

Sorption of Nickel by *Hypnea Valentiae*: Application of Response Surface Methodology

M.Rajasimman and K.Murugaiyan

Abstract—In this work, sorption of nickel 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 nickel 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 nickel were found to be: pH – 5.1, temperature – 36.8°C, sorbent dosage – 5.1 g/L, metal concentration – 100 mg/L and contact time – 30 min. At these optimized conditions the maximum removal of nickel was found to be 91.97%. A coefficient of determination R^2 value 0.9548 shows the fitness of response surface methodology in this work.

Keywords—Optimization, Metal, *Hypnea valentia*, Response surface methodology, Red algae

I. INTRODUCTION

WASTEWATER generated by the electroplating process often contains high concentrations of nickel ions, which would impose severe effects on the aquatic environment and must be properly treated before discharge. As a consequence, increasing attention is being centered on removal and recovery of nickel from various waste streams. Traditional methods such as chemical precipitation have been used to remove nickel from wastewater. 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 that can 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

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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 [1-8].

RSM is a collection of statistical techniques for designing experiments, evaluating the effects of factors and searching for the optimum conditions. It is widely used for multivariable optimization studies in several biotechnological processes, process conditions, fermentation, biosorption of metals, food processing etc. [9-16]. In RSM, several factors are simultaneously varied. The objectives of the present investigation were to quantify the sorption of nickel to unmodified *hypnea valentiae* and to optimize the process parameters for the sorption of nickel using *hypnea valentiae* using RSM.

II. MATERIALS AND METHODS

A. 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 μ m particle size were then directly used as sorbents without any pretreatment.

B. Preparation of Solution

Batch experiments were performed with a magnetic stirrer at 200 rpm using 250 mL beakers containing test solutions. The stock Nickel solution (1g/L) was prepared by dissolving of Nickel sulphate ($\text{NiSO}_4 \cdot \text{H}_2\text{O}$) of analytical grade in deionised water. Other concentrations were prepared by dilution of this stock solution and fresh dilutions were used in each experiment. The pH of the solutions was adjusted by using 0.1M HCl and 0.1M NaOH.

C. 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 nickel in the Central composite design. In order to describe the effects of pH, adsorbent dosage, temperature, initial nickel concentration and processing time on percentage removal of nickel batch experiments were conducted. The coded values of the process parameters were determined by the following equation.

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (1)$$

Where x_i - coded value of the i^{th} variable, X_i - uncoded value of the i^{th} test variable and X_0 - 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

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

TABLE I
EXPERIMENTAL RANGE AND LEVELS OF INDEPENDENT PROCESS VARIABLES

Independent variable	Range and levels				
	- 2.38	-1	0	1	2.38
pH (A)	5	6	7	8	9
Temperature,(B) °C	30	35	40	45	50
Sorbent dosage,(C) g/L	4	5	6	7	8
Nickel concentration, (D) mg/L	20	40	60	80	100
Contact time, (E) min	20	30	40	50	60

where Y is the predicted response, β_i , β_j , β_{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 nickel. 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 nickel concentration using an atomic absorption spectrophotometer.

