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PROCESS OPTIMIZATION AND BIOSORPTION OF LEAD USING *ALBIZIA SAMAN* LEAF POWDER

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ABSTRACT
Water pollution is one of the signs that humans have exceeded the limits and causing health problems for living beings on earth. The present paper comprises the optimization and biosorption of lead from aqueous solution using *Albizia saman* leaf powder as biosorbent. Single Step Optimization was considered for preliminary runs with the variables agitation time, biosorbent size, pH of the solution, initial concentration of the aqueous solution, dosage of biosorbent and temperature. The Central Composite Design (CCD) was used for final runs optimization using Response Surface Methodology (RSM). Results indicated that the optimum agitation time for biosorption of lead is 50 min. The increase in mass of biosorbent lead to increase in lead (pb) ion biosorption due to the increase in the number of active biosorption sites. Maximum percentage biosorption is observed at a pH of 6 and with particle size of 53 µm. Experimental data were better described by pseudo-second-order model. The adsorption isotherm could be well fitted by the Langmuir equation followed by Freundlich and Temkin. Over and all, *Albizia Saman* leaf powder can be used as an effective natural biosorbent for the economic treatment of aqueous solutions containing lead.

Keywords **-** Albizia Saman, biosorption, optimization, isotherms, kinetics

1. INTRODUCTION
Because of its relative recent development in the planet's history, pollution is a human problem. Before the 19th century Industrial Revolution, people lived more in harmony with their immediate environment. If one or more substances have built up in resources like water, air etc., to such an extent that they cause problems for living beings, we treat it as polluted one. As industrialization has spread around the globe, the problem of pollution spread along with it. Intensive mining operations and processing of minerals to meet the increasing needs of our society have led to environmental pollution in specific locations all over the world [1]. Heavy metals are discharged from various industries such as electroplating, plastic manufacturing, textile, storage batteries, mining and metallurgical process [2]. Water pollution of toxic heavy metal ions discharged from the industries and inhabited areas is seriously harmful to the health of human beings and the eco-system. Among these heavy metals, lead may be the severe pollutant sources due to its wide applications in industries, which may produce wastewater containing lead at the concentrations higher than the recommended doses of 0.015 mg/L. Microorganisms immobilized on natural and synthetic adsorbents have been used for separation and preconcentration of heavy metals at trace levels [3, 4, 5, 6, 7]. Most studies have focused on the removal of Pb^{2+}, Cd^{2+}, and Ni^{2+} from wastewater by using various biosorbents [8]. Biosorbents are prepared from the naturally abundant or waste biomass of algae, moss, fungi or bacteria [9]. Hence the naturally and abundantly available *albizia saman* has been selected for the present study for the removal of lead from aqueous solutions.

2. MATERIALS AND METHODS
2.1 Biosorbent Preparation
Albizia saman leaves were obtained from Rajahmundry. The leaves are 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 powder 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, 30, 60, 120 & 180 mg/L), Biosorbent Dosage (10, 20, 30, 40, 50 & 60 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

The potential of dry *Albizia saman* leaf powder as a biosorbent for the biosorption of lead metal present in an aqueous solution is investigated in the present investigation. The effects of various parameters on biosorption of lead are studied. The numerical analysis of the investigation was undertaken applying CCD using RSM.

3.1 Effect of agitation time

The equilibrium agitation time is determined by plotting the % biosorption of lead against agitation time as shown in fig. 1. For 0.5g (10 mg/L) of biosorbent and 53µm of biosorbent size in the interaction time intervals of 1 to180 min 58.30 % (1.166 mg/g) of lead is biosorbed in the first 1 min. The % biosorptionis increased briskly up to 50 min reaching 79.45 % (1.589 mg/g). Beyond 50 min, the % biosorption is constant indicating the attainment of equilibrium conditions. The maximum biosorption of 79.45% (1.589 mg/g) 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) [10, 11].

3.2 Effect of biosorbent size

The percentage biosorption is increased from 72.12 (1.4424 mg/g) to 79.45 % (1.589 mg/g) as the biosorbent size decreases from 152 to 53 µm presented in fig. 2. This phenomenon is expected, as the size of the particle decreases, surface area of the biosorbent increases; thereby the numbers of active sites on the biosorbent are better exposed to the biosorbate.

