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Response surface methodology as an optimizing tool for removal of mercury from aqueous solution using *Ficus Hispida* L.

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ABSTRACT

Response surface methodology involving a 2^4 full factorial central composite design was used to optimize the biosorption process of mercury by *Ficus Hispida* L. Influence of various parameters such as temperature, pH, biosorbent loading and initial mercury concentration on biosorption process was investigated. From the analysis of variance (ANOVA) results, the significance of various factors and their influence on the response were identified. The regression coefficient (R^2) of the model was developed and the results of validation experiments conducted at optimum conditions for the removal of mercury indicate that the predicted values are in good agreement with the experimental results.

KEYWORDS

Biosorption;
Ficus Hispida;
Design of experiments;
CCD;
RSM.

INTRODUCTION

Industrial wastes and fertilizers can add excessive amount of heavy metals to the environment. Heavy metals even at very low concentrations are highly toxic, and pose a serious threat to biota and the environment[1]. Among the heavy metals mercury has the most damaging effects on human health. It can enter a human body through uptake of food (65%), water (20%) and air (15%)[2]. Continuous absorption of mercury may cause serious injuries to health such as encephalopathy, kidney damage and several others[3,4]. Several methods for the removal of toxic metals from wastewaters have been introduced and tried out[5]. Techno-economic considerations have restricted the wide scale application of these methods[6,7]. However; application of biosorption has been proved to be an effective way to heavy metal ions pollutions[1,3-6]. Successful metal biosorption, with a variety of biological materials including, microalgae, seaweeds, bacteria, fungi, crop residues, and papaya wood have been reported[8-10]. This study verifies a new biomass as metal sorbent, and demonstrates its potential for efficient removal of Mercury from aqueous solution. *Ficus Hispida* tree leaves are in great supply, inexpensive and easily available. These leaves have no commercial usage and are not eaten by livestock. Factors affecting metal ions uptake by a sorbent in a batch system include temperature, pH, biosorbent dosage, initial mercury ion concentration[10]. Thus several factors should be optimized. Here the major concern is the large number of experimental runs. To resolve this problem, some variables can be arbitrarily fixed. The application of statistical design especially, a 2^4 full factorial central composite design using response surface methodology was used for optimization of biosorption process has comparatively rarely been reported in literatures than other approaches such as industrial process or analytical research[10-13]. This study tries to develop an efficient method for achieving maximum removal of mercury ion in aqueous solutions. For this purpose, by using a 2^4 full factorial central composite design using response surface methodology was proposed[12-15].

EXPERIMENT

Preparation of biosorbent

The *Ficus Hispida* 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 ìm, which were used as biosorbent without any pretreatment for mercury biosorption.

Chemical

Analytical grades of mercury, HCl and NaOH were purchased from Merck (Mumbai, Maharastra, India). Mercury 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.

All the experiments were repeated five times and the average values have been reported. Also, blank experiments were conducted to ensure that no biosorption was taking place on the walls of the apparatus used.

Apparatus

An Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) was used for the determination of mercury ion concentration. Adsorbate pH and adsorbent weight were measured using a Systronics pH meter and a Shimatzu electronic balance.

Batch biosorption experiments

Experimental mercury solutions of desired concentrations were prepared from the stock solution with the appropriate dilutions and the pH was adjusted to 6.1 with hydrochloric acid and sodium hydroxide.

The effect of agitation time with different initial concentration of Mercury was studied by agitating 30 ml of different concentrations of metal solution with 0.1g of adsorbent of size 75 ìm at 180 rpm for 1 h. At the end of predetermined time intervals the sorbent was separated by centrifugation and the Mercury remaining in solution was analyzed by Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia). The same spectrophotometric method was used in the subsequent experiments. The amount of metal adsorbed by *Ficus Hispida* L. was calculated from the differences between metal quantity added to the adsorbent biomass and metal content of the supernatant using the following equation:

$$q=(C_0-C_f)\frac{V}{M} \quad (1)$$

Where q is the metal uptake (mg/g); C_0 and C_f the initial and final metal concentrations in the solution (mg/L), respectively; V the solution volume (mL); M is the mass of adsorbent (g).

