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The residue of alginate extraction from *Sargassum muticum* (brown seaweed) as a low-cost adsorbent for hexavalent chromium removal from aqueous solutions

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ABSTRACT

The residue of alginate extraction from the invasive brown seaweed *Sargassum muticum* harvested from the Moroccan Atlantic coast was tested as biosorbent for hexavalent chromium removal. The results revealed that biosorption of Cr(VI) was highly pH dependent, favoring higher chromium removal at very low pH values. Langmuir and Freundlich adsorption isotherms were applied to fit the experimental data. The results demonstrated that the equilibrium data were well fitted by Langmuir isotherm model. The maximum uptake capacity for Cr(VI) was about 34.8 mg/g. The kinetic studies showed that biosorption process can be described perfectly by a pseudo-second-order model. Functional groups on the biomass surface, responsible of adsorption phenomenon, have been successfully evidenced by the use of attenuated total reflectance Fourier transform infrared spectroscopy. The results gave evidence that the residue of alginate extraction from *S. muticum* could be an appropriate low-cost biosourced material for removing hexavalent chromium from aqueous solutions.

Keywords: Biosorption; Hexavalent chromium; Alginate extraction residue; *Sargassum muticum*; Seaweed

1. Introduction

Heavy metals refer to metallic chemical elements that have a relatively high density and are toxic or poisonous at low concentrations to living organisms. These pollutants are non-degradable and persistent in the environment. Heavy metal ions are widely discharged without adequate treatment into the environment from a variety of industrial activities [1]. Due to their toxic impact and accumulation tendency throughout the food chain, the heavy metal pollution represents a serious problem with dramatic ecological and human health consequences [2]. Chromium is one of the most common and highly toxic pollutants released into natural waters at elevated concentrations from industrial effluents worldwide [3]. The demand of chromium has been increasing globally due to its extensive use in various metallurgical, chemical, and leather tanning industries because of its various physicochemical properties. The corrosion resistance property of chromium expanded its application in hardened steel, stainless steel and alloys. It is also used in electroplating to produce a hard, shining surface and prevent corrosion [4,5]. Chromium is a heavy metal with oxidation states ranging from −2 to +6; however, this metal is only stable under the +3 and +6 oxidation states [6]. Hexavalent chromium (Cr(VI)) is more mobile and toxic than trivalent chromium (Cr(III)) [7]. In contact with the human cells, the Cr(VI) is rapidly reduced to Cr(III), and during the reduction process, reactive oxygen and other free radicals can be created inside the cells, which causes DNA damage. The later was supposed to be the origin of cancer initiation [4]. Therefore, in order to protect public health, the removal of

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Cr(VI) from industrial effluents is necessary before their discharge into the receiving aquatic environment.

Removal of heavy metals, especially Cr(VI), from aqueous solutions and wastewater has been challenged for a long term. Various strategies are potentially applied in wastewater treatment including traditional and separation processes, for the treatment of chromium-contaminated wastewaters such as electrochemical method, reverse osmosis, chemical precipitation, membrane filtration, ion exchange, liquid extraction, electrocoagulation, electrodialysis, evaporation and adsorption on activated carbon. Nevertheless, these technologies are often very costly, requiring high energy input or large quantities of chemical reagents [8,9]. Biosorption has emerged as an alternative and sustainable strategy for the remediation of chromium containing wastewaters as it is low cost, effective, regenerative and eco-friendly process [10]. Different types of industrial and agricultural biowastes were investigated as biosorbents of heavy metals such as rice husks [11], orange waste [12], crab shells [13], olive stone [14], eggshell [15], sugarcane bagasse [16], wheat straw [17] and tea waste [18]. New approaches developing various microbial sources, seaweed and aquatic plant-based adsorbents, as cost-effective and efficient biosorbents have also been reported [19,20].

The use of natural materials for Cr(VI) is becoming a concern for scientists and environmentalists. Among them, seaweeds have proven to possess high metal binding capacities [21]. They may be involved in clean and eco-friendly methods based on phycoremediation. Brown seaweed contains alginate biopolymer, the main component of its cellular wall, responsible for its mechanical resistance and significant sorption capacity [22,23]. The residues from alginate extraction contain many of the constituents of the raw seaweed, presenting, therefore, potential for the sorption of heavy metals [24]. Therefore, the use of this kind of waste as a biosorbent seems to be economically interesting.