3.3 Effect of pH of the aqueous solution

In order to determine the optimal value, pH of the aqueous solution is varied from 2 to 8. The pH of aqueous solution is shown against % biosorption of lead in fig 3. The % biosorption of metal is increased from 58.42 % (1.1684 mg/g) to 77.18 % (1.5436 mg/g) as pH is increased from 2 to 6 and decreased beyond pH value of 7. The predominant sorbing forms of lead are Pb^{2+} and $PbOH^{+}$ that occurr in the pH range of 4–6. This is the reason for higher biosorption of lead in the pH range of 4–6. At pH higher than 6, precipitation of lead occurred and biosorption due to biosorption is reduced [12, 13, 14].

3.4 Effect of initial concentration of lead in the aqueous solution

The effect of initial Pb2+ ion concentration is investigated in the range of 20-180 mg/L. 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 77.12% to 58.68% with an increase in C0 from 20 mg/L to 180 mg/L while the uptake capacity is increased from 1.5424 to 10.5624 mg/g [15].

3.5 Effect of biosorbent dosage

The biosorption of lead increases from 77.14% (1.5428 mg/g) to 83.78 % (0.5585 mg/g) with an increase in biosorbent dosage from 10 to 30 g/L, 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 83.78% (0.5585 mg/g) to 84.92% (0.2830 mg/g) when 'w' is increased from 30 to 60 g/L. Hence all other experiments are conducted at 30 g/L dosage.

3.6 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 slowed down and the increase is marginal. 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. 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 [16].

3.7 Isotherms

3.7.1 Langmuir isotherm

Irving Langmuir developed an isotherm named as Langmuir isotherm, which is the most widely used simple two-parameter equation. Langmuir isotherm is drawn between Ce vs Ce/ qe shown in fig 7. The equation obtained is (Ce/qe) = 2.8729 Ce + 0.05929 with a good linearity (correlation coefficient, R2=0.9791) indicating strong binding of lead ions to the surface of albizia saman leaf powder. The separation factor (RL) of 0.9219 shows favorable biosorption (0< RL<1). Hence a maximum biosorption capacity of the Albizia saman leaf powder for lead is find to be 16.8656 mg/g by Langmuir isotherms at 303K (mass of biosorbent: 10 g/L) [17, 18].

3.7.2 Freundlich isotherm

Freundlich empirical adsorption isotherm equation can be applied in case of low and intermediate concentration ranges. Freundlich isotherm is drawn between log q_e and log C_e, in fig. 8 The equation obtained is log q_e = 0.6815 log C_e – 0.2404. The resulting equation has a correlation coefficient of 0.9655. The 'n' value in the above equations is 0.6815, satisfies the condition of 0<n<1 indicating favorable biosorption. K_f is 0.5748 mg/g [19].

3.7.3 Temkin isotherm

Temkin and Pyzhev isotherm equation describes the behavior of many adsorption systems on the heterogeneous surface. 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 lead biosorption is: $q_e = 3.1546 \ln C_e - 3.8813$ with a correlation coefficient 0.9637. The best fit model is determined based on the linear regression correlation coefficient (R^2) [20].

3.8 Kinetics of biosorption

Kinetic models are used to describe the order of biosorbate – biosorbent interactions. Traditionally, the first order model of Lagergren 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 Lagergren [21]:

$(dq_t/dt) = K_1 (q_e - q_t)$

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 adsorption.

The above equation can be presented as

$\log (q_e - q_t) = \log q_e - (K_1/2.303)\, t$

$\log (q_e - q_t) = -0.02357\, t - 0.3027$; $R^2 = 0.9620$

Plot of log (q_e–q_t) versus 't' gives a straight line for first order kinetics, facilitating the computation of biosorption rate constant (K_1). If the experimental results do not follow the above equation, they differ in two important aspects:

$K_1 (q_e - q_t)$ does not represent the number of available adsorption sites and log q_e is not equal to the intercept.

In such cases, pseudo second order kinetic equation [22, 23]:

$(dq_t/dt) = K_2 (qe - qt)^2$ is applicable, where 'K_2' is the second order rate constant.

The other form of the above equation is:

$(t/q_t) = (1/ K_2 qe^2) + (1/qe)\, t$

$(t/q_t) = 0.6229\, t + 1.1720$; $R^2 = 0.9959$

The pseudo second order model 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_2.

