Korean J. Chem. Eng., 35(1), 234-245 (2018)
DOI: 10.1007/s11814-017-0239-2

pISSN: 0256-1115
eISSN: 1975-7220

Treatment of chromium-laden aqueous solution using $CaCl_2$-modified *Sargassum oligocystum* biomass: Characteristics, equilibrium, kinetic, and thermodynamic studies

Rauf Foroutan*, Reza Mohammadi*, and Bahman Ramavandi,†**

*Polymer Research Laboratory, Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran
**Environmental Health Engineering Department, Faculty of Health and Nutrition, Bushehr University of Medical Sciences, Bushehr, Iran
(*Received 25 July 2017 • accepted 26 August 2017*)

Abstract−Biosorption properties of a $CaCl_2$-modified *Sargassum oligocystum* algae biomass for removal of Cr(VI) from aqueous solutions were investigated. Experimental parameters affecting the biosorption process such as pH, contact time, biosorbent dosage, and temperature were studied. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), mapping test, energy-dispersive X-ray spectroscopy (EDX), and specific surface area were used to assess the physico-chemical properties the biosorbent. The surface area of biosorbent was found to be 35.64 m^2/g. FTIR test revealed that the active groups of -OH, -NH_2, -C-H, C-O, -C-N, and S=O were present on the surface of $CaCl_2$-modified *S. oligocystum* biomass. The kinetic behavior of the chromium biosorption by modified *S. oligocystum* biomass followed well pseudo-second order kinetic (R^2>0.999). The biosorption equilibrium occurred at 100th min of contact time. The Langmuir, Freundlich, and Dubinin-Radushkevich models were applied to describe the biosorption isotherm of Cr(VI) onto modified *S. oligocystum* biomass. According to the R_L and n parameters of the studied isotherms, the Cr(VI) biosorption process was physical and desirable. The chromium biosorption capacity of modified *S. oligocystum* biomass was found to be 34.46 mg/g. The calculated thermodynamic parameters (ΔG^o, ΔH^o, and ΔS^o) indicated that the biosorption of Cr(VI) onto modified *S. oligocystum* biomass algae was feasible, spontaneous, and exothermic under examined conditions.

Keywords: Marine Brown Algae, $CaCl_2$-modified *Sargassum oligocystum*, Biosorption, Cr(VI), Kinetics, Thermodynamic

INTRODUCTION

Heavy metal pollution is one of the most important concerns for the environment. Various industries such as mining and metallurgy, surface processing industry, fuel and energy, fertilizer and pesticide industry, metallurgy, iron and steel, and industrial nuclear energy are introducing heavy metals to environment via their waste effluents. Heavy metals are not biodegradable and can accumulate in living organisms and cause various diseases and disorders in human beings [1]. Heavy metals such as lead, cadmium, arsenic, and chromium are continuously discharged into the environment, and these metals are stable and can survive for long time periods in the environment. Among the diverse heavy metals, chromium ions especially Cr(VI) have high toxicity to living organisms. Chromium and its compounds are used in various industries such as mining and smelting steel, iron, chemical processes such as pigment, electroplating, and tanning [2]. The wastewater of these industries can cause the environmental pollution and water resources deterioration. Therefore, it is essential to control and reduce the Cr(VI) content of effluents before discharge to the environment. To remove heavy metal ions like Cr(VI) from aqueous solutions, different methods exist such as precipitation, ion exchange, reverse osmosis, electro-dialysis, coagulation, nanofiltration, flotation, electrolysis, and adsorption [3,4]. These methods have disadvantages such as high cost, high energy needs and the production of toxic sludge [5]. Recently, the adsorption method has promisingly been used for the removal of heavy metals from water and wastewater. This method, compared with other physical and chemical methods, is facile, low-cost, efficient, and easy-design [6]. In the adsorption process a variety of biosorbent can be used, because the efficiency and effectiveness of the biosorption process is dependent on the nature and characteristics of the biosorbent [7]. One of the most common biosorbents is activated carbon, which is produced from wastes and successfully used for treating wastewater. The usage of activated carbon is restricted due to high energy consumption during its production [8] and difficult recovery [9]. Taking into account of as-mentioned reasons, in recent years, low- or no-cost natural sorbents, which annually are abundantly produced, are applied for attenuating heavy metals from aqueous solution. Bentonite [10], hydroxyapatite and chitosan [7], sawdust and peanut husk [11], clay montmorillonite [12], biochar [3,13] are all some examples of natural sorbents for heavy metal removal. In current decade, biomaterials such as algae, fungi, and bacteria biomass as biosorbent were studied [14-16]. Brown algae are very useful for

†To whom correspondence should be addressed.
E-mail: ramavandi_b@yahoo.com, b.ramavandi@bpums.ac.ir

the biosorption process because they have active functional groups of carboxyl, hydroxyl and alginic acid compounds on their cell walls [17]. The cell walls of brown algae contain 10 to 40% alginic acid compounds, and it has been reported that these compounds have an important role in the removal of toxic heavy metals [18].

In this study, to remove Cr(VI) ions from an aqueous solution, the biomass of *S. oligocystum* brown algae which chemically modified by $CaCl_2$ was used. The $CaCl_2$ material was chosen as alga biomass modifier as it can prevent leaching of adsorbate from biomass and increase the stability of the biosorbent material [19]. To evaluate the biosorption process of Cr(VI) by the biosorbent, the effects of parameters such as initial pH, biosorbents dose, temperature, initial Cr(VI) concentration, and contact time were studied. The kinetic behavior of the biosorption process was evaluated by pseudo-first order, pseudo-second order, and intra-particle diffusion kinetics models. To describe the biosorption isotherm of Cr(VI) by modified biomass of *S. oligocystum*, Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models were used. Further, the thermodynamic parameters such as enthalpy (ΔH^o), entropy (ΔS^o), the Gibbs free energy (ΔG^o), and the activation energy (Ea) were studied for determining the reaction mechanism of chromium ion biosorption.

EXPERIMENTAL

1. Biomass Preparation

The raw biomass of *S. oligocystum* was collected from the northern part of the Persian Gulf, Bushehr coast, Iran. The alga was washed several times with double distilled water to remove extraneous materials and salts. After washing, the *S. oligocystum* mass was placed in an oven (80 °C) for about 24 h. The dried alga biomass was chopped, sieved (size fraction of 0.3-0.5 mm), and stored in polyethylene bottles.

The modification of the alga was carried out as follows: 20 g of algae was immersed in 0.2 M calcium chloride solution (200 mL) at a ratio of 1 : 10 (w/v) for 24 h under stirring rate of 200 rpm. After that, the alga was washed with deionized water. Then, the algae biomass was oven- dried at 80 °C for 24 h and the dried alga biomass was again sieved (because of the partial aggregation of biosorbent particles) to get a uniform particle size of 0.3-0.5 mm.

2. Preparation of the Working Solution

The stock solution of Cr(VI) (1,000 mg/L) was prepared by dissolving of 2.8289 g potassium dichromate ($K_2Cr_2O_7$) in 1 L of the deionized water. To prepare the solution with a known concentration of chromium ions (10-100 mg/L), the stock solution was diluted with the deionized water. The initial pH of experimental solutions was adjusted to the desired value by adding 1 M sodium hydroxide or hydrochloric acid.