TABLE II
CCD MATRIX FOR THE EXPERIMENTAL DESIGN AND PREDICTED RESPONSES FOR NICKEL REMOVAL

Run. No	A	B	C	D	% Nickel removal		
					Experimental	Theoretical	
1	1	1	-1	-1	1	69.2	70.78
2	1	1	1	-1	1	69.8	69.06
3	0	0	0	2.38	0	66.3	67.00
4	1	1	-1	-1	-1	70.3	70.61
5	1	-1	1	1	1	72.6	74.06
6	-1	1	1	-1	1	71.6	71.18
7	0	0	0	0	0	84.7	84.92
8	-1	-1	1	1	-1	78.4	77.37
9	-1	1	1	1	1	74.2	74.68
10	-1	-1	-1	-1	-1	77.5	78.04
11	0	0	0	0	0	84.8	84.92
12	-1	-1	1	-1	-1	80.2	80.20
13	-1	1	1	1	-1	78.9	79.15
14	0	2.38	0	0	0	77.2	78.47
15	1	-1	1	-1	-1	76.2	76.51
16	0	0	0	-2.38	0	63.2	63.65
17	-1	-1	1	1	1	74.8	73.95
18	1	-1	-1	-1	1	78.6	76.68
19	1	-1	-1	1	-1	75.3	74.76
20	0	0	0	0	-2.38	74.3	74.75
21	-1	1	1	-1	-1	73.4	74.93
22	2.38	0	0	0	0	78.7	79.03
23	1	-1	-1	-1	-1	75.9	75.45
24	-1	-1	1	-1	1	79.3	77.50
25	1	-1	1	1	-1	76.6	76.63
26	1	-1	1	-1	1	73.5	74.66
27	-2.38	0	0	0	0	80.3	81.16
28	1	1	1	-1	-1	73.4	71.96
29	0	0	0	0	0	84.9	84.92
30	1	-1	-1	1	1	75.8	75.26
31	-1	1	-1	1	-1	77.3	75.88
32	-1	-1	-1	1	1	74	74.05
33	0	0	0	0	0	84.8	84.92
34	1	1	1	1	-1	80.2	79.14
35	1	1	-1	1	1	77.9	76.41
36	0	0	0	0	0	84.9	84.92
37	1	1	-1	1	-1	75.3	76.96
38	0	0	0	0	0	84.9	84.92
39	-1	-1	-1	-1	1	76.9	78.42
40	0	0	2.38	0	0	70.1	70.62
41	-1	-1	-1	1	-1	73.9	74.40
42	-1	1	-1	-1	1	72.8	71.80
43	0	0	0	0	0	84.9	84.92
44	0	0	0	0	0	84.8	84.92
45	1	1	1	1	1	76.5	75.52
46	0	-2.38	0	0	0	83.5	83.37
47	-1	1	-1	-1	-1	74.6	72.47
48	0	0	0	0	2.38	70.2	70.89
49	0	0	-2.38	0	0	68.5	69.12
50	-1	1	-1	1	1	74.5	74.48

III. RESULTS AND DISCUSSION

A. Experimental design by RSM

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 nickel using the red algae. A Model F-value of 44.26 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 353.44 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 0.9683. This implies that more than 96% 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. For a good statistical model, R^2 value should be close to 1.0. The adjusted R^2 value corrects the R^2 value for the sample size and for the number of terms in the model. The value of the Adj R^2 (0.9464) is also high to advocate for a high significance of the model. If there are many terms in the model and the sample size is not very large, the adjusted R^2 may be noticeably smaller than the R^2 . Here in this case the adjusted R^2 value is lesser than the R^2 . The Pred R^2 0.8891 are in reasonable agreement with the Adj R^2 . The value of CV is also low as 1.60 indicate 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 >26 , which indicates an adequate signal.

The experimental results are analyzed through RSM to obtain in empirical model for the best response. The results of theoretically predicted response are shown in Table 2. The mathematical expression of relationship to the response with variables are shown below

$$Y = 84.93 - 0.44*A - 1.03*B + 0.31*C + 0.70*D - 0.81*E + 0.18*A*B - 0.27*A*C + 0.74*A*D + 0.21*A*E + 0.075*B*C + 1.76*B*D - 0.26*B*E + 0.21*C*D - 0.77*C*E - 0.18*D*E - 0.86*A^2 - 0.71*B^2 - 2.66*C^2 - 3.47* D^2 - 2.14*E^2 \quad (3)$$

where Y is the percentage removal of nickel.

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. 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 model terms are significant. In this case, A, B, D, E, AD, BD, CE, A^2 , B^2 , C^2 , D^2 and E^2 are significant model terms for the sorption of nickel. Values greater than 0.10 indicate the model terms are not significant. This implies that the linear and square effects of pH, temperature, sorbent dosage, nickel concentration and contact time are more significant factors.

