ISSN : 0974 - 7435 Volume 11 Issue 5

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 11(5), 2015 [170-177]

Hexavalent chromium removal from aqueous solution by adsorbents prepared from seaweed *Cystoseira tamariscifolia*

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ABSTRACT

The objective of this study is to assess the uptake of hexavalent chromium from aqueous solutions onto *Cystoseira tamariscifolia* algae raw and chemically modified. The biosorption data of hexavalent chromium by marine brown algae *Cystoseira tamariscifolia*, which was raw (RC) and chemically modified by hydrochloric acid (AC), has been used for kinetic studies based on fractional power, Elovich, pseudo-first order, pseudo-second order and intraparticle diffusion rate expressions. Four parameter biosorption isotherm models, Freundlich, Langmuir, Dubinin – Radushkevich, Temkin are tested for their applicability. The time-dependent Cr(VI) biosorption data were well-described by fractional power and Elovich kinetic model. Among the two-parameter models, the Langmuir model produces the best fit. Comparing our results with other previous work on the brown algae, shows the value of materials developed from *Cystoseira tamariscifolia* and allows us to offer them as adsorbent materials.

KEYWORDS

Hexavalent chromium;
Cystoseira tamariscifolia;
Biosorption;
Kinetics;
Equilibrium models.

INTRODUCTION

The presence of toxic heavy metals in water resulting from rapid industrialization and technological advances is a world wide environmental problem[1-4]. One of the heavy metals that have been a major focus in water and wastewater treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties[5-7]. Chromium has been considered as one of the top 16th. toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern[8]. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production[9]. Extensive use of chromium results in large quantities of chromium containing effluents which need an exigent treatment. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard (United States Environmental Protection Agency). In addition, World Health Organization standard for

Cr(VI) concentration in drinking water is 0.05 mg/L[10,11].

Removal of heavy metals from aqueous effluents has conventionally been accomplished through a range of abiotic processes[12-14]. However, these processes can be expensive and not fully effective. Recently, increasing interest in the application of materials of biological origin in heavy metals removal from diluted, large volume solutions has been observed. Sorption with biomaterials has become an alternative to traditional methods of industrial wastewaters treatment, such as precipitation, adsorption, coagulation …[15-17] and it is relatively inexpensive, non-hazardous, and may permit recovery of the metals from the sorbing biomass[18]. The potential of nonviable brown seaweeds in the recovery of heavy metal ions from aqueous effluents has been well demonstrated[19,20].

The objective of this study was to evaluate the adsorption capacity of chromium on substrates obtained from the brown seaweed *Cystoseira tamariscifolia*. The choice of the latter is mainly based on purely economic considerations, because we are always looking for natural materials with no obvious utility in order to exploit them for very specific tasks, either in its raw state or after certain operations do not require large investments in energy supply or material. The main objective is to enhance this marine natural resource and use for water-pollution control and preservation of ecological balance.

MATERIALS AND METHODS

Biomass and chemical modification

The brown alga *Cystoseira tamariscifolia* was collected from the Dar Bouaaza beach (Casablanca), Morocco in December 2009. The alga was washed with running water and with deionized water. The washed biomass was oven-dried at 60 °C for 24 h, crushed with an analytical mill, sieved (size fraction of 0.50 mm). The resulting dried biomass was designated as the raw biomass (RC) in the present study.

A 100 g raw biomass was activated in 1M solution of hydrochloric acid at 25 °C for 2h and the mixture was separated by centrifugation and washed thoroughly with distilled water. It was dried in an oven at 60 °C for 24 h resulting dried biomass was designated as the actived biomass (AC).

Sorption experiments and analytical method

All the experiments were conducted at a constant temperature of 25±1 °C and at a constant pH = 5.8 to be representative of environmentally relevant conditions. Batch kinetics and equilibrium sorption experiments were carried out in 250mL Erlenmeyer flasks containing Potassium dichromate solutions (100 mL) of known concentrations, which varied from 30 to 50 mg /l. Known amounts of biomass, were added to each flask and the mixtures were shaken on the rotary shaker.