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 50 min. Lagergren and pseudo plots for biosorption of lead with biosorbent size 53 µm of *Albizia saman* leaf powder are drawn in figs. 10 & 11. As the correlation coefficient values for the pseudo second order kinetics is 0.99 which is better than first order kinetics (R^2=0.962), very well describes the biosorption mechanism of lead using *Albizia saman* leaf powder.

3.9 Thermodynamics of biosorption

The process of 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 Van't Hoff's plots for the biosorption data obtained at initial concentrations of the lead are shown in fig. 12. The equation obtained is log q_e / C_e = –0.41701(1/T) + 0.5921. The correlation coefficient is 0.9568. In the present study, the enthalpy change is ΔH is 7.9845 J/mole is positive indicating that the biosorption is endothermic. The value of ΔS is 11.3370 J/mole is also positive indicating the irreversibility of process, ΔG is 3427.1334 J/mole is negative indicating the spontaneity of biosorption.

3.10 Optimization of the selected parameters using CCD

In order to determine an optimum condition for lead ions removal, the parameters having greater influence over the response are to be identified. In the present study, the relationship between four independent variables and percent of lead ions biosorption is fitted well with the quadratic model. The regression equation for the optimization of lead biosorption: % biosorption of lead (Y) is a function of the $W (X_1)$, $C_o (X_2)$, $pH (X_3)$, and $T (X_4)$. Table–1 presents the coded levels and Table–2 represents the variations in the corresponding coded values of four parameters and response based on experimental runs and predicted values proposed by CCD design.

$$Y = -452.007 + 0.429 X_1 + 0.369 X_2 + 5.846 X_3 + 3.347 X_4 - 0.006X_{12} - 0.015X_{22} - 0.548 X_{32} - 0.006 X_{42} + 0.004 X_1X_2 - 0.010 X_1X_3 + 0.026 X_2X_3 + 0.002 X_3X_4 \quad \text{-------------------------------- (1)}$$

Interpretation of the regression analysis:

The results of above regression model for Eq. (1) (in the form of analysis of variance ANOVA) are compiled in Table-3. In general, the Fischer's 'F-statistics' value ($=MS_{model}/MS_{error}$), 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} = 33852) and a very low probability value (P_{model} > F=0.000000). More over, the computed F-value ($F_{0.05}$ (14.15) = MS_{model}/MS_{error} = 33852) is greater than that of the tabular F-value ($F_{0.05}$ (14.15) tabulars = 2.42) at the 5% level, indicating that the treatment differences are significant.

The significance of the regression coefficient of the parameter can be verified by the Student's t-test as a tool, while 'P' values signify the pattern of interaction among the factors. From the Table–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-4, it is found that the X_1, X_2, X_3, X_4, X_1^2, X_2^2, X_3^2, X_4^2 X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_3X_4 have high significance to explain the individual and interaction effect of biosorption variables on the biosorption of lead to predict the response.

A positive sign of the coefficient represents a synergistic effect which means response (% biosorption of lead increases with the increase in effect, while a negative sign indicates an antagonistic effect which means response (% biosorption of lead) decreases with the increase in effect. The optimal set of conditions for maximum percentage biosorption of lead is pH = 6.0250, biosorption dosage (w) = 31.7191 g/L, initial lead concentration (C_o) = 19.8996 mg/L and temperature = 304.0673 K. The extent of biosorption of lead calculated at these optimum conditions is 84.90612%. Fig. 13 shows the comparison between the % biosorption obtained through experiments and predicted. The correlation coefficient (R^2) provides a measure of the models variability in the observed response values. The closer the R^2 value to 1, the stronger the model is and it predicts the response better. In the present study the value of the regression coefficient (R^2 = 0.99997) indicates that 0.003% of the total variations are not satisfactorily explained by the model. The ANOVA Table-3 can be used to test the statistical significance of the ratio of mean square due to regression and mean square due to residual error.

Figs. 15 to 20 were represented as a function of two factors at a time, holding other factors fixed at zero level for the Interaction effects of biosorption variables.

