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Biosorption performance of *Albezia lebbeck* pods powder for the removal of lead: Application of statistical method

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ABSTRACT

The impact of industries on ground water resources is immense and only through good pollution prevention practices the contamination and deterioration of ground water sources will decrease. Biosorption a promising method for removal of metal ions from aqueous solution is under taken for the present experimentation. This paper determines the thermodynamics, isotherms and kinetic studies on biosorption of lead ions from an aqueous solution onto low cost biosorbent from waste plant namely *Albizia lebbeck* pods powder. The biosorption was carried out in a batch process varying six parameters. Results have shown that the biosorption of lead increases with an increase in biosorbent dosage and decreases with increase in biosorbent size. A significant increase in percentage removal of lead is observed as pH is increased from 1 to 6 and the percentage removal is maximum at ph = 6. Freundlich, Temkin and Langmuir models are applied to describe the equilibrium isotherms. The kinetic study showed that biosorption of lead followed pseudo second order kinetics. Various thermodynamic parameters such as change in enthalpy, entropy and gibb's free energy are also determined. The Box-Behnken Design (BBD) was used for optimization using Response Surface methodology. The ANOVA of the regression model demonstrated that the model is highly significant which is evident from Fisher test.

***Keywords*: Biosorption, optimization, Albizia lebbeck pods powder, Box-Behnken Design, Isotherms, Kinetics**

1. INTRODUCTION

Water resources are of critical importance to both natural ecosystem and human development but enhanced industrial activity after the industrial revolution has led to the discharge of chemicals, which caused environmental and public health problems. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations **[1, 2]**. The studies made on investigation of economic and effective methods for the removal of heavy metals have resulted in the development of new separation technologies. Biological treatment, ion exchange, coagulation, electrochemical operation and filtration are commonly applied to the treatment of industrial effluents **[3, 4]**. Recent research on biosorption has shown that biomaterials containing acidic groups such as hydroxyls and carboxyls were effective in binding metal cations **[6]**. Other biomaterials containing weak basic groups such as amides and amines are efficient for adsorbing metal anions **[7]**.There are three major factors affecting metal biosorption behavior **[8]**. Recently efforts are being made to harness this phenomenon into a technique for the detoxification of metal bearing industrial effluents by removing or eventually also recovering the metals **[9]**. Biosorption removal of toxic heavy metals is especially suited as a 'polishing' waste water treatment step because it can produce close to drinking water quality from initial metal concentrations of 1-100 mg/L to final concentrations < 0.01-0.1 mg/L **[10,11]**. Alternatively due to its low cost even the unprocessed, once through used up metal laden biosorbent can be disposed of by either incineration or it could be landfilled, having a rather small volume when compared to the wastewater – the biosorption process serves to reduce the overall waste volume **[12-21]**. . A multitude of biomass types comprising fungal biomass, bacterial biomass, algae, peat etc., have been studied for their biosorption of metals **[16, 18, 19, 20]**. Agricultural wastes such as tree bark, peanut skin, hull, tobacco, tomato root tissues and plants waste have been used to remove heavy metals from water **[22-24]**.

2. EXPERIMENTAL PROCEDURE

2.1 Biosorbent

Albezia lebbeck pods were obtained from A.U. Engg college premises in Visakhapatnam. The A.L. pods was washed thrice with tap water and once with distilled water in order to remove adhering mud, impurities etc. It was dried in sunlight for one week until all the moisture was evaporated. The crispy A.L. pods were then crushed and grinded to powder, separated using British Standard Sieves (BSS) and stored in dry vacuum packs to prevent moisture content and readily used as biosorbent.

