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Biosorption of chromium (Cr) onto algae (Ulva.lactuca): application of isotherm and kinetic models.

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Abstract

The biosorption of chromium (VI) ions to *Ulva.lactuca* studied in a batch system with respect to the concentration, initial pH and initial metal ion concentration. The algal biomass exhibited the highest chromium (VI) adsorption capacity at 20°C, at the initial pH value of 3.0. Biosorption capacity increased from 0.70 to 1.08 mg g^{-1} with an increase in initial chromium (VI) concentration from 29.14; 38.28; 58.47 mgL^{-1}. Freundlich and Langmuir isotherm models were tried to represent the equilibrium data of chromium (VI) biosorption depending on concentration. Equilibrium data fitted very well to the Langmuir model in the studied concentration range of chromium (VI) ions at all the concentrations studied. The pseudo second-order kinetic model was also applied to experimental data assuming that the external mass transfer limitations in the system can be neglected and biosorption is sorption controlled.

Keywords: *Biosorption; chromium (VI); Ulva.lactuca; Isotherms; Kinetics*

1. Introduction

The increasing concentration of heavy metals in waters is manly due to effluent discharges from industries. Pollution of natural waters by metal ions has become a major issue all over the world because metal concentrations in waters often exceed the admissible values. Consequently, industries are required to diminish the contents of heavy metals in their effluents to acceptable levels. As a result, scientists are studying new and alternative technologies to remove trace metals from polluted waters [1] and industrial effluents. Hexavalent chromium species, Cr(VI), are highly toxic agents that act as carcinogens, mutagens, and teratogens in biological systems [2]. Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery. However, these technology processes have considerable disadvantages including incomplete metal removal, requirements for expensive equipment and monitoring system, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [3][4]. Many works describing metals biosorption on suspended biomass [5][6] and on fixed on different type of matrixes [9][8] among others have been published. The advantages of using dead aquatic algae for metal removal relays on its high efficiency as biosorbents, easy handling, no nutrient requirements, low costs, and they can be easily collected along the shore tide. The present work aims to investigate the biosorption potential of Ulva.lactuca [9] for removal of chromium (VI) from aqueous solution. Experimental parameters affecting biosorption process such as pH, contact time, biomass dosage and temperature were studied. The equilibrium biosorption data were evaluated by Langmuir and Freundlich isotherm models. The biosorption mechanism was also investigated in terms of pseudo-first-order and pseudo-second-order kinetics.

1.1. Kinetic modeling

In order to investigate the mechanism of biosorption and potential rate controlling step such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. When the biomass is employed as a free cell suspension in a well-agitated batch system, all the cell wall binding sites are made readily available for metal uptake so the effect of external film diffusion on biosorption rate can be assumed not significant and ignored in any engineering analysis [10][11]. The kinetic models included the pseudo first-order and pseudo second-order, equations can be used in this case assuming that measured concentrations are equal to cell surface concentrations. The first-order rate expression of Lagergren [12][13] based on solid capacity is generally expressed as follows:

$$Q_t = Q_m(1-e^{-K_{1,ad}t}) \qquad (1)$$

Where Q_m and Q_t are the amounts of adsorbed metal ions on the biosorbent at equilibrium and at time t, respectively (mgg^{-1}) and $k_{1,ad}$ is the rate constant of first-order biosorption (min^{-1}). After integration and applying boundary conditions, $t = 0$ to $t = t_{max}$ and $Q_t = 0$ to $Q_t = Q_m$; the integrated form of Eq. (1) becomes

$$\ln(Q_m - Q_t) = \ln(Q_m) - \frac{1}{2{,}303}.K_{1,ad}.t \qquad (2)$$

A straight line of $ln(Q_m–Q_t)$ versus t suggests the applicability of this kinetic model [12][14]. In order to fit Eq. (2) to experimental data, the equilibrium sorption capacity, Q_m, must be known. In many cases Q_m is unknown and as adsorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. For this reason it is necessary to obtain the real equilibrium sorption capacity, Q_m, by extrapolating the experimental data to $t = t_{max}$ or by using a trial and error method. Furthermore in most cases the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 10–30 min

of the sorption process. The pseudo second-order equation is also based on the sorption capacity of the solid phase. Contrary to the other model it predicts the behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step [12][15]. If the rate of sorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equation is expressed as:

$$\frac{dQ_t}{dt} = k_{2,ad}(Q_m - Q_t)^2 \quad (3)$$

Where $k_{2,ad}$ is the rate constant of second-order biosorption (g $mg^{-1}min^{-1}$). For the boundary which is the integrated rate law for a second-order reaction. Eq. (3) can be rearranged to obtain.

