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Characterization of Thermostructural Damages Observed in a Seaweed Used for Biosorption of Cadmium

Effects on the Kinetics and Uptake

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Abstract

The effect of drying *Sargassum filipendula* on the kinetics and uptake of cadmium was studied. The maximum uptake was not reduced when oven-dried biomass was used for cadmium concentrations from 10.0 to 500.0 mg/L. Kinetics indicated better performance of the *in natura* biomass. Drying at 333 K affected the uptake capacity. Results fit the Langmuir model better than the Freundlich. This process followed pseudo-second-order kinetics. Thermogravimetric and infrared analysis confirmed that no structural damage occurred after drying, and no differences between the biomasses were observed. Temperatures from 303 to 328 K affected cadmium uptake capacity.

Index Entries: Cadmium; kinetics; *Sargassum filipendula*; thermal effects; uptake capacity; biosorption.

Introduction

In the last few years, there has been an increasing concern about using biomasses for the recovery of metals from industrial solutions. This information has been confirmed in a recent review from Ahluwalia and Goyal *(1)* wherein *Aspergillus niger, Penicillium chrysogenum, Rhizopus nigricans, Ascophyllum nodosum, Sargassum natans, Chlorella fusca, Oscillatoria anguistissima, Bacillus firmus*, and *Streptomyces* sp. are presented as potential biosorbents under investigation. Authors say that lead, zinc, cadmium, chromium, copper, and nickel are potential targets for these studies. They also say that uptake capacities may range from 5.0 to 641.0 mg/g, indicating a wide

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variability of biomasses and structural polysaccharides. The critical conclusion of the review paper is that information about different biosorbents is still inadequate for process scale-up and design, and also that the appropriate biomass choice and proper operational conditions need to be identified.

In order to fill part of this technological gap in the literature, a few authors are trying to establish the operational parameters for possible scale-up of processes or to confirm the feasibility of using certain types of biomasses for the accumulation of metals. Martins et al. *(2)* studied the adsorption of cadmium and zinc ions by the aquatic moss *Fontinalis antypiretica*, focusing on temperature, pH, and water hardness. Some process parameters, such as equilibrium data and pH were studied by Pavasant et al. *(3)* who investigated the green macroalga *Caulerpa lentillifera* as a biosorbent material. Padilha et al. *(4)* studied the effect of the counter ions on the uptake capacity of copper by a brown seaweed. Karthikeyan et al. *(5)*, Villar et al. *(6)*, and Martins et al. *(2)* also investigated some physico-chemical properties that may affect the biosorption process, and drew specific conclusions for individual metal-biosorbent combinations. The objective of the present work was to investigate the impact of drying *S. filipendula* at 303 and 333 K on cadmium uptake capacity and rate.

Materials and Methods

Seaweed Biomass

The brown seaweed *S. filipendula* (*Phaeophyceae*, *Ectocarpales*, *Fucales*, and *Sargassaceae*) used in this work was harvested from the sea and sampled. Seaweed was collected in the city of Recife, Pernambuco State, Brazil, at the Atlantic Ocean (W34°53′55″) in January 2006. Only one batch of seaweeds was collected (5.0 kg) for use in experiments. Other studies from the group indicated that the polysaccharide content of the seaweeds was practically the same during the whole year, with changes observed in the mannuronic and guluronic acids content. However, the total alginate content (mannuronic plus guluronic acid blocks) remains constant.

Part of the harvested biomass was extensively washed with distilled water to remove particulate material from its surface, and was oven-dried at 343 K for 24 h. Part of the harvested biomass was only sun-dried at an average temperature of 303 K (*in natura* biomass) for 24 h. One kilogram of biomass was subsampled for use in these experiments. In order to ensure that homogeneous samples were used, standard sampling techniques were applied. Dried biomass was cut, ground in a mortar with a pestle, and then sieved. The fraction with a diameter of 0.3–0.7 mm was selected for use in the biosorption tests. After drying, the biomass was stored in a dessicator.

