Kinetics, Modeling, Thermodynamic Analysis and Optimization of Biosorption Parameters for Biomass of Sargassum Wighiti using Response Surface Methodology

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Abstract: In the present study, the central composite design matrix (CCD) and response surface methodology (RSM) by design expert version 8.0.5 (Stat Ease, USA) have been applied to design the experiments to evaluate the interactive effects of five important variables viz., 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) for full response surface estimation on biosorption of chromium (VI) ion using the dry biomass of *sargassum wighiti*. Batch mode experiments were carried out to assess the biosorption equilibrium. Kinetic and isotherm studies were carried out, the thermodynamic parameters like standard Gibb's free energy ($\Delta G\circ$), enthalpy ($\Delta H\circ$) and entropy ($\Delta S\circ$) were evaluated. The optimum conditions for maximum uptake of chromium (VI) ions from an aqueous solution of 100 mg/L were as follows: sorbent size (0.5284 mm), sorbent dosage (4.8798 g), temperature (34.16 °C), contact time (5 hours 58 minutes) and agitation speed (151.2 rpm). Analysis of variance (ANOVA) showed a high coefficient of determination value ($R^2 = 0.9446$) and satisfactory prediction second-order regression model was derived.
Key words: *sargassum wighiti,* Biosorption, Response surface methodology, Optimization.

Introduction

Chromium is ubiquitous and its presence in the natural world is bilateral (i.e) it exists in trivalent and hexavalent oxidation states. The pervasive attribute of Cr (III) makes it an essential micronutrient (requirement is 50 to 200 μg per day) that bolsters the body in metabolizing sugar, protein and fat. Cr (VI) has an anthropogenic nascent and its non-quotidian naturally [1]. The carcinogenic properties of the hexavalent form make it more noxious [2]. The abundant use of chromium compounds are burgeon in industries such as leather tanning, pigments and paints, mining, textile dyeing, leather tanning, electroplating, pulp and paper, aluminum conversion coating operations, plants producing industrial inorganic chemicals and wood treatment units [3]. These industries are decimating our environment by predominantly releasing the Cr(VI) into the wastewater in various aspects ,such as leather tanning, electroplating, manufacturing of dye, paint and paper are just few examples [4] and natural processes also, like volcanic action and weathering of rocks [5].

The contamination of water resources due to unsystematic disposal of chromium metals has triggered a worldwide concern for the last few decades. Enervating the environment, the discharge limits of both Cr (III) and Cr (VI) have been instituted by most industrial countries. Their concentration in industrial wastewaters ranges from 0.5 to 270mg/l. The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1mg/l

and in potable water is 0.05 mg/l [6, 7]. The Ministry of Environment and Forest (MoEF); Government of India has set Minimal National Standards (MINAS) of 0.1 mg/l for safe discharge of effluent containing Cr (VI) in surface water [8]. The imposition of strict regulations increased the demand for innovative treatment technologies to remove metals from wastewater and to attain today's toxicity driven concentration limits. Many efforts have been made recently to find cheaper pollution control methods and materials [9, 10]. Conventional techniques for heavy metal removal, including chemical precipitation, electrochemical precipitation, ion exchange reduction, solvent extraction, membrane separation, adsorption, evaporation, concentration and reverse osmosis emulsion are frequently inefficient and uneconomical when applied for heavy metals removal in low concentrations [11].

Exploration for new and ingenious treatment technologies has emphasized the attention on the metal binding capacities of non conventional materials such as paper mill sludge [12], seaweed biosorbent [13], tannin gel particles [14], sugar beet pulp [15], wheat bran [16], leaf mould [17], coniferous leaves [18], activated groundnut husk carbon [19], coconut husk and palm pressed fibers [20], coconut shell, wood and dust coal activated carbons [21], coconut tree sawdust carbon [22], used tyres carbon [23], cactus, olive stone/cake, wool, charcoal, and pine needles [24], rice husk carbon [25], moss [26], sphagnum moss peat [27], hazelnut shell carbon [28, 29], almond shell carbon [30], corncob [31], cow dung carbon [32], agricultural wastes [33], waste slurry [34], carbon slurry [35], lignocellulosic solid wastes [36], charred rice husk ,activated charcoal and eucalyptus bark [37] have been reported in literature.

