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Special Issue on Metal Ions Removal from Liquid Effluents: Part One
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34   **Abstract**
35
36   In this work, biosorption of trivalent chromium by the marine brown algae *Sargassum muticum* was
37   studied in a batch system. The effect of the solution pH on Cr(III) uptake by *Sargassum* was
38   investigated. Kinetics and equilibrium experiments were conducted at different pH values (3.0, 4.0 and
39   5.0). Equilibrium data are well described by the Langmuir and Langmuir-Freundlich isotherms and
40   kinetics follows the pseudo-second-order model, at different pH values. The two mass transfer models
41   give comparable results, but they did not provide a perfect representation of the sorption data. The
42   homogeneous diffusivity, D_h, was found to be around 1.6×10^{-8} cm^2 s^{-1} for 100 mg l^{-1} Cr(III)
43   concentration.
44   *Sargassum muticum* was compared with the brown algae *Laminaria hyperborean* and the red algae
45   *Gelidium sesquipedale* in terms of uptake capacity. The maximum uptake capacities for *Sargassum*,
46   *Laminaria* and *Gelidium* were, respectively, 56 ± 3, 70 ± 4 and 18 ± 1 mg Cr(III) g^{-1}, at pH = 5.
47
48   **Keywords:** *Sargassum*, *Gelidium*, *Laminaria*, Equilibrium, Kinetics, Marine Algae
49

53

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62   effluents detoxification using solar radiation.
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research interests include colour removal from textile wastewaters using low-cost adsorbents, heavy metal removal from contaminated waters by biosorption, formation and fate of disinfection by-products and biogeochemical transformations in surface waters. He has published about 40 papers in peer-reviewed environmental journals and presented over 80 communications in international conferences. He is member of the International Water Association.

Nomenclature

a_p specific area of thin plate particles (cm^{-1})

C_i and C_f initial and final metal concentrations in the solution (mg l^{-1})

C_{eq} residual metal concentration in solution (mg l^{-1})

$C_b(t)$ concentration of metal species in the liquid phase (mg metal l^{-1})

C_{b_0} initial metal concentration in the liquid phase (mg l^{-1})

D_h homogeneous diffusion coefficient inside the particle (cm^2 s^{-1})

L half of the thin plate thickness (cm)

$k_{1,ads}$ biosorption constant of pseudo-first-order equation (min^{-1})

$k_{2,ads}$ biosorption constant of pseudo-second-order equation (min^{-1} g mg^{-1}).

K_L equilibrium constant for the Langmuir equation (l mg^{-1})

K_{LF} equilibrium constant for the Langmuir-Freundlich equation (l mg^{-1})

k_p mass transfer coefficient for intraparticle diffusion (cm s^{-1})

n empirical dimensionless parameter

q metal uptake (mg metal g^{-1} of the biosorbent)

q_{eq} amount of the metal adsorbed on the biosorbent at equilibrium (mg g^{-1})

q_L and q_{LF} maximum amount of metal per unit weight of biosorbent to form a complete monolayer on the surface, respectively for Langmuir and Langmuir-Freundlich equation (mg g^{-1})

$\langle q(z,t) \rangle$ average metal concentration in the solid phase (mg g^{-1})

q_t concentration of metal in the sorbent at time t (mg g^{-1})

$r_{ads}(i)$ initial biosorption rate (mg g^{-1} min^{-1})

V volume of solution (l)

$y_b(t)$ and $y(x,t)$ dimensionless metal concentrations in liquid and solid phase

$\langle y(x,t) \rangle$ dimensionless metal concentration inside the particle

y_{eq} dimensionless metal concentration in the solid phase

x dimensionless axial coordinate inside the particle

z distance to the symmetry plane (cm)

W dry weight of biosorbent (g)

ξ dimensionless factor for the batch capacity

τ_d particle diffusion time constant (s)

1 Introduction

Chromium main uses are in alloys, such as stainless steel, chrome plating leather tanning, and metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating; it is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; to make moulds for the firing of bricks (WHO, 1988).

Chromium(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health harmful effects as well, for instance skin rashes (WHO, 1988).

Chromium, and most trivalent chromium compounds, have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals, but a long-term exposure to Cr(III) is known to cause allergic skin reactions and cancer (Lide, 2006).

Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops (Lide, 2006).

Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal bearing wastewaters in surface waters, can damage the gills of fish that swim

near the point of discharge. Chromium can cause respiratory problems in animals, a lower ability to fight disease, birth defects, infertility and tumour formation (Lide, 2006).

