Evaluation of biosorption potential of Gracilaria corticata for the removal of hexavalent chromium from aqueous solutions using response surface methodology

K. Kumaraguru

Department of Petrochemical Technology, Anna University-BIT Campus, Tiruchirappalli - 620024, India
kumaraguruautt@gmail.com

P. Sureshkumar

Department of Biotechnology, Anna University-BIT Campus, Tiruchirappalli - 620024, India
drsureshbiotech2003@gmail.com

ABSTRACT

In this study, the biosorption of chromium (VI) on *Gracilaria corticata* biomass marine algae, was investigated in a batch and continious system. The influence of process parameters including sorbent size (0.176 - 1.503 mm), sorbent dosage (3 -7 g/l), temperature (25 - 45°C), contact time (2 - 10 hrs) and agitation speed (50 - 250 rpm) on the sorption of chromium (VI) were performed using a full factorial central composite design (CCD). This result of the studies indicates that the optimum biosorption conditions of sorbent size, sorbent dosage, temperature, contact time and agitation speed were 0.5284 mm, 5.12 g, 35°C , 2 hours 58 minutes and 140 rpm, respectively. A higher value coefficient of determination R^2 0.9799 evidenced the fitness of response surface methodology. The Langmuir and Freundlich isotherm models were applied to the equilibrium data. The Langmuir adsorption model was better than the other model. The maximum adsorption capacity of *Gracilaria corticata* was found to be 62.5 mg/g. The thermodynamic parameters like enthalpy ($\Delta H\circ$) and entropy ($\Delta S\circ$) were 34.57 (kJ/mol) and 0.1308 (kJ/mol K) respectively. The results showed that the biosorption of chromium (VI) by *Gracilaria corticata* is more endothermic and spontaneous.

Indexing terms/Keywords

Chromium (VI), *Gracilaria corticata* , Biosorption, CCD, Optimization

1. INTRODUCTION

Hexavalent chromium (Cr (VI)) is widely used in various process industries such as leather tanning, pigments and paints, mining, textile dyeing, electroplating, pulp and paper, aluminum conversion coating operations etc. It is a toxic heavy metal often existing in the industrial waste stream. Cr (VI) is known to be a strong oxidant and an acute carcinogen [1]. Therefore the removal of Cr (VI) from waste streams is essential to protect environmental health. The permissible level of Cr (VI) for discharge into surface water is 0.1 mg/L and portable water is 0.05 mg/L [2,3]. The Ministry of Environment and Forest (MOEF);Government of India has set Minimal National Standard (MINAS) of 0.1 mg/L for safe discharge of chromium containing effluent to surface water[4]. The stricter regulations are needed to achieve the demand for innovative treatment technologies to remove metal ions from wastewater. The conventional techniques for removing heavy metals from industrial wastewaters are precipitation [5], adsorption [6], reduction [7], membrane process [8], ion exchange [9] and solvent extraction [10]. In addition, these conventional treatment processes are limited due to technological or economic constraints. However, biosorption represent attractive and cost effective alternative for decontamination of ionic pollutants such as heavy metal ions. Bacteria, fungi, algae and agricultural waste are considered as the class of biosorbent [11]. Several recent publications were utilized for various inexpensive and locally abundantly available biosorbents like barley straw [12], peanut hulls [13], neem bark [14], waste tea leaves [15],sago waste[16],hazel nut shell [17],cocoa shells [18], tea waste [19], palm kernel fibre [20] and orange peels [21]. Among these biosorbent, seaweeds are inexpensive and abundantly available. It is based on the submissive withholding of metal ions by functional groups and active sites present in the biomass [22-24]. It has numerous discrete advantages over other conventional techniques such as low-cost, eco-friendly, high efficiency, without additional nutrient supply, regeneration of biosorbent and feasibility of metal extraction etc., [25]. Among various classifications of marine algae, red seaweeds were found to be a most effective biosorbent for different heavy metal ions due to their well in seizing of various metal ions [26]. However, *Gracilaria corticata*, common red seaweed have been identified as potent biosorbent owing to the presence of binding site such as carboxyl sulphonate amine and hydroxyl group[27]. There is no literature report on optimization of biosorption process for removal of chromium (VI) with *Gracilaria corticata* using response surface methodology (RSM). The central composite design (CCD) was utilized to obtain the experimental design matrix. This approach has minimum number of actual experiments executed while allowing into possible interaction between process parameters studied and their effect on biosorption capacity of Cr (VI) on to *Gracilaria corticata*. The prime objective of this work was to acquire the potential of the marine algae *Gracilaria corticata* to remove hexavalent chromium ions from aqueous solutions. The influence of process parameters including sorbent size, sorbent dosage, temperature, contact time and agitation speed on the sorption of chromium (VI) were performed using a full factorial central composite design (CCD) in batch process. The different thermodynamic and isotherm models were achieved for their effectiveness in correlating the experimental data.

2. MATERIALS AND METHODS

2.1 Adsorbent

Raw *Gracilaria corticata* was collected from CSMCRI (Central Salt and Marine Chemical Research Institute) marine algae research station.(Mandapam, Tamilnadu, India). The collected alga was washed with deionized (DI) water several times to remove impurities. The washing process continued until the pH of wash solution was equal to DI water. The washed algae were then wholly dried in sunlight for ten days. Dried weight of algae was incurred after drying it at 105°C for 24 hours. Dry algae were then sliced in to small pieces and were pulverized using domestic mixer. In this study the dry powder biomass in the range of 0.176mm to 1.503mm particle size were utilized for sorption experiments without any chemical pretreatment.

2.2 Adsorbate

The stock solution containing 1000 mg/L of Cr (VI) was prepared by dissolving required amount of AR-Grade $K_2Cr_2O_7$ in DI water. Required initial concentration of Cr (VI) standards were prepared by appropriate dilution of the above stock Cr (VI) standard solution. The concentrate in the test solution was determined by spectrophotometer a wavelength corresponding to the maximum absorbance 540 nm [28]. Batch adsorption experiments were performed after proper dilution of stock solution.

