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Evaluation of process parameters for biosorption of chromium (VI) using full factorial design and response surface methodology

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ABSTRACT

The present study is focused on evaluation and optimization of biosorption of hexavalent chromium (Cr (VI)) using marine algae, Sargassum sp. Biosorption kinetics of Cr (VI) was studied using Langmuir and freundlich isotherms. It was found that the adsorption of Cr (VI) by Sargassum sp. could be modeled effectively by Langmuir isotherms (R2 value of 0.994). A Full Factorial Design (FFD) was used to determine the significance of process parameters like, pH, biomass concentration and biomass immobilization on biosorption efficiency. It was found that pH has the maximum effect on biosorption efficiency whereas immobilizing the biomass did not seem to be significant. Central Composite Design (CCD) followed by response surface methodology (RSM) was employed to investigate the process conditions for maximum chromium adsorption. The optimum conditions for the biosorption were found to be pH 1.17 and biomass concentration of 0.3% at an initial Chromium concentration of 100ppm.

KEYWORDS

Biosorption;
Sargassum sp;
Chromium (VI);
Full factorial design (FFD);
Central composite design (CCD);
Response surface method (RSM).

INTRODUCTION

Wastewater contaminated with heavy metal is a common environmental hazard. The metal ions that are dissolved in waste water reach the top of the food chain (Bioaccumulation) and thus become a threat to human health as they are toxic[1]. Heavy metals are released during industrial and mining processes, which are threat to living organisms. It therefore becomes important to develop technologies for effective removal of heavy metals from waste waters[2]. Chromium is considered to be a toxic metal and a microelement. Hexavalent chromium is more toxic than trivalent chromium. Chromium containing effluents are mostly discharged from electroplating and tanning industries[3]. Thus the removal of Cr (VI) from industrial waste water is essential before discharging it into water[4]. Conventional technologies are not effective as they cannot be used for the removal of metal concentrations smaller than 100mg/l. Moreover, they are expensive and require wide spaces for installation, which results in a high production of sewage which has to be discharged[5]. Seaweeds, agriculture by-products and wastes, together with other materials like bracken fern or lignin have been proposed as low cost alternatives to traditional methods[6]. Marine macro algae have been chosen, among many biosorbents, due to their high binding ability and low cost. Moreover, an adequate reinforcement of seaweeds can provide an increase in their adsorption capacity, stabilization and attrition characteristics, making this biomass suitable for practical uses[7]. The raw algal biomass is stabilized by the main cations present in seawater, such us, Na+,K+,Ca2+ and Mg2+. As a result of simple physical treatment with acid, protons substitute these ions bound to active sites, and then, an increase in the maximum adsorption capacity and an improvement in the biomass stability are obtained[8].

Brown algae are one of the most commonly used biosorbents Sargassum muticum is large brown seaweed, varying in colour from dark brown to pale, yellowish brown depending on the season and the growing conditions. The raw and protonated S. muticum have also been used for the treatment of real wastewaters from an electroplating industry[6]. It is typically found in tropical countries and abundant in coastal areas, and it is easily collected on beaches without any environmental damage[9].

Nonviable biomass is not biologically active and its metal uptake can be regarded as a passive adsorption process and, thus, be correlated with mathematical sorption models as the Langmuir and Freundlich equations[10]. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Freundlich isotherm model is used to estimate the adsorption intensity of the sorbent towards the adsorbent[11]. Biosorptive metal uptake can be quantitatively evaluated from the above stated experimental biosorption equilibrium isotherms. The two widely accepted models for single solute systems, the Langmuir and Freundlich isotherms, are described by Equations. (1) and (2), respectively:

$$q^* = (qmaxbC^*)/(1+bC^*) \qquad (1)$$

where qmax and b are Langmuir constants

$$Q^* = a\,(C^*)^n \qquad (2)$$

and a and n are the Freundlich constants[12].

Optimization of biosorption of heavy metals by the classical method involves changing one independent variable while maintaining all others at a fixed level which is extremely time consuming and expensive for a large number of variables. To overcome this difficulty, experimental Central composite design under response surface methodology can be employed to optimize the biosorption of heavy metals[13]. In a multivariate experiment, all of the important variables are changed during each run of trials. The need for this arises because the variables often interact with each other. This will show the best direction to move within the multidimensional space defined by the major variables[14].

The objective of the present work is to study the kinetic parameters and optimize biosorption of Cr (VI) in aqueous solution by using Sargassum sp. in a batch experiment. Kinetic modeling of Sargassum sp. was studied using mathematical models; Langmuir and Freundlich equations. Optimization experiments were carried out by maintaining fixed concentrations of Cr (VI) (100ppm) and by optimizing for pH and biomass concentrations. A central composite design (CCD) followed by response surface methodology (RSM) employed to optimize process parameters.

MATERIALS AND METHODS

Chemical reagents

Pottasium dichromate ($K_2Cr_2O_7$), Calcium Chloride ($CaCl_2$), sodium alginate and 1, 5 Diphenylcarbazide (GR) were the predominant chemicals used for the study. All chemicals used in this study were analytical grade and were purchased from Merck India Pvt. Ltd.