After the sorption was reached, the change in Cr(VI) concentration due to sorption was determined colorimetrically (Shimadzu 1240 spectrophotometer) according to Standard Methods[21]. A purple-violet colored complex was developed in the reaction between Cr(VI) and 1,5-diphenylcarbazide in acidic condition. Absorbance was measured at wavelength (λ) 540 nm.

Chromium uptake capacities

The amount of Cr(VI) sorbed at equilibrium, q ($mg.g^{-1}$), which represents the metal uptake, was calculated from the difference in metal concentration in the

TABLE 1: Kinetic biosorption models.

Model	Equation	linear expression
Fractional power	$q_t = k_p.t^v$	$\mathrm{Ln}\, q_t = v.\mathrm{Ln}\, t + \mathrm{Ln}\, k_p$
Elovich	$q_t = \frac{1}{\beta_E}.\mathrm{Ln}(\alpha_E.\beta_E.t)$	$q_t = \frac{\mathrm{Ln}(\alpha_E.\beta_E)}{\beta_E} + \frac{1}{\beta_E}.\mathrm{Ln}t$
pseudo-first order	$q_t = q_{e,1P}(1-e^{-k_{1p}.t})$	$\mathrm{Ln}(q_e-q_t) = -k_{1p}.t + \mathrm{Ln}\, q_{e,1P}$
pseudo-second order	$q_t = \frac{k_{2p}.q_{e,2P}^2.t}{1 + k_{2p}.q_{e,2P}.t}$	$\frac{1}{q_t} = \frac{1}{k_{2p}.q_{e,2P}.t} + \frac{1}{q_{e,2P}}$
Intraparticle diffusion	$q_t = k_D.t^{1/2} + C_D$	-

TABLE 2 : Two parameter biosorption isotherm models

Model	Equation	linear expression
Freundlich	$q_e = K_F . C_e^n$	$Lnq_e = LnK_F + n. LnC_e$
Langmuir	$q_e = \frac{q_{m,L} . K_L . C_e}{1 + K_L . C_e}$	$\frac{1}{q_e} = \frac{1}{q_{m,L} . K_L . C_e} + \frac{1}{q_{m,L}}$
Dubinin – Radushkevich	$q_e = q_{m,DR} . e^{-(B.\varepsilon^2)}$	$Lnq_e = Lnq_{m,DR} - \frac{R^2 T^2}{E^2} [Ln\left(1+\frac{1}{C_e}\right)]^2$
Temkin	$q_e = B_T . Ln(K_T . C_e)$	$q_e = B_T . LnK_T + B_T . LnC_e$

aqueous phase before and after adsorption, according to the following equation[22]:

$$q = \frac{(C_0 - C_e)}{m}$$

C_0 and Ce are the initial and equilibrium concentration of Cr(VI) in solution (mg.l^{-1}), respectively and m is the mass of dry seaweed (g).

Fractional power[23], Elovich[24], pseudo-first order[25], pseudo-second order[24] and intraparticle diffusion[26] rate equations have been used for modeling the kinetics of Cr(VI) sorption (TABLE 1).

To examine the relationship between sorbed and aqueous concentration at equilibrium, various two-parameter sorption isotherm models like Freundlich[27], Langmuir[28], Dubinin – Radushkevich[29], Temkin[30] isotherms were used for fitting the data (TABLE 2).

RESULTS AND DISCUSSION

Kinetic study

Studies on the adsorption kinetics of chemical compounds in aqueous solution are usually performed for small ranges of initial concentrations of chemical and adsorbent. The objective was primarily to study the apparent kinetics of adsorption of chromium on four supports that have been already prepared[31].

