Optimization of Biosorption Performance of *Casuarina* Leaf Powder for the Removal of Lead Using Central Composite Design

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Abstract

　　Rapid industrialization, urbanization and increase in population have led to increasing the pollution levels. Heavy metal pollution of water is of major concern now-a-days as water is the basic need for mankind. The present investigation is removal of lead from aqueous solutions using a new biosorbent *Casuarina* leaf powder. The cumulative effects of operating parameters such as initial metal ion concentration, pH of the aqueous solution, biosorbent dosage and temperature on the lead biosorption were analyzed using Response Surface Methodology (RSM). For obtaining the mutual interaction between the variables and optimizing these variables, a 2^4 full factorial central composite design was employed. According to ANOVA results, the proposed quadratic model for CCD fitted very well to the experimental data. The optimal set of conditions for maximum percentage biosorption of lead is found to be pH=4.988, biosorption dosage (w) =35.37 g/L, initial lead concentration (Co)=18.0555 mg/L and temperature=306.47 K and the % of biosorption calculated at these values found to be 95.73%. The Langmuir isotherm fitted well with a correlation factor of 0.9944, followed by Freundlich and Temkin. The entire biosorption process followed pseudo second order kinetics. By applying the Van't Hoff equation the thermodynamic parameters such as enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy ($\Delta G°$) were evaluated which described the biosorption process as spontaneous, irreversible and endothermic in nature. The optimized values obtained through central composite design and one factor at a time process is in good agreement.

Keywords: Biosorption; *Casuarina* leaf powder; Central composite design; Isotherms; Kinetics

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 $1/4^{th}$ of the land of whole ecosystem. The contaminated water may cause anemia, headache, chills, diarrhea and reduction in hemoglobin formation [1]. The influence of pollution on the global environment, through activities such as rapid industrialization, urbanization and mining operations often lead to an increase in the discharge of toxic metals, such as lead, nickel, chromium, cobalt, copper, cadmium etc., into the environment, which results in a contamination of water. These heavy metal contaminants are hazardous to the environment, because they do not naturally degrade [2]. Beyond certain limits, heavy metals are toxic to living organisms and may cause serious hazard to public health [3]. Environmental engineers and scientists are faced with the challenging task to develop appropriate low cost technologies for effluent treatment [4].

　　Traditional methods for removal of lead ions from solution include chemical precipitation, ion exchange, electrodialysis and membrane separations. All these methods have various disadvantages, specifically, high capital investment and operating cost, incomplete removal, low selectivity and high energy consumption. Therefore, there is a need for a cost effective treatment method that is capable of removing low concentrations of lead from solution For the last decades, biosorption or sorption of contaminants by sorbents of natural origin has gained important credibility due to the good performance and low cost of these complexing materials [5-10]. A multitude of biomass types comprising fungal biomass, bacterial biomass, algae, peat etc., have been studied for their biosorption of metals [11-14]. 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 [15-17].

　　In view of the above, the authors tried to use a novel biosorbent *Casuarina* leaf powder to remove lead from aqueous solutions and report the application of Response Surface Methodology using Central Composite Design to develop a mathematical model and predict the response and check the adequacy of the model. The objectives of the present study include identifying the maximum lead uptake capacity of the *Casuarina* leaves powder with respect to various governing parameters. In addition, biosorption isotherms were described by using Langmuir, Freundlich and Temkin models and the kinetic experimental data were correlated by the pseudo first and second order kinetic models. Thermodynamics for biosorption of lead on *Casuarina* leaves powder is also studied and fitted in to Van't Hoff equation.

Experimental Procedure

Biosorbent

　　Casuarina leaves were collected from the surroundings of Bapatla, Guntur. The *Casuarina* leaves were washed thrice with tap water and once with distilled water in order to remove adhering surface impurities. The leaves were dried in sunlight until all the moisture was evaporated. The crispy *Casuarina* leaves were then grinded in a ball mill to powder, separated using British Standard Sieves (BSS) and stored in dry air tight packs to prevent moisture penetration and readily used as biosorbent.

Preparation of metal solutions

Test solutions containing lead ions were prepared from Pb $(NO_3)_2$ at different concentrations ranging from 25, 50, 100, 150, 200, 250 mg/L. The pH of each test solution was adjusted to the appropriate value by using 0.1 N HNO_3 or 0.1 N NaOH solutions. All the chemicals used in preparing the stocks are of analytical grade and the water used is double distilled water prepared from Millipore ELIX-10 unit.

Batch sorption studies

The biosorption was carried out in a batch process by contacting a pre-weighed amount of the *Casuarina* leaves powder with a known volume of aqueous solution. Experiments were conducted in 250 ml Erlenmayer flasks containing 50 ml of 20 mg/L metal solution using single step optimization procedure. The flasks containing aqueous solution and biosorbent 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 and 180 min) and centrifuged at 14000 rpm and the supernatant liquid was analyzed in Atomic Absorption Spectrophotometer (AAS) - Shimadzu make AA-6300 for final concentrations. Similarly the other variables were varied for a wide range: Biosorbent Size (63, 75 and 105 μm), pH of the aqueous solution (2, 3, 4, 5, 6, 7 and 8), Initial concentration of lead solution (20, 50, 80, 120 and 150 mg/L), Biosorbent dosage (5, 10, 15, 20, 25, 30, 35, 40 and 50 g/L) and Temperature (283, 293, 303, 313 and 323 K).

