

Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon

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Abstract

Biosorption of heavy metals can be an effective process for the removal of toxic chromium ions from wastewater. In this study, the batch removal of toxic hexavalent chromium ions from aqueous solution, saline water and wastewater using marine dried green alga *Ulva lactuca* was investigated. Activated carbon prepared from *U. lactuca* by acid decomposition was also used for the removal of chromium from aqueous solution, saline water and wastewater. The chromium uptake was dependent on the initial pH and the initial chromium concentration, with pH ~1.0, being the optimum pH value. Langmuir, Freundlich, Redlich-Peterson and Koble-Corrigan isotherm models were fitted well the equilibrium data for both sorbents. The maximum efficiencies of chromium removal were 92 and 98% for *U. lactuca* and its activated carbon, respectively. The maximum adsorption capacity was found to be 10.61 and 112.36 mg g⁻¹ for dried green alga and activated carbon developed from it, respectively. The adsorption capacities of *U. lactuca* and its activated carbon were independent on the type of solution containing toxic chromium and the efficiency of removal was not affected by the replacing of aqueous solution by saline water or wastewater containing the same chromium concentration. Two hours were necessary to reach the sorption equilibrium. The chromium uptake by *U. lactuca* and its activated carbon form were best described by pseudo second-order rate model. This study verifies the possibility of using inactivated marine green alga *U. lactuca* and its activated carbon as valuable material for the removal of chromium from aqueous solutions, saline water or wastewater.

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1. Introduction

Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain and hence in the human body. Water pollution by chromium is of considerable concern, as this metal has found widespread use in metal finishing, leather tanning, electroplating, nuclear power plant, textile industries, and chromate preparation [1]. Chromium is an element of 6th group in the latest IUPAC Periodic Table, exists in the environment mainly in Cr³⁺ and Cr⁶⁺ states. Cr³⁺ is non-toxic and an essential species to mammals since it helps the body to control blood-sugar levels when present in trace concentrations, but toxic to fish when its concentration in water exceed 5.0 mg L⁻¹ [2]. Cr⁶⁺ is a powerful epithelial irritant and is toxic to many plants, aquatic animals,

bacteria and confirmed as human carcinogen [3,4]. Most industries in developed countries discharge wastewater into surface water containing Cr⁶⁺ after reduction to the trivalent state [4]. The disadvantage of this treatment method is the high cost of chemicals used for the reduction purposes and incomplete reduction of Cr⁶⁺ which may produce toxic sludge due to surface adsorption of Cr⁶⁺ onto the Cr³⁺ hydroxide precipitate [4]. It is therefore necessary to explore viable technologies for controlling the concentration of Cr⁶⁺ in aqueous discharges.

Surface adsorption is found to be an important basis for the treatment of toxic chromium contaminated water [4], where, numerous adsorbents such as clay [5], tires and sawdust [6] and zeolite [7] were used. Biosorption is a potential alternative to traditional treatment processes of metal ions removal [8–10]. Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake [11]. The phenomenon of biosorption has been described in a wide range of non-living biomass such as bark [12], lignin [13] and

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peanut hulls [14] as well as living biomass like fungi [15], yeast [16], aquatic plants [17] and algae [18]. Marine algae, a renewable natural biomass proliferate ubiquitously and abundantly in the littoral zones of world [19]. These biomasses have attracted the attention of many investigators as organisms to be tested and used as new supports to concentrate and adsorb metal ions [20,21].

Activated carbon has undoubtedly been the most popular and widely used as adsorbent in wastewater treatment applications throughout the world. However, activated carbon remains an expensive material since higher the quality of activated carbon, the greater its cost [22]. Therefore, searching for a low cost activated carbon and other adsorbent materials are of great important for the wastewater treatment [23–26].

The purpose of the present study is to evaluate the biosorption capacity of the dried green alga *Ulva lactuca* for removal of Cr^{6+} from aqueous solution, natural seawater, synthetic seawater and real wastewater [27]. Furthermore, this is the first time to develop an activated carbon from green alga *U. lactuca* and study its adsorption capacity for toxic Cr^{6+} . In addition, kinetics and reaction mechanism were investigated.

2. Materials and methods

2.1. Biomass

Green alga *U. lactuca* was collected from Abo-Quir Bay, Alexandria, Egypt and washed with seawater, tap water, and then distilled water several times. The clean alga was sun dried for 7 days followed by oven drying at $105\text{ }^{\circ}\text{C}$ for 24 h, and the dried alga was milled and sieved to $\leq 0.063\text{ mm}$ [24,25].

2.2. Activated carbon

The dried green alga *U. lactuca* 0.5 kg was added in small portion to 400 mL of 98% H_2SO_4 and the resulting mixture was kept for 24 h at room temperature followed by refluxing in fume hood for 5 h. After cooling, the reaction mixture was poured onto ice water (2 L) and filtered. The filtrate was washed repeatedly with distilled water and soaked in 1% NaHCO_3 solution to remove any remaining acid. The sample was then washed with distilled water until pH of the activated carbon reached 6, dried in an oven at $160\text{ }^{\circ}\text{C}$ for 48 h and sieved to the particle size $\leq 0.063\text{ mm}$ and kept in a glass bottle until used [9].

2.3. Preparation of synthetic solution

A stock solution of 1.0 g L^{-1} was prepared by dissolving the 5.657 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 1.0 L distilled water. Concentrations ranged between 5 and 100 mg L^{-1} were prepared from the stock solution to have the stander curve. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. All the adsorption experiments were carried out at room temperature ($25 \pm 2\text{ }^{\circ}\text{C}$). The initial pH is adjusted with 1 M HCl or 1 M NaOH.

2.4. Simulation studies

Synthetic seawater was prepared by dissolving 35 g NaCl in 1 L distilled water. Different weights of chromium were dissolved in the synthetic seawater to obtain different concentrations of Cr^{6+} .

Natural seawater was collected from Eastern Harbor, Alexandria, Egypt and filtered using Whatman no. 40 filter paper. The clear natural seawater was used to prepare different concentrations of Cr^{6+} .

Wastewater was collected from El-Emoum drain (contains several industrial effluents and agriculture drain from Alexandria Governorate) near lake Maruit, Alexandria, Egypt. The collected wastewater was filtered through Whatman no. 40 filter paper and used for preparing different concentrations of Cr^{6+} .

2.5. Batch biosorption studies

The effect of pH on the equilibrium adsorption was investigated by employing different initial concentration of Cr^{6+} (50 mg L^{-1}) and different alga and its activated carbon dosages. The pH values were adjusted with diluted HCl and NaOH solutions. The suspensions were shaken at room temperature ($25 \pm 2\text{ }^{\circ}\text{C}$) using agitation speed (200 rpm) for the minimum contact time required to reach the equilibrium. The concentration of Cr^{6+} in solution was measured according to standard method introduced by Gilcreas et al. [28] using UV–vis spectrophotometer (Milton Roy, Spectronic 21D) using silica cells of path length 1 cm at wavelength λ 540 nm. All the experiments are duplicated and only the mean values are reported. The maximum deviation observed was less than 5%.

Adsorption of Cr^{6+} was studied using different weights of green alga and its activated carbon in 100 mL solution of 20, 30 and 50 mg L^{-1} of initial Cr^{6+} concentration and initial pH 1.0.

