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*Research Article*

# Application of the Statistical Design for the Sorption of Lead by *Hypnea valentiae*

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**Abstract** In this work, sorption of lead from aqueous solution on *Hypnea valentiae*, red macro algae, was investigated. Batch experiments have been carried out to find the effect of various parameters such as pH, temperature, sorbent dosage, metal concentration and contact time on the sorption of lead using *Hypnea valentiae*. Response surface methodology (RSM) is employed to optimize the process parameters. Based on the central composite design, quadratic model was developed to correlate the process variables to the response. The most influential factor on each experimental design response was identified from the analysis of variance (ANOVA). The optimum conditions for the sorption of lead were found to be as follows: pH: $5.1$, temperature: $36.8\,°\mathrm{C}$, sorbent dosage: $5.1\,\mathrm{g/L}$, metal concentration: $100\,\mathrm{mg/L}$ and contact time: $30\,\mathrm{min}$. At these optimized conditions the maximum removal of lead was found to be $91.97\%$. A coefficient of determination ($R^2$) value of $0.9548$ shows the fitness of RSM in this work.

**Keywords** optimization; metal; *Hypnea valentiae*; response surface methodology; red algae

## 1 Introduction

Lead is one of the most widely used non-ferrous metals in electroplating industry, metallurgical industry, metal finishing industries, tannery operations, chemical manufacturing, mine drainage and battery manufacturing [2, 8]. Its presence in the environment causes problems to human being. The specific problem associated with lead is the accumulation in the food chain and persistence in nature [3]. As a consequence, increasing attention is being centered on removal and recovery of lead from various waste streams. Traditional methods such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes have been used to remove lead from wastewater [22, 25]. However, these technologies are most suitable in situations where the concentrations of the heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentrations, or when very low concentrations of heavy metals in the treated water are required. Hence new technologies are required to reduce heavy metal concentrations to environmentally acceptable levels at affordable costs.

Biological approaches, especially application of sorbents, have been suggested in the last decade. The advantages offered by sorbents are higher metal loading capacity and greater selectivity for transition and heavy metals. Marine algae have been found to be potential suitable sorbents because of their cheap availability, relatively high surface area and high binding affinity. The use of marine algae for heavy metal removal has been reported by several authors [5, 9, 10, 12, 15, 16, 17, 23, 24]. *Hypnea valentiae* is a red algae widely found in the Atlantic Ocean: from North Carolina, USA, to the Caribbean, south to Brazil, east to Herault, France and the Mediterranean; in the Canary Islands. In Indian Ocean, from the Arabian Sea south to Madagascar, Mauritius and south to the Andaman Sea. *Hypnea valentiae* is a carrageenan yielding plant. It is also edible and the freshly gathered seaweed is commonly prepared as salad.

RSM is a collection of statistical techniques for designing experiments, building models, evaluating the effects of factors and searching for the optimum conditions. It is widely used for multivariable optimization studies in several biotechnological processes such as optimization of media, process conditions, production, fermentation, biosorption of metals, food processing and so on [1, 6, 7, 13, 14, 18, 19, 20]. In RSM, several factors are simultaneously varied. The objectives of the present investigation were to quantify the sorption of lead to unmodified *Hypnea valentiae* and to optimize the process parameters for the sorption of lead using *Hypnea valentiae* using response surface methodology.

## 2 Materials and methods

### 2.1 Preparation of adsorbent

The red colored marine algae *Hypnea valentiae* was used in the present study. It was collected from the coastal belt of Gulf of Mannar, Tamilnadu, India. The collected algae were washed with deionized water several times to remove impurities. The washing process was continued till the wash water contains no dirt. The washed algae was then completely dried in sunlight for 10 days. The dried algae was then cut into small pieces and was powdered using domestic mixer. In the present study, the powdered materials in the range of 500–700 $\mu$m particle size were then directly used as sorbents without any pretreatment.

### 2.2 Preparation of solution

Batch experiments were performed with a magnetic stirrer at 200 rpm using 250 mL beakers containing test solutions. The stock lead solution (1 g/L) was prepared by dissolving of Lead (II) nitrate of analytical grade in deionized water. Other concentrations were prepared by dilution of this stock solution and fresh dilutions were used in each experiment.