Among these indigenously acquirable biomaterials, seaweeds are often considered attractive as they are affordable and readily available [38]. These biomaterials are known to sequester metals from aqueous streams, and are extravagantly available in most of the domain of world's ocean. Marine algae, in specific brown seaweed, have been identified as potent biosorbents due to the presence of several functional groups, such as sulfonate, carboxyl, amine and hydroxyl groups [39]. They also provide advantages in biosorption such as their macroscopic structures impart a convenient basis for the yield of biosorbent particles suitable for application to the sorption process.

The prime objective of this work was to acquire the potential of the marine algae Sargassum wighiti to remove hexavalent chromium ions from aqueous solutions. The consequence of temperature, sorbent dosage, contact time, sorbent size and agitation speed was analyzed using a factorial experimental design. The factorial experimental design methodology involves transforming all variables from one experiment to the other. As the variables can influence each other and the ideal value for one of them can depend on the values of the others, the interaction between the parameters was studied and optimized utilizing response surface methodology.

Materials and Methods

Adsorbent

The marine algae sargassum wighiti, brown colored, is used in the present study. Raw sargassum wighiti was collected from CSMCRI (Central Salt and Marine Chemical Research Institute) marine algae research station. (Mandapam, Tamilnadu, India). The collected algae were washed with deionized (DI) water several times to remove impurities. The washing process persisted 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 chopped 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 experiment without any chemical pretreatment.

Adsorbate

The stock solution containing 1000 ppm 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 at wave length corresponding to the maximum absorbance 540 nm [40]. All chemicals obtained from MERK (Delhi) including $K_2Cr_2O_7$ of analytical grade.

Experimental design by RSM

A full factorial design, which comprehends all viable factor combinations in each of the factors, is a efficacious tool for interpreting 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 various temperature, sorbent size, contact time, sorbent dosage and agitation speed 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:

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

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

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

where Y is the predicted response, βi, βj, βij are coefficients were computed from regression, they implies the linear, quadratic and cross products of x_1, x_2, x_3 on response.

A statistical program package Design Expert 8.0.5, was utilized for regression analysis of the data procured and to estimate the coefficient of the regression equation. The equations were corroborated by the statistical tests called the ANOVA analysis. The importance of every term in the equation is to evaluate the morality of fit in each case. Response surfaces were drawn to estimate the individual and interactive effects of test variable on percentage removal of chromium (VI). The optimal values of the test variables were first obtained in coded units and then converted to the uncoded units.

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

Experimental procedure

Removal of Cr (VI) ions from the known concentration of aqueous solutions onto *sargassum wighiti* was performed on the batch scale. Experiments were carried out as per the design expert software. For each 100 ml solution, a desired quantity of *s.wighiti* was added in 250 ml volumetric flask. The mixture was agitated on the mechanical shaker. After biosorption, the contents of the beakers were 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 were determined. The response, i.e., removal efficiency of *s.wighiti* was calculated as

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

　　　　where C_o, C_i are the initial and final concentration of metal ion. All experiments were carried out in triplicate and the mean values were reported.

　　　　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, q_e (mg/g), was calculated by:

