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ORIGINAL ARTICLE

A systematic analysis of hexavalent chromium adsorption and elimination from aqueous environment using brown marine algae (*Turbinaria ornata*)

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Abstract

In this study, chromium (VI) adsorption was explored using *Turbinaria ornata* as sorbent and the effects of parameters like temperature, sorbent size, contact time, sorbent dose, and agitation speed were improved using the response surface method. The optimal condition for maximum adsorption of Cr (VI) was found as solution temperature (33.6 °C), sorbent size (0.786 mm), contact time (215 min), agitation speed (117 rpm), and adsorbent dose (2.7 g/l). The maximum removal percentage was found to be 95.25%. The investigational data was also studied using various adsorption models. From the Langmuir model, it was observed that a maximum Cr (VI) uptake of 44.95 mg/g was achieved. Thermodynamic constraints such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ have been assessed and it has been originating that the sorption procedure was impulsive and heat releasing in nature. A high R^2 value, low root mean square error (RMSE), and mean absolute percentage error (MAPE) suggest that the Cr (VI) adsorption follows the pseudo-first-order model. The characterization of absorbent was studied by FTIR and SEM. The FTIR exposed the connection of some functional groups such as carboxylic acid, hydroxyl, and amino in the adsorption of Cr ions. From all of our data, we conclude that the *Turbinaria ornata* explored in this work displayed good potential for chromium elimination from synthetic solutions.

Keywords *Turbinaria ornata* · Chromium · Biosorption · Response surface methodology · Optimization

1 Introduction

The major worldwide ecological problem is due to the presence of heavy metal ions as contaminate in the water. Due to the increase in industrialization throughout the world, especially over a past few decades, production of more than ten thousand of new chemicals results annually. These new chemicals are utilized by chemical process industries and then discharged into the effluent stream. Also, increased consumption of various pesticides, salinity of road, lethal substances from mining locations, used motor oil, and chemical fertilizers in agriculture contributes towards the contamination of groundwater. The rate of increase in the world population demands pressure on the limited water resources. Most importantly, it would be impossible to summarize the prime causes responsible for water pollution and other types of environmental degradation in any community [1]. The main aim of wastewater handling is to reject or decrease toxins to levels that do not cause any adverse effects on the aquatic environment. Due to the increase in the alertness health of human and environmental hazards allied with ecological impurities, stricter guidelines are essential to attain the demand for novel treatment knowledge to eliminate contaminants from wastewater [2].

The big issue for humans and aquatic lives is the release of heavy metals into the channel of water over industrial activities. The most harmful and lethal impurities are cadmium, chromium, copper, lead, and mercury. Among the top 16 toxic metals, chromium is one of them which cause health effects to human [3]. Cr (VI) is highly lethal compared with Cr (III) [4]. By reacting to the DNA structure block and few protein molecules, it defectively influences the human being. Cr (VI) toxicity has undesirable effects like irritation of the

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skin, ulceration, asthma, and severe diarrhea. It damages the tissues of the kidney, the cardiovascular issues, the liver, and the nerve. Expose of high chromium in the digestive zone and lungs causes cancer [5–8]. Consequently, extensive discharges of chromium into water sources of drinking water are to be controlled by the use of permissible standards and a strict mechanism for ecological control [9]. The maximum admissible limit of Cr (VI) in drinking water is 0.05 mg l^{-1} (EPA). It is likely to eliminate lethal metals from the marine medium by various methods, such as electrodialysis, electrochemical precipitation, ultrafiltration, reverse osmosis, emulsion liquid membrane, and exchange of ions [10–15]. Compared to traditional techniques, biosorption has some major advantages. It has comparatively low costs, it is also effective in diluting solutions, it reduces the development of chemical and/or biological sludges, it does not need any addition of nutrients, the biosorbent may be regenerated, and it allows metals to be recovered [16–21].

Recently, several investigators have attained adequate removal of chromium (VI) by employing cheap, naturally and widely available biomass as sorbents like rice straw [22], *Sterculia guttata* shell [23], Gulmohar fruit shell [24], fish scales and eggshells [25], *Leucaena leucocephala*-activated carbon [26], mangrove leaf powder [27], garlic stem and horse chestnut shell [28], avocado kernel seeds, *Juniperus procera* sawdust, *Mangifera indica* bark and papaya peel [29], longan seed [30], and algae [31–34]. These adsorbents are more economic than the resins or activated carbon. Furthermore, most of these biomasses are composed of major components of functional groups joint with polysaccharides, proteins, hemicellulose, lignin, and cellulose [35].

The functional groups present in algae play a vital role in the selective surface attachment of the solute. Brown algae are well known for their superior ability, when compared to other types of algae, in the adsorptive removal of pollutants due to the presence of functional groups such as amine, carboxylic acid, hydroxyl, imidazole, phosphate, and phenolic, in their cell wall. This leads to increased affinity with the metal ions in the aqueous medium [36]. The algae are also available in plenty. The presence of functional groups and less cost makes algae a better choice for the adsorption process [36, 37]. So far, the brown alga, *Turbinaria ornata*, is not utilized for chromium (VI) sorption. Hence, the novelty of the present work is the use of these brown algae for the removal of chromium (VI) ions. The applications for batch adsorption were implemented under various criteria such as adsorbent quantity, time of influence, temperature, sorbent dosage, agitation speed, and pH. Additionally, this research completed kinetic models, adsorption equilibrium isotherms, SEM, FTIR, and thermodynamics study.

2 Materials and methods

2.1 Preparation of biosorbents

Turbinaria ornata was obtained from the CSMCRI (Central Salt and Marine Chemical Research Institute) research station of marine algae (Mandapam, Tamil Nadu, India). The collected algae were washed with water to remove contaminations. The cleaned *Turbinaria ornata* was sun-dried for 10 days. Then, the sun-dried algae were further dried at 105 °C. Finally, the *Turbinaria ornata* was then chopped into small bits and a household mixer was employed to pulverize them. In this work, *Turbinaria ornata* in the range of 0.176 to 1.503 mm particle size (using 80 mesh and 10 mesh) was used without any chemical pretreatment for sorption experimentations.

2.2 Synthetic Cr (VI) solution

The synthetic Cr (VI) solution was prepared by dissolving the required quantity of $K_2Cr_2O_7$ in double-distilled water. This solution was utilized for the preparation of other concentrations of Cr (VI) by dilution. The spectrophotometer was used to measure the metal concentration in the test solution at the wavelength of 540 nm [38]. All chemicals were obtained from MERCK (Delhi) including analysis grade $K_2Cr_2O_7$.

2.3 Response surface methodology (RSM)

In RSM, the central composite design was utilized to evaluate the effects of sorbent size, sorbent dose, temperature, contact time, and agitation speed concurrently covering the spectrum of variables for chromium removal. The ranges of these factors were evaluated by Eq. (1) [39]:

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

where x_i is the coded value of the i th variable and X_i and X_0 are uncoded values of the i th variable and i th variable at the center point respectively.

The range and levels of individual variables were given in Table 1.

A quadratic polynomial Eq. (2) was formed by applying the RSM to forecast the efficiency as a function of variables.

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

Table 1 Range of factors for Cr (VI) sorption

Independent variable	Levels and range					
		−2.38	−1	0	+1	+2.38
Sorbent dosage (g/100 ml)	X_1	0.1	0.2	0.3	0.4	0.5
Average sorbent size (mm)	X_2	1.503	1.057	0.564	0.389	0.176
Agitation speed (rpm)	X_3	50	100	150	200	250
Temperature (°C)	X_4	25	30	35	40	45
Contact time (h)	X_5	2	4	6	8	10

where Y is the predicted Cr (VI) removal efficiency and β_i, β_j, and β_{ij} are coefficients which denote the linear, quadratic, and cross products of x_1, x_2, and x_3 on response.