2.3 Characterization of *Gracilaria corticata*

Scanning electron microscopic studies was conducted to examine the surface texture and porosity of the adsorbent. FT-IR spectrometer (PERKIN – ELMER) was employed to observe the type of functional groups in *Gracilaria corticata* responsible for metal adsorption. HACH-DR-4000 UV–visible Spectrophotometer was used for determination of Cr (VI) content in standard and treated solution. The pH of the solution was measured with a Sartorius 420A pH Meter. All chemicals obtained from MERK (Delhi) including $K_2Cr_2O_7$ of analytical grade.

2.4 Experimental design by RSM

The optimization of Cr (VI) removal was carried out by five independent variables (temperature, sorbent size, contact time, sorbent dosage and agitation speed) with ten replicates at centre points, according to central composite design (CCD). The ranges and the levels of the process variables analyzed in the experiments are given in Table 1.

Table 1.Experimental range and levels of independent variables

Independent variable		Range and levels				
		-2.378	-1	0	1	2.378
Sorbent dosage, g/l00 ml	A	3	4	5	6	7
Average sorbent size, mm	B	1.503	1.057	0.564	0.389	0.176
Agitation speed, rpm	C	50	100	150	200	250
Temperature,°C	D	25	30	35	40	45
Contact time, hrs	E	2	4	6	8	10

The coded values of the process variables were investigated by the following equation

$$x_i = \frac{X_i - X_0}{\Delta x} \tag{1}$$

Where xi is the coded value of the ith variable, Xi the uncoded value of the ith test variable and X0 the uncoded value of the ith test variable at center point. The amount of metal removal (Y) was taken as the response of the design experiments. The response for the quadratic polynomial equation model for predicting the optimum value was expressed according to Eq. (2).

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

where Y is the predicted response, βi, βj, βij are coefficients estimated from regression, they represent the linear, quadratic and cross products of x_1, x_2, x_3 on response. Percentage adsorption was studied with a standard RSM design called central composite design (CCD). The equations were validated by the statistical tests called the ANOVA analysis. The significance of each term in the equation is to predict the best fit in each case. Response surfaces were drawn to determine the individual and interactive effects of test variable on percentage removal of Cr (VI).

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Fifty two experiments were investigated in duplicate according to the scheme mentioned in Table 2. consists of 52 sets of coded conditions expressed in natural values. Design Expert Version 8.0. (Stat Ease, USA) was used for regression and graphical analysis of the data obtained. The optimum conditions of the selected process variables were obtained by solving the regression equation and by analyzing the response surface 3D plots. The variability of the dependent variable was defined by the multiple coefficient of determination, R^2 and the model equation was used to determine the optimum value and consequently to reveal the interaction between the factors within the specified. The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

2.5 Experimental procedure

Removal of Cr (VI) ions from the known concentration of aqueous solutions onto *Gracilaria corticata* was performed on the batch scale. Experiments were carried out according to the central composite design (CCD) matrix as per the design expert software. For each 100 ml solution, a desired quantity of *Gracilaria corticata* was added in 250 ml volumetric flask. The mixture was agitated on the mechanical shaker. After biosorption, the supernatant of the beakers was centrifuged at 4000 rpm for 3 min and the sorbent was successfully separated from aqueous solution. The supernatant of the solutions were analyzed for residual metal ion concentration using an UV-vis spectrophotometer at 540nm. From the noted absorbance value the initial and final concentration of the metal ions was determined. The response, i.e., removal efficiency of *Gracilaria corticata* was calculated as

$$Y(\%) = \frac{C_0 - C_i}{C_0} \times 100 \qquad (3)$$

Where Co, Ci are the initial and final concentration of metal ion. All experiments were carried out in duplicate and the mean values were reported. The maximum deviation was found to be ± 4%. The process variables temperature, sorbent dosage, contact time, sorbent size and agitation speed were optimized and at these optimized conditions, the effect of pH and initial metal ion concentration were studied. The amount of equilibrium adsorption, qe (mg/g), was calculated by:

$$q_e = \frac{V(C_0 - C_e)}{M} \qquad (4)$$

where C_0 and Ce (mg/l) are the liquid-phase concentrations of Cr(VI) at initial and equilibrium, respectively. V (l) is the volume of the solution and M (g) is the mass of dry sorbent used.

Table 2.Experimental design in term of coded factors and results of central composite design (CCD)

Std. Order	Obs	A	B	C	D	E	% Cr (VI) Removal	
							Experimental	Predicted
23	1	0.00	0.00	0.00	0.00	0.00	75.23	72.89
52	2	1.00	1.00	-1.00	-1.00	1.00	89.55	88.61
38	3	1.00	-1.00	-1.00	1.00	1.00	66.55	64.06
37	4	-1.00	-1.00	1.00	-1.00	-1.00	70.53	67.46
51	5	1.00	1.00	1.00	-1.00	1.00	63.23	60.72
40	6	-1.00	-1.00	-1.00	-1.00	1.00	58.75	56.94
44	7	-1.00	-1.00	1.00	-1.00	1.00	56.66	59.04
5	8	0.00	0.00	0.00	0.00	0.00	75.23	72.89
13	9	0.00	0.00	0.00	0.00	0.00	75.23	72.89
43	10	-1.00	1.00	1.00	-1.00	-1.00	52.25	55.61
3	11	-1.00	1.00	-1.00	-1.00	1.00	53.65	55.58
15	12	1.00	-1.00	1.00	1.00	1.00	62.85	62.85
10	13	1.00	-1.00	1.00	1.00	-1.00	59.15	58.49
28	14	0.00	0.00	0.00	0.00	2.38	70.36	68.64
50	15	-1.00	-1.00	-1.00	-1.00	-1.00	55.25	66.27
39	16	-1.00	1.00	1.00	-1.00	1.00	50.33	50.64
31	17	0.00	0.00	0.00	0.00	0.00	75.23	72.89
27	18	1.00	-1.00	-1.00	-1.00	-1.00	70.11	68.96
34	19	0.00	0.00	0.00	0.00	0.00	75.23	72.89
29	20	-2.38	0.00	0.00	0.00	0.00	48.46	48.93
19	21	-1.00	1.00	1.00	1.00	-1.00	59.85	62.37
24	22	0.00	-2.38	0.00	0.00	0.00	72.65	66.06
35	23	0.00	0.00	0.00	0.00	0.00	75.23	72.89