The kinetic study of biosorption of hexavalent chromium was used to determine the contact time necessary to reach equilibrium. During the contact time, the solution is kept under constant stirring and at constant temperature and pH (pH = 5.8 and T = 25 °C).A mass of 2 g/L of each support and RC crude media activated AC are dispersed in a solution of the chromium to an initial concentration equal to C_0 = 50 mg/L. Figure 1 shows the variation of the residual concentration C_{res} versus time t.

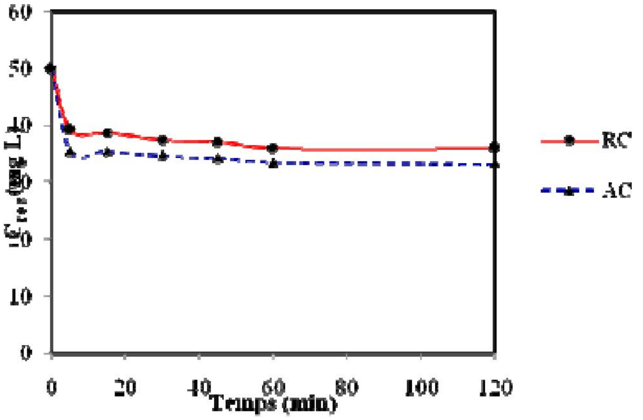

Figure 1 : Kinetics (residual concentration of chromium C_{res} vs. time) of Cr(VI) on various forms (RB and AB) of *Cystoseira tamariscifolia*.

These curves show two quite clear: A first branch reflects a rapid decrease of the residual concentration of chromium C_{res} for 20 minutes. A second branch is characterized by a gradual change of the residual concentration of chromium C_{res} until the balance of biosorption from 60 minutes.

The experimental adsorption capacities of activated biomass are higher than those of raw biomass, and the adsorption capacity of the biomass *Cystoseira tamariscifolia*, it increased by 7.02 mg/g to 8.35 mg/g.

All the kinetic parameters of biosorption media (RC) and (AC) are determined from the straight linearity according to the equations of the models described in TABLE 1. In considering the reliability of the proposed kinetic models, we calculated the correlation coefficients of the equations and the kinetic constants of each model. These are grouped in TABLES 3 and 4.

From the values of correlation coefficients R^2 of these tables we can conclude that the model of fractional power (91.9% to 89.4% for RC and AC) and the Elovich model (91.1% for RC and 89% AC) are closer to the experimental results of adsorption kinet-

TABLE 3 : Kinetic model parameters for Cr(VI) biosorption on biomasses RC of *Cystoseira tamariscifolia*

Model	linear expression	R^2	Model parameters
Fractional power	$y = 0,093x + 1,517$	0,919	$\upsilon = 9,3.10^{-2}$ $k_p = 4,558$ $\upsilon.\ k_p = 0,424\ mg.g^{-1}.min^{-1}$
Elovich	$y = -0,035x + 3,996$	0,361	$k_0 = -3,5.10^{-2}\ mg.g^{-1}.min^{-1}$ $q_{e,0} = 3,996\ mg.g^{-1}$
pseudo-first order	$y = 0,0023x + 1,730$	0,738	$k_1 = -2,3.10^{-3}\ min^{-1}$ $q_{e,1} = 5,641\ mg.g^{-1}$
pseudo-second order	$y = -0,069x + 1,548$	0,840	$k_{1P} = 6,9.10^{-2}\ min^{-1}$ $q_{e,1P} = 4,702\ mg.g^{-1}$
Intraparticle diffusion	$y = 0,575x + 4,334$	0,911	$\alpha_E = 1078,7\ mg.g^{-1}.min^{-1}$ $\beta_E = 1,739\ g.mg^{-1}$
Fractional power	$y = -0,0004x + 0,177$	0,722	$k_2 = -4.10^{-4}\ g.mg^{-1}.min^{-1}$ $q_{e,2} = 5,649\ mg.g^{-1}$
Elovich	$y = 0,206x + 0,148$	0,721	$k_{2P} = 0,718\ g.mg^{-1}.min^{-1}$ $q_{e,2P} = 6,756\ mg.g^{-1}$
pseudo-first order	$y = 0,540x + 2,536$	0,641	$k_D = 0,540\ mg.g^{-1}.min^{-1/2}$ $C_D = 2,536\ mg.g^{-1}$