The response model coefficient was assessed using a multiple regression analysis system that was comprised in the RSM. The fit quality of the models was assessed from their correlation and determination coefficients.

Different statistical analytical methods were used to find the investigational error, model fitness, and statistical implication of the terms in the model when fitting the model. The model was confirmed through the statistical tests called variance analysis (ANOVA). The importance of any term in the equation is to assess in each case the morality of fit. Response surfaces have been drawn to estimate the individual and interactive effects of factors on chromium removal efficiency.

2.4 Batch experimentation

Trials were conducted as per the software of design experts (Stat Ease, 8.0.5 USA). A desired amount of marine algae (0.1–0.5 g), as per the design given in Table 2, was added into each 250-ml conical flasks containing 100 ml of 100 ppm Cr (VI) solution. A water bath shaker was employed for agitation and maintaining the temperature of the solution as per the design. The speed was varied between 50 and 250 rpm. The substances in the flask were centrifuged at 4000 rpm for 3 min after biosorption and the solution was separated from biomass and analyzed.

The separated solution was examined at 540 nm for Cr (VI) concentration using a UV–Vis spectrophotometer (SHIMADZU UV -2450). The absorbance value for initial and final Cr (VI) concentration was found. The triplicate mean value of the experiments was reported.

The Cr (VI) removal was estimated by Eq. (3):

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

The uptake, q_e (mg/g), was estimated by Eq. (4):

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

where C_o (mg/l) is the initial Cr (VI) concentration and C_e (mg/l) is the equilibrium Cr (VI) concentration. Y is the removal efficiency in percentage, V (L) is the solution volume, and M (g) is the biomass weight.

2.5 Point of zero charge (pH_{ZPC}) and pH effect

The point of zero charge of sorbent (pH_{zpc}) was found at different pH ranging from (2 to 12) using the procedure given by Sarojini and coworkers [40]. The pH effect was studied at the optimized conditions of other parameters. The influence of solution pH was analyzed at optimum conditions for a pH range (2 to 7). The pH was attuned by adjusting essential amounts of acid or base.

2.6 Biosorbent characterization

2.6.1 Scanning electron microscope

SEM for new and algae loaded with Cr (VI) was taken. Dehydrated biosorbent samples were tested using a SEM (JEOL JSM 6360 Japan) by standard procedure.

2.6.2 Study by Fourier transform infrared spectroscopy

The FTIR spectrometer (Perkin-Elmer Spectrum One FT-IR 4200) was engaged to investigate the category of functional groups responsible for adsorption in biomass. The investigation was made between 4000 and 400 cm^{-1}.

2.7 Thermodynamics of Cr (VI) sorption

At optimum conditions, the temperature has been varied from 293 to 3 13 K in order to study the thermodynamic aspects of the sorption process.

$$\Delta G^\circ = -RT \ln K_C \tag{5}$$

where ΔG° is the standard Gibbs free energy (kJ/mol), ΔH° is the enthalpy changes (kJ/mol), and ΔS° is the entropy (kJ/mol K). The following equations (Eqs. (6) and (7)) were employed to find the properties [41]:

Table 2 CCD for sorption of Cr (VI)

Obs	X_1	X_2	X_3	X_4	X_5	Cr (VI) removal, %	
						Experimental	Theoretical
1	0.00	0.00	0.00	0.00	0.00	95.25	94.85
2	1.00	1.00	−1.00	−1.00	1.00	62.55	73.97
3	1.00	−1.00	−1.00	1.00	1.00	59.26	58.39
4	−1.00	−1.00	1.00	−1.00	−1.00	98.55	82.48
5	1.00	1.00	1.00	−1.00	1.00	69.33	69.2
6	−1.00	−1.00	−1.00	−1.00	1.00	63.33	66.3
7	−1.00	−1.00	1.00	−1.00	1.00	69.33	77.38
8	0.00	0.00	0.00	0.00	0.00	95.25	94.85
9	0.00	0.00	0.00	0.00	0.00	95.25	94.85
10	−1.00	1.00	1.00	−1.00	−1.00	67.65	71.51
11	−1.00	1.00	−1.00	−1.00	1.00	67.49	63.84
12	1.00	−1.00	1.00	1.00	1.00	50.55	56.1
13	1.00	−1.00	1.00	1.00	−1.00	49.56	56.31
14	0.00	0.00	0.00	0.00	2.38	59.38	56.89
15	−1.00	−1.00	−1.00	−1.00	−1.00	69.46	76.41
16	−1.00	1.00	1.00	−1.00	1.00	62.25	72.01
17	0.00	0.00	0.00	0.00	0.00	95.25	94.85
18	1.00	−1.00	−1.00	−1.00	−1.00	59.89	69.038
19	0.00	0.00	0.00	0.00	0.00	95.25	94.85
20	−2.38	0.00	0.00	0.00	0.00	58.89	56.37
25	1.00	−1.00	1.00	−1.00	1.00	68.22	68.44
26	−1.00	−1.00	1.00	1.00	1.00	62.36	63.77
27	−1.00	−1.00	−1.00	1.00	−1.00	69.55	69.69
28	1.00	1.00	−1.00	1.00	−1.00	59.88	65.25
29	0.00	0.00	0.00	0.00	−2.38	65.99	62.43
30	1.00	1.00	−1.00	−1.00	−1.00	68.55	67.18
31	1.00	−1.00	−1.00	1.00	−1.00	62.63	63.57
32	−1.00	1.00	−1.00	1.00	−1.00	63.88	65.21
33	1.00	1.00	1.00	−1.00	−1.00	48.77	57.5
34	−1.00	1.00	1.00	1.00	1.00	62.55	61.99
35	−1.00	−1.00	1.00	1.00	−1.00	65.69	75.19
36	2.38	0.00	0.00	0.00	0.00	49.23	45.75
37	0.00	0.00	0.00	0.00	0.00	95.25	94.85
38	−1.00	1.00	−1.00	1.00	1.00	48.88	54.42
39	1.00	1.00	1.00	1.00	1.00	58.44	60.45
40	0.00	2.38	0.00	0.00	0.00	98.55	95.67
41	0.00	0.00	−2.38	0.00	0.00	70.56	73.97
42	0.00	0.00	2.38	0.00	0.00	68.23	64.07
43	1.00	−1.00	−1.00	−1.00	1.00	69.23	70.24
44	0.00	0.00	0.00	−2.38	0.00	65.58	61.55
45	0.00	0.00	0.00	2.38	0.00	51.16	43.49
46	−1.00	1.00	−1.00	−1.00	−1.00	59.23	68.33
47	0.00	0.00	0.00	0.00	0.00	95.25	94.85
48	1.00	1.00	1.00	1.00	−1.00	55.13	54.98
49	1.00	1.00	−1.00	1.00	1.00	59.14	65.72
50	−1.00	−1.00	−1.00	1.00	1.00	52.25	53.29
51	0.00	0.00	0.00	0.00	0.00	95.25	94.85
52	1.00	−1.00	1.00	−1.00	−1.00	58.56	62.24