Pretreatment of biomass

Brown seaweed, Sargassum sp. collected from the west coastal region, Udupi, Karnataka, India. The collected seaweed was extensively washed with distilled water to remove particulate material, and dried at 50ºC for 24 h in hot air oven. The dried biomass was soaked in 0.2 M $CaCl_2$ solution to increase the ion exchange efficiency, the solution again kept for drying in hot air oven at 70ºC for 24 hours. The oven dried sample was ground, collected and stored in airtight containers at room temperature.

Immobilization of biomass

Alginate solution was prepared by dissolving 4 g of alginate (sodium salt) in 100 ml of distilled water with constant stirring to avoid formation of lumps. The equal quantity of pre treated algal biomass (4g) was mixed with sodium alginate solution under stirring condition to have a uniform mixture and dropped in to 6% CaCl2 solution using 3mm syringes. The immobilized beads were washed with water and stored at 40ºC.

Preparation of stock solution

The stock solution of chromium (1000 ppm) was prepared by dissolving an accurate quantity of $K_2Cr_2O_7$ in deionized distilled water. Chromium solutions of different concentrations were obtained by diluting the stock solution.

Batch biosorption studies

In the biosorption batch experiments, 0.1 g of 0.2M $CaCl_2$ treated Sargassum sp. were added to a 100 mL metal solution of varying concentration, of which pH was maintained or initially adjusted at 2.0. The solution was then stirred at 250 rpm. The samples were withdrawn at different time intervals. The Cr (VI) concentration was determined by standard colorimetric method[15]. This procedure is meant to measure only hexavalent chromium present in solution by the reaction with 1, 5 diphenylcarbazide in the acid medium. A red-violet complex is formed, the absorbance measured at 540 nm. Percentage of metal removal at any instant of time was determined by the following equation:

Heavy metal removal (%) = ((Ci-Cf)/Cf)*100 (3)

Where, Ci and Cf represent initial and final metal concentration (mg/L) at any instant of time, respectively.

Kinetic studies

0.1g of pretreated Sargassum sp was mixed with 100 mL of Cr (VI) solution of different concentrations: 25, 50, 100, 150, 200, 250 ppm. The experiment was carried out at a constant agitation of 250 rpm and pH was maintained at a constant value of 1.5. Aliquots of samples were collected at different time intervals from each flask (from 25 to 250 ppm) to determine Cr (VI) concentration.

The adsorption data obtained from biosorption studies was analyzed using Langmuir and Freundlich isotherm models. Freundlich and Langmuir isotherm is the (traditional) earliest and simplest known model explains the characteristics of adsorption. The linearized form of Langmuir equation (Eq. 4), helps to predict the characteristics of adsorption material and the Langmuir constants.

(Ceq/q) = (1/qmaxb)+(Ceq/qmax) (4)

where q is amount of metal accumulated by biosorbent material (mg/g); Ceq is the metal residual concentration in solution (mg/L); qmax is the maximum specific uptake corresponding to the site of saturation (mg/g) and b is Langmuir equation constant which represents ratio of adsorption and desorption rates.

The Freundlich isotherm is well known model fits for sorption of metals to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that binding strength decreases with the increasing degree of site occupation. The linearized form of the Freundlich equation was used to analysis the data obtained from biosorption studies (Eq. 5).

Log Qe = logkf + (1/nlogCe) (5)

Where, Ce is the equilibrium concentration of the adsorbate (mg/L) and Qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Kf and n are Freundlich equilibrium coefficients.

Statistical analysis

The conditions for the biosorption of chromium from aqueous solutions of K2Cr2O7 were evaluated using statistical optimization techniques. The three factors, viz., pH, concentration of biomass and immobilization of biomass are tested for the biosorption of chromium and their corresponding ranges are shown in the TABLE 1. A 2^3 full factorial design (FFD) yielding eight sets of experiments was employed to predict the significant factors contributing affecting biosorption of chromium. To predict the optimal value of pH (2-9) and biomass concentration (0.1-0.5), a central composite design (CCD) with five coded levels was implemented (TABLE 1). The central composite design employed pH and biomass concentrations as parameters in order to fit an empirical second-order polynomial model (TABLE 1).

The quadratic equation for predicting the model behavior is of the form

$$Y=b_1x_1+b_2x_2+b_{11}x_1^2+b_{22}x_2^2+b_{12}x_1x_2$$

where Y is the response variable, b is the regression coefficient, and x is the coded level of the independent

TABLE 1 : Variables with uncoded values for full factorial design (FFD) and central composite design (CCD)

	FFD levels		CCD Levels				
Parameter	-1	1	-α	-1	0	1	α
pH (A)	2	9	1	2	4	6	7
% Biomass (B)	0.1	0.5	0.02	0.1	0.3	0.5	0.58
Immobilization(C)	No	Yes	not considered for CCD				

variable[16]. A second order model equation obtained for biosorption of chromium using MINITAB 15 was also used to describe response surface methodology. Statistical significance of the terms in the regression equations was examined

RESULTS AND DISCUSSION

Effect of initial concentration on biosorption

The effect of initial concentration (25-250ppm) of chromium solution on biosorption by Sargassum sp was studied. The initial concentration of metal solution generates an important driving force to overcome all mass transfer resistance of Cr(VI) between the aqueous and solid phases. The initial biosorption rate of Cr(VI) by Sargassum sp increased with increasing initial Cr(VI) concentration which is depicted in Figure 1(a & b).