$$\frac{t}{Q_t} = \frac{1}{k_{2,ad}Q_m^2} + \frac{1}{Q_m}t \quad (4)$$

If second-order kinetics are applicable, the plot of t/Q_t against t of Eq. (4) should give a linear relationship, from which Q_m and $k_{2,ad}$ can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand [12][16].

1.2. Equilibrium modeling

1.2.1. Isotherm modeling

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Classical adsorption models (Langmuir and Freundlich) were used to describe the equilibrium between adsorbed metal ions on the algal cell (Q_m) and metal ions in solution (C_e) at a constant temperature. The Langmuir equation which is valid for monolayer sorption on to a surface a finite number of identical sites and is given by Eq. (5).

$$Q_e = \frac{Q_m.K_L.C_e}{1 + K_L.C_e} \quad (5)$$

Where Q_m $(mg.g^{-1})$ is the maximum amount of metal ion per unit weight of alga to form a complete monolayer on the surface bound at high C_e, and K_L $(l.mg^{-1})$ is a constant related to the affinity of the binding sites.Q_m represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. Q_m and K_L can be determined from the linear plot of C_e/Q_e versus C_e [17][18]. .

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by Eq. (6).

$$Q_e = K_F.C_e^{1/n_F} \quad (6).$$

Where K_F and n_F are the Freundlich constants characteristic of the system. K_F and n_F are indicators of adsorption capacity and adsorption intensity, respectively. Eq. (2) can be linearized in logarithmic form and Freundlich constants can be determined. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model [17][18].

2. Materials and methods

2.1. Algal biomass preparations

Marine green algae (ulva-lactuca) were collected at room temperature 22 ° C (on) at the Moroccan Atlantic coast at the level of the beach of Rabat (34 ° 03' North latitude, and 6 ° 46' West longitude at an altitude of 79 m). These algae have been rinsed in sea water and polyethylene plastic bags previously rinsed with distilled water acidified to pure nitric acid, upon arrival at the laboratory, the algae are again rinsed with distilled water.

For biosorption studies, the algal biomass was washed in running tap water followed by distilled water 4–5 times, for removing from its surface interfering ions and other undesired materials, such as, sand particles and debris. The biomass was then eventually kept on a filter paper to reduce the water content. The biomass was then sun dried for four days followed by drying in an oven at 70 °C for 48 h and subsequently, it was ground on an agate stone pestle mortar and sieved, to select the particles between <1000 µm for use.

2.2. FTIR analysis

FTIR spectroscopy was used to confirm the presence of the functional groups in samples and to observe the chemical modification after chromium biosorption. Infrared spectra were recorded in the 4000–400 cm^{-1} region using a Fourier Transform infrared Spectrometer, JASCO model 4000.

2.3. Batch biosorption

The stock solution of Cr (VI) at the concentration of 58.47mgL^{-1} was prepared using $K_2Cr_2O_7$ and deionized water. This stock solution was used for the preparation of test solutions by dilution. The initial pH was controlled with NaOH 0.1M and HCl 0.1M. The biomass in amount of 2g was added to the solution in order to analyze his influence over biosorption process. Then, the suspension was maintained under agitation on a reciprocal shaker at 500 rpm for 100min. After this time, the equilibrium pH was measured and the chromium solution was filtrated on a cellulose filter membrane (pore size 4.5µm). Next, the filtrate was acidified with HNO_3 and analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometry) in order to determine the final metal concentration.