Cadmium Solutions

A stock cadmium solution (1000.0 mg/L) was prepared by dissolving cadmium chloride (Merck, Darmstadt, Germany) in 100 mL of deionized

distilled water (DDW) and quantitatively diluted to 1000 mL using DDW. Cadmium solutions of different concentrations were prepared by appropriate dilution of the stock solution with DDW.

Determination of Cadmium Concentration by Atomic Absorption Spectrometry

The concentration of cadmium in the solutions before and after the equilibrium was determined by atomic absorption spectrometry, using a Perkin-Elmer (Frankfurt, Germany) Analyst 300 atomic absorption spectrometer equipped with a deuterium arc background corrector and an air-acetylene burner, and was controlled by an IBM personal computer. The hollow cathode lamp was operated at 4 mA, and the analytical wavelength was set to 228.8 nm. Glassware and polypropylene flasks used were immersed overnight in 10% (v/v) HNO_3 and rinsed several times with DDW.

Infrared Spectrometry

The scope and versatility of infrared spectrometry as a qualitative analysis tool have been substantially increased by the internal reflectance technique, also known as attenuated total reflectance. When a material is placed in contact with the reflecting surface, the beam loses energy at those wavelengths whereby the material absorbs because of an interaction with the penetrating beam. This attenuated radiation, when measured and plotted as a function of wavelength, is an absorption spectrum that is characteristic of the material and is similar to an infrared spectrum obtained in the normal transmission mode. Using this technique, qualitative infrared absorption spectra are easily obtained from most solid materials without the need for grinding or dissolving or making a mull *(7)*. A Perkin-Elmer Spectrum One fourier transform infrared was used in the infrared spectrometry analysis of *S. filipendula* biomass.

Thermogravimetric Analysis of the Biomass

Thermogravimetry (TG) or thermogravimetric analysis (TGA) provides a quantitative measurement of weight changes associated with thermally induced transitions. For example, TG can directly record the loss in weight as a function of temperature for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or material owing to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The rates of these thermally induced processes are often a function of the molecular structure. Changes in weight result from physical and chemical bonds forming and breaking at elevated temperatures. TG data are useful in characterizing materials as well as in investigating the thermodynamics and kinetics of the reactions and transitions that result from the application of heat to these materials.

TG, a valuable tool in its own right, is perhaps most useful when it complements differential thermal analysis (DTA). Virtually, all weight-change processes absorb or release energy and are thus measurable by DTA, but not all energy-change processes are accompanied by changes in weight. This difference in the two techniques enables a clear distinction to be made between physical and chemical changes when samples are subjected to both DTA and TG tests. In TG, the weight of the sample is continuously recorded as the temperature is increased. In this case, the biomass was placed in a crucible that was positioned in a furnace on a quartz beam attached to an automatic recording balance (Rigaku, model TAS 100, Japan) with a rate of 10°C/min and 30 mL/min of nitrogen.

Batch Biosorption Studies

Batch biosorption experiments were performed using 50.0 mg of dried biomass (dried at 343 K or *in natura*), which was added to 25 mL of cadmium solution in 100-mL polypropylene flasks. The flasks were placed on a rotating shaker (Tecnal, Brazil) with constant shaking at 150 rpm (1.5*g*). For the kinetic study, two cadmium concentrations were tested: 10 mg/L and 100 mg/L. Three temperatures were selected: 303, 313, and 328 K; and the working pH was that of the solution (pH = 4.5). The biosorption time ranged from 3 to 300 min. At predetermined times, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman no. 40, ashless). The equilibrium isotherms were determined using similar experimental conditions, by varying the initial cadmium concentration from 10 to 500 mg/L and using an equilibrium time equal to 2 h.

