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Biosorption of hexavalent chromium from aqueous solution by six brown macroalgae

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ABSTRACT

The biosorption potential of six brown macroalgae viz. *Nizamuddina zanardinii*, *Stoechospermum marginatum*, *Cystoseira indica*, *Dictyota cervicornis*, *Padina australis,* and *Sargassum glaucescens*, for the removal of hexavalent chromium (Cr(VI)) was investigated in the present study. Optimum conditions were determined by studying the effect of initial solution pH, biomass dosage, initial Cr(VI) concentration, and contact time on Cr(VI) removal by the macroalgae. Cr(VI) sorption was found to be highly pH dependent and maximum sorption was obtained at pH 1.0. Freundlich isotherm model showed the best fit with the equilibrium data. The removal rate of Cr(VI) was relatively rapid during the first 30 min, although the rate decreased gradually and the sorption reached equilibrium in about 70 min for *S. marginatum*, 90 min for *N. zanardinii,* and 150 min for *D. cervicornis*, *P. australis*, *S. glaucescens,* and *C. indica*. Different kinetic models such as pseudo-first-order, pseudo-second-order, and intra-particle diffusion model were tested, and the experimental data was in agreement with the pseudo-second-order model. The results of the present study suggest that brown macroalgae could be used as effective biosorbents for Cr(VI) removal from aqueous solution.

Keywords: Biosorption; Brown macroalgae; Biosorbents; Hexavalent chromium; Water treatment

1. Introduction

Heavy metal pollution is a serious and widespread environmental problem due to the persistent and non-biodegradable properties of these contaminants causing toxic effects to human health and other living organisms [1]. Chromium and its compounds are widely used in many industrial applications including electroplating, chromate manufacturing, alloy reparation industries, metal cleaning and processing, leather tanning, and wood preservation [2]. As a result, the effluents of these industries may contain elevated concentrations of chromium. Hexavalent chromium (Cr (VI)) and Cr(III) are the most common forms present in the aquatic environment. Cr(VI) compounds are more toxic than Cr(III) due to their high water solubility and mobility. Cr(III) is insoluble and thus immobile under ambient conditions. Chromium has been recognized as one of the most toxic pollutants

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[3], due to carcinogenic and mutagenic effects on living organisms [4]. Cr(VI) exists in water as oxyanion such as chromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$). It causes different health problems such as epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage by ingestion. Also, chronic exposure to Cr(VI) causes intestine cancer [5]. To meet environmental regulations, effluents or water contaminated with chromium must be treated before discharge.

Traditional methods, such as chemical reduction/precipitation, solvent extraction, ion exchange, membrane separation, etc. have been commonly employed for stripping toxic metals from wastewaters. But all these methods have several disadvantages, such as high cost, high reagent or energy requirements, and generation of toxic sludge [6]. Further, these processes might become ineffective or extremely expensive when metal concentration in wastewater is between 10–100 mg/L [7].

Compared to conventional techniques, biosorption process has emerged as one of the economical and efficient approaches for the remediation of metal bearing wastewaters because of eco-friendly characteristics, low cost, high uptake capacity, lack of toxicity constraints, less sludge production, availability of biosorbents worldwide with possibility of regeneration, and effectiveness to treat waters with very low levels of contamination, normally in the order of ppb [8].Various types of biomass, including bacteria [9], yeast [10], fungi [11], and algae [12] have been evaluated as efficient biomass materials for Cr(VI) removal. Metal uptake capacity of algal biomass is either comparable or sometimes higher than chemical sorbents, which has been explained due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing functional groups such as amino, hydroxyl, carboxyl, and sulfate, which can act as binding sites for metals [13]. Among the various forms of algae, brown algal biomass has been found to show higher metal uptake capacities due to higher alginate and fucoidan contents [14]. Many previous studies have reported considerable biosorption potential of different biomasses for Cr(VI) [6,15]. The objective of the present study was to optimize the operational parameters for Cr(VI) biosorption by different macroalgae. Six marine brown macroalgae were selected as biosorbents namely, *Nizamuddina zanardinii*, *Stoechospermum marginatum*, *Cystoseira indica*, *Dictyota cervicornis*, *Padina australis,* and *Sargassum glaucescens* to investigate Cr (VI) removal from aqueous solution. The effect of different operational parameters such as, initial solution pH, contact time, biomass dosage, and initial Cr(VI) concentration were studied on Cr(VI) biosorption. The experimental data was also examined to different kinetic and equilibrium models.