4. FIGURES AND TABLES

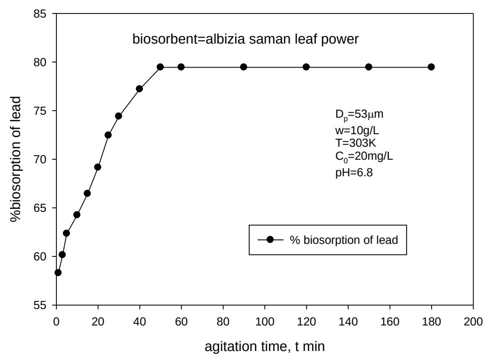

Fig. 1 Effect of agitation time on % biosorption of lead

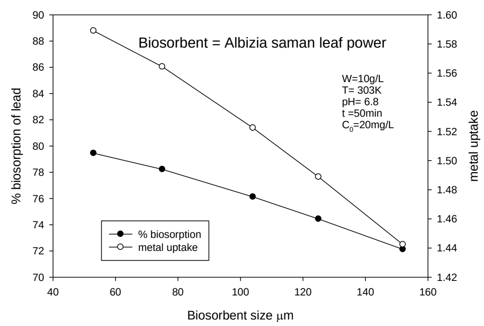

Fig. 2 Variations in % biosorption of lead using biosorbent size

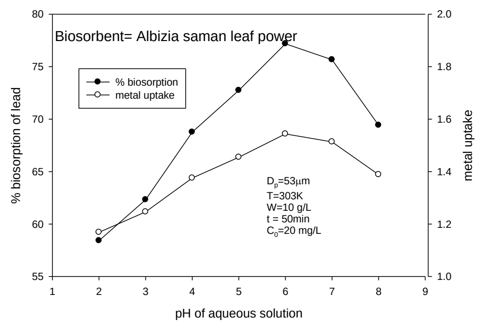

Fig. 3 Effect of pH on % biosorption of lead

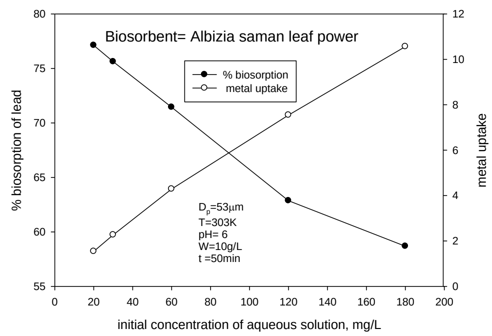

Fig. 4 Effect of initial concentration for the biosorption of lead

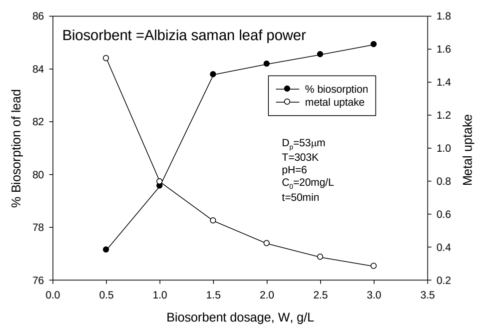

Fig. 5 Effect of biosorbent dosage on % biosorption of lead

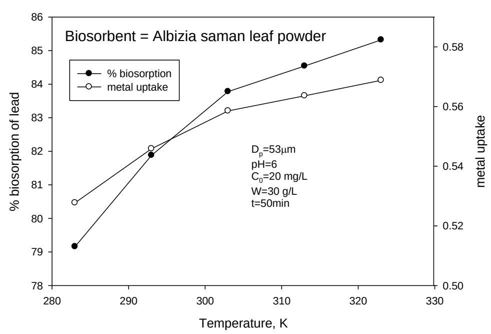

Fig. 6 Effect of temperature for the biosorption of lead

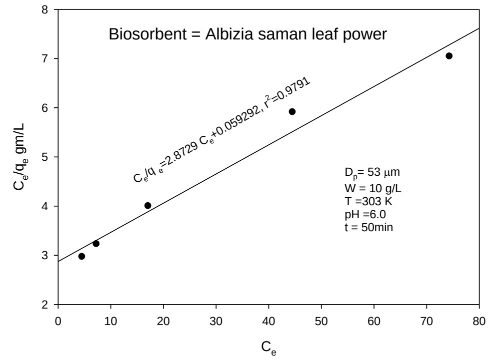

Fig. 7 Langmuir isotherm for biosorption of lead

