OPTIMIZATION OF PROCESS VARIABLES FOR THE BIOSORPTION OF CHROMIUM USING *Hypnea valentiae*

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Abstract: In this study, *Hypnea valentiae,* a red alga is used as a sorbent for the removal of chromium from aqueous solutions. The biosorption potential of *Hypnea valentiae* was investigated in batch experiments. The process parameters were optimized using response surface methodology. Based on the central composite design, quadratic model was developed to correlate the 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 maximum biosorption of chromium are pH – 2.8, temperature – 48.2°C, sorbent dosage – 5.3 g/L, metal concentration – 103 mg/L and contact time – 27 min. At these optimized conditions the maximum removal was found to be 94.5%.

Key words: *Hypnea valentiae,* optimization, RSM, chromium, algae, biosorption

1. Introduction

Toxic heavy metals are detrimental to human health and ecosystem stability. The removal and recovery of heavy metals from wastewater is important in the protection of the human health and environment. The most toxic metals are aluminium, chromium, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead. The major industries that contribute to water pollution by chromium are mining, leather tanning, textile dyeing, electroplating, plants producing industrial inorganic chemicals etc. Chromium (Cr) bearing wastewater resulted from all these industries must be disposed off after treatment. Traditional methods such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes have been used to remove chromium 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 greater selectivity for transition and heavy metals. Marine algae have been found to be potential suitable sorbents because of their low cost, relatively high surface area and high binding affinity. The use of marine algae for heavy metal removal has been reported by several authors (TIEN, 2002; JALALI *et al*., 2002; PRASANNAKUMAR *et al*., 2007; DENG *et al*., 2007; OZER *et al*., 2009).

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 processes (RAVIKUMAR *et al*., 2005; KORBAHTI, 2007; ALEBOYEH *et al.,* 2008; GARG *et al*., 2008; RAJASIMMAN *et al*., 2009; RAJESHKANNAN *et al*., 2009). So far no work has been carried out for the removal of chromium using *H. valentiae.* Hence the objectives of the present investigation are to quantify the biosorption of chromium to unmodified *H. valentiae* and to optimize the process parameters for the biosorption of chromium using *H. valentiae* using response surface methodology.

2. Materials and methods

2.1 Preparation of adsorbent

The red colored marine alga *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 continued till the wash water contained no dirt. The washed alga was then completely dried in sunlight for 10 days. The dried alga 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 μm particle size were then directly used as sorbents without any pre-treatment.

2.2 Preparation of solution

Batch experiments were performed with a magnetic stirrer (REMI, India) at 200 rpm using 250 mL beakers containing test solutions. The stock chromium solution (1 g/L) was prepared by dissolving potassium dichromate (SD fine chemicals, India) 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 chromium in the Central Composite Design. The coded values of the process parameters were determined by the following equation:

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

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 are given in Table 1. The experiment design is 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

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

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.

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

Independent variable	Range and levels				
	- 2.38	**-1**	**0**	**1**	**+2.38**
pH (A)	1	2	3	4	5
Temperature, (B) °C	25	35	45	55	65
Sorbent dosage, (C) g/L	3	4	5	6	7
Chromium concentration, (D) mg/L	50	75	100	125	150
Contact time, (E) min	10	20	30	40	50

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 chromium.

After biosorption, 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 chromium concentration using an atomic absorption spectrophotometer (ELICO, India).

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 biosorption of chromium using the red alga. A Model *F*-value of 94.93 implies that the model is significant. The Fisher *F*-test with a very low probability value ($P_{model} > F = 0.0001$) demonstrates a very high significance for the regression model. The fitness of the model is checked by the determination coefficient (R^2). The coefficient of determination (R^2) was calculated to be 0.9850. This implies that more than 98.5 % of experimental data was compatible with the data predicted by the model (Table 2) and only less than 1.5 % 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.

Table 2. CCD matrix for the experimental design and responses for chromium removal.