The introduced brown seaweed *Sargassum muticum* invaded the Atlantic coast of Morocco with large populations esteemed at 1,500 tons dry weight annually. *S. muticum* provide alginate yield about 25.6% dry weight that correspond approximately to an annual production of 375 tons of alginate and 1,125 tons of waste [25]. In this context, the present study investigates the potential use of the waste of alginate extraction from this invasive seaweed in Morocco as biomaterial for hexavalent chromium removal.

2. Material and methods

2.1. Extraction of alginate and preparation of the biosorbent

S. muticum was harvested at low tide in spring 2015 from the Northwestern Atlantic coast of Morocco at the south of El Jadida city (33°14′47.5″ N 8°32′31.9″W; Fig. 1). The samples were washed and then dried in an oven at 60°C for 24 h. The extraction of alginate was performed according to the method described by Calumpong et al. [26]. Dried algal biomasses were soaked in 2% formaldehyde during 24 h at room temperature, washed with water and then added to 0.2 M HCl and left for 24 h. Then after, the sample was washed again with distilled water before extraction with 2% sodium carbonate during 24 h. The soluble fraction was collected by centrifugation, and the polysaccharides were precipitated by three volumes of ethanol. The residue of this extraction was protonated by adding 0.1 mol/L HCl under constant shaking until stabilization at pH 5. The acidified biomass was rinsed with deionized water and then dried in an oven at 60°C and then grounded to be used in biosorption experiments.

2.2. Batch adsorption studies

The biosorption of Cr(VI) on the residue of alginate extraction from *S. muticum* was investigated in batch mode. Different parameters were studied such as the effect of solution pH (range 1–9), biosorbent dose (0.01–1.5 g/100 mL), contact time (5–300 min) and initial chromium concentration (50–200 mg/L). Adsorption experiments were carried out in 250 mL volumetric flask using 100 mL Cr(VI) solution with the required amount of adsorbent. The mixtures were agitated by mechanical stirrer. The sample was collected and centrifuged at 4,000 rpm during 10 min. The supernatant was collected, and the concentration of remaining Cr(VI) ions was determined using the standard colorimetric method [27] based on the reaction established between hexavalent chromium and 1,5-diphenylcarbazide in acid solution. A red-violet complex is formed and measured spectrophotometrically at 540 nm

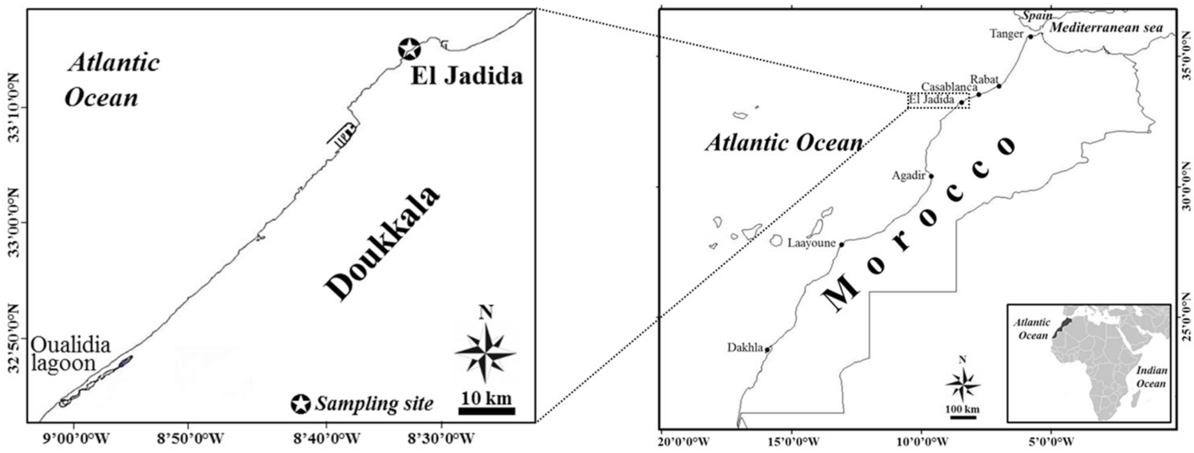

Fig. 1. Sampling site (✪) of *Sargassum muticum*.

