

Chromium and zinc uptake by algae *Gelidium* and agar extraction algal waste: Kinetics and equilibrium

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Abstract

Biosorption of chromium and zinc ions by an industrial algal waste, from agar extraction industry has been studied in a batch system. This biosorbent was compared with the algae *Gelidium* itself, which is the raw material for agar extraction, and the industrial waste immobilized with polyacrylonitrile (composite material). Langmuir and Langmuir-Freundlich equilibrium models describe well the equilibrium data. The parameters of Langmuir equilibrium model at pH 5.3 and 20 °C were for the algae, $q_L = 18 \text{ mg Cr(III) g}^{-1}$ and $13 \text{ mg Zn(II) g}^{-1}$, $K_L = 0.0211 \text{ mg}^{-1} \text{ Cr(III)}$ and $0.0261 \text{ mg}^{-1} \text{ Zn(II)}$; for the algal waste, $q_L = 12 \text{ mg Cr(III) g}^{-1}$ and $7 \text{ mg Zn(II) g}^{-1}$, $K_L = 0.0331 \text{ mg}^{-1} \text{ Cr(III)}$ and $0.0421 \text{ mg}^{-1} \text{ Zn(II)}$; for the composite material, $q_L = 9 \text{ mg Cr(III) g}^{-1}$ and $6 \text{ mg Zn(II) g}^{-1}$, $K_L = 0.0321 \text{ mg}^{-1} \text{ Cr(III)}$ and $0.0341 \text{ mg}^{-1} \text{ Zn(II)}$. The biosorbents exhibited a higher preference for Cr(III) ions and algae *Gelidium* is the best one. The pseudo-first-order Lagergren and pseudo-second-order models fitted well the kinetic data for the two metal ions. Kinetic constants and equilibrium uptake concentrations given by the pseudo-second-order model for an initial Cr(III) and Zn(II) concentration of approximately 100 mg l^{-1} , at pH 5.3 and 20 °C were $k_{2,\text{ads}} = 0.04 \text{ g mg}^{-1} \text{ Cr(III) min}^{-1}$ and $0.07 \text{ g mg}^{-1} \text{ Zn(II) min}^{-1}$, $q_{\text{eq}} = 11.9 \text{ mg Cr(III) g}^{-1}$ and $9.5 \text{ mg Zn(II) g}^{-1}$ for algae; $k_{2,\text{ads}} = 0.17 \text{ g mg}^{-1} \text{ Cr(III) min}^{-1}$ and $0.19 \text{ g mg}^{-1} \text{ Zn(II) min}^{-1}$, $q_{\text{eq}} = 8.3 \text{ mg Cr(III) g}^{-1}$ and $5.6 \text{ mg Zn(II) g}^{-1}$ for algal waste; $k_{2,\text{ads}} = 0.01 \text{ g mg}^{-1} \text{ Cr(III) min}^{-1}$ and $0.18 \text{ g mg}^{-1} \text{ Zn(II) min}^{-1}$, $q_{\text{eq}} = 8.0 \text{ mg Cr(III) g}^{-1}$ and $4.4 \text{ mg Zn(II) g}^{-1}$ for composite material. Biosorption was modelled using a batch adsorber mass transfer kinetic model, which successfully predicts Cr(III) and Zn(II) concentration profiles. The calculated average homogeneous diffusivities, D_h , were 4.2×10^{-8} , 8.3×10^{-8} and $1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for Cr(III) and 4.8×10^{-8} , 9.7×10^{-8} and $6.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for Zn(II), respectively, for *Gelidium*, algal waste and composite material. The algal waste has the lower intraparticle resistance. © 2007 Elsevier B.V. All rights reserved.

Keywords: Biosorption; Chromium(III); Zinc(II); Algae *Gelidium*; Algal waste; Kinetics; Equilibrium

1. Introduction

Chromium is essentially used in the metallurgical processing of ferrochromium alloys and other metallurgical products, mainly in stainless steel, and, to a much lesser extent, in the refractory processing of chrome bricks and chemical processing to make chromic acid and chromates. Chromium in the form of trivalent compounds is an essential nutrient as well as zinc. Although trivalent chromium is less toxic than hexavalent chromium, a long-term exposure to trivalent chromium is known to cause allergic skin reactions and cancer [1].