Process optimization

Final experimental runs for optimization were obtained through Response Surface Methodology using Central Composite Design with 2^4 factorial runs, 6-central points and 8-axial points. Design of Experiments (DoE) obtained based on the above optimization technique 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. For the optimization of biosorption, the regression equation is written in terms of % biosorption of lead (Y) as function of the parameters having greater influence over the response i.e. pH (X_1), Co (X_2), w (X_3), and T (X_4). Based on experimental runs and predicted values proposed by CCD design, the following equation represents multiple regression analysis of the experimental data for the biosorption of lead:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{11} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{44} x_4^2 + b_{14} x_1 x_4 + b_{24} x_2 x_4 + b_{34} x_3 x_4$$

Results and Discussion

Effect of agitation time

Duration of equilibrium biosorption is defined as the time required for heavy metal concentration to reach a constant value during biosorption. The equilibrium agitation time is determined by plotting the % biosorption of lead against agitation time as shown in figure 1 for the interaction time intervals between 1 to 180 min. For 63 μm size of 10 g/L biosorbent dosage mixed in 50 mL of aqueous solution $(C_o=20$ mg/L), 50.4% of lead is biosorbed in the first one minute and reached to 55.7% after 5 minutes of biosorption. The % biosorption is increased briskly up to 60 min reaching 86.5%. Beyond 60 min, the % of biosorption is constant indicating the attainment of equilibrium conditions. The maximum biosorption of 86.5% is attained for 60 min of agitation time. 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. Therefore, all other experiments are conducted at this agitation time.

Effect of biosorbent size

The variations in % biosorption of lead from the aqueous solution with biosorbent size are drawn in figure 2 with percentage biosorption of lead as a function of biosorbent size. The percentage of biosorption is decreased from 86.9% to 80.2% as the biosorbent size increases from 63 to 105 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.
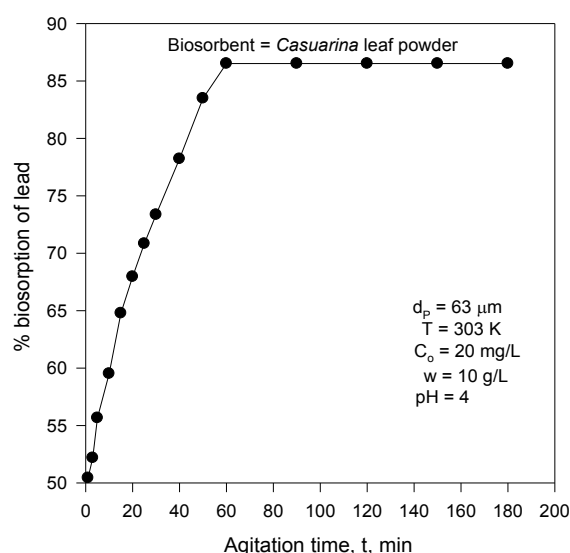

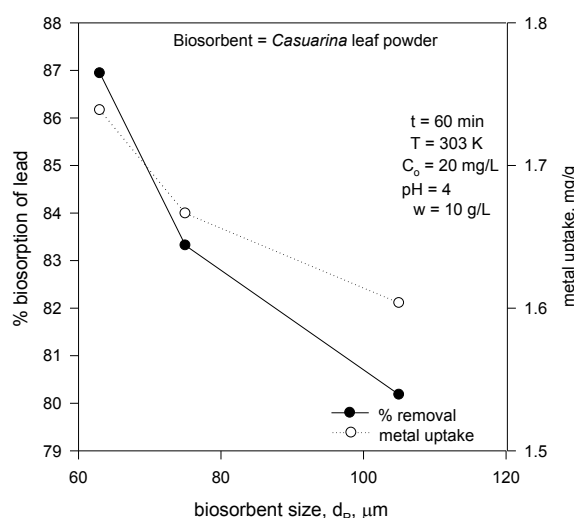**Figure 1:** Effect of agitation time on % biosorption of lead.

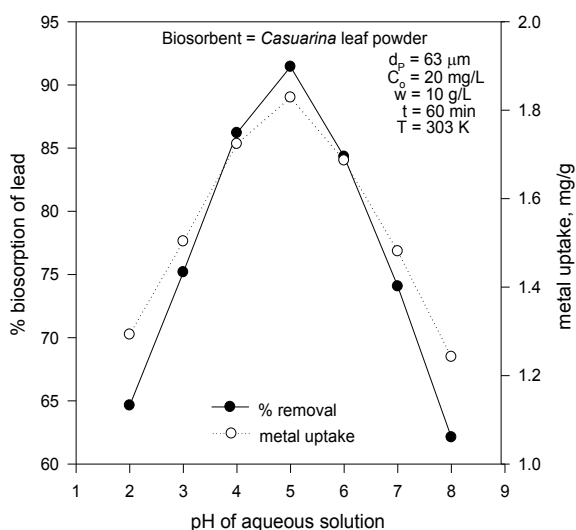**Figure 2:** % Biosorption of lead as a function of biosorbent size.

Effect of pH

Biosorption is controlled by pH by the influence of surface charge of the biosorbent, the degree of ionization and the species of biosorbate. In the present investigation, effect of pH on lead biosorption is obtained in the pH range of 2 to 8 of the aqueous solution (C_o=20 mg/L) using 10 g/L of 63 μm size biosorbent. The effect of pH of aqueous solution on % biosorption of lead is shown in figure 3. The % biosorption of lead is increased from 64.6% to 91.4% as pH is increased from 2 to 5 and decreased beyond the pH value of 6. Percentage of biosorption is decreased to 62.1% from 84.3% for pH variation of 6 to 8. Since the pH of aqueous solution influences the solution chemistry of the heavy metals, the binding of metal ions by surface functional groups is strongly pH dependent. The increase in % removal when pH increases from 2 to 5 could be due to decrease in competition between hydrogen ions and metal species for appropriate sites on the biosorbent surface and also by the decrease in positive surface charge on the adsorbent. However, with increasing pH above 5 lead tends to hydrolyze and precipitate instead of adsorption and adsorbent was deteriorated with accumulation of metal ions, making the true adsorption studies unpredictable.