2. Materials and methods

2.1. Biosorbents preparation

The brown macroalgae *N. zanardinii*, *S. marginatum*, *C. indica*, *D. cervicornis*, *P. australis,* and *S. glaucescens*, were used as biosorbents for the biosorption of Cr(VI) in the present study. Marine algae samples were collected from Oman Sea coastal water, Chabahar, Iran, in March 2010. The wet algae were washed several times with tap water followed by distilled water to remove extraneous debris and salts. Wet algal biomasses were sun-dried for 72 h, and then dried in an oven (Lab Tech, LDO-060 E, USA) at 70˚C for 24 h. The dried algae biomasses were cut and grinded in a blender and subsequently, were sieved through an ASTM Standard sieve (106–250 μm) to obtain uniform particle size.

2.2. Preparation and analysis of metal solution

All chemicals used in this study were of analytical grade. An accurately weighed quantity of potassium dichromate ($K_2Cr_2O_7$, Aldrich Corporation) was added to milli-Q water to prepare a stock solution (1,000 mg/L). The stock solution was diluted further to prepare solutions of desired concentrations throughout the study. The initial solution pH was adjusted by diluted NaOH and/or HCl (1 M). Biosorption studies were conducted in batch mode using 100 mL Erlenmeyer flasks. Pre-weighed dried biomass was added to each flask and constantly agitated at 27˚C, until the equilibrium was reached. At achieving equilibrium, samples were filtered through 0.2 μm membrane filter (Orange Scientific, GyroDisc CA-PC, Belgium). The initial and equilibrium Cr(VI) ions concentrations were analyzed using an UV/Vis spectrophotometer (Hach, DR/4000 Spectrophotometer, USA) at 540 nm complexing with 1,5-diphenylcarbazide in acidic medium [16]. The biosorption capacities were then obtained by mass balance calculations. All the experiments were performed in triplicates and average values are reported.

2.3. Batch biosorption studies

The Cr(VI) biosorption on the six species of algal biomass were investigated in batch mode by agitating flasks containing 50 mL of Cr(VI) solution using a platform shaking incubator (Labcon, FSIM-SPO16, USA) at 180 rpm to achieve equilibrium. The effect of initial solution pH (1.0–5.0), biosorbents dosage (0.5–3.0 g/L), and contact time (0–180 min) on the biosorption rate and capacity were studied. To obtain biosorption isotherms, the biosorbents (2 g/L) were suspended in Cr(VI) solutions (5–100 mg/L). Biosorption kinetics experiments were also carried out in 500 mL Erlenmeyer flasks containing 250 mL Cr(VI) solution using a known amount (2 g/L) of biosorbent in a rotary shaker at 180 rpm and 27˚C for various time intervals (0–180 min). Samples were taken at different time intervals, filtered, and analyzed for remaining metal ions concentration.

The amount of Cr(VI) ions adsorbed per unit mass of the adsorbent at equilibrium conditions, q_e (mg/g), was calculated by Eq. (1):

$$q_e = V\frac{C_0 - C_e}{m} \qquad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of chromium solution, respectively, V is the volume of solution (L) and m is the mass of algae (g). Biosorption efficiency was determined by (Eq. (2)):

$$\text{Sorption } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) (mg/L).

3. Results and discussion

3.1. Effect of initial solution pH

The solution pH is an important parameter in the adsorption of any solute because it has a large influence on its solubility and adsorption capacity [17], among other properties. As solution pH of chromium containing wastewater is usually acidic [18], solutions of different pH values ranging from 1.0–5.0 were used to examine the effect of solution pH on Cr(VI) sorption by biomasses and the results are shown in Fig. 1. The sorption percentage of metal was found to be favored by acidic pH range of 1.0–2.0 and maximum sorption of Cr(VI) by brown algae was observed at pH 1.0. By increasing the solution pH, removal efficiency of Cr(VI) decreased. A sharp decrease in removal efficiency of brown algae was observed at pH 2.0 and removal percentage became almost constant between pH 3.0–5.0. This can be explained on the basis of zero point of charge of biomass. In general, an isoelectric point at solution pH ca. 3.0–4.0 is determined for all algal species [19]. The algal surface have positive charge when solution pH is less than the isoelectric point pH (acidic solution), and vice versa when solution pH is greater than the isoelectric point pH (alkaline solution) [20]. In solution, Cr(VI) is observed as anionic species such as CrO_4^{2-} and $HCrO_4^-$. At lower initial pH, the acidic solution favors biosorption of the negatively charged Cr(VI) species onto algae surface, thus the removal efficiency increases. The results of the present study are in agreement with previously published literature where biosorption of Cr(VI) has been investigated by non-living green algae [6] and tobacco biomass [21].