B. 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 nickel are shown in Figs 1-

TABLE III
ANALYSIS OF VARIANCE (ANOVA) FOR RESPONSE SURFACE QUADRATIC MODEL

Source	Coefficient factor	F	P-value Prob> F
Model	84.93	44.26	< 0.0001 ^a
A	-0.44	5.61	0.0247 ^a
B	-1.03	30.89	< 0.0001 ^a
C	0.31	2.88	0.1005
D	0.70	14.34	0.0007 ^a
E	-0.81	19.20	0.0001 ^a
A*A	-0.86	27.62	<0.0001 ^a
B*B	-0.71	18.81	0.0002 ^a
C*C	-2.66	265.16	<0.0001 ^a
D*D	-3.47	449.56	<0.0001 ^a
E*E	-2.14	171.46	<0.0001 ^a
A*B	0.18	0.71	0.4071
A*C	-0.27	1.63	0.2120
A*D	0.74	11.72	0.0019 ^a
A*E	0.21	0.97	0.3322
B*C	0.075	0.12	0.7303
B*D	1.76	66.91	<0.0001 ^a
B*E	-0.26	1.48	0.2329
C*D	0.21	0.92	0.3464
C*E	-0.77	12.73	0.0013 ^a
D*E	-0.18	0.71	0.4071
Residual			
Lack of fit		353.44	<0.0001
Pure Error			
Cor Total			
Pure Error			
Cor Total			

^a – significant variable

R^2 - 0.9683; Adj R^2 - 0.9464; C.V. % - 1.60; Pred R^2 - 0.8891; Adeq Precision - 26.93

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 figures it was observed that the elliptical nature of the contour in 3D-response surface graphs depict 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.

Earlier studies indicated that pH of solutions strongly affected heavy metal removal. Figs. 1-4 show the effect of initial pH of the solution on the removal of nickel. The sorption capacity of *hypnea valentiae* was low at initial pH 3.0, but increased considerably from 72% to 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 nickel at low pH (3.0) could be attributed to the competition of the binding sites on the *H. valentiae* for H^+ ions whereby nickel cannot become easily bound to the sites [17]. It was clear that the optimum pH of nickel removal by *hypnea valentiae* was found to be 5 ± 0.1 .

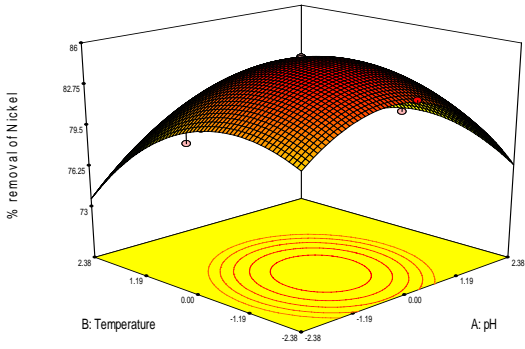


Fig. 1. The 3D plot showing the effects of pH, temperature and their mutual interaction on nickel removal

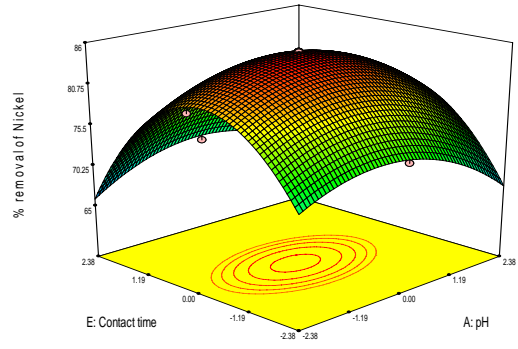


Fig. 4. The 3D plot showing the effects of pH, contact time and their mutual interaction on nickel removal