Zinc is mainly used as a protective coating of other metals, such as iron and steel. It is also applied in galvanizing, brass, alloys, wrought zinc, pigments/chemical and others (including the use in veterinary and human medicines, as feed additive, and in cosmetics). Poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhoea have been reported after a single or short-term exposure to concentrations of zinc in water or beverages of 1000–2500 mg l^{-1} . Inhalation exposure to zinc chloride following the military use of “smoke bombs” has resulted in effects that include interstitial oedema, interstitial fibrosis, pneumonitis, bronchial mucosal oedema, ulceration and even death under extreme exposure conditions in confined spaces [2].

Methods proposed for zinc and chromium removal from wastewaters are chemical precipitation, chemical oxidation or

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reduction, adsorption and ion exchange, although these are often expensive and ineffective at low metal concentrations [3–5]. Recently, it has been confirmed that various biosorbents are able to effectively remove chromium, as brown seaweed *Ecklonia* sp. [3] and *Sargassum* [4], milled peat, waste industrial *Mucor meihi* biomass [6], etc., and zinc, as sugar industry waste (bagasse fly ash) [7], dewatered waste activated sludge from the Anglesea wastewater treatment plant [5], aquatic moss *Fontinalis antipyretica* [8], brown seaweed *Sargassum* sp. [9], etc.

Removal of chromium(III) and zinc(II) from water by biosorption, using algal waste from agar extraction, either directly or as a composite material and dead biomass of algae *Gelidium* can be a promising process. Large quantities of algal waste are generated and can be reused before final disposal. On the other hand, the waste material is cheaper than other commercially available adsorbents.

2. Biosorption equilibrium and kinetics

2.1. Equilibrium models

The Langmuir isotherm assumes that all adsorbed species interact only with a site, adsorption is limited to a monolayer, and adsorption energy of all sites is identical and independent of the presence of adsorbed species on neighbouring sites. The model is represented by the following equation [10]:

$$q_{\text{eq}} = \frac{q_L K_L C_{\text{eq}}}{1 + K_L C_{\text{eq}}} \quad (1)$$

where C_{eq} and q_{eq} represent the residual metal concentration in solution and the amount of the metal adsorbed on the biosorbent at equilibrium, respectively, q_L the maximum amount of the metal per unit weight of biosorbent to form a complete monolayer on the surface, and K_L is a coefficient related to the affinity between the sorbent and the metal ions.

The Langmuir-Freundlich (LF) isotherm, derived from the Langmuir and Freundlich models, is represented by the following equation [11]:

$$q_{\text{eq}} = \frac{q_{\text{LF}} K_{\text{LF}} (C_{\text{eq}})^{(1/n)}}{1 + K_{\text{LF}} (C_{\text{eq}})^{(1/n)}} \quad (2)$$

where K_{LF} is the equilibrium constant, q_{LF} the maximum amount of metal per unit weight of biosorbent and n is an empirical dimensionless parameter. If $n = 1$ Eq. (2) becomes the Langmuir equation.

2.2. Kinetic models

Kinetic models are used to examine the controlling mechanism of the biosorption process, mass transfer or chemical reaction. The two sorption kinetic models used in this study are based on the Ritchie equation [12]. From the general form of the Ritchie equation, the pseudo-first-order Lagergren model [13] and the second-order kinetic model [14] can be deduced:

First-order Lagergren model:

$$q_t = q_{\text{eq}} [1 - \exp(-k_{1,\text{ads}} t)] \quad (3)$$

Second-order model:

$$q_t = \frac{q_{\text{eq}}^2 k_{2,\text{ads}} t}{1 + k_{2,\text{ads}} q_{\text{eq}} t} \quad (4)$$

where q_t is the concentration of ionic species in the sorbent at time t (mg metal g⁻¹ biosorbent), $k_{1,\text{ads}}$ the biosorption constant of pseudo-first-order Lagergren equation (min⁻¹) and $k_{2,\text{ads}}$ is the biosorption constant of pseudo-second-order equation (min⁻¹ g biosorbent mg⁻¹ metal).

