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Adsorption studies of hexavalent chromium ions on the dead biomass of *Cystoseira indica*

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RESEARCH ARTICLE

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ABSTRACT

The biosorption of hexavalent chromium ions from aqueous solution was investigated using acid-modified dead biomass of the abundantly available brown marine alga *Cystoseira indica* from Karachi coastal area of Pakistan. The biosorbent was characterized by infrared spectroscopy and scanning electron microscopy. The optimum biosorption conditions, *i.e.*, biosorbent dosage, contact time, initial metal ion concentration, pH, and temperature, were determined by carrying out batch-mode experiments. The sorption behavior was established by the Langmuir and Freundlich isotherms, which showed that although the uptake of metals was more feasible on a heterogeneous surface, homogeneous surface conditions seemed to exist at the same time. The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ calculated at different temperatures ranging from 298 to 318 K demonstrated that the biosorption was a spontaneous and exothermic process under the experimental conditions applied.

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1. Introduction

Contamination of wastewater due to considerable quantities of heavy metals released from various industries especially mining, metallurgy and electroplating, leads to severe health hazards owing to their non-biodegradability and accumulation in the environment. Therefore, it is necessary to eliminate these contaminants from industrial effluents for safe disposal [1]. According to World Health Organization (WHO), the toxic metals including chromium, nickel, copper, cobalt, lead, mercury, cadmium and zinc need significant attention for water pollution control [2]. Among these metals, the presence of chromium ions in aqueous sources is the most hazardous; it exists in the environment in two oxidation states, *i.e.*, Cr(III) and Cr(VI), out of which Cr(VI) is more mobile and toxic to living beings since it results in serious problems ranging from skin allergies to various cancer diseases because of its carcinogenic and mutagenic potential. The permissible limits for hexavalent chromium before its discharge into water bodies and drinking water are 0.10 and 0.05 mg/L, respectively [3,4].

Chromium primarily finds its way into the environment through industrial processes such as electroplating, tanning, dyeing, and metal finishing [5]. Due to the detrimental effects of chromium(VI), its removal from industrial effluents by the implementation of economical and environmentally friendly water treatment procedures is an extremely significant step in the protection of the environment and human health. Conventional treatment methods such as chemical precipitation, chemical oxidation and reduction, ion exchange, membrane separation, solvent extraction, electrodialysis, coagulation, adsorption using activated carbon and lime ash, *etc*. are not often feasible due to their high treatment cost, continuous input of chemicals required and the toxic sludge produced [6-8]. On the other hand, the biosorption technology, based on the interactions between toxic metals and the binding functional groups present on the cell wall structure of microorganisms, has emerged as a cost–effective and eco-friendly technique due to high metal uptake capacity, less toxicity, less sludge formation, easy availability of biosorbents with an opportunity of regeneration and efficiency to eliminate contaminants at low concentration levels [9].

Over the last few decades, several bacterial, algal, and fungal biomass, agricultural by-products, and industrial wastes have originated as efficient biosorbents to remove hexavalent chromium from aqueous solutions [10]. Among all these, algal biomass, especially brown seaweed, has sorption capacity

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analogous to chemical adsorbents due to the presence of polysaccharides, proteins or lipids on the surface of their cell walls that carry functional groups such as hydroxyl, amino, carboxyl and sulfate, which act as binding sites for metals [9,11]. Kumar *et al.* found that the blue green algae *Anabaena* species is an economical biosorbent for the removal of hexavalent chromium from the plating effluent [12]. *Turbinaria vulgaris*, a genus of brown algae, has been found to be an efficient biosorbent for the removal of Cr(VI) from industrial effluent [13]. Moreover, studies confirm the use of *Sargassum sp.* as an efficient biosorbent for the eradication of chromium, cadmium, copper, nickel, zinc, *etc.* [14]. Previously, Esmaeili and colleagues used activated carbon prepared from red algae *Gracilaria* and brown algae *Sargassum sp.* for the elimination of Cr(VI) from industrial wastewater and found them valuable for 91.53 and 91.98% removal, respectively [15]. Koutahzadeh and co-workers employed six brown macroalgae, *i.e.*, *Nizamuddina zanardinii, Stoechospermum marginatum, Cystoseira indica, Dictyota cervicornis, Padina australis* and *Sargassum glaucescens* for eradicating hexavalent chromium from aqueous solution and found them quite efficient biosorbents [16]. Recently, Musa *et al.* developed *Chlorella vulgaris* and *Spirulina platensis* pretreated with sulfuric acid as a suitable, efficient, and environmentally friendly biomass for the 100% removal of chromium(VI) and iron(II) from aqueous solutions [17].