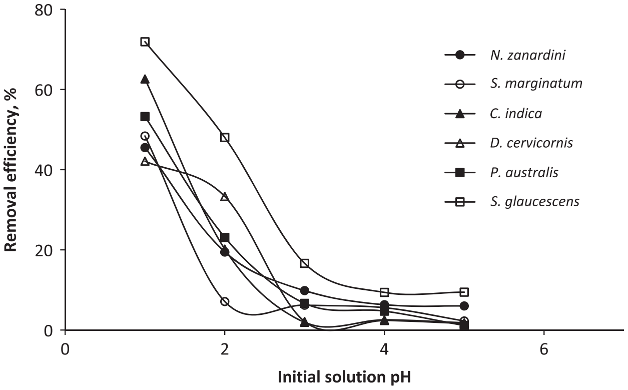

Fig. 1. Effect of initial solution pH on removal efficiency of Cr(VI) by six brown macroalgae biomasses, $[Cr(VI)]_o = 50$ mg/L, algae dose = 2 g/L, $T = 27$˚C, contact time = 180 min.

3.2. Effect of biomass dosage

One of the important parameters, which is generally used for the wastewater treatment studies is biomass dosage, which determines the potential of biosorbent to remove pollutant at a given initial concentration [22]. The experiment was conducted with 50 mg/L test solution of Cr(VI), 150 min of contact time, initial solution pH 1.0, varying algae dosage from 0.5 to 3 g/L in 50 mL metal solution at 27˚C, and the results are shown in Fig. 2. The biomass dosage significantly influenced Cr(VI) removal efficiency i.e. the biosorption of Cr(VI) increased with increasing biomass dosage. Maximum removal percentage was observed with biomass dosage of 2 g/L for *P. australis, S. marginatum,* and *C. indica* and 3 g/L for *N. zanardinii, D. cervicornis,* and *S. glaucescens.* Removal of Cr(VI) was found to increase with increase in biomass dosage due to availability of greater number of active sites on biomass [6]. The lower Cr(VI) removal efficiency occurred with increased biomass dosage, higher than 2 g/L for *P. australis, S. marginatum,* and *C. indica,* and higher than 3 g/L for *N. zanardinii, D. cervicornis,* and *S. glaucescens* as a consequence of particle aggregation of biomass at

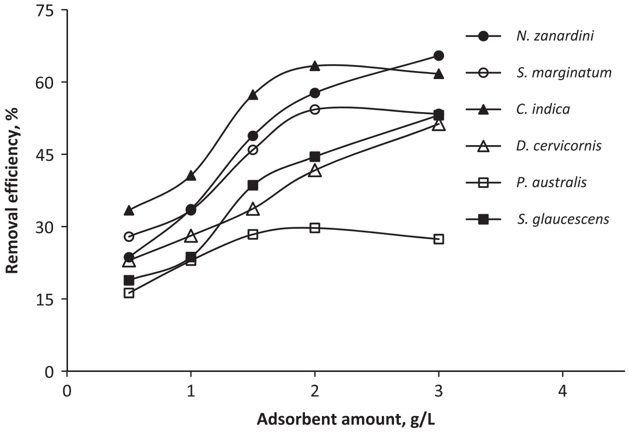

Fig. 2. Effect of different adsorbent dosage on removal efficiency of Cr(VI) by six brown macroalgae biomasses, [Cr(VI)]$_o$ = 50 mg/L, pH = 1.0, T = 27˚C, contact time = 180 min.

higher dosage, which results in the decrease of effective surface area for biosorption [1].