The initial biosorption rate ($r_{\text{ads}}(i)$) can be calculated from:

$$\left. \frac{dq}{dt} \right|_{t=0} = r_{\text{ads}}(i) \quad (5)$$

So,

$$r_{\text{ads}}(i) = k_{1,\text{ads}} q_{\text{eq}} \quad (6)$$

and

$$r_{\text{ads}}(i) = k_{2,\text{ads}} q_{\text{eq}}^2 \quad (7)$$

for the pseudo-first order Lagergren (Eq. (6)) and pseudo-second order (Eq. (7)) models, respectively.

2.3. Mass transfer models

For a quantitative description of the biosorption process dynamics, the following assumptions have been made [15]: (i) negligible external diffusion, corresponding to an adequate stirring rate; (ii) sorption rate controlled by homogeneous diffusion inside the particle or linear driving force approximation (LDF); (iii) isothermal process; (iv) equilibrium between bounded and soluble metal concentrations, as formulated by Langmuir isotherm; (v) particles assumed as uni-dimensional thin plates.

2.3.1. Homogeneous diffusion model

Mass conservation inside the particles

$$\frac{\partial y(x, t)}{\partial t} = \frac{1}{\tau_d} \frac{\partial^2 y(x, t)}{\partial x^2} \quad (8)$$

where τ_d is the time constant for diffusion of ionic species into the particle (min). The initial and boundary conditions for Eq. (8) are:

$$t = 0, \quad y_b(0) = 1 \quad (9)$$

$$0 \leq x < 1, \quad y(x, 0) = 0 \quad (10)$$

$$x = 1, \quad y(1, 0) = \frac{K_L C_{b0}}{1 + K_L C_{b0}} \quad (11)$$

$$x = 0, \quad \frac{\partial y(x, t)}{\partial x} = 0 \quad \forall t \quad (12)$$

$$x = 1, \quad \frac{\partial y(x, t)}{\partial t} = -\frac{\xi}{\tau_d} K_L C_{b0} [1 - y(x, t)]^2 \left[\frac{\partial y(x, t)}{\partial x} \right]_{x=1} \quad (13)$$

Dimensionless variables:

$$x = \frac{z}{L}; \quad y_b(t) = \frac{C_b(t)}{C_{b_0}};$$

$$y(x, t) = \frac{q(z, t)}{q_L}; \quad \langle y(x, t) \rangle = \frac{\langle q(z, t) \rangle}{q_L};$$

$$y_{eq} = \frac{q_{eq}}{q_L}; \quad \xi = \frac{Wq_L}{VC_{b_0}}$$

where V is the metal solution volume (l), W the mass of biosorbent (g), $C_b(t)$ and $\langle q(z, t) \rangle$ are, respectively, the concentration of metal species in the liquid phase (mg metal l^{-1}) and the average metal concentration in the solid phase (mg metal g^{-1} biosorbent), z the distance (expressed in cm) to the symmetry plane, C_{b_0} the initial metal concentration in the liquid phase (mg metal l^{-1}), $y_b(t)$ and $y(x, t)$ the dimensionless metal concentrations in liquid and solid phase, $\langle y(x, t) \rangle$ the dimensionless average metal concentration inside the particle, y_{eq} the dimensionless metal concentration in the solid phase, given by the equilibrium law, and ξ is the dimensionless factor for the batch capacity. A collocation on finite elements method was used to solve the nonlinear parabolic PDE with the initial and boundary conditions for each model equation [16].

2.3.2. Linear driving force (LDF)

If the average metal concentration inside the particle is used instead of a concentration profile, the following equations are considered:

Kinetic law:

$$\frac{d\langle y(t) \rangle}{dt} = k_p a_p [y_{eq} - \langle y(t) \rangle]; \quad a_p = \frac{1}{L} \quad (14)$$

where k_p is the mass transfer coefficient for intraparticle diffusion (cm s^{-1}) and a_p is the specific area of the thin plates particles (cm^{-1}).

