International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1413-1420, April-June 2013

Application Of Response Surface Methodology For The Biosorption Of Lead Using Grewia Orbiculata

Rakesh Namdeti*, King Pulipati

Environmental Pollution Control Engineering Laboratory, Department of Chemical Engineering, Andhra University College of Engineering, Visakhapatnam-530 003, A.P, India.

***Corres. author : rakesh_nandeti@yahoo.co.in ,Ph: +91-9949402042.**

Abstract: Response surface methodology was used to study the cumulative effect of the various parameters namely, temperature, pH, biosorbent loading, initial lead ion concentration and to optimize the process conditions for the maximum removal of lead. For obtaining the mutual interaction between the variables and optimizing these variables, a 2^4 full factorial central composite design using response surface methodology was employed. The analysis of variance (ANOVA) of the quadratic model demonstrates that the model was highly significant. The model was statistically tested and verified by experimentation. A maximum lead removal of 83.7% was obtained using the biosorption kinetics of lead under optimum conditions.
Keywords: Biosorption; *Grewia Orbiculata*; Design of experiments; Central composite design; Response surface methodology.

Introduction

With rapid industrial development, problems related to pollution are becoming severe. Unfavorable alterations in the environment result in change of energy flow in the universe, and also in its chemical and physical composition. It adversely affects human life through water resources, agriculture and biological products[1]. Heavy metals present in the industrial effluents remain as alarming pollutants due to their nondestructive nature, toxicity, bioaccumulation and subsequent biomagnifications[2]. Lead (Pb) is one of the most important heavy metals, since it poses a great danger for humans, if accumulated in larger amounts. Petrol combustion globally contributes an estimated 60% of total lead emission. Auto-exhaust lead pollution is the main route to introduce lead in soil and vegetation[3] Lead is widely used in battery manufacturing, printing, pigments, fuels, photographic materials and paint industry[4,5]. There is an increasing trend in the use of plant biomass for removal and possible recovery of metal ions from industrial wastes by biosorption. This is a potential alternative to existing technologies (chemical precipitation, reverse osmosis and solvent extraction), which have significant disadvantages, such as high chemical or energy requirements and generation of toxic sludge or other products that need disposal[6]. Biosorption is an innovative technology using inactive and dead biomasses to remove heavy metals from aqueous solutions. This biological phenomenon could be explained by considering different kinds of chemical and physical interactions among the functional groups present in the cell wall and the heavy metals in solution[7]. The biosorbent used in this study is Grewia Orbiculata leaves powder, in which the adsorption takes place on surface of insoluble cell walls of the leaves. The insoluble cell walls of the Grewia Orbiculata leaves are largely made up of cellulose and hemi celluloses, lignin, condensed tannins and structural proteins[8].

This work is primarily aimed at evaluating the effects of temperature, pH, biosorbent loading, initial lead ion concentration on the percentage removal of lead and statistically optimizing these variables for maximum removal of lead efficiently and economically. The application of statistical experimental design in biosorption techniques, results in higher percentage yields, less treatment time with minimum costs. Most optimization studies during the development of a process involve variation of one factor at a time, keeping all other factors constant. But the experiments conducted using the factorial designs, enable all factors to vary simultaneously. This helps in quantifying linear, square and interactive effects of the test variables. Another important advantage is that, the experimental designs could be changed progressively until a fitted model is found to describe the studied phenomenon[9,10]. Response surface methodology (RSM) is an empirical statistical technique employed for multiple regression analysis of quantitative data obtained from statistically designed experiments by solving the multivariate equations simultaneously. The graphical representation of these equations are called as response surfaces, could be used to describe the individual and cumulative effect of the test variables on the response and to determine the mutual interaction between the test variables and their subsequent effect on the response[11,12]. In this study, 2^4 full factorial central composite design using response surface methodology was employed.