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32	24	0.00	0.00	0.00	0.00	0.00	75.23	72.89
41	25	1.00	-1.00	1.00	-1.00	1.00	69.89	72.38
11	26	-1.00	-1.00	1.00	1.00	1.00	53.85	53.07
20	27	-1.00	-1.00	-1.00	1.00	-1.00	59.46	62.17
2	28	1.00	1.00	-1.00	1.00	-1.00	64.83	67.28
8	29	0.00	0.00	0.00	0.00	-2.38	78.15	78.484
21	30	1.00	1.00	-1.00	-1.00	-1.00	61.65	60.96
25	31	1.00	-1.00	-1.00	1.00	-1.00	60.95	61.28
16	32	-1.00	1.00	-1.00	1.00	-1.00	73.85	71.39
17	33	1.00	1.00	1.00	-1.00	-1.00	55.51	56.72
26	34	-1.00	1.00	1.00	1.00	1.00	49.14	58.65
14	35	-1.00	-1.00	1.00	1.00	-1.00	48.35	57.74
33	36	2.38	0.00	0.00	0.00	0.00	54.26	49.99
1	37	0.00	0.00	0.00	0.00	0.00	75.23	72.89
6	38	-1.00	1.00	-1.00	1.00	1.00	69.86	69.26
49	39	1.00	1.00	1.00	1.00	1.00	64.15	65.21
42	40	0.00	2.38	0.00	0.00	0.00	76.35	79.31
9	41	0.00	0.00	-2.38	0.00	0.00	65.65	64
48	42	0.00	0.00	2.38	0.00	0.00	62.58	64.54
45	43	1.00	-1.00	-1.00	-1.00	1.00	62.47	68.76
47	44	0.00	0.00	0.00	-2.38	0.00	69.43	68.89
18	45	0.00	0.00	0.00	2.38	0.00	60.14	62.34
46	46	-1.00	1.00	-1.00	-1.00	-1.00	59.25	67.15
22	47	0.00	0.00	0.00	0.00	0.00	75.23	72.89
30	48	1.00	1.00	1.00	1.00	-1.00	56.65	59.92
12	49	1.00	1.00	-1.00	1.00	1.00	38.25	49.96
36	50	-1.00	-1.00	-1.00	1.00	1.00	49.48	54.45
4	51	0.00	0.00	0.00	0.00	0.00	75.23	72.89
7	52	1.00	-1.00	1.00	-1.00	-1.00	69.07	74.55

3. RESULTS AND DISCUSSION

To explore the positions and numbers of the functional groups existing for the binding of Cr (VI) on to *Gracilaria corticata* FT-IR spectra of native and Cr (VI) loaded adsorbents were recorded. The surface structure of biosorbent before and after biosorption was analyzed by scanning electron microscope (SEM).

3.1 Morphological Analysis

In order to investigate the surface morphology of the *Gracilaria corticata* , SEM micrographs were taken before and after Cr(VI) biosorption and are presented in Fig. 1(a&b). Before Cr(VI) uptake, the biosorbent is characterized by irregular and porous surface. Following metal ions biosorption, pores are absent on the surface of Cr(VI) loaded *Gracilaria corticata*, suggesting the biosorption of Cr(VI) onto *Gracilaria corticata*. In addition, the appearance of a molecular cloud over the surface of Cr(VI) biosorbent confirms the binding of Cr(VI) ions to the functional groups present in *Gracilaria corticata*.

3.2 FT-IR spectra analysis

The FT-IR spectra of *Gracilaria corticata* before and after sorption of Cr(VI) ions were used to determine the vibrational frequency changes of functional groups in the adsorbent. The spectra of sorbents were measured within the range of 400–4000 cm-1 wave number. All spectra were plotted by the same scale on the transmittance axis for the raw and Cr(VI) loaded biomass. The FT-IR spectra of the *Gracilaria corticata* displayed a number of absorption peaks, indicating the complex nature of the adsorbent. Fig. 2 (a&b) shows the fundamental peaks of the adsorbent before and after use. In *Gracilaria corticata*, the absorption peak around 3384.5 cm-1 indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed at 2361.3 cm-1 can be assigned to stretching vibration of the C–H group. The peaks around 1661 cm-1 is due to C=O group and around 1425.3 cm-1 correspond to the C=C aromatic or may be due to the asymmetric and symmetric stretching C=O vibrations. The strong C–O band at 1036.03 cm-1 due to –OCH3 group. The