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	10,566.56	20	528.33	71.45	< 0.0001
A	215.33	1	215.33	29.12	< 0.0001
B	35.7	1	35.7	4.83	0.0356
C	1.69	1	1.69	0.23	0.6356
D	655.12	1	655.12	88.59	< 0.0001
E	57.63	1	57.63	7.79	0.0089
AB	77.31	1	77.31	10.46	0.0029
AC	330.76	1	330.76	44.73	< 0.0001
AD	2.82	1	2.82	0.38	0.5414
AE	254.7	1	254.7	34.44	< 0.0001
BC	16.73	1	16.73	2.26	0.1426
BD	25.92	1	25.92	3.51	0.0706
BE	62.55	1	62.55	8.46	0.0067
CD	0.69	1	0.69	0.093	0.762
CE	49.8	1	49.8	6.73	0.0143
DE	79.82	1	79.82	10.79	0.0025
A^2	3505.61	1	3505.61	474.08	< 0.0001
B^2	234.48	1	234.48	31.71	< 0.0001
C^2	1789.32	1	1789.32	241.98	< 0.0001
D^2	3311.45	1	3311.45	447.82	< 0.0001
E^2	2260.67	1	2260.67	305.72	< 0.0001
Residual	229.23	31	7.39		
Lack of fit	229.23	22	10.42		
Pure error	0	9	0		
Cor total	10,795.79	51			

$$K = q_e / C_e \tag{6}$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

2.8 Regeneration

The reusability of the biosorbent was studied using HCl in the concentration range of 0.1 to 0.5 M. The experimental cycle of sorption–desorption was repeated till five cycles and the quantity of desorbed metal was estimated. The desorption efficiency was found using Eq. (8) [42, 43].

$$\text{Desorption efficiency} = \frac{\text{Quantity of Cr (VI) desorbed}}{\text{Quantity of Cr (VI) adsorbed}} X100 \tag{8}$$

2.9 Equilibrium isotherm study

Langmuir, Freundlich, Dubinin-Radushkevich (DR), and Temkin isotherms were used to find the lined isotherms specifically, to regulate the Cr (VI) sorption mechanism on to marine algae.

2.9.1 Langmuir isotherm

Langmuir [44] planned a philosophy to define the sorption on metal surfaces of the vapor molecules. The isotherm Langmuir adsorption has successfully been used in many other real monolayer adsorption sorption processes. Langmuir's adsorption model is assumed that inter-molecular forces decrease quickly with distance, thus predicting that the adsorbed monolayer covers exist on the outside surface of the adsorbent. Sorbent has a finite c in theory. Equation (9) defines the Langmuir isotherm.

$$q_e = \frac{q_{\max} K_a C_e}{1 + K_a C_e} \tag{9}$$

where C_e (g/l) is the equilibrium concentration of Cr (VI), q_e (g/g) is the equilibrium metal uptake quantity, q_{max} (mg/g), and K_a (L/mg) are Langmuir constants, respectively, connected to sorption volume and sorption energy. The equilibrium (q_e) is estimated using Langmuir isotherm from the experimental data.

2.9.2 Freundlich isotherm

Freundlich [45] reported the empirical calculation used to define non-homogenous systems.

$$q_e = K_F Ce^{1/n} \tag{10}$$

where K (mg/g) is the capacity of biosorption and 1/n (mg/g) is a measure of the intensity of sorption. Favorable adsorption means the value of n should be between 1 and 10.

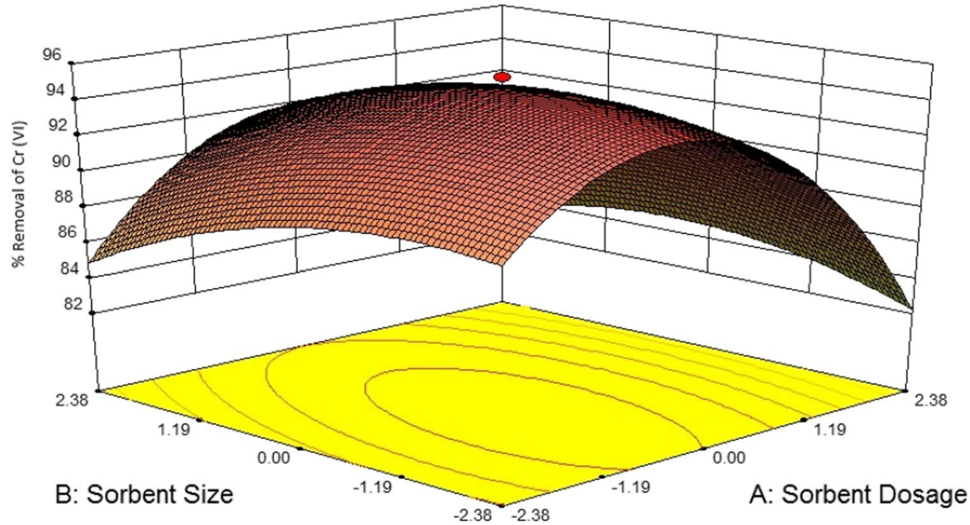
2.9.3 D-R isotherm

The isotherm *D-R* [46] is given by,

$$\begin{aligned} q_e &= q_m exp(-D\varepsilon^2) \\ \varepsilon &= RTln(1 + 1/C_e) \end{aligned} \tag{11}$$

where D is the isotherm constant Dubinin-Radushkevich (gmmol/J) and q_m is the maximum sorption capacity (mg/g).

Fig. 1 Effect of sorbent dosage and sorbent size on Cr (VI) removal



The constant D gives the mean free adsorption energy per adsorbate molecule.

2.9.4 Temkin isotherm

The Temkin isotherm [47] is

$$q_e = \frac{RT}{\Delta Q}\ln\left(K_T C_e\right) \quad (12)$$

where K_T is the Temkin model constant (L/mg), Q is the adsorption heat (J), q_e is the equilibrium adsorbent amount (mg/g), R is the universal gas constant (J/gmmole-K), and T is the temperature (K).

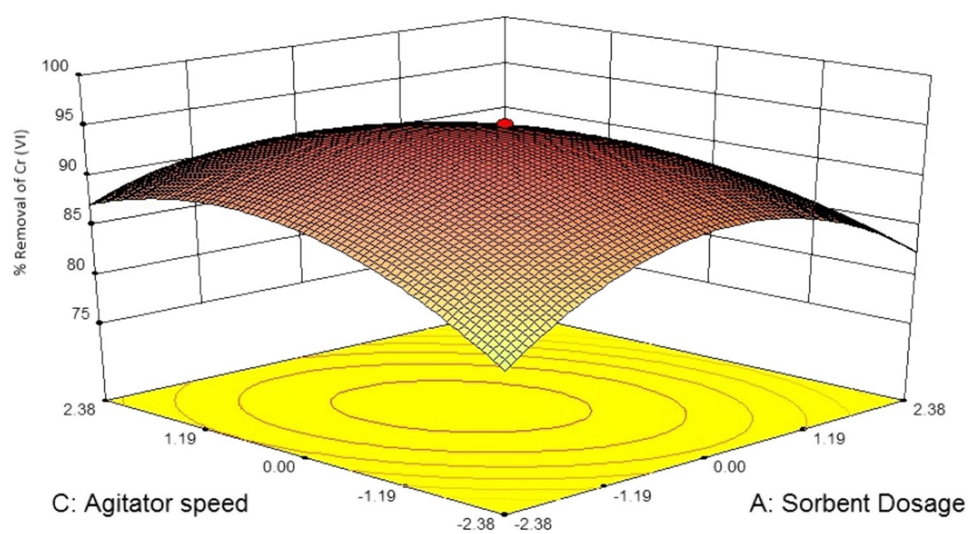
3 Results and discussion

3.1 Statistical analysis for Cr (VI) sorption onto *Turbinaria ornata*

CCD has been used to study the effects of factors considered in this study, on Cr (VI) sorption. In Table 1, a summary of the independent parameters and their range and level was presented. The five parameters remained identified as potential parameters for Cr (VI) sorption from the results of previous literature [48].