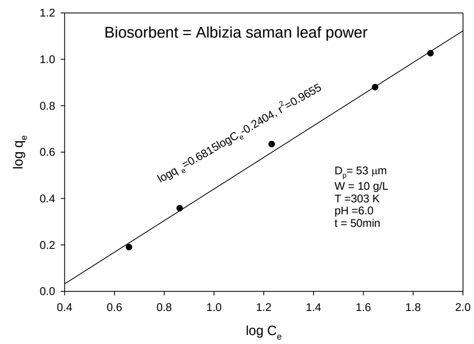

Fig. 8 Freundlich isotherm for biosorption of lead

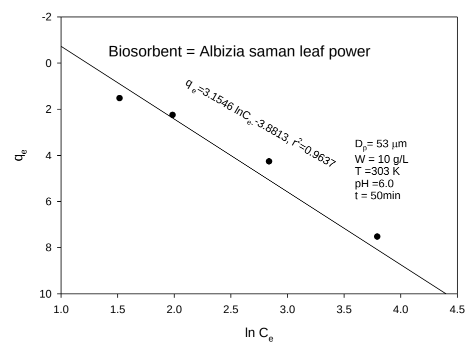

Fig. 9 Temkin isotherm for biosorption of lead

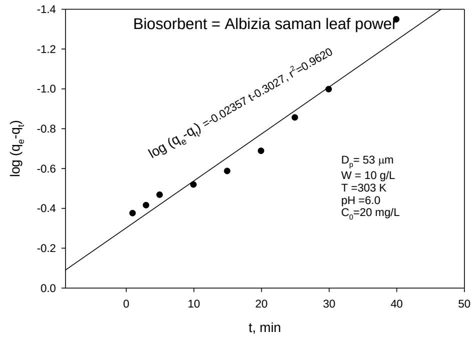

Fig. 10 First order kinetics for biosorption of lead

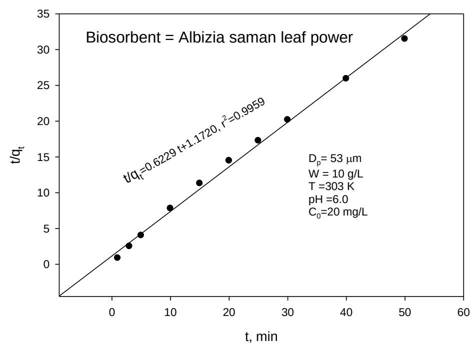

Fig. 11 Second order Kinetics for biosorption of lead

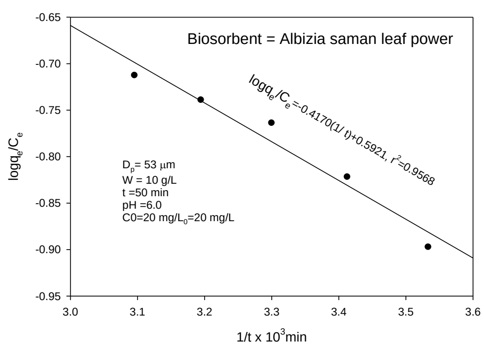

Fig. 12 Vant Hoff's plot for biosorption of lead

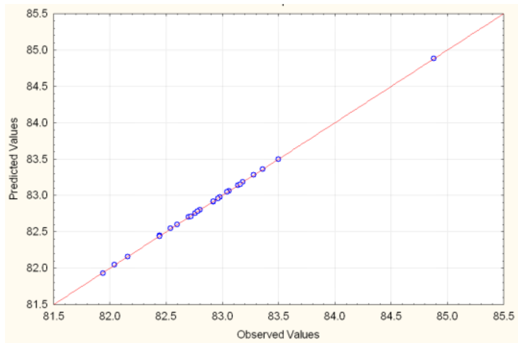

Fig. 13 Predicted vs Observed

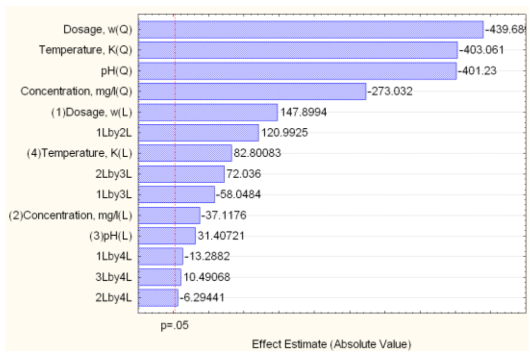

Fig. 14 Pareto Chart

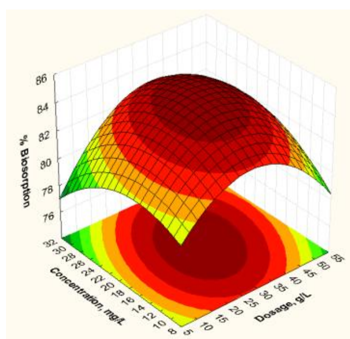

Fig. 15 Surface contour plot for the effects of dosage and initial concentration of lead on % biosorption