Central composite design (CCD)

With the identification of the parameters having the statistically significant influence on the response a CCD[16] 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_oe"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. (2):

$$X_i = X_i - x_i / Äx_j \,(i=1, 2, 3, ….k) \quad (2)$$

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. 3) are calculated with the statistical package STATISTICA 6.0 (Stat-Ease Inc., Tulsa, OK, USA) to estimate the response of the dependent variable:

$$\begin{aligned} Y = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 \\ & + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 \\ & + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \end{aligned} \quad (3)$$

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.

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RESULTS AND DISCUSSION

Development of regression model equation

In the present study, CCD for four variables (temperature, pH, bbiosorbent dosage, Initial ion concentration), each with five levels (±1 for the factorial points, 0 for the center points and ±_for the axial points), was used as the experimental design model. The model has the advantage that it permits the use of relatively few combinations of variables for determining the complex response function[17]. A total of 30 experimentswere required to be performed to calculate 14 coefficients of the second order polynomial equation. The biosorption of mercury ion estimated as biosorption capacity of *Ficus Hispida* was taken as the response of the system.

Optimization of the selected parameters using CCD

The experiments with different pH values of 2– 10, different mercury 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 mercury were given in TABLE 1. A 2^4 – factorial CCD design, with eight axial points (α= “4) and six replications at the center points (*n*o=6) mercurying 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 mercury (*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 mercury:

$$\begin{aligned}\mathbf{Y} &= \mathbf{-346.66 + 21.713X_1 + 0.548X_2}\\ &\mathbf{+ 4.213X_3 + 0.291X_4 - 0.304X_1^2}\\ &\mathbf{- 2.218X_2^2 - 134.896X_3^2 - 0.006X_4^2}\\ &\mathbf{+ 0.424X_1X_2 - 0.03X_1X_3 - 0.001X_1X_4}\\ &\mathbf{+ 12.825X_2X_3 + 0.077X_2X_4 + 0.12X_3X_4}\end{aligned} \qquad \mathbf{(4)}$$

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 mercury 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 mercury 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 = 153.918) 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

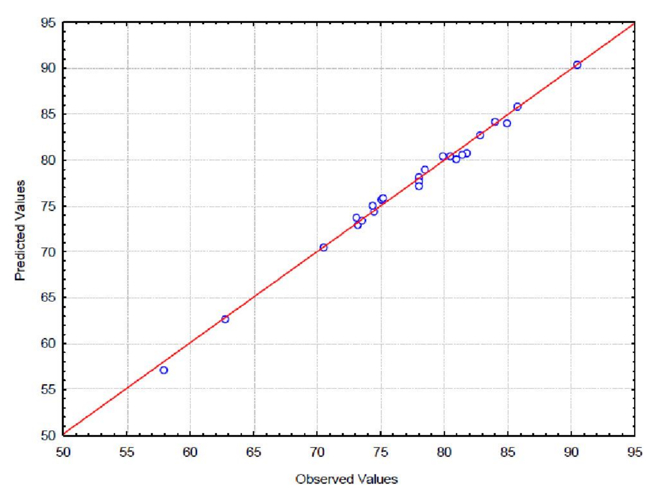

Figure 1 : Parity plot showing the distribution of observed vs. predicted values of percentage biosorption of mercury with *Ficus Hispida* L.

better. In this present study, the value of the correlation coefficient (R^2 = 0.9949) indicated that 99.49 % of the variability in the response could be explained by the model. In addition, the value of the adjusted correlation coefficient (Adj R^2 = 0.9884) was also very high to advocate for a high significance of the model. From TABLE 3 it was observed that the linear effects of X_1 ($p<0.05$) and X_4 ($p<0.05$) are more significant when compared to X_2 ($p=0.851$) and X_3 ($p=0.86$) and the coefficients X_1^2, X_2^2, X_3^2, X_4^2 are more significant as $p<0.05$. Among the interaction terms X_1X_2, X_2X_3 and X_2X_4 ($p<0.05$) were highly significant on the biosorption capacity.