Since former researchers have reported that chemically modified adsorbents possess enhanced adsorption efficiency compared to the natural ones [18], therefore, in this study, an attempt has been made to develop an economical biosorbent using modified dead biomass of *Cystoseira indica*, a brown marine alga for the removal of Cr(VI) ions from aqueous solutions. The influence of different parameters such as biosorbent dose, contact time, initial metal ion concentration, pH of solution, and temperature was investigated. Adsorption characteristics with Langmuir and Freundlich isotherms and thermodynamic parameters were evaluated to obtain a better understanding of the biosorption mechanism. The biosorbents were characterized by infrared (IR) spectroscopy and scanning electron microscopy (SEM).

2. Experimental

2.1. Preparation of biosorbent

The biomass sample of *Cystoseira indica,* a brown alga, was arranged from Blunji area of the Karachi coast, Pakistan. It was thoroughly washed with distilled water to remove any excess material and dried in an electric oven at 40±2 °C for one hour. The moisture-free biomass was manually chopped to cut down into small pieces and then ground to make fine powder with the help of a mechanical grinder to pass through 200 mesh sieve. The dead biomass sample thus obtained was used for further experimental work.

2.2. Modification of biosorbent

A part of the prepared natural biosorbent was subjected to acid pretreatment using 0.1 N HCl with continued soaking for 24 hours. The biosorbent was then filtered and thoroughly washed with distilled water until a neutral product was obtained that was dried in an electric oven at 60±2 °C for 24 hours.

2.3. Characterization of biosorbent

Both the natural and chemically modified samples of biosorbent were characterized by infrared spectroscopy using Thermo Nicolet IR 200 (USA) and their surface morphology was studied using scanning electron microscope S-3700N Hitachi Japan.

2.4. Adsorption studies

2.4.1. Preparation of standard solutions

The stock solution of chromium(VI) (1000 ppm) from Fluka chemicals was diluted with distilled water to prepare work standards of the required strength.

2.4.2. Biosorption experiments

Batch experiments were carried out to optimize the sorption parameters by varying the biosorbent dosage (0.1, 0.2, 0.3, 0.4 and 0.5 g), contact time (10, 20, 30, 40, 50 and 60 minutes), initial metal ion concentration (5, 10, 15, 20 and 25 mg/L), pH (ranging from 1 to 7) and temperature (25, 30, 35, 40 and 45 °C). In each experiment, weighed quantity of biosorbent was added to a specific volume of standard solution and after adjusting the desired pH, the mixture was kept at ambient temperature for constant contact time. Therefore, the obtained solution was filtered through Whattman filter paper No. 41. The residual metal ion concentration of chromium was determined in the filtrate solutions by an atomic absorption spectrometer (Hitachi Z-8000) and the percentage removal of metal from the solution was calculated using Equation (1):

$$\%\text{Removal}=\frac{(C_0\text{-}C_e)}{C_0}\times 100 \tag{1}$$

where, C_0 is the initial metal ion concentration in mg/L and C_e is the metal ion concentration at equilibrium in mg/L [19].

Similarly, the biosorption capacity, q_e was calculated for each experiment in mg/g according to Equation (2):

$$q_e=\frac{(C_0\text{-}C_e)\times V}{m} \tag{2}$$

where, C_0 is the initial metal ion concentration in mg/L; C_e is the equilibrium metal ion concentration in mg/L; V is the volume of metal ion solution in L and m is dry mass of the biosorbent in g [20].

3. Results and discussion

3.1. Infrared spectroscopy of biosorbents

IR spectra of natural, acid-treated, and chromium(VI) adsorbed *Cystoseira indica* were recorded in the range of 4000-400 cm^{-1} to identify surface functional groups and are presented in Figure 1a-c. Figure 1a illustrates multiple bands of numerous intensities combined to form broad bands along with a distinct band in the region between 3800 and 3300 cm^{-1}, associated with free or bonded O-H and N-H stretching vibrations. The absorption bands of relatively less intensity between 3500 and 3400 cm^{-1} are specifically assigned to the stretching vibrations of free N-H group of primary amines, so, the band at 3438 cm^{-1} is related to these vibrations. The bands of minor intensities in the range of 3300-3000 cm^{-1} appear due to the stretching vibrations of unsaturated alkyl chains whereas the weak band at 2924 cm^{-1} corresponds to the asymmetric stretching vibrations of alkyl chains [20,21]. The band of medium intensity at 1627 cm^{-1} appears due to the stretching modes of C=O of the amide group. The absorption band at 1385 cm^{-1} is observed due to the bending vibrations of C-H group of alkanes. The weak band in the region of 1200-800 cm^{-1} is attributed to C-OH stretching vibrations of carboxylic acids, since the carboxylic group is the most abundant functional group in brown algae due to the presence of alginate polymer.