Run No.	A	B	C	D	E	% chromium removal	
						Experimental	**Theoretical**
1	1	1	-1	-1	1	65.2	66.50
2	1	1	1	-1	1	76.3	75.51
3	0	0	0	2.38	0	82.5	81.37
4	1	1	-1	-1	-1	69.2	68.84
5	1	-1	1	1	1	79.2	80.92
6	-1	1	1	-1	1	80.3	80.93
7	0	0	0	0	0	93.6	93.41
8	-1	-1	1	1	-1	74.6	73.72
9	-1	1	1	1	1	83.2	82.13
10	-1	-1	-1	-1	-1	79.8	80.67
11	0	0	0	0	0	93.5	93.41
12	-1	-1	1	-1	-1	83.6	82.78
13	-1	1	1	1	-1	86.2	86.73
14	0	2.38	0	0	0	82.2	81.18
15	1	-1	1	-1	-1	83	83.71
16	0	0	0	-2.38	0	79.6	79.17
17	-1	-1	1	1	1	70.8	71.67
18	1	-1	-1	-1	1	78.4	78.82
19	1	-1	-1	1	-1	79.6	79.24
20	0	0	0	0	-2.38	82.3	81.37
21	-1	1	1	-1	-1	87.6	88.72
22	2.38	0	0	0	0	75	73.84
23	1	-1	-1	-1	-1	77.2	78.60
24	-1	-1	1	-1	1	76.2	77.55
25	1	-1	1	1	-1	80.6	80.42
26	1	-1	1	-1	1	81.9	81.02
27	-2.38	0	0	0	0	76.3	75.90
28	1	1	1	-1	-1	80.3	80.76
29	0	0	0	0	0	93.6	93.41
30	1	-1	-1	1	1	83.1	82.66
31	-1	1	-1	1	-1	80.6	81.75
32	-1	-1	-1	1	1	76.2	76.44
33	0	0	0	0	0	93.4	93.41
34	1	1	1	1	-1	83.1	84.55
35	1	1	-1	1	1	76.4	77.40
36	0	0	0	0	0	93.6	93.41
37	1	1	-1	1	-1	76.8	76.55
38	0	0	0	0	0	93.4	93.41
39	-1	-1	-1	-1	1	79.9	78.36
40	0	0	2.38	0	0	76.2	75.44
41	-1	-1	-1	1	-1	74.2	75.56
42	-1	1	-1	-1	1	73.8	74.93
43	0	0	0	0	0	93.5	93.41
44	0	0	0	0	0	93.5	93.41
45	1	1	1	1	1	82.3	82.47
46	0	-2.38	0	0	0	80.9	80.36
47	-1	1	-1	-1	-1	81.2	79.80
48	0	0	0	0	2.38	76.8	76.17
49	0	0	-2.38	0	0	67.7	66.90
50	-1	1	-1	1	1	80.1	80.07

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 (0.9746) is also high to advocate for a high significance of the model. The Pred R^2 0.9451 is in reasonable agreement with the Adj R^2. 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

$$\text{\% removal of chromium} = 93.38 - 0.43\,A + 0.17\,B + 1.79C + 0.46\,D - 1.09\,E - 3.27\,A^2 - 2.23\,B^2 - 3.93C^2 - 2.32D^2 - 2.58\,E^2 - 2.22\,AB + 0.75AC + 1.44AD + 0.63\,AE + 1.70BC + 1.77BD - 0.64\,BE - 0.98CD - 0.73CE + 0.80\,DE \quad (3)$$

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, C, D, E, AB, AC, AD, AE, BC, BD, BE, CD, CE, DE, A^2, B^2, C^2, D^2, E^2 are significant model terms for the biosorption of chromium. Values greater than 0.10 indicate the model terms are not significant. This implies that the linear, square and interactive effects of pH, temperature, sorbent dosage, chromium concentration and contact time are more significant factors.

Table 3. Analysis of variance (ANOVA) for Response surface quadratic model

Source	Coefficient factor	*F* value	*P*
Model	93.38	94.93	< 0.0001[a]
A	-0.43	6.54	< 0.0160[a]
B	0.17	1.01	0.0328
C	1.79	111.85	< 0.0001
D	0.46	7.41	0.0109
E	-1.09	41.58	<0.0001
A*A	-3.27	477.44	<0.0001
B*B	-2.23	221.62	<0.0001
C*C	-3.93	687.34	<0.0001
D*D	-2.32	239.54	<0.0001
E*E	-2.58	297.47	<0.0001
A*B	-2.22	126.72	<0.0001
A*C	0.75	14.56	0.0007
A*D	1.44	53.27	<0.0001[a]
A*E	0.63	10.33	0.0032
B*C	1.70	74.45	<0.0001
B*D	1.77	80.02	<0.0001
B*E	-0.64	10.53	0.0030
C*D	-0.98	24.87	<0.0001
C*E	-0.73	13.61	0.0009
D*E	0.80	16.30	0.0004
Residual			
Lack of fit		235.65	<0.0001
Pure Error			
Cor Total			

Std. Dev.-1.12 ; R^2 0.9850; Adj. R^2-0.9746; Pred. R^2 - 0.9451; C.V.% - 1.38; Adeq Precision - 37.158

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. 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 chromium are shown in Figs 1-4. 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.

Figure 1-4 shows the effect of solution pH on chromium removal. The results indicate that the percentage removal of chromium varies from 65% to 93% in the pH range 1 to 5, suggesting that the removal was highly pH-dependent. The biosorption capacity of *H. valentiae* was high at initial pH 2.8, but decreased considerably from 93% to 71% as the pH of experimental solution increased to 5.0. From Fig. 1 it was observed that the biosorption of chromium increased from 65% to 93% with increase in temperature from 25 to 49°C. A maximum biosorption of 93% chromium has been obtained at 49°C. This suggests that biosorption between seaweed and chromium 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 biosorption, diffusion and penetration of chromium ions within the pores of seaweed causing increased biosorption (SALEEM *et al*., 2007).