additional peak at 613.47 cm-1 can be assigned to bending modes of aromatic compounds. A minor shift is observed in case of –OH group.
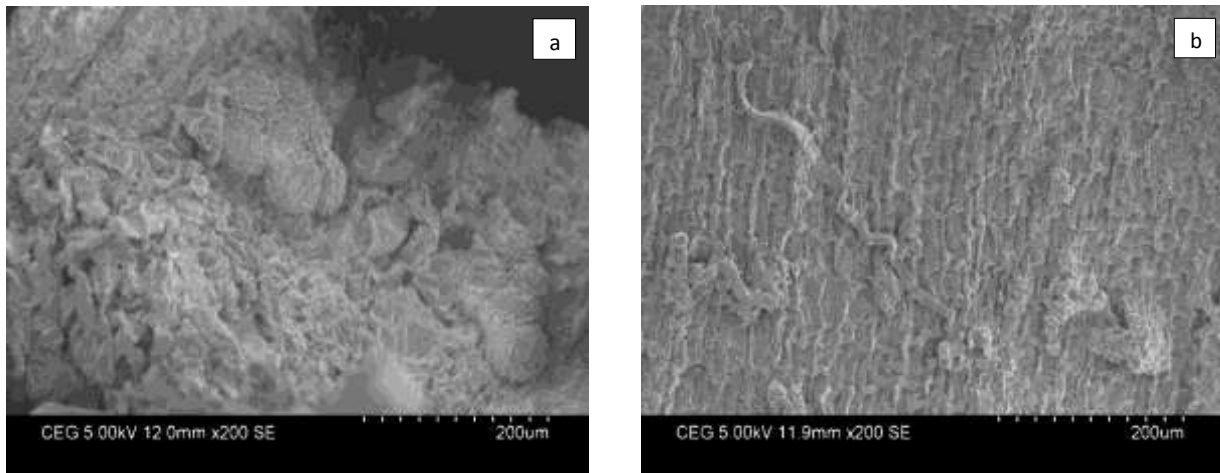

Fig. 1: SEM analysis (a) SEM picture of virgin *Gracilaria corticata*, (b) SEM picture of Cr(VI) loaded *Gracilaria corticata*
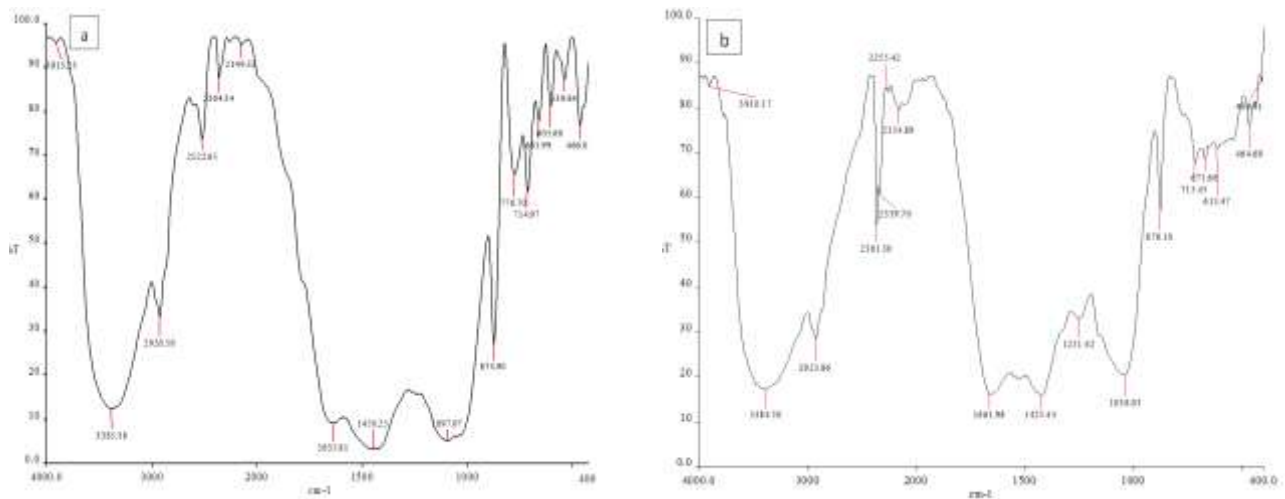

Fig. 2: FT IR analysis (a). FTIR spectrum of virgin *Gracilaria corticata*, (b) FTIR spectrum of Cr(VI) loaded *Gracilaria corticata*

3.3 Experimental design and fitting of quadratic model

The experimental results for each trial performed were given in Table 2. The relationship between the five different independent process variables was drawn by second order polynomial equation for % removal of chromium (VI). Equation (5) represents the mathematical model relating the % of ions removal with the independent process variables and the second order polynomial coefficient for each term of the equation determined through multiple regression analysis using the Design Expert 8.0.

% removal of Cr(VI) = 88.6 + 2.3*A - 0.61* B -1.94*C + 0.092*D - 0.39*E - 0.8*A*B + 0.41 *A*C - 0.90*A*D + 2.25*A*E - 1.77*B*C + 3.50*B*D + 0.85*B*E - 1.4*C*D + 0.23*C* E + 0.94* D*E - 8.12*A2 - 4.24* B2 - 5.16*C2 - 5.31*D2 - 3.36* E2

(5)

The result of the study indicates that the selected model was found to be significant due to the F- value which was 29.19. Further the value of "Prob>F" was less than 0.05 implies that the selected terms are significant. Hence A, C, AD, AE, BC, BD, BE, CD, DE, A2, B2, C2, D2, E2 are significant model terms. Hoeever the Predicted R2 of 0.9242 was well agreement with the the adjusted R^2 of 0.9669. in addition the regression coefficient R^2 is 0.9799 which was expressed by fit of the model. This indicates that the prediction of experimental data is reasonably satisfactory (Table 3).

