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ORIGINAL ARTICLE

Biosorptive removal of lead (II) ions from aqueous solutions using *Cystoseira stricta* biomass: Study of the surface modification effect

Abdelkader Iddou [a,b], Mohamed Hadj Youcef [b,*], Abdallah Aziz [a], Mohand Said Ouali [a]

[a] *Laboratoire de valorisation des matériaux et traitement des nuisances, Département de chimie, Faculté des sciences et sciences de l'ingénieur, Université de Mostaganem, BP 992 Mostaganem, Algeria*
[b] *Department of Chemistry, Faculty of Sciences, University of Science sand Technology of Oran-Mohamed Boudiaf (USTO-MB), P.O. Box 1505, El Mnaouer, Oran 31000, Algeria*

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Abstract A brown marine alga, *Cystoseira stricta*, has been studied for its biosorption capacities of the heavy metallic ion, the Pb(II), in aqueous solutions. The brown alga (C) has been used without previous treatment and with chemical treatment to acid (H_2SO_4 1 M: CS) and to sodium hydroxide (NaOH 1 M: CB). The results have shown the influence of the particle size of the biomaterial on the extraction-removal of Pb(II). The application of the Langmuir adsorption model revealed the maximum capacities of adsorption of each material (C, CS, CB). The one specific to *C. stricta* treated by a solution of sodium hydroxide 1 M (CB) was the most important (65 mg g^{-1}). The established isotherms at different temperatures showed that this parameter affects the adsorption. The best results are obtained for a temperature of 25 °C, in comparison with those recorded at 50 °C. Finally, the results of this study showed that *C. stricta* can be a good potential biosorbent of heavy metals, in particular, when it is treated by a basic solution.

* Corresponding author.
E-mail addresses: iddouaek@yahoo.fr (A. Iddou), hadjyoucef_med@yahoo.com (M. Hadj Youcef), ouali@univ-mosta.dz (M.S. Ouali).

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1. Introduction

The accumulation of wastes in the environment leads to their dispersion on soils, superficial waters, atmosphere and particularly aquifers that constitute reservoirs for drinking water. To find a solution to the dispersion of the pollutants in the environment, one might think of the remediation definite as being the use of chemical or biological processes for the elimination of the polluting substances due to accidental or purposeful discharges (Vullo, 2003). These processes of remediation can be used in-situ or ex-situ; such is the case of the industrial or urban effluents.

The industrial activities are usually considered responsible for the contamination by the heavy metals (i.e. Cu, Zn, Pb, Cd, Cr, Ni ...); in which their impact depends strictly on their behaviour and their response to the physico-chemical and biological conditions of the medium. Besides, the remediation of the polluted media requires some very expensive processes. The heavy metals, being non biodegradable can be dispersed among air, water and soil (under all type of oxidation states) or can be incorporated to the living species.

The most important processes that induce the accumulation of the heavy metals on suspended matters and sediments are the adsorption processes and the formation of complexes (Hursthouse, 2001; Kalbitz and Wennrich, 1998).

The present work achieved in the field of the removal of the heavy metals permitted the use of several types of supports: stone olive (Blazquez et al., 2005), industrial wastes (Iddou and Ouali, 2005), microscopic fungi (Bayramoglu et al., 2005), bacteria (Wang et al., 2003), algae of soft water (Haq Rahmani and Sternberg, 1999; Tien, 2002), marine micro-algae (Arica et al., 2005; Abu Al-Rub et al., 2006), aquatic mosses (Bleuel et al., 2005), and marine macro-algae (Kaewsarn and Yu, 2001; Jalali et al., 2002; Aksu, 2002; Vijayaraghavan et al., 2005).

Lead is a heavy metal ion toxic to the human biosystem, and is among the common global pollutants arising from increasing industrialization. The accumulation of relatively small amounts of lead over a long period of time in human body can lead to the malfunctioning of the organs and chronic toxicity (Khurshid and Qureshi, 1984). According to the WHO, the maximum permissible limit (MPL) of lead in drinking water is 0.05 mg/L (WHO, 1984).

In this work, *Cystoseira stricta* is used as a novel biosorbent for the removal of Pb(II) from aqueous solutions. The aim of this study is to establish a comparison between the adsorption capacity of the chemically treated alga and the non-treated one. Some parameters affecting biosorption like size of biosorbent particles, chemical treatments, and temperature are investigated, and data on adsorption isotherm are obtained and fitted to common isotherms models, Langmuir and Freundlich.

