 60 g/L. The samples thus obtained are filtered and analyzed using AAS to get the residual concentration of lead in aqueous solutions.

Thermodynamics:

The following procedure is followed to determine the effect of temperature on the rate of biosorption and to evaluate the enthalpy of biosorption (ΔH), entropy of biosorption (ΔS) and Gibbs free energy (ΔG). 50 mL of aqueous solution containing 20 mg/L of lead is taken in each of five conical flasks. 10 g/L of 53 μm size biosorbent is added in each of these flasks. Rest of them are also shaken in an orbital shaker for optimum agitation time for five different temperatures 283, 293, 303, 313 and 323 K. These samples are filtered. The lead concentrations of the filtrates are determined by using AAS. The values of parameters investigated are compiled in table – 2.

Table 2

Experimental conditions investigated

S.No.	Parameter	Values Investigated
1	Agitation time, t, min	1, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 & 180
2	Biosorbent size, dP, μm	53, 74, 104, 125 and 152
3	Biosorbent dosage, w, g/L	10, 20, 25, 30, 35, 40, 45, 50 & 60
4	Initial lead concentration, C_0, mg/L	20, 50, 100, 150 and 160
5	pH of aqueous solution	2, 3, 4, 5, 6, 7 and 8
6	Temperature, K	283, 293, 303, 313 & 323

RESULTS & DISCUSSION

Present study illustrates the potential of *Cassia siamea* pods powder as biosorbent for the biosorption of lead present in aqueous solution. Effect of several parameters are evaluated on biosorption were analysed. This measured data comprises of the initial and final concentrations of the metal in aqueous solution, temperature of the aqueous solution, pH of the aqueous solution, biosorbent dosage, biosorbent size and agitation time. Batch experiments were conducted to obtain the data.

Equilibrium studies:

The percentage biosorption of lead from the experiment is found to be $= \dfrac{C_o - C_e}{C_o} \times 100$

The amount of lead biosorbed per unit mass of the biosorbent, q_t in mg/g is computed by using the expression:

$$q_t = \frac{C_o - C_e}{w}$$

The effects of various parameters on biosorption of lead are discussed below.

Effect of agitation time:

The equilibrium agitation time is determined by plotting the % biosorption of lead against agitation time as shown fig. 1 for the interaction time intervals between 1 to 180 min. For 53 μm size of 10 g/L biosorbent dosage, 61.5 % (1.23 mg/g) of lead is biosorbed in the first 5 min. The % biosorption is increased briskly upto 40 min reaching 72 % (1.44 mg/g). Beyond 40 min, the % biosorption is constant achieving equilibrium conditions [10].
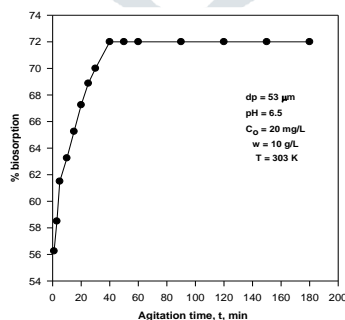

Fig. 1 Effect of agitation time on % biosorption of lead

The maximum biosorption of 72 % (1.5495 mg/g) is attained for 40 min of agitation time with 10 g/L of 53 μm size biosorbent mixed in 50 mL of aqueous solution ($C_0 = 20$ mg/L). The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of lead. As time increases, more amount of lead gets biosorbed onto the surface of the biosorbent due to Vanderwaal's forces of attraction and resulted in decrease of available surface area. The biosorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the biosorbent

capacity is exhausted. The maximum percentage of biosorption is attained at 40 minutes and remains to be constant. From here on, further experiments are done considering this agitation time.

Effect of biosorbent size:

The variations in % biosorption of lead from the aqueous solution with biosorbent size are obtained. The results are drawn in Fig.2 with percentage biosorption of lead as a function of biosorbent size displays percentage biosorption is raised from 66.44 (1.3288 mg/g) to 72 % (1.44 mg/g) with reductions in biosorbent size from 152 to 53 μm. As the particle looses its size, surface area gains to a greater extent, this phenomenon is as expected; thereby the number of active sites present on the biosorbent are better exposed to the biosorbate [11].
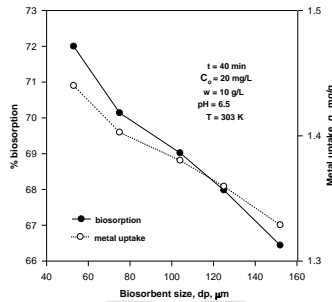