TABLE 4 : Kinetic model parameters for Cr(VI) biosorption on biomasses AC of *Cystoseira tamariscifolia*

Model	linear expression	R^2	Model parameters
Fractional power	$y = 0,051x + 1,873$	0,894	$\upsilon = 5,1.10^{-2}$ $k_p = 6,507$ $\upsilon.\ k_p = 0,331\ mg.g^{-1}.min^{-1}$
Elovich	$y = -0,038x + 5,165$	0,283	$k_0 = -3,8.10^{-2}\ mg.g^{-1}.min^{-1}$ $q_{e,0} = 5,165\ mg.g^{-1}$
pseudo-first order	$y = 0,0013x + 1,987$	0,820	$k_1 = -1,3.10^{-3}\ min^{-1}$ $q_{e,1} = 7,293\ mg.g^{-1}$
pseudo-second order	$y = -0,051x + 1,197$	0,804	$k_{1P} = 5,1.10^{-2}\ min^{-1}$ $q_{e,1P} = 3,310\ mg.g^{-1}$
Intraparticle diffusion	$y = 0,397x + 6,416$	0,890	$\alpha_E = 4,122.10^{6}\ mg.g^{-1}.min^{-1}$ $\beta_E = 2,518\ g.mg^{-1}$

ics. By cons, we note that the theoretical data from other models move away from the experimental data. To better demonstrate the effectiveness of the model of fractional power and Elovich model, we reported in Figures 2 and 3 modeling the kinetics of chromium biosorption of these two models respectively on the biomass RC and AC.

Equilibrium isotherm models

With a view to assess the adsorption capacity of chromium on each algal support prepared, a study of adsorption isotherms was carried out. Recall that adsorption isotherm is also known as saturation curve and it shows the variation of the amount adsorbed q_t depending on the residual concentration at equilibrium Ce (q_t = f (Ce)) at a temperature T and a consistent pH (T = 25 °C, pH = 5.8).

In order to determine the nature of the adsorption isotherm of chromium on the media, we made solutions containing chromium at initial concentrations constant C_0 = 50 mg / L, and for each medium we introduced

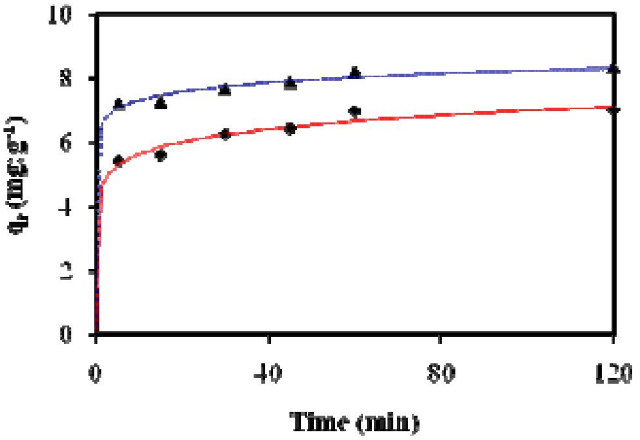

Figure 2 : Modeling the kinetics of chromium biosorption of the fractional power model. (♦ : RC, ▲: AC, — model RC, — model AC)