3.3. Effect of Cr(VI) concentration

Effect of varying initial concentration of Cr(VI) on the biosorption rate at optimum biosorbent dosage, initial solution pH 1.0, agitation speed 180 rpm, and temperature 27˚C was investigated. As can be seen from Fig. 3, the biosorption capacity (q_e) of Cr(VI) onto all brown macroalgae increased with an increase in initial Cr(VI) concentration indicating that the initial concentration provided a dominant driving force to overcome the mass transfer resistance between the aqueous and solid phases [23,24]. Another reason for the increased biosorption capacity might be attributed to the fact that increasing the initial metal concentration increases the probability of contact between chromium ions and biosorbent. Increased sorption capacity with increased sorbate concentration has previously been reported in biosorption studies of dyes [25] and metals [26].

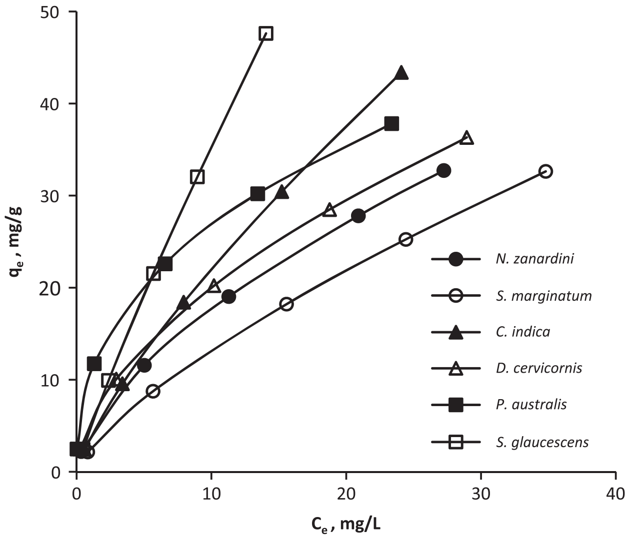

Fig. 3. Isotherm plots for Cr(VI) sorption onto six brown macroalgae biomasses (algae dose = 2 g/L, pH = 1.0, T = 27˚C, contact time = 180 min).

3.4. Effect of contact time

The effect of contact time for biosorption of Cr(VI) was studied with biomass dosage of 2 g/L and initial metal concentration of 50 mg/L at 27˚C for 3 h. As can be seen in Fig. 4, Cr(VI) removal was rapid during the first 30 min of contact time and, thereafter, the biosorption rate decreased gradually and the sorption process reached equilibrium in about 70 min for *S. marginatum*, 90 min for *N. zanardinii,* and 150 min for *D. cervicornis*, *P. australis*, *S. glaucescens,* and *C. indica*. In case of physical biosorption, most of the sorbate were adsorbed within a short contact time [27]. The high removal sorption capacity in the first few minutes might be due to the availability of a larger number of vacant surface sites. After that, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between Cr(VI) adsorbed on the algal biomasses and in solution phase [28]. Similar results were reported by other researchers in biosorption studies of dyes [29,30] and Cr(VI) [1].

3.5. Kinetic modeling

Kinetic modeling during sorption process can be counted as a plan to design optimum operating

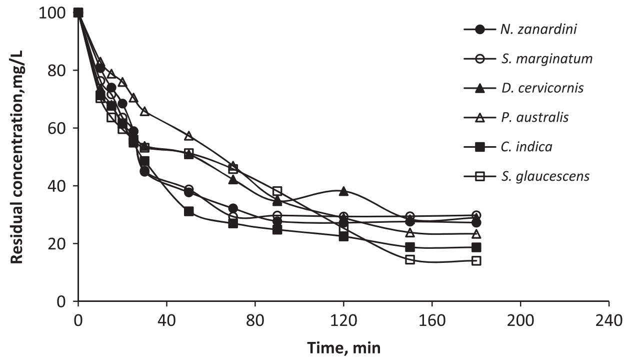

Fig. 4. Effect of contact time on removal efficiency of Cr(VI) by six brown macroalgae biomasses, [Cr(VI)]$_o$ = 50 mg/L, algae dose = 2 g/L, pH = 1, T = 27˚C, contact time = 180 min.

conditions for full-scale biosorption process. For determining the biosorption kinetics of Cr(VI) by six brown macroalgae, three kinetic models, viz. Lagergren's pseudo-first-order, pseudo-second-order model, and intra-particle diffusion model were applied and their respective correlation coefficients (R^2) estimated by linear fitting of experimental data collected at variable time are presented in Table 1 and Fig. 5. The linear form of the pseudo-first-order rate equation is shown below [31] (Eq. (3)):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \qquad (3)$$

where q_e and q_t (mg/g) are the amount of Cr(VI) sorbed onto mass of algae at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order kinetics. The values of k_1, $q_{e,}$ and R^2 are listed in Table 1. In the pseudo-first-order kinetic model, the results show that the experimental data did not fit well to the pseudo-first-order kinetic model because of the low linear regression coefficients (0.73–0.92) for all brown macroalgae. Also, significant difference was observed between calculated and experimental uptake values. It was seen that pseudo-first-order kinetic model did not fit well for the complete data range of contact time and can only be applied for preliminary stage of biosorption.