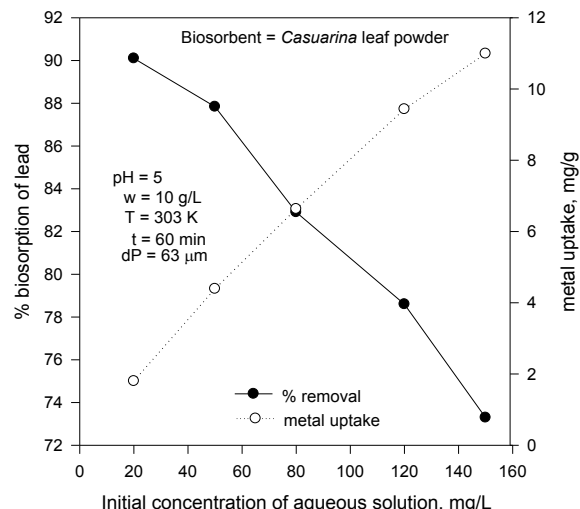## Effect of initial concentration of lead

The effect of % biosorption on initial concentration of lead in the aqueous solution is shown in figure 4. The percentage biosorption of lead is increased from 73.3% to 90.1% with decrease in C_0 from 150 mg/L to 20 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.
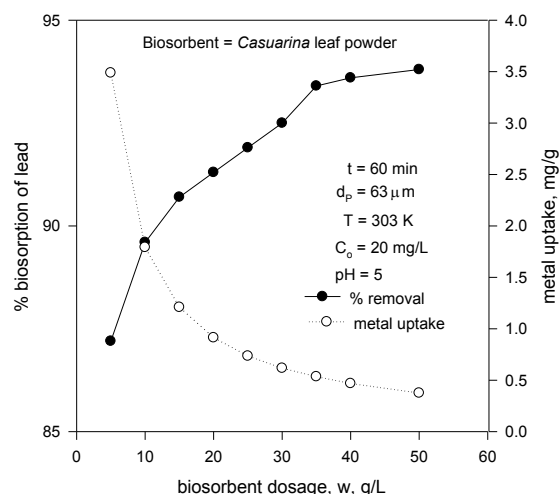
Effect of biosorbent dosage

The percentage biosorption of lead is drawn against biosorbent dosage for 63 μm size biosorbent in figure 5. The biosorption of lead increased from 87.2% to 93.4% with an increase in biosorbent dosage from 5 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 marginal from 93.4% to 93.8% when 'w' is increased from 35 to 50 g/L. Hence all other experiments are conducted at 35 g/L dosage.

**Figure 4:** Variation of initial concentration with % biosorption of lead.

Figure 5: Dependency 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 figure 6. Lead uptake marginally increased from 92.2 to 94.6% with increasing temperature from 283 K to 323 K indicating that the biosorption of lead on to *Casuarina* leaf powder is endothermic process. Adsorption processes are normally exothermic and as the temperature increases the % adsorption decreases in accordance with Le Chatelier principle. The reverse phenomena could be activation of non living biomass under moderate temperatures and Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to decrease in the viscosity of the solution.

Isotherms

Langmuir isotherm: Irving Langmuir developed an isotherm

Figure 3: Observation of pH along with % biosorption of lead.
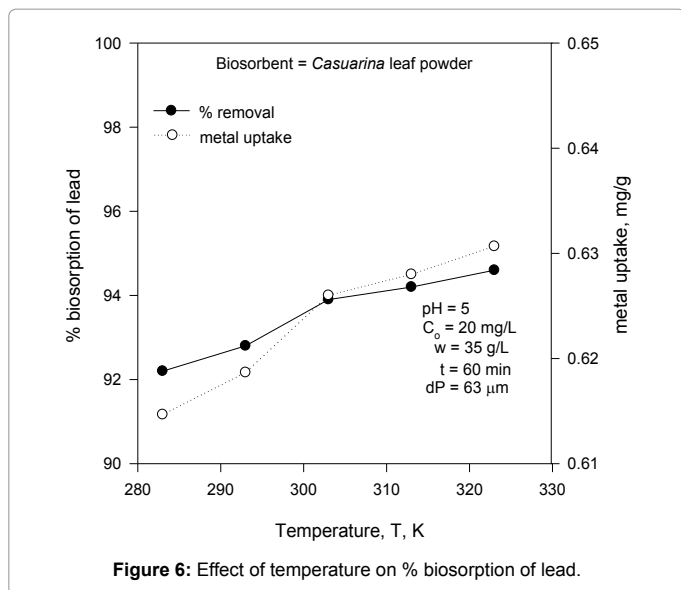
Figure 6: Effect of temperature on % biosorption of lead.

named Langmuir isotherm. It is the most widely used simple two-parameter equation. The Langmuir relationship is hyperbolic and the equation is:

$$q_e/q_m = bC_e/(1+bC_e) \tag{1}$$

Equation (5.1) can be rearranged as

$$(C_e/q_e) = 1/(bq_m) + C_e/q_m \tag{2}$$

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 figure 7. The equation obtained is $C_e/q_e = 0.0663142C_e + 1.0222246$ with a good linearity (correlation coefficient, $R^2 \sim 0.9944$) indicating strong binding of lead ions to the surface of *Casuarina* leaf powder. The maximum metal uptake of (q_m) 15.0797 mg/g is observed and the separation factor obtained (R_L) is 0.88617, indicating favorable biosorption.

Freundlich isotherm: Freundlich presented an empirical biosorption isotherm equation that 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

$$q_e = K_f C_e n \tag{3}$$

Where, K_f (mg) represents the biosorption capacity when metal equilibrium concentration and n represents the degree of dependence of biosorption with equilibrium concentration. The above equation is represented as

$$\ln q_e = \ln K_f + n \ln C_e \tag{4}$$

Freundlich isotherm is drawn between $\ln C_e$ and $\ln q_e$ (Figure 8). The

obtained equation is $\ln q_e = 0.600397 \ln C_e + 0.274637$; for the present data. The resulting equation has a correlation coefficient of 0.9832. The 'n' value (0.600397) in the above equations satisfies the condition of $0 < n < 1$ indicating favorable biosorption. The K_f obtained was 1.882075.