2.2 Batch Sorption studies

Preliminary experiments were conducted in 250 ml Erlenmayer flasks containing 50 ml of 20 mg/L metal solution using single step optimization procedure. The flasks were agitated on an orbital shaker at 180 rpm and samples were taken at predetermined time intervals (1, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 & 180 min) & centrifuged at 14000 rpm and the supernatant liquid was analysed in Atomic Absorption Spectrophotometer (AAS) for final concentrations. Similarly the other variables were varied in a wide range: Biosorbent Size (53, 75, 104, 125 & 152 µm), pH of the aqueous solution (2, 3, 4, 5, 6, 7 and 8), Initial concentration of lead solution (25, 40, 80, 120 & 160 mg/L), Biosorbent Dosage (10, 20, 30, 40, & 50 g/L) and Temperature (283, 293, 303, 313 & 323 K).

2.3 Process Optimization

Final experimental runs for optimization were obtained through Response Surface Methodology from Design of Experiments (DoE) using STATISTICA software. The extent of biosorption of lead calculated at the preliminary optimum conditions is verified with the final runs for the optimum conditions.

3. RESULTS AND DISCUSSION

In the present investigation, the potential of dry *Albizia Lebbeck* pods powder as a biosorbent for removal of lead present in an aqueous solution is investigated. The effects of various parameters are:

3.1 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, 64.45 % of lead is biosorbed in the first 5 min. The % biosorption is increased briskly up to 50 min reaching 78.3 %. Beyond 50 min, the % biosorption is constant indicating the attainment of equilibrium conditions. The maximum biosorption of 78.3 % is attained for 50 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) **[25,26]**.

3.2 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. The percentage biosorption is increased from 72.36% to 78.34 % as the biosorbent size decreases from 152 to 53 µm. This phenomenon is expected, as the size of the particle decreases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases.

3.3 Effect of pH

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 is increased from 55.22 % to 76.16% as pH is increased from 2 to 6 and decreased beyond the pH value of 6 **[27]**. % biosorption is decreased from pH 7 to 8 reaching 68.18 % from 74.38 %. 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 **[28, 29]**.

3.4 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 76.14 % to 61.32 % with an increase **[30]** in C_0 from 20 mg/L to 160 mg/L. Such behavior can be attributed to the increase in the amount of concentration of the aqueous solution to the unchanging number of available active sites on the biosorbent.

3.5 Effect of biosorbent dosage

The biosorption of lead increased from 76.14 % to 82.98 % with an increase in biosorbent dosage from 10 to 40 g/L is shown in fig. 5. 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 marginal from 82.98 % to 83.68 % when 'w' is increased from 40 to 60 g/L. Hence all other experiments are conducted at 40 g/L dosage.

3.6 Effect of Temperature

When temperature was lower than 303 K, lead uptake increased with increasing temperature, but when temperature was over 303 K, the lead uptake increased very marginally (fig. 6). 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 **[31]** while at higher temperature, the plant powder were 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.

3.7 Isotherms

3.7.1 Langmuir Isotherm

Irving Langmuir **[32, 33]** developed an isotherm named Langmuir isotherm. It is the most widely used simple two-parameter equation. Langmuir isotherm is drawn for the present data and shown in fig. 7. The equation obtained is $C_e/q_e = 0.0565\ C_e + 2.871$ with a good linearity (correlation coefficient, R^2~0.9976) indicating strong binding of lead ions to the surface of *Albizia Lebbeck* pods powder.

3.7.2 Freundlich Isotherm

Freundlich **[34]** presented an empirical biosorption isotherm equation that can be applied in case of low and intermediate concentration ranges. 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 It is easier to handle mathematically in more complex calculations. Freundlich isotherm is drawn between log C_e and log q_e in fig. 8 for the present data. The resulting equation log q_e = 0.7246log C_e - 0.2798; has a correlation coefficient of 0.9924.

3.7.3 Temkin Isotherm

Temkin and Pyzhev **[35]** 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 equation obtained for lead biosorption is: $q_e = 3.2144 \ln C_e - 4.0314$ with a correlation coefficient 0.9758. 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 0.9976, followed by Freundlich and Temkin isotherms with correlation coefficients of 0.9924 and 0.9758 respectively.