Experiment

The *Grewia Orbiculata* L. leaves were collected near K.L University campus of Guntur, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt particles. Then the dried leaves were powdered using domestic grinder and the powder size of 75-212 μm, which were used as biosorbent without any pretreatment for lead adsorption. Analytical grades of Pb $(NO_3)_2$, HCl and NaOH were purchased from Merck (Mumbai, Maharastra, India). Lead ions were prepared by dissolving its corresponding nitrate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and NaOH.

Central composite design (CCD)

With the identification of the parameters having the statistically significant influence on the response a CCD[13] was used to optimize the levels of these parameters. The full CCD, based on three basic principles of an ideal experimental design, primarily consists of (i) a complete 2^n factorial design, where n is the number of test parameters, (ii) n_o center points ($n_o \geq 1$) and (iii) two axial points the axis of each design parameters at a distance of $2^{n/4}$ from the design center. The total number of design points is $N= 2^n+2n+n_o$. For statistical calculations, the parameters X_i are coded as x_i according to Eq. (1):

$$X_i = X_i - x_i / \Delta x_j \quad (i=1, 2, 3, \ldots.k) \qquad (1)$$

where x_i is dimensional value of an independent parameter, X_i is the real value of an independent parameter, x_i^- is the real value of the independent parameter at the center point and x_j is the step change. The second degree polynomials (Eq. 2) are calculated with the statistical package STATISTICA 6.0 (Stat-Ease Inc., Tulsa, OK, USA) to estimate the response of the dependent variable:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2$$

$$+ b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \qquad (2)$$

Where Y is predicted response, X_1, X_2, X_3,X_4 are independent parameter,b_0 is offset term, b_1, b_2, b_3, b_4 are linear effects , b_{11}, b_{22}, b_{33}, b_{44} are squared effects and b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, b_{34} are interaction terms.

Results and Discussion

Optimization of the Selected Parameters Using CCD

The experiments with different pH values of 2– 10, different lead concentrations of 20–100 mg/L, different biosorbent dosages of 0.1–0.5 g/L and different temperatures of 30–50 ^{0}C were coupled to each other and varied simultaneously to cover the combination of parameters in the CCD. The levels and ranges of the chosen independent parameters used in the experiments for the removal of lead were given in **Table 1.** A 2^4 – factorial CCD design, with eight axial points ($\alpha = \sqrt{4}$) and six replications at the center points (*n*o=6) leading to a total number of 30 experiments (Table 2) was employed for the optimization of the parameters. The calculated regression equation for the optimization of medium constituents showed that percentage removal of lead (Y) was function of the temperature (X_1), pH (X_2), biosorbent loading (X_3) and initial concentration (X_4). Multiple regression analysis of the experimental data resulted in the following equation for the biosorption of lead:

$$Y = -333.349 + 21.237X_1 - 7.397X_2 + 17.138X_3 + 0.535X_4 - 0.299X_1^2 - 2.209X_2^2 - 145.938X_3^2 - 0.007X_4^2 + 0.516X_1X_2 - 0.035X_1X_3 - 0.003X_1X_4 + 12.8X_2X_3 + 0.078X_2X_4 - 0.051X_3X_4 \quad (3)$$

