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Response surface methodology approach for optimization of lead(II) adsorptive removal by *Spirogyra* sp. biomass

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

In this work, various variables that affected the lead(II) removal efficiency by thermally activated adsorbent prepared from *Spirogyra* species were simultaneously optimized using the experimental design method. Preliminary experiments showed that the effect of four variables of adsorbent dosage (0.1 – 1.0 g/L), sample pH (3 – 9), initial concentration (50 - 100 mg/L), and temperature (25 – 45 °C) were important. Therefore, response surface methodology (RSM) based on central composite design (CCD) was performed to find a relationship between these factors on lead(II) removal efficiency as response. The statistical parameters of the derived model were R^2 = 0.9899 and F value = 10852.54. The response surface diagrams were plotted based on the defined model to show the effects of the variables on lead(II) adsorption efficiency. Finally, non-linear optimization was carried out and under the defined optimum conditions the predicted lead(II) removal efficiency with 95% confidence level was found 97.6±2.3%, which is in agreement with the experimental response of 96.9±1.3%.

KEYWORDS
adsorption; lead(II); optimization; response surface methodology; *Spirogyra*

1. INTRODUCTION

The presence of heavy metal ions in the aquatic environment is a matter of great concern to researchers because of their toxic nature, increasing levels of discharge, and other adverse effects of receiving wastewaters. Unlike most organic pollutants, heavy metals are non-degradable and cannot be detoxified biologically and therefore, are the main toxic pollutants in industrial wastewater. They have been found to be the major contaminants of surface and ground water. These metal ions are let out by a variety of industries such as plating, paint and dyes, glass operations, lead batteries, electroplating, mining, and smelters (Jalali et al., 2002; Senthilkumar et al., 2007). Among the heavy metals, lead is one of the most toxic elements, even at lower concentrations. It affects the central nervous system, kidneys, liver, and gastrointestinal system, and it may directly or indirectly cause disease such as anemia, encephalopathy, hepatitis, and nephritic syndrome (Repo et al., 2013). The conventional methods for the removal of lead ions from aqueous solution are chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment, and sorption (Alves et al., 2008; Repo et al., 2010). Most of these methods have been found to be limited because they often involve high capital and operational cost and may also be associated with the generation of secondary wastes. In all these techniques, adsorption appears to be particularly competitive and an effective process for the removal of heavy metals at trace level (Zhao et al., 2013;

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Srivastava et al., 2015). Even though commercially, activated carbon with a high surface area, micro-porous character, and high adsorption capacity has proven its potential as an adsorbent for the removal of heavy metals from industrial wastewater, it is expensive with relatively high operating costs (Sivarajasekar and Baskar, 2015a; Karthik et al., 2016a). Hence, low-cost adsorption method has attracted many researchers because it does not require complicated regeneration process (Sivarajasekar, 2007, 2016; Sivarajasekar et al., 2008; Sivarajasekar and Bhaskar, 2014a, 2015b; Vijayaraghavan and Yun, 2008; Sivarajasekar, 2014). Among various biosorbents reported in the literature, *Spirogyra* species were identified as a promising biosorbent (Sivarajasekar et al., 2009; Karthik et al 2016a; Karthik et al 2016b).

However, an extensive research has been done on the biosorptive removal of lead(II) (Chen 2012; Holan and Volesky, 1994; Davis et al., 2003; Ibrahim 2011; Repo et al., 2010; Srivastava et al., 2015; Zhao et al., 2013), and in the majority of these studies, the effect of different parameters, such as adsorbent dosage, sample pH, contact time and pollutant concentration on the pollutant removal percent/adsorption capacity of adsorbent were investigated. Despite the numerous studies, no definite relationship exists between these parameters and their interactions to reach the highest adsorption capacity/removal efficiency for adsorption of lead(II) onto *Spirogyra* sp.

Several statistical methodologies have been used for optimizing the process variables such as Taguchi, genetic algorithm, neural network, iterative mathematical search technique, metaheuristic search technique, heuristic search technique, simulated annealing (Morgan 1991; Sivarajasekar and Bhaskar, 2014b) and response surface methodology (RSM) (Korbahti and Rauf, 2009). RSM is a statistical method which applied quantitative data from appropriate experiments to solve multivariate equation, in order to obtain the optimal conditions for reaching the best response. Central composite design (CCD) is the most popular class of RSM that involves three steps: (i) designing the experiments, (ii) estimating the coefficients in a mathematical model and (iii) predicting the response and the model validation.