Kinetics of biosorption

The isotherms of experimental results are shown in Figure 2a and Figure 2b. The behavior of biosorption characteristics of biomass was explained well with Langmuir isotherm model compared to freundlich isotherm.

Statistical analysis

Full factorial design (FFD)

Adsorption of chromium metal ions depends on the surface area, it exposed and pH of the solution. Hence, the surface area to adsorption was varied via immobilization of algae (dried) in alginate. The global optimum value of adsorption of chromium ions was investigated by varying pH, biomass concentration and immobilization between two levels (cf. TABLE 2). One factor at a time design cannot be used to in this case since factor-factor interaction and errors associated with each batch dominates the individual factor response. Moreover, parameters are less than five; hence the factorial design has to be adopted than other screening techniques, such as Plackett-Burman design, to predict the significance of parameters on chromium adsorption. Hence, full factorial design approach (2^3) was employed to predict the significant factors resulting in the maximum adsorption of chromium with interaction data. The results were analyzed using MINITAB 14. Percentage chromium adsorbed was calculated using equation 3. The experimental runs were randomized to minimize the errors in the response (TABLE 2). It was observed that the total chromium adsorbed varied from 20.31 % to 97.91 % in the experimental runs performed.

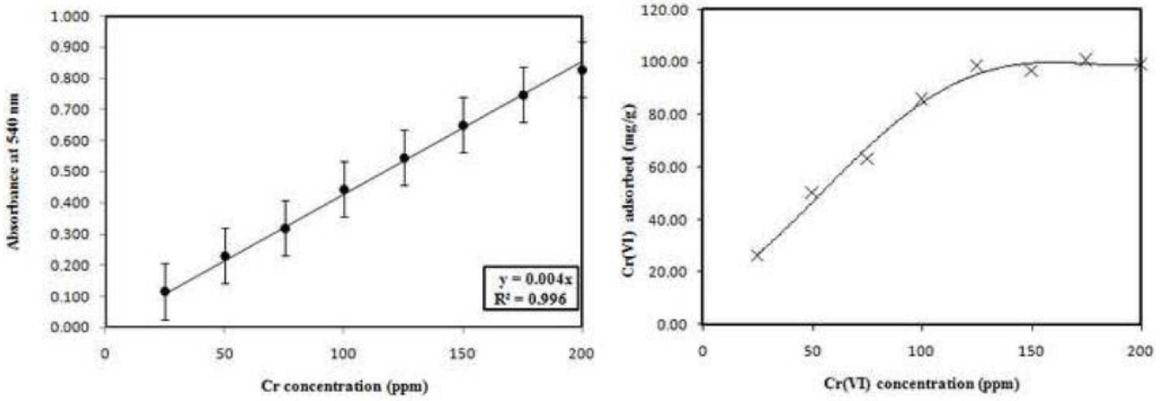


Figure 1a and 1b : Biosorption kinetics at initial concentration (100ppm) by sargassum sp

Regression coefficients and main effect

Based on the data obtained, main effects and coef-

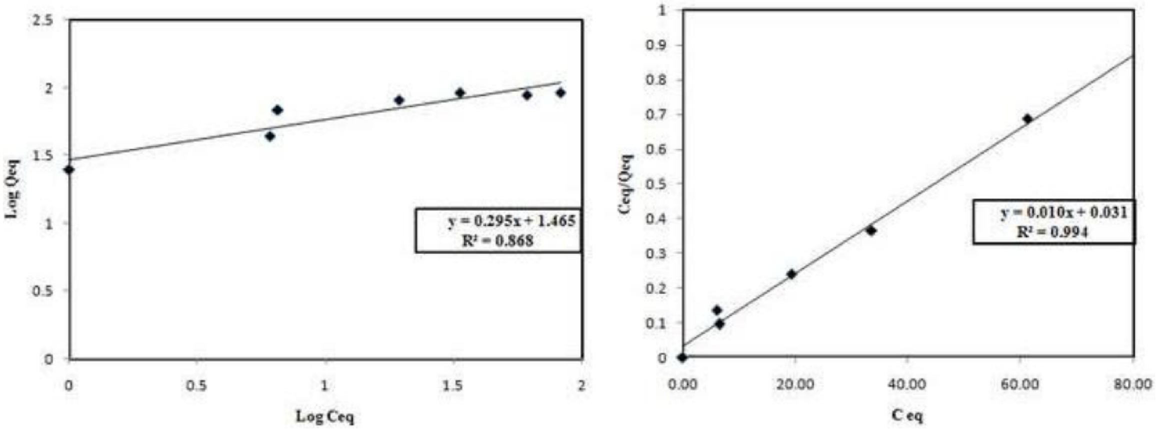


Figure 2a and 2b : Langmuir isotherm for biosorption of cr(VI) by sargassum species (qmax=100; b=0.32; R2=0994) and Freundlich isotherm for biosorption of cr(VI) by sargassum species (n=3.38; kf=4.327; R2=86.8)