### 2.3 Experimental design by RSM

A full factorial design, which includes all possible factor combinations in each of the factors, is a powerful tool for understanding complex processes for describing factor interactions in multifactor systems. RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously.

The experiments with different pH, adsorbent dosage, temperature, initial metal concentration and processing time were employed simultaneously covering the spectrum of variables for the removal of lead in the Central composite design. In order to describe the effects of pH, adsorbent dosage, temperature, initial lead concentration and processing time on percentage removal of lead, batch experiments were conducted. The coded values of the process parameters were determined by the following equation:

$$x_i = \frac{X_i - X_o}{\Delta x}, \quad (1)$$

where $x_i$ is the coded value of the $i$th variable, $X_i$ is the uncoded value of the $i$th test variable and $X_0$ is the uncoded value of the $i$th test variable at center point. The range and levels of individual variables were given in Table 1. The experiment design was given in Table 2 along with experimental data and predicted responses. The regression analysis was performed to estimate the response function as a second-order polynomial

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=l}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j, \quad (2)$$

| Independent variable | Range and levels | | | | |
|---|---|---|---|---|---|
| | −2.38 | −1 | 0 | 1 | +2.38 |
| pH (A) | 3 | 4 | 5 | 6 | 7 |
| Temperature, (B) °C | 25 | 30 | 35 | 40 | 45 |
| Sorbent dosage, (C) g/L | 3 | 4 | 5 | 6 | 7 |
| Lead concentration, (D) mg/L | 30 | 60 | 90 | 120 | 150 |
| Contact time, (E) min | 10 | 20 | 30 | 40 | 50 |

**Table 1:** Experimental range and levels of independent process variables.

where $Y$ is the predicted response, $\beta_i$, $\beta_j$, $\beta_{ij}$ are coefficients estimated from regression; they represent the linear, quadratic and cross products of $x_1$, $x_2$, $x_3$ on response.

A statistical program package "Design Expert 7.1.5" was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the ANOVA analysis. The significance of each term in the equation is to estimate the goodness of fit in each case. Response surfaces were drawn to determine the individual and interactive effects of test variable on percentage removal of lead. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

After sorption, the contents of the beakers were centrifuged at 4500 rpm for 3 min and the sorbent was successfully separated from aqueous solution. The supernatants were analyzed for residual lead concentration using an atomic absorption spectrophotometer.

## 3 Results and discussion

### 3.1 Fitting models

Experiments were performed according to the CCD experimental design given in Table 2 in order to search for the optimum combination of parameters for the sorption of lead using the red algae. A Model $F$-value of 30.63 implies that the model is significant. There is only a 0.01% chance that a "Model $F$-Value" this large could occur due to noise. The Lack of Fit $F$-value of 222.51 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit $F$-value" this large could occur due to noise.

The Fisher $F$-test with a very low probability value ($P_{\text{model}} > F = 0.0001$) demonstrates a very high significance for the regression model. The goodness of fit of the model is checked by the determination coefficient ($R^2$). The coefficient of determination ($R^2$) was calculated to be 0.9548. This implies that more than 95% of experimental data was compatible with the data predicted by the model (Table 2) and only less than 4% of the total variations are not explained by the model. The $R^2$ value is always between 0 and 1, and a value $> 0.75$ indicates aptness of the model.