Mass conservation in the fluid inside the closed vessel:

$$\langle y(t) \rangle = \frac{1}{\xi} (1 - y_b(t)) \quad (15)$$

Initial condition:

$$t = 0 \quad y_b(t) = 1 \quad \langle y(t) \rangle = 0 \quad (16)$$

By replacing Eq. (15) and the dimensionless Langmuir equation in Eq. (14) we will obtain the following expression, which can be solved analytically considering the initial condition:

$$\frac{1}{k_p a_p} \frac{dy_b(t)}{dt} + \left(\frac{\xi K_L C_{b_0}}{1 + K_L C_{b_0} y_b(t)} + 1 \right) y_b(t) = 1 \quad (17)$$

Supposing a parabolic profile inside the particle, $k_p a_p = 3D_h/L^2 = 3/\tau_d$, where $k_p a_p$ is the mass transfer intraparticle resistance (min^{-1}), D_h is the homogeneous diffusion coefficient inside the particle ($\text{cm}^2 \text{s}^{-1}$), and L is half of the thin plate thickness (cm).

3. Material and methods

3.1. Biosorbents

Untreated algal waste from the agar extraction industry or granulated by the addition of Polyacrylonitrile (PAN) were used in this study, as well as algae *Gelidium*, which is the raw material for agar extraction. The characteristics and preparation mode of these materials were presented in previous works [17,18].

3.2. Chromium and zinc solutions

Chromium(III) and zinc(II) solutions were prepared by dissolving a weighted quantity of nonhydrated chromium(III) nitrate (Carlo Erba, 98%) and anhydrous zinc(II) chloride (Merck, 98%) in distilled water. The initial pH of each solution was adjusted to 5.3 with HCl and NaOH 0.01 M solutions.

3.3. Sorption kinetic studies

In order to determine the contact time required to reach equilibrium, biosorption dynamic experiments were performed. Batch experiments were carried out in a 1-l capacity glass vessel, equipped with a cooling jacket (Grant type VFP) to ensure a constant temperature of 20 °C during the experiment. The pH was monitored and controlled with a WTW 538 pH/temperature meter. For kinetic experiments the vessel was filled with 0.5 l of distilled water and a known weight of adsorbent was added. The suspension was stirred for 10 min (magnetic stirrer Heidolph MR 3000) and the metal solution (0.5 l) was added. Suspension was maintained at pH 5.3, with a stirring rate of 600 rpm and a temperature of 20 °C. Samples (5 ml) were taken out at pre-determined time intervals ranging from 1 to 10 min after addition of the metal solution. Samples were centrifuged (Eppendorf Centrifuge 5410) and the supernatant stored for Cr(III) and Zn(II) analysis.

3.4. Sorption equilibrium studies

The experiments were performed in duplicate, using 100 ml Erlenmeyer flasks at pH 5.3 and 20 °C. The initial metal concentration changed from 10 to 300 mg l^{-1} . A given amount of biomass was suspended in 100 ml of metal solution and stirred at 100 rpm. Solution pH was adjusted by using 0.01 M NaOH and HCl solutions. The temperature was maintained constant by using a HOTTECOLD thermostatic refrigerator. Once equilibrium was reached, 1 h later, samples were taken out and centrifuged (Eppendorf Centrifuge 5410) and the supernatant analysed for the remaining Cr(III) and Zn(II).

3.5. Analytical procedure

Metal concentration was determined by Atomic Absorption Spectrometry (GBC 932 Plus Atomic Absorption Spectrometer). The amount of metal adsorbed per gram of biosorbent was

calculated as follows:

$$q = \frac{V(C_i - C_f)}{W} \quad (18)$$

where q is the metal uptake (mg metal g^{-1} of the biosorbent), C_i and C_f the initial and final metal concentrations in the solution (mg l^{-1}), V the volume of solution (l), and W is the dry weight of the added biosorbent (g).

4. Results and discussion

4.1. Equilibrium

Fig. 1(a) and (b) presents obtained equilibrium data for Cr(III) and Zn(II) adsorption on algae *Gelidium*, algal waste and composite material. Experimental equilibrium data correlates well with predicted values by Langmuir and Langmuir-Freundlich adsorption isotherms. Model parameters, including statistical ones are presented in Tables 1 and 2. It was found no statistical difference between the two models, using the test- F for a 95% probability level. So, results will be compared using the Langmuir model. Algae *Gelidium* is the best biosorbent as it can accumulate a higher quantity of metal ions and, in general, the uptake capacity is higher for Cr(III) than Zn(II).