Table 3.Analysis of variance (ANOVA) for response surface quadratic Model

Source	Sum of square	DF	Mean square	F	P>F
Model	8051.48	20	402.57	75.43	< 0.0001
A	230.54	1	230.54	43.20	< 0.0001
B	16.15	1	16.15	3.03	0.0919
C	163.56	1	163.56	30.65	< 0.0001
D	0.37	1	0.37	0.069	0.7946
E	6.48	1	6.48	1.21	0.2790
AB	20.76	1	20.76	3.89	0.0576
AC	5.36	1	5.36	1.00	0.3240
AD	25.64	1	25.64	4.80	0.0360
AE	162.32	1	162.32	30.41	< 0.0001
BC	100.26	1	100.26	18.79	0.0001
BD	391.82	1	391.82	73.41	< 0.0001
BE	23.28	1	23.28	4.36	0.0450
CD	63.26	1	63.26	11.85	0.0017
CE	1.62	1	1.62	0.30	0.5852
DE	28.44	1	28.44	5.33	0.0278
A^2	3865.52	1	3865.52	724.26	< 0.0001
B^2	1055.75	1	1055.75	197.81	< 0.0001
C^2	1563.20	1	1563.20	292.89	< 0.0001
D^2	1651.66	1	1651.66	309.46	< 0.0001
E^2	663.48	1	663.48	124.31	< 0.0001
Residual	165.45	31	5.34		
Lack of Fit	162.59	22	7.39	23.19	< 0.0001
Pure Error	2.87	9	0.32		
Cor Total	8216.93	51			

3.4 Response surface estimation for maximum removal of chromium (VI)

The biosorption capacities of the red marine algae *Gracilaria corticata* over different combinations of independent variables were analyzed through 3D view of response surface plots as shown in Fig. 3(a-f). Response surface plots were represented as a function of two factors at a time, maintaining other factors at fixed levels. The response surface curves were plotted to know the interaction of the variables and to find the optimum level of each variable for maximum response. The nature of the response surface curves indicates the interaction between the variables. The elliptical curve shows good interaction and circular shape of the curve no interaction between the two variables. From plots it was observed that the elliptical nature of the contour in graphs showed the mutual interactions of all independent 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 coefficients in Eq. 5 gives the positive and negative contribution of independent variables such as agitation speed, sorbent dosage, sorbent size, temperature and contact time on the removal of chromium. The interactions of, 'sorbent dosage and contact time', 'sorbent size and contact time', 'agitation speed and temperature', 'sorbent dosage and temperature', 'agitation speed and contact time', 'sorbent size and agitation speed' have positive effect, Whereas the interactions of 'sorbent dosage and agitation speed', 'temperature and contact time', 'sorbent dosage and sorbent size'', 'sorbent size and temperature' have negative effect on chromium removal. The response surface curves were plotted to know the interaction of the variables and to find the Optimum conditions for percentage removal of chromium (VI) using *Gracilaria corticata* biomass were obtained by using RSM. Second order polynomial models obtained in this study were utilized for each response in order to find the optimum conditions. The optimum values obtained by substituting the respective coded values of variables are: sorbent size (0.5284 mm), sorbent dosage (5.12 g), temperature (35°C), contact time (2 hours 58 minutes) and agitation speed (140 rpm). At this condition the maximum percentage chromium removal was calculated. The sequential quadratic programming in MATLAB 7 is utilized to solve the second-degree polynomial regression Eq. (5). The optimal values predicted from the MATLAB were found to be within the design region. This showed that the model acceptably explains the influence of the selected variables on the percentage removal of chromium (VI).

3.5 Thermodynamic analysis

The effect of the temperature on the biosorption of Cr (VI) ions in *Gracilaria corticata* was studied in the range of 293, 303 and 413 K. An increase in temperature from 293 K to 413 K increases the specific uptake of Cr (VI) by *Gracilaria corticata*. Further increasing the temperature from 303.K to 318.K decreases the specific uptake of Cr(VI). This is probably caused by a change in the texture of the sorbent and a loss in the sorption capacity due to material deterioration [13]. Thermodynamic parameters such as standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) change of biosorption can be evaluated from the following Eqs. (6) and (7) [29].

$$\Delta G^\circ = -RT \ln K_C \qquad (6)$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \qquad (7)$$

Where R is the universal gas constant (8.314×10^{-3} kJ/mol K), T is the temperature in Kelvin and K_C is the equilibrium constant, ($K_C = qe/Ce$). ΔH° and ΔS° were obtained from the slope and intercept of the plot of ΔG vs T as shown in Fig 4. The calculated thermodynamic parameters were listed in Table 4.
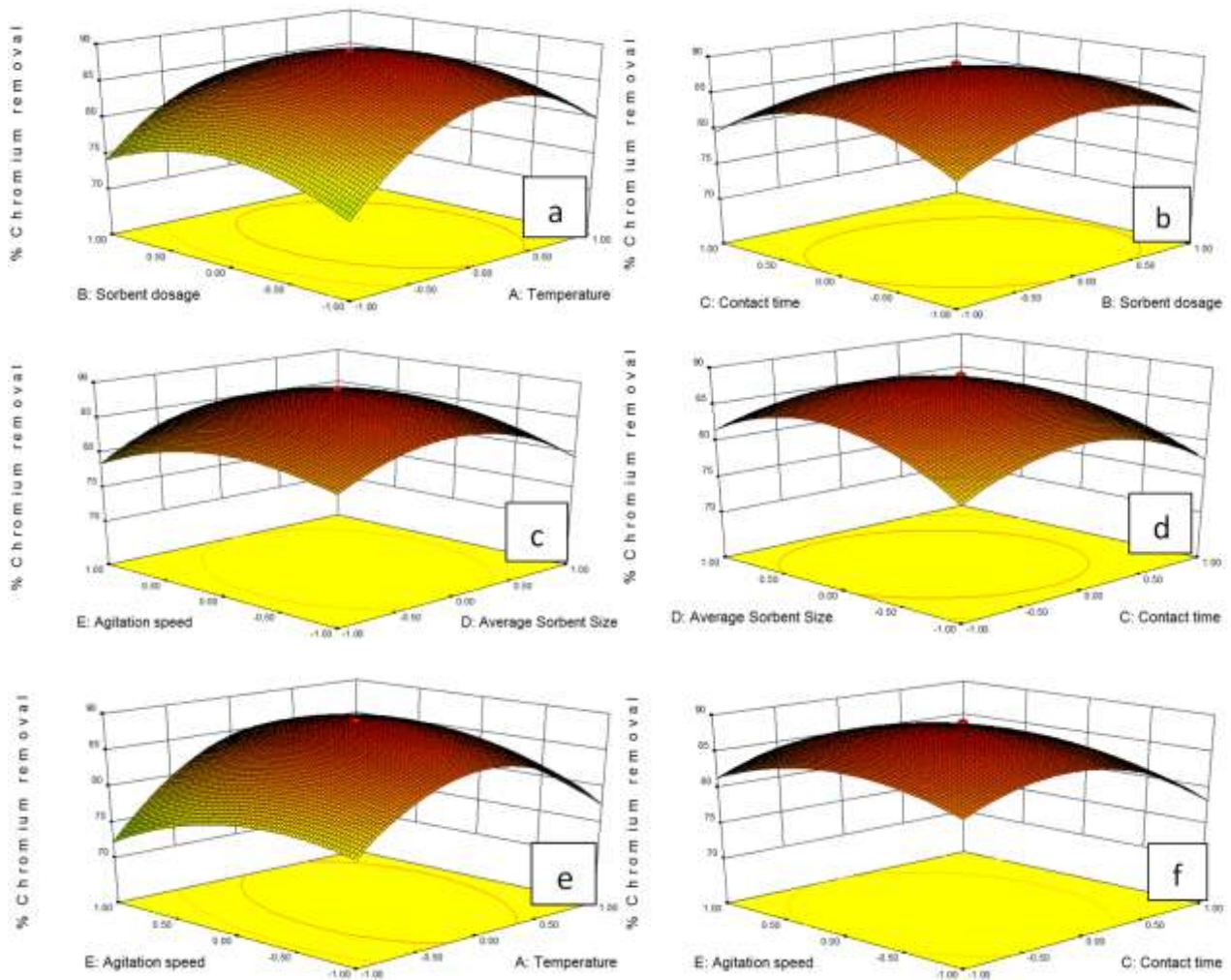