TABLE 1 : Experimental range and levels of the independent parameters for mercury biosorption onto *Ficus Hispida* L.

Independent Parameters	Range and Level				
	-2	**-1**	**0**	**+1**	**+2**
Temperature (X_1), K	30	35	40	45	50
pH (X_2)	4	5	6	7	8
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 mercury with *Ficus Hispida* L.

Run no.	Coded values				Real values				% Biosorption of mercury	
	x_1	x_2	x_3	x_4	X_1	X_2	X_3	X_4	Observed	Predicted
1	-1	-1	-1	-1	35	5	0.2	40	83.96	84.17625
2	-1	-1	-1	1	35	5	0.2	80	81.68	80.77458
3	-1	-1	1	-1	35	5	0.4	40	79.89	80.51625
4	-1	-1	1	1	35	5	0.4	80	77.96	78.07458
5	-1	1	-1	-1	35	7	0.2	40	73.14	72.99792
6	-1	1	-1	1	35	7	0.2	80	74.98	75.73625
7	-1	1	1	-1	35	7	0.4	40	74.42	74.46792
8	-1	1	1	1	35	7	0.4	80	78.02	78.16625
9	1	-1	-1	-1	45	5	0.2	40	78.02	77.77458
10	1	-1	-1	1	45	5	0.2	80	73.05	73.81292
11	1	-1	1	-1	45	5	0.4	40	73.46	73.51458
12	1	-1	1	1	45	5	0.4	80	70.47	70.51292
13	1	1	-1	-1	45	7	0.2	40	74.38	75.07625
14	1	1	-1	1	45	7	0.2	80	77.98	77.25459
15	1	1	1	-1	45	7	0.4	40	75.14	75.94625
16	1	1	1	1	45	7	0.4	80	78.49	79.08459
17	-2	0	0	0	30	6	0.3	60	62.74	62.66583
18	2	0	0	0	50	6	0.3	60	57.82	57.1825
19	0	-2	0	0	40	4	0.3	60	82.78	82.8025
20	0	2	0	0	40	8	0.3	60	80.93	80.19583
21	0	0	-2	0	40	6	0.1	60	85.74	85.88917
22	0	0	2	0	40	6	0.5	60	84.92	84.05917
23	0	0	0	-2	40	6	0.3	20	81.38	80.70583
24	0	0	0	2	40	6	0.3	100	80.48	80.4425
25	0	0	0	0	40	6	0.3	60	90.37	90.37
26	0	0	0	0	40	6	0.3	60	90.37	90.37
27	0	0	0	0	40	6	0.3	60	90.37	90.37
28	0	0	0	0	40	6	0.3	60	90.37	90.37
29	0	0	0	0	40	6	0.3	60	90.37	90.37
30	0	0	0	0	40	6	0.3	60	90.37	90.37

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

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TABLE 3 : Coefficients, t-statistics and significance probability of the model for biosorption of mercury onto *Ficus Hispida* L.

Term	Coefficient	Value	Standard error of coefficient	t-value	p-value
Constant	b_0	-346.66	21.73984	-15.9459	0.000000a
X_1	b_1	21.713	0.66474	32.6629	0.000000a
X_1^2	b_{11}	-0.304	0.00748	-40.6852	0.000000a
X_2	b_2	0.548	2.86291	0.1915	0.8516
X_2^2	b_{22}	-2.218	0.18708	-11.8542	0.000000a
X_3	b_3	4.213	23.33923	0.1805	0.86005
X_3^2	b_{33}	-134.896	18.70816	-7.2105	0.000017a
X_4	b_4	0.291	0.1167	2.4928	0.029888a
X_4^2	b_{44}	-0.006	0.00047	-13.0903	0.000000a
$X_1 * X_2$	b_{12}	0.424	0.03908	10.8495	0.000000a
$X_1 * X_3$	b_{13}	-0.3	0.3908	-0.7677	0.458854
$X_1 * X_4$	b_{14}	-0.001	0.00195	-0.7165	0.488629
$X_2 * X_3$	b_{23}	12.825	1.954	6.5634	0.000041a
$X_2 * X_4$	b_{24}	0.077	0.00977	7.8557	0.000008a
$X_3 * X_4$	b_{34}	0.12	0.0977	1.2282	0.244986