Pseudo-second-order kinetic model [32] was also tested for the present study (Eq. (4)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

where q_e and q_t have the same meaning as mentioned previously, and k_2 is the rate constant for the pseudo-second-order kinetics. To calculate the values of k_2 and q_t, the intercept and the slope of the linear plots (t/q_t) vs. t were obtained for biosorption of Cr(VI) onto six brown macroalgae. The correlation coefficient, R^2, was found to be higher than 0.95 for all the biosorbents. The model parameters are listed in Table 1. It is clear that correlation coefficient (R^2) value for pseudo-second-order model is higher and this model certainly describes the sorption kinetics of Cr(VI) onto brown macroalgae biomasses. The biosorption uptake values of Cr(VI) obtained from pseudo-second-order model were 43.48, 41.67, 47.62, 40.00, 52.63, and 50.00 mg/g, for *N. zanardinii*, *S. marginatum*, *C. indica*, *D. cervicornis*, *P. australis*, and *S. glaucescens*, respectively. These results suggest that the sorption of Cr(VI) onto

Table 1
Kinetic parameters obtained from pseudo-first-order, pseudo-second-order and intra-particle diffusion model for Cr(VI) biosorption by six brown macroalgae ($pH = 1.0$, $T = 27 \pm 2$°C, $[Cr(VI)]_o = 50$ mg/L, algae dose = 2 g/L)

Biomass		Pseudo-first-order				Pseudo-second-order				Intra-particle diffusion		
	$q_{e,\ cal}$	$k_1 \times 10^2$ (1/min)	q_e (mg/g)	R^2	$q_{e,\ cal}$	$k_2 \times 10^2$ (g/mg min)	q_e (mg/g)	R^2	$q_{e,\ cal}$	$k_{id} \times 10^1$ (mg g min$^{-0.5}$)	C (mg/g)	R^2
N. zanardinii	32.89	3.60	32.95	0.82	37.49	0.08	43.48	0.98	42.19	2.62	7.10	0.80
S. marginatum	27.11	3.30	27.19	0.88	37.16	0.11	41.67	0.99	40.68	2.32	9.53	0.78
C. indica	49.01	3.70	49.06	0.88	41.55	0.08	47.62	0.99	45.47	2.71	9.08	0.88
D. cervicornis	24.29	1.90	25.13	0.92	35.12	0.11	40.00	0.99	37.91	2.13	9.39	0.94
P. australis	55.12	2.90	55.42	0.90	38.93	0.03	52.63	0.99	41.78	3.19	−1.06	0.98
S. glaucescens	50.13	2.60	50.60	0.73	42.18	0.06	50.00	0.96	43.32	2.69	7.19	0.97

macroalgae biomasses was controlled by chemisorption and probably took place through surface exchange reactions until the surface active sites were fully occupied; then, the Cr(VI) ions diffused into the biomass network for further interactions. However, the metal ions diffusion within the particle was reported to be much slower than the movement of the metal ions from solution to the external solid surface, because of the greater mechanical obstruction to movement presented by the surface molecules or surface layers and the restraining chemical attractions between Cr(VI) ions and biosorbents [33].

The intra-particle diffusion model was also tested in order to verify the influence of mass transfer resistance on the binding of chromium ions to the biosorbent surface. The intra-particle diffusion model [34] is expressed as:

$$q_t = k_{\mathrm{id}} t^{1/2} + C \tag{5}$$

where q_t (mg/g) is the amount of Cr(VI) sorbed at time t, C (mg/g) is the intercept, and k_{id} (mg/g min$^{0.5}$) is the intra-particle diffusion rate constant. Correlation coefficient values for sorption of Cr(VI) onto *N. zanardinii*, *S. marginatum*, *C. indica,* and *D. cervicornis* were found to be in the range of 0.80–0.94 and the linear plot of intra-particle diffusion model between the metal ions and macroalgae biomasses did not pass through the origin (Fig. 4). Based on R^2

