Biosorption performance of Quisqualis Indica leaves powder for the removal of Lead and Statistical Optimization

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Abstract- *Environmental protection has gained tremendous scope now days by majority of countries through Green Revolution. The reason behind this comprises of Industrial pollution and eradication of green forests. The solution for the prominent problem has led researchers to various solutions where as biosorption has gained more momemtum and importance since its ease at handling. Biosorption handles a low-cost natural biosorbent for the removal of heavy metals like lead, etc. The present experimentation comprises of removing lead from industrial effluents using Quisqualis Indica leaf powder. The parameters involved in this study are biosorbent particle size, pH of the aqueous solution, biosorbent dosage, contact time, initial lead metal concentration and temperature. The biosorption was rapid and increased by the decrease in biosorbent particle size. The pH experiments showed that the significant biosorption takes place at a pH of 5. The increase in mass of biosorbent leads to increase in lead ion biosorption due to the increase in the number of biosorption sites. Experimental data were better described by pseudo-second-order model. The adsorption isotherms could be well fitted by the isotherms.*

Keywords- quisqualis indica, biosorption, Response Surface Methodology(RSM), Central Composite Design (CCD), Isotherms, Kinetics.

I. INTRODUCTION

Water is an essential ingredient for the existence of life. However, the large amounts of pollutants that fill our waterways each year are largely unknown. In recent days water pollution due to heavy metals is an issue of great environmental concern. Since the number of health problems associated with heavy metal contamination continuous to rise, the removal of these pollutants from wastewaters has received great attention. Heavy metal pollution occurs directly by effluents from industries, refineries and waste treatment plants and indirectly by the contaminants that enter the water supply from soils/ground water systems and from the atmosphere via rain water [1]. Mining and metallurgical waste waters are considered to be the major sources of heavy metal contamination [2]. Modern industry is, to a large degree

responsible for contamination of the environment. Lakes, rivers and oceans are being overwhelmed with many toxic contaminants. Among toxic substances reaching hazardous levels are heavy metals [3]. Removal and recovery of heavy metals are very important with respect to environmental and economical considerations [4]. Heavy metals cannot be destroyed chemically as organic pollutants. Therefore, several treatment technologies have been developed for eliminating heavy metal from solution such as chemical precipitation, ultra filtration, adsorption and ion exchange [5]. However, most of these methods may be ineffective, extremely expensive, generation of secondary pollution and ineffectiveness for low metal concentration. Hence, there is a crucial need for the development of a method that is not only cost effective and economic, but can be easily implemented [6]. The search for newer methods of removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials [7].It can be considered as an alternative technology in industrial wastewater treatment [8]. Some confusion has prevailed in the literature regarding the use of the terms "bioaccumulation" and "biosorption" based on the state of the biomass. Herein, therefore, bioaccumulation is defined as the phenomenon of living cells; whereas, biosorption mechanisms are based on the use of dead biomass [9]. The term 'biosorption' refers to the passive non metabolically– mediated process of metal binding by biomass [10]. The use of adsorbents of biological origin has emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies [11]. Thus this study is aimed to investigate the potential use of dead plant waste for the removal of lead. The parameters were optimized for all the lead metal sorption studies. Studies were performed on lead solution with Quisqualis Indica leaf powder as biosorbent.

II. MATERIALS AND METHODS

Preparation of Lead stock solution:

Pb(NO₃)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 ppm (mg/L) of lead stock solution. Synthetic lead samples 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 ppm 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 180 mg/L) are prepared.

Preparation of Quisqualis Indica leaves(red algae) powder

Quisqualis Indica leaves were collected from Visalakshinagar in Visakhapatnam. Quisqualis Indica leaves were washed thoroughly with water, distilled water and dried in sunlight. After completely drying the biosorbent, dry mass was grinded and the obtained powder was separated into different sizes (53, 75, 105, 125 and 152 μm) using BSS sieves. These size fractions were stored in air tight packing for further use as biosorbent.

Experimental Procedure

To 50 mL of the lead ion solution added 10 g/L of biosorbent in each of 250 mL Erlenmeyer flasks. The flasks were incubated in a shaker at a speed of 180 rpm for different agitation times (1, 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150, 180 min). The samples were filtered by Whatman filter paper and analyzed for lead concentration in an Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer AAnalyst 200 model).

Preliminary experimental runs for the biosorption of lead using Quisqualis Indica leaves powder has been developed by assigning five experimental modes, as listed below, varying one parameter and keeping the other four parameters constant for the equilibrium agitation time period of 25 min.