The coefficients of the regression model were calculated and listed in Table 3. They contain one block term, four linear, four quadratic and six interaction terms. The significance of each coefficient was determined by student's *t*-test and *p*-values and listed in **Table 3.** The larger the magnitude of the *t*-value and smaller the *p*-value, the more significant was the corresponding coefficient. This implies that the linear, quadratic and interaction effects of temperature, pH, biosorption dosage and initial concentration of lead are highly significant as is evident from their respective *p*-values in (**Table 3).** The parity plot (Figure 1) showed a satisfactory correlation between the experimental and predicted values of percentage removal of lead indicating good agreement of model data with the experimental data. The results of the second order response surface model, fitting in the form of ANOVA were shown in **Table 4**. The Fisher variance ratio, the *F*-value (= S_r^2 / S_e^2), is a statistically valid measure to test the significance and adequancy of the model. The greater the *F*-value above unity, it is more certain that the factors adequately explain the variation in the data about its mean, and the estimated factor effects are real. The ANOVA of the regression model demonstrated that the model was highly significant, as is evident from the Fisher's *F*-test (*F*model = 374.11) and a very low probability value (*P*model > *F*=0.000000). More ever, the computed *F*-value ($F_{0.05(14.15)} = S_r^2/Se^2 = 374.11$) was greater than the tabular *F*-value ($F_{0.05(14.15)\ tabulars} = 2.46$) at the 1% level, indicating that the treatment differences were significant. 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 this present study, the value of the correlation coefficient (R^2 = 0.9979) indicated that 99.79 % of the variability in the response could be explained by the model. In addition, the value of the adjusted correlation coefficient (Adj R^2 = 0.9952) was also very high to advocate for a high significance of the model. The response surface plots of percentage biosorption of lead versus the interactive effect of pH, initial lead concentration, biosorbent dosage and temperature were shown **in the Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, and Figure 7.**

Each response plot represents a number of combinations of two test parameters with the other parameter maintained at zero levels. The maximum percentage biosorption of level is indicated by the surface confined in the smallest curve (circular or elliptical) of the response plot. The optimal set of conditions for maximum percentage biosorption of lead is pH = 4.72, initial concentration of lead in aqueous solution = 58.523 mg/L, biosorbent dosage = 0.271 g/L and temperature = 39.23^{0}C. The extent of biosorption of lead at these optimum conditions was 83.775%. The optimum values of variables for lead biosorption from regression equation were shown **in table 5.**

Table.1. Experimental range and levels of the independent parameters for lead biosorption onto *Grewia Orbiculata* L.:

Independent Parameters	Range and Level				
	-2	**-1**	**0**	**+1**	**+2**
Temperature (X_1), K	30	35	40	45	50
pH (X_2)	3	4	5	6	7
Adsorbent Dosage(X_3), g/L	0.1	0.2	0.3	0.4	0.5
Initial Concentration (X_4), mg/L	20	40	60	80	100

Table 2: CCD matrix showing coded and real values along with the observed and predicted values for percentage biosorption of lead with *Grewia Orbiculata* L.:

Run no.	Coded values				Real values				% Biosorption of zinc	
	x_1	**x_2**	**x_3**	**x_4**	**X_1**	**X_2**	**X_3**	**X_4**	**Observed**	**Predicted**
1	-1	-1	-1	-1	35	4	0.2	40	77.13	77.26292
2	-1	-1	-1	1	35	4	0.2	80	74.85	74.53125
3	-1	-1	1	-1	35	4	0.4	40	73.06	73.58292
4	-1	-1	1	1	35	4	0.4	80	71.13	71.26125

5	-1	1	-1	-1	35	6	0.2	40	65.67	65.75125
6	-1	1	-1	1	35	6	0.2	80	68.99	69.24958
7	-1	1	1	-1	35	6	0.4	40	67.59	67.19125
8	-1	1	1	1	35	6	0.4	80	71.19	71.09959
9	1	-1	-1	-1	45	4	0.2	40	69.15	69.50792
10	1	-1	-1	1	45	4	0.2	80	64.97	65.62625
11	1	-1	1	-1	45	4	0.4	40	65.76	65.75792
12	1	-1	1	1	45	4	0.4	80	62.1	62.28625
13	1	1	-1	-1	45	6	0.2	40	68.19	68.31625
14	1	1	-1	1	45	6	0.2	80	70.92	70.66458
15	1	1	1	-1	45	6	0.4	40	69.1	69.68625
16	1	1	1	1	45	6	0.4	80	72.32	72.44458
17	-2	0	0	0	30	5	0.3	60	56.7	56.8025
18	2	0	0	0	50	5	0.3	60	51.02	50.3925
19	0	-2	0	0	40	3	0.3	60	75.95	75.37917
20	0	2	0	0	40	7	0.3	60	73.98	74.02583
21	0	0	-2	0	40	5	0.1	60	78.91	78.6525
22	0	0	2	0	40	5	0.5	60	77.02	76.7525
23	0	0	0	-2	40	5	0.3	20	72.98	72.53917
24	0	0	0	2	40	5	0.3	100	72.65	72.56583
25	0	0	0	0	40	5	0.3	60	83.54	83.54
26	0	0	0	0	40	5	0.3	60	83.54	83.54
27	0	0	0	0	40	5	0.3	60	83.54	83.54
28	0	0	0	0	40	5	0.3	60	83.54	83.54
29	0	0	0	0	40	5	0.3	60	83.54	83.54
30	0	0	0	0	40	5	0.3	60	83.54	83.54