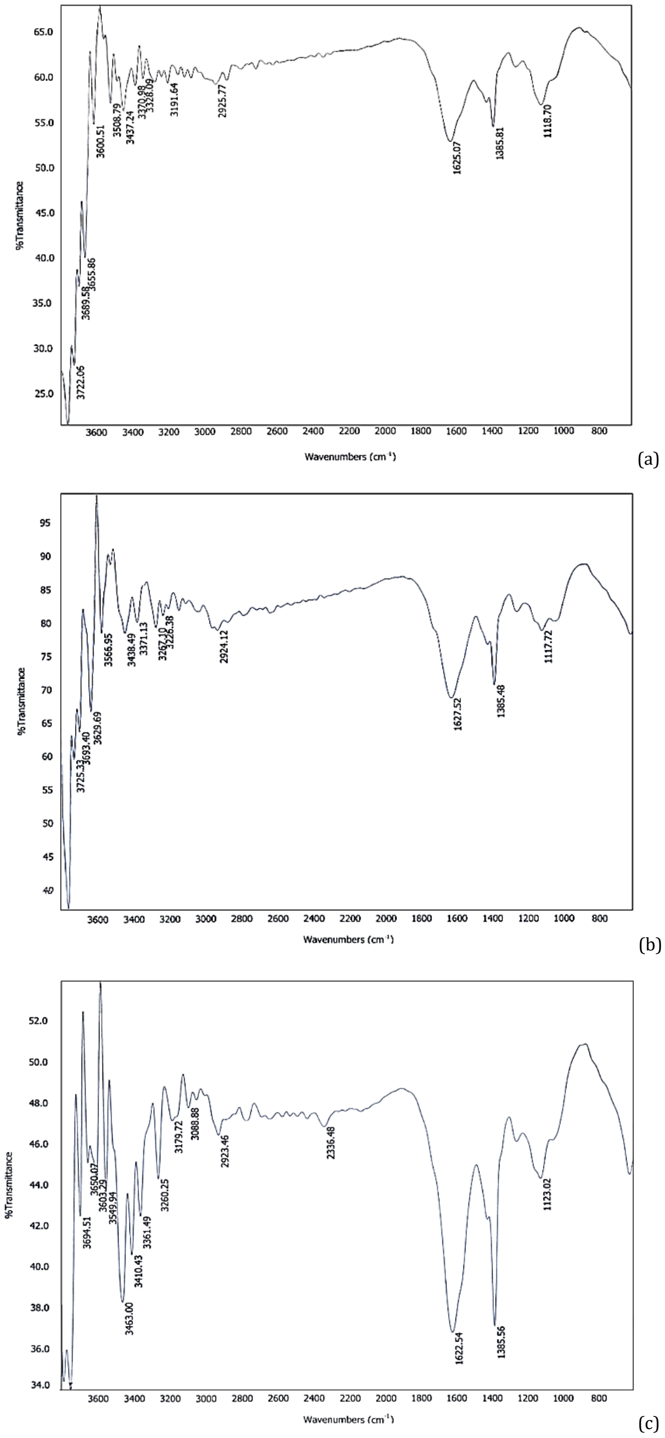

Figure 1. IR spectra of (a) natural *Cystoceira indica* biomass, (b) acid-treated *Cystoceira indica* biomass, and (c) Chromium(VI) adsorbed *Cystoceira indica* biomass.

The broad band below 1000 cm^{-1} results from long alkyl chains [22,23]. Figure 1b shows similar bands for acid-treated biomass but more intense compared to the natural one indica-ting the presence of enhanced quantity of surface functional groups that have high tendency to bind with metal ions and hence, play a vital role in defining the adsorption capacity of an adsorbent. For the Cr(VI) adsorbed biosorbent (Figure 1c), distinct bands in the frequency range below 1800 cm^{-1} can be observed. The difference between IR spectra before and after biosorption confirm the binding of chromium (VI) ions to the functional groups present on the surface of biomass. Rangabhashiyam *et al.* detected slight shifts of the 2,921 and 1,064 cm^{-1} bands and an additional absorption band for the Cr(VI)-loaded biosorbent at 1322 cm^{-1} [24]. Scientists have observed that acid modification results in activation of surface hydroxyl groups [25].

3.2. Scanning electron microscopy of biosorbents

The surface morphology of the acid-treated *Cystoseira indica* biosorbent was studied using scanning electron microscopy at 1000 and 2000× magnifications and micro-graphs are shown in Figure 2a-b.