TABLE 2 : Experimental design for FFD with response results

Run	Variables			% chromium adsorbed		
	pH	Biomass	Immobilization	Response 1	Response 2	Average Response
1	9	0.1	No	34.11	33.18	33.64
2	9	0.5	No	30.70	23.10	26.90
3	9	0.1	Yes	33.18	20.31	26.74
4	2	0.1	Yes	58.60	54.26	56.43
5	2	0.1	No	68.06	71.32	69.69
6	9	0.5	Yes	40.00	42.48	41.24
7	2	0.5	Yes	95.04	97.05	96.05
8	2	0.5	No	97.83	97.98	97.91

TABLE 3 : Selection of a satisfactory model for Cr (VI) removal, ANOVA table

Regression coefficients					ANOVA Table			
Term	Effect	Coefficient	T	P	Source	DF	F	P
Constant		56.1	55.06	0.000	**Main Effects**	3	213.3	0.000
A	-47.95	-23.98	-23.53	0.000	**2-Way Interactions**	3	25.93	0.000
B	18.83	9.42	9.24	0.000	**3-Way Interactions**	1	1.42	0.268
C	-1.96	-0.98	-0.96	0.364	**Residual Error**	8		
A*B	-14.95	-7.48	-7.34	0.000	**Pure Error**	8		
A*C	5.68	2.84	2.79	0.024	**Total**	15		
B*C	8.2	4.1	4.02	0.004				
A*B*C	2.42	1.21	1.19	0.268				
R square = 98.90%					F crit (0.05,1,8) = 5.317			
R square(predicted) = 95.60%					T crit (0.05,8) = 2.306			

ficients for the model equation (Eq. 2) were calculated and presented in TABLE 3. The main effects represent deviations of the average between high and low levels for respective variables[17]. The codified equation for a

2^3 FFD model is

$$Y=\beta_0+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_1 2X_1X_2+\beta_{13}X_1X_3+\beta_{23}X_2X_3+\beta_{123}X_1X_2X_3 \quad (2)$$

In the above equation, β0 represents the global mean and β1, β2, β3, … β123 represents the regression coefficient corresponding to the main factor effects and interactions[14]. The predicted model (Eq. 3) could explain the experimental behaviour of the significant parameters on chromium adsorption and R2 of the predicted model is 0.99.

$$Y=56.1-23.98X_1+9.42X_2-0.98X_3-7.48X_1X_2+2.84X_1X_3+4.1X_2X_3+1.21X_1X_2X_3 \quad (3)$$

Analysis of variance (ANOVA)

The significance of the model was tested using ANOVA (TABLE 3). TABLE 3 shows that the main effects and the two way interactions were of 95% significant (p<0.05). The main effect of immobilization of biomass and three way interaction were insignificant with 95% confidence (p>0.05). Hence, the predicted model can be re-written on elimination of the insignificant terms as,

$$Y=56.1-23.98X_1+9.42X_2-7.48X_1X_2+2.84X_1X_3+4.1X_2X_3$$

The goodness of fit can be interpreted from the R^2 value and R^2 value of the modified model was 98.9. The R2 is the proportion of variability in the response value explained by the model[18]. Hence, the predicted model can able to explain 98.9 % variation in the percentage chromium adsorption. F value of the model at 95% confidence level (Fcalc) is 213.3 which higher than that of the table value (Fcrit (0.05,1,8) = 5.317) confirmed the adequacy of the model. Higher F value (=25.93) was observed for 2 way interactions which indicates the significance of interaction, whereas 3 way interactions was found to be insignificant. Student's t-test was employed to find the relative importance of individual parameters and their interaction and the results are illustrated in Pareto chart (Figure 3). In Pareto chart, a vertical line indicates 95% confidence level (for n=8) and the corresponding t-value is 2.306. From the Pareto chart, it was evident that immobilization of cell