Batch 1: pH was varied as 2, 3, 4, 5, 6, 7 and 8. keeping the biosorbent dosage, biosorbent size, initial lead ion concentration and temperature constant. (t= 60 min)

Batch 2: Biosorbent size varied as 53, 75, 105, 125 and 152 μm , keeping the other parameters constant. (t= 25 min)

Batch 3: Initial Lead ion concentration was varied as 20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L, keeping the other parameters constant. (t= 25 min)

Batch 4: Keeping pH, biosorbent size, initial lead ion concentration and temperature as constants, the biosorbent

dosage was varied as 2 g/L, 5g/L, 10 g/L, 15 g/L, 20 g/L, 25 g/L, 30 g/L, 35 g/L, 40 g/L and 60 g/L. (t= 25 min)

Batch 5: The data was generated by keeping four variables constant and the temperature of the aqueous solution was varied as 283 K, 293 K, 303 K, 313 K and 323 K. (t= 25 min)

III. RESULTS AND DISCUSSION

Effect of agitation time:

The equilibrium agitation time is determined by plotting % biosorption of lead against agitation time in fig. 1 for the interaction time intervals of 1 min to 180 min. For 10 g/L of 53 μm size biosorbent, 20% (0.4 mg/g) of lead is biosorbed in the first min. The % biosorption is increased briskly up to 25 min reaching 60% (1.2 mg/g). From 25 min onwards, there is no change in biosorption indicating the attainment of equilibrium conditions. The rate of biosorption is fast because adequate surface area of the biosorbent is available for the biosorption of lead. As agitation time increases, more amount of lead is adsorbed onto the surface of the biosorbent due to Vanderwaal's forces of attraction and resulted in decrease of available surface area. The biosorbent, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the biosorbent is exhausted [12].
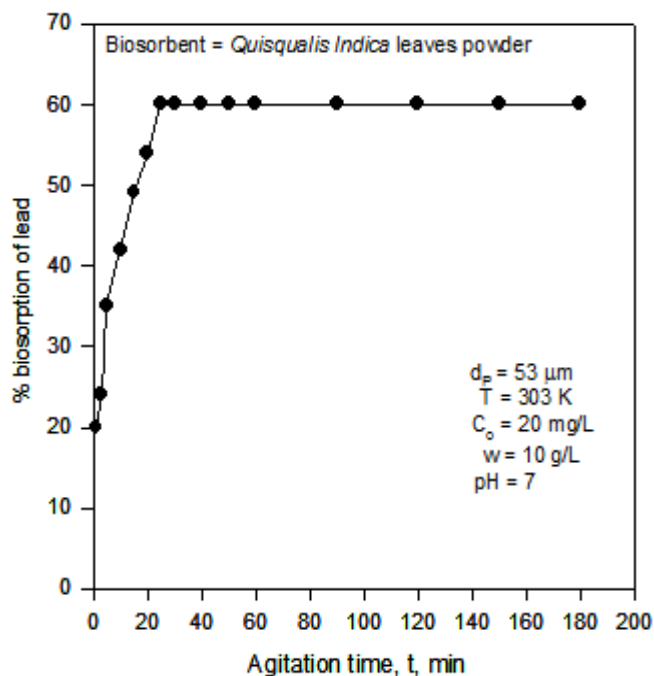

Effect of biosorbent size:

The variations in % biosorption of lead from the aqueous solution with biosorbent size (53, 75, 105, 125 and 152μm) are obtained. The results are drawn in fig. 2 with