In result of chromium toxicity, discharge limits have been regulated by most industrialized countries. Conventional treatment of these effluents rich in chromium, as chemical precipitation, oxidation/reduction, ion exchange and others, are extremely expensive (reagents consumption, safe disposal of toxic sludge, technology) or inefficient for chromium removal from diluted solutions (Volesky, 2003).

Nowadays, it has been confirmed that several low cost biological materials are able to effectively remove chromium by sorption, as brown seaweed *Ecklonia sp.* (Yun et al., 2001), *Sargassum* (Kratochvil et al., 1998), *Laminaria japonica* (Kang et al., 2004), blue-green algae *Spirulina sp.* (Chojnacka et al., 2005), peat (Ma and Tobin, 2003), waste industrial *Mucor meihi* biomass (Tobin and Roux, 1998), *Saccharomyces cerevisiae* residual cells from brewing industries (Ferraz et al., 2004), etc. Metal uptake by biosorption is the result of a combination of different reactions that can occur in the cell wall, as complexation, coordination and chelation of metals, ion exchange, adsorption and microprecipitation (Volesky, 2003). The binding of chromium ions (Cr^{3+} and $CrOH^{2+}$) by protonated brown alga *Ecklonia* biomass was attributed to carboxylic groups in the pH range 1-5, and the uptake capacity increased with pH. An equilibrium model including the hydrolysis reactions that chromium undergoes in the aquatic phase and the Cr^{3+} and $Cr(OH)^{2+}$ reactions with the binding sites was able to predict the equilibrium data (Yun et al., 2001). Carboxyl groups are acidic, so at low pH they will be protonated and thereby become less available for binding metals, which explains why the uptake of many metals increases with increasing pH (Crist et al., 1991).

Protonated or Ca-form *Sargassum* seaweed biomass bound up to 40 mg g^{-1} of Cr(III) by ion exchange at pH 4. An ion-exchange model assuming that only species taken up by the biomass was $Cr(OH)^{2+}$ successfully fitted the experimental biosorption data for Cr(III) (Kratochvil et al., 1998).

Waste industrial *Mucor meihi* biomass was found to be an effective biosorbent for the removal of chromium from industrial tanning effluents. Sorption levels of 1.15 and 0.7 mmol g^{-1} were observed at pH 4 and 2, respectively. Acid elution of biosorbed chromium increased with decreasing eluant pH to a maximum value of *ca*. 30% at pH near zero (Tobin and Roux, 1998).

Kinetic, equilibrium and dynamic (packed bed column) adsorption studies have been performed successfully, using as adsorbate Pb(II), Cu(II), Cd(II) and Zn(II) ions, and the red algae *Gelidium sesquipedale* as biosorbent (Vilar et al., 2006a, Vilar et al., 2006c, , 2007).The metal ion uptake was attributed to the carboxylic groups present in the structure of the algae, determined by potentiometric titration (Vilar, 2006). A continuous model, considering a heterogeneous Sips distribution of the binding equilibrium constants fitted well the equilibrium experimental data (Vilar et al., 2006c). The kinetic data in batch and continuous systems were also well described by a mass transfer model (Vilar et al., 2006a, 2006b, Vilar et al., 2007).

Until now biosorption of trivalent chromium by algae *Sargassum muticum* has not been described. Large quantities of these algae are available in the Portuguese coast and can be used for metal removal. Ria Formosa, in the south of Portugal, has been invaded by *Sargassum muticum*, putting in danger the ecosystem biodiversity. So, it's a matter of concern to remove this algal biomass, and find out an interesting application for the large quantities available.

2 Material and methods

2.1 Biosorbents

The brown seaweeds *Sargassum muticum* and *Laminaria hyperborea* were collected along Portuguese northern coast. The red algae *Gelidium sesquipedale* was harvested from central and southern coast. The algae were washed with tap water and distilled water to remove most salts, air-dried during two days to remove odours and most water and, after that, dried at 60ºC and crushed in a mill. Algal particles were then sieved (AS200 digit Retsch shaker) to obtain a fraction of 0.5-0.85 mm. The equivalent length and width of the particles were about 2.5 mm and 0.6 mm, respectively, and thickness 0.1 mm.