3. Batch Experiments of Cr(VI) Biosorption

The biosorption of Cr(VI) using modified biomass of *S. oligocystum* brown algae was carried out in a 250 mL of Erlenmeyer flask containing 100 mL of Cr(VI) solution. The effects of parameters such as initial pH, biosorbent dosage, temperature, contact time, and concentration of chromium ion were studied on the efficiency of biosorption process. To investigate the effect of pH on the efficiency of biosorption, the initial pH of 2 to 11 was evaluated. The effect of pH was examined at the conditions of biosorbent dose of 3 g/L, initial Cr(VI) concentration of 10 mg/L, contact time of 100 min, solution temperature of 25 °C, and stirring speed of 400 rpm. After determining the optimum pH, the effects of other parameters such as temperature (25-55 °C), biosorbent dose (0.5-9 g/L), initial Cr(VI) concentration (10-100 mg/L), and contact time (5-180 min) were determined. It is noteworthy that the effects of as-mentioned parameters were studied on efficiency of biosorption process at optimum pH. After the defined contact time, the solution was filtered using Whatman-42 μm filter paper. The amount of Cr(VI) in the filtrate was determined at wavelength of 540 nm using a UV-visible spectrophotometer (Varian, Cary 100 Scan) according to the 1,5-diphenylcarbazide method [20]. The amount of biosorbed metal ion per unit of the biosorbent mass (q_e, mg/g) and removal efficiency (%) of metal ions were calculated using Eqs. (1) and (2), respectively:

$$q_e = \left(\frac{C_i - C_e}{W}\right) \times V \tag{1}$$

$$R(\%) = \left(\frac{C_i - C_t}{C_i}\right) \times 100 \tag{2}$$

where: C_i, C_t and C_e are the initial, defined time, and equilibrium chromium ion concentrations (mg/L), W is the mass of biosorbent (g), V is the volume of solution (L). All tests were triplicated to ensure the reproducibility and the average values were reported herein. The blank samples were also provided for each test.

4. Apparatus and Instruments

The solution pH was analyzed using a digital pH-meter (Metrohm 744, Germany). To investigate the surface morphology of fresh *S. oligocystum*, fresh $CaCl_2$-modified *S. oligocystum* algae, and used $CaCl_2$-modified *S. oligocystum* algae, the scanning electron microscopy (SEM), mapping, and energy-dispersive X-ray spectroscopy (EDX) tests were done using the TESCAN MIRA3-FEG instrument. Functional groups and elemental composition of *S. oligocystum* fresh, fresh $CaCl_2$-modified *S. oligocystum* algae, and used $CaCl_2$-modified *S. oligocystum* algae were also determined using Fourier transform infrared spectroscopy (FTIR, Broker Victor 22). The tests were performed in a heater stirrer (Yellow MAG HS 7) equipped with a magnet.

5. Measurement the Specific Surface Area

To do this, the modified *S. oligocystum* alga was soaked in different concentrations of methylene blue (1-20 mg/L) to plot a calibration graph. The methylene blue concentration was measured using spectrophotometer at 600 nm wavelength. One gram of the modified *S. oligocystum* algae was added to methylene blue solution with concentration of 18 mg/L and was agitated at 200 rpm for 1 h. The prepared solution was passed through the 0.42 μm Whatman filter paper and the final concentration of dye in the filtrate was analyzed. Finally, the specific surface area was calculated using Eq. (3) [21]:

$$S_{MB} = \frac{C_{opt} \times A_{MB} \times A_V}{M V_{MB}} \tag{3}$$

where: S_{MB} (m^2/g) is the specific surface area of the modified *S. oligocystum* algae, C_{opt} (mg/mg) is the number of methylene blue mole-

cules adsorbed by the biosorbent, A_{MB} is the surface occupied by a molecule of methylene blue, A_v Avogadro number (6.02×10^{23} molecules/mol), and MV_{MB} (g/mol) is the methylene blue molecular weight (319.85 g/mol).

RESULTS AND DISCUSSION

1. The Biosorbent Properties

The elements, morphology, and distribution of elements in the

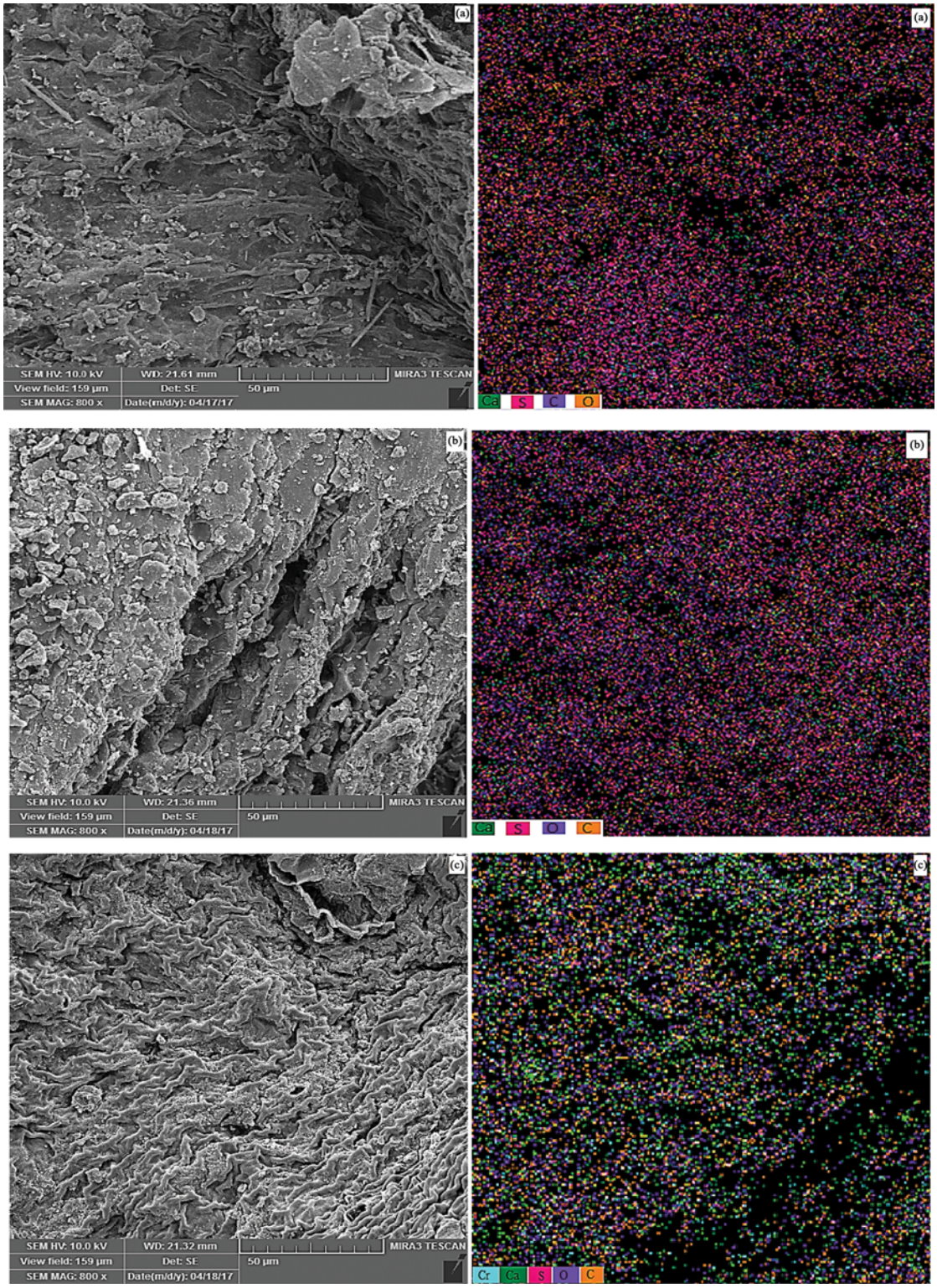

Fig. 1. Morphology, mapping, and elemental analysis of (a) un-modified, (b) modified alga, and (c) used modified *S. oligocystum* algae for Cr(VI) biosorption.