Temkin isotherm: Temkin and Pyzhev isotherm equation describes the behavior of many biosorption systems on the heterogeneous surface and it is based on the following equation
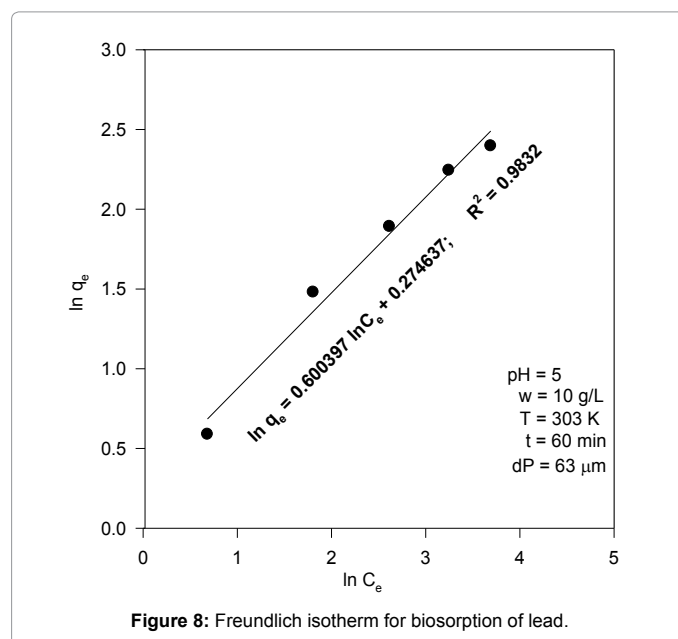
$$q_e = RT \ln(A_T C_e)/b_T \tag{5}$$

The linear form of Temkin isotherm can be expressed as

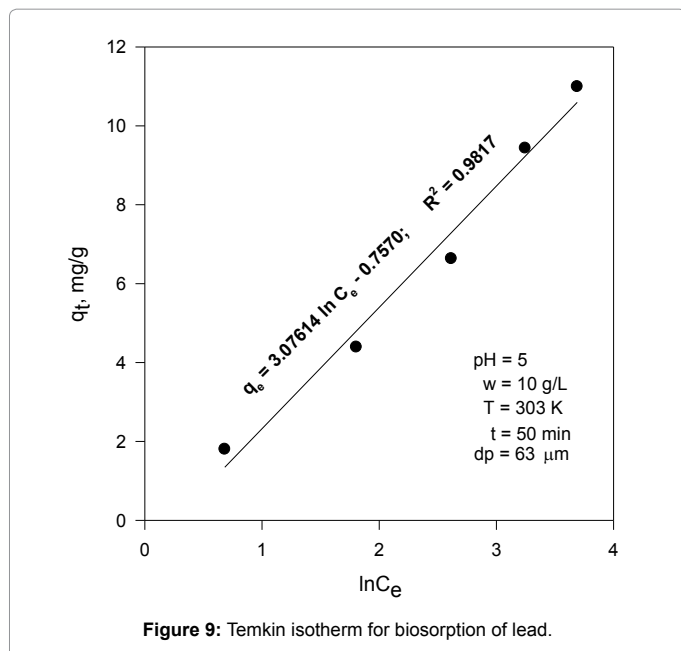$$q_e = (RT/b_T) \ln(A_T) + (RT/b_T) \ln(C_e) \tag{6}$$

The present data are analysed according to the linear form of Temkin isotherm and the linear plot is shown in figure 9. The equation obtained for lead biosorption is: $q_e = 3.07614 \ln C_e - 0.7570$ with a
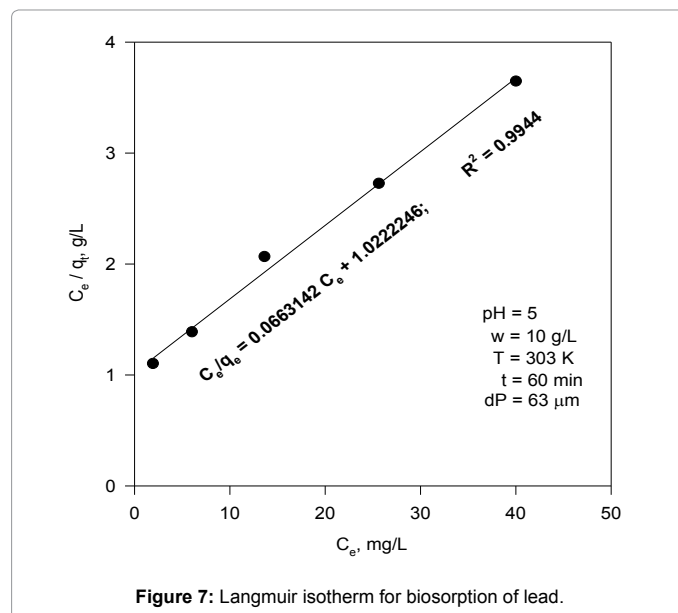
Figure 7: Langmuir isotherm for biosorption of lead.

Figure 8: Freundlich isotherm for biosorption of lead.

Figure 9: Temkin isotherm for biosorption of lead.

correlation coefficient 0.9817. The best fit model is determined based on the linear regression correlation coefficient (R^2). From the figure 7-9, it is found that biosorption data are well represented by Langmuir isotherm with higher correlation coefficient of 0.9944, followed by and Freundlich and Temkin isotherms with correlation coefficients of 0.9832 and 0.9817 respectively. The validity of Langmuir model suggests the adsorption process is monolayer and adsorption of each molecule has equal activation energy. The isotherm constants are given in table 1.