2.2 Chromium solutions

Chromium(III) solutions were prepared by dissolving a weighted quantity of nonahydrated chromium (III) nitrate (Carlo Erba, 98%) in distilled water. Solution pH values were controlled during kinetic and equilibrium experiments to 5.0, 4.0 and 3.0 by addition of HNO_3 0.01/0.1 M and NaOH 0.01/0.1 M solutions.

4

2.3 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-liter capacity glass vessel, equipped with a cooling jacket (Grant type VFP) to ensure a constant 20 ºC temperature 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 at 600 rpm stirring rate (magnetic stirrer Heidolph MR 3000) for initial solution pH correction, and then the metal solution (0.5 l of a 200 mg l⁻¹ solution, which leads to an initial concentration of 100 mg l⁻¹) was added maintaining the same stirring rate. 5 ml samples were taken out at pre-determined time intervals ranging from 1 to 10 minutes after addition of the metal solution. Samples were centrifuged (Eppendorf Centrifuge 5410) and the supernatant stored for Cr(III) analysis.

2.4 Sorption equilibrium studies

The experiments were performed in duplicate, using 100 ml Erlenmeyer flasks, at pH = 5.0, 4.0 and 3.0 and temperature 20ºC. The initial metal concentration was changed between 10 and 200 mg l⁻¹. A given amount of biomass was suspended in 100 ml metal solution and stirred at 100 rpm. The solution pH was adjusted by using 0.01 M NaOH and HCl solutions and temperature was maintained constant (20ºC) by using a HOTTECOLD thermostatic refrigerator. Once equilibrium was reached, samples were taken out and centrifuged (Eppendorf Centrifuge 5410) for Cr(III) analysis in the supernatant.

2.5 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 from the metal mass balance.

3. Results and discussion

3.1 Equilibrium

Biosorption of Cr(III) ions by *Sargassum muticum* is highly pH dependent, as can be seen in Fig. 1. The pH influences both metal binding sites on the cell surface and metal chemistry in solution. According to the chromium speciation diagram in aqueous solution (Haug and Smidsrod, 1970), for the pH range 1.5-5, the predominant Cr(III) species in solution are Cr^{3+} and $Cr(OH)^{2+}$ ($Cr(OH)^{+}$ also exists at this pH range but in a very low concentration). For pH < 2.5, $Cr(OH)^{2+}$ is no more present in solution, and Cr^{3+} starts to precipitate as $Cr(OH)_3$ at pH > 5.0. Two major species, Cr^{3+} and $Cr(OH)^{2+}$, can bind with functional groups present on the surface of the biosorbent.

INSERT FIG.1

As the pH increases, the active sites, such as carboxyl and sulphate groups carry negative charges and subsequently attract metal ions. So, biosorption onto cell surfaces increases. Yun et al. (2001) studied the biosorption of trivalent chromium on brown alga *Ecklonia* biomass, and concluded that, even at pH > 3.35, the contribution of Cr^{3+} binding to the chromium uptake was significant (identical concentrations of Cr^{3+} and $Cr(OH)^{2+}$ in aqueous phase), indicating that Cr^{3+} has higher affinity to the binding sites than $Cr(OH)^{2+}$.

Fig. 2 presents obtained equilibrium data for Cr(III) adsorption on algae *Sargassum muticum* at three different pH (3.0, 4.0 and 5.0). Two equilibrium models were used to describe the equilibrium data:

Langmuir isotherm equation (Langmuir, 1918):

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

Langmuir-Freundlich (LF) isotherm, derived from the Langmuir and Freundlich models (Sips, 1948):

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

265 where C_{eq} and q_{eq} represent the residual metal concentration in solution and the amount of the metal
266 adsorbed on the biosorbent at equilibrium, respectively, q_L and q_{LF} are the maximum amount of metal
267 per unit weight of biosorbent to form a complete monolayer on the surface, K_L is a coefficient related
268 to the affinity between the sorbent and the metal ions, K_{LF} is the equilibrium constant, and n is an
269 empirical dimensionless parameter.

270
271 **INSERT FIG. 2**
272
273 Experimental equilibrium data are well predicted by Langmuir and Langmuir-Freundlich adsorption
274 isotherms. Model parameters, including statistical ones, are presented in Tables 1 and 2. No statistical
275 difference was found between the two models, as given by the application of the test F for a 95%
276 confidence level. So, results will be compared using Langmuir model.