Fig. 2 Variation of % biosorption with biosorbent size

Effect of pH

pH controls biosorption by influencing the surface change of the biosorbent, the degree of ionization and the species of biosorbate. In the present investigation, lead biosorption data are obtained in the pH range of 2 to 8 of the aqueous solution ($C_0 = 20$ mg/L) using 10 g/L of 53 μm size biosorbent. The effect of pH of aqueous solution on % biosorption of lead is shown in Fig. 3. The % biosorption of lead has gone up from 51.72 % (1.3072 mg/g) to 70.18 % (1.4036 mg/g) as pH is increased from 2 to 6 and decreased beyond the pH value of 6 [12]. % biosorption is decreased from pH 7 to 8 reaching 69.22 % (1.3844 mg/g) from 65.36 % (1.3072 mg/g). Low pH depresses biosorption due to competition with H^+ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Lead ions replace H^+ ions bound to the biosorbent.
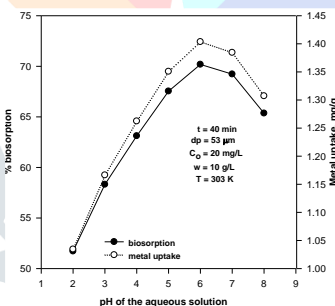

Fig. 3 Dependence of % biosorption on pH of aqueous solution

Effect of initial concentration of lead:

The effect of initial concentration of lead in the aqueous solution on the percentage biosorption of lead is shown in Fig.4. The percentage biosorption of lead is decreased from 70.18 % (1.4036 mg/g) to 53.52 % (10.664 mg/g) with an increase **[13]** in C_0 from 20 mg/L to 200 mg/L. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent.
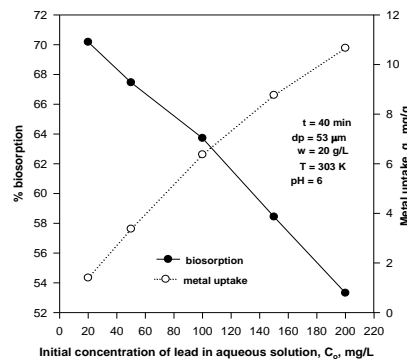

Fig. 4　% biosorption as a function of initial concentration of lead

Effect of biosorbent dosage:

The percentage biosorption of lead is drawn against biosorbent dosage for 53 μm size biosorbent in Fig. 5. The biosorption of lead increased from 70.1 % (1.402 mg/g) to 79 % (0.45143 mg/g) with an increase in biosorbent dosage from 10 to 35 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for lead biosorption would be more. The change in percentage biosorption of lead is minimal from 79 % (0.45143 mg/g) to 80.3 % (0.267667 mg/g) when 'w' is increased from 35 to 60 g/L. Hence all other experiments are conducted at 35 g/L dosage [13].
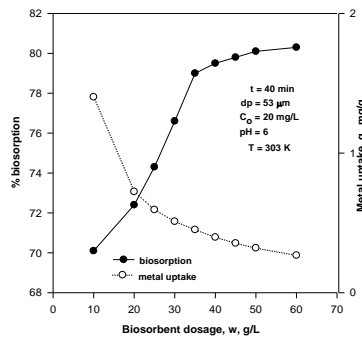

Fig. 5 Dependence of % biosorption of lead on biosorbent dosage

Effect of Temperature:

The effect of temperature on the equilibrium metal uptake was significant. The effect of changes in the temperature on the lead uptake is shown in Fig.6. When temperature was lower than 303 K, Lead uptake increased with increasing temperature, but when temperature was over 303 K, the results were on the contrary. This response suggested a different interaction between the ligands on the cell wall and the metal. Below 303 K, chemical biosorption mechanisms played a dominant role in the whole biosorption process, biosorption was expected to increase by increase in the temperature [15] while at higher temperature, the plant powder was in a nonliving state, and physical biosorption became the main process. Physical biosorption reactions were normally exothermic, thus the extent of biosorption generally is constant with further increasing temperature.
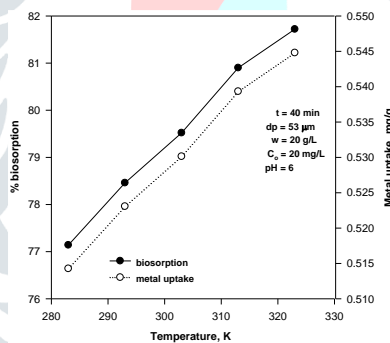

Fig. 6 Dependence of % biosorption of lead on biosorbent temperature

Langmuir isotherm:

Irving Langmuir [16] developed an isotherm named Langmuir isotherm. It is the most widely used simple two-parameter equation. This simple isotherm is based on following assumptions:
Biosorbates are chemically biosorbed at a fixed number of well- defined sites
Each site can hold only one biosorbate species
All sites are energetically equivalent
There are no interaction between the biosorbate species
The Langmuir relationship is hyperbolic and the equation is:

$q_e/q_m = bC_e /(1+bC_e)$ …….. (1)

Equation (5.1) can be rearranged as

$(C_e/q_e) = 1/(bq_m) + C_e/q_m$

From the plots between (C_e/q_e) and C_e, the slope $\{1/(bq_m)\}$ and the intercept $(1/b)$ are calculated. Further analysis of Langmuir equation is made on the basis of separation factor, (R_L) defined as $R_L = 1/(1+bC_e)$

$0< R_L <1$	indicates	favorable adsorption
$R_L >1$	indicates	unfavorable adsorption
$R_L = 1$	indicates	linear adsorption
$R_L = 0$	indicates	irrepressible adsorption

Langmuir isotherm is drawn for the present data and shown in Fig. 7.   The equation obtained 'n' $C_e/q_e = 0.05131 \, C_e + 3.92823$ with a good linearity (correlation coefficient, $R^2 \sim 0.99889$) indicating strong binding of lead ions to the surface of *Cassia siamea* pods powder.
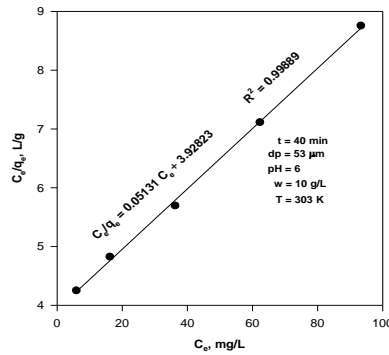
Fig. 7   Langmuir isotherm for biosorption of lead

Freundlich isotherm**:**

Freundlich [17] presented an empirical biosorption isotherm equation, which can be applied in case of low and intermediate concentration ranges. It is easier to handle mathematically in more complex calculations.

The Freundlich isotherm is given by

$$q_e = K_f C_e^n$$

where K_f (mg) represents the biosorption capacity when metal equilibrium concentration and n represents the degree of dependence of biosorption with equilibrium concentration Taking logarithms on both sides, we get

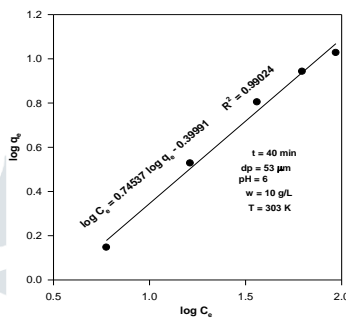$$\log q_e = \log K_f + n \log C_e$$

Fig. 8   Freundlich isotherm for biosorption of lead

Freundlich isotherm is drawn between $\log q_e = 0.74537 \log C_e + 0.39991$; $\log C_e$ and $\log q_e$ in Fig. 8 for the present data. The resulting equation has a correlation coefficient of 0.99024.

The 'n' value in the above equations satisfies the condition of $0 < n < 1$ indicating favorable biosorption.

Temkin isotherm**:**

Temkin and Pyzhev [**18**] isotherm equation describes the behavior of many biosorption systems on the heterogeneous surface and it is based on the following equation

$$q_e = RT \ln(A_T C_e)/b_T$$

The linear form of Temkin isotherm can be expressed as

$$q_e = (RT/b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$$

where $A_T = \exp[b(0) \times b(1)/RT]$

         $b(1) = RT/b_T$ is the slope

    $b(0) = (RT/b_T) \ln(A_T)$ is the intercept and

         $b = RT/b(1)$

The present data are analysed according to the linear form of Temkin isotherm and the linear plot is shown in fig. 9. The equation obtained for chromium biosorption is:

q_e = 1.61849 ln C_e + 0.28591 with a correlation coefficient 0.97529. The best fit model is determined based on the linear regression correlation coefficient (R^2). From the Figs 7, 8 & 9 it is found that biosorption data are well represented by Langmuir isotherm with higher correlation coefficient of 0.99889, followed by Freundlich and Temkin isotherms with correlation coefficients of 0.99024 and 0.97519 respectively.
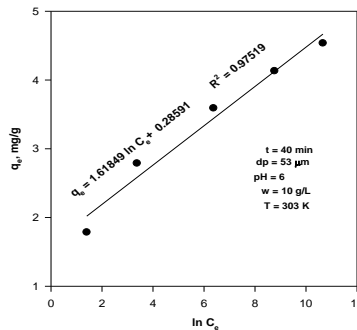

Fig. 9 Temkin isotherm for biosorption of lead

Table – 3

Isotherms constants

Langmuir	Freundlich	Temkin
q_m = 19.4893	K_f = 2.51136	A_T = 1.1932
K_L = 0.01306	n = 0.74537	b_T = 1556.476
R^2 =0.99889	R^2 =0.99024	R^2 =0.97519

Kinetics of biosorption

The order of biosorbate – biosorbent interactions have been described using kinetic model. Traditionally, the first order model of Lagergren [19] finds wide application. In the case of biosorption preceded by diffusion through a boundary, the kinetics in most cases follows the first order rate equation of Lagrangen:

$(dq_t/dt) = K_{ad} (q_e - q_t)$

where q_e and q_t are the amounts adsorbed at t, min and equilibrium time and K_{ad} is the rate constant of the pseudo first order biosorption.