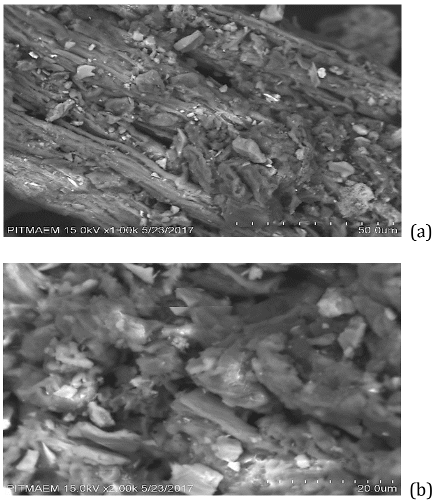

Figure 2. SEM micrographs of the acid-treated *Cystoceira indica* biomass at (a) 1000× and (b) 2000× magnification.

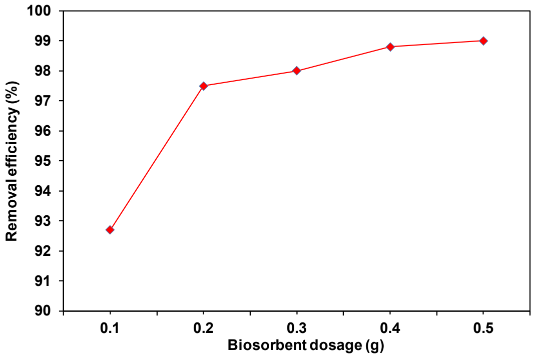

Figure 3. Effect of dosage on Cr(VI) adsorption.

The micrographs show a highly porous surface, since acid activation strongly influences the pore size, as well as pores distribution of the biomass. As reported by the former scientists that the activation step produces an extensive external surface comprising of a large number of mesopores and macropores. Furthermore, the subsequent drying step releases volatile matter from the surface, leaving empty spaces, producing a porous structure with quite irregular cavities, resulting in a high surface area responsible for the improved sorption capacity of the biomass [26].

3.3. Adsorption studies

3.3.1. Effect of biosorbent dosage

The adsorption of Cr(VI) on the treated biosorbent was studied as a function of biosorbent dosage, and equilibrium was determined for the maximum uptake of metal. In a series of experiments, the dosage of biosorbent was varied, that is, 0.1, 0.2, 0.3, 0.4 and 0.5 g keeping contact time (30 minutes), initial metal ion concentration (10 ppm), pH (5-6) and temperature (30 °C) constant, and the results are shown in Figure 3. It can be seen that as the biosorbent dose increases from 0.1 to 0.2 g, a significant increase occurs from 92.70 to 97.50% in the biosorption efficiency, followed by a minor increase at 0.3 g dose, that is, 98%. The substantial increase in the sorption capacity from 0.1 to 0.2 g of biosorbent dose can be attributed to the increased surface area that makes more active sites available. A further increase in the quantity of biosorbent leads to a consistent metal removal with a minor change, as a result of which an equilibrium was established. Therefore, 0.2 g of the biosorbent was found to be sufficient for removing a considerable quantity of Cr(VI) since, in common practice, the optimal biosorbent dose can be defined as the minimum quantity required for a sufficient level of removal efficiency. Moreover, it has been suggested by the scientists that at lower biosorbent dosage, the metal to biosorbent ratio increases as more quantity of metal is retained by the biosorbent until saturation point is attained; higher biosorbent dosage on the other hand, inhibits metal uptake by the active sites. Previous scientists have reported similar observations for a variety of algal biomasses used for the removal of hexavalent chromium ions [11,16,27].

3.3.2. Effect of contact time

The effect of contact time on the biosorption of chromium for the modified biosorbent was studied by varying the contact time from 10 to 60 minutes while all other parameters were kept constant (Figure 4). This information is considered to be essential for designing a sorption system and finding out the rate at which metal uptake takes place [10]. The results revealed that the biosorption of Cr(VI) was low within the first 20 minutes with a maximum removal efficiency of 66.9%, but it increased abruptly in the next 10 minutes and reached 97.2% and therefore, the equilibrium was achived after 30 minutes. Therefore, it seems to be insignificant to continue the biosorption process for more than 30 minutes, since a further increase in the contact time from 40 to 60 minutes resulted in negligible change in the metal removal with 98.0, 98.35 and 99.02% efficiencies. It is believed that the biosorbent that rapidly sorbs high concentrations of metal ions from solutions and reaches

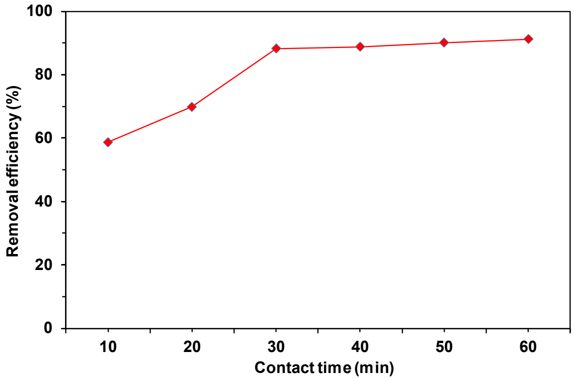

Figure 4. Effect of contact time on Cr(VI) adsorption.