percentage biosorption of lead on a function of biosorbent size. The percentage biosorption is increased from 40 to 60 % as the biosorbent size decreases from 152 to 53μm. This phenomenon is expected, as the size of the particle decreases, surface area of the adsorbent increases, thereby the number of active sites on the adsorbent are better exposed to the adsorbate [13].
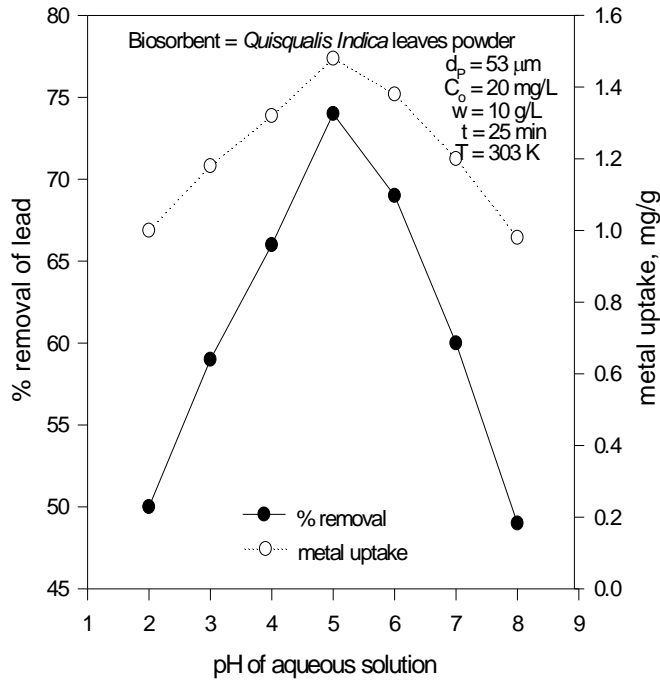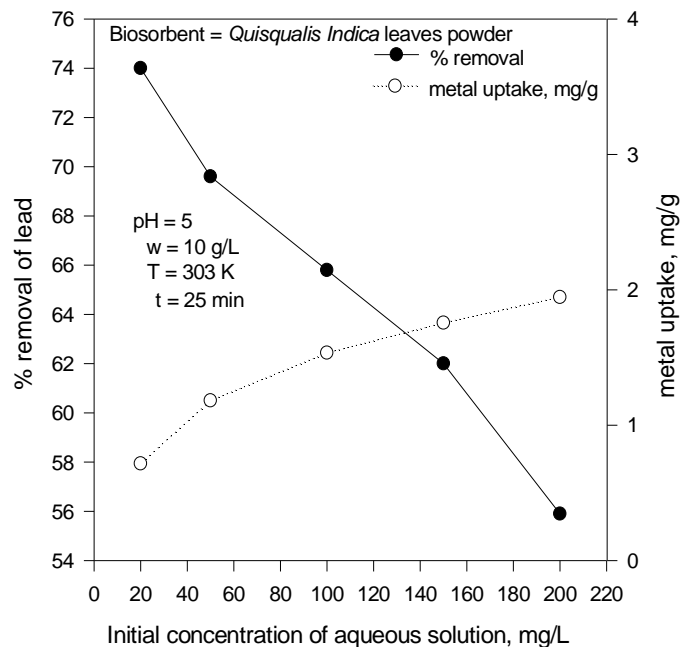

Effect of pH:

pH controls biosorption by influencing the surface change of the biosorbent, the degree of ionization and the species of adsorbate. In the present investigation, biosorption data are obtained varying of the aqueous solution pH in the range of 2 to 8 (C_o = 20 mg/L) using 10 g/L of 53μm size biosorbent. The effect of pH of aqueous solution on lead biosorption is drawn in fig. 3. The rate of biosorption is increased from 50 % (1.0 mg/g) to 74 % (1.48 mg/g) as pH is increased from 2 to 5 and biosorption decreased beyond pH value of 5. Low pH depresses biosorption of lead, 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 (or forming part of the surface functional groups such as –OH–, –SO_4–, etc) [14].
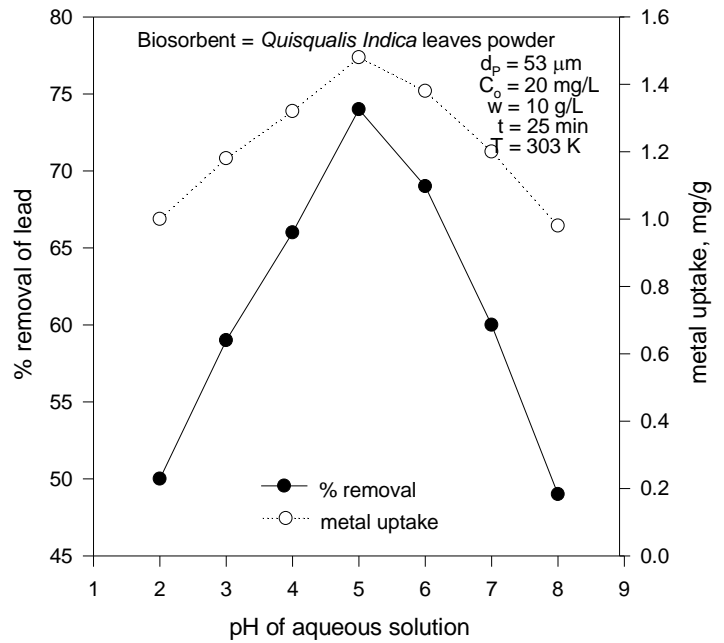
Effect of initial concentration of lead:

The effect of initial concentration of lead in the aqueous solution on percentage biosorption of lead is shown in fig. 4. The change in % biosorption is decreased as concentration is increasing from 20 to 200 mg/L. The percentage biosorption of lead is decreased from 74 % (0.716 mg/g) to 55.9 % (1.94 mg/g) with an increase in C_o from 20 to 200 mg/L. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the biosorbent [15].