3.8 Kinetics of biosorption

The order of biosorbate – biosorbent interactions have been described using kinetic model. Traditionally, the first order model of Lagergren **[36]** 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 first order biosorption.

$\log (q_e - q_t) = -0.3828 - 0.0279t$

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: $K_{ad} (q_e - q_t)$ does not represent the number of available biosorption sites and log q_e is not equal to the intercept. In such cases, pseudo second order kinetic equation **[37]**:

$(dq_t/dt) = K (q_e - q_t)^2$ is applicable,

where 'K' is the second order rate constant.

Rearranging the terms, we get the linear form as:

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

$(t/q_t) = 0.6431\, t + 0.7029.$

The pseudo second order model **[38]** 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 *Albizia Lebbeck* pods powder in the interaction time intervals of 1 to 180 min are drawn in figs. 10 & 11.

3.9 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).
The ΔH is related to ΔG and ΔS as $\Delta G = \Delta H - T\,\Delta S$

The Vant Hoff's equation is

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

$\log (q_e / C_e) = -0.4783\, (1 / T) + 0.77525$

Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. The Vant Hoff's plot for the biosorption data obtained is shown in fig. 12. The corresponding values are ΔG = -4488.519382, ΔH = 9.158078 and ΔS = 14.84382.

3.10 Optimization using Box Behnken Design (BBD)

The experiments conducted with different pH values ranging from 5–7, different biosorption dosages of 30–50 g/L and different lead concentrations of 10–30 mg/L and varied simultaneously to cover the combination of parameters in BBD. The levels and ranges of the chosen independent parameters are given in Table-5.1. Table-5.2 is employed for the optimization of the parameters. The regression equation for the optimization of the biosorption of lead: % biosorption of lead (Y) is function of the biosorption dosage, w (X_1), initial lead concentration, C_0 (X_2) and pH (X_3). Multiple regression analysis of the experimental data has resulted in the following equation for the biosorption of lead:

$$Y = 48.89 + 8.23 X_1 + 0.417 X_2 + 0.0755 X_3 - 0.675 X_1^2 - 0.00495 X_2^2 - 0.00175 X_3^2 \quad \text{-------------} (1)$$

The result of above regression model in the form of analysis of variance (ANOVA) for Eq. (1) is given in Table-5.3. In general, the Fischer's 'F-statistics' value ($F=MS_{model}/MS_{error}$), where MS (mean square) with a low probability 'P' value indicates high significance of the regression model.

The ANOVA of the regression model demonstrates that the model is highly significant, as is evident from the Fisher's F-test (F_{model} = 2188.8093) and a very low probability value ($P_{model} > F$=0.000000). More ever, the computed F-value ($F0.05\,(14.15) = MS_{model} / MS_{error}$ = 0.4924821/0.000225) is greater than the tabular F-value ($F_{0.05}$ (14.15) tabulars = 3.56) at the 5% level, indicating that the treatment differences are significant. From the Table-5.4, we can observe that, the larger the value of t and smaller the value of P, more significant is the corresponding coefficient term. By analyzing the ‘t’ values and ‘P’ values from Table-5.4, it is found that the X_1, X_2, X_3, X_1^2 , X_2^2, and X_3^2.have high significance to explain the individual and interaction effect of biosorption variables on the biosorption of lead to predict the response. The optimal set of conditions for maximum percentage biosorption of lead is pH = 6.09630, biosorption dosage (w) = 42.12121 g/L and initial lead concentration (C_o) = 21.57143 mg/L. The extent of biosorption of lead calculated at these optimum conditions is 83.57285 %. Fig. 13 shows the comparison between the % biosorption obtained through experiments, which are in good agreement with predicted values. In fig. 14 pareto chart depicts the variables which have significance at 95 % conf level. Fig. 15 (a, b, c) shows the response surface contour plots for different variables effects. The experimental optimum values are compared with those predicted by BBD in table-5 and are in close agreement.