| Run. no. | A | B | C | D | D | Lead removal (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Experimental | Theoretical |
| 1 | 1 | 1 | −1 | −1 | 1 | 79.4 | 77.73 |
| 2 | 1 | 1 | 1 | −1 | 1 | 72.3 | 75.30 |
| 3 | 0 | 0 | 0 | 2.38 | 0 | 87.4 | 87.02 |
| 4 | 1 | 1 | −1 | −1 | −1 | 73.2 | 75.58 |
| 5 | 1 | −1 | 1 | 1 | 1 | 81.2 | 81.26 |
| 6 | −1 | 1 | 1 | −1 | 1 | 78.1 | 79.40 |
| 7 | 0 | 0 | 0 | 0 | 0 | 90.9 | 90.88 |
| 8 | −1 | −1 | 1 | 1 | −1 | 78.8 | 78.26 |
| 9 | −1 | 1 | 1 | 1 | 1 | 79.4 | 80.45 |
| 10 | −1 | −1 | −1 | −1 | −1 | 79.8 | 78.92 |
| 11 | 0 | 0 | 0 | 0 | 0 | 90.8 | 90.88 |
| 12 | −1 | −1 | 1 | −1 | −1 | 79.3 | 81.14 |
| 13 | −1 | 1 | 1 | 1 | −1 | 77.9 | 79.52 |
| 14 | 0 | 2.38 | 0 | 0 | 0 | 84.3 | 82.77 |
| 15 | 1 | −1 | 1 | −1 | −1 | 76.4 | 77.16 |
| 16 | 0 | 0 | 0 | −2.38 | 0 | 79.8 | 78.62 |
| 17 | −1 | −1 | 1 | 1 | 1 | 77.6 | 77.64 |
| 18 | 1 | −1 | −1 | −1 | 1 | 74.3 | 74.87 |
| 19 | 1 | −1 | −1 | 1 | −1 | 79.2 | 80.29 |
| 20 | 0 | 0 | 0 | 0 | −2.38 | 73.2 | 72.71 |
| 21 | −1 | 1 | 1 | −1 | −1 | 82.3 | 81.00 |
| 22 | 2.38 | 0 | 0 | 0 | 0 | 80.1 | 79.14 |
| 23 | 1 | −1 | −1 | −1 | −1 | 75.5 | 74.27 |
| 24 | −1 | −1 | 1 | −1 | 1 | 78.9 | 77.99 |
| 25 | 1 | −1 | 1 | 1 | −1 | 80.4 | 81.63 |
| 26 | 1 | −1 | 1 | −1 | 1 | 74.3 | 74.26 |
| 27 | −2.38 | 0 | 0 | 0 | 0 | 81.4 | 80.81 |
| 28 | 1 | 1 | 1 | −1 | −1 | 77.5 | 76.65 |
| 29 | 0 | 0 | 0 | 0 | 0 | 91.1 | 90.88 |
| 30 | 1 | −1 | −1 | 1 | 1 | 84.3 | 83.41 |
| 31 | −1 | 1 | −1 | 1 | −1 | 80.1 | 80.68 |
| 32 | −1 | −1 | −1 | 1 | 1 | 79.3 | 80.47 |
| 33 | 0 | 0 | 0 | 0 | 0 | 91.0 | 90.88 |
| 34 | 1 | 1 | 1 | 1 | −1 | 82.3 | 82.52 |
| 35 | 1 | 1 | −1 | 1 | 1 | 85.1 | 87.67 |
| 36 | 0 | 0 | 0 | 0 | 0 | 90.9 | 90.88 |
| 37 | 1 | 1 | −1 | 1 | −1 | 84.5 | 83.00 |
| 38 | 0 | 0 | 0 | 0 | 0 | 90.9 | 90.88 |
| 39 | −1 | −1 | −1 | −1 | 1 | 77.6 | 79.27 |
| 40 | 0 | 0 | 2.38 | 0 | 0 | 75.0 | 73.27 |
| 41 | −1 | −1 | −1 | 1 | −1 | 78.9 | 77.59 |
| 42 | −1 | 1 | −1 | −1 | 1 | 83.4 | 82.51 |
| 43 | 0 | 0 | 0 | 0 | 0 | 91.1 | 90.88 |
| 44 | 0 | 0 | 0 | 0 | 0 | 91.1 | 90.88 |
| 45 | 1 | 1 | 1 | 1 | 1 | 84.5 | 83.69 |
| 46 | 0 | −2.38 | 0 | 0 | 0 | 77.9 | 77.87 |
| 47 | −1 | 1 | −1 | −1 | −1 | 79.0 | 80.61 |
| 48 | 0 | 0 | 0 | 0 | 2.38 | 75.6 | 74.53 |
| 49 | 0 | 0 | −2.38 | 0 | 0 | 75.2 | 75.37 |
| 50 | −1 | 1 | −1 | 1 | 1 | 86.2 | 85.10 |

**Table 2:** CCD matrix for the experimental design and predicted responses for lead removal.

For a good statistical model, $R^2$value should be close to $1.0$. The value of the Adj $R^2$ $(0.9236)$ is also high to advocate for a high significance of the model. The Pred $R^2$ $0.8387$ are in reasonable agreement with the Adj $R^2$. The value of CV is also low as $4.96$ indicates that the deviations between experimental and predicted values are low. Adeq Precision measures the signal-to-noise ratio. A ratio greater than $4$ is desirable. In this work, the ratio is found to be $> 18$, which indicates an adequate signal.