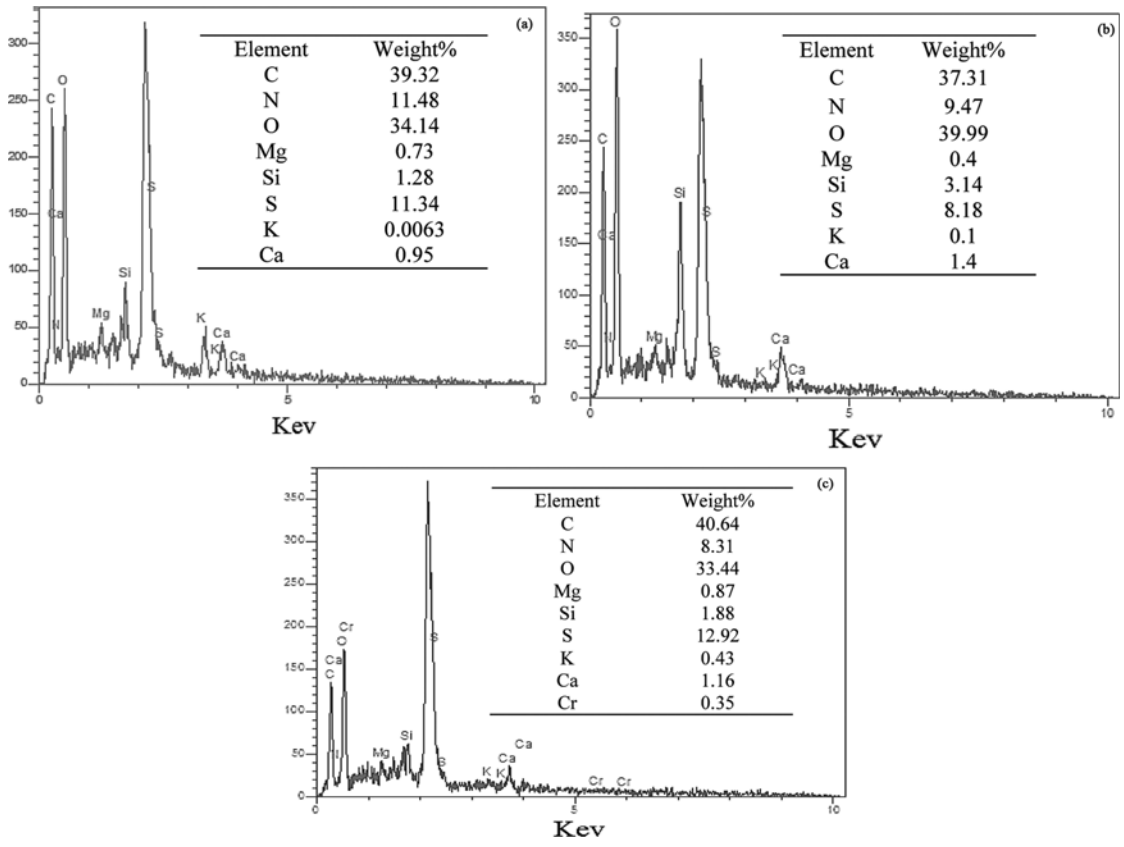

Fig. 1. Continued.

biosorbent before and after chemical modification as well as after Cr(VI) biosorption are depicted in Fig. 1. The results indicate that the surface of raw algae has a few pores and low amounts of calcium ion. On the other hand, after chemical modification of the alga by calcium chloride, the pores and the amount of calcium ion in its surface increased. The opening up of the pores after the calcium chloride treatment could be justified by the removal of some organic compounds with low molecular mass, or by the degradation of polysaccharides or proteins from the alga biomass skeleton as a result of hydrolysis reaction which occurs during the modification. Such interpretation has been presented by Bulgariu and Bulgariu [22] for alkaline treated algae waste biomass. Following the biosorption of chromium ion, the biosorbent surface has undergone some changes in the surface, resulting from the biosorption of the adsorbate. Such results can also be seen using EDX and mapping analyses (Fig. 1). The success of modification of the algae surface with $CaCl_2$ as well as the biosorption of chromium contaminant can be easily tracked by the EDX and mapping analyses.

To investigate and obtain information about the nature and functional groups in the utilized biosorbent, the FTIR test was also used. The results are provided in Fig. 2(a)-(c). The strong and broad peak at 3,442.94-3,838.84 cm^{-1} is associated with hydroxyl (-OH) and amine ($-NH_2$) groups present in the algae biomass. The peak at 2,950 and 2,991 cm^{-1} is related to the presence and vibration of -C-H functional group in the algae biomass. Before modification of the algae and biosorption of Cr(VI), a peak is observed at 2,525 cm^{-1}, which can be a result of vibration of $-NH_2^+$, $-NH^+$, and -NH in the algae biomass. This peak disappeared following the modification. The peaks at 1,117-1,804 cm^{-1} can be attributed to the C-O functional group in the algae biomass [23]. Some peaks are observed within 1,100-865 cm^{-1} which can be attributed to stretching of -C-N functional group and S=O band [2].

Following the biosorption of Cr(VI), significant changes occurred in the vibrations of the functional groups in the biosorbent. The peak related to hydroxyl or amine group in the biosorbent was moved to 3,442.47-3,842.3 cm^{-1}. Further, after the biosorption of chromium ion, the peak associated with the carboxyl group was transferred to 1,533-1,693 cm^{-1} and some peaks were observed at 845 and 997 cm^{-1}, which can be a result of vibrations of Cr-O and Cr=O [24]. The results confirm that functional groups such as amine, carboxyl, hydroxyl, and S=O have been involved in the biosorption process of Cr(VI).

The specific surface area of the modified *S. oligocystum* biomass was determined as 35.64 m^2/g, which is suitable in comparison with other sorbents such as *Tamarix hispida* modified by lanthanum [25], *Sargassum angustifolium* modified with molybdate [17], cantaloupe peel [3], bimetal-Chitosan [24], and *Conocarpus erectus* biochar [26], which are used for removal of different contaminants.

2. The Effect of Initial Solution pH

The initial solution pH is one of the most important and effective parameters in the metal ions biosorption. The biosorption process of metal ions onto a biosorbent surface is dependent on the interactions between the biosorbent surface and metal ions. In

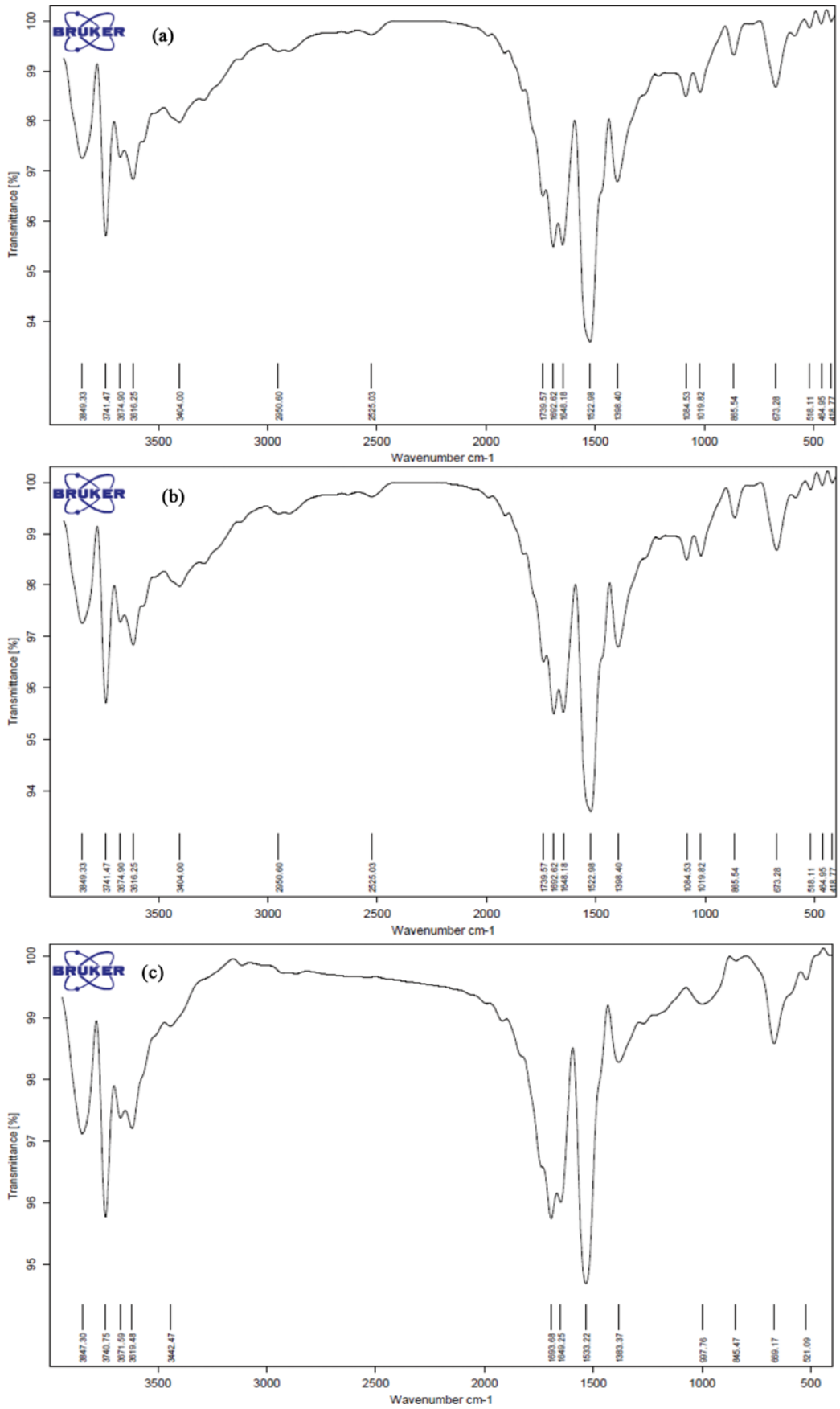

Fig. 2. FTIR spectra of *S. oligocystum* algae: (a) raw, (b) modified, (c) Cr(VI)-loaded modified.