4. FIGURES AND TABLES

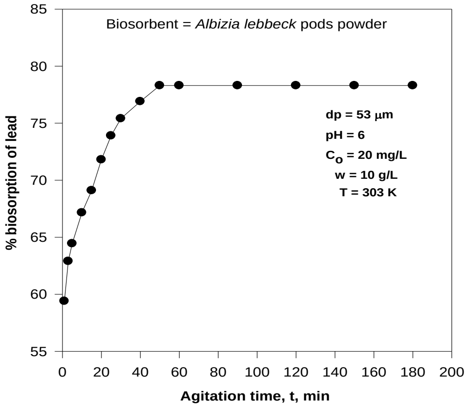

Fig. 1 Effect of agitation time on % biosorption of lead

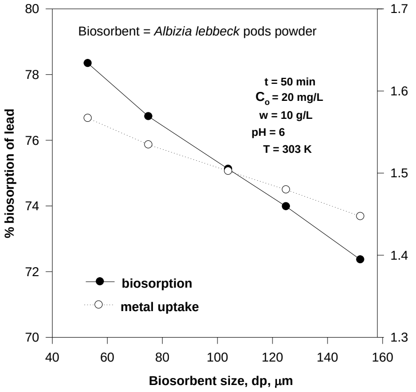

Fig. 2 % Biosorption of lead as a function of biosorbent size

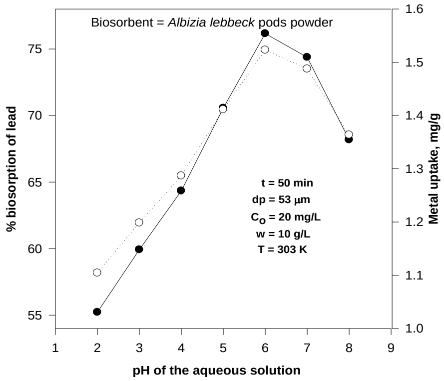

Fig. 3 Observation of pH along with % biosorption of lead

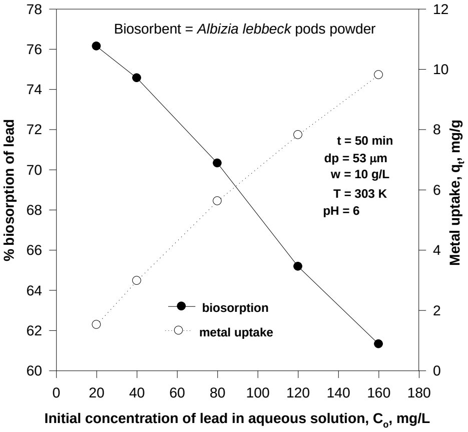

Fig. 4 Variation of initial concentration with % biosorption of lead

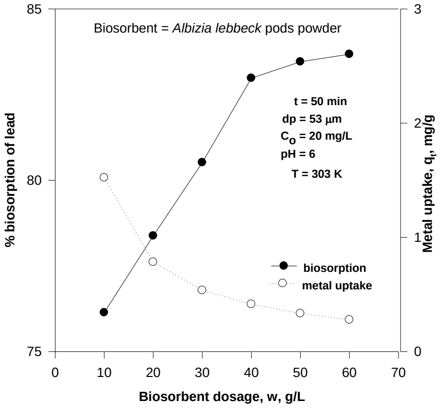

Fig. 5 Dependency of % biosorption of lead on biosorbent dosage

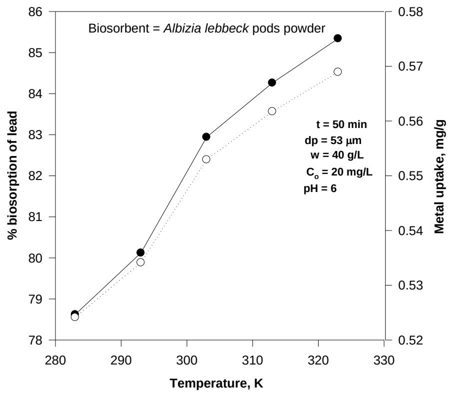