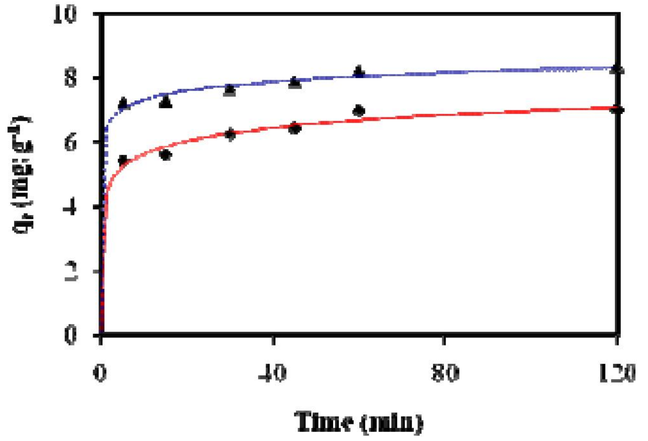

Figure 3 : Modeling the kinetics of chromium biosorption of the Elovich model. (♦ : RC, ▲ : AC, — model RC, — model AC)

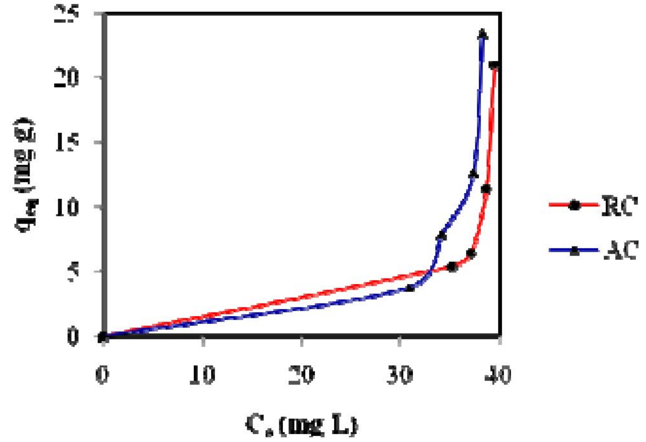

Figure 4: Equilibrium isotherms of biosorption of chromium on biomass RC and AC.

TABLE 5 : Isotherms model parameters for Cr(VI) biosorption on RC

Model	linear expression	R^2	Model parameters
Freundlich	y = 11,45x - 39,29	0,858	n = 11,45 $K_F = 8{,}64.10^{-18}$ L.g$^{?1}$ $q_{m,F} = 245{,}344$ mg.g^{-1} n>1 : adsorption faible
Langmuir	y = 45,21x - 1,085	0,927	$K_L = 2{,}39.10^{-2}$ L.g$^{?1}$ $q_{m,L} = 0{,}921$ mg.g^{-1} $R_L = 0{,}45$
Dubinin – Radushkevich	y = -8151x + 7,897	0,835	$B = 1{,}32.10^{-3}$ J^2.mol$^{?2}$ $q_{m,DR} = 2689{,}2$ mg.g^{-1} E = 27,429 J.mol$^{?1}$
Temkin	y = 123,9x - 438,4	0,746	$B_T = 123{,}9$ J.mol?1 $K_T = 2{,}9.10^{-2}$ L.g$^{?1}$ ΔQ = 19,98 J $q_{m,T} = 46{,}29$ mg.g^{-1}

TABLE 6 : Isotherms model parameters for Cr(VI) biosorption on AC

Model	linear expression	R^2	Model parameters
Freundlich	y = 2,294x - 5,585	0,842	n = 2,294 $K_F = 3{,}75.10^{-3}$ L.g$^{?1}$ $q_{m,F} = 29{,}641$ mg.g^{-1} n>1 : adsorption faible
Langmuir	y = 7,139x - 0,121	0,947	$K_L = 1{,}69.10^{-2}$ L.g$^{?1}$ $q_{m,L} = 8{,}264$ mg.g^{-1} $R_L = 0{,}54$
Dubinin – Radushkevich	y = -971,6x + 3,374	0,776	$B = 1{,}58.10^{-4}$ J^2.mol$^{?2}$ $q_{m,DR} = 29{,}195$ mg.g^{-1} E = 79,446 J.mol$^{?1}$
Temkin	y = 24,87x - 74,00	0,657	$B_T = 24{,}87$ J.mol?1 $K_T = 5{,}1.10^{-2}$ L.g$^{?1}$ ΔQ = 99,57 J $q_{m,T} = 23{,}29$ mg.g^{-1}