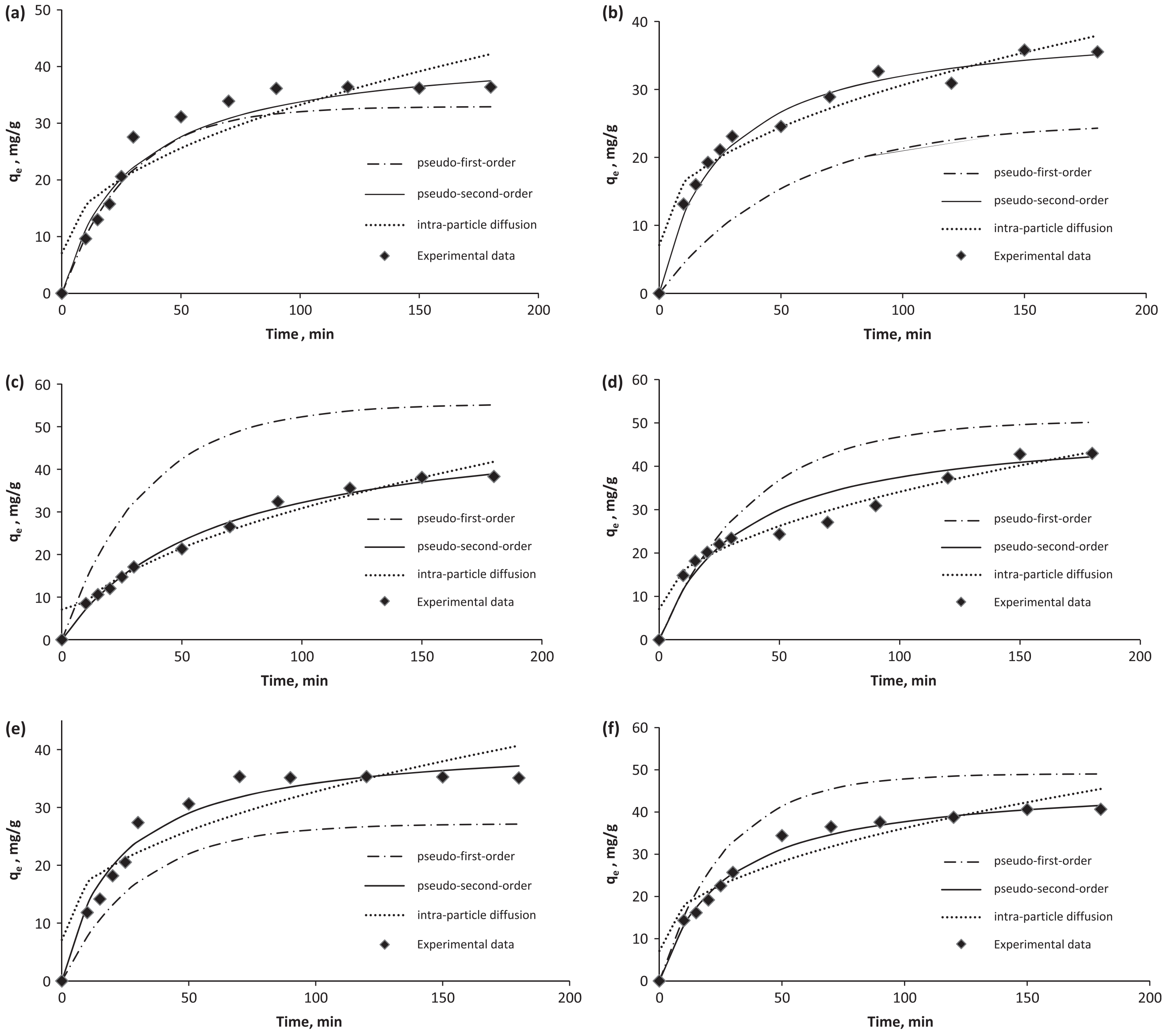

Fig. 5. Kinetic plots for Cr(VI) sorption onto *N. zanardinii* (a), *S. marginatum* (b), *C. indica* (c), *D. cervicornis* (d), *P. australis* (e), and *S. glaucescens* (f) biomass, $[\mathrm{Cr(VI)}]_o = 50$ mg/L, algae dose = 2 g/L, pH = 1, $T = 27$°C, contact time = 180 min.

values, the intra-particle diffusion model was not appropriate in describing the kinetics of Cr(VI) on macroalgae. The results indicated that there was not a degree of boundary layer control and this further showed that the intra-particle diffusion was not the rate-limiting step for Cr(VI) adsorption onto biosorbents. It suggested that the resistance to mass transfer was not involved in the Cr(VI) kinetics [35,36].