The adsorption capacity of the gravel was determined by following the method used for soil adsorption capacity [19]. The experiment adsorption capacity was calculated with the following equation [19][20]:

$$Q_t = (C_0 - C_t)\frac{V_l}{M_S} \quad (7)$$

Where Q_t is adsorption capacity; C_t is the final concentration; C_0 is the initial concentration; V_l is the volume of the solution; M_s is the mass of the gravel.

The percentage of removed Cr(VI) ions in solution was calculated using following equation,

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (8)$$

3. Results and Discussions

3.1. FTIR analysis

The FTIR spectra of *Ulva.lactuca* with and without metal-loaded are shown in Fig. 1b. The carboxyl ions give rise to two bands: a strong asymmetrical stretching band at 1628 cm^{-1} and a weaker symmetrical band at 1416 cm^{-1}. When the biomass was loaded with the chromium ion, the strong asymmetrical stretching band was shifted to 1603 cm^{-1}, so it led to the conclusion on the participation of carboxyl groups in the metal uptake.

The FTIR analysis also shows broad bands at 3280 cm^{-1} that represent bounded single bond OH and single bond NH groups (very involved in the biosorption process). The band at 1028 cm^{-1} was due to the single bond C single bond O stretching of alcoholic groups. On the other hand, single bond CH stretch could be ascribed to the band that appeared at 2920 cm^{-1}. The bands at 1224 cm^{-1} that represent single bond SO_3 stretching, mainly present in sulfonic acids of polysaccharides, such as fucoidan [21][22][23], and there is a difference before and after biosorption that could implicate that these groups were involved in metal complexation by Ulva.lactuca.

At the same time, the band at 1535 cm^{-1} in the spectrum of native *Ulva.lactuca* disappears in the spectrum of Cr (VI)-loaded Ulva.lactuca. This behavior reflects the interaction between the amino groups and the metal ions [22][23].

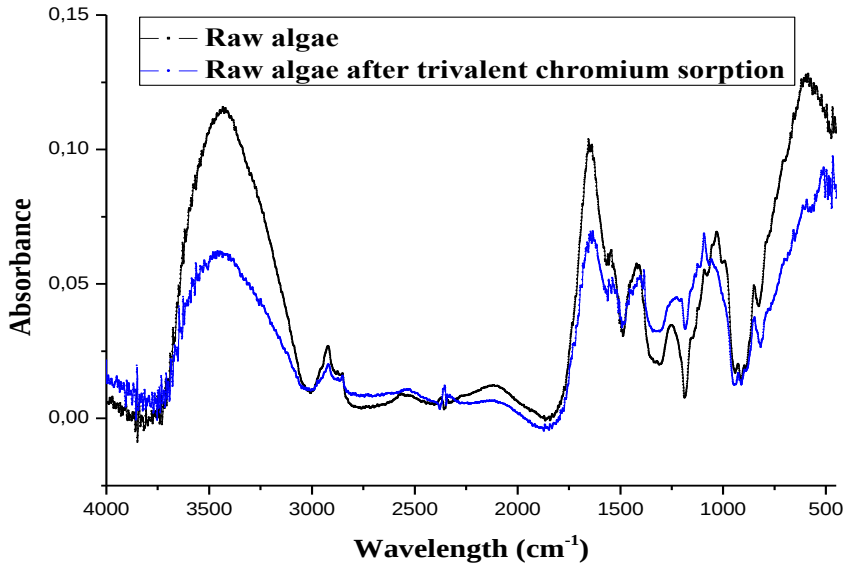

Fig. 1. FTIR spectra of *Ulva.lactuca* before and after Cr (VI) biosorption.

3.2. Effect of pH on Cr (VI) biosorption

pH is one of the most important parameter which affects any biosorption system [24]. Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the adsorbent. Hence, metal sorption is critically linked with pH. Not only different metals show different pH optima for their sorption but may also vary from one kind of biomass to the other [25]. The pH of the system determines the adsorption capacity due to its influence on the surface properties of the WAQI and different ionic forms of the chromium solutions. Change of the adsorption capacity of Cr(VI) on Ulva.lactuca with pH is shown in Fig. 2. From Fig. 2, it was observed that the maximum adsorption occurred at pH 2.0. Almost 96.40% of Cr(VI) removal was observed at this pH at 29.14 mg L−1 Cr(VI) concentration. Dominant form of Cr(VI) at initial pH of 2