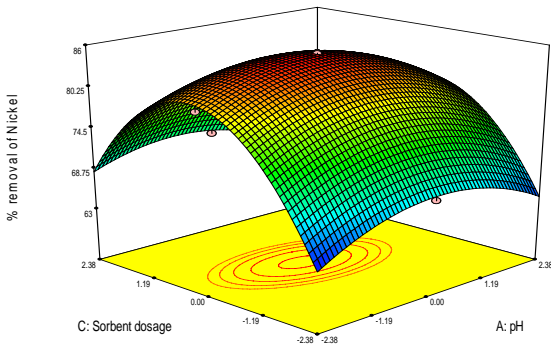


Fig. 2. The 3D plot showing the effects of pH, sorbent dosage and their mutual interaction on nickel removal

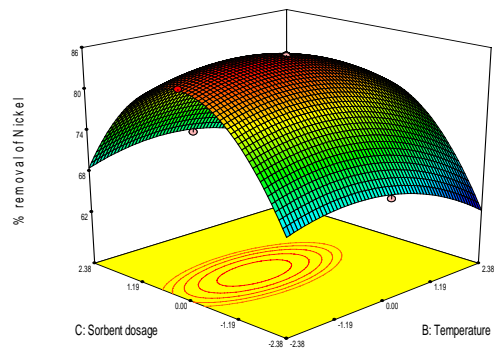


Fig. 5. The 3D plot showing the effects of temperature, sorbent dosage and their mutual interaction on nickel removal

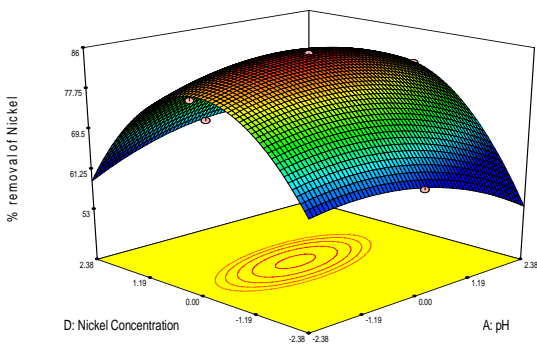


Fig. 3. The 3D plot showing the effects of pH, nickel concentration and their mutual interaction on nickel removal

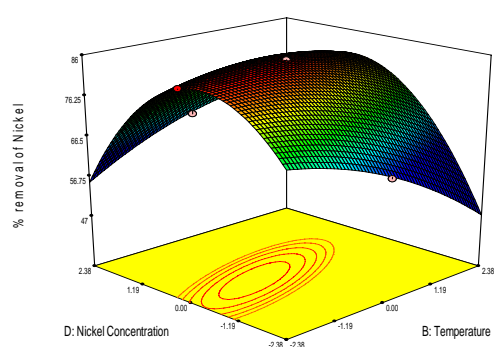


Fig. 6. The 3D plot showing the effects of temperature, nickel concentration and their mutual interaction on nickel removal

From Figs.5-7, it was observed that the sorption of nickel increased from 69% to 91% with increase in temperature from 25 to 38°C. A maximum sorption of 91% nickel has been obtained at 36±1°C. This suggests that sorption between seaweed and nickel 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 [18]. 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 [19].

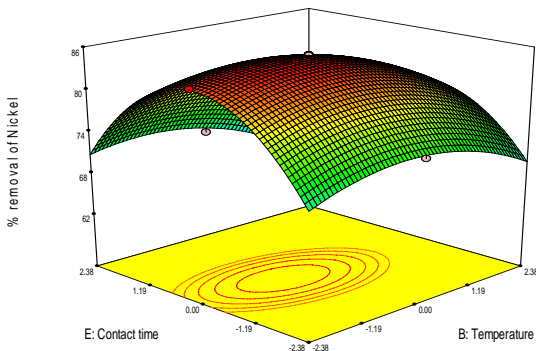


Fig. 7. The 3D plot showing the effects of temperature, contact time and their mutual interaction on nickel removal

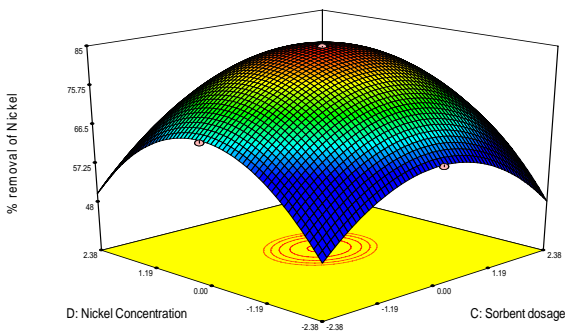


Fig. 8. The 3D plot showing the effects of sorbent dosage, nickel concentration and their mutual interaction on nickel removal