Table 2 shows the experimental result obtained from each trial and Cr (VI) removal predicted by the II-order polynomial equation which relates the response with the five different independent process variables. Equation (13) gives the

Fig. 2 Effect of sorbent dosage and agitation speed on Cr (VI) removal



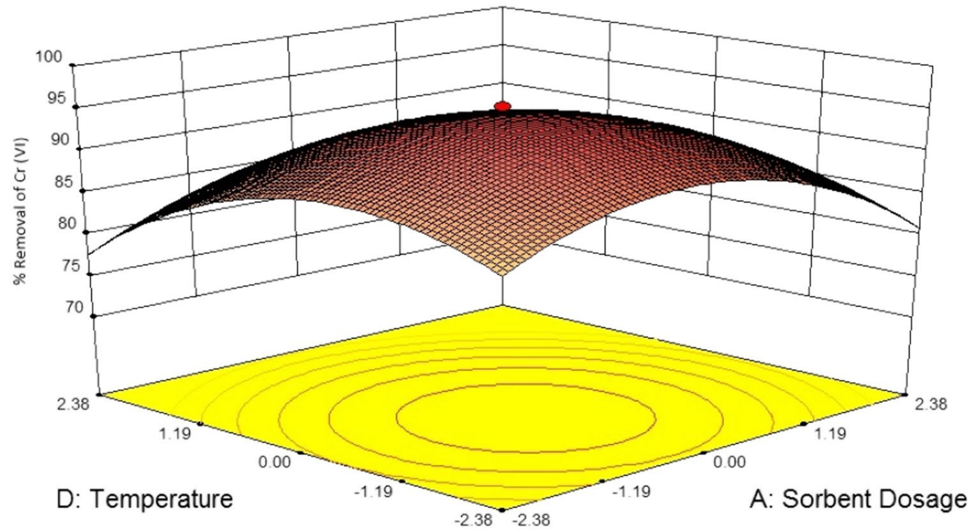


Fig. 3 Effect of sorbent dosage and temperature on Cr (VI) removal

mathematical model associated with the percentage removal of Cr (VI) ions.

The regression equation for the determination of output response for Cr (VI) was found as follows.

$$\begin{aligned}\text{Cr (VI) removal efficiency, } \% =& 94.85 - 2.23 * A - 0.91 * B \\ &+ 0.20 * C - 3.89 * D - 1.15 * \mathrm{E} \\ &+ 1.55 * A * \mathrm{B} - 3.22 * A * C \\ &+ 0.30 * A * D + 2.82 * A * E \\ &- 0.72 * B * C + 0.90 * B * D \\ &+ 1.40 * B * E - 0.15 * C * D \\ &+ 1.25 * C * E - 1.58 * D * E \\ &- 7.73 * A^2 - 2.00 * B^2 - 5.52 * C^2 \\ &- 7.51 * D^2 - 6.21 * E^2\end{aligned} \quad (13)$$

3.2 Analysis of variance (ANOVA)

From Table 3, the importance of the model was suggested by the model F-value of 71.45. Standards of "Prob > F" less than 0.05 specify model terms are important. The significant terms were identified based on the F value, whose value less than 0.05 shows the importance of the term for the sorption process. The linear effect of sorbent dose, sorbent size, temperature and contact time, the square effect of all the terms, and interactive effect of AB, AC, AE, BE, CE, and DE are found to be important for the Cr (VI) sorption process using *Turbinaria ornata*. The predicted R^2 value of 0.9127 is in line with the adjusted R^2 value of 0.9651.

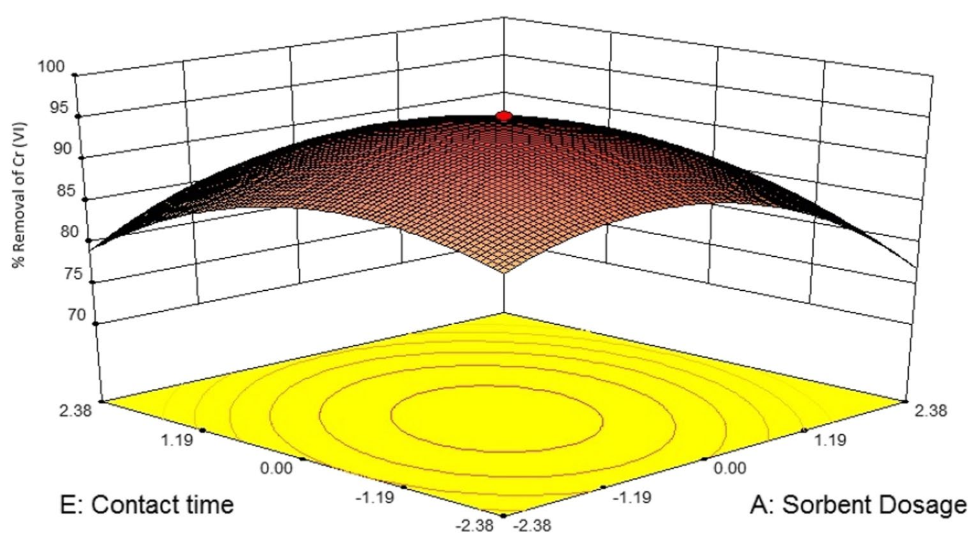


Fig. 4 Effect of sorbent dosage and contact time on Cr (VI) removal

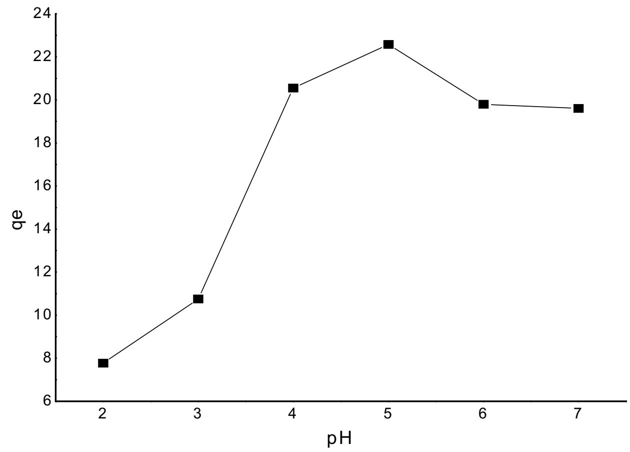


Fig. 5 Effect of pH on the sorption capacity of *Turbinaria ornata*

3.3 Optimization of process variables for Cr (VI) removal using *Turbinaria ornata*

Brown marine algae, *Turbinaria ornata*, biosorption capacity was investigated by means of various factors like sorbent dosage, average sorbent size, agitation speed, temperature and contact time using surface plots (Figs. 1, 2, 3, and 4). The plots of the surface response were signified as a function of two features at a time, keeping other features at fixed levels. The surface response curve nature dictates the interaction between the factors [31]. The oval shape is well interactive and the circular curve does not interact with the two variables. It has been observed from plots that the elliptical contour shows the mutual interaction of all the parameters. There was a virtual important interaction between each of the two parameters, and the maximum projected to yield as specified in the contour diagrams by the surface confined in the smallest ellipse [31].