Nieboer and McBryde [19] introduced the parameter $X_m^2(r_{\text{cryst}} + 0.85)$ as a measure for the strength of covalent bonding, where 0.85 stands for the contribution of N or O donors to the bond distance, X_m is the Pauling electronegativity [20] and r_{cryst} is the Shannon crystal radii [21]. This criterion confirms that the relative contribution of covalent bonding is similar for both ions, 4.05 Å for Cr(III) and 4.07 Å for Zn(II). According to the (z^2/r_{hyb}) criterion, where z is the cation charge and r_{hyb} is the nightingale hydrated ion radii [22], the strength of ionic bonds is higher for Cr(III) (1.95 \AA^{-1}) than for Zn(II) (0.93 \AA^{-1}). Using the criteria ΔX_m (1.9 for Zn(II) and 1.8 for Cr(III)) or $1 - \exp(-\Delta X_m^2/4)$ (0.59 for Zn(II) and 0.56 for Cr(III)), it can be concluded that the binding of Zn is more ionic (electrostatic) than the binding of Cr, but the difference is small. The parameter for the total binding strength, $\xi = z^2/r_{\text{hyb}}/1 - \exp(-\Delta X_m^2/4)$, is 1.6 for Zn(II) and 3.5 for Cr(III), which confirms the higher uptake of Cr(III) ions by the biosorbents.

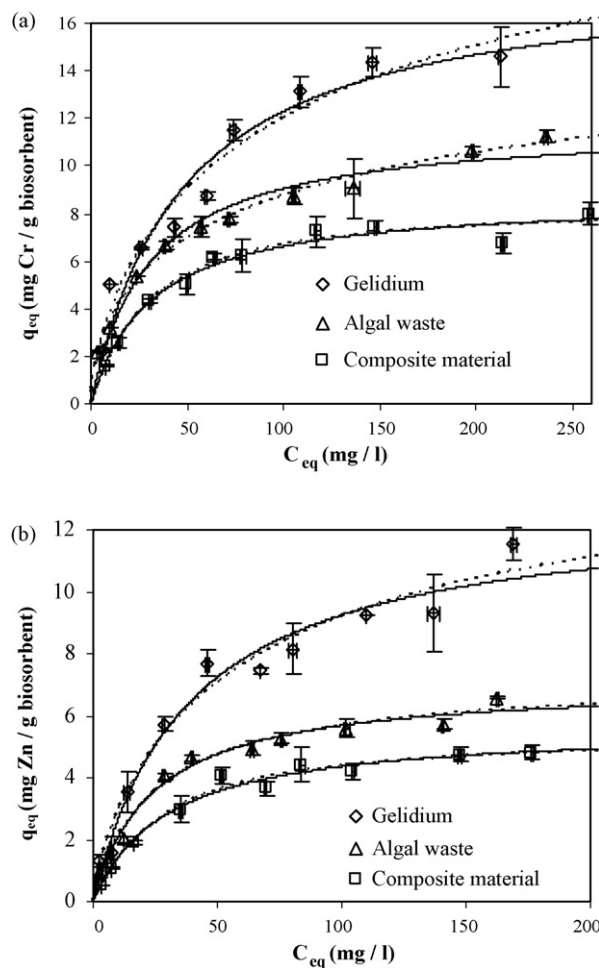


Fig. 1. Cr(III) (a) and Zn(II) (b) biosorption isotherms for algae *Gelidium*, algal waste and composite material (c). (---) Langmuir-Freundlich model, (—) Langmuir model (average $q_{\text{eq}} \pm$ standard deviation).

4.2. Kinetics

4.2.1. Kinetic models

In general, biosorption is rapid, occurring mainly in the first 20 min. The adsorption process is faster at an initial stage, during occupation of high affinity sites and gradually decreases with time until saturation.