X_1= Temperature, X_2= pH, X_3= Biosorbent loading, X_4= Initial Concentration

Table.3. Coefficients, t-statististics and significance probability of the model for biosorption of lead onto *Grewia Orbiculata* L.:

Term	Coefficient	Value	Standard error of coefficient	t-value	p-value
Constant	b_0	-333.349	12.60581	-26.4441	0.000000[a]
X_1	b_1	21.237	0.41757	50.8572	0.000000[a]
X_1^2	b_{11}	-0.299	0.00479	-62.4747	0.000000[a]
X_2	b_2	-7.397	1.65237	-4.4766	0.000937[a]
X_2^2	b_{22}	-2.209	0.11982	-18.4394	0.000000[a]
X_3	b_3	17.138	14.36005	1.1934	0.257811
X_3^2	b_{33}	-145.938	11.98185	-12.1799	0.000000[a]
X_4	b_4	0.535	0.07180	7.4463	0.000013[a]
X_4^2	b_{44}	-0.007	0.00030	-22.9253	0.000000[a]
$X_1 * X_2$	b_{12}	0.516	0.02503	20.6159	0.000000[a]
$X_1 * X_3$	b_{13}	-0.035	0.25029	-0.1398	0.891317
$X_1 * X_4$	b_{14}	-0.003	0.00125	-2.2973	0.042231[a]
$X_2 * X_3$	b_{23}	12.800	1.25146	10.2280	0.000001[a]
$X_2 * X_4$	b_{24}	0.078	0.00626	12.4454	0.000000[a]
$X_3 * X_4$	b_{34}	0.051	0.06257	0.8190	0.430151

X_1= Temperature, X_2= pH, X_3= Biosorbent dosage, X_4= Initial Concentration.

[a]Significant ($p \leq 0.05$)

Table.4. ANOVA for the entire quadratic model for biosorption of lead onto *Grewia Orbiculata* L.:

Source of variation	Sum of squares (SS)	Degrees of freedom (D.F)	Mean squares (MS)	F-value	Probe>F
Model	1312.535	14	93.752	374.11	0.00000
Error	2.756	15	0.2506		
Total	1315.29	29			