Metal Uptake

The cadmium uptake was calculated by the simple concentration difference method. The initial concentration (C_0 [mg/L]) and metal concentration at any time (C_t [mg/L]), respectively, were determined and the metal uptake (q [mg metal adsorbed/g adsorbent]) was calculated from the mass balance as follows (Eq. 1):

$$q = \frac{(C_0 - C_t)V}{1000w} \tag{1}$$

where V is the volume of the solution in milliliter before addition of seaweed, and w, mass of the sorbent in gram. Preliminary experiments had shown that cadmium adsorption losses to the flask walls and to the filter paper were negligible.

Equilibrium Modeling

Modeling the equilibrium data is fundamental for industrial applications of biosorption. It gives information for comparison of different

biomaterials under different operational conditions for designing and optimizing operating procedures. In order to examine the relationship between sorbed (q_e) and aqueous concentrations (C_e) at equilibrium, the biosorption isotherm models of the Langmuir (Eq. 2) and Freundlich (Eq. 3) isotherms were tested for fitting our data.

$$\text{Langmuir isotherm} \quad q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{2}$$

$$\text{Freundlich isotherm} \quad q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

where C_e is the liquid-phase concentration of metal at equilibrium (mg/L), K_L the Langmuir constant (L/mg), q_e the metal uptake at equilibrium (mg/g), Q_0 the maximum metal uptake capacity at equilibrium (mg/g), and K_F and n the Freundlich parameters.

Kinetic Modeling

Two different kinetic models were used to fit the experimental data of cadmium biosorption on *S. filipendula*. The pseudo-first-order Lagergren model (Eq. 4):

$$\log(q_e - q) = \log q_e - \frac{k_{1,\,ads}}{2.303} t \tag{4}$$

where q_e (mg/g) and q (mg/g) are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time (t), respectively. And $k_{1,\,ads}$ is the Lagergren rate constant, and the pseudo-second order model is represented in Eq. 5 *(2,8)*:

$$\frac{t}{q} = \frac{1}{k_{2,\,ads} q_e^2} + \frac{1}{q_e} t \tag{5}$$

where $k_{2,\,ads}$ is the rate constant for second-order biosorption (g/mg/min).

Results and Discussion

Infrared Spectrometry

Results about the infrared spectra of both *in natura S. filipendula* and oven-dried *S. filipendula* biomasses are presented in Fig. 1. A comparison between the two infrared spectra indicates that no marked differences were observed.

Pavasant et al. *(3)* studied the biosorption of cadmium by the green macroalgae *C. lentilifera* suggesting the possibility of coupling between metal species and types of functional groups such as carboxylic (O–H bending),

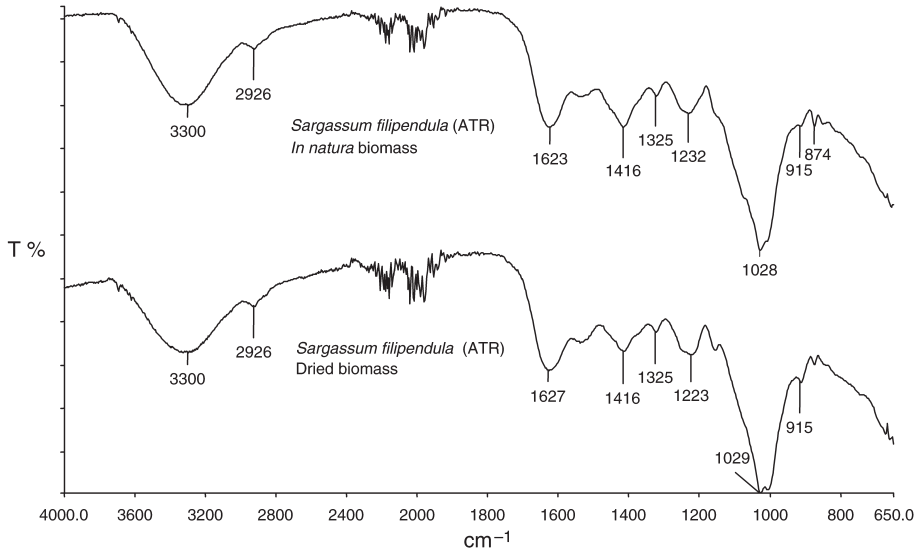

Fig. 1. Infrared spectra of *in natura S. filipendula* and oven-dried *S. filipendula* biomasses.

amine (N–H and C–N stretching), amide (N–H), amino (C–O), sulfonyl (S=O stretching), and sulfonate (S=O stretching).