277
278 **INSERT TABLES 1 AND 2**
279
280 Fig. 3 compares the adsorption behaviour of three different algae species, brown algae *Sargassum*
281 *muticum* and *Laminaria hyperborea*, and red algae *Gelidium sesquipedale*, at pH = 5 and T = 20ºC.
282 Brown algae present a higher uptake capacity for chromium than red algae *Gelidium*, because they
283 have more surface carboxyl groups ($\approx$ 2.6 mmol g^{-1}) (Figueira et al., 2000, Lodeiro et al., 2005) when
284 compared with algae *Gelidium* ($\approx$ 0.36 mmol g^{-1}) (Vilar, 2006). Carboxyl groups are mainly due to
285 alginic acid (brown algae) and agarose (*Gelidium*). The values of $q_L \times K_L$ presented in Table 1,
286 indicate metal ions affinity for surface groups. Results show that metal ions bind with brown algae
287 functional groups more easily than with algae *Gelidium*. Alga *Laminaria* is the best biosorbent as it
288 can accumulate a greater amount of metal ions, principally for equilibrium concentrations higher than
289 20 mg l^{-1}.

290
291 **INSERT FIG. 3**
292
293 The adsorption of trivalent chromium ions has been studied, using different kinds of biosorbents: crab
294 shell (*Chinonecetes opilio* obtained as waste from a crabmeat processing plant) (q_L = 21 mg g^{-1}, pH =
295 5.0, T = 30ºC) (Kim, 2003), *Sargassum sp.* (Brazilian coast) (q_L = 60 mg g^{-1}, pH = 5.0, T = 30ºC)
296 (Cossich et al., 2002), a residue of *Sargassum sp.* seaweed obtained after extraction of biological
297 cosmetics (q_L = 300 mg g^{-1}, pH = 6.0, T = 55ºC) (Carmona et al., 2005), brown seaweed *Ecklonia sp.*
298 (seashore of Pohand, Korea) (q_L = 34 mg g^{-1}, pH = 4, T = 20ºC), algal biomass *spirogyra spp.* treated
299 with 0.2 M CaCl$_2$ (q_L = 30.21 mg g^{-1}, pH = 5, T = 25ºC) (Bishnoi et al., 2006), carrot residues (q_L = 40
300 mg g^{-1}, pH = 5.0, T = 25ºC) (Nasernejad et al., 2005), bacterium *Pseudomonas aeruginosa* (q_L= 7 mg g^{-1}
301 ^{1}, pH not given, T = 25ºC) (Kang et al., 2006), milled peat form supplied by Bord and Mona
302 (Newbridge, Co. Kildare, Ireland) (q_L = 21 mg g^{-1}, pH = 5, T = 22-25ºC) (Ma and Tobin, 2003), yeast
303 *Candida tropicallis* (q_L = 4.6 mg g^{-1}) and filamentous bacterium *Streptomyces noursei* (q_L = 1.8 mg g^{-1})
304 (Mattuschka et al., 1993). These results show that the brown algae studied in this work are similar to
305 the best biosorbents presented above, with respect to Cr(III) uptake capacity.

306
307 *3.2 Kinetics*
308
309 *3.2.1 Kinetic models*
310
311 Fig. 4 shows that biosorption is a fast process, occurring mainly in the first 40 minutes. The adsorption
312 process takes place in two different stages: an initial and fastest stage, when high affinity and more
313 accessible sites are occupied and a second stage that corresponds to the occupation of low affinity and
314 more internal sites (Vilar, 2006).

315
316 **INSERT FIG. 4 (a) AND (b)**
317
318 In this work, two kinetic models were used (Lagergren, 1898, Ho and McKay, 1998):
319 Pseudo-first-order model   Pseudo-second-order model

320 $$q_t = q_{eq}\left[1 - exp\left(-k_{1,ads}t\right)\right] \quad (3) \qquad q_t = \frac{q_{eq}^2\, k_{2,ads}\, t}{1 + k_{2,ads}\, q_{eq}\, t} \quad (4)$$

321   where q_t is the concentration of ionic species in the sorbent at time t (mg metal g^{-1} biosorbent), $k_{1,ads}$ is

322   the biosorption constant of pseudo-first-order equation (min^{-1}) and $k_{2,ads}$ is the biosorption constant of

323   pseudo-second-order equation (min^{-1} g biosorbent mg metal^{-1}).