In this study, we applied the experimental design as a highly efficient optimization method to optimize the adsorption process for the removal of lead(II) using a freshly prepared thermally activated *Spirogyra* sp. We investigated the interaction between the parameters and optimal condition using limited experiments and the RSM was employed to find a predicting reliable model under CCD.

2. MATERIALS AND METHODS

2.1. Preparation of Spirogyra adsorbent

All the chemicals used in this study were purchased from Sigma Aldrich Co. and of analytical grade. The *Spirogyra* species was obtained from fresh water ponds at Erode District, Tamil Nadu, India. The sampling sites were chosen because of minimal heavy metal pollution. The collected algal biomass was rinsed with distilled deionized water to remove attached particulate materials. Upon arrival in the laboratory the algae samples were first washed with carbon tetra chloride to elute the chlorophylls and dried at 60 ^{o}C in a hot air oven for 12 h. The dried biomass was thermally activated in the muffle furnace by keeping it at 300 ^{o}C for 1 h under controlled nitrogen environment. The resultant material Thermally Activated *Spirogyra* sp. (TAS) was pulverized and further used for the batch adsorption experiments.

2.2. Batch adsorption experiments

For the adsorption experiments, the desired amount of TAS was added to 100 mL of lead(II) solution in 250 mL Erlenmeyer flasks and kept in an orbital shaker. After 3 h, the solution was filtered using a 0.45 µm syringe filter and analyzed for residual lead(II) concentration. The lead(II) removal percentage (R, %) and lead(II) adsorption capacity (Q, mg/g), were calculated by the following equations respectively:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$Q = \frac{C_0 - C_t}{m} \times V \quad (2)$$

where, C_o and C_t (mg/L) are the lead(II) concentrations at initial and t time (min) respectively. m (g) is the adsorbent amount and V (L) is the solution volume. The lead(II) concentrations (C) were measured using a JASCO V-670 UV-Visible spectrophotometer (Japan) at a wavelength of 520 nm, using PAR reagent (2,4-pyridyl azoresorcinol) as a complexing agent.

3. RESULTS AND DISCUSSION

3.1. Characterizations of TAS

The specific surface area of TAS was measured using a surface analyzer (Micromeritics ASAP 2020) and it was observed to be 0.96 m^2/g. Surface morphology was examined by using a scanning electron microscope (SEM: JSM–6390LV–JEOL Ltd., Japan). The SEM image of prepared adsorbent is shown in Figure 1. It was evident from the micrographs that the biosorbent showed well-defined rod clusters in net/mat format. Fourier transmission infra-red (FTIR) analysis was done using a Thermo Nicolet, Avatar 370 FTIR spectrometer over a spectral range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}. The peaks recorded in the FTIR spectra such as 2918, 1661, 3412 and 1057 can be assigned to carboxyl (C-H), carbonyl (C = O), amine (N-H) and carbonyl (C-O) groups respectively. It is a clear indication that TAS surface was full of functional groups due to which TAS could behave as a good adsorbent.

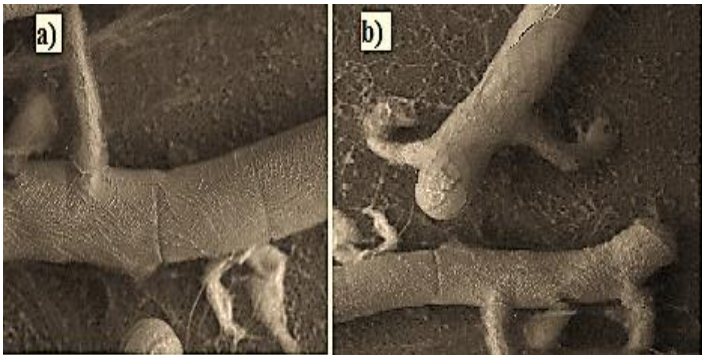

Figure 1. SEM images of prepared TAS.

3.2. Experimental design

Univariate methodology as a conventional method is still used in optimization procedure, but it requires a great experimental run which is time consuming, costly, and especially the variables interactions are not considered. The multivariate techniques are fast as well as effective and provide optimization of more than one variable, simultaneously. RSM is one of the multivariate techniques to evaluate optimization process which have been used for optimization of different process. CCD as a type of RSM method is an independent, rotatable, orthogonal and quadratic design (Mason et al., 2003).