2.6. Equilibrium isotherms

Adsorption equilibrium isotherms were studied using green alga and its activated carbon dosages of 0.2, 0.3, 0.5, 1.0 and 1.5 g and 0.2, 0.3, 0.4, 0.5 and 0.7 g, respectively, per 100 mL of aqueous Cr^{6+} solutions of initial concentrations ranged from 5 to 50 mg L^{-1} for green alga and $5\text{--}250\text{ mg L}^{-1}$ for activated carbon using initial pH 1.0. For these experiments, the screw-cap conical flasks were shaken at a speed of 200 rpm and room temperature ($25 \pm 2\text{ }^{\circ}\text{C}$) for the required contact time. Then, the solution was filtered through a $0.45\text{ }\mu\text{m}$ membrane filter. The Cr^{6+} uptake was calculated by the simple concentration difference methods. The initial concentration C_0 (mg L^{-1}) and Cr^{6+} concentrations at any time, C_t (mg L^{-1}) respectively, were determined and the metal uptake q_t ($\text{mg metal adsorbed per g adsorbent}$) was calculated by using the following mass balance equation as follows:

$$q_t = \frac{(C_0 - C_t)V}{m_s} \quad (1)$$

where C_0 and C_t are the Cr^{6+} concentrations (mg L^{-1}) initially and at a given time t , respectively, V the volume of the Cr^{6+}

solutions (L) and m_s is the weight of green alga or its activated carbon (g).

The percentage of removed Cr^{6+} ions ($R\%$) in solution was calculated using Eq. (2):

$$R(\%) = \frac{C_0 - C_t}{C_0} 100 \quad (2)$$

2.7. Theory and data evaluation

The adsorption dynamics describes the chromium uptake rate by green alga *U. lactuca* and its activated carbon have been studied using different kinetic models to identify the type of reaction rate. The kinetics of Cr^{6+} adsorption onto the green alga *U. lactuca* and its activated carbon were analyzed using pseudo first-order [29] and pseudo second-order [30]. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of adsorption of Cr^{6+} .

The pseudo first-order equation [29] is generally expresses as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption capacity at equilibrium and at time t (min), respectively, k_1 (L min^{-1}) is the rate constant of pseudo first-order adsorption. The integrated linear form of Eq. (3) can be expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (4)$$

A straight line of $\log(q_e - q_t)$ versus t suggests the applicability of this kinetic model. The q_e and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo second-order adsorption kinetic rate equation is expressed as follows [30]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo second-order adsorption. The integrated form of Eq. (5) can be expressed as follows:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (6)$$

which is the integrated rate law for a pseudo second-order reaction. The linear form of Eq. (6) can be obtained as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The plot of (t/q_t) versus t of Eq. (7) should give a straight line if second-order kinetic model is applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

Four models were used to fit the experimental data, Langmuir isotherm [31], Freundlich isotherm [32], Redlich-Peterson

isotherm [33] and Koble-Corrigan isotherm [34]. The Langmuir equation may be written as:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (8)$$

The above equation can be rearranged to the following four linear forms:

Langmuir-1:

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} C_e \quad (9)$$

Langmuir-2:

$$\frac{1}{q_e} = \frac{1}{K_a Q_m} \frac{1}{C_e} + \frac{1}{Q_m} \quad (10)$$

Langmuir-3:

$$q_e = Q_m - \left(\frac{1}{K_a} \right) \frac{q_e}{C_e} \quad (11)$$

Langmuir-4:

$$\frac{q_e}{C_e} = K_a Q_m - K_a q_e \quad (12)$$

where C_e is the equilibrium concentration (mg L^{-1}); q_e the amount of metal ion sorbed (mg g^{-1}); Q_m the q_e for a complete monolayer (mg g^{-1}); K_a is the sorption equilibrium constant (L mg^{-1}). A plot of C_e/q_e versus C_e (Langmuir-1), $1/q_e$ versus $1/C_e$ (Langmuir-2), q_e versus q_e/C_e (Langmuir-3) and q_e/C_e versus q_e (Langmuir-4) should indicate straight lines.

The Freundlich equation may be written as:

$$q_e = K_F C_e^{1/n} \quad (13)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (14)$$

The constants K_F and $1/n$ of the Freundlich model are the constants indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and the constant indicative of the intensity of the adsorption, respectively.

Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (15)$$

It has three isotherm constants, A , B and g ($0 < g < 1$), which characterize the isotherm. Its limiting behavior is summarized: where $g = 1$.

Eq. (15) can be converted to a linear form by taking logarithms:

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B) \quad (16)$$

Three isotherm constants, A , B and g can be evaluated from the linear plot represented by Eq. (16) using a trial and error optimization method.

Koble-Corrigan model is another three parameter empirical model for the representing equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm-type models and is given by Eq. (17) [34]:

$$q_e = \frac{aC_e^n}{1 + bC_e^n} \quad (17)$$

where a , b and n are the Koble-Corrigan parameters, respectively.

3. Results and discussion

3.1. Effect of pH on biosorption

The initial pH of the metal solution is an important parameter affecting biosorption of metal ions [35]. Therefore, the effect of initial pH on the removal of Cr^{6+} using dried green alga *U. lactuca* and its activated carbon was studied (Fig. 1). It is clear from Fig. 1 that the adsorption of Cr^{6+} decreases with increase in pH from 1.0 to 11.0. The maximum removal was occurred at initial pH 1.0 for both of green alga and activated carbon. This behavior can be explained by the nature of the biosorption at different pH, the type of ionic state of functional group of sorbent and the metal chemistry [36]. Adsorption of Cr^{6+} below pH 3.0 suggests that bind of the negatively charged chromium species occurred through electrostatic attraction to the positively charged functional groups on the surface of sorbent cell wall due to the presence of more functional groups carrying positive charges at $\text{pH} < 3$. While at $\text{pH} > 3$ the sorbent cell wall possesses more functional group carrying net negative charges which tend to repulse the metal anions. However, there is removal at $\text{pH} > 3.0$ but the rate of removal is reduced, which could be considered the presence of other mechanism such as physical adsorption on the surface of sorbent [37].

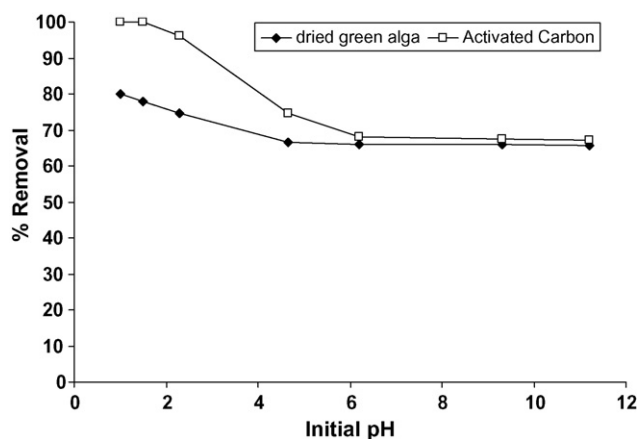


Fig. 1. Effect of initial pH on the percentage of removal of 50 mg L^{-1} Cr^{6+} using 5 g L^{-1} of dried green alga *U. lactuca* and its activated carbon.