324   Kinetic data in Fig. 4 are fitted by the pseudo-first order and the pseudo-second order models. The
325   performance of both models was compared by using the F Test, which let us to conclude that the
326   pseudo-second-order model fits better the kinetic data for the three pH values (95% confidence level).
327   Model parameters are presented in Tables 3 and 4. The values of q_{eq} confirm a stronger chromium
328   uptake at high pH values, as it was concluded from the equilibrium experiments. The initial
329   biosorption rate ($r_{ads}(i)$) was calculated as:

330
$$r_{ads}(i) = k_{1,ads}\, q_{eq} \qquad (5) \qquad \text{and} \qquad r_{ads}(i) = k_{2,ads}\, q_{eq}^2 \qquad (6)$$

331   for the pseudo-first order and pseudo-second order models, respectively. The initial biosorption rate
332   increases with pH due to the increase of the affinity of the metal ions to the binding sites.

333
334   **INSERT TABLES 3 AND 4**

335
336   *3.2.2 Mass transfer models*

337
338   In order to describe the dynamics of the biosorption process two mass transfer models were developed,
339   a homogeneous diffusion model and a linear driving force model, that can be solved analytically
340   (Rodrigues, 1974). The following assumptions were considered: (i) - negligible external diffusion, for
341   an adequate stirring rate (600 rpm); (ii) - sorption rate controlled by homogeneous diffusion inside the
342   particle or linear driving force approximation (LDF); (iii) - isothermal process; (iv) - equilibrium
343   between bound and soluble metal concentrations, as formulated by Langmuir isotherm; (v) - particles
344   as uni-dimensional thin plates.

345
346   *Homogeneous Diffusion Model*
347   Mass conservation inside the particles gives:

348
$$\frac{\partial\, y(x,t)}{\partial\, t} = \frac{1}{\tau_d}\frac{\partial^2 y(x,t)}{\partial\, x^2}\,,\ \tau_d = \frac{L^2}{D_h} \qquad (7)$$

349   where τ_d is the time constant for diffusion of ionic species into the particle (min), D_h is the
350   homogeneous diffusion coefficient inside the particle (cm^2 s^{-1}), and L is half of the thin plate thickness
351   (cm).
352   The initial and boundary conditions for Eq. (7) are:

353           $t = 0 \quad y_b(0) = 1$ (8)

354           $0 \le x < 1 \quad y(x,0) = 0$ (9)

355           $x = 0 \quad \dfrac{\partial\, y(x,t)}{\partial\, x} = 0 \quad \forall t$ (10)

356           $x = 1 \quad \dfrac{\partial\, y(x,t)}{\partial\, t} = -\dfrac{\xi}{\tau_d} K_L\, C_{b_0}\left[1 - y(x,t)\right]^2 \left[\dfrac{\partial\, y(x,t)}{\partial\, x}\right]_{x=1}$ (11)

357   Dimensionless variables:

358
$$x = \frac{z}{L};\quad y_b(t) = \frac{C_b(t)}{C_{b_0}};\quad y(x,t) = \frac{q(z,t)}{q_L};$$

359
$$\langle y(x,t)\rangle = \frac{\langle q(z,t)\rangle}{q_L};\quad y_{eq} = \frac{q_{eq}}{q_L};\quad \xi = \frac{W\, q_L}{V\, C_{b_0}}$$

360   where V is the metal solution volume (l), W the mass of biosorbent (g), $C_b(t)$ and $\langle q(z,t)\rangle$ the
361   concentration of metal species in the liquid phase (mg metal l^{-1}) and the average metal concentration in
362   the solid phase (mg metal g^{-1} biosorbent), respectively, z the distance (cm) to the symmetry plane, x the
363   dimensionless axial coordinate inside the particle, C_{b_0} the initial metal concentration in the liquid
364   phase (mg metal l^{-1}), $y_b(t)$ and $y(x,t)$ the dimensionless metal concentrations in liquid and solid

365   phase, $\langle y(x,t)\rangle$ the average metal concentration inside the particle, y_{eq} the dimensionless metal

366   concentration in the solid phase, given by the equilibrium law, and ξ the dimensionless factor for the

367   batch capacity. A collocation on finite elements method was used to solve the nonlinear parabolic PDE

368   with the initial and boundary conditions for each model equation (Madsen and Sincovec, 1979).

369

370   *Linear Driving Force (LDF)*

371   If the average metal concentration inside the particle is used instead of a concentration profile, the

372   following equations are obtained:

373   Kinetic law:

374
$$\frac{d\langle y(t)\rangle}{dt} = k_p\, a_p \left[y_{eq} - \langle y(t)\rangle \right]; \quad a_p = \frac{1}{L} \tag{12}$$

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

376   the thin plate particles (cm^{-1}).