| Source | Coefficient factor | $F$ value | $P$ value |
|---|---|---|---|
| Model | 90.85 | 30.63 | $< 0.0001$[a] |
| A | −0.35 | 2.35 | $< 0.0359$[a] |
| B | 1.03 | 20.04 | 0.0001 |
| C | −0.44 | 3.66 | 0.0456 |
| D | 1.77 | 58.86 | 0.0001 |
| E | 0.38 | 2.74 | 0.0495 |
| A*A | −1.92 | 89.50 | $< 0.0001$ |
| B*B | −1.86 | 83.83 | $< 0.0001$ |
| C*C | −2.92 | 206.67 | $< 0.0001$ |
| D*D | −1.42 | 48.73 | $< 0.0001$ |
| E*E | −3.04 | 224.55 | $< 0.0001$ |
| A*B | −0.094 | 0.12 | 0.7288 |
| A*C | 0.17 | 0.40 | 0.5335 |
| A*D | 1.84 | 47.10 | 0.0001[a] |
| A*E | 0.062 | 0.054 | 0.8171 |
| B*C | −0.46 | 2.90 | 0.0991 |
| B*D | 0.35 | 1.71 | 0.2014 |
| B*E | 0.39 | 2.09 | 0.1586 |
| C*D | −0.39 | 2.09 | 0.1586 |
| C*E | −0.87 | 10.68 | 0.0028 |
| D*E | 0.63 | | 0.0254 |
| Residual | | | |
| Lack of fit | | 222.51 | $< 0.0001$ |
| Pure error | | | |
| Cor total | | | |

Std dev: 1.51; $R^2$: 0.9548; adjusted $R^2$: 0.9236; predicted $R^2$: 0.8387; adeq precision: 18.47; CV (%): 1.87

**Table 3:** Analysis of variance (ANOVA) for response surface quadratic model.

The experimental results are analyzed through RSM. The results of theoretically predicted response are shown in Table 2. The mathematical expression of relationship to the response with variables are shown as follows:

$$\begin{aligned} Y = {} & 90.85 - 0.35*A + 1.03*B - 0.44*C + 1.77*D \\ & + 0.38*E - 0.094*AB + 0.17*AC + 1.84*AD \\ & + 0.062*AE - 0.46*BC + 0.35*BD + 0.39*BE \\ & - 0.39*CD - 0.87*CE + 0.63*DE - 1.92*A^2 \\ & - 1.86*B^2 - 2.92*C^2 - 1.42*D^2 - 3.04*E^2, \end{aligned} \tag{3}$$

where $Y$ is the percentage removal of lead and A, B, C, D and E are the coded values of the test variables, pH, temperature (°C), sorbent dosage (g/L), lead concentration (mg/L), and contact time (min), respectively.

The results of multiple linear regressions conducted for the second-order response surface model are given in Table 3. The significance of each coefficient was determined by Student's $t$-test and $P$-values, which are listed in Table 3.