Effect of biosorbent dosage:

The percentage biosorbent of lead is drawn against biosorbent dosage for 53 μm size biosorbent in fig. 5. The biosorption is increased from 74 % (1.48 mg/g) to 89% (0.445 mg/g) with an increase in biosorbent dosage from 2 to 40 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 89% (0.445 mg/g) to 91% (0.3033 mg/g) when 'w' is increased from 40 to 60 g/L. Hence all other experiments are conducted a 40 g/L dosage [16].
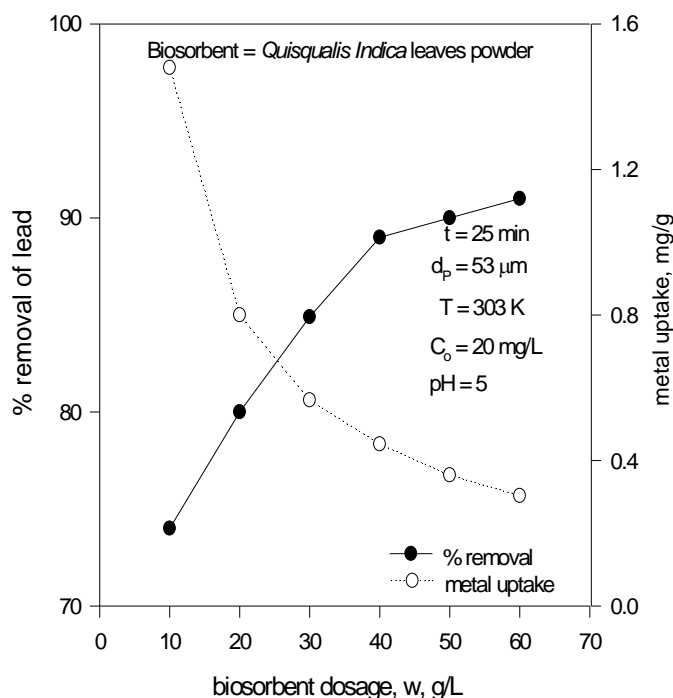

Effect of Temperature:

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 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 [17].
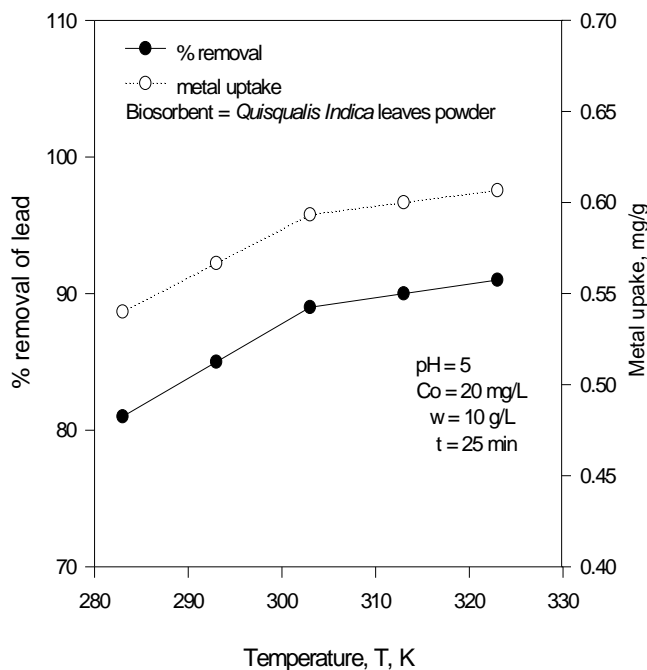
IV. OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY (RSM)

Optimization of biosorption conditions using CCD

The optimum condition for the four independent variables on the extent of lead biosorption is formed within the quadratic model. Levels of different process variables for percentage biosorption are shown in table–1. Regression equation for the optimization of biosorption is:

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

Table-2 represents
- ✓ Response based on experimental runs
- ✓ Relative in variations coded values of four parameters
- ✓ Predicted values proposed by CCD design

Table–1
Levels of different process variables in coded and un-coded form for % biosorption of Lead using Quisqualis Indica leaves powder

Variable	Name	Range and levels				
		-2	-1	0	1	2
X_1	pH of aqueous solution	3	4	5	6	7
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30
X_3	Biosorbent dosage, w, g/L	20	30	40	50	60
X_4	Temperature, T, K	283	293	303	313	323