Kinetics

The order of biosorbate – biosorbent interactions have been described using kinetic model. 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:

$$(dq_t/dt) = K_{ad} (q_e – q_t) \qquad (7)$$

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 lagergren first order biosorption.

The above equation can be presented as

$$\int (dq_t/ (q_e – q_t)) = \int K_{ad}dt \qquad (8)$$

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

$$\log (q_e – q_t) = \log q_e – (K_{ad}/2.303) t \qquad (9)$$

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}).

The pseudo second order kinetic equation given below:

$$(dq_t/dt) = K (q_e – q_t)2 \qquad (10)$$

Where, 'K' is the second order rate constant.

Substituting these values in above equation, we obtain:

$$1/ (q_e – q_t) = Kt + (1/q_e) \qquad (11)$$

Rearranging the terms, we get the linear form as:

$$(t/q_t) = (1/ Kq_e^2) + (1/q_e) t \qquad (12)$$

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. The first order and the second order kinetics plots are given in figures 10 and 11 respectively. The rate equations obtained and comparative lead uptake capacities are given in table 2 and table 3 respectively. The correlation coefficients indicate that the system under consideration is more appropriately described by pseudo-second order model. The regression coefficient of 0.9897 shows that that the model can be applied for the entire adsorption process. The confirmation of pseudo second order kinetics indicates that in the adsorption process, concentrations of both adsorbent and adsorbate are involved in rate determining step. In the range of studied parameters, the metal uptake is very good for *Casuarina* leaf powder.

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). 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

Langmuir	Freundlich	Temkin
q_m = 15.0797	k_f = 1.882075	A_T = 0.781859
b = 0.06487	n = 0.600397	b_T = 818.9295
R^2 =0.9944	R^2 =0.9832	R^2 =0.9817

Table 1: Isotherms constants.
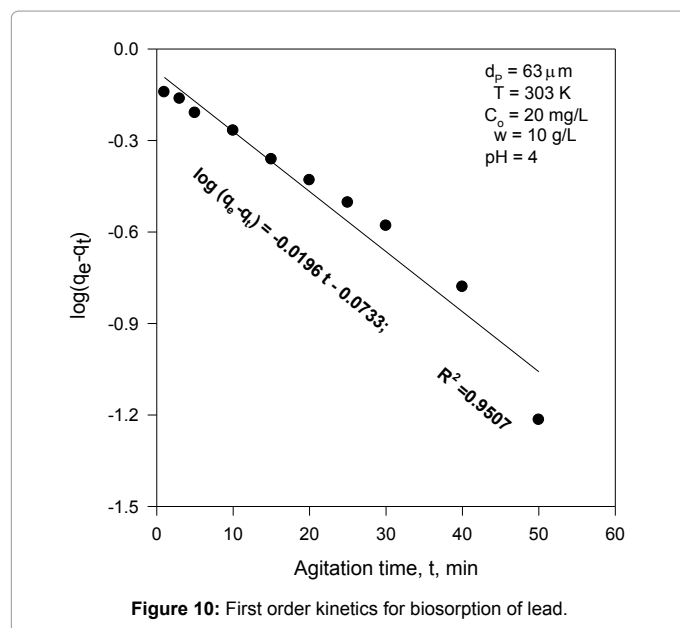
Figure 10: First order kinetics for biosorption of lead.
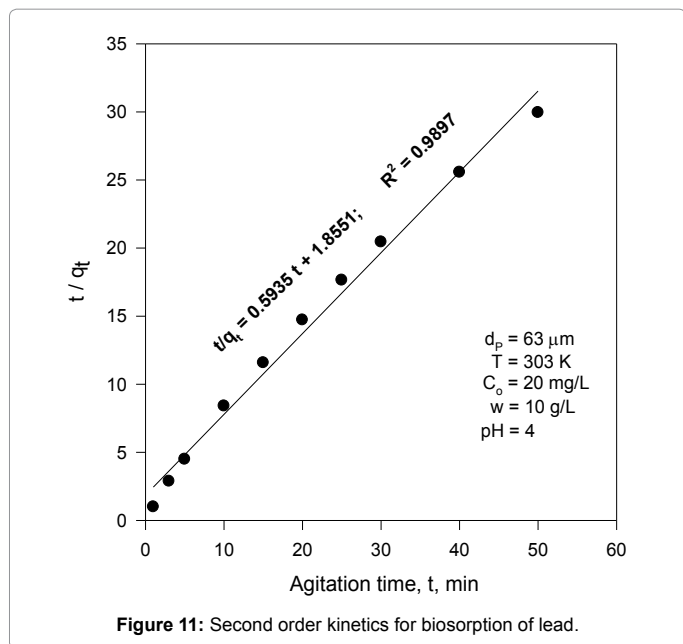
Figure 11: Second order kinetics for biosorption of lead.

Order	Equation	K, min^{-1}	R^2
First order	log (q_e-q_t)=−0.019698 t−0.073348	0.04513	0.9507
Second order	t/q_t=0.5935 t + 1.85514	0.18987	0.9897

Table 2: Rate Equations and coefficients for biosorption of lead on Casuarina leaf powder.