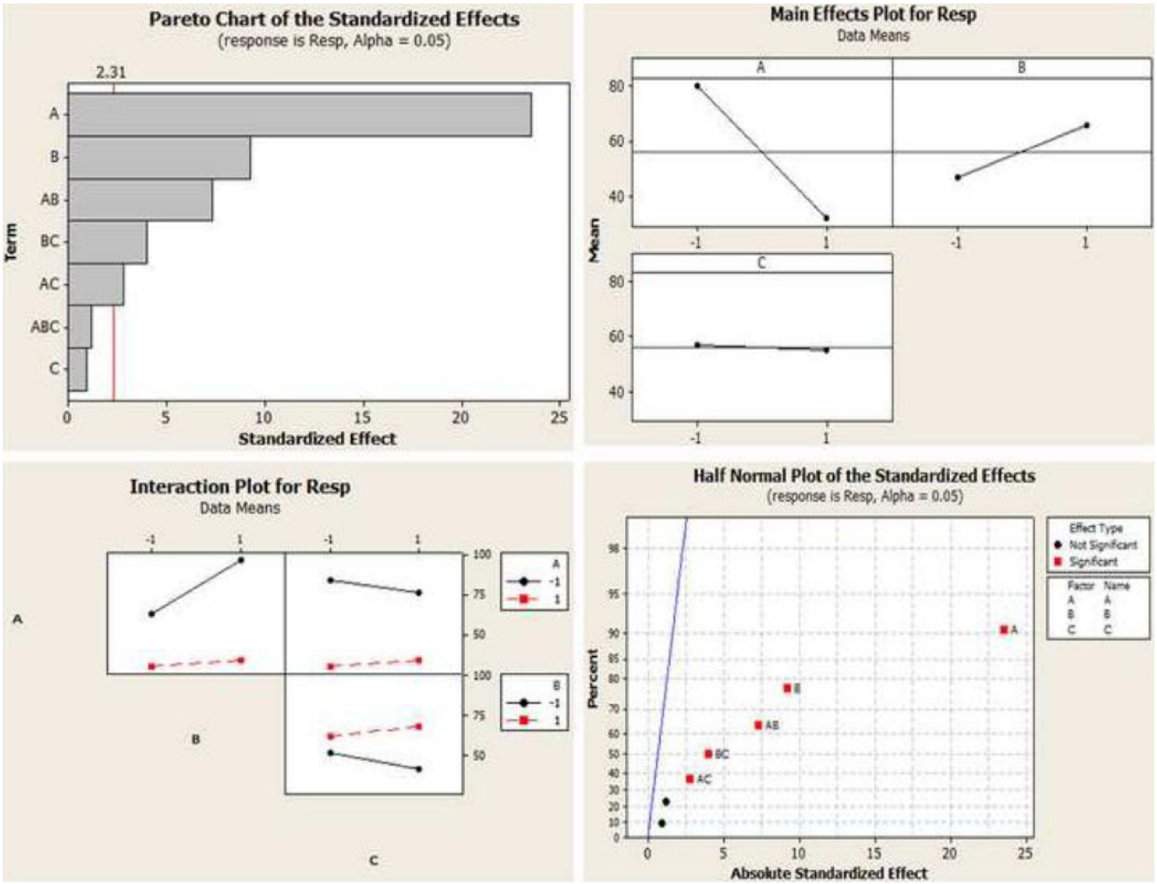
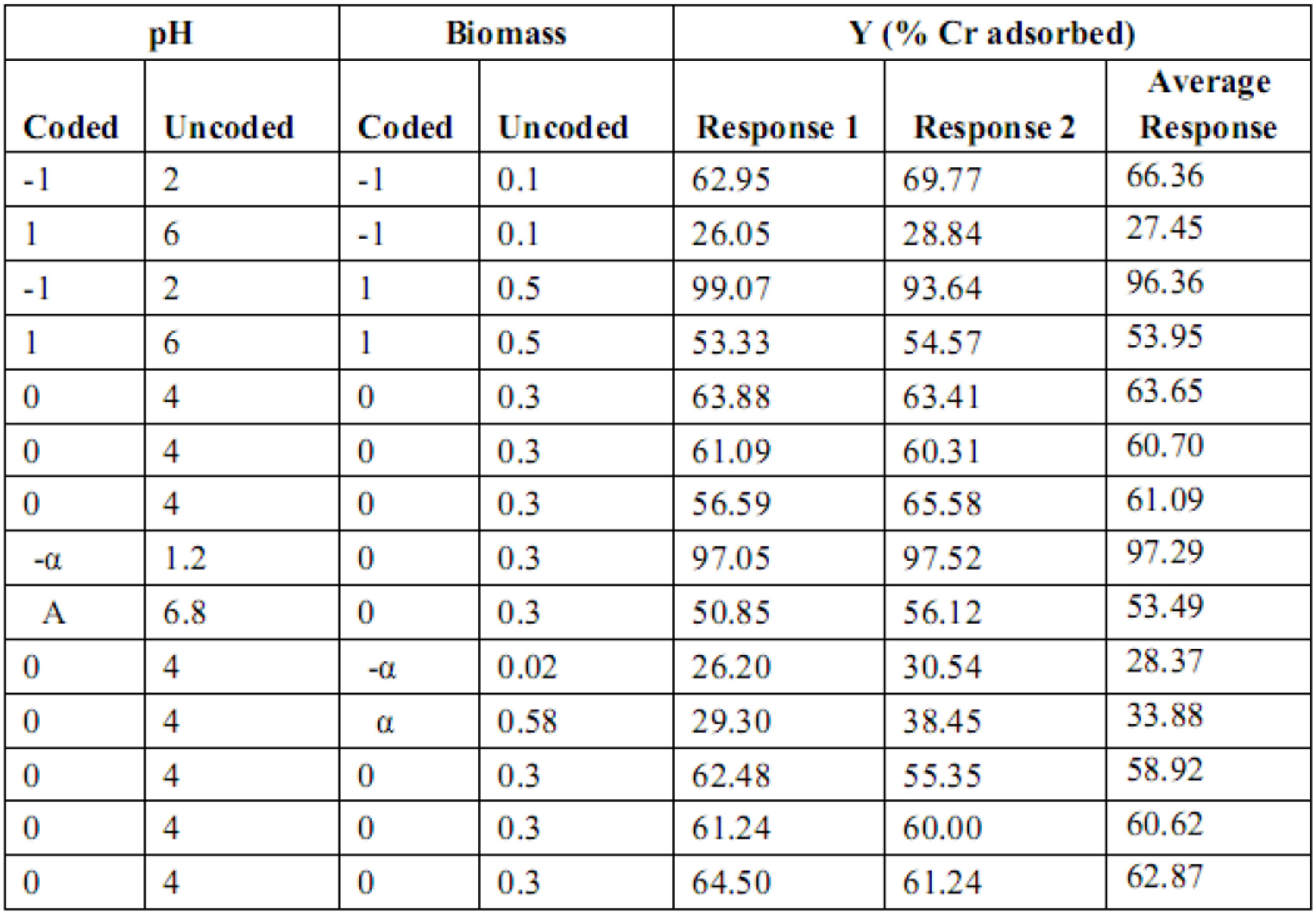