2. Materials and methods

Marine alga samples, *C. stricta*, have been picked from the Mostaganem coast (West Algeria). Alga was washed with running water several times, in order to get rid of all impurities, in particular the shellfish and mostly the sand. A rinsing with the distilled water has been done lastly. Alga was then dried with free air during 72 h. This operation allows us to eliminate the surplus of water. After, the drying was completed in a sweating-room at 80 °C for 24 h. The obtained biomaterial was noted (C).

The alga sample was ground with the mortar made of porcelain, and then sifted to obtain a particle size in the range 0.25–0.5 and 1 mm. The obtained biomaterials were noted C/0.25–C/0.5 and C/1.

The aqueous solutions of Pb(II) have been prepared by dissolving the desired quantity from its nitrate salt (Prolabo quality) in DDW. The residual concentrations of lead have been measured at 283.8 nm by the atomic absorption spectrophotometer (type Pye Unicam SP9) using an acetylene/air flame. In order to appreciate the influence of the particle size, Isotherms were established with a metallic solution volume of 100 mL at initial concentrations of Pb(II) ranging from 10 to 100 mg dm^{-3}, and 0.1 g of material. The suspensions were adjusted to pH 3 and shaken for 30 min.

The biomaterial, *C. stricta*, has been treated by two solutions, one acid (H_2SO_4 1 M) and the other alkali (NaOH 1 M). A ratio of 10% (m/v) has been selected for the activation that has been taken place in a hot refluxed ball.

After 2 h of heating, the biomaterials were washed with distilled water until stabilization of the pH (5.5 and 7.2) was achieved for the activated biomaterials with acidic and basic solutions, respectively.

The obtained biomaterials were noted: CS for Cystoseira activated with the sulphuric acid 1 M and CB for Cystoseira activated with sodium hydroxide 1 M.

Isotherms have been established at different temperatures of 25, 30, 40 and 50 °C. For that, a volume of 100 mL of solution of Pb(II) was put in contact with a mass of 0.1 g of each biomaterial. The concentrations of lead chosen in order to establish the isotherms were 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg dm^{-3}.

The adsorption isotherms of Pb(II) on *C. stricta* have been obtained for a concentration of biomass of 1 g dm^{-3} and an initial pH of the suspension is equal to 3. The contact time has been fixed at 30 min.

3. Results and discussion

3.1. Effect of biosorbent's particle size

The surface of contact between the biosorbent and metallic cations in solution plays an important role in adsorption processes (Blazquez et al., 2005; Teixeira Tarley and Aruuda, 2004). The adsorption isotherms established (Fig. 1) for different particle sizes at pH 3 show that in the case of using pheophycea biomass (C), one can note the influence of this parameter. Indeed, the removal of Pb(II) is more important

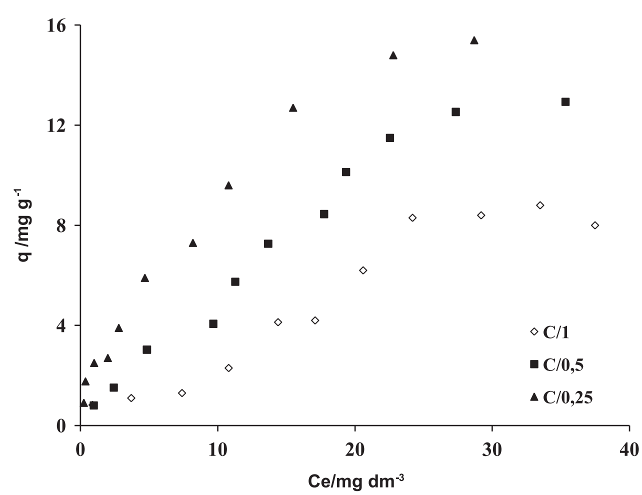

Figure 1 Effect of *Cystoseira stricta* adsorbent (C) particle size on removal of Pb(II).

when the particle sizes decrease. In addition, the recorded adsorption capacities (q) are inversely proportional to the particle size and therefore the values of the highest capacities are obtained for the particle size of 0.25 mm. The same observations have been reported by Benguella and Beniassa, 2002, and Ho and McKay, 2001. On the other hand, one can observe that the differences between the values of the adsorption capacities of the materials C/0.25 (15.4 mg g^{-1}) and C/0.5 (12.9 mg g^{-1}) are not very important. Thus the particle's diameter 0.5 mm of biomaterials is used in the following experiments.