using a Metash 5200 spectrophotometer. The pH value at point of zero charge (pH_{pzc}) was determined by fast alkalimetric titration according to Fiol and Villaescusa [28] modified protocol: 1 g of biomass was put into contact with 50 mL of 0.01 M KNO_3 solution at different pH values (1–12). The suspensions were agitated for 24 h. The value of pH_{pzc} has been determined from the curve that cuts the pH_i line of the plot $pH_f - pH_i$ vs. pH_i, where pH_i and pH_f are, respectively, the initial and final pH values of KNO_3 solutions.

2.3. Characterization of biomass

Morphological characterization and chemical elemental composition of the biosorbent were performed using scanning electron microscopy (SEM) Hitachi S-3400N equipped with an energy-dispersive X-ray spectroscopy (EDS; Noran with a silicon drift detector). Specimens for SEM–EDS characterizations were metalized by sputtering. The energy of the acceleration beam employed was 15 kV.

The identification of functional groups on the biosorbent surface was performed by infrared spectroscopy. The samples were dried at 50°C for 3 h in an oven before analysis. The infrared spectra were recorded with Thermo Scientific Nicolet iS50 FT-IR in an attenuated total reflectance (ATR) mode. A total of 32 scans were averaged for each sample at 4 cm^{-1} resolution, and the infrared spectra were then plotted and analyzed with the OMNIC 9.1 software.

3. Results and discussion

3.1. Biosorbent characterization

The chemical elemental composition and microstructure of protonated residue before and after biosorption of chromium were analyzed by SEM–EDS. The SEM micrographs (Fig. 2) show irregular and porous structure on the surface of the biosorbent. EDS spectra (Fig. 2) illustrate the presence of Mg, Na, Al, Si, S, Cl, K and Ca. Those ions are considered as common elements of seaweeds [24,29]. Calcium is the major element present in the biosorbent with a concentration of about 33%. EDS spectra do not show the characteristic signal of chromium for biosorbent before adsorption (Fig. 2(A)). After sorption equilibrium, chromium is detected in the biomass (Fig. 2(B)). These results are similar to those reported in the literature [4,24].

The changes in the functional groups and surface properties of the biosorbent can be confirmed by ATR Fourier transform infrared (ATR-FTIR) analysis. Infrared analysis before and after adsorption of Cr(VI) onto protonated residue of alginate extraction could lead to a shift or reduction in bands and also extinction of some peaks, suggesting the contribution of some functional groups such as –OH, –NH and C–O groups in Cr(VI) adsorption. Fig. 3 shows that adsorption of Cr(VI) onto biomass leads to significant spectral changes. This suggests that there was a metal-binding process taking place on the surface of the biomass used. FTIR spectra show broad band at 3,360 cm^{-1} that represent bounded OH and NH groups [4]. The intensity of this band decreases considerably due to the reaction between the biomass and hexavalent chromium. The bands located in the wave number region 2,800–3,000 cm^{-1} can be attributed to aliphatic methylene–CH stretch [30]. The carboxyl ions are detected due to two bands: an asymmetrical stretching band at 1,632 cm^{-1} and symmetrical band at 1,415 cm^{-1} [29]. After Cr(VI) biosorption, the residue was loaded with the chromium ion, and the asymmetrical stretching band was shifted to 1,604 cm^{-1}. Therefore, it can be suggested that the carboxyl groups are involved in the metal uptake. The band located at 1,740 cm^{-1} can be assigned to C=O stretching [4]. The band centered at 1,509 cm^{-1} could be due to the stretching band of –NH [31], which disappears after contact with Cr(VI). This behavior indicates the interaction between the amino groups and the chromium ions [32]. The band located at 1,260 cm^{-1} can be attributed to $–SO_3$ stretching, mainly present in sulfonic acids of polysaccharides, such as fucoidan [33]. The small displacement in this band frequency from 1,260 cm^{-1} to 1,247 cm^{-1} can be due to the binding of metal ions to the sulfate group [34]. The band situated at 1,131 cm^{-1} is due to the –C–O stretching. These results related to Cr(VI) adsorption are coherent to those observed in the literature [29,34–36].