Authors	Biosorbent	q_t, mg/g
S.A. Abo-El-Enein [18]	rice husk ash	158
Erdal Kenduzler [19]	Amberlyst 36	88
Vijayaraghavan [20]	Sargassum	20.2
Fuat Guzel [21]	black carrot	5.003
Mustafa Tuzen [22]	Pseudomonas aeruginosa	5.83
Present investigation	***Casuarina* leaf powder**	15.0797

Table 3: Lead uptake capacities for different biosorbents.

$$\Delta G = \Delta H - T \, \Delta S \qquad (13)$$

$\Delta S < 1$ 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

$$\log (q_e / C_e) = \Delta H/(2.303\ RT) + (\Delta S/2.303\ R) \qquad (14)$$

$$\log (q_e / C_e) = -\,0.40566\,(1 / T) + 1.029489 \qquad (15)$$

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 reversibility of process. The negative value for ΔG indicates the spontaneity of biosorption, whereas the positive value indicates non spontaneity of sorption. Experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 323 K. The Van't Hoff's plot for the biosorption data obtained is shown in figure 12. From the plot the equation obtained is log $(q_e /C_e) = -\,0.40566$ $(1 / T) + 1.029489$. The values obtained from the equation are $\Delta G =$ -5964.899, $\Delta H = 7.7672$ and $\Delta S = 19.71177$. ΔH is positive indicating that the biosorption is endothermic. The negative value of ΔG indicates

the spontaneity of biosorption. As ΔS is more than zero, it indicates the irreversibility of biosorption.

Optimization using Response Surface Methodology (RSM)

In order to determine an optimum condition for Pb ions removal, the parameters having greater influence over the response is to be identified. In the present study, the relationship between four independent variables and percent of Pb ions biosorption fitted well with the quadratic model. Levels of different process variables in coded and un-coded form (Table 4), Results from CCD (Table 5), Analysis of variance (ANOVA) (Table 6), Estimated regression coefficients (Table 7) and Comparison of optimum values obtained from CCD and experimentation (Table 8) for biosorption of lead using *Casuarina* leaf powder are presented below. For the optimization of biosorption the regression equation: % biosorption of lead (Y) is function of the

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	3	4	5	6	7
X_4	Temperature, T, K	283	293	303	313	323

Table 4: Levels of different process variables in coded and un-coded form for biosorption of lead using *Casuarina* leaf powder.

Run no.	$X_1(w)$	$X_2(C_o)$	$X_3(pH)$	$X_4(T)$	% biosorption of cobalt	
					Experimental	Predicted
1	-1.0000	-1.0000	-1.0000	-1.0000	93.18	93.21
2	-1.0000	-1.0000	-1.0000	1.0000	93.67	93.65
3	-1.0000	-1.0000	1.0000	-1.0000	93.19	93.18
4	-1.0000	-1.0000	1.0000	1.0000	93.59	93.60
5	-1.0000	1.0000	-1.0000	-1.0000	92.2	92.21
6	-1.0000	1.0000	-1.0000	1.0000	92.79	92.82
7	-1.0000	1.0000	1.0000	-1.0000	92.89	92.91
8	-1.0000	1.0000	1.0000	1.0000	93.51	93.50
9	1.0000	-1.0000	-1.0000	-1.0000	93.8	93.78
10	1.0000	-1.0000	-1.0000	1.0000	94.17	94.20
11	1.0000	-1.0000	1.0000	-1.0000	93.29	93.31
12	1.0000	-1.0000	1.0000	1.0000	93.74	93.71
13	1.0000	1.0000	-1.0000	-1.0000	91.98	92.01
14	1.0000	1.0000	-1.0000	1.0000	92.62	92.60
15	1.0000	1.0000	1.0000	-1.0000	92.28	92.27
16	1.0000	1.0000	1.0000	1.0000	92.83	92.84
17	-2.0000	0.0000	0.0000	0.0000	94.34	94.30
18	2.0000	0.0000	0.0000	0.0000	94.21	94.20
19	0.0000	-2.0000	0.0000	0.0000	94.13	94.12
20	0.0000	2.0000	0.0000	0.0000	92.28	92.25
21	0.0000	0.0000	-2.0000	0.0000	90.71	90.67
22	0.0000	0.0000	2.0000	0.0000	90.89	90.88
23	0.0000	0.0000	0.0000	-2.0000	93.77	93.73
24	0.0000	0.0000	0.0000	2.0000	94.75	94.74
25	0.0000	0.0000	0.0000	0.0000	95.6	95.60
26	0.0000	0.0000	0.0000	0.0000	95.6	95.60
27	0.0000	0.0000	0.0000	0.0000	95.6	95.60
28	0.00000	0.0000	0.0000	0.0000	95.6	95.60
29	0.00000	0.0000	0.0000	0.0000	95.6	95.60
30	0.00000	0.0000	0.0000	0.0000	95.6	95.60

Experimental conditions [Coded Values] and observed response values of central composite design with 2^4 factorial runs, 6- central points and 8- axial points. Agitation time fixed at 60 min and biosorbent size at 63 µm

Table 5: Results from CCD for cobalt biosorption by *Casuarina* leaf powder.

Source of variation	SS	df	Mean square(MS)	F-value	*P*> F
Model	53.85109	14	3.8465	4649.27	0.0000
Error	0.01241	15	0.0008273		
Total	53.8635				

df, degree of freedom; SS, sum of squares; F, factor F; *P*, probability.
R^2=0.99977; R^2 (adj): 0.99955

Table 6: Analysis of variance (ANOVA) of lead biosorption for entire quadratic model.

Terms	Regression coefficient	Standard error of the coefficient	t-value	*P*-value
constant	-280.353	5.533036	-50.669	0.000000
X_1	1.233	0.047130	26.151	0.000000
X_2	-0.013	0.000220	-61.134	0.000000
X_3	0.694	0.046155	15.036	0.000000
X_4	-0.024	0.000220	-109.843	0.000000
X_1*X_1	12.272	0.232115	52.871	0.000000
X_2*X_2	-1.204	0.005492	-219.326	0.000000
X_3*X_3	2.071	0.033977	60.965	0.000000
X_4*X_4	-0.003	0.000055	-61.816	0.000000
X_1*X_2	-0.008	0.000288	-26.511	0.000000
X_1*X_3	-0.022	0.001438	-15.385	0.000000
X_1*X_4	-0.000	0.000144	-0.782	0.446215[a]
X_2*X_3	0.037	0.001438	25.468	0.000000
X_2*X_4	0.001	0.000144	5.998	0.000024
X_3*X_4	-0.000	0.000719	-0.608	0.551990[a]

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

Table 7: Estimated regression coefficients for the lead biosorption onto *Casuarina* leaf powder.