TGA of the Biomass

The results of the TGA of the biomass are presented in Fig. 2.

Results clearly indicate that there is a continuous loss of mass as a function of increasing temperature. From these results, it is possible to obtain an estimation of weight of biomass lost at the two temperatures used. For *in natura* biomass (sun dried at 303 K), the approximate weight loss is negligible, around 2.5%. On the other hand, for the oven-dried biomass (333 K) the weight loss is considerable, reaching 10%. Heating the biomass in an inert environment results in a loss of mass, which was probably associated with water. The DTA curve shows a significant thermal effect at 333 K.

Effect of the Initial Cadmium Concentration on Biosorption Equilibrium

Figure 3 presents the results obtained when the Langmuir model was used to fit the experimental data; and Fig. 4 shows the experimental data fit for the Freundlich model (Table 1). The corresponding constants and the correlation coefficients (R) associated with each linearized form of both equilibrium models, for both types of biomasses and for temperatures tested, are presented in Table 1. The results indicate that the Langmuir isotherm best fits the experimental data over the experimental range studied because it has higher correlation coefficients. Statistically distinct results

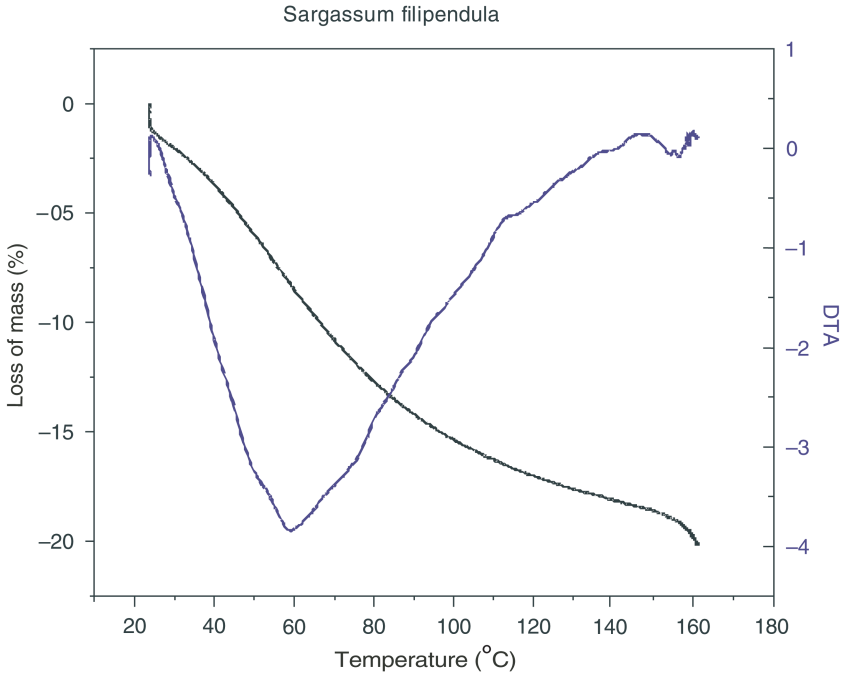

Fig. 2. Plot of loss of mass of *S. filipendula* biomass as a function of increasing temperature and DTA analysis.