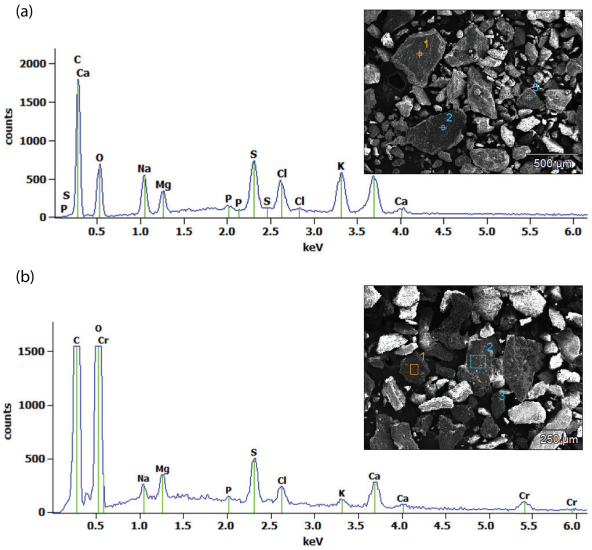

Fig. 2. SEM–EDS analysis of the residue of alginate extraction before (a) and after (b) hexavalent chromium biosorption.

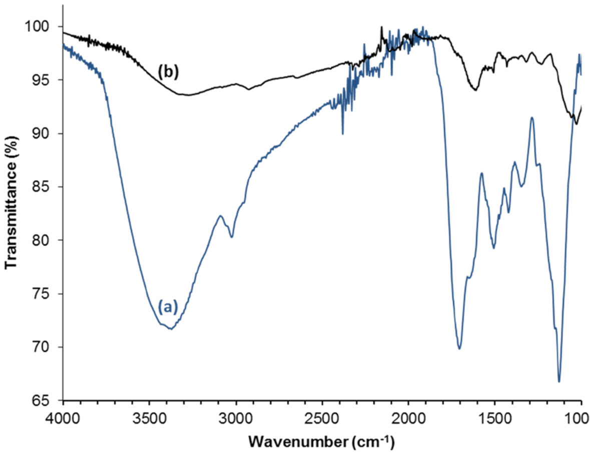

Fig. 3. FTIR spectra of protonated residue of alginate extraction from *S. muticum* before (a) and after (b) Cr(VI) biosorption.

3.2. Effect of pH

The effect of pH on chromium removal by the residue of alginate extraction is presented in Fig. 4. Obtained results showed that Cr(VI) removal is more favored at very low pH values. The mechanism by which metal ions are adsorbed onto the surface of the adsorbent has been a matter of considerable debate. Different mechanisms, such as electrostatic forces, ion exchange and chemical complexation [37], must be taken into consideration while examining the effect of pH on adsorption efficiency. One of the commonly proposed mechanisms is electrostatic attraction/repulsion between adsorbent and adsorbate. Many studies have claimed that Cr(VI) can be removed from the aqueous phase through an adsorption mechanism, whereby anionic Cr(VI) ion species bind to the positively charged groups of nonliving biomass [38,39]. In this study, the mechanism of hexavalent chromium removal by the residue of alginate extraction seems to be electrostatic attraction process where maximum metal adsorption at pH 2 seems to be due to a net positive charge on algal surface. At low pH values, chromium ions ($HCrO_4^-$ and $Cr_2O_7^{2-}$) have a tendency to bind the protonated active sites of the biosorbent [40]. But as pH of the solution increases, algal cell wall components becomes more and more negatively charged due to functional groups, which repulse the negatively charged chromate ions thereby affecting Cr(VI) adsorption on the algal surface [7]. To verify the surface charge of biosorbent at different pH value, the pH_{pzc} was determined according to Fiol and Villaescusa [28] modified protocol. The pH_{pzc} corresponds to the pH value of the solution, when the surface charge density is equal to zero. The obtained pH_{pzc} is about 5.9. It means that at pH values <5.9, the surface area of the alginate residue is positively charged and, at pH 1–2, strongly attracts the negatively charged chromium species.