Variable	CCD	Experimental value
pH of aqueous solution	4.9884	5.0
Biosorption dosage, w, g/L	35.3702	35
Initial cobalt concentration, mg/L	18.0555	20
Temperature, K	306.4727	303
% biosorption	95.7337	93.9

Table 8: Comparison of optimum values obtained from CCD and experimentation.

pH (X_1), Co (X_2), w (X_3), and T (X_4). Based on experimental runs and predicted values proposed by CCD design.

$$Y = -280.353 + 1.233\,X_1 + 0.694\,X_2 + 12.272\,X_3 + 2.071\,X_4 - 0.013\,X_1^2 - 0.024\,X_2^2 - 1.204\,X_3^2 - 0.003\,X_4^2$$

$$- 0.008\,X_1X_2 + 0.022\,X_1X_3 + 0.000\,X_1X_4 + 0.037\,X_2X_3 + 0.001\,X_2X_4 + 0.000\,X_3X_4 \qquad (16)$$

From the Central Composite Design, the Pareto Chart (Figure 13), Observed Vs Predicted values plot (Figure 14) and Surface contour plot (Figures 15 a-f) for biosorption of lead on to *Casuarina* leaf powder are presented below. The optimal set of conditions for maximum percentage biosorption of lead is pH= 4.9884 biosorption dosage (w) =35.3702 g/L, initial lead concentration (Co) =18.0555 mg/L and temperature=306.4727 K and the % of biosorption calculated at these values found to be 95.73%.

Conclusions

The analysis of the experimental and theoretical data resulted that the equilibrium agitation time for lead biosorption is 60 minutes. The % removal of lead from an aqueous solution increases with a decrease in the particle size of the biosorbent and increases with increase in biosorbent dosage. With an increase in the initial concentration of
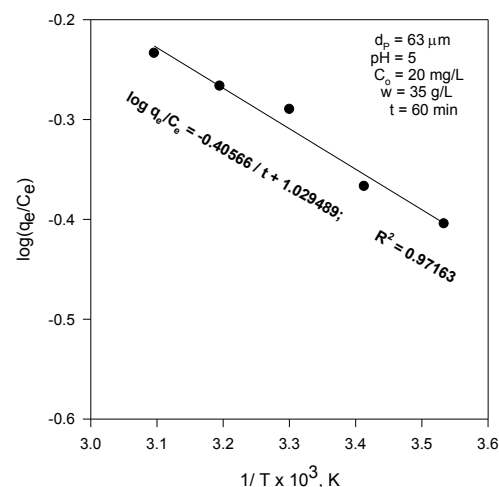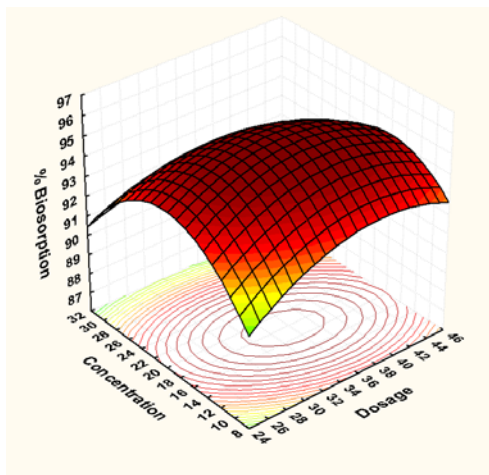

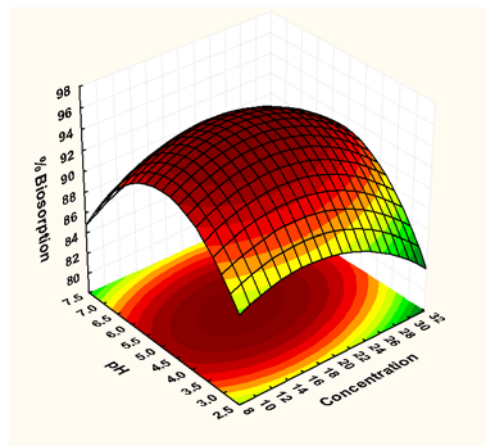**Figure 12:** Van't Hoff's plot for biosorption of Lead.
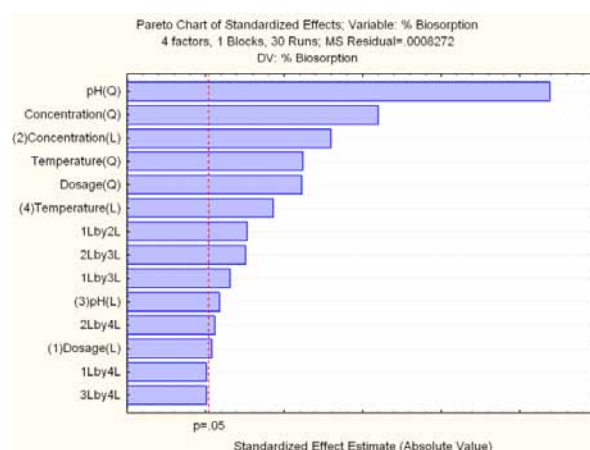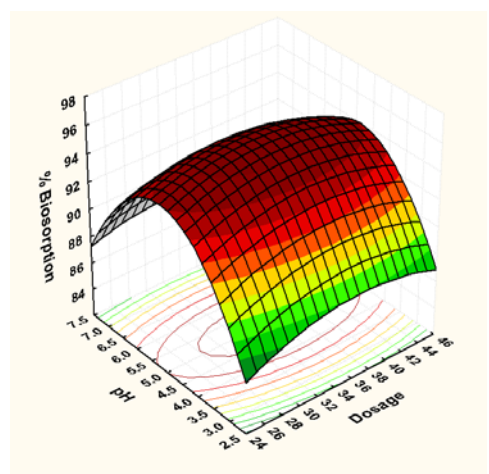