The above equation can be presented as $\int (dq_t/(q_e - q_t)) = \int K_{ad} \ dt$

Applying the initial condition $q_t = 0$ at t = 0, we get

log ($q_e - q_t$) = log q_e – (K_{ad}/2.303) t

log ($q_e - q_t$) = – 0.47433 – 0.29122 t R^2 = 0.9679

Plot of log ($q_e - q_t$) versus 't' gives a straight line for first order kinetics, facilitating the computation of adsorption rate constant (K_{ad}). If the experimental results do not follow the above equation, they differ in two important aspects:

i) $K_{ad} (q_e - q_t)$ does not represent the number of available biosorption sites and

ii)log q_e is not equal to the intercept.

In such cases, pseudo second order kinetic equation: $(dq_t/dt) = K (q_e - q_t)^2$ is applicable, where

'K' is the second order rate constant.

The other form of the above equation is: $(dq_t/(q_e–q_t)^2) = Kdt$

let $q_e - q_t$ = x ; dq_t = dx ; 1/ x = K x + C ; C = 1/ q_e at t = 0 and x = q_e

Substituting these values in above equation, we obtain:

1/($q_e - q_t$) = Kt + (1/q_e)

Rearranging the terms, we get the linear form as:

$(t/q_t) = (1/ Kq_e^2) + (1/q_e) t.$

$(t/q_t) = 0.68976\, t + 0.62144.$ $R^2 = 0.9999$

The pseudo second order model [20] based on above equation, considers the rate -limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the biosorbate and biosorbent. If the pseudo second order kinetics is applicable, the plot of (t/q_t) versus 't' gives a linear relationship that allows computation of q_e and K.

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 20 mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagragen plots of log (q_e-q_t) versus agitation time (t) for biosorption of lead the biosorbent size (53 μm) of *cassia siamea* pods powder in the interaction time intervals of 1 to 40 min are drawn in figs. 10 & 11.
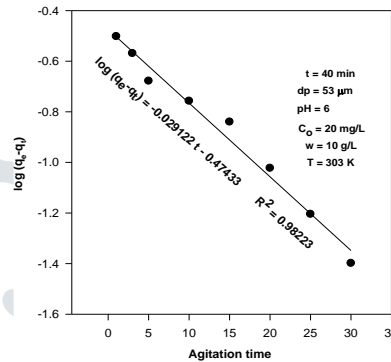

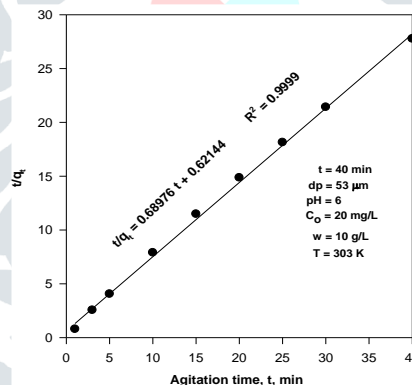Fig.10 First order kinetics for biosorption of lead

Fig. 11 Second order kinetics for biosorption of lead

Table–4 Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	log (q_e-q_t) = -0.02912 t - 0.47433	0.06706 min^{-1}	0.9822
Pseudo second order	t/q_t = 0.68976 t + 0.62144	0.7656 g/(mg-min)	0.9999

Thermodynamics of biosorption:

Biosorption is temperature dependant.   In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of biosorption (ΔH), change in entropy of biosorption (ΔS) and change in Gibbs free energy (ΔG) [21].

 Enthalpy is the most commonly used thermodynamic function due to its practical significance. The negative value of ΔH will indicate the exothermic/endothermic nature of biosorption and the physical/chemical in nature of sorption.   It can be easily reversed by supplying the heat equal to calculated ΔH.

The ΔH is related to ΔG and ΔS as $\Delta G = \Delta H - T \Delta S$

$\Delta S < 1$ indicates that biosorption is impossible whereas $\Delta S > 1$ indicates that the biosorption is possible. $\Delta G < 1$ indicates the feasibility of sorption.