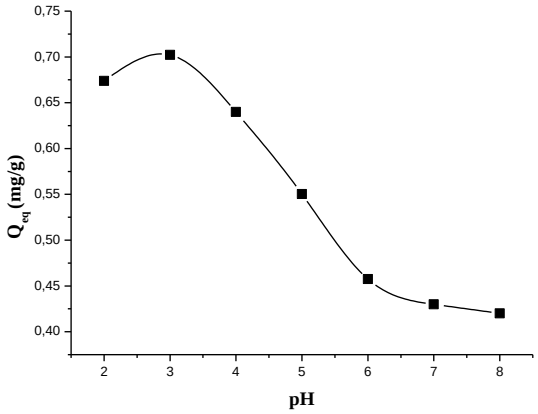

Fig. 2. Effect of pH on the adsorption of Cr (VI) on the *Ulva.lactuca* algae.

Dominant form of Cr(VI) at initial pH of 2 is $HCrO^{4-}$ [25] and increasing the pH will shift the concentration of $HCrO^{4-}$ to other forms, CrO_2^{2-} and $Cr_2O_7^{2-}$. The Ulva.lactuca biomass, which serve as a matrix of –COOH and NH_2 groupe, which in turn takes part in binding of metal ions. The interaction of the matrix with the Cr ions is determined by the extent of protonation of the cell wall functional groups, which in turn depend upon the solution pH. The increased binding of Cr (VI) ions at acid pH can explained due to the electrostatic binding to positively charged groupe such as amines in the Ulva.lactuca cell wall. Adsorption of hexavalent Cr(VI) varies as a function of pH, with H_2CrO_4, $HCrO^-_4$, $Cr_2O^{2-}_7$, and CrO^{2-}_4 ions present as dominant species. At pH acid, $HCrO^-_4$ was the dominant species.

3.3. Effect of contact time and concentration

Next the effect of initial chromium (VI) ion concentration was studied. This was carried out by changing the initial chromium (VI) ion concentration from 29.14 mgL^{-1} to 58.47 mgL^{-1} for the algae. The equilibrium adsorption of chromium (VI) ion and yield is shown in Table 2.

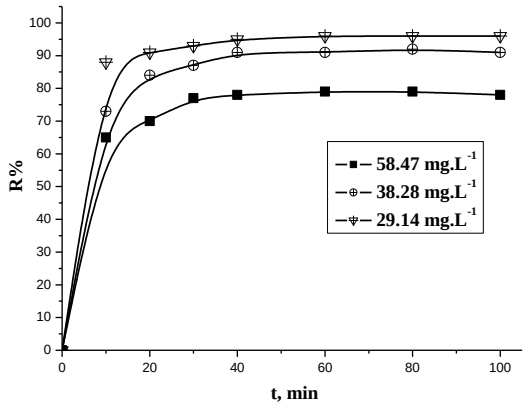

Fig.3. Effect of initial due concentration on biosorption of Cr (VI) onto biomass ulva.lactuca, pH=2, T°=20°c, M_{algae}=2g.

Fig. 3 shows the comparative data of the effect of contact time on the extent of biosorption of Cr (VI) on the biomass at 29.14 to 58.47mgL^{-1} initial chromium concentration at pH 2.0 and temperature 20°C for the algae biomass. It has been observed that the metal adsorption rate is high at the beginning for the algal biomasses and then high slowly till saturation levels were completely reached at equilibration point (60 min). The initial rapid phase may involve physical adsorption or ion exchange at cell surface and the subsequent slower phase may involve other mechanisms such as complexation, micro-precipitation or saturation of binding sites. An increase in adsorption was observed from (96%) 0.72 to (79%) 1.08 mg g^{-1} for raw alga with 29.14; 38.28 and 58.47 mg L^{-1} initial concentration of Cr (VI). Note that there are several parameters, which determine the adsorption rate such as structural properties of both sorbate and biosorbent (e.g. protein and carbohydrate composition and surface charge density, topography and surface area). The amount of biosorbent, initial concentration of metal ions and existence of other ions (which may compete with the ions of interest for the active biosorption sites) also affect the adsorption rate.