Table–2

pH	Concentration	Dosage	Temperature	Observed	Predicted
4	15	30	293	87.2	54.7467
4	15	30	313	88.6	22.9333
4	15	50	293	88.8	288.7033
4	15	50	313	89.8	57.4700
4	25	30	293	84	17.8933
4	25	30	313	85.4	185.6900
4	25	50	293	85.2	52.2000
4	25	50	313	87	20.5767
6	15	30	293	86.4	20.6433
6	15	30	313	87.8	188.2000
6	15	50	293	88.2	55.2500
6	15	50	313	89.6	23.3867
6	25	30	293	87.2	186.9500
6	25	30	313	88.2	554.1167
6	25	50	293	88.4	21.9067
6	25	50	313	89.8	189.6533
3	20	40	303	81.6	47.1733
7	20	40	303	82.8	182.1467
5	10	40	303	93.5	58.6333
5	30	40	303	88.4	188.0467
5	20	20	303	88.8	187.1433
5	20	60	303	90.2	56.6367
5	20	40	283	91	57.2233
5	20	40	323	94.6	193.1567
5	20	40	303	94.5	93.5667
5	20	40	303	94.5	93.5667
5	20	40	303	94.5	93.5667
5	20	40	303	94.5	93.5667
5	20	40	303	94.5	93.5667
5	20	40	303	94.5	93.5667

Regression Equation:

$$Y = -13296.08 - 1533.03 X_1 - 318.71 X_2 + 187.02 X_3 - 69.45 X_4 + 5.27 X_1^2 + 0.30 X_2^2 + 0.07 X_3^2 + 0.08 X_4^2 + 10.16 X_1X_2 - 4.98 X_1X_3 + 4.98 X_1X_4 - 1.0 X_2X_3 + 1.0 X_2X_4 - 0.5 X_3X_4 --- (2)$$

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 (% biosorption of lead) lowers with an increase in effect. Most desirable set conditions for maximum percentage biosorption of lead are pH =5.0191, biosorption dosage (w) = 42.3150 g/L, initial lead concentration (C_o) =17.9782 mg/L and temperature = 309.1499 K. The intensity of biosorption of lead calculated at these desirable conditions is 94.89%. The experimental values are in good conjugation with predicted values.

Table–3
ANOVA of BPB dye biosorption for entire quadratic model

Source of variation	SS	df	Mean square(MS)	F-value	P > F
Model	386.8042	14	27.6288	45541.978	0.00000
Error	0.0091	15	0.0006066		
Total	386.8133	29			

Interpretation of residual graphs:

Normal probability plot (NPP) is a graphical technique used for analyzing whether or not data set is normally distributed to greater extent. This NPP plot is used to check normality of data obtained. The difference between the observed and the predicted values from the regression can be termed as residual. Fig. 6 & 7 exhibits normal probability plot for the present data. It is evident that the experimental data are reasonably aligned implying normal distribution.

Fig 6. Pareto Chart

Fig. 7 Normal probability plot

Interaction effects of biosorption variables:

Three-dimensional view of response surface plots [Fig. 8 (a) to (f)] exhibit % biosorption of the lead using Quisqualis Indica leaves powder for different combinations of independent 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 plots that the % biosorption of lead is maximal at low and high levels of the variables.   But a dead region prevails where increasing or decreasing trend in % biosorption is not found. This behavior conforms that there is a presence of optimum for the biosorption variables in order to maximize % biosorption. The role played by all the variables are so vital in % biosorption of lead and seen clearly from the plots.
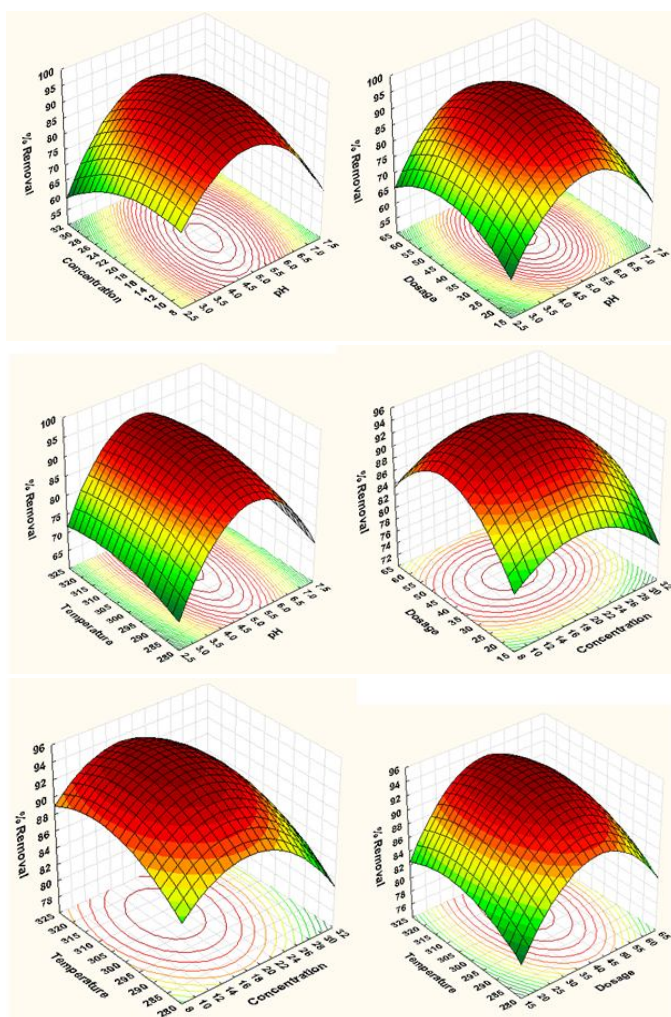
Fig. 8 (a) to (f)