Figure 3 : Pareto chart of effects on the chromium removal efficiency %. (A: pH, B: biomass concentration and C: immobilization), b. main effects plot, c. interaction plot for response and d. half normal probability plot

TABLE 4 : Experimental design (coded and uncoded levels) and results of the central composite design (CCD) for the adsorption of chromium (%)



pH		Biomass		Y (% Cr adsorbed)		
Coded	Uncoded	Coded	Uncoded	Response 1	Response 2	Average Response
-1	2	-1	0.1	62.95	69.77	66.36
1	6	-1	0.1	26.05	28.84	27.45
-1	2	1	0.5	99.07	93.64	96.36
1	6	1	0.5	53.33	54.57	53.95
0	4	0	0.3	63.88	63.41	63.65
0	4	0	0.3	61.09	60.31	60.70
0	4	0	0.3	56.59	65.58	61.09
-α	1.2	0	0.3	97.05	97.52	97.29
A	6.8	0	0.3	50.85	56.12	53.49
0	4	-α	0.02	26.20	30.54	28.37
0	4	α	0.58	29.30	38.45	33.88
0	4	0	0.3	62.48	55.35	58.92
0	4	0	0.3	61.24	60.00	60.62
0	4	0	0.3	64.50	61.24	62.87

and 3- way interactions were relatively insignificant on percentage of chromium adsorption. From full factorial design, it was evident that pH has the maximum significance on biosorption of chromium followed by concentration of biomass. Immobilization of algal biomass doesn't improve the efficiency. Hence, pH and biomass concentration were further carried out for optimization studies. To optimize the conditions for maximum chromium adsorption, central composite design was employed with these two parameters.

Central composite design (CCD)

Central composite design (CCD) was used to optimize the significant parameter obtained from full factorial design (FFD). Further optimization of Cr (VI) removal was done by considering four corner points (2n, four axial points (2n) and 6 replicates at the centre point for each of the two variables, giving rise to fourteen runs in a single set of the experiment. The variable n represents the number of variables and in this study, pH and biomass concentration were considered as variables (n=2). From the FFD results, it is evident that pH greater than 7 (alkalinity) does not help in improving the adsorption efficiency, therefore the acidic pH (range from 1.2 to 6.8) was selected for CCD.

Biomass concentration was operated in the range between 0.02 and 0.58. The complete experimental design and results are shown in TABLE 4. Regression analysis was conducted to fit the response function with the experimental data. In order to check the statistical significance of the second-order model equation, F-test (ANOVA) was done and data is shown in TABLE 5.

An analysis of variance (ANOVA) of regression model was conducted to determine the significant effect of each variable on the response. The ANOVA table and regression coefficients for the quadratic model equations are shown in TABLE 5. To check the significance of the model and individual terms, F values and t values were compared with standard tabular values.

TABLE 5 : Analysis of variance (ANOVA) for full quadratic equation

Regression Coefficients				ANOVA Table			
Term	**Coef**	**T**	**P**	**Source**	**DF**	**F**	**P**
Constant	61.3049	75.680	0.000	**Blocks**	1	1.610	0.218
Block	0.6733	1.270	0.218	**Regression**	5	218.270	0.000
pH	-16.0536	-22.884	0.000	**Linear**	2	332.600	0.000
Biomass	8.3462	11.897	0.000	**Square**	2	206.490	0.000
pH*pH	7.4415	10.191	0.000	**Interaction**	1	13.160	0.002
Biomass*Biomass	-12.2271	-16.745	0.000	**Residual Error**	21		
pH*Biomass	3.5988	3.627	0.002	**Lack-of-Fit**	3	1.510	0.246
				Pure Error	18		
				Total	27		
R square value 98.11%				F crit (0.05,5,21) = 2.685			
R square (predicted) 96.76%				T crit (0.05,21) = 2.079			