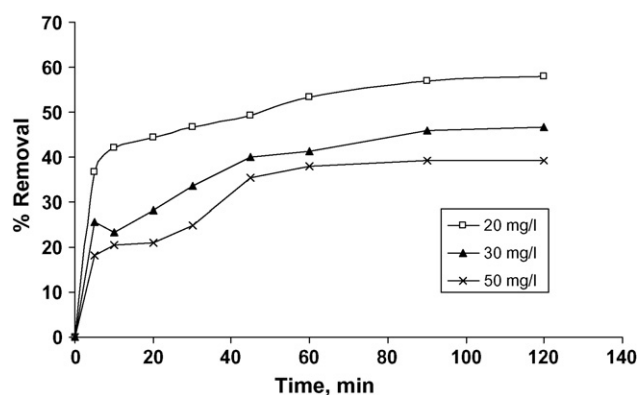


Fig. 2. The effect of time on the percentage of removal for different Cr^{6+} concentrations at pH 1.0 and room temperature using 3 g L^{-1} of dried green alga *U. lactuca*.

3.2. The effect of biosorption time

The effect of the contact time on biosorption of Cr^{6+} at 2 g L^{-1} dried green alga and activated carbon concentration has been shown in Figs. 2 and 3, respectively. As can be seen from Figs. 2 and 3, with the beginning of biosorption, the uptake of Cr^{6+} ions increased quickly, after 10 min, the change became slow. The biosorption process of Cr^{6+} on both of dried green alga *U. lactuca* and its activated carbon was speedy and in 40 min, the process of biosorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed Cr^{6+} ions did not significantly change with time. So, the removal efficiency was high and 120 min was selected as the time of biosorption equilibrium. The efficiency of adsorption increases from 70 to 96 with various algal doses. It can be concluded that the adsorption of Cr^{6+} with activated carbon is much more efficient than that of green alga *U. lactuca*. This may be due to net work pore structure of activated carbon and other factor that is generated during the activation process which exhibit high specific surface area [38].

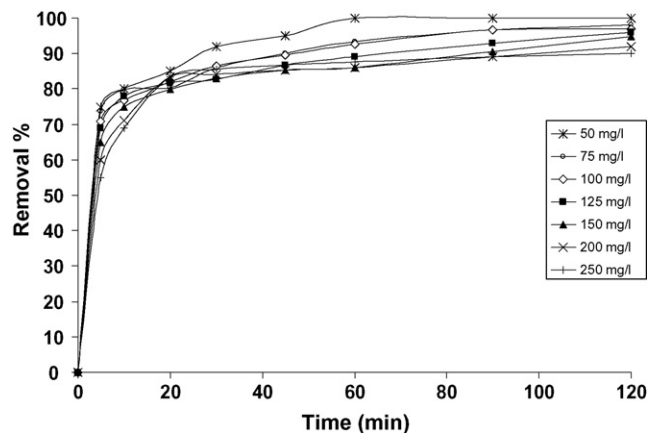


Fig. 3. The effect of time on the percentage of removal for different Cr^{6+} concentrations at pH 1.0 and room temperature using 2 g L^{-1} of activated carbon developed from green alga *U. lactuca*.

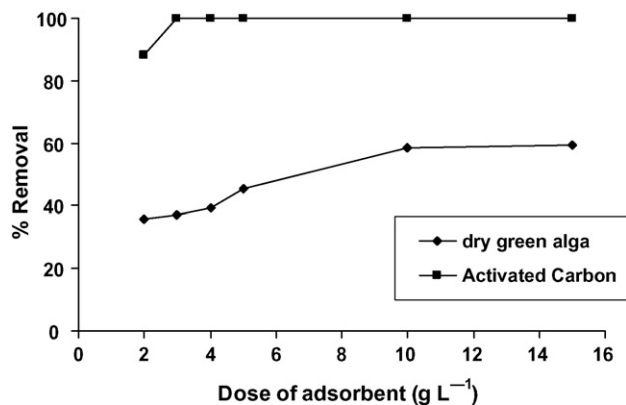


Fig. 4. The effect of green alga *U. lactuca* and activated carbon doses on the percentage of removal of Cr^{6+} at pH 1.0 and room temperature using 30 mg L^{-1} metal ion concentration.

3.3. Effect of adsorbent dose on biosorption

The effects of algal doses and its activated carbon on the removal of Cr^{6+} from aqueous solutions were investigated using different adsorbent concentration $2\text{--}15$ and $2\text{--}7 \text{ g L}^{-1}$ of green alga *U. lactuca* and its activated carbon, respectively. Since biosorption is highly dependent on the initial adsorbent concentration, the extent of biosorption is proportional to specific area. Specific area can be defined as the portion of the total area that is available for biosorption [39]. The results are presented in Fig. 4 which indicated that the percentage of removal of metal ions increase with increasing doses of both adsorbents. This result was accepted because increasing adsorbent doses provides greater surface area and more pore volume will be available for the biosorption [40–45].

3.4. Effect of metal ion concentration on biosorption

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases [39]. Fig. 5 represented the effect of different initial concentrations of Cr^{6+}

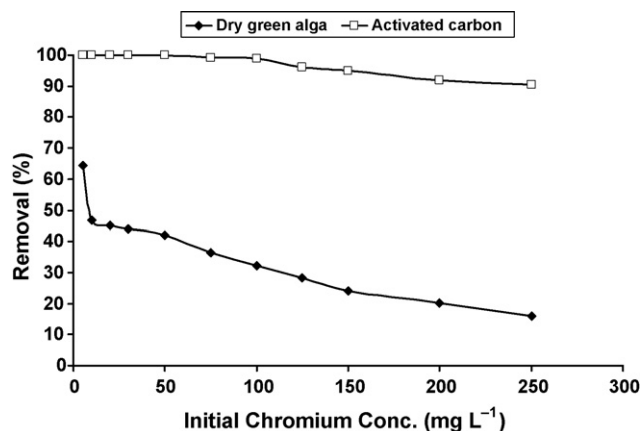


Fig. 5. The effect of initial concentration of metal ion on the percentage of removal of Cr^{6+} at pH 1 and room temperature using 2 g L^{-1} green alga *U. lactuca* and activated carbon doses.

($5\text{--}250 \text{ mg L}^{-1}$) on biosorption of Cr^{6+} using green alga *U. lactuca* and its activated carbon. The results show that the equilibrium concentration of Cr^{6+} increased with increasing adsorbate concentration. It showed that the increase in initial concentration of Cr^{6+} led to decrease in the percentage of removal for both adsorbents. When initial chromium concentrations increased from 5 to 50 mg L^{-1} , the removal percents decreased from 66 to 45% for dried green alga and when initial chromium concentrations changed from 5 to 250 mg g^{-1} , the percentage of removals were decreased from 100 to 90% for the activated carbon. This was due to the saturation of the sorption sites on adsorbents.

3.5. Adsorption isotherm

Adsorption isotherms are important for the description of how adsorbate will interact with an adsorbent and are critical in optimizing the use of adsorbent. Equilibrium studies in adsorption give the capacity of the adsorbent. It is described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. In order to investigate the adsorption isotherm, four equilibrium models were analyzed.