In the present work, the influence of four parameters namely, pH, adsorbent dosage, initial concentration and temperature on the lead(II) removal efficiency, as response, was evaluated by CCD. Then, the effect of variables on the response which contributed to building of a surface was considered by the RSM. The graphical relationship between these variables and response (R, %) was obtained based on the mathematical modeling equation for removal efficiency of lead(II). Finally, the analysis of variance (ANOVA) was applied for evaluating the model and analysis of data.

3.3. Model development by CCD

Due to the small number of factors, there is no need for screening of the factors by factorial design, so CCD was used directly which was firstly presented by Box and Wilson (Box et al., 1978). Generally, a CCD approach fork factors, coded as (χ_1,..., χ_k), including three parts: (i) a factorial design, formed by a total of $n_f = 2^k$ points with the coordinates of $\chi_i = -1$ or $\chi_i = +1$, for i =1,..., k, (ii) an axial part, containing $n_{ax} = 2k$ points with all their coordinates null excluding the point with a certain value of α (or −α), ranges from 1 to √k; (iii) a total of n_c runs at the center of the experimental region to attain some properties such as orthogonality or rotatability to fit quadratic polynomials. In order to get a good estimate of experimental error, the center points are usually repeated.

A CCD is made rotatable and orthogonal by the choice of suitable axial point, α, which can be calculated from the following equations (Box et al., 1978):

$$\alpha = \sqrt[4]{N_f} \quad (3)$$

$$\alpha = \sqrt{\frac{\sqrt{(N_f+N_a+N_0)N_f}-N_f}{2}} \quad (4)$$

where N_f, N_a and N_o are the numbers of factorial points, axial points and center points respectively. Using Equation (3), the axial spacing was ±2.0 and then, N_o was obtained 6. For the f number of variables, the number of needed design points (N) can be obtained using Equation (5):

$$N = 2^f + 2f + N_0 \quad (5)$$

Therefore, 30 experiments had to perform for CCD design, in the studied case, which were randomized in two blocks, to the same reasons as mentioned for the factorial design section. The ranges of factors were defined in the Table 1.

Firstly, the values of the responses were transformed to the power of three values for removal efficiency of lead(II) (not shown), according to the recommendation of Box-Cox plot. The ANOVA table for CCD design matrix is represented in Table 2 which can be used to select a suitable response surface model, the significances of the model equation and the model terms. As it can be seen in Table 2, the model F-value is 10852.54, implying the significance of model. Also, the value of "Probability > F" less than 0.050 for a factor indicating the significance of its effect. Based on a higher F- and R-value and also, lower lack of fit and prediction error sum of squares (PRESS), a quadratic response surface model was selected to fit the experimental data. The regression coefficients values were calculated via the multiple linear regression models, in backward mode, to exclude non-significant effects from the model. Accordingly, the predictive model for the removal percentage of lead(II) using TAS adsorbent in terms of the coded factors can be presented by the following equation:

$$R(\%) = 76.48 - 7.56\,X_1 + 6.56X_2 + 2.49X_3 - 4.03X_4 + 4.15X_1X_2 + 3.68X_1X_3 - 3.17X_1X_4 - 3.18X_2X_3 + 4.59X_2X_4 + 5.05X_3X_4 - 1.67X_1^2 - 1.50\,X_2^2 - 0.20X_3^2 - 3.28X_4^2 \quad (6)$$

Table 1. Factors, factor notation, and their levels in CCD.

Factor	Levels				
	−α	−1	0	+1	+α
Sample pH, X_1	1.5	4	6.5	9	11.5
Adsorbent dose, X_2 (g/L)	0.1	0.4	0.7	1.0	1.3
Initial lead(II) concentration, X_3 (mg/L)	25	50	75	100	125
Temperature, X_4 (°C)	15	25	35	45	50

The F-value was obtained as 1.206 for lack of fit indicates that there is no significant experimental error and confirms the validity of the predicted model. Other statistical parameters of the predicted model for the adsorptive removal of lead(II) over TAS are listed in Table 3. The coefficient of variation (CV) of 0.25% and standard deviation of 0.18 are reasonably low. Also, it demonstrates the low value of 2.16 for the PRESS, calculated by Equation (7):

$$\text{PRESS} = \sum_{i=1}^{n}(e_{i,-i})^2 \qquad e_{i,-i} = y_i - \hat{y}_{i,-i} \qquad (7)$$

where $e_{i,-i}$, y_i and $\hat{y}_{i,-i}$ are residual, the experimental value and the predicted value respectively. R^2 parameter, as a measure of variation amount around the mean value, was evaluated 0.990 for the model which is defined as follows:

$$R^2 = 1 - \frac{SS_{resid}}{SS_{model}+SS_{resid}} \qquad (8)$$

where SS_{resid} and SS_{model} are the residual sum of squares and model sum of squares respectively.