3.2. Effect of the chemical treatment on the biosorption of Pb(II)

Fig. 2 shows the scanning electron micrography (SEM) images of alga before and after chemical treatment. It clearly appears that the modification operated on the biomaterial does not affect its global morphology. One can also note that the treatment with acid causes the appearance of thin remnants on the surface, which risks affecting the adsorption capacity of the matrix. The treatment with sodium hydroxide causes the appearance free and especially enough porous surface; which foretells an increase in the adsorption capacity of the biomass. The same behaviours have been observed on the active coal modified by the citric acid (Chen et al., 2003).

3.3. Adsorption isotherms

The adsorption capacities of the different biomaterials, towards the metallic cation Pb(II) in aqueous solution at pH 3, have been calculated by using the Langmuir isotherm model, expressed by the following equation:

$$q = \frac{q_{max} b C_e}{1 + b C_e} \quad (1)$$

where q refers to the adsorbed amount of Pb(II) pergram of material (mg g^{-1}), q_{max} is the maximum adsorption capacity of the biomaterial (mg g^{-1}), C_e is the equilibrium concentration of Pb(II) (mg dm^{-3}), and b is a constant related to the adsorption energy.

Eq. (1) can be re-arranged to yield:

$$\frac{1}{q} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \quad (2)$$

The Figs. 3–5 show the plots of the sorption isotherms according to the linearized Langmuir model (Eq. (2)) at different temperatures. In the considered concentration range, it appears that the obtained results are in good compliance with this model. With the correlation coefficients higher than 0.9, the Langmuir model reveals a monolayer adsorption in which the biomass surface is not completely saturated (Bai and Abraham, 2002). The maximum adsorption capacity found is

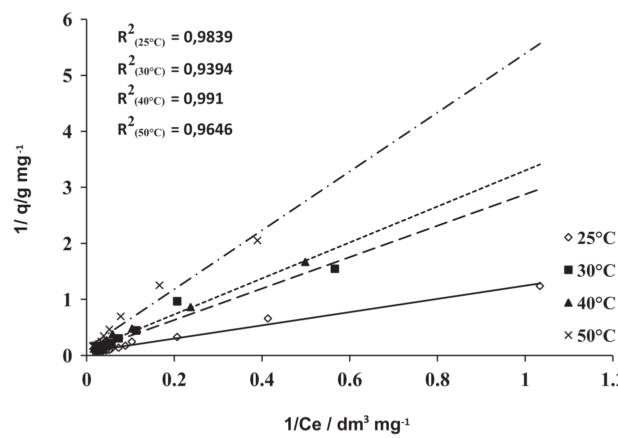

Figure 3 Adsorption of Langmuir isotherms of Pb(II) on C at different temperatures.