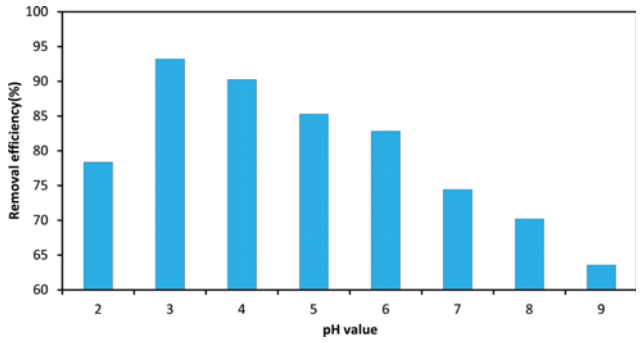

Fig. 3. Effects of pH (mixing rate: 400 rpm, biosorbent dose: 3 g/L, contact time: 100 min, C_0: 10 mg/L, temperature: 25 °C).

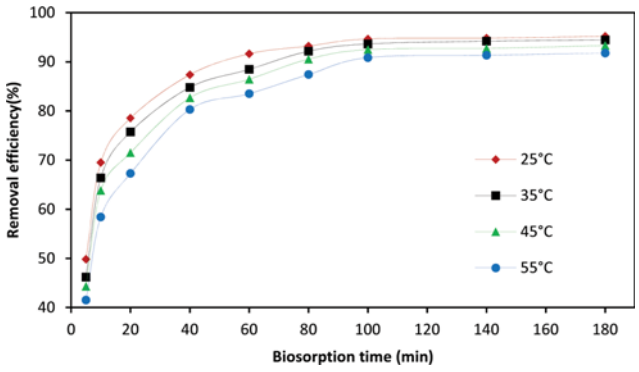

Fig. 4. Effects of temperature and contact time (mixing rate: 400 rpm, biosorbent dose: 3 g/L, C_0: 10 mg/L, pH: 3).

this regard, there are various theories including ion exchange, adsorption, chemical adsorption, complex formation, adsorption-complex, and reduction-adsorption [2] which affect the metal removal in the biosorption process. The initial pH effect on the Cr(VI) biosorption efficiency was studied and results depicted in Fig. 3. The maximum chromium(VI) biosorption of 93.22% using the biosorbent was obtained at the initial pH of 3. Thus, the initial solution pH of 3 was selected as an optimal value for rest of the tests. Chromium(VI) is a substance which can be converted to different forms such as dichromate ($Cr_2O_7^{2-}$), hydrochromate ($HCrO_7^-$), H_2CrO_4 or chromate (CrO_4^{2-}) in the aqueous solution with different pHs. Also, at pH=1 the chromium ion could be changed to $H_2CrO_4^+$, but the concentration of this form of chromium diminishes rapidly with increasing the initial pH. When the solution pH lies between 2-6, the chromium ions exist in different forms of $HCrO_4^-$, $Cr_2O_7^{2-}$, and $Cr_3O_{10}^{2-}$ [27]. However, when pH falls within the range of 1-3, chromium ion has mostly the form of $HCrO_4^-$ [28]. The size of $HCrO_4^-$ ion (44 cm^3/mol) is smaller than the size of $Cr_2O_7^-$ (73 cm^3/mol). Thus, $HCrO_4^-$ form of chromium can easily permeate into layers and active sites of the biosorbent and adhere to them [29]. In addition to the size of chromium metal ion, another factor that can be effective in chromium ion removal is the presence of proton (H^+) on the biosorbent surface. At low pHs, the biosorbent surface is surrounded by proton, which can enhance the interactions between the active surface of biosorbent and chromium ion. Based on Fig. 3, for solution pH of >3 the removal efficiency of chromium ion is decreased. At high pHs, the extent of negative charge (OH^-) inside the system increases and the biosorbent's surface finds a negative charge. Therefore, a repulsive force is developed between Cr(VI) and the surface of biosorbent, whereby electrostatic force is weakened [3], which can cause diminished efficiency of the biosorption process of chromium ion.

3. The Effect of Solution Temperature and Contact Time

The time of contact is one of the important and effective parameters in the biosorption process, and the process occurs rapidly at initial contact times, after which the biosorption rate increases gradually [30]. The effect of contact time on Cr(VI) removal efficiency is shown in Fig. 4. This figure suggests that the biosorption efficiency of chromium ion using the modified *S. oligocystum* biomass increases with the prolongation of contact time, which has occurred across different temperatures. A rapid increase in the removal efficiency was observed within 5-60 min, and after the initial time of 100 min (as the optimal time), no significant change was observed in the Cr(VI) biosorption efficiency. Increased sorption rate of chromium ion at initial times is due to the presence and availability of free active sites and the existence of different active groups on the biosorbent surface, which are required for interaction with the adsorbate, enhance the biosorption capacity and rate [31].

Another important and effective parameter in the biosorption process is the solution temperature. Temperature in biosorption processes is influential through microbial cells, with adsorption mechanisms being dependent on energy [32]. In addition, at high temperatures, the structure of biomasses can undergo damage, followed by devastation of active sites [33]. Thus, this parameter can affect biosorption efficiency and capacity and it is essential that its effect be investigated. The effect of temperature on chromium ion biosorption efficiency using the modified *S. oligocystum* biomass is shown in Fig. 4. The maximum chromium ion removal was determined at 25 °C, within 100 min of contact time and at initial pH of 3. The decreasing of the removal efficiency with the elevation of solution temperature, suggesting that the biosorption process is exothermic. The results also suggest that during the biosorption process, no permanent chemical bond is formed. This situation can be a result of various factors, including increased tendency of the adsorbed metal to be released into the solution, shrinkage and change of active sites on the biosorbent surface at high temperatures, increased mobility of chromium ion and its greater tendency to separate off the active sites, and diminished boundary layer between the solid phase (sorbent) and liquid phase [2].

4. The Effect of Biosorbate and Biosorbent Concentration

Fig. 5(a) represents the effect of biosorbent dose on Cr(VI) removal efficiency as well as the biosorption capacity. The Cr(VI) removal efficiency was increased from 51.39 to 95.88% with increasing of the biosorbent dose from 0.5 to 9 g/L, while the biosorbent capacity declined from 10.27 to 1.06 mg/g. The elevation of removal efficiency with increasing of the biosorbent dose is a result of the number of available active sites on the biosorbent surface [34]. This phenomenon indicates that the maximum removal occurs following a certain value of the biosorbent dose and after which with increasing the amount of biosorbent, the extent of metal ion

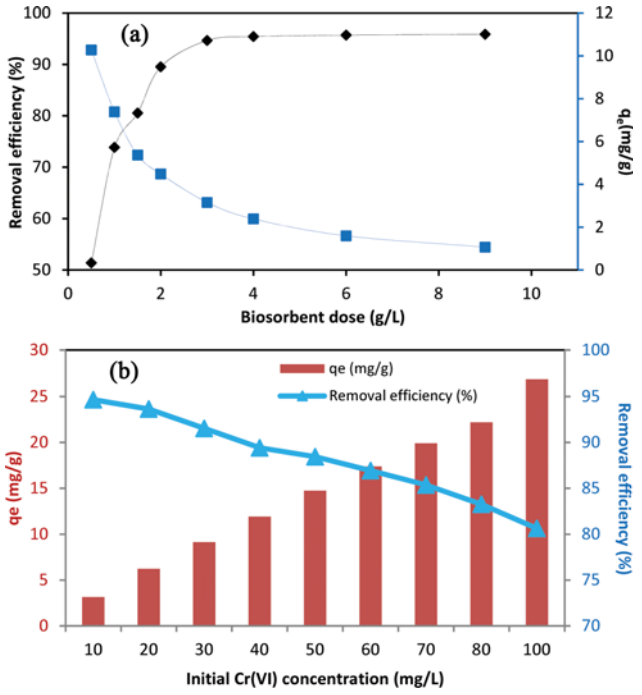

Fig. 5. (a) Effects of biosorbent dose on removal efficiency and biosorption capacity (b) effects of Cr(VI) concentration on biosorption capacity (mixing rate: 400 rpm, temperature: 25 °C, pH: 3, contact time: 100 min).

adsorbed by the biosorbent and free ion inside the solution remains constant. It can be ascribed to the partial aggregation of biosorbent particles at high dosage and thus decreased active sites available of the biosorbent [34].