Figure 13: Pareto Chart.
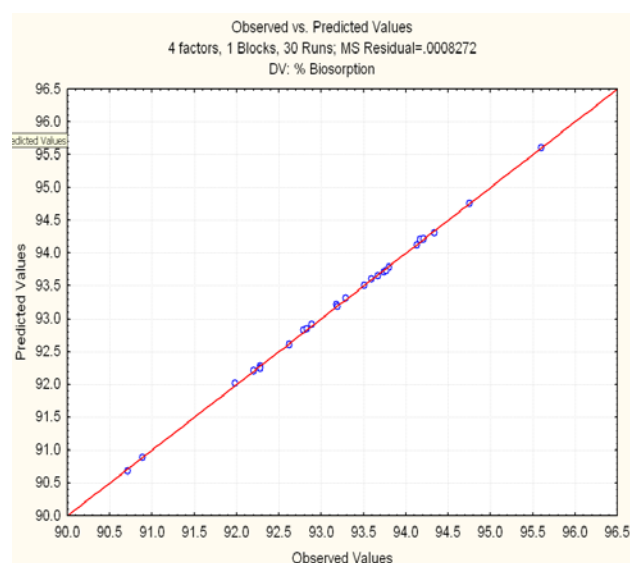
Figure 14: Observed Vs Predicted values plot for % biosorption of lead.
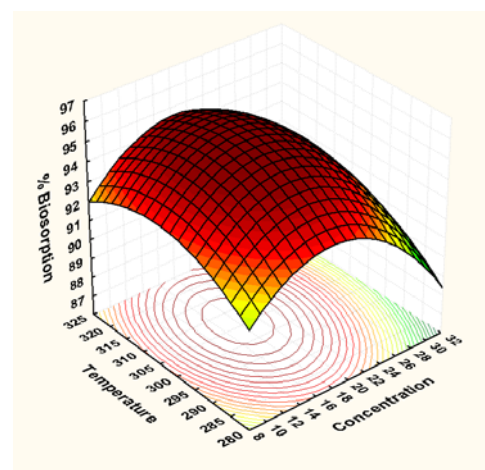
Figure 15a: Surface contour plot for the effects of dosage and concentration of lead on % biosorption.
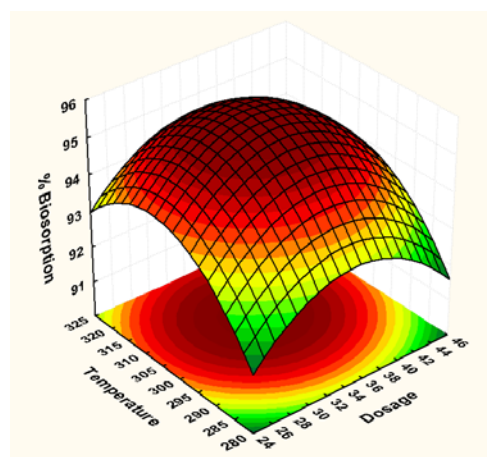

Figure 15d: Surface contour plot for the effects of concentration of lead and pH on % biosorption of lead.
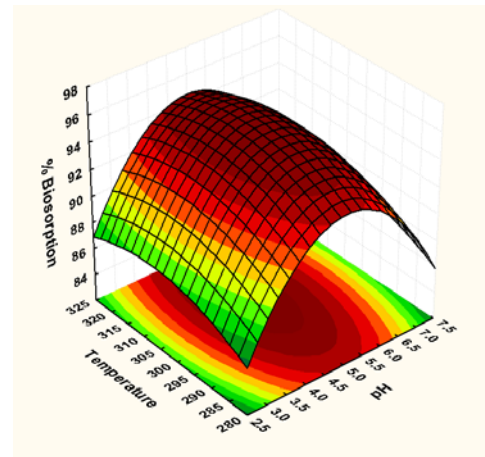

Figure 15b: Surface contour plot for the effects of dosage and pH on % biosorption of lead.

Figure 15e: Surface contour plot for the effects of concentration of lead and temperature on % biosorption of lead.

Figure 15c: Surface contour plot for the effects of dosage and temperature on % biosorption of lead.

Figure 15f: Surface contour plot for the effects of pH and temperature on % biosorption of lead.

lead in the aqueous solution, the percentage removal of lead from the aqueous solution is decreased. Percentage removal of lead from the aqueous solution increases significantly with increase in pH from 2 to 5, thereafter percentage removal decreases for further increase in pH. In the range of variables studied, percentage removal is increased from 50.44% to 93.9%. The maximum uptake capacity of 15.0797 mg/g is obtained at temperature 303 K. The kinetic studies show that the biosorption of lead is better described by pseudo second order kinetics It is also found that the data are well represented by Langmuir isotherm with higher correlation coefficient of 0.9944, followed by Freundlich and Temkin isotherms. The biosorption of lead on to *Casuarina* leaf powder is irreversible, spontaneous and endothermic in nature. 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 (95.73%) onto *Casuarina* leaf powder is observed when the processing parameters are set as follows: pH = 4.988, w = 35.37 g/L, C_o =18.0555 mg/L and T=306.47 K**.** Therefore the above said *Casuarina* leaf powder is effective and efficient biosorbent and is capable of removing lead.

Acknowledgements

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