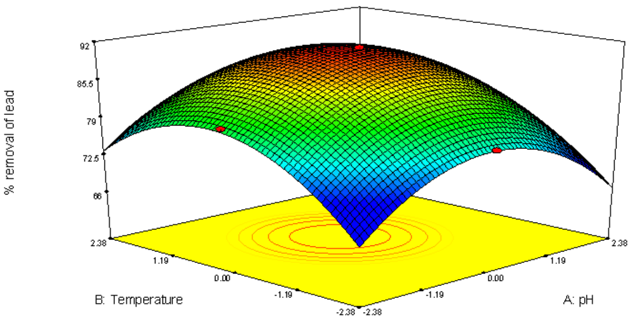


**Figure 1:** 3D plot of lead removal (%) showing interactive effect of pH and temperature.

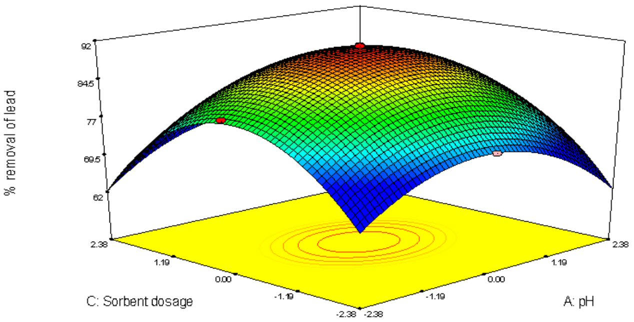


**Figure 2:** 3D plot of lead removal (%) showing interactive effect of pH and sorbent dosage.

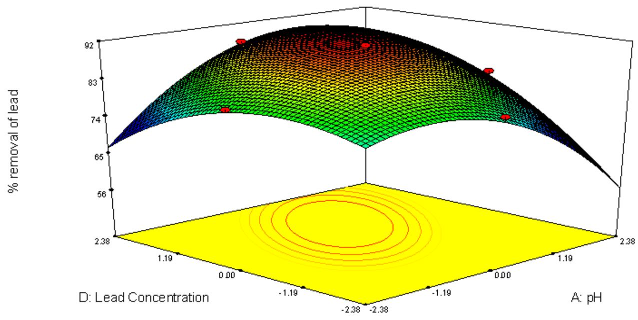


**Figure 3:** 3D plot of lead removal (%) showing interactive effect of pH and lead concentration.

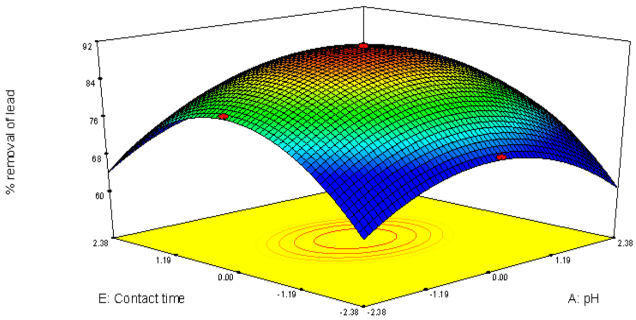


**Figure 4:** 3D plot of lead removal (%) showing interactive effect of pH and contact time.

The larger the magnitude of the $t$-value and smaller the $P$-value, the more significant is the corresponding coefficient. Values of "Prob $>$ $F$" less than $0.0500$ indicate that the model terms are significant. In this case, A, B, C, D, E, AD, BD, CE, $A^2$, $B^2$, $C^2$, $D^2$ and $E^2$ are significant model terms for the sorption of lead. Values greater than $0.10$ indicate that the model terms are not significant. This implies that the linear and square effects of pH, temperature, sorbent dosage, lead concentration and contact time are more significant factors. The most significant individual terms are temperature and lead concentration.

### 3.2 Response surfaces and contour plots

Response surface plots as a function of two factors at a time, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors. These plots can be easily obtained by calculating from the model, the values taken by one factor where the second varies with constraint of a given $Y$ value. The response surface curves were plotted to understand the interaction of the variables and to determine the optimum level of each variable for maximum response. The response surface curves for the removal of lead are shown in Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The nature of the response surface curves shows the interaction between the variables. The elliptical shape of the curve indicates good interaction of the two variables and circular shape indicates no interaction between the variables. From the figures, it was observed that the elliptical nature of the contour in 3D-response surface graphs depicts the mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted yield as indicated by the surface confined in the smallest ellipse in the contour diagrams.

The magnitude of $P$ and $F$ values in Table 3 indicates the maximum positive contribution of pH, temperature, sorbent dosage and lead concentration and negative contribution of contact time on the removal of lead. It implies increased lead removal with increase in pH, temperature, sorbent dosage and lead concentration and this is clearly depicted in Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The quadratic terms of pH, temperature, sorbent dosage, lead concentration and contact time have negative effect on lead removal. Further, the interactions of all the process variables have positive effect on lead removal.