Critical values

The predicted optimal set of conditions for maximum percentage biosorption of lead is:

pH of aqueous solution= 5.0191,
biosorption dosage = 17.9782 g/L,
Initial lead ion concentration = 42.3150 mg/L and
Temperature = 309.1499 K.
The extent of biosorption of lead at these optimum conditions is 94.89045 %.

It is evident that experimental values of % biosorption are in close agreement with that of predicted by Central Composite Design.   Experiments are conducted in triplicate with the above predicted optimal set of conditions and the % percentage biosorption of lead is 94.89 %, which is closer to the predicted % biosorption.

V. ISOTHERMS

Langmuir isotherm:

Langmuir isotherm [18–19] is the most widely used simple two- parameter equation.

From the plots between (C_e/q_e) and C_e, the slope $\{1/(K_L q_m)\}$ and the intercept $(1/q_m)$ can be calculated.
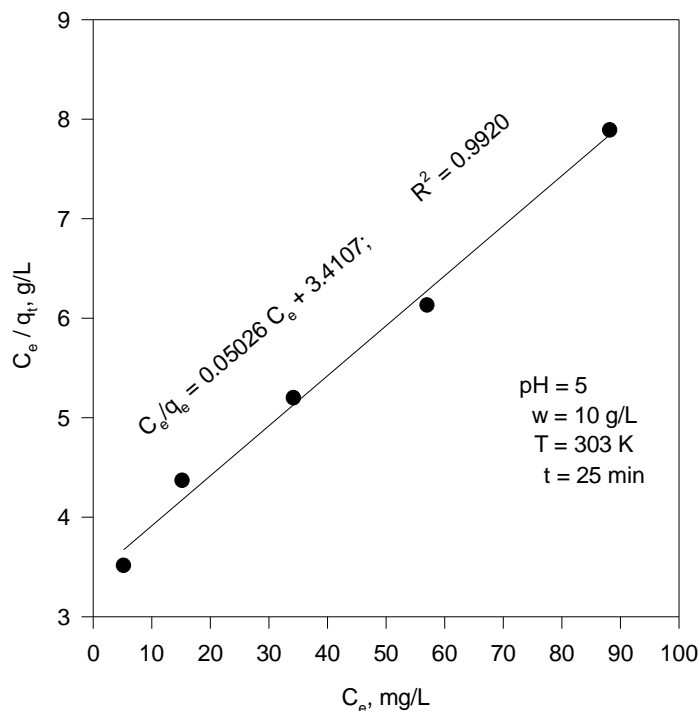

Fig. 9. Langmuir isotherm for % biosorption

Freundlich isotherm:

Freundlich [20] presented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges.
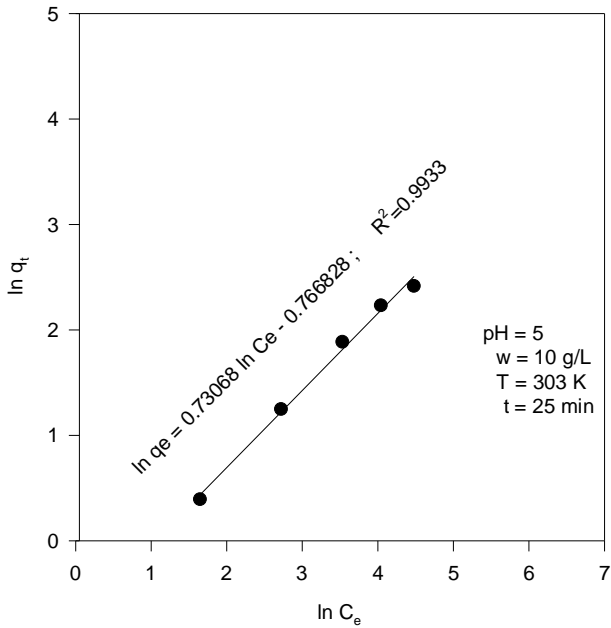
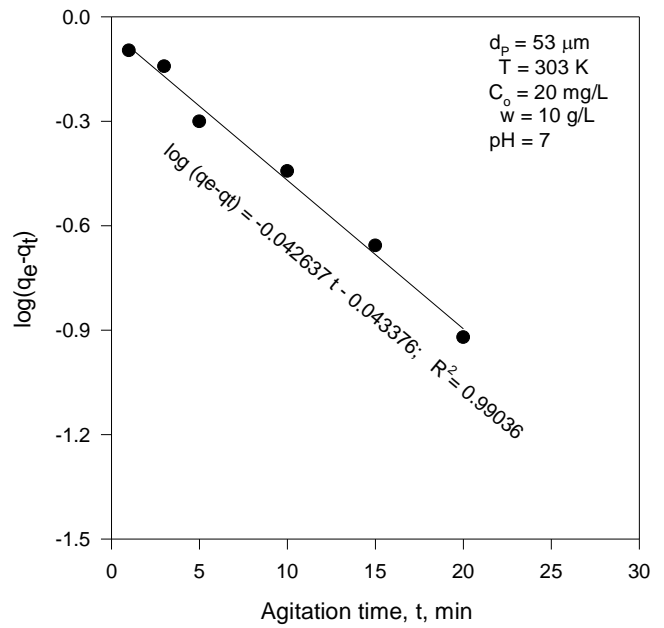Fig. 10 Freundlich isotherm for % biosorption

Temkin isotherm:

Temkin and Pyzhev isotherm **[21]** equation describes the behavior of many adsorption systems on the heterogeneous surface.
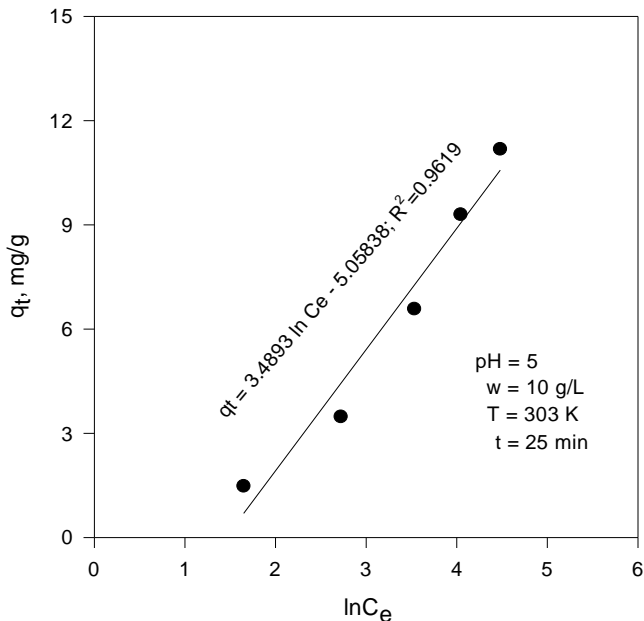

Fig. 11. Temkin isotherm for % biosorption

VI. KINETICS

The order of adsorbate – adsorbent interactions have been described using kinetic models. Traditionally, the Lagergren first order model **[22]** finds wide application.