3.4. Biosorption kinetic modeling

In order to examine the controlling mechanism of biosorption process such as mass transfer and chemical reaction, kinetic models were used to test the experimental data. The Lagergren first-order and the Ritchie second-order kinetic

models [16], were applied for the biosorption of Cr (VI) ions on the biomass. The comparison of experimental biosorption capacities and the theoretical values estimated from the above two equations and are presented in Table 1. According to the values in Table 2, the correlation coefficients for the linear plots of t/Q_t against t for the second order equation were greater than 0.99 for the algae biomass for a contact time of 100min (Fig. 4a and 4b). The theoretical Q_m values for all the studied chromium (VI) ion were very close to the experimental Qm values in the case of second order kinetic model. These results suggest that the second-order mechanism is predominant and the biosorptions may be the ratelimiting step that controls the biosorption process [15]. On the other hand, the theoretical Qm values estimated from the first order kinetic model gave significantly different values compared to experimental values, and the correlation coefficients were also found to be slightly lower. These results showed that the biosorption systems were not described by the first order kinetic model.

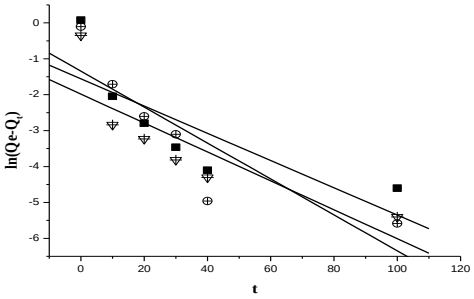

Fig. 4a. Pseudo first-order sorption kinetics of Cr (VI) onto green alga *Ulva lactuca* at various initial chromium concentrations.

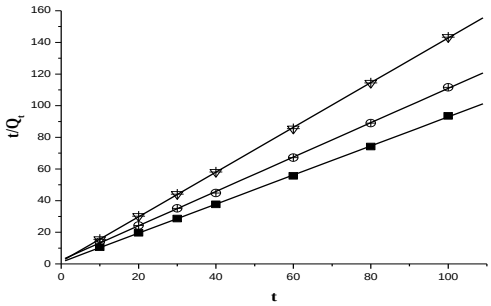

Fig. 4b. Pseudo second-order sorption kinetics of Cr (VI) onto green alga Ulva.lactuca at various initial chromium concentrations

Table 1. Comparison of the first and second-order adsorption rate constants at different concentrations of Cr (III).

Metal ion			First-order kinetic model			Second order kinetic model		
	C_0(mg/l)	$Q_{m,exp}$ (mg/g)	Q_m (mg/g)	$K_{1,ad}$	R^2	Q_m (mg/g)	$K_{2,ad}$	R^2
Cr(II)	58,47	1,08	0,21	0,09	0,640	1,09	0,77	0,999
	38,28	0,88	0,26	0,12	0,764	0,92	0,84	0,999
	29,14	0,72	0,12	0,09	0,704	0,71	1,31	0,999

3.5. Adsorption isotherms

Modeling of adsorption isotherms The linearized Freundlich and Langmuir adsorption isotherms of cadmium (II) ions obtained at the temperatures of 20, 35 and 43°C are given in Figs. 5a and 5b. The Freundlich and Langmuir adsorption constants evaluated from the isotherms at different temperatures with the correlation coefficients presented in Table 3. As seen from the tables, there is a very high regression. Correlation coefficients (>0.99) were found at the all temperatures studied. The higher correlation coefficients show that both the Freundlich and Langmuir models are very suitable for describing the biosorption equilibrium of chromium (VI) by the algal cells in the studied concentration range. An adsorption isotherm is characterized by certain constants the values of which express the surface properties and affinity of the sorbent and can also be used to find the adsorptive capacity of biomass for the chromium (VI). From Table 2, the magnitude of K_F and n_F; the Freundlich constants, showed easy uptake of chromium (VI) from wastewater with a high adsorptive capacity of the dried Ulva-lactuca, especially at 43°C. The highest K_F and n_F values were found as 0.31 and 2.06, respectively, at this temperature value. Table 3 also indicates that n is greater than unity, indicating that chromium (VI) ions are favourably adsorbed by dried *Ulva-lactuca* at all the temperatures studied. The values of K_F and n determined from the Freundlich plots decreased with the raise in temperature. Values of Q_m and K_L for different temperatures have been calculated from the Langmuir plots in Fig. 5a and 5b the results are also tabulated in Table 2. The maximum capacity Q_m determined from the Langmuir isotherm defines the total capacity of the biosorbent for chromium (VI) (4,02 mg/g). The adsorption capacity of chromium (VI) also increased with the increasing temperature.