Earlier studies indicated that pH of solutions strongly affected heavy metal removal. Figures 1, 2, 3, and 4 show the effect of initial pH of the solution on the removal of lead. The sorption capacity of *Hypnea valentiae* was low at initial pH 3.0, but increased considerably from 72% to

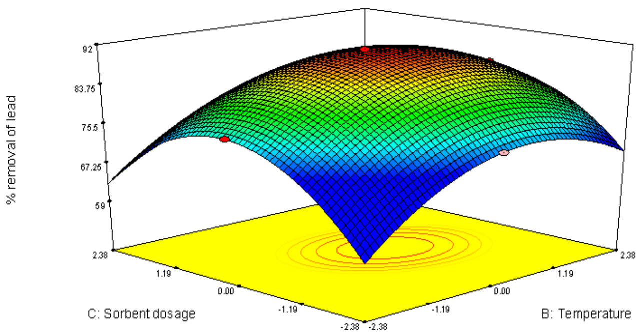


**Figure 5:** 3D plot of lead removal (%) showing interactive effect of temperature and sorbent dosage.

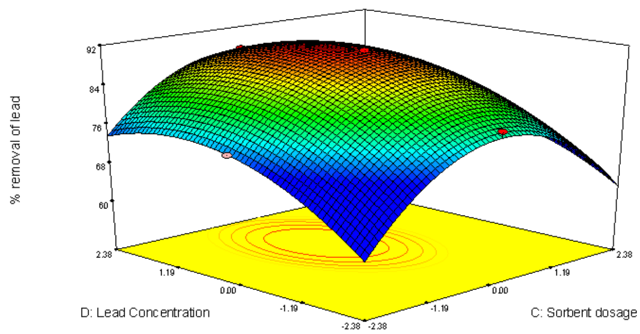


**Figure 8:** 3D plot of lead removal (%) showing interactive effect of sorbent dosage and lead concentration.

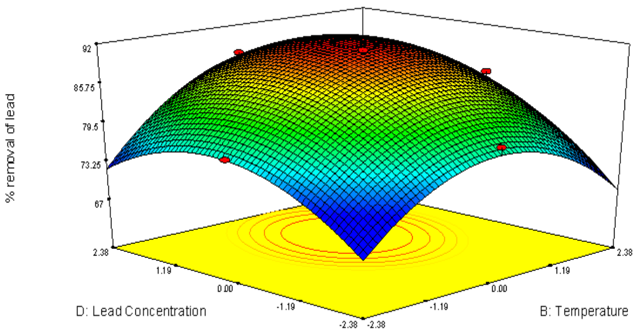


**Figure 6:** 3D plot of lead removal (%) showing interactive effect of temperature and lead concentration.

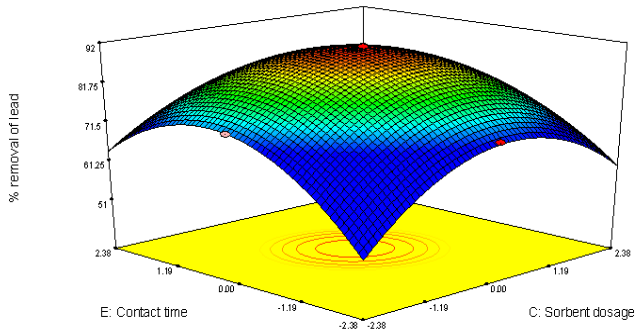


**Figure 9:** 3D plot of lead removal (%) showing interactive effect of sorbent dosage and contact time.

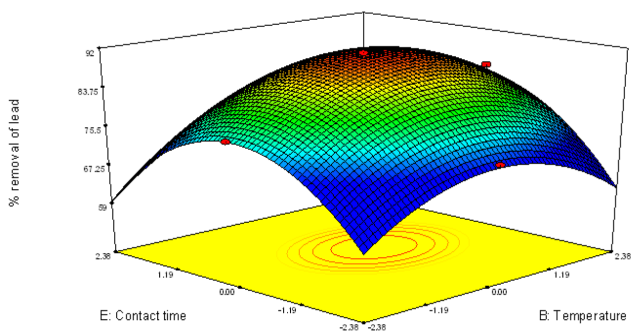


**Figure 7:** 3D plot of lead removal (%) showing interactive effect of temperature and contact time.

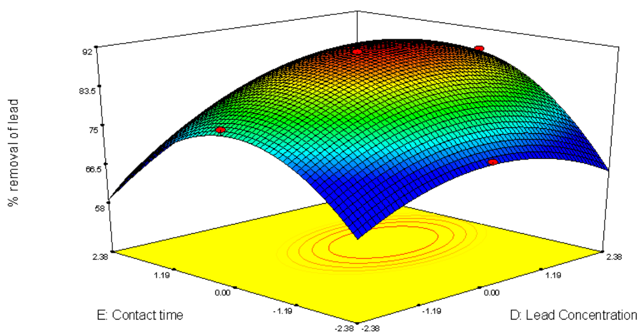


**Figure 10:** 3D plot of lead removal (%) showing interactive effect of lead concentration and contact time.

$91\%$ as the pH of experimental solution increased to $5.5$. On further increase in pH, the removal efficiency decreases. The metal sorption mechanism depends on the surfaces of sorbent and nature of the physicochemical interaction of ions. The decreased sorption of lead at low pH (3.0) could be attributed to the competition of the binding sites on the *H. valentiae* for H+ ions whereby lead cannot become easily bound to the sites [26]. It was clear that the optimum pH of lead removal by *Hypnea valentiae* was found to be $5 \pm 0.1$.

From Figures 5, 6, and 7, it was observed that the sorption of lead increased from $69\%$ to $91\%$ with increase in temperature from 25 °C to 38 °C. A maximum sorption of $91\%$ lead has been obtained at $36 \pm 1$ °C. This suggests that sorption between seaweed and lead could involve a combination of chemical interaction and physical adsorption. With the increase in temperature, pores in the seaweed enlarge, resulting in increased surface available for the sorption, diffusion and penetration of cadmium ions within the pores of seaweed causing increased sorption [21]. Also, increasing temperature is known to increase the diffusion rate of adsorbate molecules within pores as a result of decreasing solution viscosity and will also modify the equilibrium capacity of the adsorbent for a particular adsorbate [11].

The sorbent dosage used for the treatment studies is an important parameter, which determines the potential of sorbent to remove lead at a given initial concentration. As shown in Figures 8 and 9, the removal of lead increased with an increase in sorbent dosage. From the investigations of findings, it was shown that the removal of lead increased up to $5$ g/L and thereafter it decreases. The decrease in sorption capacity may be due to splitting effect of concentration gradient between sorbate and sorbent with increasing seaweed concentration causing a decrease in the amount of lead adsorbed onto unit weight of *Hypnea valentiae*. Therefore, the optimum value of sorbent dosage was found to be $5 \pm 0.2$ g/L.