The quality of the fit of model was expressed by adjusted R^2 (R^2_{adj}) and predicted R^2 (R^2_{pred}) in Equations (9) and 10, respectively, which should be within 0.20 of each other (Box et al., 1978; Evans, 2003).

$$R^2_{adj} = 1 - \frac{n-1}{n-p}\left(\frac{SS_{Error}}{SS_{total}}\right) = 1 - \frac{(n-1)}{(n-p)}(1-R^2) \quad (9)$$

$$R^2_{adj} = 1 - \left(\frac{PRESS}{SS_{total}-SS_{block}}\right) \qquad (10)$$

In these equations, n is the number of experiments and p is the number of model parameters including intercept and any block coefficient. The R^2_{pred} and the R^2_{adj} values for the above model for the lead(II) removal percentage onto TAS were obtained 0.9898 and 0.9866 respectively.

The statistical significance was checked with the adequate precision ratio, presenting in Equations (11) and (12) (Evans 2003).

$$adequate\ precision = \left[\frac{\max(\bar{y})-\min(\bar{y})}{\sqrt{\bar{V}(\bar{y})}}\right] \qquad (11)$$

$$\bar{V}(\bar{y}) = \frac{1}{n}\sum_{i=1}^{n}\bar{V}(\bar{y}) = \frac{p\sigma^2}{n} \qquad (12)$$

where ý, p and n are the predicted value, the number of model parameters and the number of experiments respectively, and σ^2 is the residual mean square from ANOVA table. As it can be seen in Table 3, the adequate precision was obtained 474.9779 (> 4.0), indicating the model adequacy.

The normal probability and studentized residuals plot for the lead(II) removal efficiency by TAS is shown in Figure 2. In this figure, the points follow a straight line indicates that the residuals follow a normal distribution. Moreover, checking the plots of residuals versus different variables such as predicted values, run order, and factors (not shown) indicated a nearly constant variance over the variable ranges.

Table 2. Analysis of variance (ANOVA) for CCD.

Source	Sum of squares	df	Mean square	F Value	p-value, Probability > F
Model	4867.592	14	347.6851	10852.54	< 0.0001
X_1	1371.838	1	1371.838	42820.12	< 0.0001
X_2	1032.938	1	1032.938	32241.80	< 0.0001
X_3	148.2551	1	148.2551	4627.59	< 0.0001
X_4	389.5398	1	389.5398	12158.98	< 0.0001
$X_1 X_2$	275.643	1	275.643	8603.84	< 0.0001
$X_1 X_3$	217.1939	1	217.1939	6779.42	< 0.0001
$X_1 X_4$	160.3389	1	160.3389	5004.76	< 0.0001
X_2C	161.3535	1	161.3535	5036.43	< 0.0001
$X_2 X_4$	336.9978	1	336.9978	10518.95	< 0.0001
X_3X_4	407.7371	1	407.7371	12726.98	< 0.0001
X_1^2	76.21905	1	76.21905	2379.08	< 0.0001
X_2^2	61.7743	1	61.7743	1928.20	< 0.0001
X_3^2	1.06425	1	1.06425	33.22	< 0.0001
X_4^2	295.6689	1	295.6689	9228.92	< 0.0001
Residual	0.480558	15	0.032037		
Lack of Fit	0.339758	10	0.033976	1.21	0.4427
Pure Error	0.1408	5	0.02816		
Cor Total	4868.072	29			