The Vant Hoff's equation is

$\log (q_e / C_e) = \Delta H/(2.303\ RT) + (\Delta S/2.303\ R)$

$\log (q_e / C_e) = -3.51874\ (1/T) + 0.19022$

Where (q_e/C_e) is called the biosorption affinity.

If the value of ΔS is less than zero, it indicates that the process is highly reversible. If ΔS is more than or equal to zero, it indicates the irreversibility of process. The negative value for ΔG indicates the sorption's spontaneity. Whereas the positive value indicates is non spontaneity of sorption.

Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of $\Delta G°$ indicated the spontaneity of the process. The positive values of $\Delta H°$ and $\Delta S°$ showed the endothermic nature and irreversibility of Cu(II) and Pb(II) biosorption, respectively.

Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. the plots indicating the effect of temperature on biosorption of lead for different initial metal concentrations are shown in Fig.12. The Vant Hoff's plots for the biosorption data obtained at various initial concentrations of the lead are shown in Fig.12
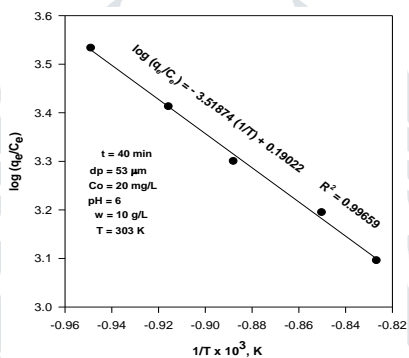

Fig. 12   Vant Hoff's plot for biosorption

Optimization using Response Surface Methodology (RSM):
Optimization of biosorption conditions using CCD
The effects of four independent variables (biosorbent dosage, initial concentration of lead in aqueous solution, pH and temperature) on lead biosorption are analyzed using Central Composite Design (CCD). The optimum conditions for the four independent variables on the extent of lead biosorption are formed within the quadratic model. Levels of different process variables for percentage biosorption are shown in table –5.

Table–5

Levels of different process variables in coded and un-coded form for

% biosorption of lead using *cassia siamea* pods powder

Variable	Name	Range and levels				
		-2	-1	0	1	2
X_1	Biosorbent dosage, w, g/L	25	30	35	40	45
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30
X_3	pH of aqueous solution	4	5	6	7	8
X_4	Temperature, T, K	283	293	303	313	323

Regression equation for the optimization of biosorption is:

% biosorption of lead (Y) is function of dosage (X_1), initial concentration (X_2), pH of aqueous solution (X_3), and Temperature of aqueous solution (X_4).

The multiple regression analysis of the experimental data has yield the following equation:

$$Y = -782.155 + 3.215 X_1 + 0.0245 X_2 + 8.481 X_3 + 5.13 X_4 - 0.02 X_1^2 - 0.031 X_2^2 - 1.008 X_3^2 - 0.008 X_4^2 - 0.003 X_1X_2 - 0.001 X_1X_3 - 0.006 X_1X_4 + 0.028 X_2X_3 + 0.003 X_2X_4 + 0.009 X_3X_4$$

----- (2)

Table-6 represents the results obtained in CCD. The response obtained in the form of analysis of variance (ANOVA) from regression eq.2 is put together in table–6. Fischer's 'F-statistics' value is defined as MS_{model}/MS_{error}, where MS is mean square. Fischer's 'F-statistics' value, having a low probability 'p' value, indicates high significance.