Fig. 6 Effect of temperature on % biosorption of lead

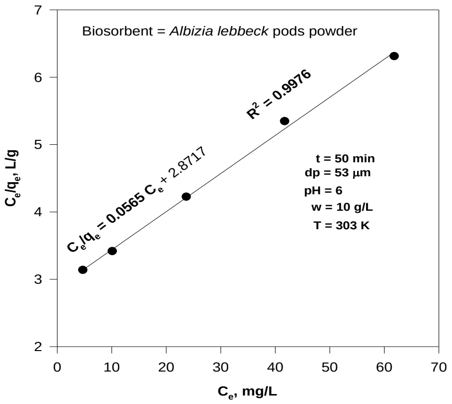

Fig. 7 Langmuir isotherm for % biosorption of lead

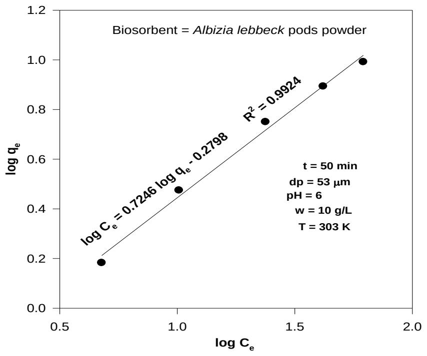

Fig. 8 Freundlich isotherm for % biosorption lead

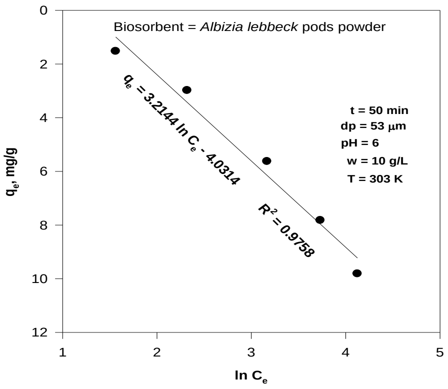

Fig. 9 Temkin isotherm for % biosorption of lead

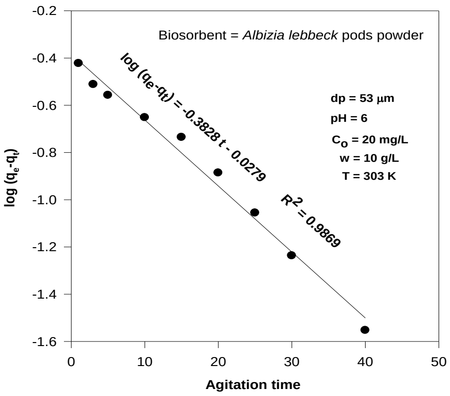

Fig. 10 First order kinetics for % biosorption of lead

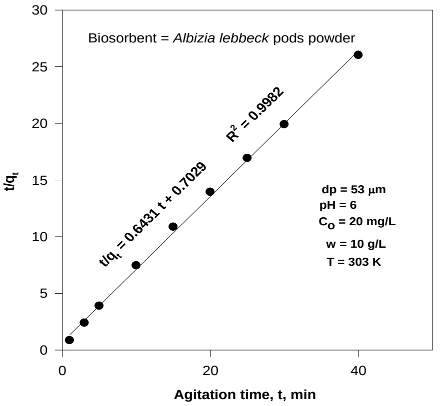

Fig. 11. Second order kinetics for % biosorption of lead

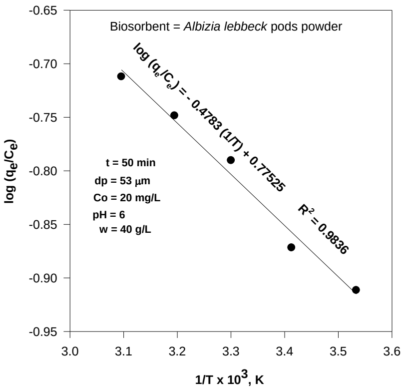

Fig. 12 Vantoff's plot for % biosorption of Lead