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

where C_0 and C_e (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	% Removal of Cr (VI)	
							Experimeental	Theoritical
23	1	0.00	0.00	0.00	0.00	0.00	81	80.87
52	2	1.00	1.00	-1.00	-1.00	1.00	50	56.29
38	3	1.00	-1.00	-1.00	1.00	1.00	46	44.88
37	4	-1.00	-1.00	1.00	-1.00	-1.00	60	59.52
51	5	1.00	1.00	1.00	-1.00	1.00	55	54.02
40	6	-1.00	-1.00	-1.00	-1.00	1.00	50	50.1
44	7	-1.00	-1.00	1.00	-1.00	1.00	55	60.07
5	8	0.00	0.00	0.00	0.00	0.00	81	80.87
13	9	0.00	0.00	0.00	0.00	0.00	81	80.87
43	10	-1.00	1.00	1.00	-1.00	-1.00	50	53.6
3	11	-1.00	1.00	-1.00	-1.00	1.00	50	47.03
15	12	1.00	-1.00	1.00	1.00	1.00	35	42.11
10	13	1.00	-1.00	1.00	1.00	-1.00	35	38.81
28	14	0.00	0.00	0.00	0.00	2.38	48	44.31
50	15	-1.00	-1.00	-1.00	-1.00	-1.00	55	56.24
39	16	-1.00	1.00	1.00	-1.00	1.00	50	55.96
31	17	0.00	0.00	0.00	0.00	0.00	81	80.87
27	18	1.00	-1.00	-1.00	-1.00	-1.00	46	51.37
34	19	0.00	0.00	0.00	0.00	0.00	81	80.87
29	20	-2.38	0.00	0.00	0.00	0.00	45	41.05
19	21	-1.00	1.00	1.00	1.00	-1.00	55	54.82
24	22	0.00	-2.38	0.00	0.00	0.00	60	57.46
35	23	0.00	0.00	0.00	0.00	0.00	81	80.87
32	24	0.00	0.00	0.00	0.00	0.00	81	80.87
41	25	1.00	-1.00	1.00	-1.00	1.00	55	54.95
11	26	-1.00	-1.00	1.00	1.00	1.00	50	49.04
20	27	-1.00	-1.00	-1.00	1.00	-1.00	52	54.96
2	28	1.00	1.00	-1.00	1.00	-1.00	46	50.65
8	29	0.00	0.00	0.00	0.00	-2.38	51	45.53
21	30	1.00	1.00	-1.00	-1.00	-1.00	50	49.69
25	31	1.00	-1.00	-1.00	1.00	-1.00	48	48.27
16	32	-1.00	1.00	-1.00	1.00	-1.00	53	54.15
17	33	1.00	1.00	1.00	-1.00	-1.00	35	40.74
26	34	-1.00	1.00	1.00	1.00	1.00	48	48.92
14	35	-1.00	-1.00	1.00	1.00	-1.00	53	56.69
33	36	2.38	0.00	0.00	0.00	0.00	35	30.79
1	37	0.00	0.00	0.00	0.00	0.00	81	80.87
6	38	-1.00	1.00	-1.00	1.00	1.00	38	41.62
49	39	1.00	1.00	1.00	1.00	1.00	43	45.24

42	40	0.00	2.38	0.00	0.00	0.00	60	55.39
9	41	0.00	0.00	-2.38	0.00	0.00	55	49.75
48	42	0.00	0.00	2.38	0.00	0.00	54	49.09
45	43	1.00	-1.00	-1.00	-1.00	1.00	52	56.12
47	44	0.00	0.00	0.00	-2.38	0.00	53	48.91
18	45	0.00	0.00	0.00	2.38	0.00	41	36.93
46	46	-1.00	1.00	-1.00	-1.00	-1.00	47	51.37
22	47	0.00	0.00	0.00	0.00	0.00	81	80.87
30	48	1.00	1.00	1.00	1.00	-1.00	40	40.14
12	49	1.00	1.00	-1.00	1.00	1.00	46	49.10
36	50	-1.00	-1.00	-1.00	1.00	1.00	32	40.63
4	51	0.00	0.00	0.00	0.00	0.00	81	80.87
7	52	1.00	-1.00	1.00	-1.00	-1.00	47	45.54

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

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	10135.93	20	506.80	26.42	< 0.0001
A-Sorbent Dosage	198.76	1	198.76	10.36	0.0030
B-Sorbent Size	5.19	1	5.19	0.27	0.6065
C-Agitation Speed	0.16	1	0.16	8.260E-003	0.9282
D-Tempeture	308.20	1	308.20	16.07	0.0004
E-Contact Time	13.45	1	13.45	0.70	0.4088
AB	9.03	1	9.03	0.47	0.4977
AC	215.28	1	215.28	11.22	0.0021
AD	7.03	1	7.03	0.37	0.5493
AE	236.53	1	236.53	12.33	0.0014
BC	5.28	1	5.28	0.28	0.6035
BD	81.28	1	81.28	4.24	0.0480
BE	19.53	1	19.53	1.02	0.3207
CD	2.53	1	2.53	0.13	0.7189
CE	75.03	1	75.03	3.91	0.0569
DE	157.53	1	157.53	8.21	0.0074
A^2	3738.20	1	3738.20	194.90	< 0.0001
B^2	1162.74	1	1162.74	60.62	< 0.0001
C^2	1725.20	1	1725.20	89.95	< 0.0001
D^2	2670.43	1	2670.43	139.23	< 0.0001
E^2	2332.50	1	2332.50	121.61	< 0.0001
Residual	594.59	31	19.18		
Lack of Fit	594.59	22	27.03		
Pure Error	0.000	9	0.000		
Cor Total	10730.52	51			