Another effective parameter for evaluation of biosorption processes is equilibrium biosorption. The equilibrium biosorption is stated when the concentration of metal ions in the aqueous solution is in a dynamic equilibrium with the amount of metal ion connected to the biosorbent surface [35]. The biosorption capacity of metal ions is a function of initial concentration of metal ions inside aqueous solutions. Fig. 5(b) shows the effect of initial Cr(VI) concentration (10-100 mg/L) on the biosorption capacity. With increase the initial chromium concentration from 10 to 100 mg/L, the biosorption capacity increased from 3.15 to 26.88 mg/g, whereas the removal percentage of Cr(VI) diminished from 94.67 to 80.64% (see Fig. 5(b)). The reduction of removal efficiency and the elevation of biosorption capacity with increasing the initial chromium concentration can be explained by the limitation of active sites available on the biosorbent surface and completion of all active sites, respectively [35].

5. Biosorption Isotherms Study

The isotherm study gives us informative parameters which are essential for designing adsorption systems. To examine the biosorption isotherm and equilibrium data different isotherm models including Langmuir, Freundlich, and D-R were used.

Langmuir isotherm model assumes that the biosorption of metal ions occur at a single-layer and homogeneous surfaces without any interaction between the adjacent sites on the biosorbent. This model also states some information about the biosorption capacity and equilibrium behavior of the biosorption process [36]. The linear relation of Langmuir model is expressed as follows:

$$\frac{C_e}{q_e}=\frac{1}{K_L Q_m}+\frac{C_e}{Q_m} \quad (4)$$

where: Q_m and K_L represent the biosorption capacity (mg/g) and biosorption energy (L/g), respectively, which are considered as constants of Langmuir model. They are obtained through measuring the slope and intercept of plotting C_e/q_e versus C_e. Another important parameter that explains the features of Langmuir equation is the intensity of biosorption (R_L). The value of R_L represents the status of biosorption isotherm model. If $R_L>1$, $R_L=0$, $R_L=1$, and $0<R_L<1$, the process is reported as undesirable, irreversible, linear, and desirable, respectively [37]. The R_L value is obtained using Eq. (5):

$$R_L=\frac{1}{1+K_L C_0} \quad (5)$$

The Freundlich model is an empirical model that is used as a criterion for explaining isothermal behavior of a sorbent in the biosorption process of heavy metal ions from aqueous solutions. This model is employed for explaining biosorption process in the heterogeneous and multilayered surfaces [38]. The linear form of Freundlich model is as follows:

$$\ln q_e=\ln K_f+\frac{1}{n}\ln C_e \quad (6)$$

where: K_f and n are the constants of Freundlich model, representing the relationship between the biosorption capacity and the biosorption intensity, respectively. To determine 1/n and K_f parameters, $\ln q_e$ is plotted against $\ln C_e$. The value of n has been reported to be 1-10 [2]. This parameter represents the physical and chemical type of the biosorption process. If n=1, the biosorption process is linear, if n>1 it is desirable and physical, and if n<1 it is desirable and chemical [39].

The D-R isotherm model is used for investigation and analysis of the sorption process isotherm with a high regularity degree. This model is similar to Langmuir model and is not used for homogeneous surfaces or constant sorption potentials. Further, D-R model is also applied for determination the physically or chemically type of the biosorption process [40]. The linear form of D-R model is as follows:

$$\ln q_e=\ln q_m-\beta\varepsilon^2 \quad (7)$$

where: β (mol^2/J^2) and q_m (mg/g) represent the constants of D-R model; ε is Pulani potential which is determined by '$\varepsilon=RT\ln(1+1/C_e)$' equation, R is the universal constant of gases (8.314 J/mol K), and T is the absolute temperature (K). The β and q_m constants of D-R isotherm model is obtained from the slope and intercept of plotting $\ln q_e$ versus ε^2.

The value of β represents the average energy of biosorption (E) which is obtained from Eq. (8):

$$E=\frac{1}{\sqrt{2\beta}} \quad (8)$$

The average value of free energy of the biosorption determines the

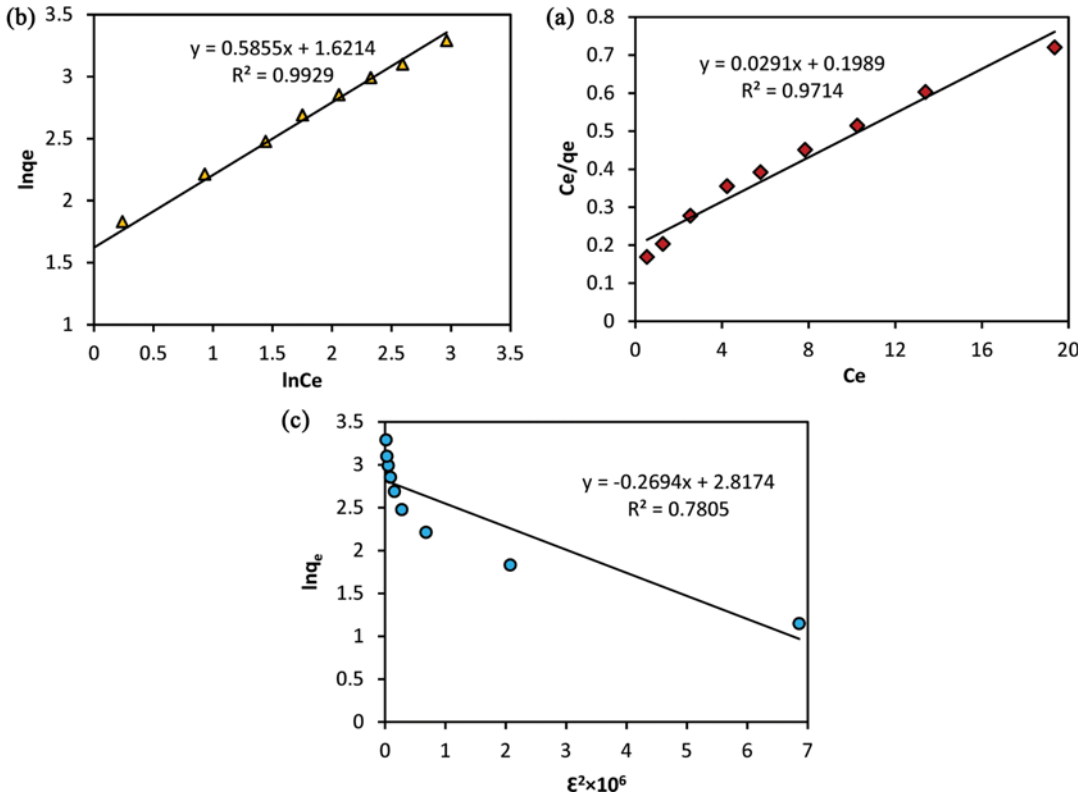

Fig. 6. The biosorption isotherm plot of (a) Langmuir, (b) Freundlich, and (c) D-R models for biosorption of Cr(VI) by modified *S. oligocystum* algae.

type of process. If the value falls within the range of 8-16 KJ/mol, then the biosorption process is of ion exchange type. On the other hand, if the value is lower than 8 KJ/mol, the biosorption mechanism is of physical type [2].