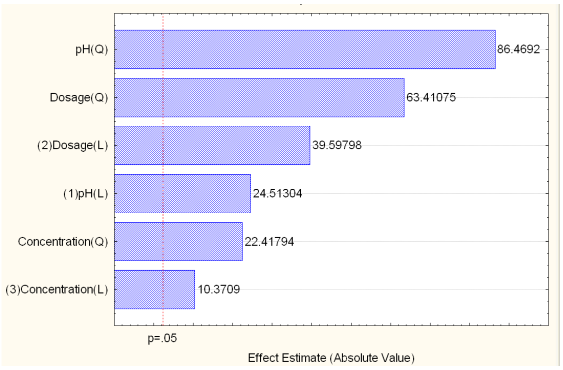

Fig. 13 Pareto Chart

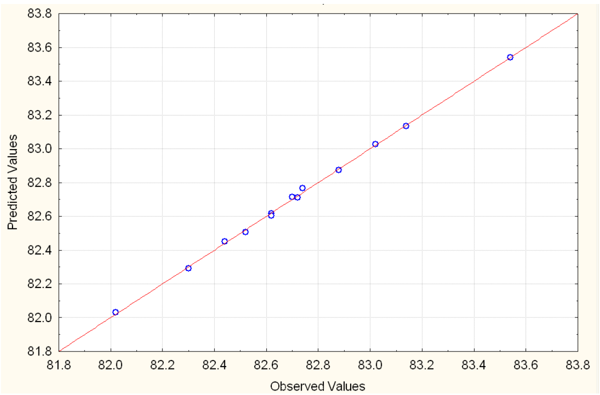

Fig. 14 Observed Vs Predicted Values

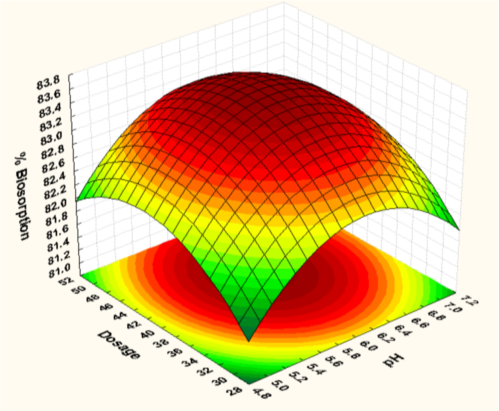

Fig. 5.15 (a) Surface contour plot for the effects of dosage and pH of lead on % biosorption

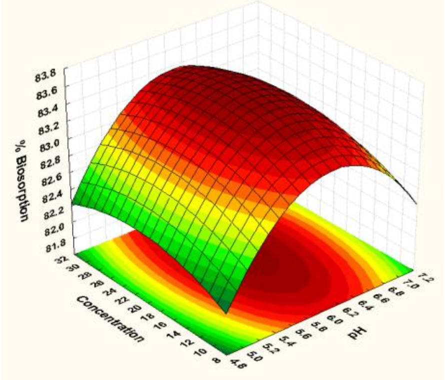

Fig. 5.15 (b) Surface contour plot for the effects of pH and initial concentration of lead on % biosorption

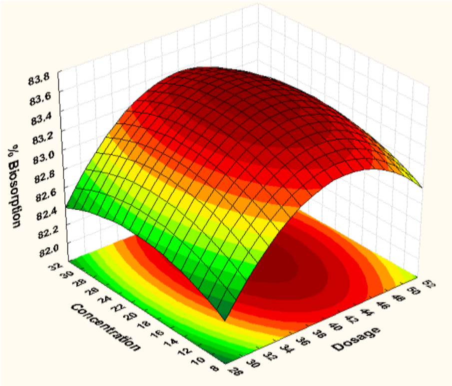

Fig. 5.15 (c) Surface contour plot for the effects of dosage and initial concentration of lead on % biosorption