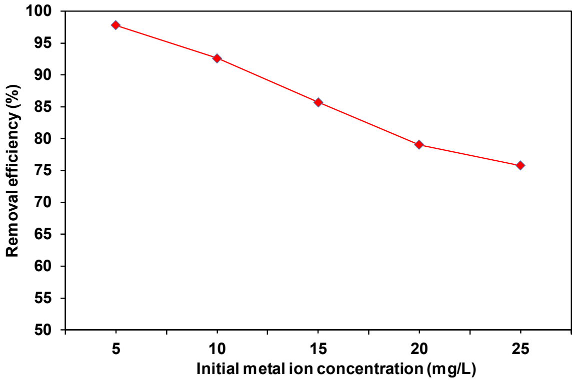

Figure 5. Effect of the initial concentration of metal ion on Cr(VI) adsorption.

the pseudo-equilibrium state in a comparatively short time is known to be an ideal one [10]. Researchers have observed that in the biosorption process the rate of metal uptake is usually high at the initial stage owing to a large surface area of the biosorbent resulting in the availability of more binding sites; this earlier fast step may involve physical phenomena like adsorption or ion exchange taking place at the cell surface. In the second phase, as time passes, the biosorption rate starts to slowly decrease until the saturation level is reached at equilibrium, the reason being that the availability of active sites on the surface decreases and the rate is controlled by the rate at which biosorbate is carried to the interior sites of the biosorbent, this step may comprise other mechanisms such as complexation or microprecipitation [11].

Koutahzadeh and co-workers reported similar results for the biosorption of Cr(VI) using various algal bimoasses, and the optimal contact time to achieve equilibrium was found to be approximately 70 minutes for *Steochospermum marginatum*, 90 minutes for *Nizamuddinia zanardinii*, and 150 minutes for *Dictyota cervicornis*, *Pandinaaustralis*, *Sargassum glaucescens*, and *Cystoseira indica* [16].

3.3.3. Effect of initial metal ion concentration

A series of experiments was conducted to investigate the effect of initial concentration of metal ions at different concentrations of the sorbate *i.e.*, 5, 10, 15, 20 and 25 ppm while unvarying all the other process parameters (Figure 5). The figure shows that increase in Cr(VI) ions concentration leads to a prominent decrease in sorption efficiency. The maximum biosorption was observed at 5 mg/L i.e. 97.80% removal efficiency whereas a regular decrease in the sorption efficiency took place till it reached 75.76%, as the concentration of metal ions was increased from 10 to 25 mg/L. Therefore, 5 mg/L was found to be the optimal initial concentration of metal ions for biosorption on acid-treated *Cystoseira indica* biomass. The higher metal uptake in the beginning is believed due to the presence of more active sites at lower metal ion concentration in the solution leading to an intervening driving force that suppresses the mass transfer resistance of metal ions between the liquid phase and the solid phase [11]. Most scientists have observed that after a certain concentration of metal ions, the percentage of removal of Cr(VI) starts to decrease, which can be explained by the fact that at higher concentrations the active binding sites become saturated and therefore the metal ions are diffused to the surface of the biosorbent by intraparticle diffusion at a relatively slower rate [4,10].

3.3.4. Effect of pH

Influence of pH on the biosorption efficiency of modified *Cystoseira indica* biomaass for Cr(VI) was studied by varying the pH from 1 to 7 and results are presented in Figure 6. It can be seen from the figure that as the pH was increased, significant quantities of metal ions were sorbed by the biosorbent and the metal uptake showed a consistent increase up to a maximum of 98.1% at pH = 5 that remained almost the same at pH = 6. However, a further increase in pH to 7, lead to a prominent decrease in biosorption, that is, 87.1%. This behavior can be explained by the fact that under highly acidic conditions, the surface hydroxyl groups involved in the biosorption process are minimized and the biosorbent is positively charged due to the presence of more hydrogen ions; therefore, an electrostatic attraction is developed between the biosorbent and Cr(VI) anions such as HCr_2O^{7-}, $HCrO^{4-}$, CrO_4^{2-} and $Cr_2O_7^{2-}$ present in the solution; all these factors result in the reduction of metal ions removal.