3.3. Effect of biosorbent dose

To test the effect of biosorbent dose, different amounts of biosorbent, ranging from 0.01 to 1.5 g, were suspended in 100 mL Cr(VI) solution (50 mg/L) under optimized conditions of pH and for 4 h of contact time. The effect of adsorbent dose on the removal of metal for the treated alginate extraction residue is shown in Fig. 5. The amount of adsorbent significantly influences the extent of Cr(VI) adsorption. The biosorption of metal ions increases with increasing biomass dosage. The percentage of chromium elimination increases with adsorbent dose and reaches a value of 100% at an adsorbent dose of 1 g/100 mL. This is mainly attributed to the increase of the number of available adsorption sites by increasing the adsorbent dose.

3.4. Effect of initial chromium concentration

The initial metal ion concentration strongly influences the metal uptake from aqueous solutions by adsorbents. The biosorption of Cr(VI) by the studied protonated residue was carried out at different initial Cr(VI) concentrations, and the results are presented in Fig. 6. As it can be seen, the removal percentage decreases from 100% to 9.5% with an increase in the Cr(VI) concentration from 50 to 200 mg/L. Similar results

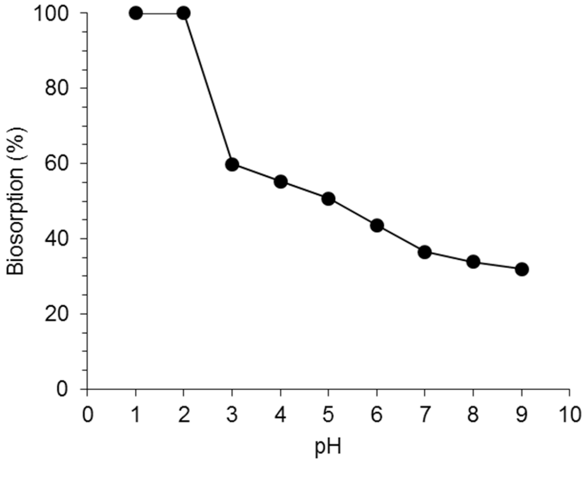

Fig. 4. Effect of pH on the Cr(VI) adsorption onto the residue of alginate extraction.

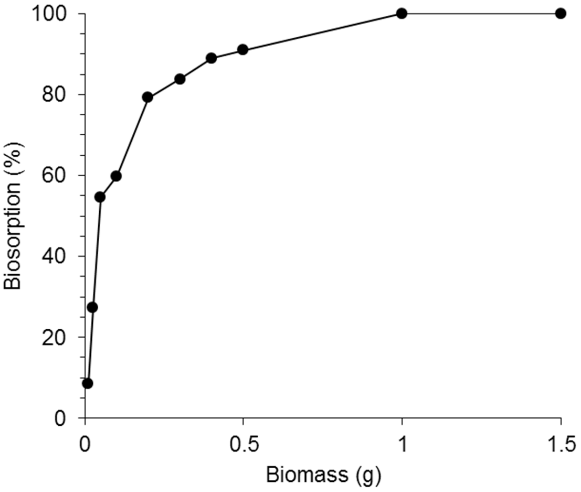

Fig. 5. Effect of biomass dosage on the adsorption of Cr(VI) onto the residue of alginate extraction.

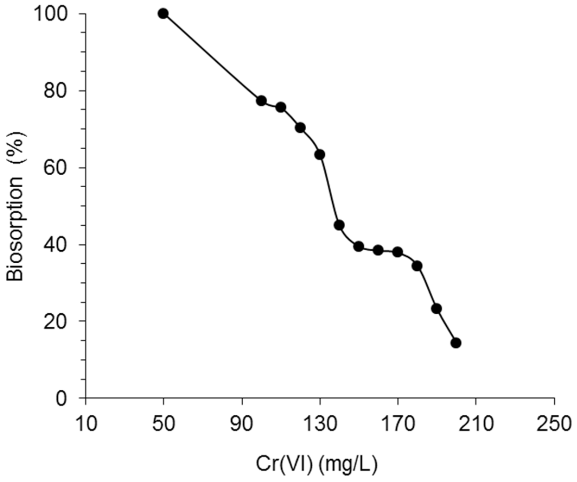

Fig. 6. Cr(VI) removal by the residue of alginate extraction as a function of initial metal concentration.

were obtained with other adsorbent/adsorbate system. Metal ions are adsorbed on active sites of the surface of the adsorbent while with the increase of metal ion concentration all active sites are saturated and no more vacant sites are available [41].