Table–1 Levels of different process variables in coded and un-coded form for % biosorption of lead using *Albizia lebbeck* pods powder

Variables	Coded levels		
	-1	0	1
Biosorbent dosage, w, g/L	30	40	50
Initial concentration, Co, mg/L	10	20	30
pH of aqueous solution	5	6	7

Table–2 Results from BBD for biosorption of lead using *Albizia lebbeck* pods powder

Run No.	X_1	X_2	X_3	% biosorption of lead	
				Experimental	Predicted
1	-1	-1	0	82.02000	82.03000
2	1	-1	0	82.30000	82.29000
3	-1	1	0	82.44000	82.45000
4	1	1	0	82.72000	82.71000
5	-1	0	-1	82.52000	82.50500
6	1	0	-1	82.74000	82.76500
7	-1	0	1	82.62000	82.61500
8	1	0	1	82.88000	82.87500
9	0	-1	-1	82.62000	82.60500
10	0	1	-1	83.02000	83.02500
11	0	-1	1	82.70000	82.71500
12	0	1	1	83.14000	83.13500
13	0	0	0	83.54000	83.54000
14	0	0	0	83.54000	83.54000
15	0	0	0	83.54000	83.54000

Table–3 Analysis of variance (ANOVA) for the entire quadratic model

Source of variation	Sum of squares (SS)	d.f.	Mean squares (MS)	*F*-value	Probe >*F*
Model	2.954893	6	0.492482	2188	0.0000
Error	0.001800	8	0.000225		
Total	2.956693				

Table –4 Coefficients, *t*-statistics and significance probability of the model

Term	Reg Coeff	Standard error of coefficient	t-value	*P*-Value
Mean/Interc.	48.8900	0.31678	154.333	0.000000
(1)Dosage, w, g/L(L)	8.23000	0.09382	87.7165	0.000000
Dosage, w, g/L(Q)	-0.6750	0.00780	-86.469	0.000000
(2)Concentration, Co, mg/L(L)	0.41700	0.00626	66.5340	0.000000
Concentration, Co, mg/L(Q)	-0.0049	0.00007	-63.410	0.000000
(3)pH (L)	0.07550	0.00316	23.8380	0.000000
pH (Q)	-0.0017	0.00007	-22.417	0.000000

Table–5 Comparison between optimum values from experimentation and BBD

Variable	**Experimental**	**BBD**
Biosorbent dosage, w, g/L	40	42.12121
Initial lead concentration, mg/L	20	21.57143
pH of aqueous solution	6	6.09630
% biosorption	**82.94**	**83.57285**

5. CONCLUSION

The equilibrium, kinetic and thermodynamic studies are carried out for biosorption of lead experimentally and the analysis of the experimental data resulted in the following conclusions. The equilibrium agitation time for lead biosorption is 50 minutes. The percentage biosorption of lead decreased with the increase in biosorbent size from 53 µm (78.34 %) to 152 µm (72.36 %). Percentage biosorption of lead from the aqueous solution increased significantly with the increase in pH from 2 (55.22 %) to 6 (76.16 %). The optimum dosage for biosorption is 40 g/L. The maximum uptake capacity of 17.1526 mg/g is obtained at 303 K. The maximum biosorption of lead (83.57285 %) onto *Albizia Lebbeck* pods powder is observed when the processing parameters are set as pH = 6.0963, w = 42.12121 g/L and C_o = 21.57143 mg/L using BBD. This investigation also revealed the endothermic nature of biosorption as ΔH (9.158078) is positive, irreversible nature of biosorption as ΔS (14.84382) is positive and spontaneity of biosorption as indicated by negative ΔG ($\Delta G = -4488.519382$ J/mole). Hence the above said *albezia lebbeck* pods powder is effective and efficient biosorbent and is capable of removing lead.

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