The sorbent dosage used for the treatment studies is an important parameter, which determines the potential of sorbent to remove nickel at a given initial concentration. As shown in Figs. 8 & 9, the removal of nickel increased with an increase in sorbent dosage. From the investigations of findings, it was shown that the removal of nickel 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 amount of nickel adsorbed onto unit weight of *hypnea valentiae*. Therefore, the optimum value of sorbent dosage was found to be 5±0.2 g/L.

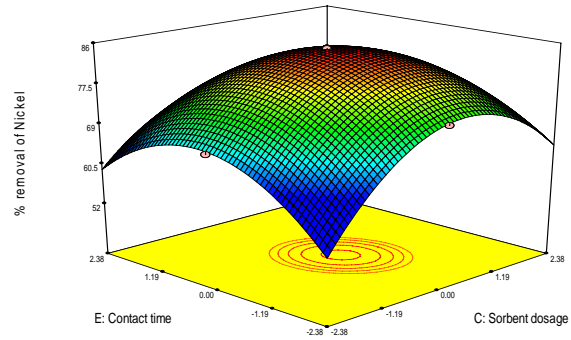


Fig. 9. The 3D plot showing the effects of sorbent dosage, contact time and their mutual interaction on nickel removal

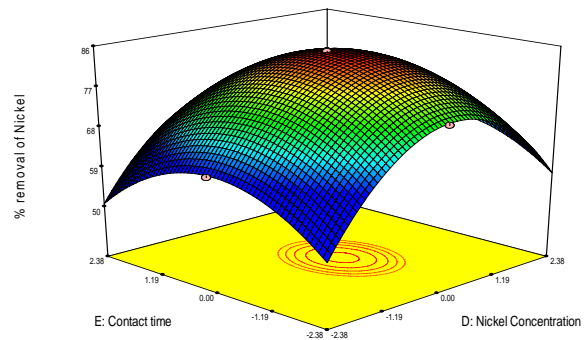


Fig. 10. The 3D plot showing the effects of nickel concentration, contact time and their mutual interaction on nickel removal

The nickel sorption of *hypnea valentiae* is depicted in Fig. 10. Percentage removal of nickel has been found to be higher in the concentration range of nickel 100 - 115 mg/L; a maximum nickel removal of 91% has been obtained for *hypnea valentiae* algae. The increase of nickel sorption capacity of sorbent with an increase in nickel concentration is probably due to higher interaction between metal ions and the sorbent. A similar result has been reported by Das and Guha (2007) [20] for chromium (III) removal by biomass of *Termitomyces clypeatus*. As seen in Fig. 10, the percentage of nickel removal increased by contact time up to 30 min. After that point, there was no considerable change in nickel removal. Therefore, optimum contact time was considered as 30 min. The studies of the contour plot (Figs. 1-10) also reveal the optimum region of the process conditions for the removal of nickel using the red algae *hypnea valentiae*.

C. Optimum Condition for Nickel Removal

Optimum conditions for the removal of nickel 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: pH – 5.1, temperature – 36.8°C, sorbent dosage – 5.1 g/L, nickel concentration – 100 mg/L, contact time – 30 min. At this point, the maximum nickel removal was found to be 92%.

IV. CONCLUSION

The sorption of nickel on *hypnea valentiae*, a red algae, was investigated in a batch system. The sorption conditions of nickel 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 nickel sorption capacity of sorbent. The optimum conditions were determined as initial pH - 5.1, temperature – 36.8°C, biosorbent concentration - 5.1 g/L, initial nickel concentration - 100 mg/L and contact time – 30 min. From this study, it can be concluded that the nickel 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 nickel 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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