R^2= 0.9979; Adjusted R^2= 0.9952

$F_{0.01(14,15)} = Sr^2 / Se^2 = 374.11 > F_{0.01(14,15)}$Tabular = 2.46

Pmodel > F = 0.000000

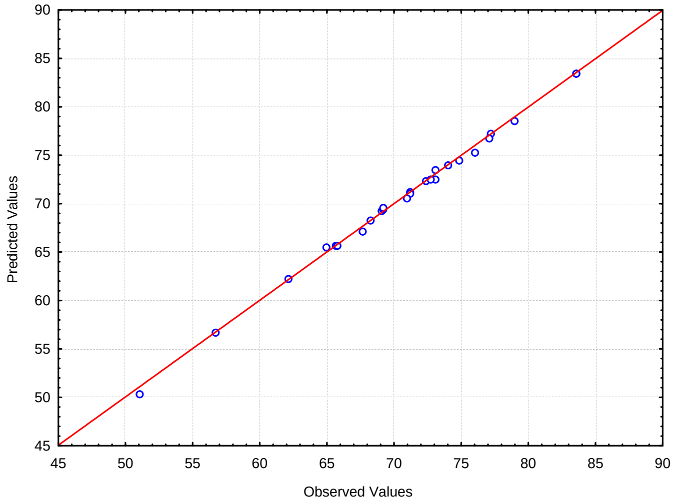

Figure.1. Parity plot showing the distribution of observed vs. predicted values of percentage biosorption of lead with *Grewia Orbiculata* L.

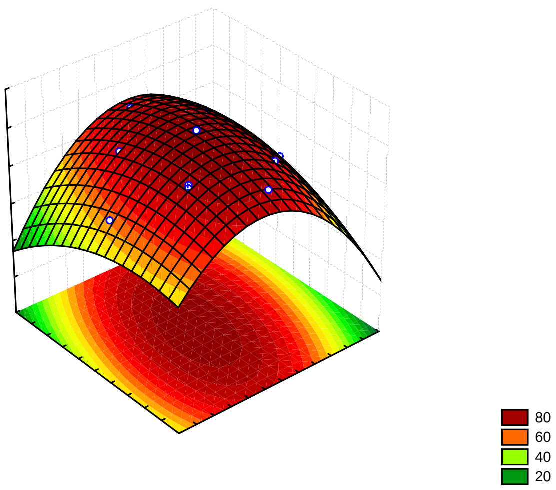

Figure.2. Response surface plot of the effects of pH and temperature on percentage biosorption of lead by *Grewia Orbiculata* L.

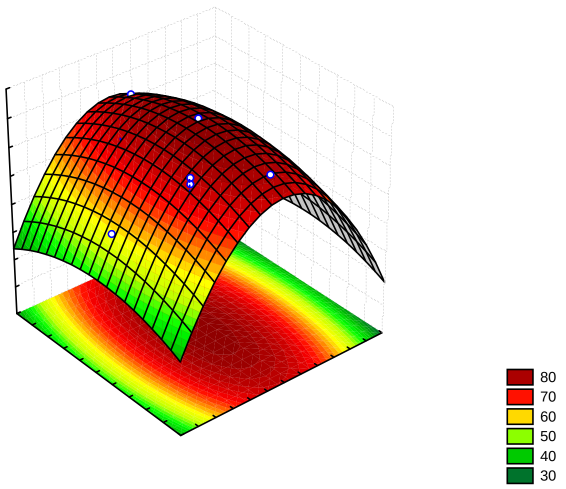

Figure.3. Response surface plot of the effects of biosorbent dosage and temperature on percentage biosorption of lead by *Grewia Orbiculata* L.

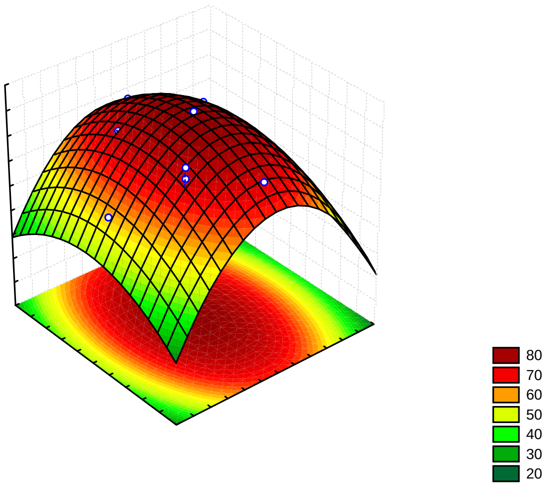

Figure.4. Response surface plot of the effects of inicial metal concentration and temperature on percentage biosorption of lead by *Grewia Orbiculata* L.