The plotting and the parameters of Langmuir, Freundlich, and D-R isotherm models are provided in Fig. 6(a)-(c) and Table 1, respectively. The results indicate that the correlation coefficient (R^2) determined for Freundlich isotherm (0.9929) is larger than R^2 values for Langmuir (0.9714) and D-R (0.7805), suggesting that the Cr(VI) biosorption process using the modified *S. oligocystum* biomass follows Freundlich isotherm, and proved that the biosorption of Cr(VI) occurs on heterogeneous surfaces. The value of n and K_f parameters of Freundlich model was determined to be 1.707 and 5.06, respectively. The n value suggesting that the biosorption process is physical and desirable.

Table 1. Results of isotherm modeling

Model	Parameter	Value
Langmuir	Q_m (mg/g)	34.36
	K_L (L/mg)	0.146
	R^2	0.9714
	R_L	0.064-0.406
Freundlich	n	1.707
	K_f (mg/g (L/mg)$^{1/n}$)	5.060
	R^2	0.9929
D-R	E (KJ/mol)	1.36
	q_m (mg/g)	16.73
	$\beta\times10^6$ (mol^2/J^2)	0.269
	R^2	0.7805

The maximum value of biosorption capacity (Q_m) and Langmuir constant (K_L) were determined as 34.36 mg/g and 0.146 L/mg, respectively. The maximum biosorption capacity of the modified *S. oligocystum* algae is suitable in comparison with other sorbents used for the chromium removal (see Table 2). Further, the Q_m parameter for simple *S. oligocystum* biomass was notably lower than those obtained for modified one, showing the effectiveness of the modification method. Different values of R_L for initial Cr(VI) concentrations of 10-100 mg/L were determined within the range of 0.064-0.406. Based on this parameter, it is reaffirmed that the biosorption process is a desirable process.

Based on D-R model, the maximum biosorption capacity (q_m) and free energy (E) were attained 16.73 mg/g and 1.36 KJ/mol, respectively (see Table 1). Considering the value of free energy, it is concluded that the chromium biosorption process by the modified *S. oligocystum* algae biomass is physical.

6. Biosorption Kinetic Study

Study of kinetic data provides important information about the mechanism of biosorption process. To examine biosorption the kinetic behavior of the Cr(VI) biosorption process from aqueous solutions, pseudo-first order, modified pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic models were used.

Table 2. Comparison of potentials of various algal biomasses for chromium ions biosorption

Sorbent	Q_{max} (mg/g)	Reference
Spirulina sp.	90.91	[16]
Activated red alga *Pterocladia capillacea*	66	[41]
Spirulina platensis extract	41.12	[42]
Modified *Sargassum oligocystum* brown algae	34.36	Present work
Chemically modified seaweed *Cystoseira indica*	26-34	[43]
Raw green alga *Oedogonium hatei*	31	[32]
Ulva lactuca (green algae)	27.6	[44]
Simple *Sargassum oligocystum* brown algae	21.57	Present work
Chlamydomonas reinhardetti (acid treated)	21.2	[45]
Spirogyra sp.	14.7	[46]
Dried red alga *Pterocladia capillacea*	12	[41]
Fucus spiralis (brown algae)	5.4	[44]

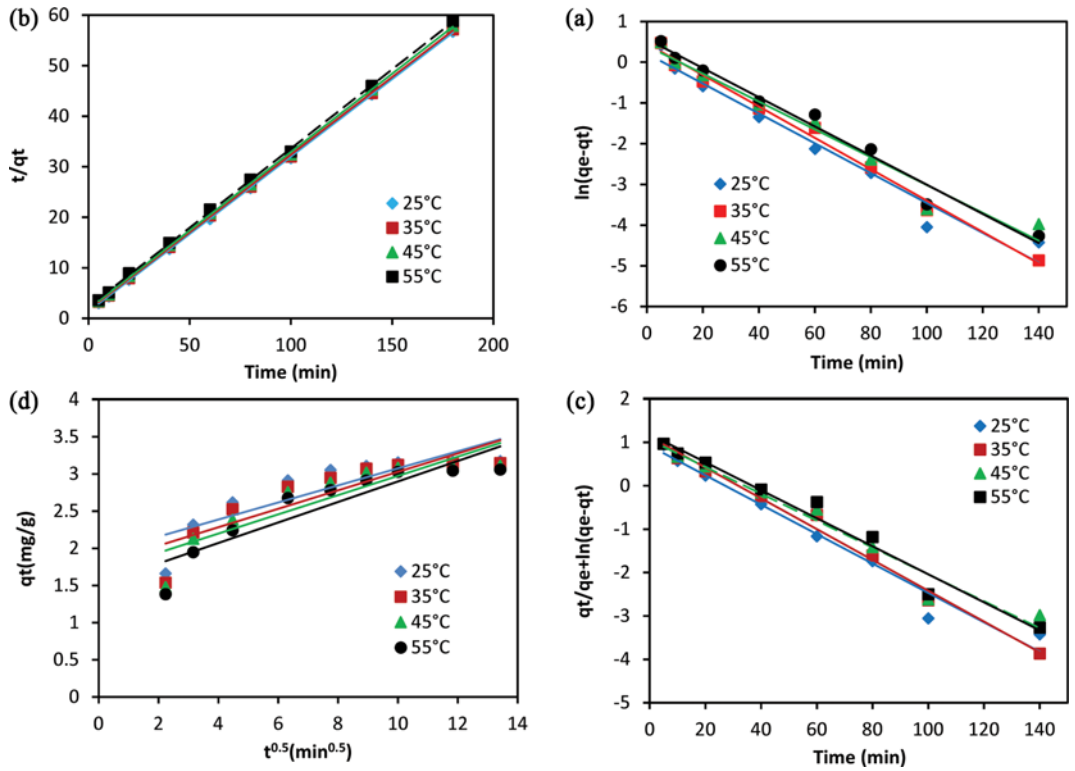

Fig. 7. Kinetic model of (a) pseudo-first order, (b) pseudo-second order, (c) modified pseudo-first order, and (d) intra-particle diffusion.

When the concentration of solute is high, the sorption process follows pseudo-first order kinetic model. The linear equation of pseudo-first order kinetic model (Eq. (9)) and its modified form (Eq. (10)) are described as follow [47]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

$$\frac{q_t}{q_e} + \ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

where: q_t (mg/g) denotes the amount of Cr(VI) adsorbed per gram of biosorbent at studied time and k_1 (1/min) is the biosorption constant. To calculate the biosorption rate constant (k_1), $\ln(q_e - q_t)$ and $q_t/q_e + \ln(q_e - q_t)$ are plotted against t (Figs. 7(a) and (c)).

One of the practical models for describing the kinetic behavior of the biosorption is pseudo-second order model. When concentration of the solute in the solution is low, the biosorption process follows this model. According to the pseudo-second order model, the rate of occupation of biosorption sites by the heavy metal ions is proportional to the square of the number of empty active sites on the biosorbent [48]. The linear equation of the pseudo-second order kinetic model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

Table 3. Modeling results of biosorption kinetic

Models	Parameters	Solution temperature (°C)			
		25	35	45	55
Pseudo-first order	k_1 (min^{-1})	0.0367	0.0385	0.0342	0.0358
	$q_{e(cal)}$ (mg/g)	1.236	1.576	1.494	1.797
	R^2	0.9645	0.991	0.967	0.9801
Modified pseudo-first order	k_1 (min^{-1})	0.0339	0.0355	0.031	0.0323
	$q_{e(cal)}$ (mg/g)	2.509	3.101	2.874	3.28
	R^2	0.971	0.9903	0.9683	0.9753
Pseudo-second order	k_2 (g/mg min)	0.0697	0.0569	0.0507	0.0428
	$q_{e(cal)}$ (mg/g)	3.26	3.25	3.22	3.19
	R^2	0.9999	0.9999	0.9998	0.9997
Intra-particle diffusion	k_i (mg/g $min^{0.5}$)	0.1147	0.1241	0.1294	0.1381
	C (mg/g)	1.927	1.786	1.679	1.519
	R^2	0.7363	0.7661	0.7938	0.826
$q_{e(exp)}$ (mg/g)		3.173	3.148	3.11	3.059

where: k_2 is the kinetic constant (g/mg min). To calculate the constants and parameters of the pseudo-second order kinetic model, t/q_t is plotted against t. In this way, q_e and k_2 values are obtained from slope and intercept of the regression line equation, respectively (Fig. 7(b)).