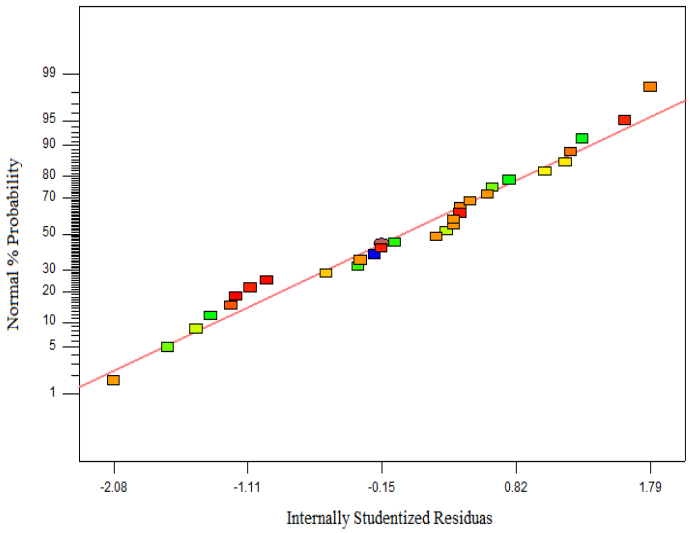

Figure 2. Normal probability plot of studentized residuals for the suggested quadratic models of lead(II) removal efficiency.

For further model evaluation, the plots of leverage and Cook's distance and difference in fits (Box et al., 1978; Evans 2003) were studied and are subsequently shown in Figures 3-5. Leverage (Box et al., 1978; Evans 2003) is a measure of how each point influences the model fit. A high leverage point represents an unexpected error in a data point which strongly influenced the model. As it can be seen in Figure 3, all the leverage values are lower than 0.8, indicated that there was no unexpected error or outliers in the model. Also, the Cook's distance (Figure 4) and difference (Figure 5) in fit plots confirmed this result. The Cook's distance (Figure 4) is a measure of how the regression changes if the case is deleted, whereas difference in fits (DFFITS, Figure 5) (Box et al., 1978; Evans 2003) is a measure of each point influence on the predicted value. In all these figures, the values were in the determined range (red line in Figures 3-5) and confirmed the reliability of the model.

Table 3. Statistical parameters for the quadratic model in Equation (6).

C.V. %	0.25		R^2	0.9896
PRESS	2.16		R^2_{adj}	0.9898
Adequate Precision	474.98		R^2_{pred}	0.9866

In order to analyse the interactions, three-dimensional plots of the model are highly recommended to visualize the relationship between the responses and the studied effective factors (Box et al., 1978; Evans 2003; Sivarajasekar et al., 2014b). Figure 6 shows the plots of response model versus two

experimental factors at the fixed value of other factors in their central levels. Figure 6a represents the effect of solution pH and adsorbent dosage. It clearly shows that the adsorbent dosage has positive effects on the removal of lead(II) whereas the removal efficiency increased with increasing of sample pH until about 6-7 and then decreased. As it can be seen in Figure 6a, the lines are not parallel which indicates that there is no interaction between adsorbent dosage and sample pH. The response surface plot for the effect of sample pH and initial concentration on the removal efficiency is shown in Figure 6b. The figure demonstrated that when initial concentration was decreased, the removal efficiency increased. Similar to previous result, there is no interaction between pH and initial concentration. As it can be seen in Figure 6c, the removal efficiency was increased by increasing the temperature and there is no interaction between these factors, as well. Similarly, there is no interaction between the adsorbent dosage and temperature (Figure 6d). The trends in Figures 6e and 6f show that there is an interaction between adsorbent dosage and initial concentration, as well as between adsorbent dosage and temperature. Due to these interactions between these factors, there is no linear relation between the response and factors.

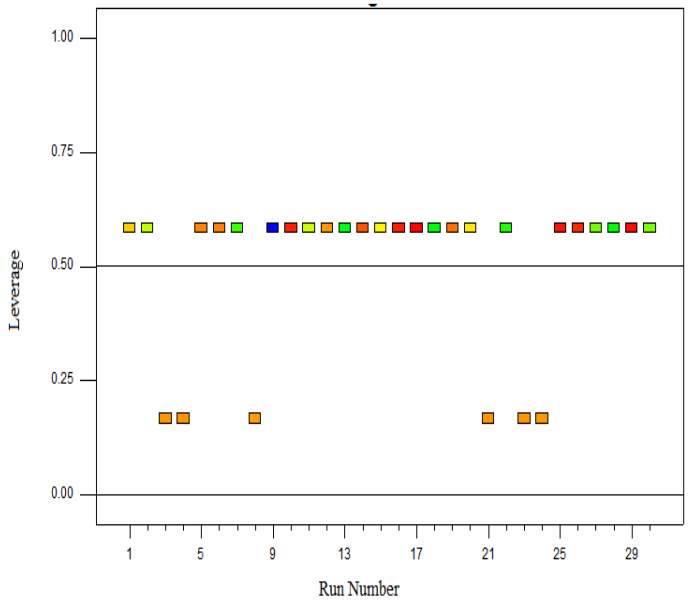

Figure 3. Leverage plot for quadratic model obtained from central composite design.