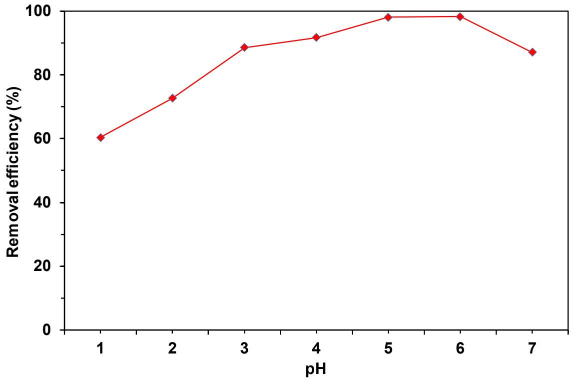

Figure 6. Effect of pH on Cr(VI) adsorption.

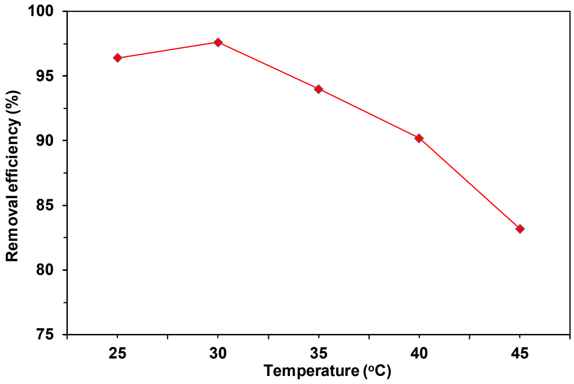

Figure 7. Effect of temperature on Cr(VI) adsorption.

Therefore, metal uptake increases to a certain pH value and then at higher pH values, interference with the diffusion of metal ions due to increase in hydroxyl ions concentration results in a lower percentage of metal ions removal [27,28]; slightly acidic conditions were selected to carry out the biosorption process.

3.3.5. Effect of temperature

Adsorption studies were carried out to investigate the effect of temperature on the sorption efficiency of hexavalent chromium on the acid-treated biosorbent. The temperature was varied from 25 to 45 °C whereas the other process parameters were kept constant, as optimized in the above experiments. The results of these experiments are illustrated in Figure 7, which shows a removal efficiency of 96.40% at 25 °C with a minor increase at 30 °C, that is, 97.60%. However, further increase in the temperature lead to a gradual decrease in the removal efficiency that reached 83.20% at 45 °C. Hence, equilibrium was achieved at 30 °C and a further rise of temperature is insignificant. It was perceived by the previous researchers that higher sorption capacity at lower temperatures was generally attributed to the easy access of chromium ions to the binding sites because of convection. On the other hand, at higher temperatures the metal ions become highly energized and this mobilization results in decreased sorption capacity [29].

3.4. Sorption isotherms

The sorption isotherms explain the distribution of the solute, *i.e.* Cr(VI), at equilibrium between the solid and liquid phases, as the metal concentration varies. The experimental data was applied to the Langmuir and Freundlich models and sorption parameters were evaluated.

3.4.1. Langmuir isotherm

This model is applied to explain the sorption capacity of the adsorbent; it defines the distribution of the adsorbate relative to the available binding sites on the surface of the sorbent and the point at which maximum adsorption leads to equilibrium [30]. The Langmuir isotherm is expressed by the following linear Equation (3),

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{3}$$

where q_e is the milligrams of adsorbate adsorbed per gram of the adsorbent at equilibrium; C_e is the adsorbate concentration in the solution at equilibrium; b is the Langmuir isotherm constant that defines the adsorption energy, and q_o measures the highest value of the theoretical adsorption capacity in mg/g.

The shape of the Langmuir isotherm and the feasibility of the adsorption process are specified by the dimensionless separation factor, R_L expressed as:

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

It indicates that the adsorption process is unfavorable for $R_L > 1$; linear for $R_L = 1$; favorable for $0 < R_L < 1$; it is irreversible for $R_L = 0$ [31].

Figure 8 shows the sorption isotherm for chromium biosorbed on acid-treated *Cystoseira indica* biosorbent. The isotherm shows the usual trend, since the initial slope is quite sharp, which corresponds to a profound increase in the sorption capacity at a lower residual metal ion concentration along with a subsequent saturation plateau attained at a higher residual metal ion concentration.

Table 1. Langmuir and Freundlich models parameters.