Fig. 3: (a) The 3D plot showing the effects of sorbent dosage, Temperature and theirmutual interaction on Cr(VI) removal, (b) The 3D plot showing the effects of sorbent dosage, contact time and theirmutual interaction on Cr(VI) removal, (c) The 3D plot showing the effects of sorbent size, agitation speed and theirmutual interaction on Cr(VI) removal, (d) The 3D plot showing the effects of sorbent size, contact time and theirmutual interaction on Cr(VI) removal, (e) The 3D plot showing the effects of Temperature, agitation speed and theirmutual interaction on Cr(VI) removal, (f). The 3D plot showing the effects of contact time, agitation speed and theirmutual interaction on Cr(VI) removal.
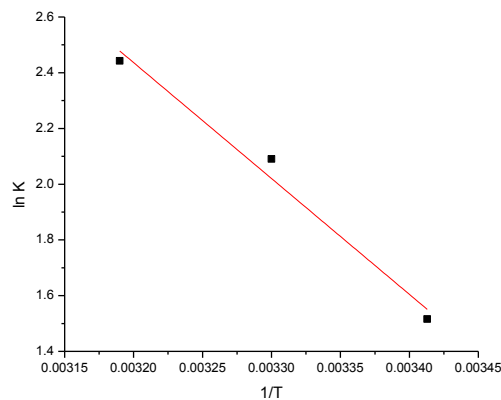

Fig. 4: Thermodynamic study

Positive values of ΔH° suggest the endothermic nature of the sorption and the negative values of ΔG° indicate the spontaneous nature of the sorption process. However, the negative value of ΔG° decreases with an increase in temperature, indicating that the spontaneous nature of sorption is inversely proportional to the temperature. Similar endothermic nature of the sorption process has been reported for other, sorbent systems [29, 30].

3.6 Equilibrium isotherm study

The experimental data was applied to linear isotherms namely, Langmuir and Freundlich to determine the sorption mechanism of Cr (VI) on *Gracilaria corticata*. The Langmuir and Freundlich isotherm model equations are in common use for describing adsorption isotherm.

3.7 Langmuir isotherm

The Langmuir isotherm is based on monolayer adsorption (constant heat of adsorption for all sites) on the active sites of the adsorbent. The data on the uptake of copper ion has been processed in accordance with the Langmuir isotherm equation. The linear form of the Langmuir isotherm is represented by the equation

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m C_e}$$

(8)