the masses of adsorbent on the volume of the adsorbate of 0.5 g/L to 5 g/L. Stirring is continued for a sufficient time to reach equilibrium (two hours). At the end of each experiment, we determine the residual concentrations of chromium, and then we deduce the sorption capacity at equilibrium Q_{eq}. The changes in adsorption capacities at equilibrium according Q_{eq} residual concentrations at equilibrium it is the equilibrium isotherms. Equilibrium isotherms of biosorption of chromium on biomass RC and AC are represented in Figure 4.

To process the experimental data, and to explain the isotherms obtained from equilibrium, we used isothermal models that have been previously described in TABLE 2. The constants characterizing each of the linear expressions of these models were determined and the data in TABLE 5 and TABLE 6 for RC and AC. Note that the reliability of these proposed models was performed by calculating the correlation coefficients R^2.

From the values of correlation coefficients R^2, we can conclude that the Langmuir model (Figure 5) is closest to the experimental results obtained in both adsorption isotherms, (92.7% for RC, and 97.4% for AC). Other models such as the Freundlich model, the model of Dubinin – Radushkevich and the model of Temkin, show significant correlation coefficients which require them to take consideration in all models made. To better demonstrate the effectiveness of these models, we reported in Figures 6, 7 and 8 respectively, the modeling of adsorption isotherms of chromium on four supports RC and AC.

Comparing our results with literature

To evaluate the biosorption of chromium on biomass RC and AC Moroccan *Cystoseira tamariscifolia*, we have shown in TABLE 7 the comparison of our results with those of the literature on the biosorption of chromium to other brown algae. The analysis of this table shows that the adsorption capacity of biomass *Cystoseira tamariscifolia* has attractive valuations relative to other algal media, which allows it to be considered for the use as biomass adsorbent materials.

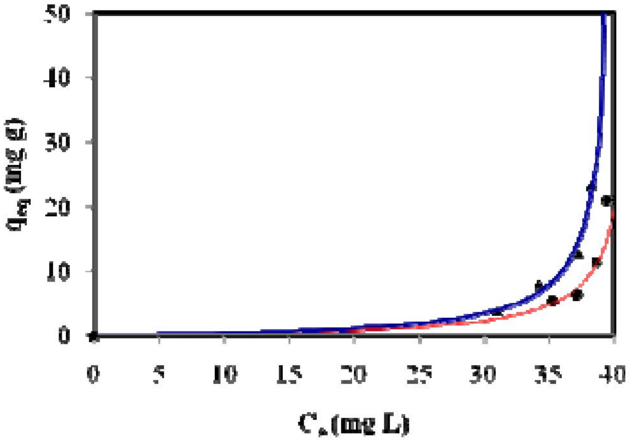

Figure 5 : The Langmuir model of adsorption isotherms of chromium. (●: RC, ▲: AC, — model RC, — model AC)

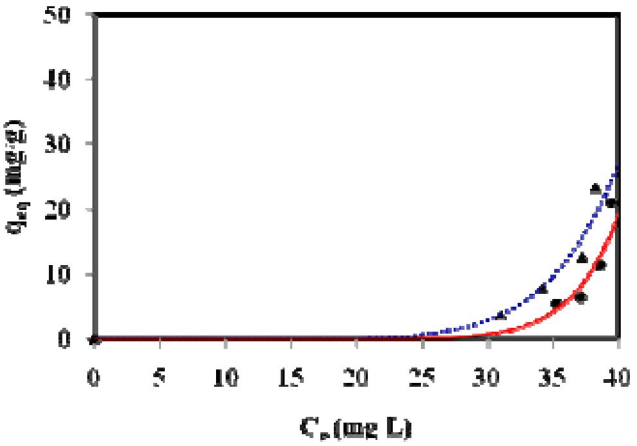

Figure 6 : The Freundlich model of adsorption isotherms of chromium. (● : RC, ▲ : AC, — model RC, — model AC)