Langmuir constants				**Freundlich constants**		
***q_m* (mg/g)**	***b* (L/g)**	***R^2***	***R_L***	***N***	***K_F***	***R^2***
7.13	4.66	0.9262	0.02	3.03	5.06	0.9983

Table 2. Thermodynamic parameters.

***T* (K)**	***K_c***	**Δ*G*° (kJ/mol)**	**Slope (-Δ*H*/R)**	**Intercept (Δ*S*°/R)**	**Δ*H*° (KJ/mol)**	**Δ*S*° (J/mol.K)**
298	9.64	-0.219	-	-	-	-
303	9.76	-0.146	707.35	-0.076	-5.881	-0.631
308	9.38	-0.352	-	-	-	-
313	9.02	-0.516	-	-	-	-
318	8.32	-0.773	-	-	-	-

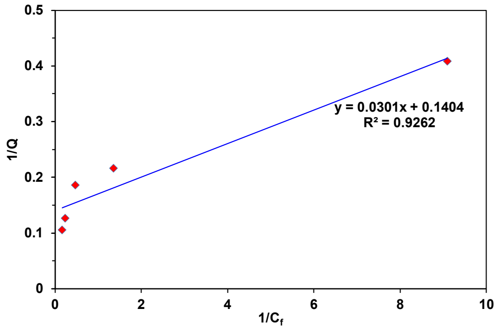

Figure 8. Langmuir isotherm for Cr(VI) adsorption.

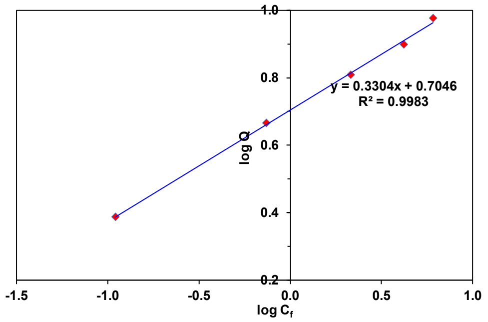

Figure 9. Freundlich isotherm for Cr(VI) adsorption.

The experimental data for the sorption isotherm were applied to the above equation, and the Langmuir constant is shown in Table 1. It can be seen that for chromium, the correlation co-efficient of the Langmuir constant, *i.e.*, R^2 is 0.9262. The table indicates that the value of R_L for chromium sorption is greater than 0 and less than 1, *i.e.*, $0 < R_L < 1$, therefore, the biosorption process is favorable. This significant sorption capacity of the biomass for Cr (VI) ions may result due to the abundance of easily accessible hydroxyl and amino groups present on its surface that provide binding sites to form metal-ligand complexes.

3.4.2. Freundlich isotherm

Freundlich model represents the adsorption of adsorbate on a heterogeneous solid surface involving strong interaction between the molecules of adsorbate. The linear form of this model is given by the Equation (5),

$$\log q = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

where, q is the milligrams of adsorbate per gram of the adsorbent at equilibrium; C_e is the concentration of sorbate in the solution at equilibrium in mg/L; K_F and n are the Freundlich constants that measure the maximum adsorption capacity and nonlinearity between concentration of adsorbate and adsorption respectively; $n = 1$ represents the linear adsorption, $n < 1$ defines the adsorption involving a chemical process whereas $n > 1$ describes the physical adsorption process for $n > 1$. The values of these constants are evaluated with the help of a graph between $\log q$ and $\log C_e$ [30].

The Freundlich isotherm for chromium (VI) ions on an acid-treated biosorbent is illustrated in Figure 9. The model was applied to evaluate the sorption data, and the values of the related constants are shown in Table 1. It can be observed that the value of correlation co-efficient (R^2) calculated for chromium biosorption is 0.9983 that confirms that the Freundlich model fitted well to the experimental data. The table shows the value of the Freundlich constant $K_F = 5.0652$ and $n = 3.03$, which confirms the bonding between the sorbate and the sorbent [32].

Sorption isotherms indicate that the correlation coefficient for Freundlich isotherm is somewhat higher than that for Langmuir isotherm which confirms that the metal uptake is more feasible on a heterogenous surface, but homogenous as well as heterogenous surface conditions simultaneously may coexist for the biosorption of hexavalent chromium ions on acid-modified *Cystoseira indica* under the experimental conditions applied [33].

3.5. Biosorption thermodynamics

The thermodynamic parameters for the biosorption process such as the free energy (Δ*G*°) in J/mol, the enthalpy change (Δ*H*°) in J/mol and the standard entropy (Δ*S*°) in

Table 3. Biosorption capacity of Cr (VI) on various materials reported in the literature.