X_1= Temperature, X_2= pH, X_3= Biosorbent dosage, X_4= Initial Concentration. [a]Significant (pd"0.05)

TABLE 4 : ANOVA for the entire quadratic model for biosorption of mercury onto *Ficus Hispida* L.

Source of variation	Sum of squares (SS)	Degrees of freedom (D.F)	Mean squares (MS)	F-value	Probe>F
Model	1316.616	14	94.044	153.918	0.00000
Error	6.72	15	0.611		
Total	1323.336	29			

R^2= 0.9949; Adjusted R^2= 0.9884; $F_{0.01(14,15)} = Sr^2/Se^2 = 153.918 > F_{0.01(14,15)}$Tabular = 2.46; *P*model > *F* = 0.000000

TABLE 5 : Optimum values of variables obtained from regression equations for the removal of mercury by *Ficus Hispida* L.

Parameter	Optimum value for mercury
Temperature, ^{0}C	39.32
pH	5.64
Biosorbent loading, g	0.26
Initial mercury concentration, mg/L	57.21
% Biosorption Predicted	90.6639
% Biosorption Observed	89.12

Interaction effects of biosorption variables

The biosorption capacities of the present biosorbent over different combinations of independent variables were visualized through three-dimensional view of response surface plots (Figures 2-7). The plots (Figures 2-7) were represented as a function of two factors at a time, holding other factors at a fixed level. All the response surface plots revealed that at low and high levels of the variables the capacity of the adsorbent was minimal, however, it was noted that there existed a region where neither an increasing nor a decreasing trend in the biosorption capacity was observed. This phenomenon conforms that there was an existence of optimum for the biosorption variables in order to maximize the biosorption capacity. Also there existed a direct

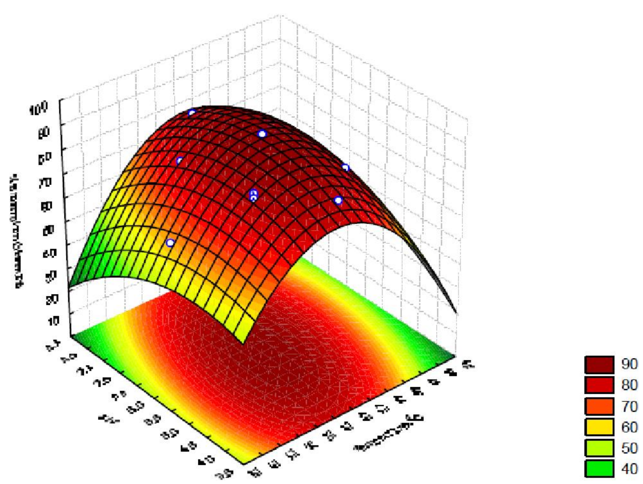

Figure 2 : Response surface plot of the effects of pH and temperature on percentage biosorption of mercury by *Ficus Hispida* L.