Amount of sorbent used for the treatment studies is an important parameter, which determines the potential of sorbent to remove chromium at a given initial concentration. As shown in Fig. 2, the removal of chromium increased with an increase in sorbent dosage (upto 5 g/L) and then decreased. Therefore, the optimum value of sorbent dosage was found to be 5.3 g/L. With increasing the quantity of seaweed, beyond this optimum condition, biosorption capacity decreases for *H. valentiae*. The decrease in biosorption capacity may be due to splitting effect of concentration gradient between sorbate and sorbent with increasing seaweed concentration causing a decrease in amount of chromium adsorbed onto unit weight of *H. valentiae*.

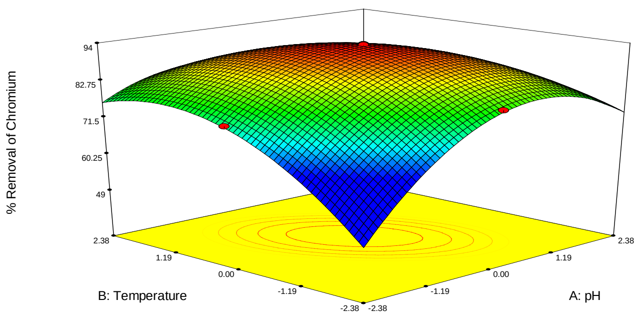

Fig. 1. 3D plot showing interactive effect of pH and temperature on Cr removal.

Percentage removal of chromium has been found to be higher at lower concentration of chromium solution (100 mg/L); a maximum chromium removal of 93% has been obtained for *H. valentiae* (Fig. 3). The increase of chromium biosorption capacity of sorbent with an increase in chromium concentration is probably due to higher interaction between metal ions and the sorbent. As seen in Fig. 4, the percentage of chromium removal increased by contact time up to 27 min. After that point, there was no considerable change in chromium removal. Therefore, optimum contact time was considered as 27 min.

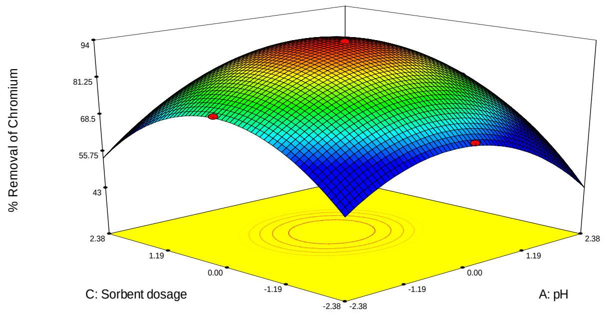

Fig. 2. 3D plot showing interactive effect of pH and sorbent dosage on Cr removal.

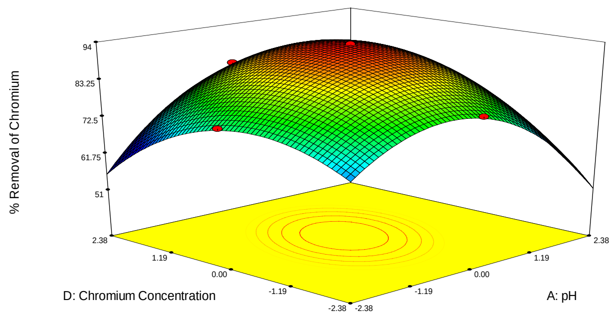

Fig. 3. 3D plot showing interactive effect of pH and chromium concentration on Cr removal.

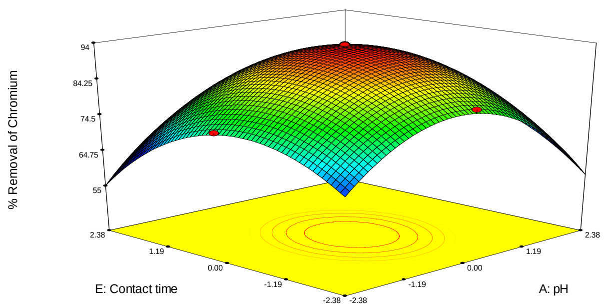

Fig. 4. 3D plot showing interactive effect of pH and contact time on Cr removal.

3.3 Optimum condition for chromium removal

Optimum conditions for the removal of chromium from aqueous solution using a red alga *H. 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 – 2.8, temperature – 48.2^{o}C, sorbent dosage – 5.3 g/L, chromium concentration – 103 mg/L, contact time – 27 min. At this point, the maximum chromium removal was found to be 94.5%.

4. Conclusions

The biosorption of chromium on *H. valentiae*, a red alga, was investigated in a batch system. The biosorption conditions of chromium on *H. valentiae* were optimized by using RSM. The relationship between the response and the independent variables was developed via the quadratic approximating function of chromium biosorption capacity of sorbent. The optimum conditions were determined as initial pH – 2.8, temperature – 48.2°C, biosorbent concentration – 5.3 g/L, initial chromium concentration - 103 mg/L and contact time – 27 min. As a result, a chemical waste containing chromium can be removed by using a red alga such as *H. 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 chromium removal. Analysis of variance showed a high coefficient of determination value (R^2 = 0.9850), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

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