Fig. 2(a) and (b) presents kinetic data fitted by pseudo-first-order Lagergren and pseudo-second-order models. The

Table 1
Estimated Langmuir equilibrium model parameters (value \pm standard deviation)

Biosorbent	Metal	Langmuir model					
		q_L (mg g^{-1})	q_L (mmol g^{-1})	K_L ($\times 10^2 \text{ l mg}^{-1}$)	R^2	S_R^2 (mg g^{-1})	$q_L \times K_L$ (l g^{-1})
<i>Gelidium</i>	Zn ²⁺	13 \pm 1	0.20 \pm 0.02	2.6 \pm 0.7	0.900	1.24	0.3 \pm 0.1
	Cr ³⁺	18 \pm 1	0.35 \pm 0.02	2.1 \pm 0.4	0.933	1.38	0.38 \pm 0.08
Algal waste	Zn ²⁺	7.1 \pm 0.2	0.110 \pm 0.003	4.2 \pm 0.5	0.973	0.11	0.30 \pm 0.04
	Cr ³⁺	11.8 \pm 0.5	0.23 \pm 0.01	3.3 \pm 0.5	0.946	0.54	0.4 \pm 0.1
Composite material	Zn ²⁺	5.7 \pm 0.3	0.087 \pm 0.005	3.4 \pm 0.6	0.941	0.15	0.19 \pm 0.04
	Cr ³⁺	8.7 \pm 0.4	0.170 \pm 0.008	3.2 \pm 0.5	0.930	0.33	0.28 \pm 0.05

Table 2
Estimated Langmuir-Freundlich equilibrium model parameters (value \pm standard deviation)

Biosorbent	Metal	Langmuir-Freundlich model				
		q_{LF} (mg g ⁻¹)	K_{LF} ($\times 10^2$ l ^{1/m} mg ^{-1/m})	n	R^2	S_R^2 (mg g ⁻¹)
Gelidium	Zn ²⁺	15 \pm 5	4 \pm 2	1.2 \pm 0.4	0.900	1.27
	Cr ³⁺	25 \pm 9	3.5 \pm 0.9	1.4 \pm 0.3	0.941	1.23
Algal waste	Zn ²⁺	7.3 \pm 0.6	5 \pm 1	1.1 \pm 0.2	0.973	0.11
	Cr ³⁺	18 \pm 5	6 \pm 1	1.7 \pm 0.3	0.964	0.35
Composite material	Zn ²⁺	5.4 \pm 0.5	3 \pm 1	0.9 \pm 0.2	0.942	0.16
	Cr ³⁺	8.3 \pm 0.6	2 \pm 1	0.9 \pm 0.2	0.932	0.34

performance of both models was compared using the test- F . Although the pseudo-second-order model is better, no significant difference exists between the two models when considering the whole experiments for a 95% confidence level.

Model parameters are presented in Tables 3 and 4. The values of q_{eq} confirm a higher chromium uptake relatively to zinc, as it was concluded in the equilibrium experiments. In general, initial biosorption rate is higher for Zn(II) than for Cr(III), because chromium ions diffusivity in solution is lower due to the higher hydrated radius (4.61 Å Cr(III) and 4.30 Å Zn(II)). The diffusiv-

ity of Cr(III) in water is 5.85×10^{-6} cm² s⁻¹ and for Zn(II) is 6.94×10^{-6} cm² s⁻¹.

4.2.2. Mass transfer models

The mass transfer models presented in this work were solved based on the operating parameters, resulting in the simulated curves shown in Fig. 3(a) and (b). Both models adjust well the experimental data, confirming that the LDF approximation can be considered, and concentration profiles inside particles are parabolic.