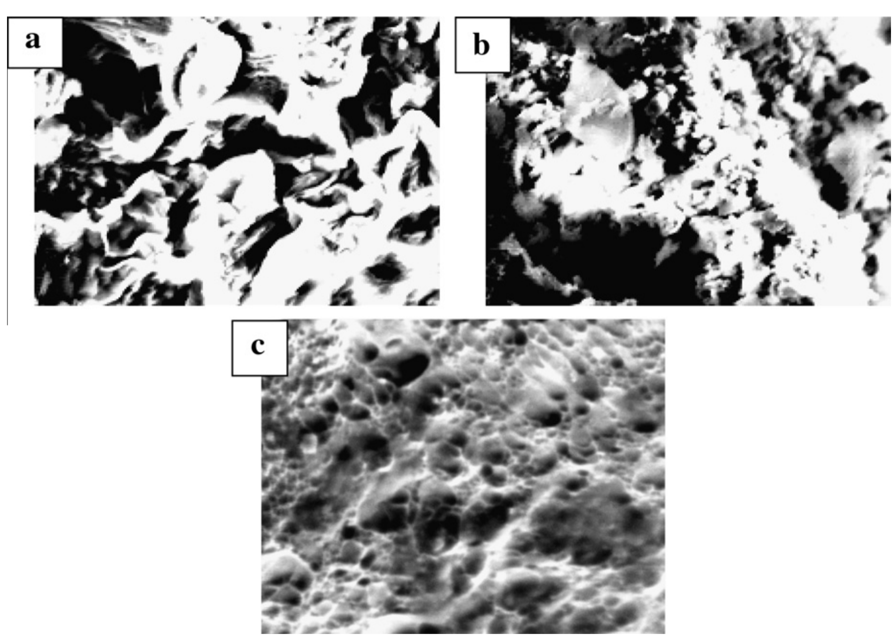

Figure 2 SEM images of the *Cystoseira stricta* surface with 1200-time magnification: (a) non-treated (C); (b) treated with sulphuric acid (CS); (c) treated with sodium hydroxide1 M (CB).

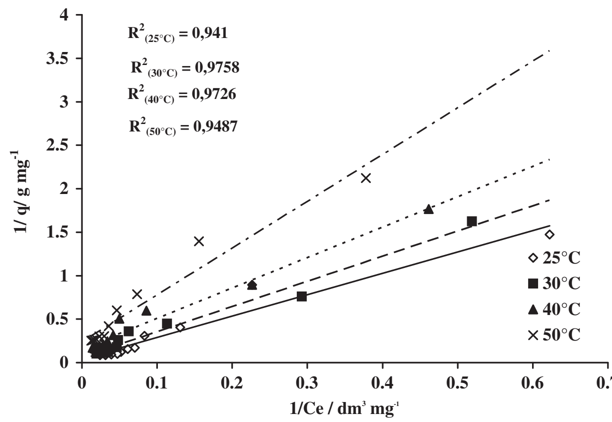

Figure 4 Adsorption of Langmuir isotherms of Pb(II) on CS at different temperatures.

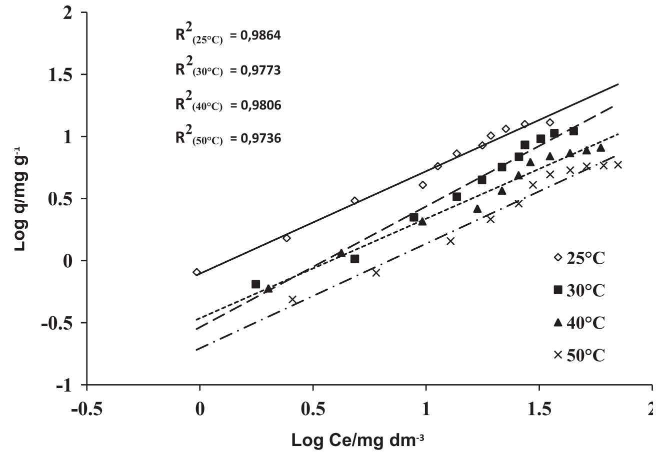

Figure 6 Adsorption of Freundlich isotherms of Pb(II) on C at different temperatures.

more important in the case of the use of the biomass treated with a solution of sodium hydroxide 1 M ($q_{max} = 64.5$ mg g^{-1}).

To explain the adsorption of the observed equilibrium in better way, the Freundlich isotherm model is also used. It is represented by the following equation:

$$q = KC_e^n \tag{3}$$

A linear form of this expression is given as:

$$\text{Log}\, q = \text{Log}\, K + n\text{Log}\, C_e \tag{4}$$

where K is the Freundlich adsorption constant, and n is the adsorption intensity.

Figs. 6–8 show the plots of the adsorption isotherms according to the Freundlich model (Eq. (4)). It appears that our results are also in good agreement with this model. The values of the two parameters K and n are calculated from the intercept and slope of the plots log q versus log C_e. The K value is maximal for the (CB) material. The minimum value estimated for the same parameter is of 0.197 and corresponds to the use of the biomass without treatment. The value of n is higher than 1 for the treated biomass and the one non-modified. This indicates that the adsorption of Pb(II) is favored (Bai and Abraham, 2002; Bayramoglu et al., 2005).