Results and Discussion

Experimental design and fitting of quadratic model

Model F-Value of 26.42 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. Lack of fit F – Value of 594.59 implies the lack of fit is significant. The Fisher F-test with a very low probability value (P $_{model}$ >F=0.001) demonstrate a very high significance for the regression model. The goodness of fit of the model is checked by determining coefficient (R^2). The coefficient of determination (R^2) was calculated to be 0.9446. This implies that more than 94.46% of experimental data was compatible with the data predicted by the model and only less than 5.54% of the total variations are not explained by the model. The value of R^2 is always between 0 and 1 and a value>0.77 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 AdjR^2 (0.9088) 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 R^2.

In this case adjusted $R^2 < R^2$. The predicted R^2 (0.7759) are in a reasonable agreement with adj R^2. The value of CV is also low as 8.02% indicate that the deviations between experimental & predicted values are low. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Here it is 18.079 which indicate the adequate signal. This model can be used to navigate the design space. Mathematical expression of relationship to the response with variables are given

$$R1 = +80.35-2.14*A-0.35*B + 0.060*C-2.67*D-0.56* E + 0.53*A*B - 2.59*A*C-0.47*A* D + 2.72*A*E - 0.41*B*C + 1.59*B*D + 0.78*B*E - 0.28*C*D + 1.53*C*E - 2.22*D*E-7.98*A^2 -4.45*B^2 - 5.42 * C^2 - 6.75* D^2 - 6.31* E^2 \quad\quad (5)$$

R1 → % Removal of Chromium VI

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, D, AC, AE, BD, DE, A^2, B^2, C^2, D^2, E^2,are significant model terms for the sorption of chromium VI.

Response Surface Estimation for Maximum Removal of Chromium (VI)

The biosorption capacities of the present marine algae over different combinations of independent variables were visualized through three-dimensional view of response surface plots (Fig. 1–10). 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 and circular shape of the curve shows good and no interaction between the two variables. From figures it was observed that the elliptical nature of the contour in graphs depicted the mutual interactions of all the variables. There was a relative significant interaction between every two variables, and there was a maximum predicted yield as indicated by the surface confined in the smallest ellipse in the contour diagrams. The magnitude of coefficients in Eq. 5 gives the positive contribution of agitation speed and negative contribution of sorbent dosage, sorbent size, temperature and contact time on the removal of Chromium. The quadratic terms of all the variables have negative effect on chromium removal. Further, the interactions of, 'sorbent dosage and sorbent size', 'sorbent dosage and contact time' 'sorbent size and temperature', 'sorbent size and contact time', 'agitation speed and contact time', have positive effect, whereas the interactions of 'sorbent dosage and agitation speed', 'sorbent dosage and temperature', 'sorbent size and agitation speed', agitation speed and temperature', 'temperature and contact time' have negative effect on chromium removal.