3.5. Kinetic study

In order to establish the optimal contact time between the biosorbent and chromium solution, adsorption capacities of chromium ions were measured as function of time (Fig. 7). The removal efficiency of Cr(VI) by the residue of alginate extraction from *S. muticum* increases with the increase of contact time and then tends to become constant. Fig. 7 *reveals* that Cr(VI) removal is relatively fast in beginning achieving about 38% in 30 min. After 60 min of contact time, the adsorption process becomes very slow, and the equilibrium is achieved at 240 min; the equilibrium time is better than that obtained in some earlier study for the elimination of Cr(VI) by raw biomass of *S. muticum* collected from the north coasts of Cuba [29] and chemically modified *Sargassum* sp. collected from Singapore West Coast [34].

The kinetic data were simulated by pseudo-first-order and pseudo-second-order kinetic models. The kinetic data fitted according to a pseudo-first-order kinetic model using Eq. (1) [42] are presented in Fig. 8:

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1.t}{2.303} \tag{1}$$

where Q_e and Q_t are the biosorption capacity (mg.g^{-1}) at equilibrium and time t, respectively, and K_1 is the constant rate (L.min^{-1}) of pseudo-first-order kinetic model, determined by linear regression using log(Q_e – Q_t) vs. time (min) plot.

The kinetic data fitted according to a pseudo-second-order kinetic model using Eq. (2) [43] are presented in Fig. 9:

$$\frac{t}{Q_t} = (\frac{1}{Q_e})t + \frac{1}{K_2 Q_e^{\ 2}} \tag{2}$$

where t is the time (min); Q_t is the uptake capacity at a given time t (mg.g^{-1}); Q_e is the equilibrium constant of sorbate ion on surface of the biosorbent (mg.g^{-1}); and K_2 is the constant rate of pseudo-second-order adsorption (g.mg^{-1}.min^{-1}) determined by plotting t/Q_t against t.

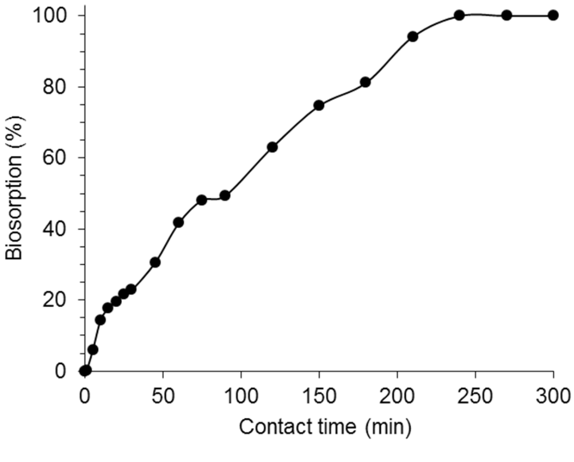

Fig. 7. Effect of contact time on the adsorption of Cr(VI) on the residue of alginate extraction.

The calculated model parameters values are listed in Table 1. The obtained results showed that the pseudo-second-order kinetic has a correlation coefficient (R^2 = 0.98) higher than that of the pseudo-first-order kinetic model (R^2 = 0.92), which means that pseudo-second-order provides the best fit for biosorption process. This means that the metal biosorption is not controlled by a pseudo-first-order model such as the diffusion through a boundary layer [44]. However, it can be concluded that biosorption of hexavalent chromium by the

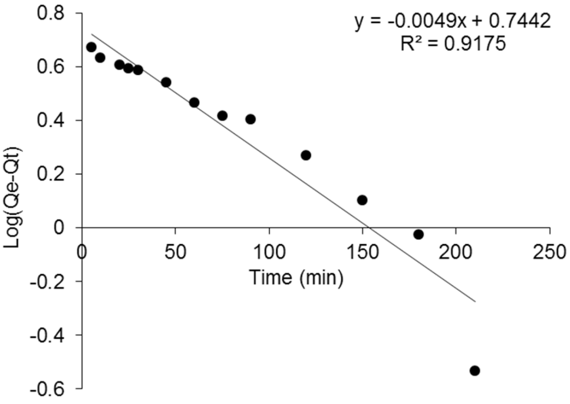

Fig. 8. Pseudo-first-order kinetic model.