Intra-particle diffusion model is also used for investigation of the kinetic behavior of adsorption process, which is an experimental model. The linear form of this model is as follows [47]:

$$q_t = k_i t^{0.5} + C \tag{12}$$

where: k_i is the constant of intra-particle diffusion rate (mg/g $min^{0.5}$). The C value presents some idea about the thickness of the boundary layer. K_i and C values are determined from the slope and intercept of q_t versus C plotting, respectively (Fig. 7(d)).

The parameters and constants determined by the applied kinetic models are presented in Table 3. Based on the mentioned results, pseudo-second order kinetic model has a higher correlation coefficient (R^2) in comparison with other models, suggesting that the chromium ion biosorption process by the modified *S. oligocystum* biomass follows this model. Further, changes in the biosorption capacity ($q_{e,cal}$) determined by pseudo-first order and modified pseudo-first order kinetic models do not follow a certain trend against temperature. On the other hand, in the pseudo-second order kinetic model the $q_{e,cal}$ changes are certain, and with increasing in the solution temperature, the amount of $q_{e,cal}$ declines. The plotting of intra-particle diffusion kinetic model is not linear, suggesting that this model had not a major contribution to the biosorption process [2]. Further, if the straight lines pass through the origin of the plotting, the intra-particle diffusion kinetic model is the only rate limiting step; if not, the biosorption process mechanism may involve other types of elementary processes [49].

The performance of Cr(VI) biosorption by the modified *S. oligocystum* biomass from aqueous media was also assessed based on the $q_{e(cal)}$ and k_2 parameters of pseudo-second order model and equations as follows [50]:

$$F_{ae} = \frac{1}{1 + k_2 q_{e(cal)} t_w} \tag{13}$$

$$R_i = k_2 q_{e(cal)} \tag{14}$$

$$t_{1/2} = \frac{1}{k_2 q_{e(cal)}} \tag{15}$$

$$t_x = \frac{S}{k_2 q_{e(cal)}} \tag{16}$$

where: F_{ae} (dimensionless) is the approaching equilibrium factor, t_w (min) is the longest contact time, R_i (min^{-1}) is the second-order rate index, $t_{1/2}$ (min) is the required contact time for reaching the initial Cr(VI) ions to the half amount by the biosorbent, t_x (min) is the required times for the given value of fractional biosorption (X, $q_t/q_{e(cal)}$) and S is equal to 'X/(1−X)'. If the value of F_{ae} within the range of 0.1-1, 0.1-0.01, and <0.01, then the kinetic is called as slightly approaching equilibrium, well approaching equilibrium, and drastically approaching equilibrium, respectively. The value of F_{ae} was obtained as 0.0238 for this study, and it indicated that the biosorption process well reached the equilibrium level. The values of R_i and $t_{1/2}$ parameters were found to be 0.227 min^{-1} and 4.405 min, respectively. The small value of half-life showed the rapid bio-

Table 4. Required contact times for various fractional biosorption values (mixing rate: 400 rpm, biosorbent dose: 3 g/L, C_0: 10 mg/L, pH: 3)

Contact time, t_x	Fractional biosorption, X	Value (min)
$t_{0.523}$	0.523	5.154
$t_{0.73}$	0.730	11.907
$t_{0.825}$	0.825	20.766
$t_{0.918}$	0.918	49.317
$t_{0.962}$	0.962	111.519
$t_{0.979}$	0.979	205.370
$t_{0.994}$	0.994	729.806
$t_{0.996}$	0.996	1096.916

sorption process. R_i is a key parameter affecting the value of fractional biosorption. Thus, it was applied to calculate the data of t_x for various X values of chromium ion biosorption by the biosorbent and the results are tabulated in Table 4. These kinetic performances are informative for designing of chromium ion biosorption systems.

7. Biosorption Thermodynamic Study

The Arrhenius relation (Eq. (17)) is used to determine the value of activation energy of the biosorption process, which represents the minimum energy to continuation the process. The linear Arrhenius relation is as follows [2]:

$$\ln k_d = \ln A_0 - \frac{E_a}{RT} \quad (17)$$

where: k_d is the equilibrium constant and determined by the equation of '$k_d=(q_e/C_e)$', Ea is the activation energy of the biosorption process (KJ/mol), R is the universal constant of gases (8.314 J/mol·K), T is the absolute temperature (K), and A_0 is the Arrhenius factor, which is dependent on the solution temperature. The parameters of A_0 and E_a are determined from the intercept and slope of the $\ln k_d$ against 1/T plot, respectively (Fig. 8). If the value of the calculated free energy lies within 5-40 KJ/mol, the biosorption process mechanism is of physical type. On the other hand, if the value lies within 40-800 KJ/mol, then the process mechanism will be chemical type [2]. In this study, the value was obtained as 15.60 KJ/mol, suggesting that the mechanism of Cr(VI) biosorption by modified *S. oligocystum* biomass is physical.

Thermodynamic parameters such as enthalpy (ΔH^o), entropy (ΔS^o), and Gibbs free energy (ΔG^o) were determined for the chromium ion biosorption by modified *S. oligocystum* biomass across different temperatures (25-55 °C). The ΔG^o parameter is determined using Eq. (18) [38]:

$$\Delta G^o = -RT\ln k_d \quad (18)$$

To determine the thermodynamic parameters of ΔH^o and ΔS^o, the following equation was used:

$$\ln k_d = \frac{-\Delta G^o}{RT} = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (19)$$

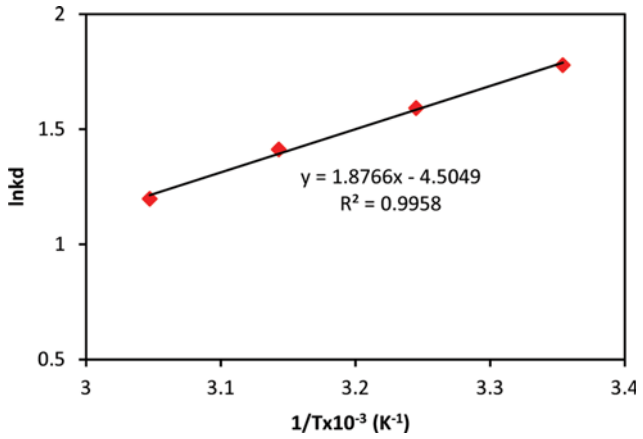

Fig. 8. Plot 1/T versus $\ln k_d$ (C_0: 10 mg/L; biosorbent dose: 3 g/L; time: 100 min; pH: 3).

Table 5. Thermodynamic results

T (°C)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol·K)	Ea (KJ/mol)
25 °C	−7.13	−15.60	−28.31	15.60
35 °C	−6.89			
45 °C	−6.64			
55 °C	−6.26			

The values of ΔH^o and ΔS^o are determined by the slope and intercept of $\ln k_d$ versus 1/T plot, respectively (Fig. 8). The thermodynamic parameters for the chromium biosorption process are provided in Table 5. The negative value of Gibbs free energy indicates that the biosorption process of chromium ion by the prepared biosorbent is thermodynamically desirable and spontaneous. Further, with elevation of temperature, the value of Gibbs free energy for the biosorption is diminished, suggesting that the extent of spontaneity of the biosorption process has declined with the elevation of temperature. The negative value of ΔH^o indicating the interactions between the biosorbent and chromium ion are exothermic. It also indicates that the biosorption process of Cr(VI) is physical, as ΔH^o<40 KJ/mol. The negative value of ΔS^o suggests that random collisions on the solid surface (biosorbent) and the solution during the biosorption process are decreased [47].