Table–6

Results from CCD for lead biosorption by *cassia siamea* pods powder

Run No.	X_1, w	X_2, C_o	X_3, pH	X_4, T	% biosorption of lead	
					Experimental	Predicted
1	-1 (30)	-1 (15)	-1 (5)	-1 (293)	80.65	80.48
2	-1 (30)	-1 (15)	-1 (5)	1 (313)	80.94	81.39
3	-1 (30)	-1 (15)	1 (7)	-1 (293)	79.24	79.03
4	-1 (30)	-1 (15)	1 (7)	1 (313)	80.45	80.28
5	-1 (30)	1 (25)	-1 (5)	-1 (293)	79.01	79.17
6	-1 (30)	1 (25)	-1 (5)	1 (313)	80.50	80.63
7	-1 (30)	1 (25)	1 (7)	-1 (293)	78.34	78.28
8	-1 (30)	1 (25)	1 (7)	1 (313)	80.10	80.08
9	1 (40)	-1 (15)	-1 (5)	-1 (293)	81.60	81.82
10	1 (40)	-1 (15)	-1 (5)	1 (313)	81.81	81.63
11	1 (40)	-1 (15)	1 (7)	-1 (293)	80.71	80.35
12	1 (40)	-1 (15)	1 (7)	1 (313)	80.45	80.51
13	1 (40)	1 (25)	-1 (5)	-1 (293)	80.32	80.25
14	1 (40)	1 (25)	-1 (5)	1 (313)	80.19	80.61
15	1 (40)	1 (25)	1 (7)	-1 (293)	79.60	79.35
16	1 (40)	1 (25)	1 (7)	1 (313)	80.11	80.05
17	-2 (25)	0 (20)	0 (6)	0 (303)	80.76	80.68
18	2 (45)	0 (20)	0 (6)	0 (303)	81.90	81.99
19	0 (35)	-2 (10)	0 (6)	0 (303)	80.99	81.14
20	0 (35)	2 (30)	0 (6)	0 (303)	79.52	79.37
21	0 (35)	0 (20)	-2 (4)	0 (303)	80.84	80.34
22	0 (35)	0 (20)	2 (8)	0 (303)	77.81	78.32
23	0 (35)	0 (20)	0 (6)	-2 (283)	78.91	79.25
24	0 (35)	0 (20)	0 (6)	2 (323)	81.20	80.86
25	0 (35)	0 (20)	0 (6)	0 (303)	82.43	83.36
26	0 (35)	0 (20)	0 (6)	0 (303)	83.55	83.36
27	0 (35)	0 (20)	0 (6)	0 (303)	83.55	83.36
28	0 (35)	0 (20)	0 (6)	0 (303)	83.55	83.36
29	0 (35)	0 (20)	0 (6)	0 (303)	83.55	83.36
30	0 (35)	0 (20)	0 (6)	0 (303)	83.55	83.36

Experimental conditions [Coded Values] and observed response values of central composite design with 24 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 40 min and biosorbent size at 53 μm

Table–7

ANOVA of lead biosorption for entire quadratic model

Source of variation	SS	df	Mean square(MS)	F-value	$P > F$
Model	69.96029	14	4.99716	28.169	0.00000
Error	2.66098	15	0.1773986		
Total	72.62127	29			

Table-8

Estimated regression coefficients for the lead biosorption onto *cassia siamea* pods powder

	Regressn	Std.Err.	t(15)	P
Mean/Interc.	-782.855	81.91128	-9.5574	0.000000
(1)Dosage, W, g/L(L)	3.215	0.69371	4.6346	0.000324
Dosage, W, g/L(Q)	-0.020	0.00322	-6.3001	0.000014
(2)Concentration, Co, mg/L(L)	0.245	0.67950	0.3602	0.723735[a]
Concentration, Co, mg/L(Q)	-0.031	0.00322	-9.6419	0.000000
(3)pH (L)	8.481	3.44074	2.4649	0.026259
pH (Q)	-1.008	0.08042	-12.5329	0.000000
(4)Temperature, T, K(L)	5.130	0.49879	10.2853	0.000000
Temperature, T, K(Q)	-0.008	0.00080	-10.2636	0.000000
1L by 2L	-0.003	0.00421	-0.6054	0.553943[a]
1L by 3L	-0.001	0.02106	-0.0475	0.962753[a]
1L by 4L	-0.006	0.00211	-2.6235	0.019178
2L by 3L	0.028	0.02106	1.3533	0.195999[a]
2L by 4L	0.003	0.00211	1.2940	0.215248[a]
3L by 4L	0.009	0.01053	0.8072	0.432142[a]

[a]insignificant ($P \geq 0.05$)

The ANOVA of the regression model is sufficiently great, as proven from the Fisher's F-test (F_{model} = 28.169) and has a very low probability value ($P_{model} > F$=0.000000). Besides, the computed F-value [$F_{0.05\ (14.15)}$ = MS$_{model}$/MS$_{error}$ = 28.169] is much higher compared to F-value ($F_{0.05\ (14.15)\ tabulars}$ = 2.42) at 5% level, suggesting that the treatment differences are sufficiently great. Student's t-test can implicate regression coefficient of the parameter, while pattern of interactions amidst all the factors can be entailed by 'p' values. It is noted from table-8 that more significant corresponding coefficient term can be possessed by having high 't' value and low 'P' value. By analyzing 't' and 'p' values from table-8 X_1, X_3, X_4, X_1^2, X_2^2, X_3^2, X_4^2 and X_1X_4 have high importance to explain the individual and interaction effects of independent variables on biosorption of lead to anticipate the response. Rest of the terms (X_2, X_1X_2, X_1X_3, X_2X_3, X_2X_4 and X_3X_4) are undistinguished in eq. 2 and are not needed to explain biosorption. The model is reduced to the following form by excluding undistinguished terms in eq.2.

$$Y = -782.155 + 3.215\ X_1 + 8.481\ X_3 + 5.13\ X_4 - 0.02\ X_1^2 - 0.031\ X_2^2 - 1.008\ X_3^2 - 0.008\ X_4^2 - 0.006\ X_1X_4$$