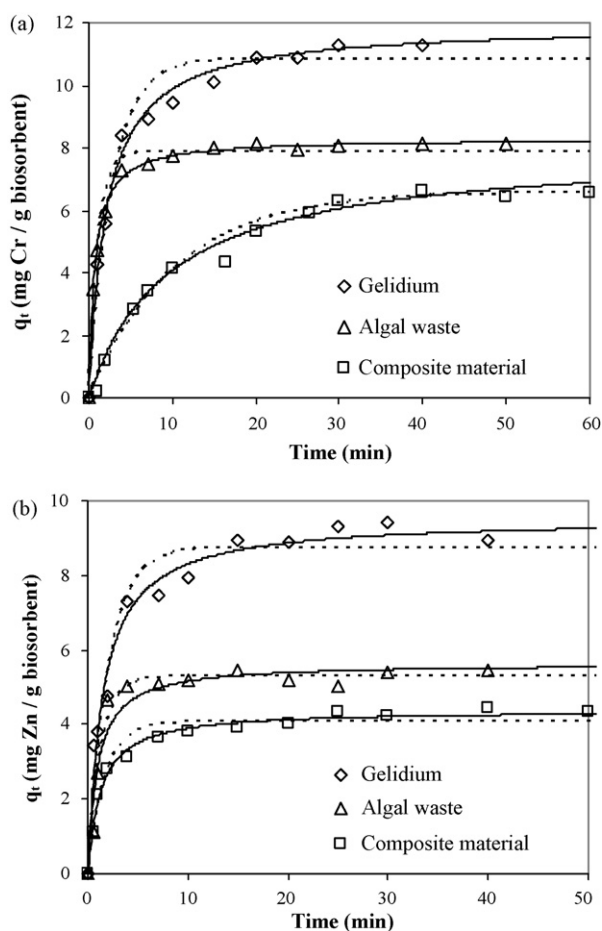


Fig. 2. Evolution of adsorbed Cr(III) (a) and Zn(II) (b) concentration on algae *Gelidium*, algal waste and composite material, with contact time: experimental data and kinetic models (---) pseudo-first-order Lagergren model, (—) pseudo-second-order model.

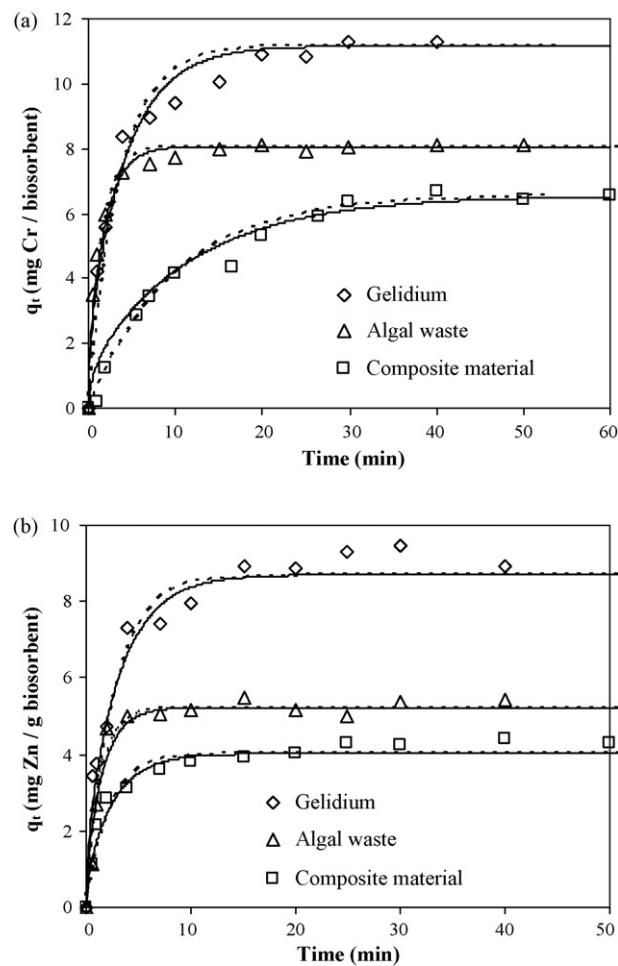


Fig. 3. Evolution of adsorbed Cr(III) (a) and Zn(II) (b) concentration on algae *Gelidium*, algal waste and composite material, with contact time: experimental data and mass transfer kinetic model.

Table 3
Estimated pseudo-first-order Lagergren model parameters (value \pm standard deviation)