where Ce is the equilibrium concentration of Cr(VI) ion in the solution (mg L−1), qe the amount of the Cr(VI) ion adsorbed at equilibrium (mg g−1), qm the amount of Cr(VI) ion required to form a monolayer, i.e., adsorption capacity of the adsorbent (mg g−1), and b is the equilibrium constant representing adsorption intensity (L mg−1). The values of qm and b can be calculated from the slope and intercept of the plot of 1/Ce vs 1/qe.
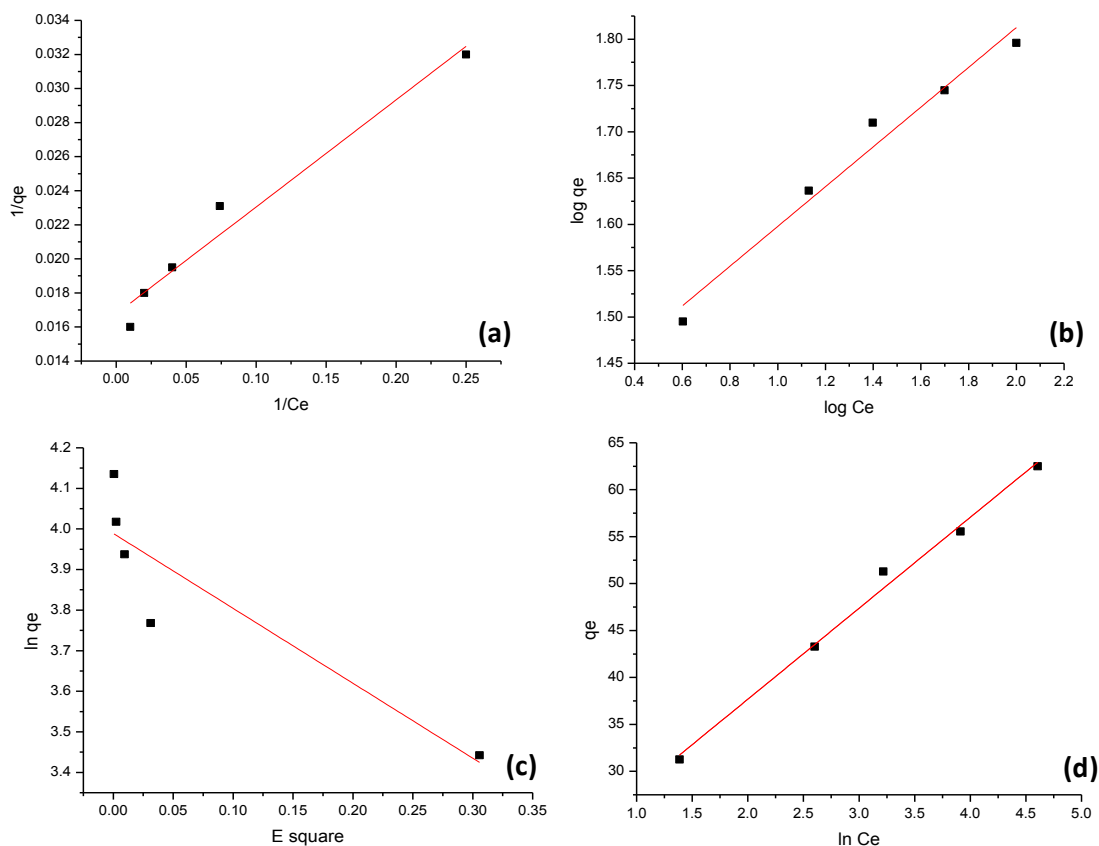

Fig. 5: (a) Langmuir isotherms (b) Freundlich isotherms (c) Dubunin-Radushkevich isotherms (d) Temkin isotherm

The constants qm and b are tabulated in Table 5. Affinity between sorbent and sorbate was represented by the constant b. In general good sorbents have a high qm and a high R^2 (0.9789). *Gracilaria corticata* have high saturation (qm) for different initial metal concentration of Cr (VI). Fig.5a shows the Langmuir plots of Cr (VI) sorption isotherms for Gracilaria *corticata* at different initial metal concentration.

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Table 4. Thermodynamic parameters for the Sorption of Cr(VI) on to *Gracilaria corticata* at different temperatures

T, K	Δ*G* (kJ/mol)	Δ*H* (kJ/mol)	Δ*S* (kJ/mol K)
293	-3.693		
303	-5.2665	34.57	0.1308
313	-6.355		

3.8 Freundlich isotherm

Freundlich isotherm is the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). It is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$
(9)

Fig. 5b shows the Freundlich plots of Cr (VI) sorption isotherms for *Gracilaria corticata* at different initial metal ion concentration and the constants Kf and n were tabulated in Table 5. The Kf and n values were calculated from the intercept and slope of the plot between log qe versus log Ce. Where Kf (mg g−1) & n (g L−1) are Freundlich constants relating multilayer adsorption capacity and adsorption intensity. From the graphs, Kf value was found to be 0.0872 and 1/n value was found as 0.9496. Usually, 1/n values between 0 and 1 indicate good sorption. In this case, the Langmuir equation fits the experimental data better than the Freundlich equation.

3.9 Dubinin-Radushkevich isotherm

Figure 5c shows the plot of lnqe versus ε2, from which the Dubinin–Radushkevich constants β and qm were calculated from the slope and intercept. The results were given in Table 5. The energy value obtained (Table 5) is 0.5204 (E < 8 kJ/mol), which indicate that all metal cation adsorptions were physical processes, since a chemical adsorption process has an E > 8kJ/mol.

Table 5. Adsorption isotherm models and their constants for the sorption of Cr (VI) on to *Gracilaria corticata*

Sl.No	Isotherm Model	Parameters	Cr (VI) Sorption at Temperature 308.15K
1	Langmuir	q_m	62.5
		b	0.266
		R^2	0.95775
2	Freundlich	K_f	1.3831
		1/n	0.21472
		R^2	0.9655
3	Dubinin- Redushkevich	q_m	53.95
		B	-1.84605
		E	0.5204
		R^2	0.76592
4	Temkin	B	9.68736
		k_T	6.6180
		R^2	0.9901
T, K	Δ*G* (kJ/mol)	Δ*H* (kJ/mol)	Δ*S* (kJ/mol K)
293	-3.693	34.57	0.1308

3.10 Temkin isotherm

Figure 5d shows the plot of qe versus ln Ce, the isotherm constants were found and given in Table 5. The correlation factors show that the Temkin model approximation to the experimental results was better than the Langmuir model. Consequently, among the four isotherm models used, the Temkins model offers the best correlation factors.

3.11 Continuous column studies in synthetic solution

The breakthrough profiles representing the influence of bed height in the continuous column study on biosorption of chromium (VI) by *Gracileria corticata* . The biosorption of Cr (VI) experiment with *Gracileria corticata* was analyzed at two different bed heights (viz. 100 mm and 150 mm) at initial concentration of 100 mg/L and constant flow rate of 5 ml/min. Figure 6a. shows the break through profile of Cr (VI) sorption for both bed heights. The increase in Cr (VI) metal ions uptake capacity was only marginal with increase in bed height. The breakthrough time and exhaustion time increased with increase in bed height.