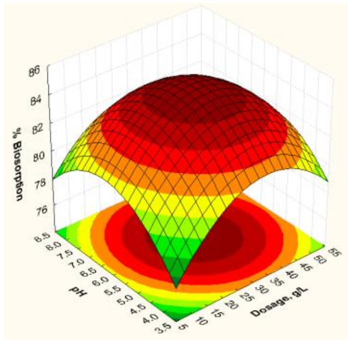

Fig. 16 Surface contour plot for the effects of dosage and pH on % biosorption of lead

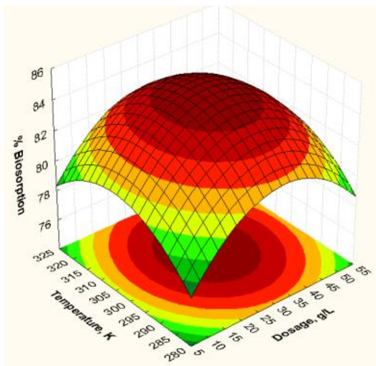

Fig. 17 Surface contour plot for the effects of dosage & Temperature on % biosorption of lead

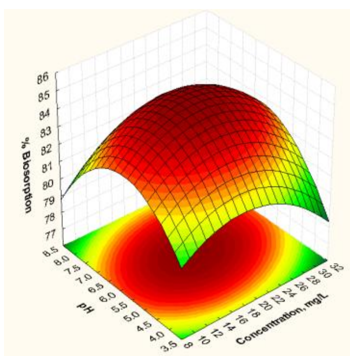

Fig. 18 Surface contour plot for the effects of initial concentration and pH on % biosorption of lead

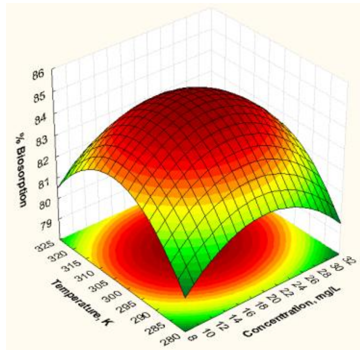

Fig. 19 Surface contour plot for the effects of initial concentration and Temperature on % biosorption of lead

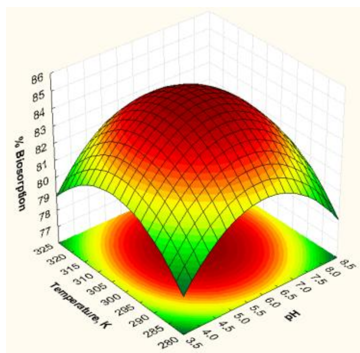

Fig. 20 Surface contour plot for the effects of pH and Temperature on % biosorption of lead

TABLE–1
Levels of different process variables in coded and un-coded form for % biosorption of lead using *Albizia saman* leaf powder

Var	Name	Range and levels				
		-2	-1	0	1	2
X_1	Biosorbent dosage, w, g/L	10	20	30	40	50
X_2	Initial concentration, Co, 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

TABLE–2 Results from CCD for lead biosorption by Albizia saman leaf powder

Runs	X_1, W	X_2, C_o	X_3, pH	X_4, T	Experimental	Predicted
1	-1.00	-1.00	-1.00	-1.00	82.70	82.70
2	-1.00	-1.00	-1.00	1.00	82.98	82.98
3	-1.00	-1.00	1.00	-1.00	82.72	82.71
4	-1.00	-1.00	1.00	1.00	83.06	83.05
5	-1.00	1.00	-1.00	-1.00	81.94	81.93
6	-1.00	1.00	-1.00	1.00	82.16	82.15
7	-1.00	1.00	1.00	-1.00	82.44	82.44
8	-1.00	1.00	1.00	1.00	82.76	82.75
9	1.00	-1.00	-1.00	-1.00	82.96	82.96
10	1.00	-1.00	-1.00	1.00	83.14	83.13
11	1.00	-1.00	1.00	-1.00	82.54	82.54
12	1.00	-1.00	1.00	1.00	82.80	82.80
13	1.00	1.00	-1.00	-1.00	83.04	83.04
14	1.00	1.00	-1.00	1.00	83.18	83.18
15	1.00	1.00	1.00	-1.00	83.16	83.15
16	1.00	1.00	1.00	1.00	83.36	83.36
17	-1.00	0.00	0.00	0.00	82.04	82.04
18	2.00	0.00	0.00	0.00	82.92	82.91
19	0.00	-2.00	0.00	0.00	83.50	83.49
20	0.00	2.00	0.00	0.00	83.28	83.28
21	0.00	0.00	-2.00	0.00	82.60	82.59
22	0.00	0.00	2.00	0.00	82.78	82.78
23	0.00	0.00	0.00	-2.00	82.44	82.43
24	0.00	0.00	0.00	2.00	82.92	82.92
25	0.00	0.00	0.00	0.00	84.88	84.88
26	0.00	0.00	0.00	0.00	84.88	84.88
27	0.00	0.00	0.00	0.00	84.88	84.88
28	0.00	0.00	0.00	0.00	84.88	84.88
29	0.00	0.00	0.00	0.00	84.88	84.88
30	0.00	0.00	0.00	0.00	84.88	84.88