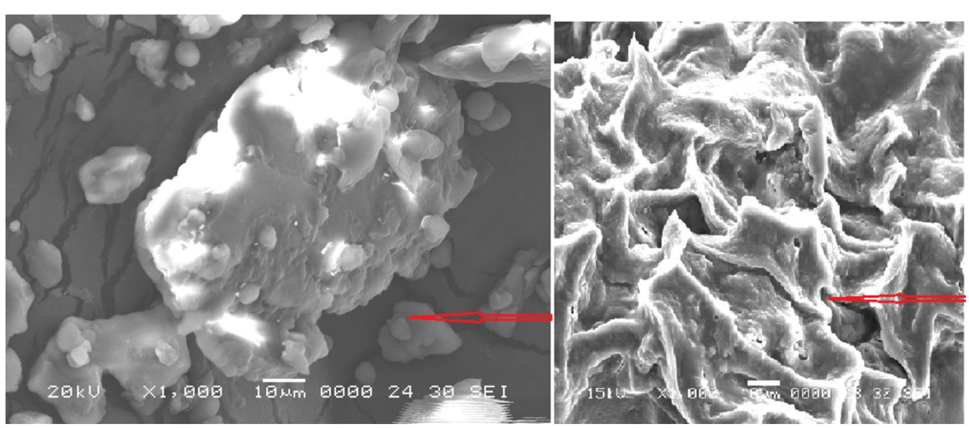
The degree of coefficients in Eq. (13) shows the positive and negative contributions of factors. All the variables' quadratic terms have a negative influence on chromium removal. In addition, the interactions' outcome of "sorbent dosage–agitation speed" and "sorbent dosage–contact time" has a positive influence. The interactions of "sorbent dosage–agitation speed," "sorbent size–temperature," "sorbent size–contact time," "agitation speed–contact time," "sorbent dose–temperature," "agitation speed–temperature," "sorbent size–agitation speed," "sorbent size–contact time," "sorbent dose–temperature," "agitation speed–contact time," "sorbent size–agitation speed," "agitation speed–temperature," and "temperature–contact time" have a negative influence on chromium elimination.

Figure 1 depicts the interactive effect of sorbent dose and size on Cr (VI) elimination. The outcomes indicate that Cr (VI) removal varies from 84 to 93% for the sorbent dosage 0.1 to 0.2 g/100 ml. Hence, the optimum sorbent dose is 2.7 g/l. Addition of seaweed above this quantity decreases the sorption of *Turbinaria ornata*. This may be due to the splitting effect of the concentration gradient between sorbate and sorbent with increasing seaweed concentration causing a decrease in the amount of chromium adsorbed onto the unit weight of *H. valentiae* [31]. This indicates that the sorbent dose had a vital effect on the uptake capacity of metal in adsorption [36].

The impact of agitation speed was investigated in the rpm range of 50 to 250. From Fig. 2, it was inferred that the maximum Cr (VI) elimination happens at 117 rpm. At very low agitation, the biomass accumulates at the bottom and decreases the Cr (VI) removal. But at higher agitation, the Cr (VI) elimination increases due to homogeneous suspension of sorbent in the solution. This is well supported by Jayakumar and groups [49].

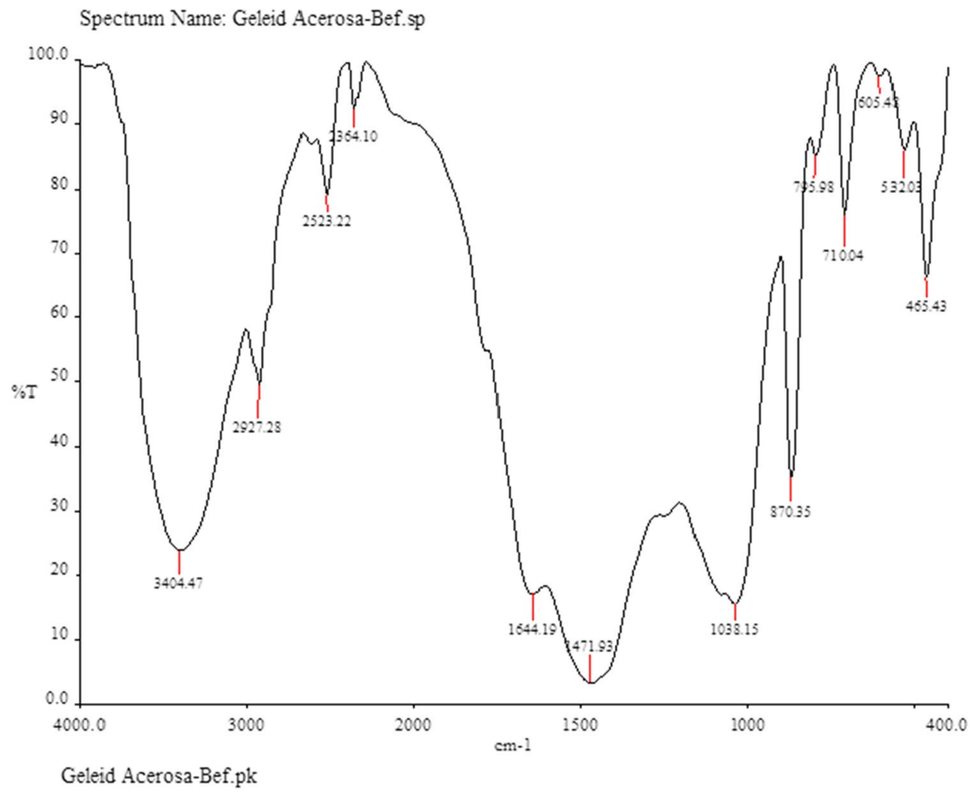
From Fig. 3, it was clear that Cr (VI) elimination improved from 75 to 92% with an escalation in temperature

Fig. 6 SEM picture of *Turbinaria ornata*. **A** Before adsorption. **B** After adsorption



A) Before adsorption B) After adsorption

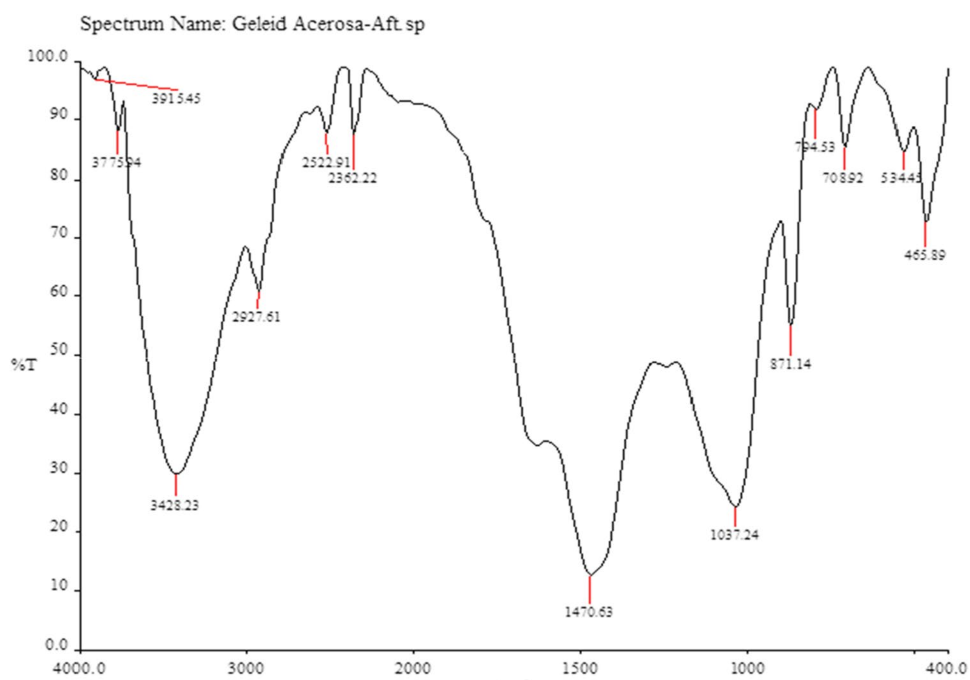
Fig. 7 FTIR picture of virgin *Turbinaria ornata*



from 25 to 33.6 °C. A maximum elimination of 93% Cr (VI) is found at 33.6 °C. It shows that sorption may be a combination of both chemical and physical adsorption. At higher temperature, the pores in the *Turbinaria ornata* enlarge lead to an increase in surface area that in turn enhances the uptake of Cr (VI) ions [50].