3.5.1. Langmuir isotherm model

The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm can be linearized in four different types of equations (Eqs. (9)–(12)) and simple linear regression will result in different parameter estimates. The four linear types of Langmuir model were applied and the best-fit is obtained using Langmuir-1 (Eq. (9)) and Langmuir-2 (Eq. (10)) as shown by high values of the regression correlation coefficient ($R^2 > 0.97$) and lower S.D. values (< 0.500). Values of the Langmuir constants, the saturated monolayer sorption capacity, Q_m , and the sorption equilibrium constant, K_a , are presented in Tables 1 and 2 for the sorption of Cr^{6+} onto dried green alga and its activated carbon. Figs. 6–9 show the applicable two linear Langmuir Eqs. (9) and (10). The maximum Cr^{6+} adsorption along with the Langmuir constants at an optimum pH of 1.0 are $9.32\text{--}10.61 \text{ mg g}^{-1}$ of alga (Table 1) and $95.24\text{--}112.36 \text{ mg g}^{-1}$ of activated carbon (Table 2). The Langmuir constant K_a can serve as an indicator of isotherm rise in the region of lower residual metal concentrations, which reflects the strength or affinity of the sorbent for solute [46].

3.5.2. Freundlich isotherm model

The applicability of the empirical Freundlich isotherm was also analyzed based on sorption on heterogeneous surface, using the same set of experimental data of dried green alga and its activated carbon, by plotting $\log(q_e)$ versus $\log(C_e)$ (Figs. 10 and 11). The constants K_F and n of the Freundlich model are, respectively, obtained from the intercept and the

Table 1
Isotherm parameters obtained for biosorption of chromium using dried green alga *Ulva lactuca*

Isotherm model	2 g L ⁻¹	3 g L ⁻¹	5 g L ⁻¹	10 g L ⁻¹	15 g L ⁻¹
Langmuir-1					
Q_m (mg g ⁻¹)	9.32	3.17	2.88	2.94	2.03
K_a (L mg ⁻¹)	0.107	0.315	0.964	0.882	1.154
R^2	0.979	0.994	0.998	0.993	0.997
Langmuir-2					
Q_m (mg g ⁻¹)	10.61	3.84	2.93	2.41	2.76
K_a (L mg ⁻¹)	0.102	0.310	0.932	1.006	1.251
R^2	0.988	0.977	0.953	0.944	0.980
Freundlich					
$1/n$	1.10	2.31	1.92	0.24	0.21
K_F (mg g ⁻¹)	0.351	0.007	0.018	1.384	1.012
(L mg ⁻¹) ^{1/n}					
R^2	0.997	0.999	0.998	0.994	0.987
Redlich-Peterson					
g	0.326	1.00	1.00	0.786	0.802
B (L mg ⁻¹) ^g	0.197	0.031	0.028	36.14	47.85
A (L g ⁻¹)	0.215	0.145	0.122	50.00	50.00
R^2	0.955	0.969	0.977	0.867	0.973

Table 2
Isotherm parameters obtained for biosorption of chromium using activated carbon developed from green alga *Ulva lactuca*

Isotherm model	2 g L ⁻¹	3 g L ⁻¹	4 g L ⁻¹	5 g L ⁻¹	7 g L ⁻¹
Langmuir-1					
Q_m (mg g ⁻¹)	95.24	62.89	50.03	40.49	46.30
K_a (L mg ⁻¹)	0.62	2.24	19.99	13.72	16.62
R^2	0.981	0.998	0.983	0.967	0.999
Langmuir-2					
Q_m (mg g ⁻¹)	112.36	75.76	55.87	45.66	45.05
K_a (L mg ⁻¹)	0.46	0.90	3.98	3.53	18.50
R^2	0.948	0.951	0.876	0.879	0.997
Freundlich					
$1/n$	0.379	0.2287	0.106	0.178	0.369
K_F (mg g ⁻¹)	34.087	37.862	41.543	33.697	65.25
(L mg ⁻¹) ^{1/n}					
R^2	0.916	0.9347	0.9477	0.7113	0.9958

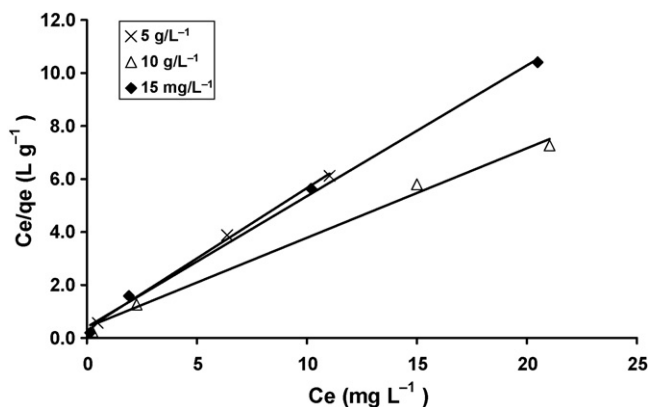


Fig. 6. Langmuir-1 isotherm obtained using the linear method for the sorption of chromium onto dried green alga *Ulva lactuca*.

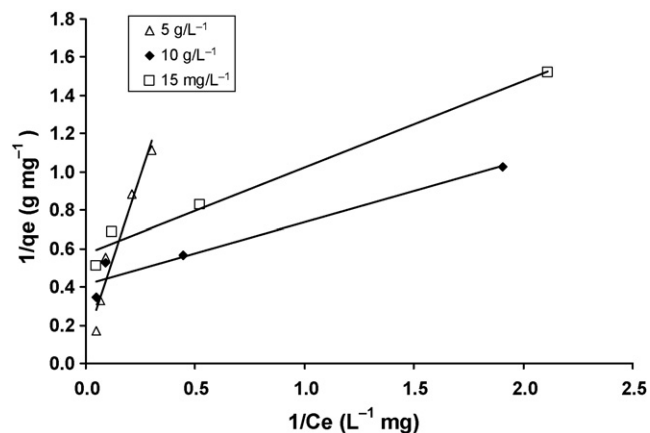


Fig. 7. Langmuir-2 isotherm obtained using the linear method for the adsorption of chromium onto dried green alga *Ulva lactuca*.

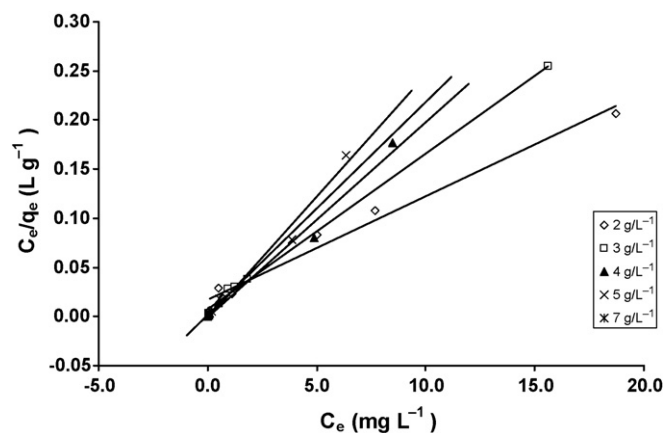


Fig. 8. Langmuir-1 isotherm obtained using the linear method for the sorption of chromium onto activated carbon from dried green alga *Ulva lactuca*.

slope of the linear plot of Figs. 10 and 11. The constant K_F can be defined as a sorption coefficient which represents the quantity of adsorbed chromium ions for a unit equilibrium concentration, while $1/n$ is a measured of the sorption intensity or surface heterogeneity. In case of $1/n = 1$, the partition between the two phases is independent of the concentration and in case

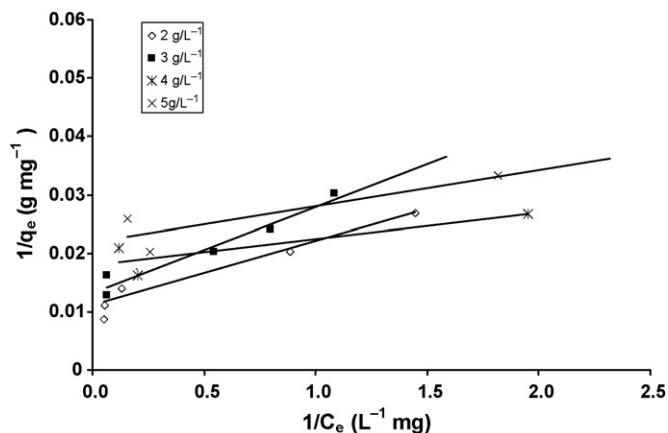


Fig. 9. Langmuir-2 isotherm obtained using the linear method for the sorption of chromium onto activated carbon from dried green alga *Ulva lactuca*.