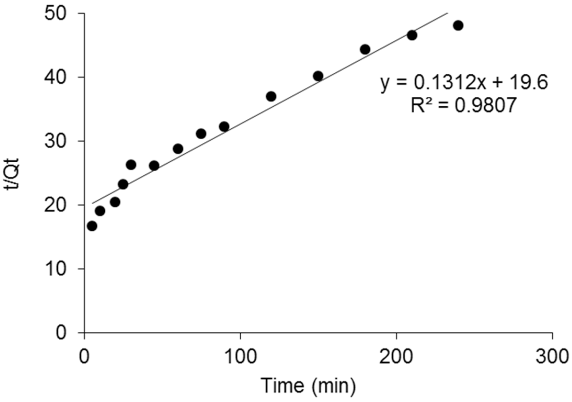

Fig. 9. Pseudo-second-order kinetic model.

Table 1
Kinetic parameters for the biosorption of hexavalent chromium onto the residue of alginate extraction from *Sargassum muticum*

Parameter	Pseudo-first order	Pseudo-second order
K_1 (L.min^{-1})	–0.01	–
K_2 (g.mg^{-1}.min^{-1})	–	0.006
Q_e experimental (mg.g^{-1})	5	5
Q_e calculated (mg.g^{-1})	2.10	7.62
R^2	0.92	0.98

residue of alginate extraction involves various mechanisms and chemical interactions between functional groups and metal ions according to a pseudo-second-order kinetic.

3.6. Modeling of biosorption isotherm

The isotherms data were analyzed using Langmuir and Freundlich models. The Langmuir adsorption isotherm has been traditionally used to quantify and contrast the performance of different biosorbents [45]. Langmuir isotherm is given by the following equation [46]:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_{\max}} \cdot \frac{1}{C_e} + \frac{1}{Q_{\max}} \tag{3}$$

where $Q_{\max}$ is the maximum biosorption capacity describing a complete monolayer adsorption (mg.g^{-1}); Q_e is the amount adsorbed at equilibrium per specified amount of biosorbent (mg.g^{-1}); C_e is the equilibrium concentration of metal ion in solution; and K_L is the adsorption equilibrium constant. The values of $Q_{\max}$ and K_L were, respectively, calculated from intercept and slope of linear plot of $1/Q_e$ vs. $1/C_e$.

The essential feature of the Langmuir isotherm can be expressed by means of a separation factor or equilibrium parameter R_L, which is calculated using the following equation [47]:

$$R_L = \frac{1}{1 + K_L . C_0} \tag{4}$$

where C_0 is the highest metal concentration (mg/L). The isotherm is unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$ and irreversible when $R_L = 0$.

The Freundlich isotherm is originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation [45]. Specifically, the Freundlich isotherm is obtained when a log-normal affinity distribution is assumed [48,49]. Freundlich sorption isotherm is given by following equation [50]:

$$Q_e = K_F . C_e^{\frac{1}{n}} \tag{5}$$

where K_F is Freundlich empirical constant relative to sorption capacity; n is an empirical constant, and rest of the terms have the usual significance. The values of the K_F and $1/n$ were calculated from the intercept and slope, respectively, from a linear plot of $\log Q_e$ vs. $\log C_e$.

The Langmuir and Freundlich isotherms constants and their corresponding correlation coefficients are presented in Table 2. From the obtained results, it can be concluded that Langmuir isotherm (Fig. 10) provides a good model for the sorption system compared with Freundlich isotherm (Fig. 11). Langmuir isotherm is based on monolayer sorption onto surface containing finite number of identical sorption sites. The value of the dimensionless parameter R_L indicates that the sorption is favorable ($0 < R_L < 1$). The magnitude of the $Q_{\max}$ was found of values (34.84 mg.g^{-1}). These results suggest that the residue of alginate extraction from *S. muticum* exhibits important hexavalent chromium uptake capacity compared with other adsorbents where $Q_{\max}$ does not exceed 10 mg.g^{-1} [51–53].