Fig. 1. The 3D plot showing the effects of sorbent dosage, sorbent size and their mutual interaction on Cr(VI) removal
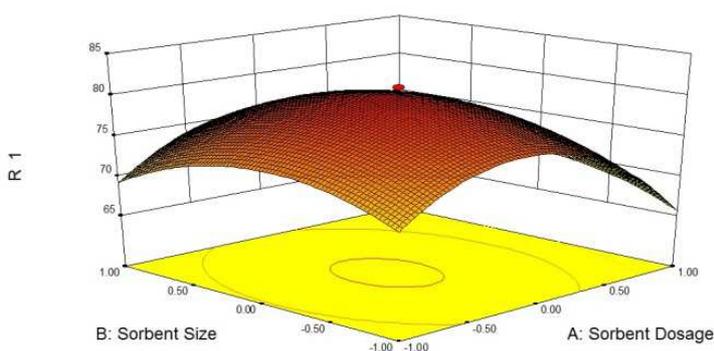
The response surface curves were plotted to know the interaction of the variables and to find the Optimum conditions for percentage removal of chromium (VI) using *s. wighiti* biomass were obtained by using RSM. Second order polynomial models obtained in this study were utilized for each response in 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 (4.8798 g), temperature (34.16 °C), contact time (5 hours 58 minutes) and agitation speed (151.2 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)

Fig. 2. The 3D plot showing the effects of sorbent dosage, agitation speed and their mutual interaction on Cr(VI) removal
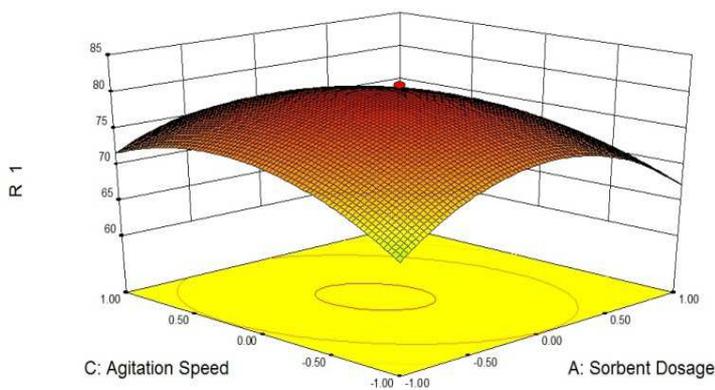
Fig. 3. The 3D plot showing the effects of sorbent dosage, Temperature and their mutual interaction on Cr(VI) removal
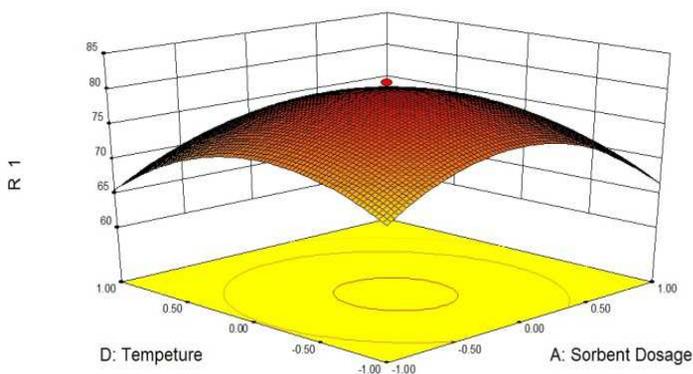
Fig. 4. The 3D plot showing the effects of sorbent dosage, contact time and their mutual interaction on Cr(VI) removal
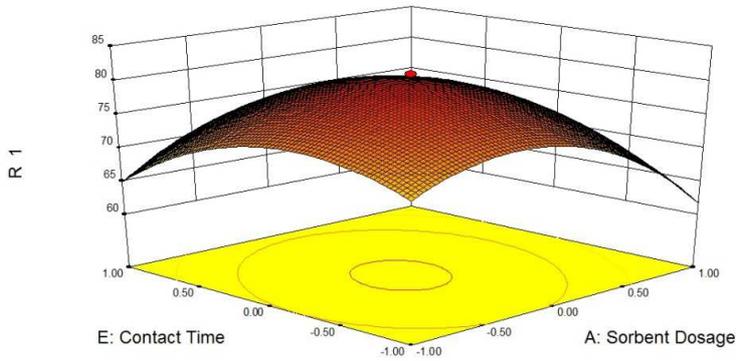