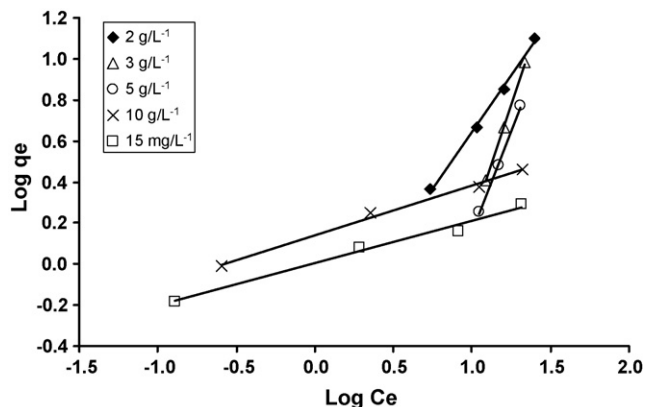


Fig. 10. Freundlich plot for chromium adsorption onto dried green alga *Ulva lactuca*.

of $1/n < 1$ is the most common and corresponds to a normal an L-type Langmuir isotherm, while $1/n > 1$ is indicative of a cooperative sorption, which involves strong interactions between the molecules of adsorbate [47]. The $1/n$ values reported in Table 1 for dried green alga were ranged from 0.21 to 2.31, which indicating a change in the type of adsorption with the change in dried alga concentration, while $1/n$ values reported in Table 2 for activated carbon were found to be lower than 1, which may indicate only one mechanism has taken place. The coefficient value obtained from Freundlich model for activated carbon was lower than that obtained from Langmuir-1 (Table 2). On the other hand, the Freundlich isotherm was more suitable for the experimental data than the linear form of Langmuir-3 and Langmuir-4 isotherm. However, the Freundlich model is more widely used but provides no information on the monolayer adsorption capacity, while the Langmuir model gives good information on the maximum monolayer adsorption capacity.

3.5.3. Redlich-Peterson isotherm model

The isotherm constants, A , B , and g of Redlich-Peterson model, were evaluated from the salvation of Eqs. (15) and (16) using SPSS computer program and reported in Table 1 for adsorption of Cr^{6+} over dried green alga. However, the Redlich-

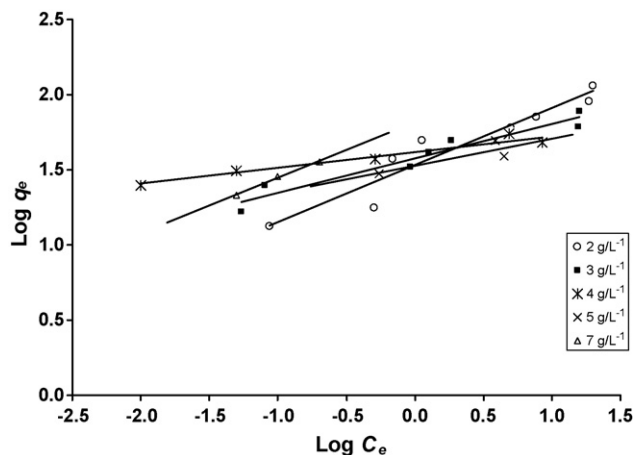


Fig. 11. Freundlich plot for chromium adsorption onto activated carbon developed from dried green alga *Ulva lactuca*.

Table 3

Biosorption isotherm Koble-Corrigan model for chromium on dried green alga *Ulva lactuca*

Chromium concentration (mg L ⁻¹)	n	A	B	R^2
5	1.23	3.480	1.959	0.916
10	2.07	40.31	50.06	0.894
20	4.80	0.088	0.029	0.403
30	0.02	0.020	0.947	0.937
50	1.27	0.035	0.014	0.659

Peterson was found to be not applicable (R^2 was very low) to the adsorption of Cr^{6+} over activated carbon. The R^2 obtained from Redlich-Peterson for adsorption of Cr^{6+} over dried green alga were ranged between 0.867 and 0.973, which are less than that obtained from Langmuir-1 and Freundlich (Table 1). The constant g showed value equal 1.0 for adsorbent doses 3 and 5 g L⁻¹, which indicates a monolayer adsorption.

3.5.4. Koble-Corrigan isotherm model

The three isotherm constants of Koble-Corrigan model were also evaluated using SPSS computer program and reported in Tables 3 and 4. This model was found to be not applicable for green alga as shown by low values of the correlation coefficient (R^2) (Table 3). The R^2 values obtained for green alga were ranged between 0.403 and 0.937, while the R^2 values obtained for activated carbon were fluctuated between 0.922 and 1.000 (Table 4). This explained the applicability of Koble-Corrigan model to the adsorption of Cr^{6+} onto activated carbon developed from dried green alga.

3.6. Adsorption kinetics studies

The kinetics of adsorption describes the rate of chromium ions uptake on dried green alga and its activated carbon which controls the equilibrium time. Two kinetics models, pseudo first-order (Eq. (4)) and pseudo second-order models (Eq. (7)), are used to analyze the sorption data and to identify the mechanism of solute adsorption onto sorbents.

3.6.1. The pseudo first-order model

Figs. 12 and 13 showed the plot of pseudo first-order for dried green alga and its activated carbon, respectively. The first-order rate constant K_1 can be obtained from the slope of the plot of $\log(q_e - q_t)$ versus time, as shown in Figs. 12 and 13. The adsorption first-order rate constants ranged

Table 4

Biosorption isotherm Koble-Corrigan model for chromium on activated carbon from dried green alga *Ulva lactuca*

Activated carbon concentration (g L ⁻¹)	n	A	B	R^2
2	0.316	33.7	0.064	0.937
3	0.288	49.0	0.248	0.925
4	0.198	81.3	0.836	0.922
5	0.680	260.0	4.320	1.000
7	0.696	267.1	4.410	1.000

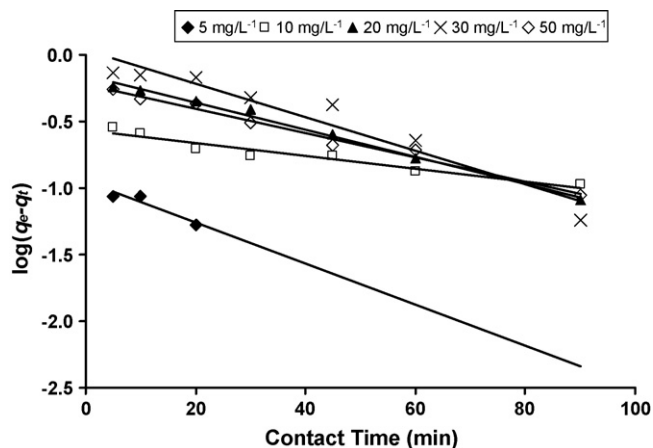


Fig. 12. Pseudo first-order sorption kinetics of Cr⁶⁺ onto dried green alga *Ulva lactuca* at various initial chromium concentrations.