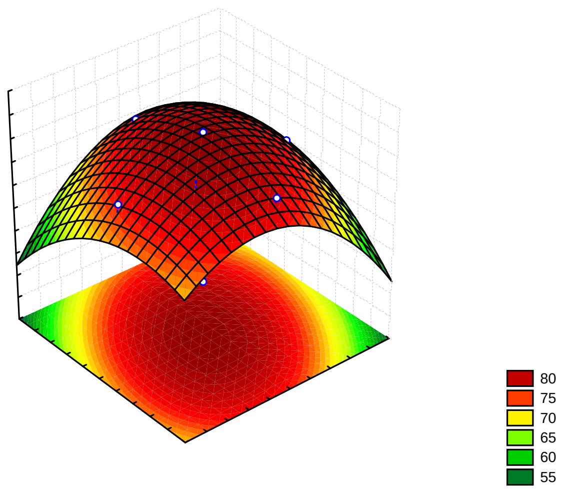

Figure.5. Response surface plot of the effects of biosorbent dosage and pH on percentage biosorption of lead by *Grewia Orbiculata* L.

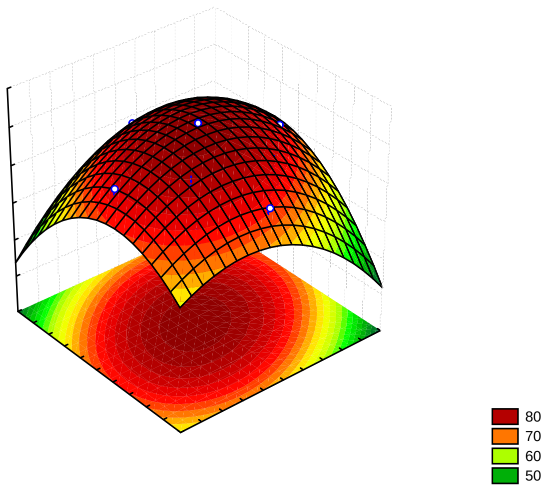

Figure.6. Response surface plot of the effects of inicial metal concentration and pH on percentage biosorption of lead by *Grewia Orbiculata* L.

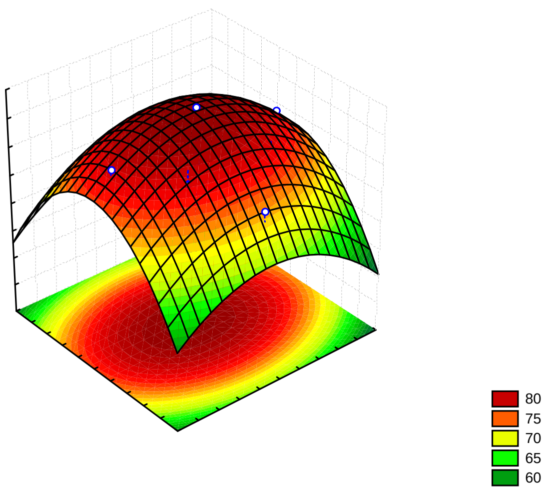

Figure.7. Response surface plot of the effects of inicial metal concentration and biosorbent dosage on percentage biosorption of lead by *Grewia Orbiculata* L.

Table.5. Optimum values of variables obtained from regression equations for the removal of lead by *Grewia Orbiculata* L.:

Parameter	Optimum value for lead
Temperature, ^{0}C	39.23
pH	4.72
Biosorbent loading, g	0.27
Initial lead concentration, mg/L	58.52

Conclusion

This work has demonstrated the use of a full factorial central composite design by determining the optimum process conditions leading to the maximum percentage removal of lead from aqueous solutions. Using this experimental design and multiple regressions, the parameters namely, temperature, pH, biosorbent loading, initial lead ion concentration were studied effectively and optimized with a lesser number of experiments. This methodology could therefore be successfully employed to study the importance of individual, cumulative and interactive effects of the test variables in biosorption and other processes.

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