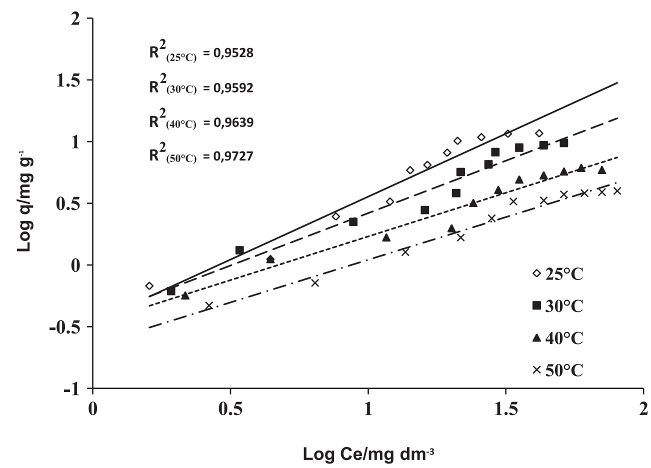

Figure 7 Adsorption of Freundlich isotherms of Pb(II) on CS at different temperatures.

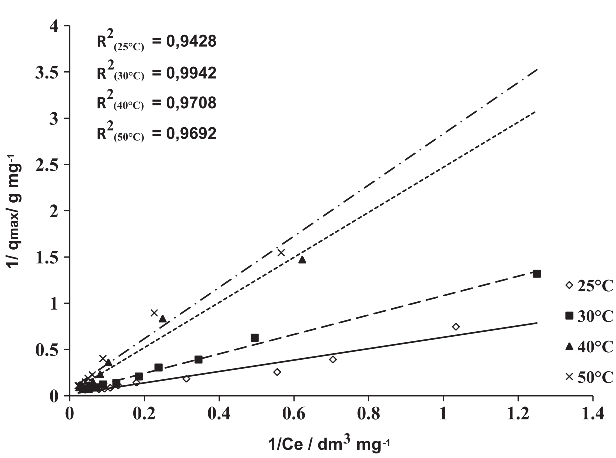

Figure 5 Adsorption of Langmuir isotherms of Pb(II) on CB at different temperatures.

The chemical treatment of alga, *C. stricta*, with 1 M solutions of sodium hydroxide and sulphuric acid, has been made in order to generate ionic sites by a superficial modification of the structure for its walls (Fourest and Roux, 1992). A particular attention can be given to alga treated with sodium hydroxide, because of the obtained results which are extensively more important than those obtained with the other materials. The treatment with sodium hydroxide usually participates in the regulation of the pH of the suspension, kept around the neutrality, which contributes to the inhibition of the majority of H_3O^+ ions activity in acidic environment. Moreover, these ions can compete with the adsorption of metallic cations, Pb(II), on the anionic active sites of the surface of the algal biomass, and which are generated by the same treatment.

The obtained Freundlich and Langmuir parameters after batch adsorption experiments of Pb(II) on non-treated and activated *C. stricta* are recapitulated in Table 1.

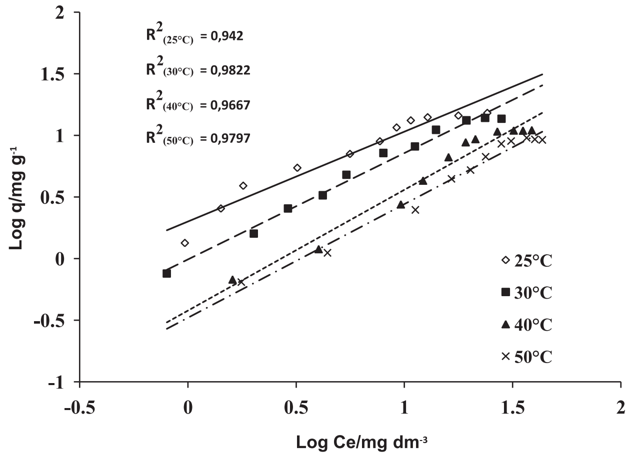

Figure 8 Adsorption of Freundlich isotherms of Pb(II) on CB at different temperatures.