Table 6. Column data and parameters obtained for synthetic and industrial effluents on *Gracileria corticata*

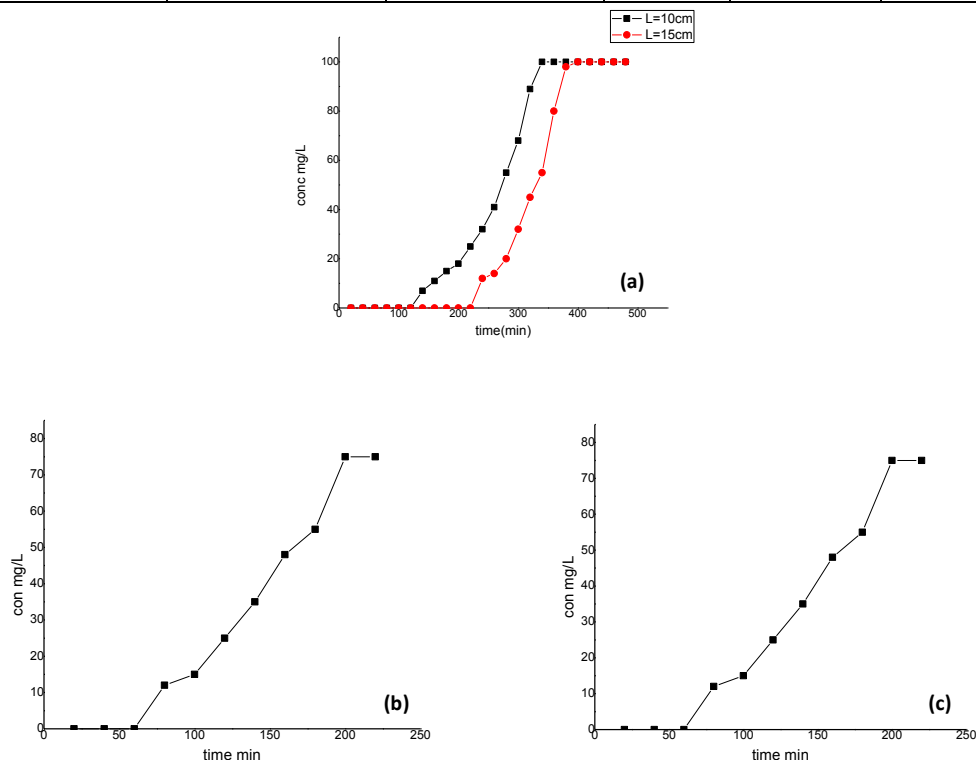| Influent	Bed height, mm	Flow rate, mL/min	t_b, min	t_s, min	Throughput volume V_{eff}, L
Synthetic solution	100	5	140	340	1.7
	150	5	240	400	2.0
Tannery industry	150	5	80	200	1.0
Electro plating industry	150	5	60	220	1.1

Fig. 6: Breakthrough curves for (a) Synthetic solution on different bed height (b) Effluent generated in the electro plating industry (c) Effluent generated in the tannery industry

3.12 Continuous column studies in industrial effluent

Electroplating & tannery effluent was pumped upwards at 5 ml/min in a continuous flow column experiment of 150 mm bed height (Table 6). Effluent samples were collected at the top of the column for different time periods and analyzed for Cr (VI) ions. All the column studies were performed at constant temperature 30°C. Figure 6b & 6c shows the breakthrough curve for Cr (VI) biosorption followed the typical S-shaped favorable curve for column operation. The column breakthrough appeared at 60 min for electroplating effluent and 80 min for tannery effluent, thereafter *Gracileria corticata* bed got rapidly saturated with Cr (VI) ions and column exhaustion appeared at 220 min for electroplating effluent and 200 min for tannery effluent.

4. CONCLUSION

For the biosorption of heavy metal Cr (VI) ions response surface methodology was used to optimize the process variables, such as sorbent size (0.176 - 1.503 mm), sorbent dosage (30 -70 g/l), temperature (25 - 45°C), contact time (2 - 10 hrs) and agitation speed (50 - 250 rpm) using marine red algae biomass *Gracilaria corticata*.. On the basis of RSM using the central composite design, found that combination of independent variables have significant effect on biosorption of Cr (VI) ions. Analysis of variance showed a high coefficient of determination value (R^2 = 0.9799), thus ensuring a satisfactory adjustment of the second order regression model with the experimental data. Maximum removal of Cr (VI) was observed 89.55%.Experimental data were analyzed using Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm models and it was found that the Temkin model presented a better fit. SEM and FTIR confirmed the presence of Cr(VI)ions on the biomass surface. Temperature affects the sorption process and the thermodynamic parameters show the spontaneous character of the sorption reaction. The findings of the present study indicates that *Gracilaria corticata* can be successfully used for separation of Cr(VI) from aqueous and industrial waste water solutions.

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Dr. K. Kumaraguru obtained his B.Tech degree in Chemical Engineering from the University of Madras in the year 2002, M,Tech degree in Chemical Process and Design from SASTRA University in the year 2004 and Ph.D in Biosorption of heavey metals from Industrial waste water at Anna University, Chennai in the year 2015. He has vast experience of over 13 years in Teaching (BharathidasanUniversity and Anna University) and Research. Her research interests include, Waste water treatment, Lube oil reclamation, Oil spill recovery and Biosorption. He is an active life member in IIChE& IPPTA. He has published several research papers in National and International Journals.

Dr. P. SURESHKUMAR, Associate Professor, Department of Biotechnology, Bharathidasan Institute of Technology, Anna University, Tiruchirappalli, Tamil Nadu, India, received his doctorate from Bharathidasan University, India in 2003. His area of research focus on identification of phytodrug targets, molecular mechanisms affected by phytodrugs, Fractionation, Identification, purification and characterization of active principles. Green nanoparticles synthesis for the application of antidiabetic , anticancer and anti-microbial activity were also underway.

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