Material	Biosorption capacity (mg/g)	Reference
Sargassumthunbergii	1.85	Wang *et al.* 2014 [35]
Dictyopteris polypodioides	21.78	Belattmania *et al.* 2015 [36]
Cinnamomum verum leaves	11.33	Saeed *et al.* 2020 [37]
Bacillus amyloliquefaciens	48.44	Ramachandran *et al.* 2022 [38]
Groundnut shell activated carbon	13.45	Vaddi *et al.* 2022 [39]
Activated *Cystoseira indica*	7.13	Present study

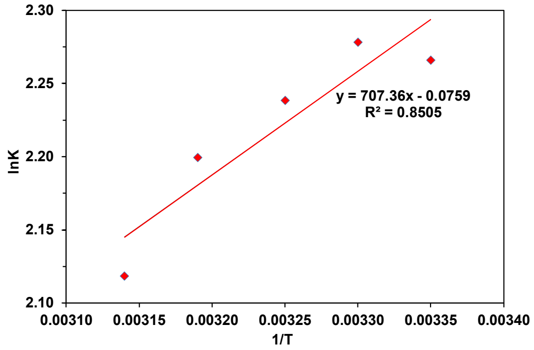

Figure 10. Plot between *lnK* and *1/T* for thermodynamic studies of Cr(VI) adsorption.

J/mol.K were calculated at temperatures varying from 298 to 318 K (Table 2) by applying the following thermodynamic Equations (6) and (7),

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

since, $\Delta G^\circ = -RT \ln K_c$ hence,

$$\ln K_c = -\frac{\Delta H}{R}T + \frac{\Delta S^\circ}{R} \tag{7}$$

where R is the universal gas constant and its value is 8.314 J/mol.K, T is the absolute temperature of the solution in Kelvin, and K_c (L/mol) is the equilibrium constant. The values ΔH° and ΔS° can be estimated from the slope and intercept, respectively, by a plot between ln K_c and *1/T*. Table 2 shows that Gibbs free energy change was found to be negative that confirms a spontaneous biosorption process. Researchers have stated that the Gibbs free energy value greater than -20 kJ/mol indicates the occurrence of physiosorption, whereas the values less than -40 kJ/mol specify the chemisorption going on. The value obtained for the energy change confirms the occurrence of the physiosorption process only since it is quite higher than -20 kJ/mol. However, the sorption isotherms prove the simultaneous involvement of the chemisorption process. The results show a negative value for the enthalpy change at optimum temperature, *i.e.,* 303 K, indicating an exothermic process taking place for biosorption. Hence, lower temperatures may lead to an increased sorption capacity as obvious from the above-mentioned results that rise in temperature after 303 K was found to be insignificant. Similarly, a negative value for the entropy change can be seen that depicts the decrease in randomness at the solid-liquid interface during the sorption process. Both the enthalpy and entropy changes specify that the enthalpy change participates mainly in generating negative Gibbs free energy, thus leading to a spontaneous biosorption process [34].

4. Conclusions

This research work was carried out using acid-modified dead biomass of the brown marine alga *Cystoseira indica* for the removal of hexavalent chromium from aqueous solutions in batch mode. The alga was obtained from the coastal area of Karachi, Pakistan, which has not been used for this study before. The optimum operating conditions were found to be 0.2 g biosorbent dosage, 30 minutes contact time, 5 mg/L initial metal ion concentration at pH = 5 and 30 °C temperature. IR spectra revealed that hydroxyl, amino, and carboxyl groups present on the surface of the biosorbent were mainly involved in the biosorption process since they have strong affinity for metal ions. SEM images confirmed the highly porous surface of the activated biosorbent, which produces a high surface area that is responsible for its enhanced sorption capacity. Sorption isotherms and thermodynamic studies demonstrate that under the present experimental conditions the biosorption was a spontaneous exothermic process involving physiosorption and chemisorption taking place together. Hence, it can be concluded that *Cystoseira indica*, a natural, eco-friendly, abundantly available, and cost-effective biomass, proved to be an efficient sorbent for the removal of Cr(VI) and can be successfully applied for the eradication of other heavy metals as well.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
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CRediT authorship contribution statement

Conceptualization: Zahid Mahmood; Methodology: Zahid Mahmood; Software: Samreen Zahra; Validation: Zahid Mahmood; Formal Analysis: Izza Ijaz; Investigation: Izza Ijaz; Resources: Zahid Mahmood; Data Curation: Zhid Mahmood; Writing - Original Draft: Samreen Zahra; Writing - Review and Editing: Samreen Zahra; Visualization: Samreen Zahra; Funding acquisition: Not available; Supervision: Zahid Mahmood; Project Administration: Zahid Mahmood.

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