3.4. Non-linear optimization

Indeed, finding the optimum values of effective factors to maximize the lead(II) removal efficiency onto TAS from the obtained model is the main objective of the optimization which was carried out using the Derringer's desirability function (Box et al., 1978; Evans 2003). According to the non-linear optimization method, the optimum values of variables were obtained as pH: 4.2, dose: 0.90 g/L, initial concentration: 50.0 mg/L, and temperature: 28.9 °C respectively. With 95% confidence level, the optimum predicted response was obtained as 97.6±2.3%. It was verified by performing the experiments in the optimized conditions, in which the experimental lead(II) removal efficiency was found to be 96.9±1.3%, which were in close agreement with the CCD model predictions.

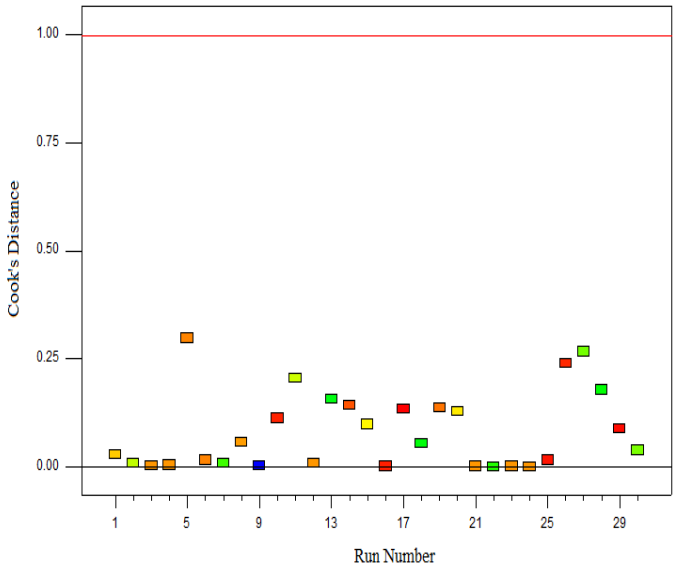

Figure 4. Cook's distance plot for model in Equation (6).

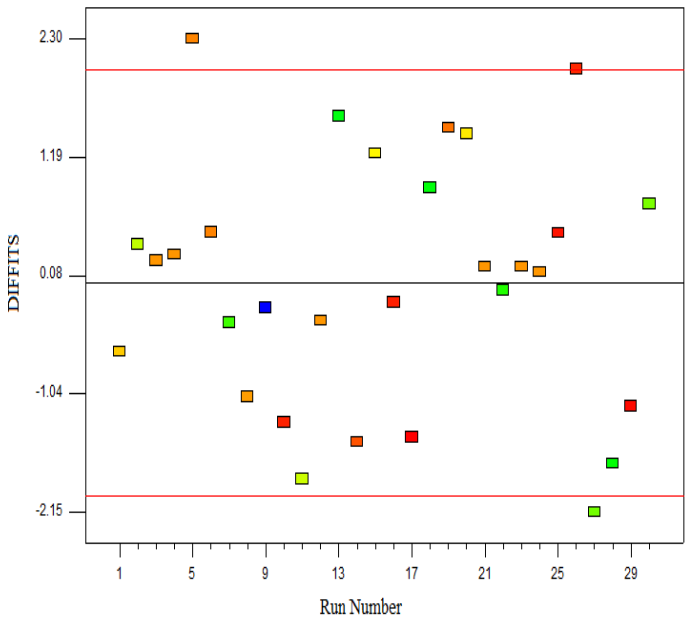

Figure 5. Difference in fits (DFFITS) plot for evaluating of the quadratic model.