Fig.5. The 3D plot showing the effects of sorbent size, agitation speed and their mutual interaction on Cr(VI) removal
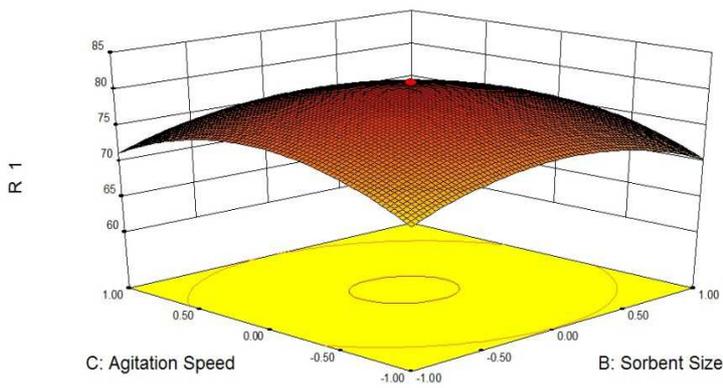

Fig.6. The 3D plot showing the effects of sorbent size, Temp and their mutual interaction on Cr(VI) removal
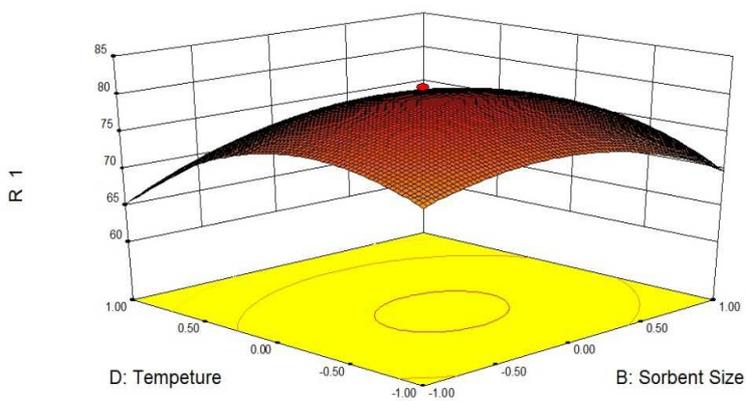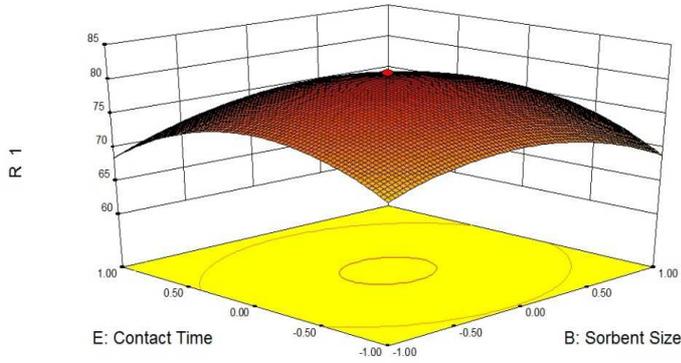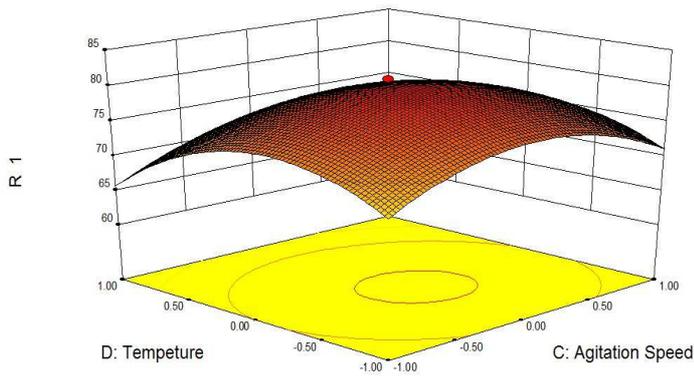
Fig.7. The 3D plot showing the effects of sorbent size, contact time and their mutual interaction on Cr(VI) removal

Fig.8. The 3D plot showing the effects of Temperature, agitation speed and their mutual interaction on Cr(VI) removal