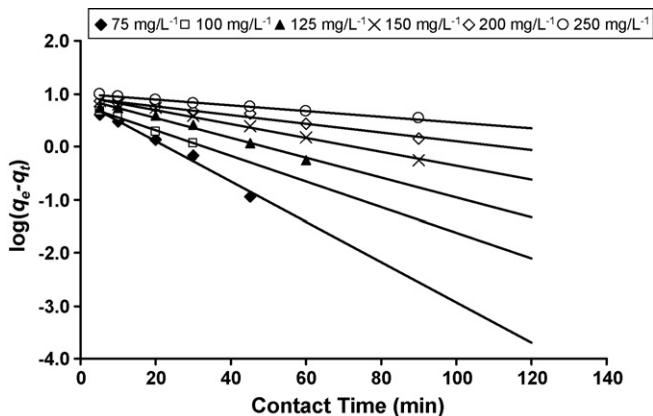


Fig. 13. Pseudo first-order sorption kinetics of Cr⁶⁺ onto activated carbon developed from dried green alga *Ulva lactuca* at various initial chromium concentrations.

between 0.013–0.071 and 0.012–0.103 min⁻¹ for dried green alga and activated carbon, respectively (Tables 5 and 6). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed that the pseudo first-order model fits well for the first 40 min and thereafter the data deviate from the theory. Thus, the model shows the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Ho and McKay [48] reported that the sorption data were represented well by the Lagergren first-order model only for the rapid initial phase that occurs for a contact time of 0–30 min. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for chromium onto dried green alga and its activated carbon for the entire sorption period. The regression coefficient values were found to be in the range of 0.795–0.996 and 0.94–0.997 while it gave predicted q_e far from the experimental q_e for both dried green alga and activated carbon, which shows that the pseudo first-order model can be applied but is not appropriate to describe the entire process and to predict the q_e .

3.6.2. The pseudo second-order model

As a result of failure in applicability of pseudo first-order, the adsorption kinetics was explained by the pseudo second-order model given by Ho and McKay Eq. (7) [48]. The second-order rate constants K_2 , the calculated q_e values and correlation coefficients were reported in Tables 5 and 6. It was observed that the pseudo second-order rate constant (K_2) decreased with increased initial concentration for both of dried green alga and its activated carbon. The calculated q_e values agree very well with the experimental values and the regression coefficients were above 0.982, which shows that the pseudo second-order model

Table 5

Comparison of the first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial Cr⁶⁺ concentration and *Ulva lactuca* concentrations

Parameter		First-order kinetic model				Second-order kinetic model		
Algae concentration	Initial Cr concentration (mg L ⁻¹)	q_e (experimental)	K_1 ($\times 10^3$)	q_e (calculated)	R^2	K_2 ($\times 10^3$)	q_e (calculated)	R^2
2 g L ⁻¹	20	4.62	16.35	2.91	0.924	14.60	4.64	0.994
	30	6.29	18.19	3.99	0.855	12.10	6.75	0.989
	50	12.57	45.14	5.01	0.996	10.94	12.92	1.000
3 g L ⁻¹	20	2.57	71.39	3.99	0.916	38.34	2.77	0.997
	30	4.62	37.56	3.57	0.950	15.72	5.06	0.992
	50	9.58	32.24	4.57	0.957	15.16	9.98	0.992
5 g L ⁻¹	20	1.80	13.13	1.14	0.828	71.67	1.65	0.991
	30	3.03	32.01	2.41	0.960	27.73	3.40	0.987
	50	5.90	31.78	2.63	0.966	26.64	6.13	0.997
10 g L ⁻¹	20	1.78	21.42	1.39	0.795	68.01	1.48	0.987
	30	1.90	21.88	1.01	0.950	54.44	1.96	0.982
	50	2.90	15.66	1.11	0.990	53.46	2.93	0.994
15 g L ⁻¹	20	1.21	23.49	1.42	0.993	66.27	1.28	0.990
	30	1.45	29.02	1.08	0.929	35.57	1.60	0.987
	50	1.97	20.96	1.66	0.985	10.95	2.00	0.997

Table 6
Comparison of the first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial Cr^{6+} concentration and Carbon *Ulva lactuca* concentrations

Parameter		First-order kinetic model				Second-order kinetic model		
Activated carbon concentration	Cr concentration (mg L^{-1})	q_e (experimental)	$K_1 (\times 10^3)$	q_e (calculated)	R^2	$K_2 (\times 10^3)$	q_e (calculated)	R^2
2 g L^{-1}	100	49.44	26.25	14.70	0.990	4.79	50.50	0.999
	150	71.16	13.82	14.32	0.971	3.87	71.43	0.997
	200	90.65	20.50	12.01	0.940	2.71	90.91	0.999
	250	115.01	16.35	14.57	0.987	1.45	114.94	0.997
3 g L^{-1}	100	33.03	39.15	8.64	0.992	11.39	33.67	1.000
	150	49.39	28.79	12.51	0.983	8.32	48.78	1.000
	200	61.46	24.18	8.26	0.975	7.67	62.11	0.999
	250	78.04	13.59	9.59	0.982	6.41	74.07	1.000
4 g L^{-1}	100	25.00	55.27	6.01	0.996	25.66	25.38	1.000
	150	37.37	30.17	9.03	0.992	8.76	38.02	0.999
	200	47.89	18.65	8.17	0.981	7.71	48.31	1.000
	250	61.28	12.44	10.12	0.990	5.72	60.98	0.998
5 g L^{-1}	100	20.00	102.94	5.94	0.993	52.59	20.20	1.000
	150	30.00	45.83	7.48	0.985	15.63	30.49	1.000
	200	38.73	27.87	8.08	0.963	9.36	39.22	0.999
	250	49.23	21.88	8.08	0.961	7.52	48.75	0.999
7 g L^{-1}	100	14.29	69.78	2.58	0.979	92.74	14.40	1.000
	150	21.43	69.32	5.23	0.987	36.03	21.69	1.000
	200	28.47	32.96	5.57	0.997	16.03	28.82	1.000
	250	35.71	24.87	6.46	0.993	14.89	35.46	1.000

can be applied for the entire adsorption process and confirms the chemisorption of Cr^{6+} onto dried green alga and its activated carbon (Figs. 14 and 15).