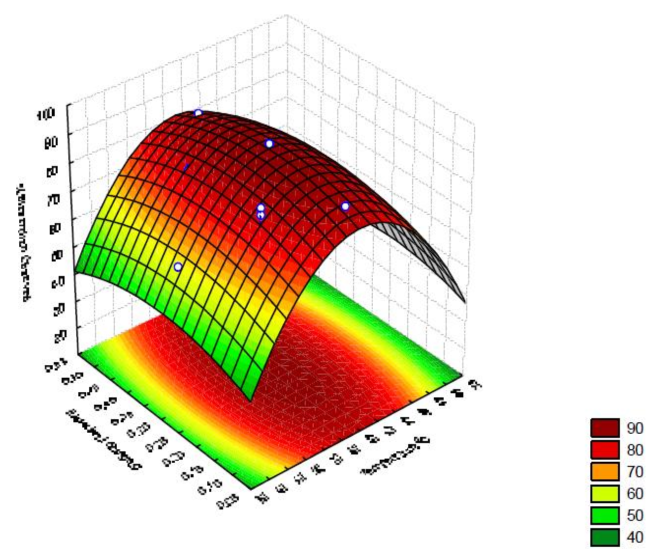

Figure 3 : Response surface plot of the effects of biosorbent dosage and temperature on percentage biosorption of mercury by *Ficus Hispida* L.

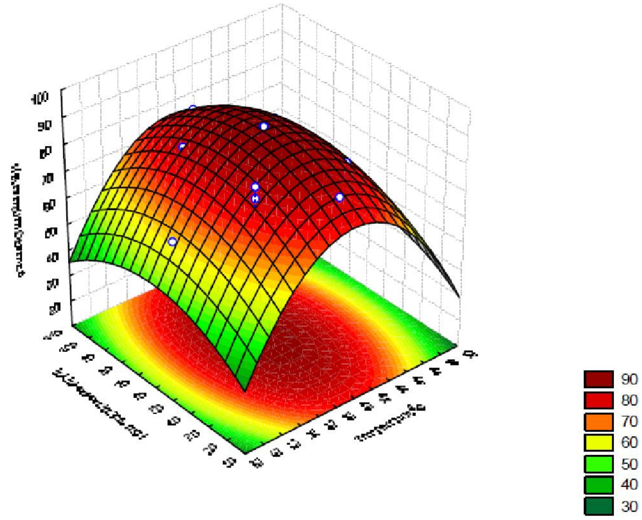

Figure 4 : Response surface plot of the effects of inicial metal concentration and temperature on percentage biosorption of mercury by *Ficus Hispida* L.

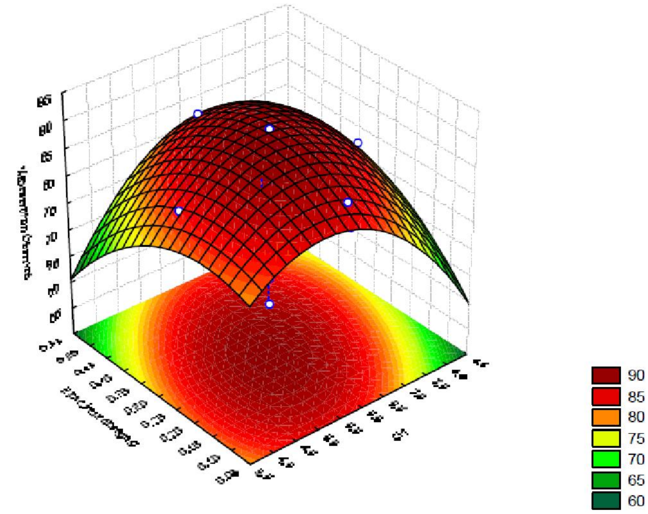

Figure 5 : Response surface plot of the effects of biosorbent dosage and pH on percentage biosorption of mercury by *Ficus Hispida* L.