The lead sorption of *Hypnea valentiae* is depicted in Figure 10. Percentage (%) removal of lead has been found to be higher in the concentration range of lead $100$–$115$ mg/L; a maximum lead removal of $91\%$ has been obtained for *Hypnea valentiae* algae. The increase of lead sorption capacity of sorbent with an increase in lead concentration is probably due to higher interaction between metal ions and the sorbent. A similar result has been reported by Das and Guha [4] for chromium (III) removal by biomass of *Termitomyces clypeatus*. As seen in Figure 10, the percentage of lead removal increased by contact time up to $30$ min. After that point, there was no considerable change in lead removal. Therefore, optimum contact time was considered as $30$ min. The studies of the contour plot (Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10) also reveal the optimum region of the process conditions for the removal of lead using the red algae *Hypnea valentiae*.

### 3.3 Optimum condition for lead removal

Optimum conditions for the removal of lead from aqueous solution using a red algae *Hypnea valentiae* were found. Second-order polynomial models obtained in this study were utilized for each response in order to determine the specified optimum conditions. The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression equation (3). The optimum values obtained by substituting the respective coded values of variables are as follows: pH: $5.1$, temperature: $36.8\,^{\circ}$C, sorbent dosage: $5.1$ g/L, lead concentration: $100$ mg/L, and contact time: $30$ min. At this point, the maximum lead removal was found to be $92\%$.

## 4 Conclusions

The sorption of lead on *Hypnea valentiae*, a red algae, was investigated in a batch system. The sorption conditions of lead on *Hypnea valentiae* were optimized by using RSM. The relationship between the response and the independent variables was developed via the quadratic approximating function of lead sorption capacity of sorbent. The optimum conditions were determined as initial pH: $5.1$, temperature: $36.8\,^{\circ}$C, biosorbent concentration: $5.1$ g/L, initial lead concentration: $100$ mg/L and contact time: $30$ min. From this study, it can be concluded that the lead can be removed by using a red algae such as *Hypnea valentiae* which is abundant and cheaply available. This study also clearly showed that response surface methodology was one of the suitable methods to optimize the operating conditions and maximize the lead removal. Analysis of variance showed a high coefficient of determination value ($R^2 = 0.9548$), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

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