Biosorbent	Metal	C_i (mg l ⁻¹)	Pseudo-first-order Lagergren model				
			q_{eq} (mg g ⁻¹)	$k_{1,ads}$ (min ⁻¹)	R^2	S_R^2 (mg g ⁻¹) ²	$r_{ads(i)}$ (mg g ⁻¹ min ⁻¹)
<i>Gelidium</i>	Zn ²⁺	85	8.8 \pm 0.3	0.48 \pm 0.08	0.951	0.56	4.2 \pm 0.7
	Cr ³⁺	100	10.8 \pm 0.3	0.35 \pm 0.05	0.960	0.59	3.8 \pm 0.6
Algal waste	Zn ²⁺	81	5.3 \pm 0.1	0.76 \pm 0.08	0.980	0.08	4.0 \pm 0.4
	Cr ³⁺	97	7.9 \pm 0.1	0.90 \pm 0.08	0.983	0.12	7.1 \pm 0.6
Composite material	Zn ²⁺	80	4.1 \pm 0.1	0.58 \pm 0.08	0.961	0.08	2.4 \pm 0.3
	Cr ³⁺	94	6.6 \pm 0.1	0.097 \pm 0.005	0.995	0.03	0.64 \pm 0.03

Table 4
Estimated pseudo-second-order model parameters (value \pm standard deviation)

Biosorbent	Metal	C_i (mg l ⁻¹)	Pseudo-second-order model				
			q_{eq} (mg g ⁻¹)	$k_{2,ads}$ (g mg ⁻¹ min ⁻¹) $\times 10^2$	R^2	S_R^2 (mg g ⁻¹) ²	$r_{ads(i)}$ (mg g ⁻¹ min ⁻¹)
<i>Gelidium</i>	Zn ²⁺	85	9.5 \pm 0.3	7 \pm 1	0.977	0.24	6 \pm 1
	Cr ³⁺	100	11.9 \pm 0.2	4.0 \pm 0.4	0.990	0.15	5.7 \pm 0.6
Algal waste	Zn ²⁺	81	5.6 \pm 0.2	19 \pm 5	0.951	0.19	6 \pm 2
	Cr ³⁺	97	8.3 \pm 0.1	17 \pm 1	0.998	0.01	11.7 \pm 0.8
Composite material	Zn ²⁺	80	4.39 \pm 0.06	18 \pm 2	0.991	0.02	3.5 \pm 0.4
	Cr ³⁺	94	8.0 \pm 0.2	1.3 \pm 0.2	0.992	0.06	0.9 \pm 0.2

Table 5
Estimated parameters for LDF and homogeneous particle diffusion models

Biosorbent	Metal	C_i (mg l ⁻¹)	LDF model		Homogeneous diffusion model	
			$k_p \times a_p$ (min ⁻¹)	τ_d (min)	τ_d (min)	D_h (cm ² s ⁻¹)
<i>Gelidium</i>	Zn	85	0.35	8.6	8.6	4.8 $\times 10^{-8}$
	Cr	100	0.25	12	10	4.2 $\times 10^{-8}$
Algal waste	Zn	81	0.70	4.3	4.3	9.7 $\times 10^{-8}$
	Cr	97	0.60	5	5	8.3 $\times 10^{-8}$
Composite material	Zn	80	0.45	6.7	6.7	6.2 $\times 10^{-8}$
	Cr	94	0.10	30	30	1.4 $\times 10^{-8}$

The values of the mass transfer intraparticle resistance, time diffusion and homogeneous diffusion coefficient are presented in Table 5. The thickness of the thin plates were determined by microscopic observations ($L = 0.05$ mm). D_h values are higher for Zn(II) ions, confirming the lower mass transfer intraparticle resistance relatively to Cr(III) ions. D_h values are higher than the diffusivity values for both ions in water, suggesting a resistance to the diffusion process.

The kinetic rate for the pseudo-first-order Lagergren equation is defined as $dq_t/dt = k_{1,ads}(q_{eq} - q_t)$. Comparing this equation with the kinetic law used in the LDF model (Eq. (14)), $k_{1,ads}$ has the same meaning that $k_p a_p$ and, both values are of the same order of magnitude, validating the assumed mechanism.

5. Conclusion

Biosorption of Zn(II) and Cr(III) ions by algae *Gelidium*, algal waste and composite material, can be considered as an innovative and effective process with good performances. Equilibrium is well described by Langmuir and Langmuir-Freundlich

models. The maximum uptake capacity indicates that algae *Gelidium* is the best biosorbent, but for low metal concentrations, similar uptake capacities were found for the three biosorbents. Biosorption kinetics is fast and is well represented by pseudo-first-order Lagergren and pseudo-second-order models. The LDF model can be considered as a simple model, with an analytical solution, to describe mass transfer resistance in the biosorption process.

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