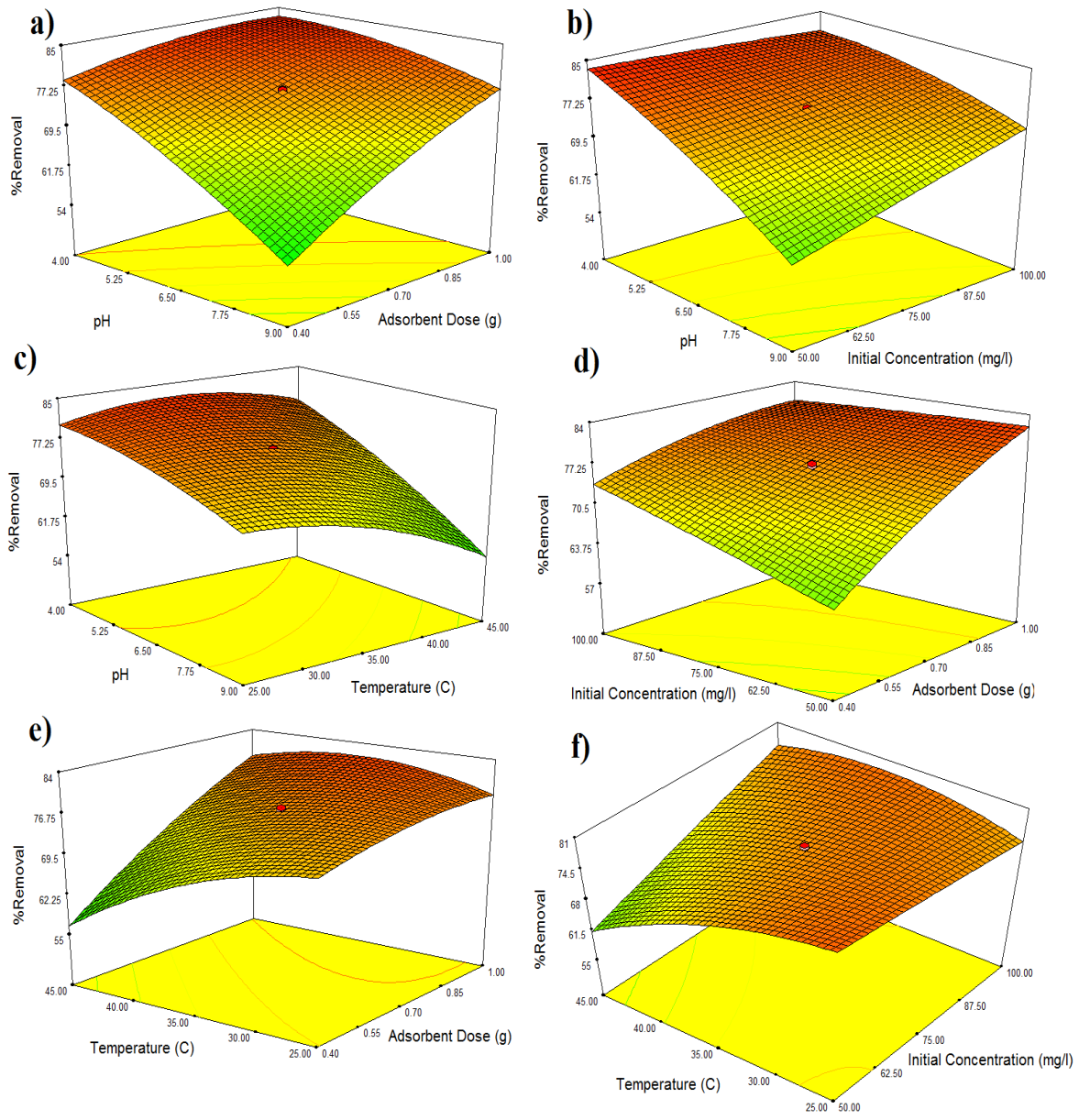

Figure 6. The response surface plots of the effect of sample pH, adsorbent dose, initial concentration, and contact time. (a) Sample pH) – Adsorbent dose, (b) Sample pH – Initial concentration, (c) Sample pH – Temperature, (d) Adsorbent dose – Initial concentration, (e) Adsorbent dose – Temperature, (f) Initial concentration – Temperature.

4. CONCLUSIONS

The statistical experimental design methodology was used for the optimization of lead(II) adsorption from aqueous solution using TAS, in order to maximize the removal efficiency. Inspection of the response surface modeling demonstrates that the lead(II) initial concentration has negative effect on the response (removal efficiency) versus the positive effect of adsorbent dosage and contact time. A quadratic model was proposed by CCD which agreed well with the experimental data (R^2 = 0.9896). Also, the optimum conditions for lead(II) removal were pH: 4.2, dose: 0.90 g/L, initial concentration: 50.03 mg/L, and temperature: 28.86 ^oC respectively, with removal efficiency of 97.6% that was in close agreement with the CCD model predictions.

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