The half adsorption time ($t_{1/2}$), the time required to uptake half of the maximal amount of Cr^{6+} adsorbed at equilibrium, was calculated from the following equation:

$$t_{1/2} = \frac{1}{K_2 q_e} \quad (18)$$

3.7. Mechanism of adsorption

The prediction of the rate-limiting step is an important factor to be considered in the adsorption process. In the solid–liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or

intra-particle diffusion, or both. Thus, the uptake of chromium ions can be controlled by either the mass transfer through the boundary film of liquid or by the intra-particle mass transfer. The external mass transfer coefficient, β_L (cm s^{-1}) of Cr^{6+} in the liquid film boundary can be evaluated by using the equation proposed by Gupta et al. [49] as followed:

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + m K_a} \right) = \ln \left(\frac{m K_a}{1 + m K_a} \right) - \left(\frac{1 + m K_a}{m K_a} \right) \beta_L S_s t \quad (19)$$

where C_t and C_0 (both in mg L^{-1}) are the concentration of the sorbent at time t and time zero, respectively, K_a (L g^{-1}) is a constant defined as the product of the Langmuir constants. The

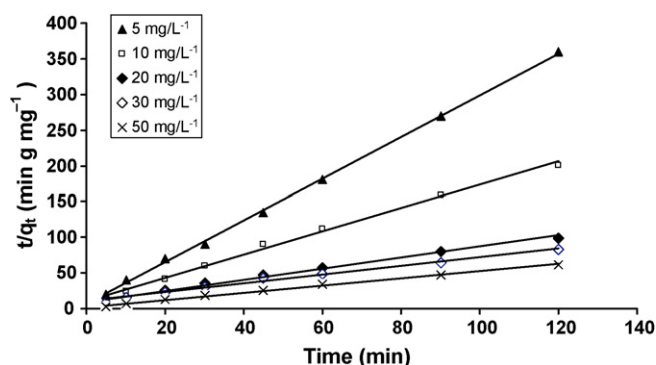


Fig. 14. Pseudo second-order sorption kinetics of Cr^{6+} onto dried green alga *Ulva lactuca* at various initial chromium concentrations.

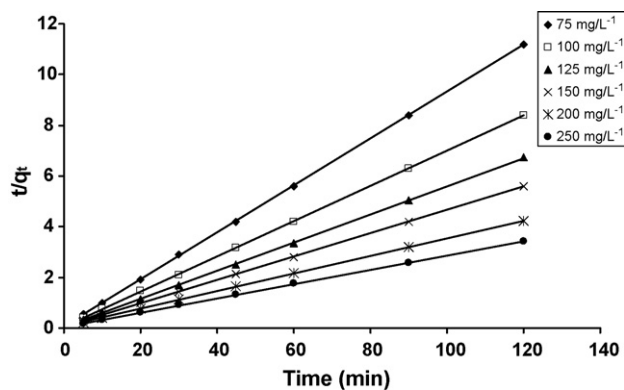


Fig. 15. Pseudo second-order sorption kinetics of Cr^{6+} onto activated carbon developed from dry green alga *Ulva lactuca* at various initial chromium concentrations.

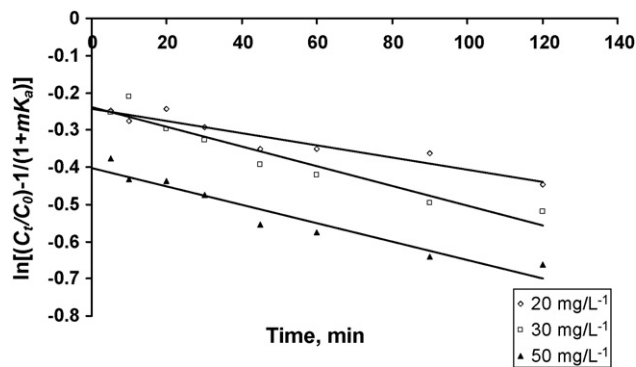


Fig. 16. Plot of mechanism of adsorption equation for the adsorption of Cr⁶⁺ onto dried green alga at pH 1.0.

m (g L⁻¹) and S_s (cm²) are the adsorbent mass and surface area, respectively.

The coefficient β_L can be calculated from the slope of the regression line of the plot of $\ln[(C_t/C_0) - (1/(1+mK_a))]$ versus t (Figs. 16 and 17). No linear relation is observed and the regression coefficient was low value for both green alga and its activated carbon. This result clearly indicates that the uptake rate is not controlled by mass transfer through a liquid film boundary such as convective mass transfer. The chromium ions are probably transported from the bulk of solution into the solid phase by intra-particle diffusion, which is often the rate-limiting step in many adsorption processes. However, at high adsorbent concentration the correlation coefficient R^2 was high and the adsorption shifted to particle diffusion at higher concentration of metal. The possibility of intra-particle diffusion is explored by using the following equation:

$$q_t = K_{dif}t^{1/2} + C \quad (20)$$

where C is the intercept and K_{dif} is the intra-particle diffusion rate constant. The values of q_t correlated linearly with values of $t^{1/2}$ (Figs. 18 and 19) and the rate constant K_{dif} directly evaluated from the slope of the regression line. The values of intercept C in Table 7 provide information about the thickness of the boundary layer, the resistance to the external mass transfer. The larger the intercept is the higher the external resistance. The R^2 values given in Table 7 are all close to unity, confirming that the

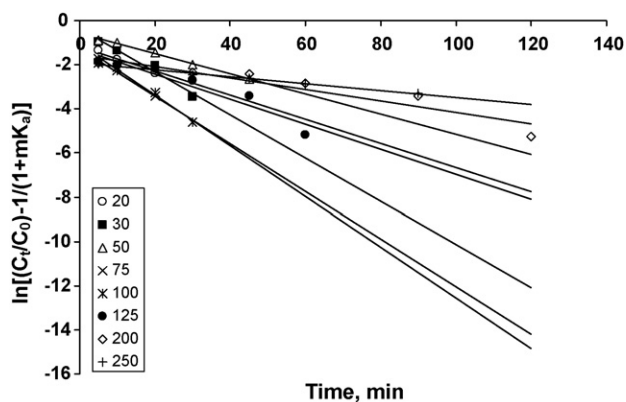


Fig. 17. Plot of mechanism of adsorption equation for the adsorption of Cr⁶⁺ onto activated carbon developed from dried green alga at pH 1.0.

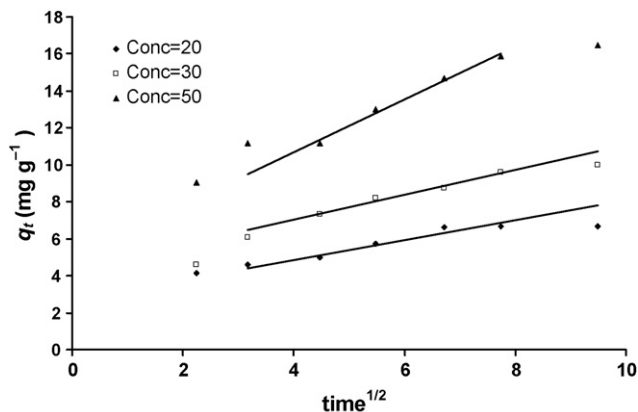


Fig. 18. Plots for evaluating intra-particle diffusion rate constant for adsorption of Cr⁶⁺ on dried green alga.

rate-limiting step is actually the intra-particle diffusion process. The intra-particle diffusion rate constant, K_{dif} , was in the range 0.053–0.285 and 0.72–1.60 mg g⁻¹ min^{-0.5} for dried green alga and its activated carbon, respectively. The linearity of the plots (Fig. 19) demonstrated that intra-particle diffusion played a significant role in the uptake of the chromium by activated carbon. This also confirms that adsorption of the chromium on the adsorbent was a multi-step process into the interior. If the steps are independent of one another, the plot usually shows two or more intersecting lines depending on the exact mechanism, the first one of these lines representing surface adsorption and the second one intra-particle diffusion. The absence of such features in the plots of activated carbon indicated that the steps were indistinguishable from one another and that the intra-particle diffusion was a prominent process right from the beginning of chromium–carbon interaction. However, still it would not give sufficient indication about which of the two steps was the rate-limiting step. Ho [50] has shown that it is essential for the q_t versus $t^{1/2}$ plots to pass through the origin if the intra-particle diffusion is the sole rate-limiting step. Since this was also not the case in both of Figs. 18 and 19, it may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the chromium–dried green alga and chromium–activated carbon interactions.