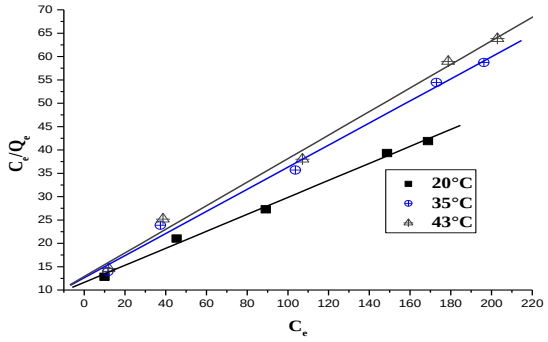

Fig. 5a. Langmuir isotherm obtained using the linear method for the sorption of chromium onto green alga Ulva.lactuca.

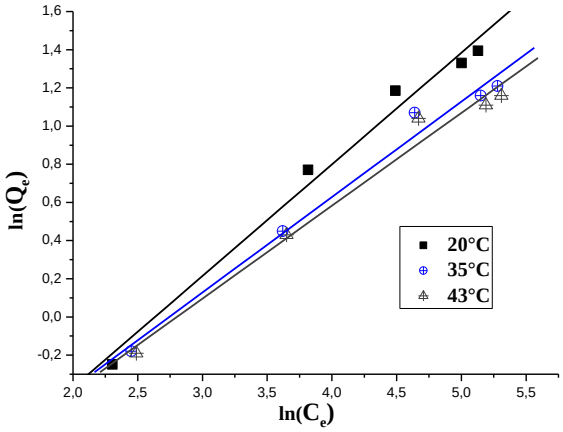

Fig. 5b. Freundlich plot for chromium adsorption onto dried green alga Ulva.lactuca.

Table 2: A comparison of the Freundlich and Langmuir adsorption constants obtained from the Freundlich and Langmuir adsorption isotherms of chromium(VI) ions at different temperatures.

t°(°c)	LANGMUIR		**FREUNDLICH**	
	Linear expression	Model parameters	Linear expression	Model parameters
20	y = 0, 25 x +11,64	k_L = 0,021 Q_m=4,02(mg.g−1) R^2=0.995	y = 0,58x -1,54	k_F=0.43 n_F=1.71>1 R^2 = 0,985
35	y = 0,26x + 12,63	k_L =0,020 Q_m=3,91(mg.g−1) R^2 = 0,992	y = 0,50x -1,37	k_F=0.31 nF=2.00 >1 R^2 = 0,985
43	y = 0,26x + 12,90	k_L =0,021 Q_m=3,82(mg.g−1) R^2 = 0,992	y = 0,49x - 1,37	k_F=0.31 n_F=2.06 >1 R^2 = 0,982

4. Conclusion

This study focused on the biosorption of chromium (VI) onto *Ulva.lactuca* algal biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time and temperature, were effective on the biosorption efficiency of chromium (VI). Biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The biosorption capacity of *Ulva.lactuca* for chromium (VI) was found to be 1.08 $mg.g^{-1}$ at pH 3 and 2g biomass dosage, 60 min equilibrium time and 23 °C. Kinetic examination of the equilibrium data showed that the biosorption of chromium ions onto *Ulva.lactuca* followed well the pseudo-second-order kinetic model. Based on all results, it can be also concluded that the *Ulva.lactuca* is an effective and alternative biomass for the removal of chromium (VI) from an aqueous solution because of its considerable biosorption capacity, being of its natural, renewable and thus cost-effective biomass.

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