Table–3
ANOVA of lead biosorption for entire quadratic model

Source of variation	SS	df	Mean square(MS)	F-value	P > F
Model	24.3289	14	1.737778	33852.82	0.0000
Error	0.00077	15	0.0000513		
Total	24.32967				

Df- degree of freedom; SS- sum of squares; F- factor F; P- probability.
R^2=0.99997; R^2 (adj):0.99994

Table–4
Estimated regression coefficients for the lead biosorption onto Albizia saman leaf powder

Terms	Regression coefficient	Standard error of the coefficient	t-value	P-value
Mean/Intercept	-452.007	1.335753	-338.391	0.000000
Dosage, w, g/L (L)	0.429	0.005629	76.293	0.000000
Dosage, w, g/L (Q)	-0.006	0.000014	-439.689	0.000000
Conc, Co, mg/L (L)	0.369	0.011310	32.663	0.000000
Conc, Co, mg/L (Q)	-0.015	0.000055	-273.032	0.000000
pH (L)	5.846	0.057298	102.035	0.000000
pH (Q)	-0.548	0.001365	-401.230	0.000000
Temperature, T, K (L)	3.347	0.008391	398.867	0.000000
Temperature, T, K (Q)	-0.006	0.000014	-403.061	0.000000
1L by 2L	0.004	0.000036	120.992	0.000000
1L by 3L	-0.010	0.000179	-58.048	0.000000
1L by 4L	-0.000	0.000018	-13.288	0.000000
2L by 3L	0.026	0.000357	72.036	0.000000
2L by 4L	-0.000	0.000036	-6.294	0.000014
3L by 4L	0.002	0.000179	10.491	0.000000

5. CONCLUSION

Both Preliminary and finals experimental runs are carried out to find out the equilibrium, isotherms, kinetics and thermodynamic parameters for biosorption of lead from an aqueous solution using Albizia saman leaf powder. The analysis of the experimental and theoretical data results in the conclusions that the equilibrium agitation time for lead biosorption is 50 minutes. The % biosorption of lead from an aqueous solution increased from 72.12 to 79.45 % with a decrease in the particle size of the biosorbent from 152 to 53 μm and increases from 77.14 to 83.78 % with increase in biosorbent dosage from 10 to 30 g/L. With an increase in the initial concentration of lead in the aqueous solution (20 to 180 mg/L), the percentage biosorption of lead from the aqueous solution is decreased from 77.12 to 58.68 %. Percentage biosorption of lead from the aqueous solution increased significantly with increase in pH from 2 to 6 (58.42 to 77.18 %). Hereafter, percentage biosorption decreases for further increase in pH from 6 to 8 (77.18 to 69.42 %). The maximum uptake capacity of 16.8656 mg/g is obtained at a temperature of 303 K. The present study involves the use of statistical experimental design to optimize process conditions for maximal biosorption of lead from aqueous solution using CCD involving RSM. The maximum biosorption of lead (84.90612 %) onto Albizia saman leaf powder is observed when the processing parameters are set as follows: pH = 6.0250, w = 31.7191 g/L, Co = 19.8996 mg/L and T = 304.0673 K. The kinetic studies showed that the biosorption of lead is better described by pseudo second order kinetics. The thermodynamic data depicted that % biosorption of lead increased with increase in temperature up to some extent.

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