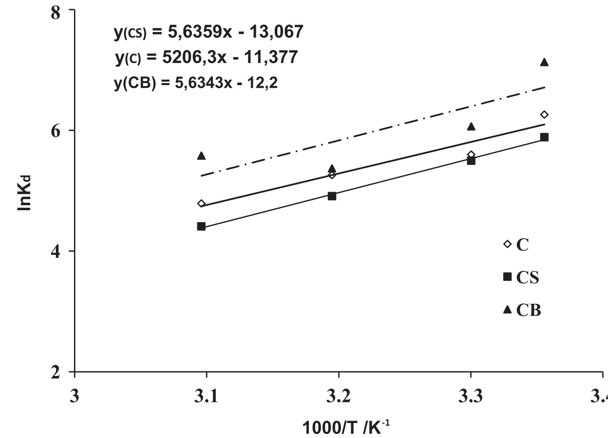

Figure 9 Plots of ln (K_d) versus $1/T$ for Pb(II) adsorption on C, CS, and CB.

3.4. Determination of the thermodynamic parameters

The thermodynamic parameters, such as the enthalpy ($\Delta H°$) and the entropy ($\Delta S°$) for the biosorption of Pb(II) with the brown alga, are calculated by using the following equation:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (5)$$

where T is the absolute temperature (K), R is the gas constant (J mol^{-1} K^{-1}), and K_d is distribution coefficient (cm^3 g^{-1}).

The standard free energy change ($\Delta G°$) is calculated from the following equation:

$$\Delta G° = \Delta H° - T\Delta S° \quad (6)$$

The plots of the variation of LnK_d versus $1/T$ are shown in the Fig. 9, and the obtained results of the values of the different parameters are summarised in Table 2.

The adsorption of Pb(II) is extensively influenced by the temperature. The negative values of the enthalpy $\Delta H°$ suggest exothermic nature of the biosorption. The values of the free energy change $\Delta G°$ of the process decrease with the increase in temperature, which indicates the feasibility of the process and the spontaneity of the adsorption phenomenon of Pb(II) on the algal *C. stricta* biomass. The negative values of entropy change $\Delta S°$ show the decreased randomness at the solid/solu-

Table 1 Adsorption isotherm constants and coefficient for the removal of Pb(II) on the three biosorbents at different temperatures.

Biosorbent	T/°C	Freundlichisotherm constants		Langmuir isotherm constants	
		K/mg g^{-1}	R^2	q_{max}/mg g^{-1}	R^2
C	25	0.7785	0.986	15.128	0.984
	30	0.290	0.977	13.605	0.939
	40	0.343	0.981	10.787	0.991
	50	0.197	0.974	7.558	0.965
CS	25	0.342	0.953	22.936	0.941
	30	0.373	0.959	16.051	0.976
	40	0.334	0.964	6.423	0.973
	50	0.225	0.973	4.172	0.949
CB	25	1.999	0.942	64.516	0.943
	30	0.986	0.982	31.746	0.994
	40	0.379	0.967	29.325	0.971
	50	0.331	0.979	14.723	0.969

Table 2 Thermodynamic parameters for the adsorption of Pb(II) on three biosorbents at different temperatures

Biosorbents	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}	$\Delta G°$/kJ mol^{-1}			
			298 K	303 K	313 K	323 K
C	−43.28	−94.59	−15.09	−14.62	−13.68	−12.73
CS	−46.86	−108.64	−14.48	−13.94	−12.85	−11.77
CB	−49.83	−108.86	−17.39	−16.85	−15.56	−14.67

tion interface during the biosorption. These results are different from the report by Aksu (Aksu, 2002) in the biosorption experiments of the nickel on *Chlorella vulgaris*.

4. Conclusion

Several algal species, proliferating along the Mostaganem coast (West Algeria), were offered to us for the tests of biosorption-removal of the heavy metal, Lead (II). Brown Alga, *C. stricta*, chosen for this study, was the most abundant. It showed a substantial potential for the removal of Pb(II) in aqueous solutions. Its efficiency depended on several parameters, among which, one is the temperature.

The results show evidence of a great potential of the exploited species. Thus, the adsorption capacity of the treated and non-treated materials is remarkable. *C. stricta*, treated with a solution of sodium hydroxide 1 M, showed higher biosorption capacity (65 mg g^{-1}).

The temperature affects negatively the adsorption process. The best results were obtained at a temperature of 25 °C, in comparison with those recorded at 50 °C.

Further experiments need to be conducted to investigate other chemical parameters which influence the biosorption process-removal of this toxic metallic cation.

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