377   Mass conservation in the fluid inside the closed vessel:

378
$$\langle y(t)\rangle = \frac{1}{\xi}\left(1 - y_b(t) \right) \tag{13}$$

379   Initial condition:

380
$$t = 0 \quad y_b(t) = 1 \quad \langle y(t)\rangle = 0 \tag{14}$$

381   Substituting Eq. (13) and the dimensionless Langmuir equation in Eq. (12) the following expression is

382   obtained, which can be solved analytically:

383
$$\frac{1}{k_p\, a_p}\frac{d\, y_b(t)}{d\, t} + \left(\frac{\xi\, K_L\, C_{b_0}}{1 + K_L\, C_{b_0}\, y_b(t)} + 1 \right) y_b(t) = 1 \tag{15}$$

384   For a parabolic profile inside the particle, $k_p\, a_p = 3\, D_h / L^2 = 3/\tau_d$, where $k_p\, a_p$ is the mass

385   transfer intraparticle resistance (min^{-1}).

386   The mass transfer models, presented in this work, were solved for the operating parameters, resulting

387   in the simulated curves presented in Figs. 5 (a) and (b). Both models adjust well the experimental data,

388   confirming that the LDF approximation can be considered. Concentration profiles inside the particle

389   for different values of dimensionless time (t/τ_p) are presented in Figure 6. It can be seen that the metal

390   concentration inside the particle follows approximately a parabolic profile for low values of (t/τ_p) and a

391   linear profile near the equilibrium. The average metal concentrations inside the particle given by the

392   two models are initially very different, but as (t/τ_p) increases they become closer and equal at

393   equilibrium.

394

395   **INSERT FIG. 5 (a), (b) AND (c)**

396

397   The values of the mass transfer intraparticle resistance, diffusion time and homogeneous diffusion

398   coefficient are presented in Table 5. The thickness of the thin plates was determined by microscopic

399   observation ($L = 0.05$ mm). D_h values are lower than the diffusivity of Cr^{3+} in water (5.85×10^{-6} cm^2 s^{-1}

400   ), suggesting that a resistance to the diffusion process exists.

401   The kinetic rate for the pseudo-first-order equation is defined as $dq_t / dt = k_{1,ads}\left(q_{eq} - q_t \right)$. When

402   compared with the kinetic law used in the LDF model (Eq. (12)), $k_{1,ads}$ has the same meaning that

403    $k_p a_p$. As, both values are of the same order of magnitude, the assumed mechanism is validated.

404

405   **INSERT TABLE 5**

406

407   **5 Conclusion**

408

409   Biosorption of Cr(III) ions by brown seaweed *Sargassum muticum* can be considered as an innovative

410   and effective process, giving good performances. Equilibrium is well described by Langmuir and

411   Langmuir-Freundlich models. The maximum uptake capacity was obtained for the highest pH within

412   the study range (3.0- 5.0). Biosorption kinetics is fast and well represented by the pseudo-second order

413   model. The LDF model can be considered as a simple model, with an analytical solution, to describe

414   mass transfer resistance in the biosorption process.

415
416 **Acknowledgements**
417
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626 **Table 1.** Estimated Langmuir equilibrium model parameters (value ± standard deviation).
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| Biosorbent | pH | Langmuir model | | | R^2 | S_R^2 $(\text{mg g}^{-1})^2$ | F_{cal} | $F_{1-\alpha}$ |
		q_L (mg g^{-1})	K_L $(\text{l mg}^{-1})\times10^2$	$q_L\times K_L$ (l g^{-1})				
Sargassum	5.0	56 ± 3	6 ± 1	3.4 ± 0.6	0.960	11.2	1.1	2.2
	4.0	33 ± 1	12 ± 1	3.9 ± 0.3	0.982	2.07	1.1	2.2
	3.0	19 ± 1	9 ± 1	1.7 ± 0.2	0.987	0.41	1.2	2.2
Laminaria	5.0	70 ± 4	4.2 ± 0.6	2.9 ± 0.6	0.971	12.9	1.9	2.1
Gelidium	5.3	18 ± 1	2.1 ± 0.4	0.38 ± 0.08	0.933	1.38	1.1	2.3

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Table 2. Estimated Langmuir-Freundlich equilibrium model parameters (value ± standard deviation).