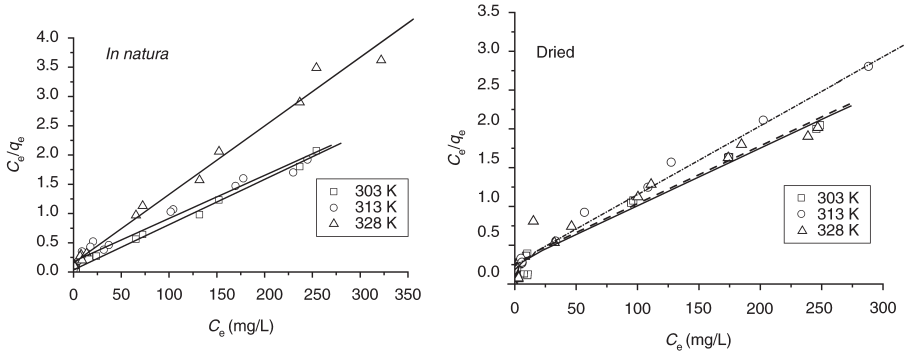

Fig. 3. Linear plots of experimental cadmium biosorption by *S. filipendula* biomass based on the Langmuir model.

were observed at an incubation temperature of 328 K (Q_0 = 85 ± 3 mg/g) and 313 K (Q_0 = 107 ± 2 mg/g) when *in natura* and oven-dried biomasses were used, respectively.

The constant K_F from the Freundlich model ranged from 9.4 ± 1.2 to 22.8 ± 1.9 when *in natura S. filipendula* biomass was used, and ranged from 13.0 ± 1.4 to 19.9 ± 2.0 when dried *S. filipendula* biomass was used. Statistically distinct results were observed for all incubation temperatures

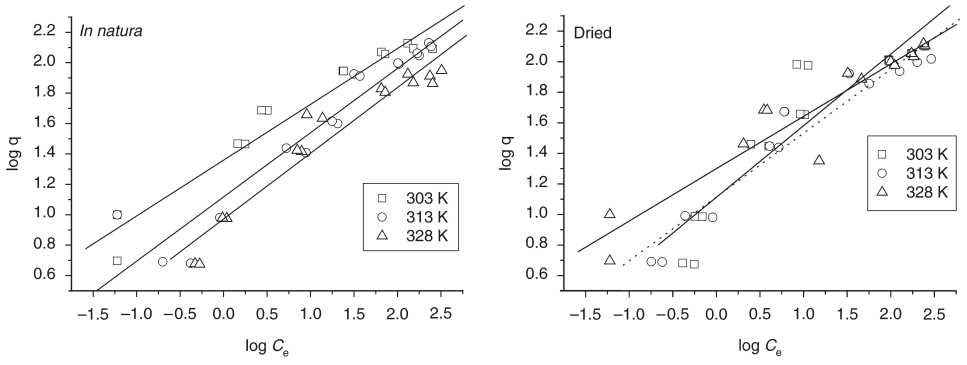

Fig. 4. Linear plots of experimental cadmium biosorption by *S. filipendula* biomass based on the Freundlich model.

Table 1
Freundlich and Langmuir Adsorption Constants Associated with Adsorption Isotherms of Cadmium(II) Ions by *S. filipendula* at Different Temperatures

	Freundlich constants			Langmuir constants		
T (K)	K_F	N	R	Q_0 (mg/g)	K_L (L/mg)	R
In natura biomass						
303	22.8 (1.9)[a]	2.7 (0.2)	0.9736	129 (2)	0.20 (0.07)	0.9981
313	13.1 (1.7)	2.4 (0.2)	0.9564	136 (7)	0.04 (0.01)	0.9843
328	9.4 (1.2)	2.3 (0.2)	0.9625	85 (3)	0.08 (0.02)	0.9936
Dried biomass						
303	13.0 (2.3)	2.1 (0.2)	0.9235	128 (3)	0.08 (0.02)	0.9962
313	13.0 (1.4)	2.4 (0.2)	0.9662	107 (2)	0.09 (0.03)	0.9962
328	19.9 (2.0)	2.9 (0.2)	0.9588	127 (7)	0.06 (0.03)	0.9766

[a]Figures in parenthesis indicate standard deviations (n = 3).

when *in natura* biomass was used, and a marked difference was observed when oven-dried biomass was used, with an incubation temperature of 328 K. The incubation temperature affected the uptake of cadmium.