In Fig. 4, it has been inferred that the elimination of Cr (VI) increased with an increment in contact time of up to 215 min. Furthermore, there is no appreciable change in the

Fig. 8 FTIR picture of Cr (VI)-loaded *Turbinaria ornata*



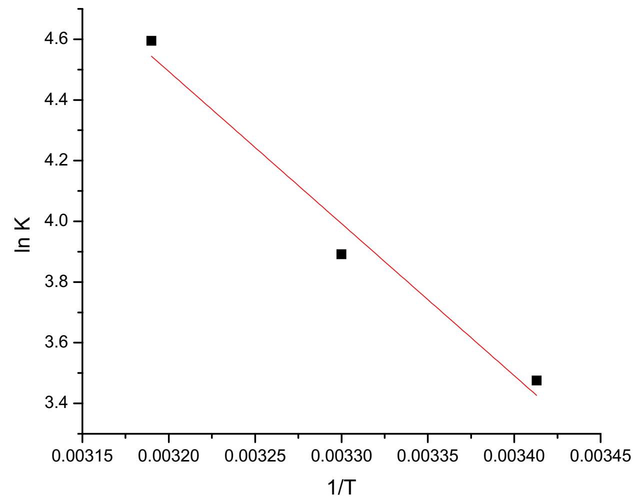


Fig. 9 Thermodynamics investigation on the sorption of Cr (VI) by *Turbinaria ornata*

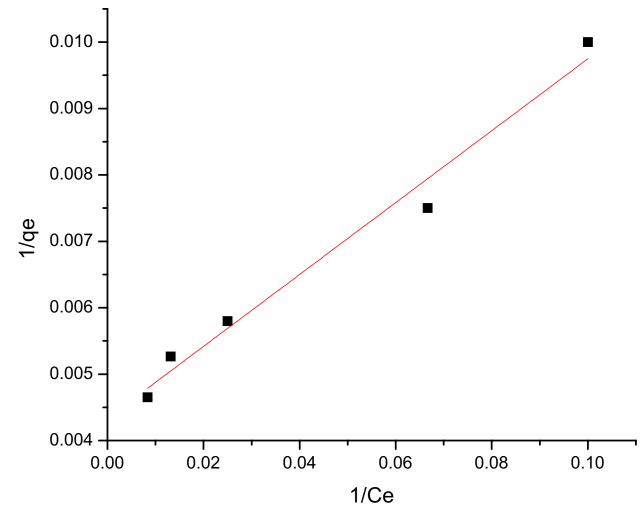


Fig. 10 Langmuir plot for biosorption of Cr (VI) on *Turbinaria ornata*

elimination of Cr (VI). Hence, a contact time of 215 min was found to be optimum. The plots (Figs. 1, 2, 3 and 4) also reveal that the optimum condition lies within the region mentioned in Table 1.

The Bhatti group [51] reported the mass transfer resistance among the aqueous and solid phases overwhelms owing to the initial metal concentration at high in solution performances as a driving force to transfer ions from the bulk solution to the sorbent surface. Similar results were achieved for the adsorption of Cr in Pakade and coworkers [52].

Using RSM, optimum conditions were obtained for the elimination of Cr (VI) using *Turbinaria ornata*. The best values found by replacing the particular coded parameter values are sorbent size at 0.7860 mm, sorbent dosage at 0.27 g/l, temperature at 33.6 °C, contact time at 215 min, and agitation speed at 117 rpm. The higher percentage deletion of chromium was obtained at this condition. It was found that the optimum values predicted from MATLAB are within the proposal area.

3.3.1 Effect of pH on biosorption

At isoelectric point (IEP), zeta potential is equal to zero. Zeta potential was evaluated at various pH from 2 to 12

Table 4 Thermodynamic properties of Cr (VI) sorption by *Turbinaria ornata*

T, K	Δ*G* (kJ/mol)	Δ*H* (kJ/mol)	Δ*S* (kJ/mol K)
293	− 8.4675	41.675	0.1707
303	− 9.804		
313	− 11.958		

and the pH_{zpc} of the sorbent was found to be 4.7. This is well supported by [53]. Above this zero-point charge, the surface of algae is negatively charged, and at lower pH, the surface charge is positive.

The influence of pH was depicted in Fig. 5. In this study, the elimination of Cr (VI) metal ions using *Turbinaria ornata* was studied by changing the pH from 2 to 7.

Table 5 Isotherm constant and their values at a temperature of 308.15 K

Isotherm model	Parameters	Values
Langmuir	q_m (mg/g)	44.95
	K_a	0.0799
	R^2	0.97578
	RMSE	1.9418
	MAPE	3.2%
Freundlich	K_f	1.77033
	1/n	0.27677
	R^2	0.90148
	RMSE	6.523
	MAPE	16.32%
Dubinin-Radushkevich	q_m (mg/g)	40.42
	B	− 256.5
	E	0.044
	R^2	0.65061
	RMSE	14.235
	MAPE	34.22%
Temkin	*B*	43.4191
	k_T	1.1993
	R^2	0.97553
	RMSE	1.9522
	SSE	3.3%

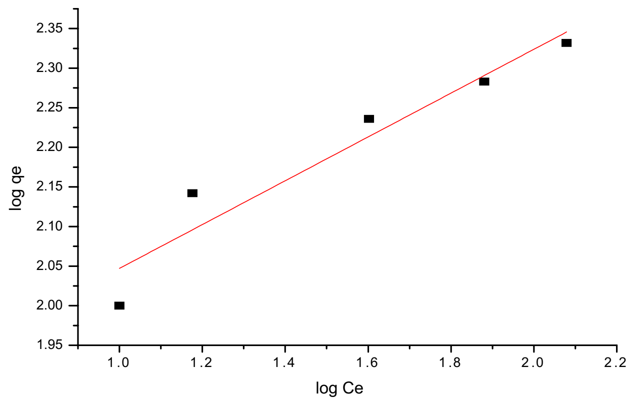


Fig. 11 Freundlich plot for biosorption of Cr (VI) on *Turbinaria ornata*

The maximum biosorption capacity of *Turbinaria ornata* for Cr (VI) ions was 99% at pH 5. At lower and higher pH values, the sorption efficiency was significantly reduced. As the pH increases from 2, on *Turbinaria ornata*, the Cr ion biosorption rises and reaches the maximum at pH 5. The increased efficiency of biosorption at pH 5 may be due to more negative binding of more positively charged metal ions on the biomass surface. In the pH, 2.0–7.0, Cr (VI) primarily occurs in the form of $HCrO^{-4}$, H_2CrO^{-4}, and CrO_2^{-4}, but $HCrO^{-4}$ dominates. Therefore, the Cr (VI) adsorption is found to be maximum at acidic conditions. This is due to the electrostatic attraction between $HCrO^{-4}$ and positively charge adsorbent surface. The Cr (VI) ions biosorption onto *Turbinaria ornata* was decreased at pH values greater than 5. This is in accordance with Murphy et al. [54].