Fig.9. The 3D plot showing the effects of contact time, agitation speed and their mutual interaction on Cr(VI) removal
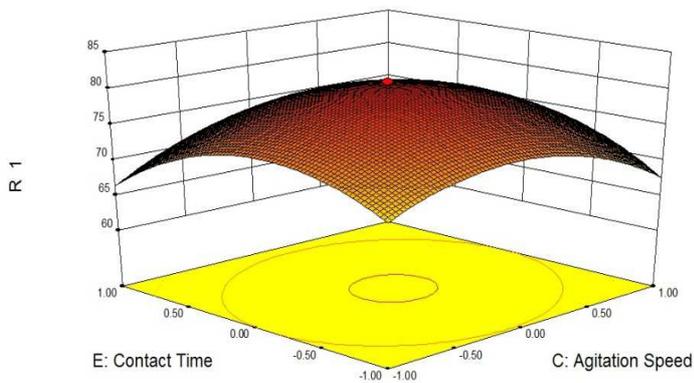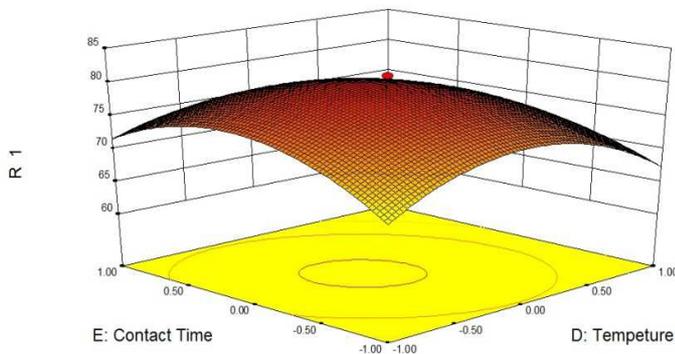
Fig.10. The 3D plot showing the effects of contact time, temperature and their mutual interaction on Cr(VI) removal

Effect of pH on Biosorption

In this study, the effect of pH on the Cr (VI) metal ions *onto S.wightii* was studied at different pH values ranging from 2 to 6. While the initial metal ion concentration (100mg/L), sorbent size (0.707-mm), sorbent dosage (4.78 mg/l), temperature (33.67°C), contact time (2 hrs) and agitation speed (150 rpm) were fixed. The maximum biosorption was found to be 82 % for Cr(VI) ions at pH 5 by *S.wightii*. The biosorption efficiency was significantly reduced at lower and higher pH values. The increased biosorption efficiency at pH 5 may be due to more negatively charged biomass surface binding more positively charged metal ions. The influence of solution pH is most important variable governing the biosorption of metal ions by biosorbents [41]. The decreased biosorption at higher pH (pH > 5) may be due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, which leads to the decreased retention capacity. It has been suggested that when pH increases, the competition from protons decreases and surface functional groups become activated, which results in increased metal biosorption and the sharpest increase in metal absorption [42]. It has been also reported that algal biomasses contain high content of carboxyl groups with mannuronic and guluronic acids on the cell wall polysaccharides and any change in solution pH could affect the biosorption process [43]. Fig.11.Effect of pH on biosorption capacity (Solution concentration = 100 mg/L, sorbent size = 0.5284 -mm, sorbent dosage = 4.8798 g, temperature = 34.16 °C, contact time = 5 hours 58 minutes and agitation speed = 151.2 rpm.

Equilibrium isotherms

The commonly used isotherm, Langmuir, was used in the present study. The nonlinear Langmuir isotherm is represented by Eqs (6):

$$q_e = (q_{max} k_a C_e)/(1+k_a C_e) \qquad (6)$$

The values of q_e and k_a can be determined from the linear plot of C_e/q_e versus C_e. The Langmuir equation is used for homogeneous surfaces. Where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the amount of chromium adsorbed at equilibrium, and q_{max} (mg/L) and k_a (L/mg) is Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

The fitting of the experimental kinetic results to Eqs. (6) was done by nonlinear regression. The fitted results and the values of the estimated parameters are presented in Table 4. Fig. 12 shows the fitted equilibrium data in Freundlich isotherm. The fitting results, i.e. isotherm parameters and the coefficients of determination, R^2, are shown in Table 4. It can be seen in Fig. 11 that Freundlich isotherm fits the data. This is also confirmed by the high value of R^2 Freundlich (0.997).