Biosorption Kinetics of Cadmium Ions

Figure 5 presents the results from the kinetic modeling of cadmium biosorption by *S. filipendula* biomass. These are based on the second-order model because it best fit the experimental data. Complete results from the modeling can be found in Table 2. Figure 5 is representative of the goodness of the fit to the second-order model in each experiment. Table 2 shows that using *in natura* and dried *S. filipendula* biomasses, did not affect the uptake capacity for initial cadmium concentrations of 10.0 and 100.0 mg/L. However, the incubation temperature proved to be a parameter that affected

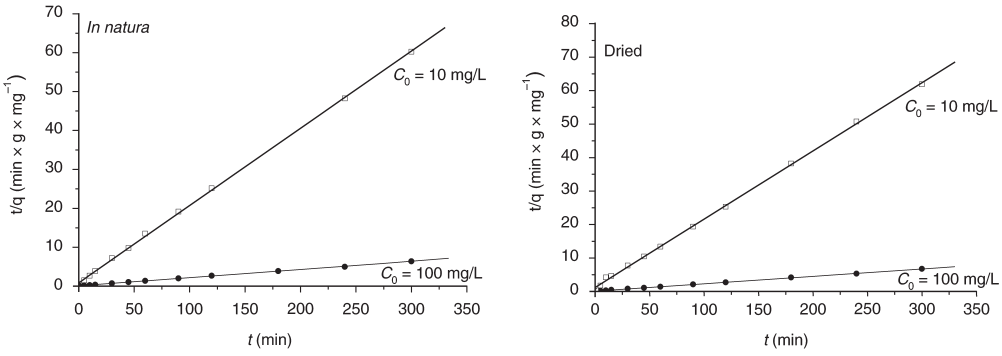

Fig. 5. Linear plots of the kinetic modeling of cadmium biosorption by *S. filipendula* biomass according to the second-order model at 303 K.

the uptake of cadmium, under certain experimental conditions. The results obtained for the parameter q_e when *in natura* biomass was tested, showed that the incubation temperature affected the uptake of cadmium. For initial cadmium concentrations of 10.0 and 100.0 mg/L, the obtained q_e values indicated that the higher the temperature, the smaller the q_e value. On the other hand, the results obtained for q_e when oven-dried *S. filipendula* biomass was used, showed that this biomass seemed to be less dependent than the *in natura* biomass with respect to the incubation temperature. For initial cadmium concentrations of 10.0 and 100.0 mg/L, the q_e value remained constant with increasing temperature, according to the second-order equation.

A comparison of the results obtained from the kinetic modeling of the experimental q_e values indicate a good fit to the pseudo-second-order model. Additionally, the correlation coefficients were close to 1.0, for all incubation temperatures tested. Hawari and Mulligan *(9)* worked with nonliving anaerobic granular biomass for the biosorption of cadmium found a q_e value of 64.0 mg/g, as predicted by the Langmuir model, in comparison with a q_e experimental value of 60.0 mg/g, which was considerably less than the results obtained in this work. Karthikeyan et al. *(5)* investigated the behavior of the green algae *Ulva fasciata* and the brown seaweed *Sargassum* sp. during the biosorption of copper. Authors found that *U. fasciata* could acquire copper up to 73.5 mg/gand *Sargassum* sp. up to 72.5 mg/g, with a rapid equilibrium and second-order kinetics. Martins et al. *(2)* observed that the aquatic moss *F. antipyretica* accumulated a maximum amount of cadmium of 28.0 mg/g biomass, independent of the temperature, with the results best fitting a Langmuir type model.