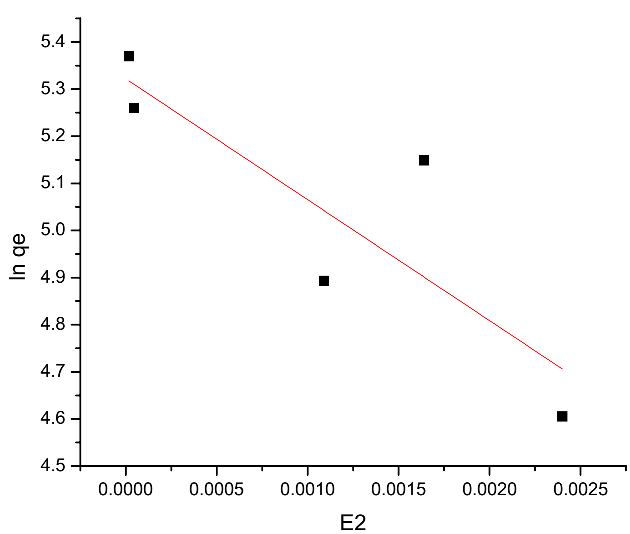


Fig. 12 Dubinin-Radushkevich isotherms for biosorption of Cr (VI) on *Turbinaria ornata*

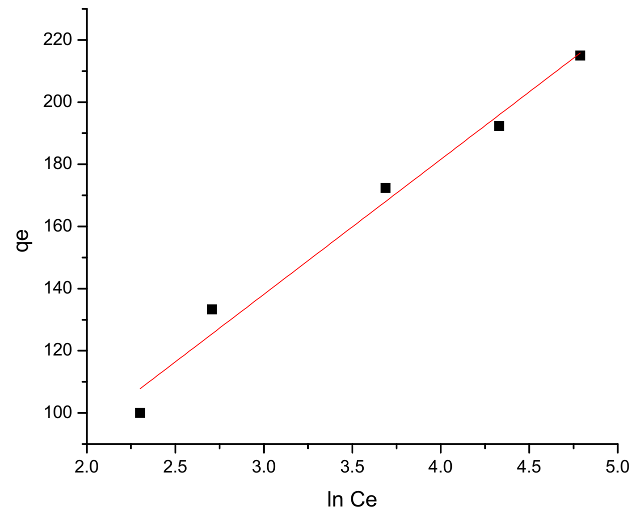


Fig. 13 Temkin isotherm for biosorption of Cr (VI) on *Turbinaria ornata*

3.4 Characterization of the biosorbent and mechanism of biosorption

3.4.1 SEM analysis

Figure 6 represents the SEM micrographs if before and after sorption experimentation. Before the adsorption of Cr (VI), the surface of algae is uneven and has a permeable surface. After sorption, the pores are occupied on the surface of *Turbinaria ornata.* It suggests that the sorption of Cr (V1) occurs on *Turbinaria ornata*. Moreover, the formation of a molecular cloud on the algae surface agrees on the binding

Table 6 Comparison of Cr (VI) uptake by various biomass

Adsorbent	Adsorption capacities (mg/g)	Reference
Rosehip seed shell	15.17	[62]
Bentonite	48.83	[63]
Natural sepiolite	37	[64]
Eggshell	10.33	[65]
Papaya peels	7.160	[66]
Banana peel	10.42	[62]
Ground nutshell	3.792	[67]
Musa acuminate bract	36.84	[68]
Irvingia gabonenis stem bark	23.26–26.18	[69]
Sagwan sawdust biochar	9.62	[70]
Bacillus strain biosorbent	106.38	[71]
Pongamia pinnata shell	96.2	[72]
Amorphous silica nanoparticles	34	[73]
Rosehip seed shell	15.17	[62]
Turbinaria ornata	44.95	Present work

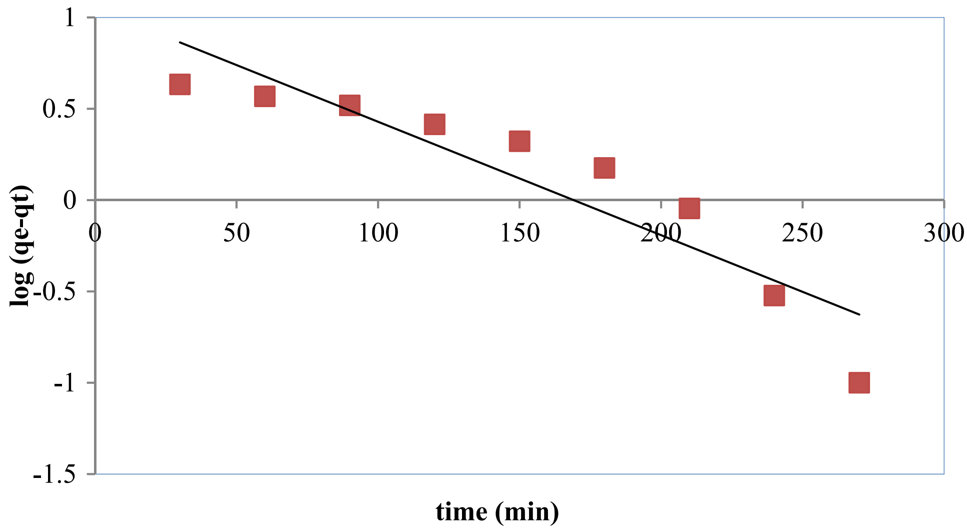


Fig. 14 PFO model for Cr (VI) sorption onto *Turbinaria ornata*

of Cr (VI) ions to the functional groups existing in *Turbinaria ornata*. In the Murphy group, similar results for Cr-loaded seaweed have been obtained [55].

3.4.2 FTIR spectra analysis

The changes in the functional groups present in the adsorbent were determined by the FTIR spectra of *Turbinaria ornata*, before and after Cr (VI) sorption. The sorbent spectra were determined in the range of 400–4000 cm^{-1}. All the spectra for the raw and Cr (VI) charged biomass were shown in Figs. 7 and 8. The FTIR spectra of *Turbinaria ornata* exhibited a number of absorption peaks, representing the adsorbent's complex nature. Figure 7 and 8 show the basic adsorbent peaks before and after *Turbinaria ornata*. The absorption peak around 3428.23 and 1470.63 cm^{-1} was specified that being free and inter-molecular bonded hydroxyl groups played a vital role in the elimination of chromium (VI) [56].

3.5 Thermodynamic study for biosorption of Cr (VI) ions by *Turbinaria ornata*

Standard enthalpy **($\Delta H°$) and entropy ($\Delta S°$)** were estimated from the intercept and slope of the plot, ln K vs $\mathbf{T^{-1}}$, as shown in Fig. 9 and presented in Table 4.

The values of $\Delta G°$ were obtained at 293, 303, and 413 K. The negative standard Gibbs free energy value shows the viability of the sorption and the impulsive nature of Cr (VI) sorption. The positive value of $\Delta H°$, which represents the binding of Cr (VI) to algae, was endothermic. This is in accordance with the literature [57, 58]. The positive entropy shows the increase in randomness at the solid/liquid boundary during biosorption [58].

3.6 Biosorption isotherms

3.6.1 Langmuir isotherm

Figure 10 shows the Langmuir plot for different initial metal concentrations of Cr (VI) sorption using ***Turbinaria ornata***. The constants q and b are tabulated in Table 5. The constant b has represented the affinity between sorbent and sorbate. In the present Cr (VI) sorption work, *Turbinaria ornata* has high uptake (q) for Cr (VI). Also, the coefficient of determination (R^2) is high for Langmuir isotherm.

3.6.2 Freundlich isotherm

Figure 11 shows the Freundlich plot of Cr (VI) sorption isotherms for *Turbinaria ornata* and the values of constants K_r and 1/n were provided in Table 5. K_r is a constant relating to the capacity of sorption and l/n is an empirical parameter

Table 7 Kinetic parameters for Cr (VI) sorption on to *Turbinaria ornata*

Pseudo-first order	
K_1 (min^{-1})	37.79
R^2	0.9862
RMSE	3.245
MAPE	5.65%
Pseudo-second order	
$k_2 \times 10^4$	1.52
R^2	0.9758
RMSE	5.645
MAPE	8.65%
IPD	
k_d (mg/g $min^{-0.5}$)	1.726
R^2	0.9491
RMSE	13.245
MAPE	16.21%