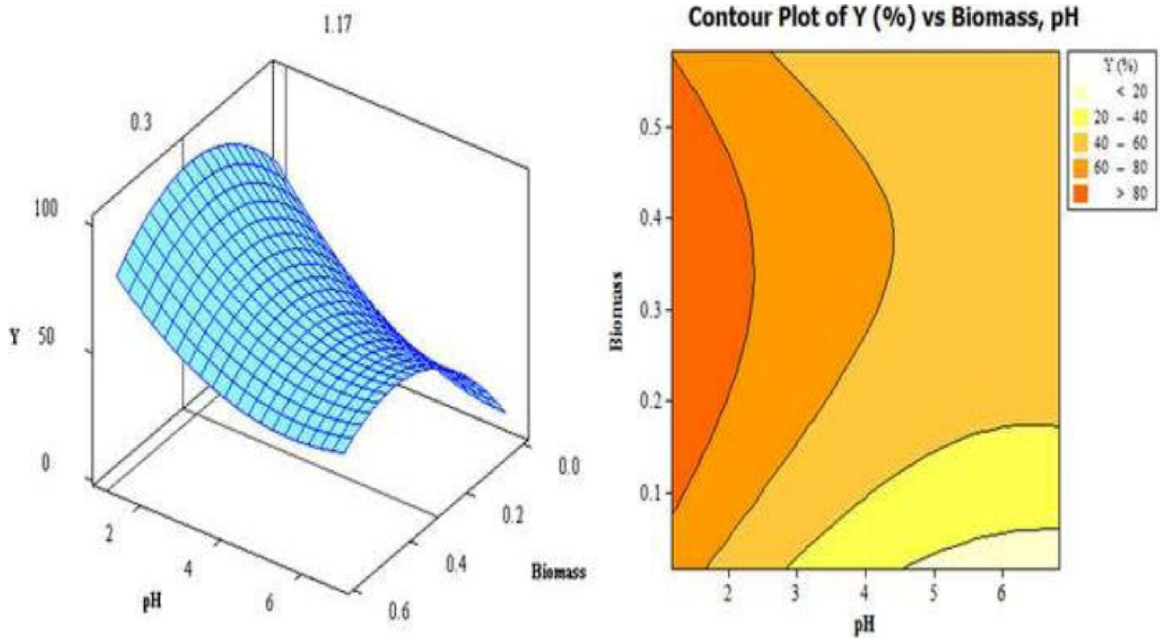


Figure 4 : Response surface and contour plots of pH and biomass concentration on adsorption of chromium (VI) with the remaining factors held constant at the middle level of the central composite experimental design in response surface methodology

The ANOVA results indicate that high R^2 value (98.11%) for the response is an indication of good fit model. It also explains that 98% of the variability in the response could be explained by the model. The F value for the model (218.27) is higher than that of the table value (Fcrit (0.05, 5, 21) = 2.685) confirms the adequacy of the model. ANOVA table also indicates the insignificant F value for 'Lack of fit' (1.510). The lack of fit measures the failure of the model to represent data in the experimental domain at points which are not included in the model[18]. In other words, based on the lack of fit, it can be concluded that the given model is a good fit for predicting the response for values which are not included in the CCD. Moreover it can also be established from the model that for Cr (VI) removal, all the main effects and second order effects were significant model terms. The final mathematical model in terms of actual factors as determined by MINITAB software is shown below

$$Y=61.3049-16.0536X_1+8.3462X_2+7.4415X_1^2-$$

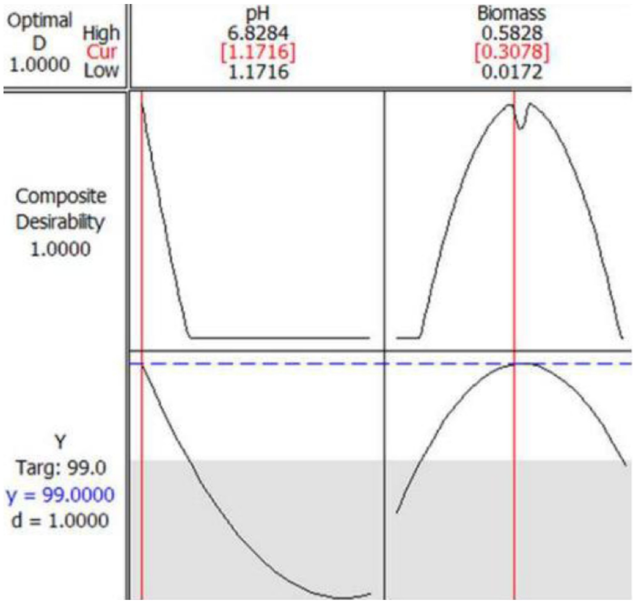


Figure 5 : Optimization plot with composite desirability

$12.2271X_2^2+305988X_1X_2$

Response surface plots

The main aim of response surface plots is to demonstrate the effect of process variables on the response and to find out optimum parameter values at which response is maximized. To investigate the effects of the two factors on the adsorption of chromium, the response surface methodology and 3D plots were used. ANOVA results reveal that pH and biomass concentration was found to have significant effects on the adsorption of chromium. 3D surface plot of pH against biomass concentration was plotted using the Minitab 14.0 (trial version) software (Figure 4 a & b). From the surface plot it was observed that as biomass concentration (%) is increased from 0.1 to 0.5, the % chromium adsorbed initially increased and then decreased after a particular biomass concentration (0.3%). Hence it can be established that a biomass concentration of 0.3% was found to be optimum for Cr (VI) adsorption by Sargassum sp. This may be due the fact that with 0.3% biomass concentration almost all the chromium would have got adsorbed, therefore further increase in biomass concentration will not result in increased chromium adsorption efficiency. It was observed that pH has a maximum effect on chromium adsorption. It was found that at any given biomass concentration, pH bore a negative effect on the response, i.e., as the pH increased the adsorption efficiency decreased. This may be due to the reason stated above in section dealing with FFD results.