3.6. Biosorption isotherms

The establishment of appropriate correlation for the equilibrium curves is important to optimize the sorption process. Isotherm models describe the equilibrium relation between the concentration of sorbate on the solution and solid phase at a constant temperature [37]. The experiments were carried out with initial chromium concentration (5, 25, 50, 75, and 100 mg/L) and other parameters were kept constant. The equilibrium data were analyzed by the Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin models.

The Freundlich isotherm was chosen to estimate the biosorption intensity of the biosorbents towards the metal ions. Freundlich model describes the interaction between adsorbate molecules and heterogeneous surfaces [38]. Freundlich expression [39] is given by following equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F and n are Freundlich constants related to the biosorption capacity and biosorption intensity, respectively. Table 2 shows the Freundlich sorption isotherm constants and the correlation coefficients. As can be seen from Table 2, the magnitude of K_F and n shows that it is possible to perform an easy separation of heavy metal ions from aqueous solutions and achieve a high biosorption capacity [40]. It was observed that the equilibrium data fitted well with the Freundlich model with a high coefficient value of greater than 0.99. Value of K_F was higher for *P. australis*, which confirm that the biosorption capacity of Cr(VI) is greater than that of the other algal biosorbents studied. The values of n is greater than 1 representing that the biosorption of Cr(VI) onto all brown macroalgae is a favorable physical process [38]. Experimental data was also modeled using the Langmuir equation. It was based on the assumption that monolayer biosorption occurs onto a surface with finite number of identical sites. Langmuir theory suggests that sorption takes place at specific homogeneous sites within the sorbent [41].

Table 2
Isotherm constants for removal of Cr(VI) by six brown macroalgae (pH = 1.0, T = 27°C, algae weight = 2 g/L)

Biomass	Langmuir model			Freundlich model			D–R model				Temkin model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g) (L/mg)$^{1/n}$	n	R^2	q_s (mg/g)	$k_{ad} \times 10^5$ (mol^2/kJ^2)	E (kJ/mol)	R^2	b_T	K_T (L/mg)	R^2
N. zanardinii	38.68	0.14	0.59	4.29	1.63	0.99	0.02	672.50	1.58	0.82	360.22	2.47	0.82
S. marginatum	46.78	0.05	0.83	2.49	1.38	0.99	5.00	672.50	0.00	0.83	327.68	1.09	0.88
C. indica	44.02	0.07	0.99	3.72	3.68	0.99	0.04	23.97	1.12	0.87	263.10	1.54	0.93
D. cervicornis	34.92	0.24	0.75	5.50	1.78	0.99	0.01	672.50	2.24	0.85	381.16	3.78	0.90
P. australis	31.36	2.00	0.59	10.52	2.46	0.99	0.00	672.50	4.08	0.85	500.12	29.23	0.87
S. glaucescens	118.33	0.04	0.92	4.65	1.14	0.99	0.03	672.50	1.29	0.88	212.67	1.78	0.91

Based on these assumptions, the Langmuir model is given by Eq. (7):

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \tag{7}$$

where q_e (mg/g) and C_e (mg/L) are the uptake of metal per unit weight of biomass and metal ions concentration in solution at equilibrium, respectively. The monolayer sorption capacity of adsorbent, q_0 (mg/g), and the Langmuir constant, K_L (L/mg), is related to the energy of biosorption. According to Table 2, the correlation coefficient (R^2) was found to be 0.99 for *C. indica* and ranged from 0.59 to 0.92 for other brown macroalgae. These results suggest that the biosorption isotherm of Cr(VI) onto *C. indica* could be described by both Freundlich and Langmuir models. Table 3 compares maximum adsorption capacities obtained in this study with those of other biomass materials reported in the literature. The adsorption capacities for chromium using the brown macroalgae are of the same order of magnitude, greater or smaller than that have been reported in literature for different biosorbents. However, it is noted that the operating conditions such as initial solution pH, temperature, initial metal ions concentrations, and the adsorbent dosage are generally different in different studies and the results should be compared with caution. The equilibrium data was also subjected to the D–R isotherm model to determine the nature of biosorption processes. This model is based on Polani's biosorption potential theory and Dubinin's minipore filling theory [42]:

$$q_e = q_s \exp(-B\varepsilon^2) \tag{8}$$

The linear presentation of the D–R isotherm equation is expressed by:

$$\ln q_e = \ln q_m - B\varepsilon^2 \tag{9}$$

where q_e is the amount of Cr(VI) adsorbed per unit weight of biomass (mol/g), q_m is the maximum biosorption capacity (mol/g), B is the activity coefficient related to biosorption mean free energy (mol^2/J^2), and ε is the Polanyi potential ($\varepsilon = RT\ \ln(1 + 1/C_e)$).

The mean free energy, E, of sorption, per molecule of sorbate, is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship [43] (Eq. (10)):

$$E = \frac{1}{\sqrt{2B}} \tag{10}$$

The biosorption mean free energy value (E) gives information about biosorption mechanism. Ion

Table 3
Comparison of biosorption capacity of six brown macroalgae for chromium (VI) with various adsorbents

Adsorbents	Uptake capacity (mg/g)	pH	T (°C)	Initial Cr(VI) concentration (mg/L)	Adsorbent dose (g/L)	Reference
Tobacco-leaf residue	113.2	1	27	100	2	[20]
Clodophara crispata	6.20	1.0–2.0	25	200	–	[46]
Pilayella littoralis	6.55	5.5	25	50	2.5	[47]
Rhizopus nigricans (polyacrylamide)	21.22	2.0	–	100	2	[48]
Neurospora crassa (AcOH pretreated)	15.85	1.0	25	250	1	[49]
Streptomyces rimosus (NaOH pretreated)	26.7	5	25	100	3	[50]
Chitosan beads	59.5	–	30	20	50	[51]
N. zanardinii	32.72	1	27	100	2	*This study*
S. marginatum	32.63	1	27	100	2	*This study*
C. indica	43.38	1	27	100	2	*This study*
D. cervicornis	36.32	1	27	100	2	*This study*
P. australis	37.82	1	27	100	2	*This study*
S. glaucescens	47.62	1	27	100	2	*This study*

exchange is dominant if the value of E is between 8.0–16.0 kJ/mol and $E < 8.0$ kJ/mol implies physical sorption process [44]. The mean biosorption energy was found to be lower than 8 kJ/mol indicating that the biosorption of Cr(VI) onto all brown macroalgae biomass mainly proceeds by physical sorption.

Temkin isotherm model was also used to fit the experimental data. The Temkin isotherm model suggests an equal distribution of binding energies over the number of exchanging sites on the surface [38]. Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [45]. The equation for Temkin isotherm is as follows (Eq. (11)):

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \tag{11}$$

where K_T is the equilibrium binding constant corresponding to the maximum binding energy, b_T is the Temkin isotherm constant, T is the temperature (K), and R is the ideal gas constant (8.315 J mol^{-1} K^{-1}). The correlation coefficients for all biosorbents were in the range of 0.82–0.93 and it can be said that the experimental data did not fit well to the Temkin isotherm model. The results indicated that the surface of brown macroalgae is heterogeneous in nature and did not possess equal distribution of binding energies on the available binding sites.

4. Conclusions

Biosorption potential of six brown macroalgae, *N. zanardinii*, *S. marginatum*, *C. indica*, *D. cervicornis*, *P. australis*, and *S. glaucescens* for Cr(VI) removal was studied as a function of different initial solution pH, biomass dosage, initial sorbate concentration, and contact time. The sorption process was found to be dependent on the solution pH, and pH 1.0 was found to be optimum for Cr(VI) biosorption. The removal of Cr(VI) increased with the increasing initial concentration at the same pH and biomass. Kinetic data of the process showed that the biosorption of Cr(VI) onto biomasses followed the pseudo-second-order kinetic model. Equilibrium was well described by Freundlich isotherms. The experimental results show that six brown macroalgae have uptake capacity for Cr(VI) in the range 31.36–118.33 mg/g. This capacity is considerably higher than a number of other types of biomasses reported in the literature. The removal rate of Cr(VI) was relatively rapid in the first 30 min, but then the rate decreased gradually. The results of the present study suggest that algal biomasses can be considered as effective and economical biosorbents for the removal of Cr(VI) from water and wastewater.

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