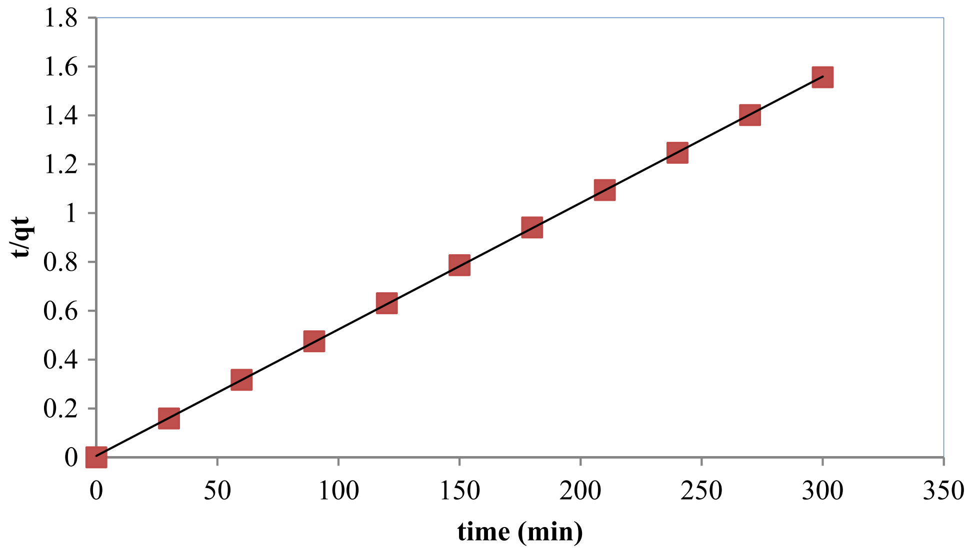


Fig. 15 Pseudo-II-order model for Cr (VI) sorption onto *Turbinaria ornata*

relating to the intensity of sorption which varies with the heterogeneity of the material. The value of K_f was found to be 1.77033 from the graphs and the value of l/n was found to be 0.27677. The 1/n value between 0 and 1 usually indicates good sorption. In this work, a value of 0.27977 specifies that the sorption of Cr (V1) onto *Turbinaria ornata* was feasible [59].

3.6.3 Dubinin-Radushkevich isotherm

Figure 12 demonstrates the plot of ln q_e versus E^2, from which the *D-R* constants, β, and q_m were estimated from the intercept and slope respectively and the values were given in Table 5. The energy value obtained in this work has $E < 8$ kJ/mol, which indicates that Cr (VI) sorption was physical since an $E > 8$ kJ/mol represents chemical adsorption [60, 61].

3.6.4 Temkin isotherm

Figure 13 shows the plot of q_e versus ln C_e, and the constants were estimated and presented in Table 5. The Langmuir model therefore provides the best correlation factors between the four isotherm models based on high R^2 value and low RMSE and MAPE values.

A comparison has been made based on uptake of Cr (VI) with some other cheap biomass and they are given in Table 6. From the comparison, it has been observed that the brown algae *Turbinaria ornata* have better sorption capacity than most of the cheap biomass utilized for Cr (VI) adsorption.

4 Sorption kinetics

The optimal time (balance) helps to determine the binding process rate. To establish the mechanism for the sorption process, several kinetic models are required. Three kinetic models were employed to investigate Cr (VI) sorption kinetics in *Turbinaria ornata*: pseudo-first, pseudo-second, intraparticle diffusion (IPD).

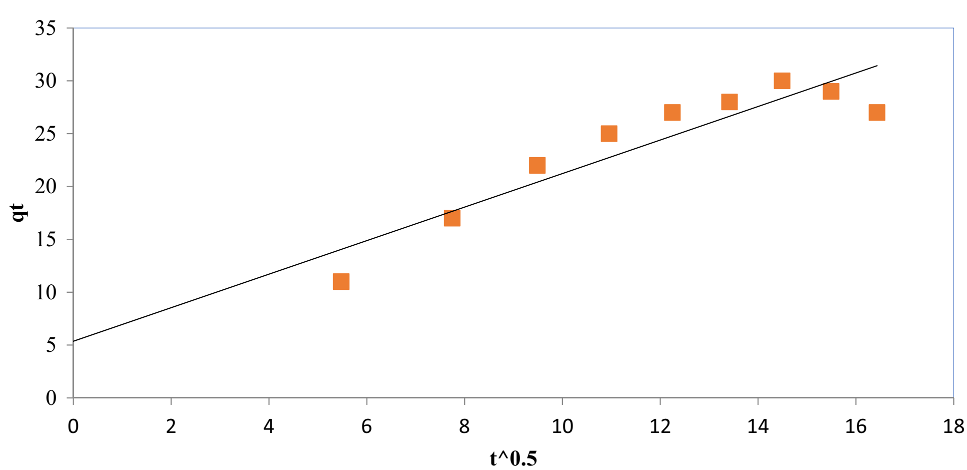


Fig. 16 IPD model for the sorption of Cr (VI) on *Turbinaria ornata*

4.1 Pseudo-first-order (PFO) model

Lagergren [74] suggested a PFO equation,

$$q = q_e\left(1 - e^{-k_1 t}\right) \tag{14}$$

where q is the sorbate concentration (mg/g), q_e is the equilibrium sorbate concentration (mg/g), and k_1 is the rate constant (min^{-1}). The parameters were calculated (Fig. 14) and reported in Table 7.

4.2 Pseudo-second-order (PSO) model

The PSO model is given by McKay et al. [75].

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{15}$$

where q_e (mg/g) is the amount of Cr (VI) adsorbed at equilibrium, q (mg/g) is the amount of Cr (VI) adsorbed at time t, k_2 (g/mg min) is the rate constant of pseudo-II order. The rate constants and R^2 values were evaluated (Fig. 15) and are given in Table 7. Based on the correlation coefficients, R^2, the PFO model fits better with the experimental data than the PSO model.

4.3 Intra-particle diffusion

Weber [76] proposed the IPD model,

$$q_e = k_d t^{0.5} \tag{16}$$

where k_d (mg/g $min^{-0.5}$) is the rate constant. The rate constants of intra-particle diffusion were calculated from Fig. 16. From Table 7, it has been found that the PSO model has a higher R^2 value and low RMSE and MAPE. This indicates that the sorption of Cr (VI) on the sorbent follows first-order kinetic model. Higher values of R^2 show a better fitness of the sorption data [77].

5 Reusability of sorbent

Reusability of the biomass offers effective economic benefits and ensures the feasible application of the algal biomass for remediation of metal-contaminated water. The desorption of Cr (VI) was investigated using different strengths of HCl and found that the effective desorption was achieved with 0.4 M HCl [49]. The biosorbent was reused for 5 cycles and the sorbed Cr (VI) was eluted with 0.4 M HCl and was depicted in Fig. 16. Also, in the first 3 cycles, more than 91% of sorbed Cr ions are desorbed from the sorbent. In the 4th and 5th cycles, the cadmium biosorption decreased to less than 80%. This loss of biosorption efficiency with an increase in cycles could be due to the amount of biomass lost. In addition, the possibilities of acid deactivation of surface active sites can inhibit the removal performance [49]. The results indicate that the *Turbinaria ornata* can be reused for five cycles in the sorption of Cr (VI).

6 Conclusions

A novel, cost-effective biomass, *Turbinaria ornata*, was used as an adsorbent for the Cr (VI) adsorption. RSM was used to determine the optimal condition of sorption for Cr (VI) onto *Turbinaria ornata.* The optimum conditions were determined as temperature (33.6 °C), sorbent size (0.786 mm), contact time (215 min), agitation speed (117 pm), and adsorbent dose (0.27 g/100 ml) solution. The maximum capacity in sorption was 44.95 mg/g. The adsorption experimental data were analyzed using various isotherm and the results show that the Cr (VI) follows Langmuir. FTIR analyses confirm the involvement of –OH, –COO, and –NH functional group in Cr (VI) adsorption onto *Turbinaria ornata*. Thus, it can be concluded that *Turbinaria ornata* can be effectively employed for the removal Cr (VI), and also, it can be tried for other metals from the effluent stream.

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