Optimization

Optimum parameter conditions at which chromium adsorption is maximized were calculated by utilizing the quadratic model equation obtained from the CCD. By applying the method of desirability function, optimum conditions were determined. Response optimizer plot is shown in Figure 5. To achieve 99% chromium adsorption pH of 1.17 and 0.3% of biomass concentration was found out to be optimum conditions with desirability of 1.00.

Validation

The adequacy of the model for predicting the response was validated using recommended optimum condition. Experiment carried out at optimum conditions (pH 1.17 and biomass concentration of 0.3%) resulted in 98.17% chromium adsorption. This suggests that by performing optimization studies using CCD has significantly improved the biosorption capacity of Sargassum sp. biomass towards chromium.

DISCUSSION

When the initial Cr(VI) concentration increased from 25 to 120 mg/L, the uptake of chromium increased from 29.07 to 98.84mg/g. Since cells offer a finite number of surface binding sites, uptake showed saturation at higher metal ion concentrations. The present study showed similarity results with Bermúdez et al. (2012)[9]. The reason for increase in biosorption of initial metal concentration by biomass is because at low concentrations of sorbate, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional biosorption becomes independent of initial concentrations. However, at higher concentrations the available sites for biosorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration[16].

The experimental results confirmed the uniform active surface present in the biomass and hence, it could not explain Freundlich model characteristics. The value of qmax, the maximum value of qe, is important to identify which biosorbent shows the highest metal uptake capacity when a large scale reactor system is considered. The maximum capacity (qmax) defined as the total capacity of biosorbent for hexavalent chromium. The data of sorption isotherm cannot be compared with other works due to the variation in the experimental conditions. Langmuir constant (b) indicates the affinity of absorbent for the binding of Cr (VI) ions (simply strong bonding of Cr (VI) to Sargassum sp biomass) at given experimental conditions. Langmuir biosorption isotherms fitted well with the Cr (VI) ion uptakes by Sargassum sp with the metal concentration ranging from 25-250 ppm. The correlation coefficients of the Langmuir curves were distinctly higher. The experimental observation implies that the monolayer biosorption were occurred on the surface of biomass and there was no interactions between adsorbed metal ions, hence, the adsorbed metal ions has no influence on the rate of adsorption.

Upon statistical analysis using FFD, it could be observed that the negative sign in the co-efficient of main effects (pH) indicated that the adsorption of chromium was maximum at lower level (-1) of pH compared to its higher level (+1), i.e., the system pH increased from low to high, i.e., from pH 2 to pH 9, the adsorption efficiency was decreased. In other words, the acidic conditions favoured the chromium adsorption. It is due the fact that pH determines the binding of metal ions to the cell wall metal binding sites[20] and as pH decreases, the net negative charges on the surface of the biomass goes on increasing which attracts positively charged chromium (VI) ions[21]. Percentage of chromium biosorption increased on changing the biomass concentration from low (0.1%) level to high (0.5%) level. The availability of large surface area for adsorption could increase the chromium adsorption in algal biomass. Immobilization of the biomass has not improved the percentage of biosorption of chromium and it might due to mass transfer problem due to entrapment. However, other types of immobilization of algal biomass, viz., immobilize on the surface of inert materials or by covalent binding are possible types of immobilization might increase the adsorption of chromium. From full factorial design, it was evident that pH has the maximum significance on biosorption of chromium followed by concentration of biomass. Immobilization of algal biomass doesn’t improve the efficiency. Hence, pH and biomass concentration were further carried out for optimization studies.

Upon evaluation using CCD, The ANOVA results proved that this model was appropriate. Additional, ANOVA analysis suggested that the adsorption of chromium was primarily determined by the linear terms pH and biomass concentration of the model, and also indicated that the quadratic terms of biomass concentration carried a negative sign and hence the effect can be considered to be negligible. In other words, based on the lack of fit, it can be concluded that the given model is a good fit for predicting the response for values which are not included in the CCD. Moreover it can also be established from the model that for Cr (VI) removal, all the main effects and second order effects were significant model terms.

CONCLUSION

The study mainly focuses on biosorption of Cr (VI) using macro algae. This work demonstrated that the seaweed sargassum sp has excellent metal uptake capacity. From the initial studies it can be accomplished that initial biosorption rate of Cr(VI) by Sargassum sp increased with increasing initial Cr(VI) concentration. The metal uptake by the algae became constant later on. The kinetic studies demonstrated that the biosorption of Chromium can be best fit using Langmuir isotherm. This work demonstrated that the factorial design is a useful tool in determining the operating variables that significantly influence the percentage of Cr(VI) removed by Sargassum sp. Factorial design employed in this study showed that the percentage removal of Cr(VI) was influenced by operating variables such as pH and biomass concentration ($p<0.05$). By the use of response surface methodology, it was found that pH of 1.17 and 0.3% of biomass concentration was found out to be optimum conditions for biosorption (desirability 1.00). It can therefore be concluded that Sargassum sp can be used as a effective biosorbents for Cr (VI) remediation from aqueous solutions chromium. Furthermore this study can also provide insights for treatment of industrial wastewater using Sargassum.

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