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| Biosorbent | pH | Langmuir-Freundlich model | | | R^2 | S_R^2 |
		q_{LF} (mg g^{-1})	K_{LF} (l mg^{-1})×10^2	n		(mg g^{-1})^2
Sargassum	5.0	50 ± 4	4 ± 1	0.8 ± 0.1	0.963	10.5
	4.0	32 ± 1	9 ± 2	0.85 ± 0.08	0.984	1.90
	3.0	22 ± 3	11 ± 2	1.3 ± 0.2	0.992	0.34
Laminaria	5.0	54 ± 2	1.1 ± 0.5	0.57 ± 0.06	0.984	6.66
Gelidium	5.3	25 ± 9	3.5 ± 0.9	1.4 ± 0.3	0.941	1.23

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723 **Table 3.** Estimated pseudo-first order model parameters (value ± standard deviation).
724

| Biosorbent | pH | C_i (mg l^{-1}) | Pseudo-first order model | | | | | F_{cal} | $F_{1-\alpha}$ |
			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})		
	5.0	102	29.6 ± 0.9	0.20 ± 0.04	0.918	8.15	6 ± 1	3.7	2.4
Sargassum	4.0	109	24.7 ± 0.6	0.22 ± 0.03	0.932	3.85	5.4 ± 0.8	3.1	2.3
	3.0	104	14.7 ± 0.3	0.16 ± 0.01	0.975	0.62	2.4 ± 0.2	2.7	2.3

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Table 4. Estimated pseudo-second order model parameters (value ± standard deviation).

Biosorbent	pH	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})
	5.0	102	31.9 ± 0.6	0.9 ± 0.1	0.977	2.21	9 ± 1
Sargassum	4.0	109	26.1 ± 0.4	1.5 ± 0.2	0.977	1.23	10 ± 1
	3.0	104	15.9 ± 0.2	1.4 ± 0.1	0.991	0.23	3.5 ± 0.3

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Table 5. Estimated parameters for the linear driving force (LDF) and homogeneous particle diffusion
models.

Biosorbent	C_i (mg l^{-1})	pH	LDF model			Homogeneous diffusion model			
			$k_p \times a_p$ (min^{-1})	τ_d (min)	S_R^2 (mg g^{-1})^2	τ_d (min)	D_h (cm^2 s^{-1})	S_R^2 (mg g^{-1})^2	D_h (average) (cm^2 s^{-1})
	102	5.0	0.12	25	15.9	25	1.7×10^{-8}	11.5	
Sargassum	109	4.0	0.12	25	6.7	25	1.7×10^{-8}	3.7	1.6×10^{-8}
	104	3.0	0.11	27	1.0	27	1.5×10^{-8}	0.5	