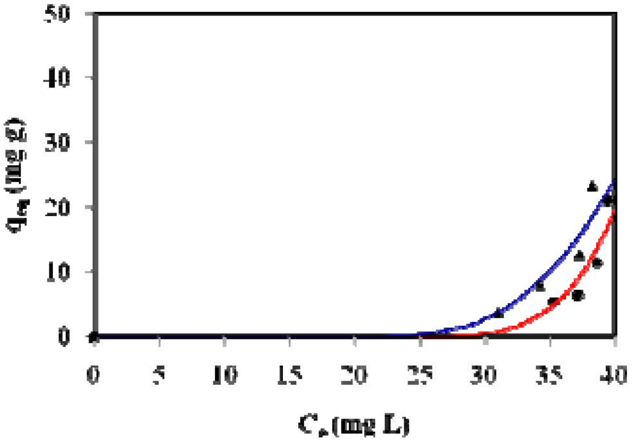

Figure 7 : The Dubinin – Radushkevich model of adsorption isotherms of chromium. (● : RC, ▲ : AC, — model RC, — model AC)

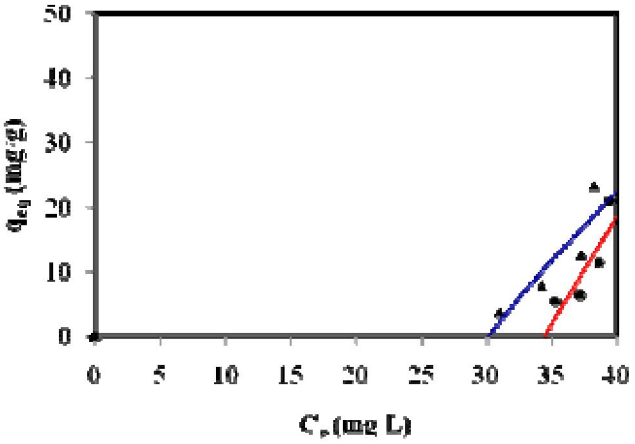

Figure 8 : The Temkin model of adsorption isotherms of chromium. (● : RC, ▲ : AC, — model RC, — model AC)

TABLE 7 : Sorption capacities for Cr(VI) using different brown seaweeds.

Brown seaweed	q (mg.g^{-1})	Refs
Padina sp.	54.60	[32]
Ecklonia	4.49mmol.g-1	[33]
Pilayella littoralis	4.68	[34]
Sargassum siliquosum	66.4	[35]
Turbinaria ornata	31	[36]
Sargassum sp.	31.72	[32]
Cystoseira indica	20.9 – 27.9	[37]
Cystoseira tamariuscifolia	21.02 – 22.41	Present study

CONCLUSIONS

The results obtained during the adsorption of chromium on both biomasses prepared from the brown seaweed *Cystoseira tamariscifolia*: RC and AC show that:

- The adsorption kinetics could be considered consistent with models of fractional power and Elovich.
- The modeling of adsorption isotherms by the Freundlich models, Langmuir, Dubinin - Radushkevich, and Temkin may simplify the interpretation of experimental data of isotherms put in games.
- All adsorptions isotherms obtained could be considered consistent with the Langmuir model.
- The comparison with the literature shows that one can use the raw materials and activated *Cystoseira tamariscifolia* in the treatment of polluted water.

All the results obtained in this work, demonstrate that we have discovered new ways of valuing the Moroccan algal biomass, giving new biomass in the field of environmental applications.

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