Villar et al. *(6)* compared the use of the red seaweed *Gelidium* sp. with an algal waste obtained from agar extraction for the biosorption of cadmium ions. They concluded that the results fitted well to the Langmuir and Redlich–Peterson models, with a maximum recovery of cadmium of

Table 2
Comparison Between Adsorption Rate Constants

	First-order kinetic model			Second-order kinetic model			
T (K)	$K_{1,\,ads}$ (min^{-1})	q_e (mg/g)	R	$K_{2,\,ads}$ (g/mg/min)	q_e (mg/g)	R	$q_{e,\,exp}$ (mg/g)
In natura biomass (C_0 = 10.0 mg/L)							
303	0.021 (0.002)	1.7 (0.2)	0.9755	0.045 (0.009)	5.04 (0.04)	0.9998	4.86 (0.14)
313	0.074 (0.008)	2.7 (0.7)	0.9686	0.106 (0.024)	4.80 (0.02)	0.9999	4.75 (0.02)
328	0.104 (0.017)	5.8 (1.8)	0.9733	0.054 (0.012)	4.71 (0.03)	0.9998	4.64 (0.02)
In natura biomass (C_0 = 100.0 mg/L)							
303	0.023 (0.005)	10.8 (2.2)	0.9077	0.007 (0.003)	47.8 (0.4)	0.9996	47.5 (0.9)
313	0.035 (0.004)	16.6 (3.6)	0.9611	0.022 (0.032)	42.8 (0.5)	0.9993	43.0 (1.2)
328	0.029 (0.016)	6.1 (1.7)	0.7862	0.061 (0.237)	41.6 (0.5)	0.9993	41.8 (1.3)
Dried biomass (C_0 = 10.0 mg/L)							
303	0.040 (0.003)	2.9 (0.3)	0.9884	0.034 (0.006)	4.91 (0.04)	0.9997	4.76 (0.06)
313	0.025 (0.011)	3.0 (1.0)	0.7288	0.234 (0.067)	4.92 (0.01)	0.9999	4.90 (0.02)
328	0.017 (0.014)	1.9 (1.1)	0.4344	0.040 (0.017)	5.07 (0.08)	0.9991	4.97 (0.02)
Dried biomass (C_0 = 100 mg/L)							
303	0.049 (0.005)	23.1 (3.5)	0.9773	0.006 (0.001)	45.2 (0.3)	0.9997	44.0 (0.9)
313	0.024 (0.003)	5.5 (0.5)	0.9605	0.021 (0.009)	46.4 (0.2)	0.9999	46.4 (0.2)
328	0.008 (0.016)	15.0 (11.7)	0.2537	0.001 (0.001)	48.3 (4.8)	0.9627	46.8 (0.3)

q_e estimated and coefficients of correlation, R associated with the pseudo-first-order Lagergren, and the pseudo-second-order kinetic models (w = 0.050 g, V = 25 mL, agitation rate 150 rpm, pH = 4.5).

[a]Figures in parenthesis indicate standard deviations (n = 3) of the numbers immediately above.

18.0 mg/g for pure *Gelidium* sp. biomass and 9.7 mg/g for the algal waste. Martins et al. *(10)* working with *Sargassum* sp. biomass for the biosorption of lead, found second-order kinetics during the uptake, which was not affected by the temperature in the range from 298 to 328 K. Their results fitted well to a Langmuir type equation, with a maximum biosorption of 1.26 mmol/g.

Conclusions

- Fourier transform infrared spectra indicated no differences between the spectra for *in natura* and oven-dried *S. filipendula* biomasses.
- TG/DTA analysis indicated a loss of mass, which was probably associated to the presence of water and a thermal effect was observed at 333 K.
- Kinetic modeling followed a pseudo-second-order model based on the similarities between the experimental and theoretical q_e values.
- Equilibrium modeling followed the Langmuir equation based on the correlation coefficients, which were close to 1.0. According to the Langmuir model, the q_e value was equal to 129.0 ± 2.0 mg/g when *in natura* biomass was used and 128.0 ± 3.0 mg/g when dry biomass was used.

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