------- (3)

A positive sign of the coefficient represents an interactive effect i.e., response (% biosorption of lead) steps up with increase in effect, whereas a negative sign implies an incompatible effect that means response lowers with an increase in effect.
Measure of the model's variability to the responses indicated is presented by correlation coefficient (R^2). As $R^2 \longrightarrow 1$, model is inviolable and the response is estimated better. In our study, R^2 = 0.96336 suggests that 3.664 % of the total variations are not adequately explained by the model. Statistical relevance of the ratio of mean due to regression and mean square due to residual error is tested with the help of ANOVA. F-values implicate that % biosorption can be sufficiently explained by the model equation. If 'P' value is lower than 0.05, the model is considered to be statistically significant at the 95 % confidence level. All square terms of all variables (P < 0.05) are in good agreement (table 8) in comparison to the linear and interaction terms X_2 = 0.245, X_1X_2 = –0.003, X_1X_3 = –0.001, X_2X_3 = 0.028, X_2X_4 = 0.003 and X_3X_4 = 0.009.
Interpretation of residual graphs:

Normal probability plot (NPP) is a graphical technique used for analyzing whether or not a data set is normally distributed to greater extent. The difference between the observed and predicted values from the regression is termed as residual. Fig. 13 exhibits normal probability plot for the present data. It is evident that the experimental data are reasonably aligned implying normal distribution.
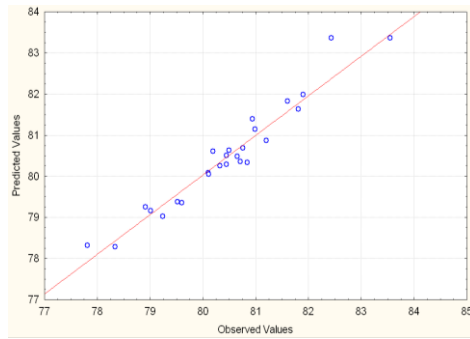
Fig. 13   Normal probability plot for % biosorption of lead

Pareto Chart

The pareto chart can be explained in such a way that P > 0.05 are significant and is presented in Fig. 14. The red line in the x-axis is P = 0.05. All the linear, quadratic and interaction terms are significant except X_2, X_2X_3, X_2X_4, X_3X_4, X_1X_2 and X_1X_3 as their p-value is less than 0.05.
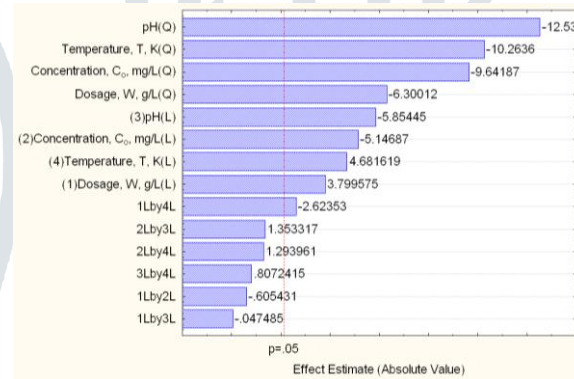

Fig. 14 Pareto Chart

Interaction effects of biosorption variables:

Three-dimensional view of response surface contour plots [Fig. 15 (a) to 15 (f)] exhibit % biosorption of the lead using *cassia siamea* pods powder for different combinations of dependent variables. All the plots are delineated as a function of two factors at a time, imposing other factors fixed at zero level. It is evident from response surface contour plots that the % biosorption is minimal at low and high levels of the variables. This behavior conforms that there is a presence of optimum for the input variables in order to maximize %

biosorption. The role played by all the variables is so vital in % biosorption of lead and seen clearly from the plots. The predicted optimal set of conditions for maximum % biosorption of lead is:

Biosorbent dosage	=	36.5051 g/L
Initial lead ion concentration	=	18.4572 mg/L
pH of aqueous solution = 5.7343		
Temperature	=	304.5429 K
% biosorption of lead	=	83.5787

The experimental optimum values are compared with those predicted by CCD in table-9. The experimental values are in close agreement with those from and CCD.