CONCLUSIONS

The potential of $CaCl_2$-modified *Sargassum oligocystum* biomass as a biosorbent was investigated for Cr(VI) removal from aqueous solutions. To investigate the characteristics of the biosorbent, FTIR, SEM, mapping, EDX, and specific surface analysis were performed. The specific surface value of the biosorbent was determined to be 35.64 m^2/g. The maximum removal efficiency (>95%) was attained at initial pH of 3, solution temperature of 25 °C, contact time of 100 min, biosorbent dose of 3 g/L, and initial chromium concentration of 10 mg/L. The removal efficiency and q_e decreased and increased with increase in the initial Cr(VI) concentration, respectively. The chromium removal efficiency decreased by increasing the solution temperature. Pseudo-second order kinetic had a higher correlation coefficient in comparison with other kinetic models. The isotherm study suggested that heterogeneous surfaces have been more effective than homogeneous surfaces for removing the chromium ion. The biosorption capacity of Cr(VI) using the prepared biosorbent was obtained 34.36 mg/g. Thermodynamic parameters including enthalpy, entropy, and Gibbs free energy were also calculated.

Hereby, considering the abundance and availability as well as based on the obtained results, it can be concluded that the modified *Sargassum oligocystum* biomass can be used as an inexpensive, facile, and suitable sorbent for removing chromium ion from aqueous media. We noted that the used biosorbent in the adsorption process could be a new source of contamination; thus, it is proposed to first desorb the chromium and recycled both adsorbate and adsorbent and finally dispose the used adsorbent in a secure landfill.

REFERENCES

1. W. Peng, H. Li, Y. Liu and S. Song, *J. Mol. Liq.*, **230**, 496 (2017).
2. M. Ahmadi, E. Kouhgardi and B. Ramavandi, *Korean J. Chem. Eng.*, **33**, 2589 (2016).
3. B. Ramavandi, G. Asgari, J. Faradmal, S. Sahebi and B. Roshani, *Korean J. Chem. Eng.*, **31**, 2207 (2014).
4. H. Chen, J. Dou and H. Xu, *Appl. Surf. Sci.* Inpress (2017).
5. K. K. Krishnani, X. Meng, C. Christodoulatos and V. M. Boddu, *J. Hazard. Mater.*, **153**, 1222 (2008).
6. A. Heidari, H. Younesi, Z. Mehraban and H. Heikkinen, *Int. J. Biol. Macromol.*, **61**, 251 (2013).
7. N. Gupta, A. K. Kushwaha and M. Chattopadhyaya, *J. Taiwan Inst. Chem. Eng.*, **43**, 125 (2012).
8. S. Veli and B. Alyüz, *J. Hazard. Mater.*, **149**, 226 (2007).
9. N. Sakkayawong, P. Thiravetyan and W. Nakbanpote, *J. Colloid Interface Sci.*, **286**, 36 (2005).
10. A. Taha, M. A. Shreadah, A. Ahmed and H. F. Heiba, *J. Environ. Chem. Eng.*, **4**, 1166 (2016).
11. Q. Li, J. Zhai, W. Zhang, M. Wang and J. Zhou, *J. Hazard. Mater.*, **141**, 163 (2007).
12. C. Chen, H. Liu, T. Chen, D. Chen and R. L. Frost, *Appl. Clay Sci.*, **118**, 239 (2015).
13. M. Shahverdi, E. Kouhgardi and B. Ramavandi, *Data in Brief*, **9**, 163 (2016).
14. A. Ebrahimi, S. Hashemi, S. Akbarzadeh and B. Ramavandi, *Chem. Data Collec.*, **2**, 36 (2016).
15. R. Foroutan, M. Madani, M. R. Farani, A. K. Kori, E. Behrad and B. Ramavandi, *Inter. J. Pharmacy Technol.*, **8**, 25133 (2016).
16. H. Rezaei, *Arab. J. Chem.*, **9**, 846 (2016).
17. F. Saberzadeh Sarvestani, H. Esmaeili and B. Ramavandi, *3 Biotech*, **6**, 254 (2016).
18. T. Vaughan, C. W. Seo and W. E. Marshall, *Bioresour. Technol.*, **78**, 133 (2001).
19. M. M. Montazer-Rahmati, P. Rabbani, A. Abdolali and A. R. Keshtkar, *J. Hazard. Mater.*, **185**, 401 (2011).
20. J. Yang, M. Yu and W. Chen, *J. Ind. Eng. Chem.*, **21**, 414 (2015).
21. Y. Yukselen and A. Kaya, *Eng. Geol.*, **102**, 38 (2008).
22. D. Bulgariu and L. Bulgariu, *J. Clean Prod.*, **112**, 4525 (2016).
23. A. Sarı and M. Tuzen, *J. Hazard. Mater.*, **171**, 973 (2009).
24. A. Ata, O. O. Nalcaci and B. Ovez, *Algal Res.*, **1**, 194 (2012).
25. N. Habibi, P. R. Najafabadi and B. Ramavandi, *Data in Brief*, **13**, 749 (2017).
26. M. Ravanipour, R. Kafaei, M. Keshtkar, S. Tajalli, N. Mirzaei and B. Ramavandi, *Data in Brief*, **12**, 471 (2017).
27. Y. Du, L. Wang, J. Wang, G. Zheng, J. Wu and H. Dai, *J. Environ. Sci.*, **29**, 71 (2015).
28. X. S. Wang, Z. Z. Li and C. Sun, *J. Hazard. Mater.*, **153**, 1176 (2008).
29. P. Mukhopadhyay, R. Chakraborty, M. Chakraborty and A. Mitra, *J. Water Process Eng.*, **6**, 32 (2015).
30. G. Asgari, B. Ramavandi and S. Farjadfard, *ScientificWorldJournal*, **2013**, 1 (2013).
31. Z. Khademi, B. Ramavandi and M. T. Ghaneian, *J. Environ. Chem. Eng.*, **3**, 2057 (2015).
32. V. Gupta and A. Rastogi, *J. Hazard. Mater.*, **163**, 396 (2009).
33. I. M. Dittert, V. J. Vilar, E. A. da Silva, S. M. G. U. de Souza, A. A. U. de Souza, C. M. Botelho, R. A. R. Boaventura, *Chem. Eng. J.*, **193**, 348 (2012).
34. P. Geetha, M. Latha, S. S. Pillai, B. Deepa, K. S. Kumar and M. Koshy, *J. Molec. Struct.*, **1105**, 54 (2016).
35. H. Fida, S. Guo and G. Zhang, *J. Colloid Interface Sci.*, **442**, 30 (2015).
36. M. Ahmadi, H. Rahmani, B. Ramavandi and B. Kakavandi, *Desal. Water Treat.*, **76**, 265 (2017).
37. M. Fooladvand and B. Ramavandi, *Indian J. Chem. Technol.*, **22**, 183 (2015).
38. F. Papari, P. R. Najafabadi and B. Ramavandi, *Desal. Water Treat.*, **65**, 375 (2017).
39. M. Ahmadi, A. H. Mahvi, Z. Doroud, B. Ramavandi and P. Teymouri, *Environ. Eng. Manag. J.*, **15**, 733 (2016).
40. S. Rangabhashiyam and N. Selvaraju, *J. Mol. Liq.*, **207**, 39 (2015).
41. A. El Nemr, A. El-Sikaily, A. Khaled and O. Abdelwahab, *Arab. J. Chem.*, **8**, 105 (2015).
42. H. W. Kwak, M. K. Kim, J. Y. Lee, H. Yun, M. H. Kim, Y. H. Park and K. H. Lee, *Algal Res.*, **7**, 92 (2015).
43. S. Basha, Z. Murthy and B. Jha, *Chem. Eng. J.*, **137**, 480 (2008).
44. V. Murphy, H. Hughes and P. McLoughlin, *Chemosphere*, **70**, 1128 (2008).
45. M. Y. Arıca, İ. Tüzün, E. Yalçın, Ö. İnce and G. Bayramoğlu, *Process Biochem.*, **40**, 2351 (2005).
46. V. Gupta, A. Shrivastava and N. Jain, *Water Res.*, **17**, 4079 (2001).
47. W. Song, B. Gao, T. Zhang, X. Xu, X. Huang, H. Yu and Q. Yue, *Bioresour. Technol.*, **190**, 550 (2015).
48. Y. Shang, X. Yu and M. E. Romero-González, *Algal Res.*, **12**, 258 (2015).
49. L. Nemeş and L. Bulgariu, *Open Chem.*, **14**, 175 (2016).
50. F. Deniz and A. Karabulut, *Ecol. Eng.*, **106**, 101 (2017).