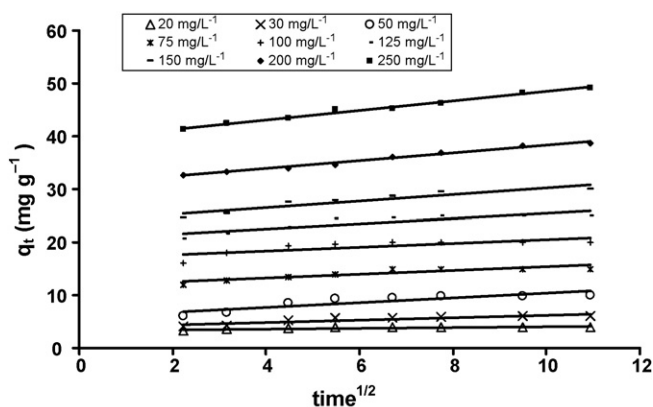


Fig. 19. Plots for evaluating intra-particle diffusion rate constant for adsorption of Cr⁶⁺ on activated carbon dried from dried green alga.

Table 7
Intra-particle diffusion models at pH 1 and different concentrations of Cr⁶⁺ and different concentration of dried green alga and its activated Carbon

Sorbents concentration (g L ⁻¹)	Cr concentration (mg L ⁻¹)	$t^{1/2}$ (min)	θ	D ($\times 10^8$) (cm ² S ⁻¹)	Intra-particle diffusion	
					K_{diff}	R^2
Dried green alga <i>Ulva lactuca</i>						
2	20	12.76	0.47	5.9	0.170	0.991
	50	3.59	0.51	20.9	0.285	0.962
3	20	6.43	0.39	11.7	0.133	0.977
	50	14.25	0.58	5.3	0.176	0.968
5	20	5.97	0.46	12.6	0.082	0.968
	50	12.09	0.59	6.2	0.246	0.963
10	20	16.77	0.80	4.5	0.129	0.982
	50	5.60	0.58	13.4	0.102	0.991
15	20	11.58	0.91	6.5	0.067	0.965
	50	4.79	0.59	15.6	0.053	0.983
Activated carbon developed from dried green alga <i>Ulva lactuca</i>						
2	125	3.83	0.960	19.59	1.60	0.977
	250	1.95	0.920	38.38	1.56	0.989
3	125	3.35	0.990	22.40	1.18	0.943
	250	0.73	0.936	102.27	1.07	0.979
4	125	2.43	1.000	30.81	0.72	0.953
	250	2.87	0.980	26.17	1.04	0.972
5	125	1.46	1.000	51.48	0.50	0.987
	250	2.67	0.985	28.07	0.89	0.989

3.8. Mass diffusivity

The mass diffusivity is mainly controlled by the surface properties of adsorbents. The transport of Cr⁶⁺ ions to the green algae and the pores of activated carbon particles, mass diffusivity, are calculated from the following equation:

$$t_{1/2} = \frac{0.03r_0^2}{D} \quad (21)$$

where D is the diffusivity (cm² s⁻¹) and r_0 (cm) is the radius of the adsorbent particle assumed to be spherical. The mass diffusivity is inversely proportional to the half-reaction time $t_{1/2}$. The values of r_0 are calculated for green alga and its activated carbon as 5×10^{-3} and 2×10^{-3} cm, the mass diffusivity increases from 4.5×10^{-8} to 20.9×10^{-8} for dried green alga and from 19.59×10^{-8} to 102×10^{-8} for activated carbon obtained from dried green alga *U. lactuca*.

3.9. Applicability

In order to study the effect of salinity and real wastewater on the capability of the green alga *U. lactuca* and its developed activated carbon to adsorb Cr⁶⁺ from its aqueous solution, a removal studies were achieved using synthetic seawater, natural seawater and real wastewater. Table 8 shows that the percentage of chromium removal from aqueous solution obtained by dissolving the chromium ion in distilled water was not affected by replacing the distilled water with synthetic seawater, natural seawater or wastewater for both of sorbents. A near 100% removal of toxic chromium from synthetic seawater, natural seawater and wastewater was detected for activated carbon developed from green alga *U. lactuca*. Moreover, the maximum adsorption capacities were not changed by the changing of the type of chromium solution. The presence of salt had no effect on the adsorption of chromium on both adsorbents, which leads to deduce that there was no interaction between the salt and the surface of the adsorbent nor the salt and the solute (Cr). Also,

Table 8
Data obtained for the adsorption of chromium from different solution using dried green alga *U. lactuca* and its activated carbon

Solution of chromium used	Dried green alga <i>U. lactuca</i>		Activated carbon	
	Removal (%)	Maximum capacity (mg g ⁻¹)	Removal (%)	Maximum capacity (mg g ⁻¹)
Distilled water	57.52	9.32	99.89	95.24
Synthetic seawater	59.55	10.5	100	96.52
Natural seawater	54.23	9.01	99.12	94.22
Wastewater	52.54	8.91	99.52	93.92

the high concentration of chromium ions may make them more preferable to be adsorbed by the adsorbents. On the other hand the real wastewater may contain very low concentrations from several metal ions that will not have much effect on the removal percentage of chromium ions. These results indicate that the two sorbents dried green alga and activate carbon of *U. lactuca* are applicable material for removal of Cr^{6+} from different types of aqueous solutions including wastewater.

4. Conclusion

A suitable indigenous dried green alga and its developed activated carbon have been identified as an effective adsorbent to remove Cr^{6+} ions from different types of aqueous solutions. The adsorption kinetic data can be described by the second-order kinetic models. The adsorption capacity is related to the pH of solution, and pH 1.0 is optimal. Furthermore, the equilibrium data of adsorption are in good agreement with the Langmuir's model. The dried green algae and its activated carbon are an inexpensive effective adsorbent for the removal of Cr^{6+} ions from aqueous solutions. The activated carbon developed from dried green alga biomass exhibited high biosorption capacity. The adsorption of Cr^{6+} was found to be pH dependent and maximum removal was observed at pH 1.0. The kinetics studies showed that both of *U. lactuca* and its activated carbon have poor fit with pseudo first-order kinetic equation while they have a well agreement with the pseudo second-order kinetic equation. Moreover, the intra-particle-diffusion was also investigated and the adsorption process was found to be controlled by the film diffusion at lower concentrations of the adsorbate and shifted to particle diffusion at high concentration. This process is environment friendly and reduces the huge amount of indiscriminate effluent discharges around the small industry concerns. It may provide an affordable technology for small and medium-scale industry.

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