Table-9

Comparison between optimum values from CCD and experimentation

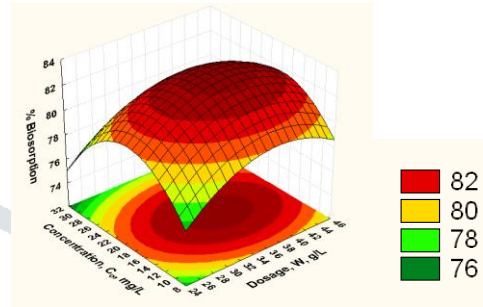| Variable	CCD	Experimental
Biosorbent dosage, w, g/L	36.5051	35
Initial lead concentration, C_o, mg/L	18.4572	20
pH of aqueous solution	5.7343	6
Temperature, K	304.5429	303
% biosorption	83.5787	79.52

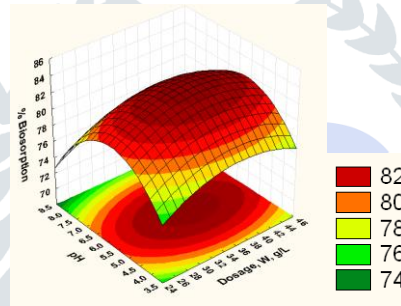Fig. 15 (a)　Surface contour plot for the effects of dosage and initial concentration of lead on % biosorption

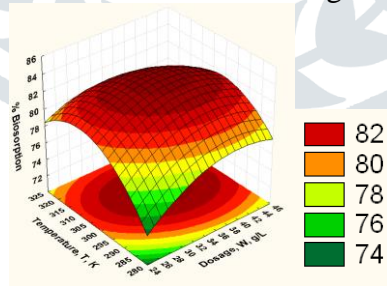Fig. 15 (b)　Surface contour plot for the effects of dosage and pH on % biosorption of lead

Fig. 15 (c)　Surface contour plot for the effects of dosage and Temperature on % biosorption of lead
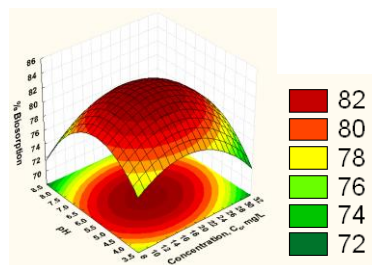

Fig. 15 (d)　Surface contour plot for the effects of initial concentration and pH on % biosorption of lead
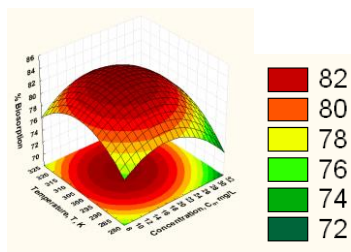
Fig. 15 (e)   Surface contour plot for the effects of initial concentration and Temperature on % biosorption of lead
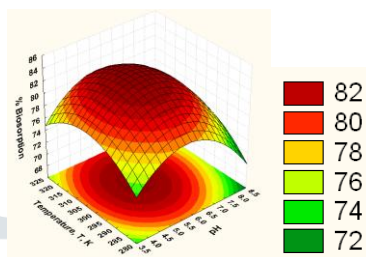

Fig. 15 (f)   Surface contour plot for the effects of pH and Temperature on % biosorption of lead

NOMENCLATURE

C_o	Initial concentration of lead in aqueous solution, mg/L
C_t	Concentration of lead in aqueous solution after 't' min, mg/L
C_e	Equilibrium adsorption concentration of lead, mg/L
t	Agitation time, min
T	Absolute temperature, K
w	Adsorbent dosage, g
b	Langmuir equilibrium constant
n	Freundlich constant for lead in the aqueous solution
d_p	Adsorbent size, μm
V	Volume of aqueous solution, mL
W	Amount of adsorbent taken per 1L of aqueous solution, gm /L
q_e	Mass of solute adsorbed per mass of adsorbent at equilibrium, mg/g
q_t	Mass of solute adsorbed per mass of adsorbent at 't' mins, mg/g
q_m	Langmuir monolayer capacity, mg/g
k	Second order rate constant, g/mg-min
k_f	Freundlich coefficient for lead in aqueous solution, L/g
k_{ad}	First order rate constant, min^{-1}
R_L	Separation factor

CONCLUSIONS

This study reports the biosorption performance of *Cassia siamea* pods powder as biosorbent for removal of lead ions from aqueous solutions. The experimental and theoretical data results are as follows:

1. The equilibrium agitation time for lead biosorption is 40 minutes.
2. Percentage biosorption of lead from the aqueous solution increases significantly with an increase in pH from 2 (51.72 %) to 6 (70.18 %).
3. The optimum dosage for biosorption is 35 g/L.
4. And through optimization method the maximum biosorption of lead (83.5787 %) onto *cassia siamea* pods powder is observed when the processing parameters are set as: pH = 5.7343, w = 36.5051 g/L, C_o = 18.4572 mg/L and T = 304.5429 K using CCD.
5. It is found that biosorption data are well represented by Langmuir isotherm model (R^2=0.99889), followed by Freundlich isotherm (R^2=0.99024) and Temkin isotherm (R^2=0.9751).
6. The pseudo-second-order equation appeared to be the best-fit model over the lagergren first order equation.

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