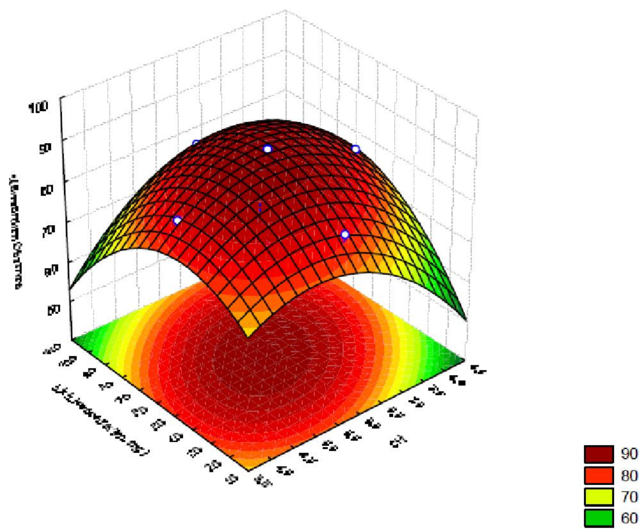

Figure 6 : Response surface plot of the effects of inicial metal concentration and pH on percentage biosorption of mercury by *Ficus Hispida* L.

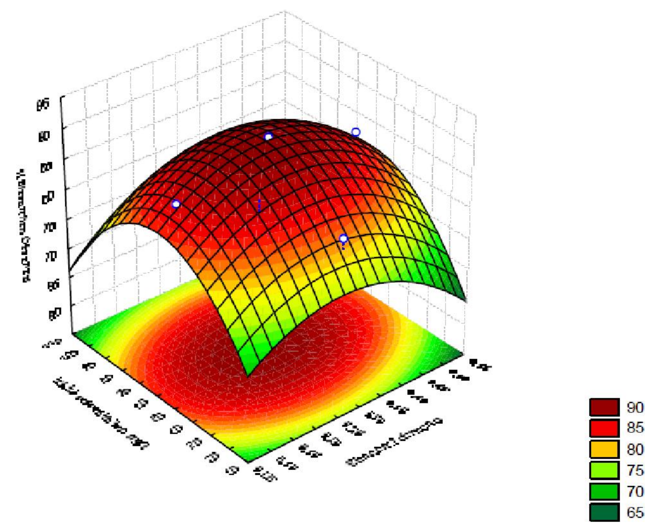

Figure 7 : Response surface plot of the effects of inicial metal concentration and biosorbent dosage on percentage biosorption of mercury by *Ficus Hispida* L.

proportional relationship between the temperature and pH (X_1 and X_2), pH and biosorbent dosage (X_2 and X_3) and pH and Initial ion concentration (X_2 and X_4) on the mercury ion uptake. These interactions were also substantiated by the fact that the interaction between them were very significant ($p < 0.5$) and was found to be solely responsible for achieving a relatively high mercury ion uptake as predicted by the model and the response contour plots (Figures 2,6,7). The curved contour lines showed that there was an interaction between the temperature and pH (X_1 and X_2), pH and biosorbent dosage (X_2 and X_3) and pH and Initial ion concentration (X_2 and X_4). Furthermore, a moderate interaction was found between temperature and biosorbent dosage (X_1 and X_3), temperature and Initial ion concentration (X_1 and X_4) and biosorbent dosage and initial ion concentration ($X_3$and X_4) as shown in Figures 3, 4, 5. The maximum predicted biosorption capacity for optimum biosorption variables was obtained through point prediction method and surface response plots are given in TABLE 5. The biosorption experiment was then performed at the optimized process conditions and it was found that the experimental data obtained was well represented by the present model Equation 4.

CONCLUSION

The development of a mathematical model for mercury biosorption process simulation and optimization on the basis of statistical design of experiments appears to be a useful tool for prediction and understanding of the interaction effects between experimental parameters. Response surface methodology and the central composite design were appropriate for determining the optimal conditions for mercury ions biosorption onto *Ficus Hispida* L. The optimal conditions of biosorption established by RSM are as follows: pH = 5.64, initial concentration of mercury in aqueous solution = 57.21 mg/L, biosorbent dosage = 0.26 g/L and temperature = 39.32^{0}C. The extent of biosorption of mercury at these optimum conditions was 90.6636% and the experimental percentage biosorption at these optimum values was 89.12.

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