Table 2
Isotherm constants related to the removal of Cr(VI) by the residue of alginate extraction from *S. muticum*

Langmuir				Freundlich		
$Q_{\max}$ (mg.g^{-1})	K_L (L.mg^{-1})	R_L	R^2	K_F	n	R^2
34.48	0.01	0.56	0.98	0.87	1.26	0.90

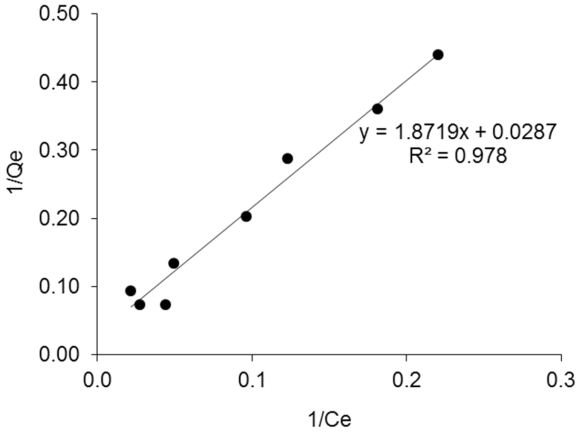

Fig. 10. Langmuir isotherm plots for Cr(VI) biosorption by the residue of alginate extraction.

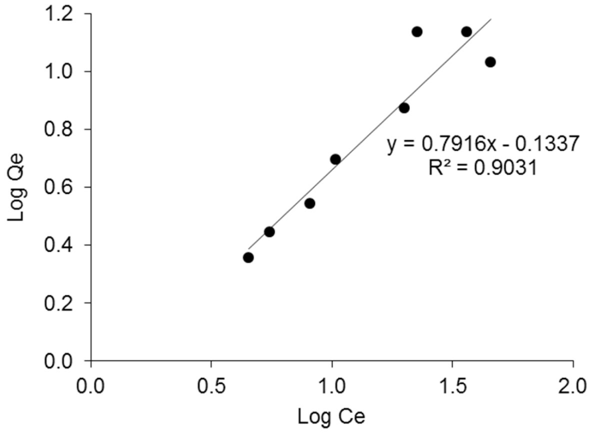

Fig. 11. *Freundlich* isotherm plots for Cr(VI) biosorption by the residue of alginate extraction.

4. Conclusion

The present study investigates the removal of hexavalent chromium from aqueous solution by the residue of alginate extraction from the invasive brown seaweed *S. muticum* collected from the Atlantic coast of Morocco. The characterization of biosorbent by FTIR spectroscopy demonstrates the contribution of functional groups especially carboxyl, hydroxyl, amino and sulfonic groups in Cr(VI) adsorption.

The pH of the solution has an important role in the chromium biosorption. At more acidic pH values, the biosorption efficiency is about 100%. The sorption process reaches the equilibrium at about 4 h. The kinetics study shows that biosorption of Cr(VI) on the extraction residue can be described by pseudo-second-order model and that experimental results are well modeled according to the Langmuir adsorption isotherm. The maximum uptake capacity was also determined and is equal to 34.48 mg.g^{-1}. The large canopies of the invasive *S. muticum* on the Northwestern Atlantic coast of Morocco, associated with important uptake capacity for hexavalent chromium, make the waste of alginate extraction from *S. muticum* a low-cost biomaterial for removing or reducing the heavy metal pollution in aquatic environment. Furthermore, to attract more usage of this algal based sorbent, strategies have to be developed for a multiple biosorption–regeneration cycles where further processing can be done to regenerate the biomass and then convert the recovered metal into usable form. Desorption seem to be particularly a perfect way to remove chromium ions from the sorbent for a renewable use of the studied algal biomaterial. Recovery of sorbed metals is in fact one of the most important aspects of any successful biosorption process development. In this context, future works must give emphasis on the selection of an appropriate elutant, which should be operative, less costly, eco-friendly and without damaging the metal-loaded biomass.

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