Table 4. Isotherm constants and kinetic models parameters for chromium (VI) adsorption on *sargassum wighiti*

Langmuir isotherm	
q_{max} (mg/g)	80.468
k_a (L/mg)	0.0426
R^2	0.9997

Fig.11. Effect of pH on biosorption capacity. (Solution concentration = 100 mg/L, sorbent size = 0.5284 mm, sorbent dosage = 4.8798 g, contact time = 5 hours 58 minutes and agitation speed = 151.2 rpm).
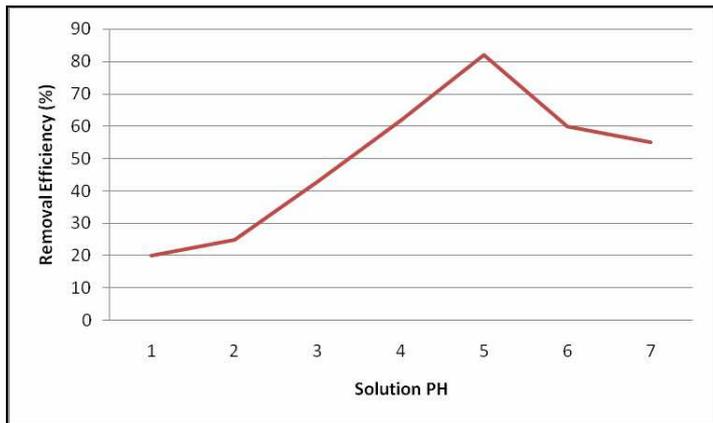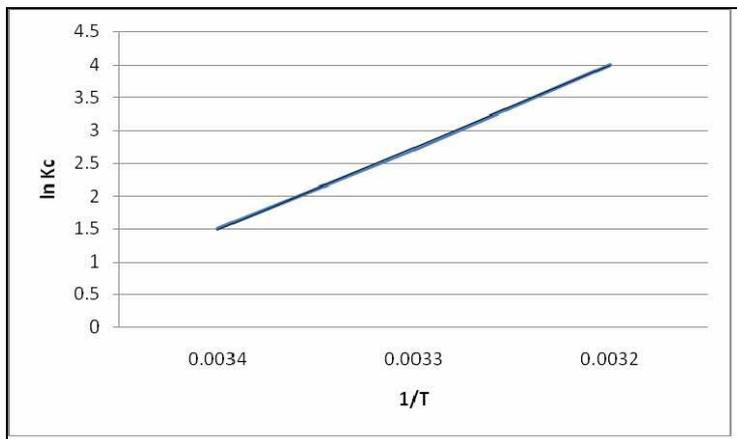

Fig12. Isotherm plot for chromium (VI) adsorption on *sargassum wighiti*

Thermodynamic study

Where ΔG^o is the standard Gibbs free energy (kJ/mol), ΔH^o is enthalpy change (kJ/mol), and ΔS^o is entropy (kJ/mol K) change of biosorption can be determined from the following Eqs. (7) and (8).

$$\Delta G^o = -RT \ln K_C \qquad (7)$$

where, K_C is the equilibrium constant.

$$\ln K_C = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (8)$$

Standard enthalpy (ΔH^o) and entropy (ΔS^o) were determined from the Van't Hoff equation; ΔH^o and ΔS^o were obtained from the slope and intercept of the plot of ln Kc vs T^{-1} as shown in Fig. 12. The standard enthalpy and entropy changes were -10.39 kJ/mol and - 1.937 J/(mol K) respectively. Negative values of ΔG^o indicate the spontaneous nature of the adsorption process. The value of ΔG^o becomes less negative with increasing temperature. This shows that a decrease in temperature favors the removal process. The negative value of ΔH^o indicates that the adsorption process is exothermic in nature. The negative values of ΔS^o suggest the probability of favorable adsorption and also the disorderliness of the adsorption at solid–liquid interface.

Conclusion

In this present study, *sargassum wighiti* algae, a cheap and commonly available biomass is used for the removal chromium (VI) from dilute aqueous solutions. The results obtained from the present investigation revealed the ability of *sargassum wighiti* biomass in removing chromium (VI) from aqueous solution. The maximum adsorption capacity was obtained (82%) at a solution pH ~6.0.

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