Fig. 12. Lagergren First order Kinetics for % biosorption

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 20 mg/L) at 303 K in the interaction time intervals of 1 min to 25 min. Lagergren plot of log (q_e-q_t) vs 't' and plot between (t/q_t) and 't' for 53 μm are drawn in figs. 14 & 15 respectively. The resulting equations and constants are shown in table – 6. As the correlation coefficient value for the pseudo second order kinetics is 0.99, we can say that the pseudo second order kinetics describes the mechanism of lead – *Quisqualis Indica leaves*powder interactions better.
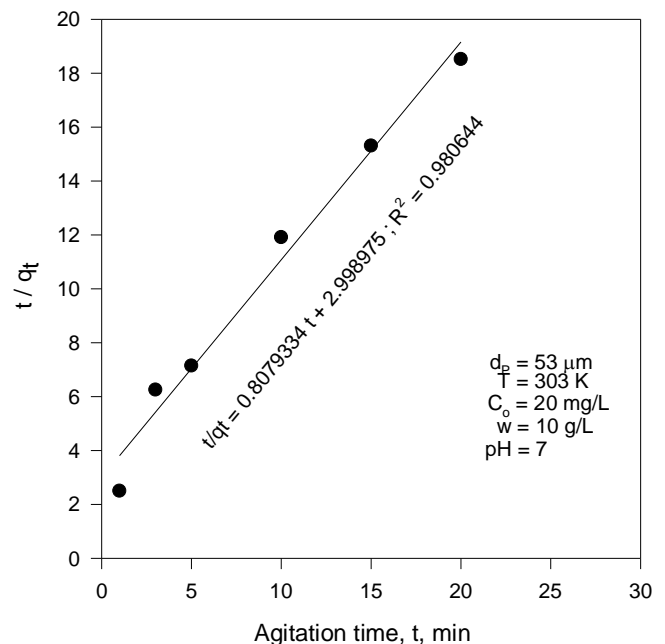

Fig. 13 Pseudo second order kinetics for % biosorption

VII. THERMODYNAMICS OF BIOSORPTION

In general, the temperature dependence of biosorption 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) [23].

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

A graph between $\log (q_e/C_e)$ and $(1/T)$, gives a slope of $-(\Delta H/2.303\,R)$ and an intercept of $\Delta S/2.303\,R$. Experiments are conducted to understand the biosorption behavior with temperature. The % biosorption increases with increase in temperature of aqueous solution. The Vant Hoff plot in fig. 16 for the present data indicates the effect of temperature on biosorption of lead. The equation obtained is:

$$\log (q_e/C_e) = -0.280\,(1/T) + 0.668 \qquad R^2 = 0.962$$

The values of ΔS, ΔG and ΔH in the present investigation are $\Delta H = 4.212$ J/mole, $\Delta S = 9.228$ J/mole-K and $\Delta G = -2791.872$ J/mole.

In the present study, 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.
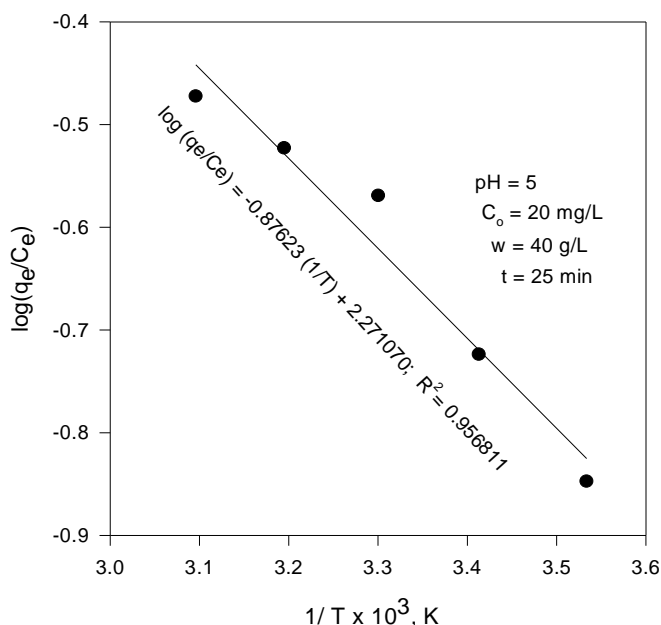

Fig. 14 Vantoff's plot for % biosorption

VIII. CONCLUSIONS

The present study involves the use of statistical experimental design to optimize process conditions for maximal biosorption of lead from aqueous solutions. These parameters were optimized using CCD involving RSM, pH of aqueous solution= 5.0191, biosorption dosage = 42.3150 g/L, Initial lead ion concentration = 17.9782 mg/L and Temperature = 309.1499 K. The significant interactions between the five parameters were observed from the contour plots. The maximum biosorption of lead (94.89%) onto *Quisqualis Indica leaves* powder was observed when the processing parameters were set as follows: pH = 5., biosorption dosage = 40.0 g/L), initial concentration of lead in aqueous solution = 20.0 mg/L and temperature = 30 ^{o}C at single step optimization. This methodology could therefore be effectively used to study the importance of individual, cumulative and interactive effects of the test parameters in biosorption and other processes. The experiment conducted at above optimum values of pH, biosorption dosage, biosorbent size, initial concentration of lead in aqueous solution and temperature yielded 94.89% biosorption of lead.

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