List of Figures

883 **Figure 1.**

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901 **Figure 2.**

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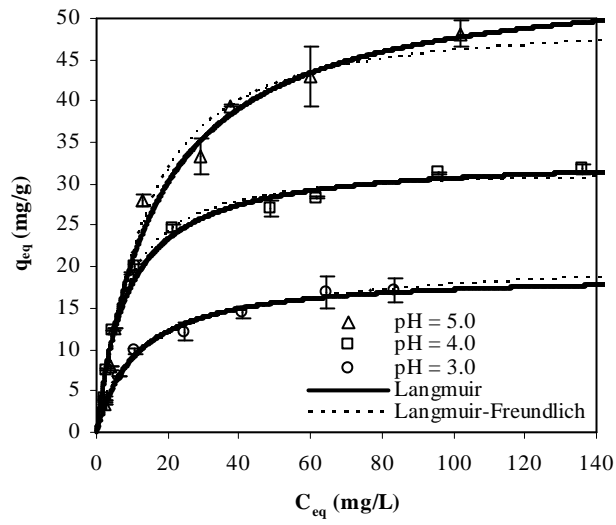
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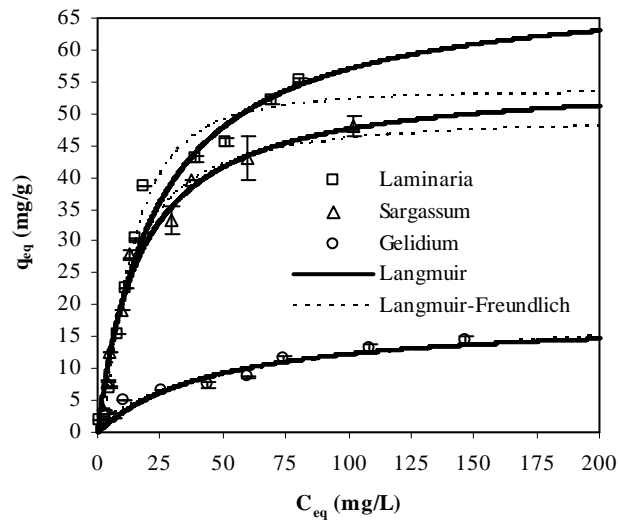
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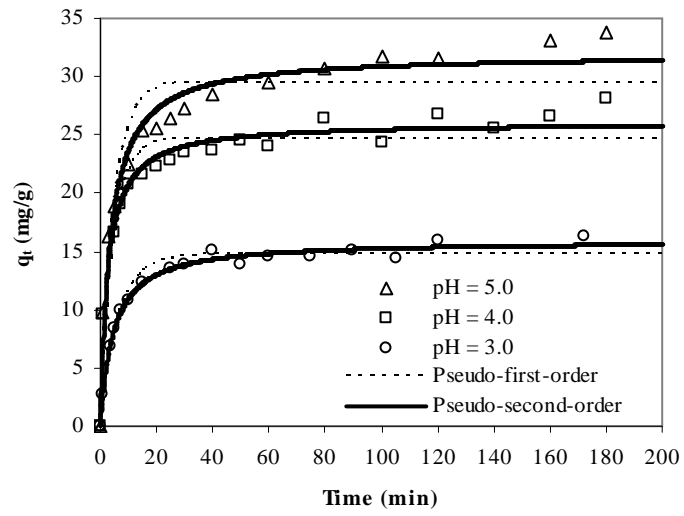
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937 **Figure 4.**

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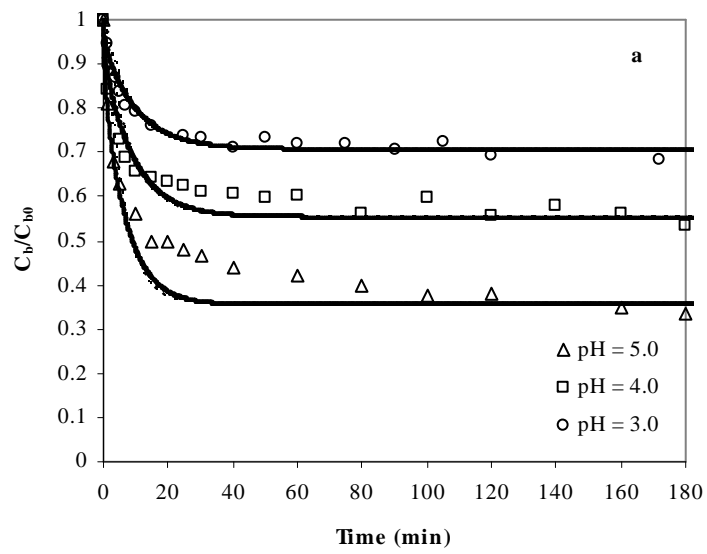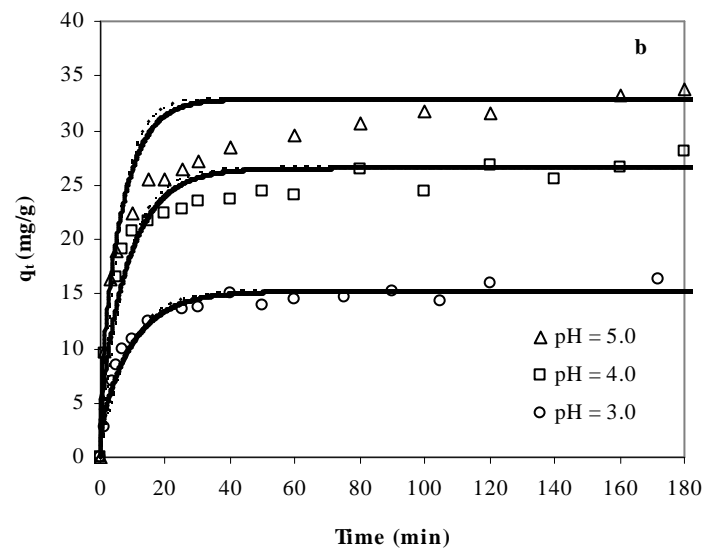
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955   **Figure 5.**

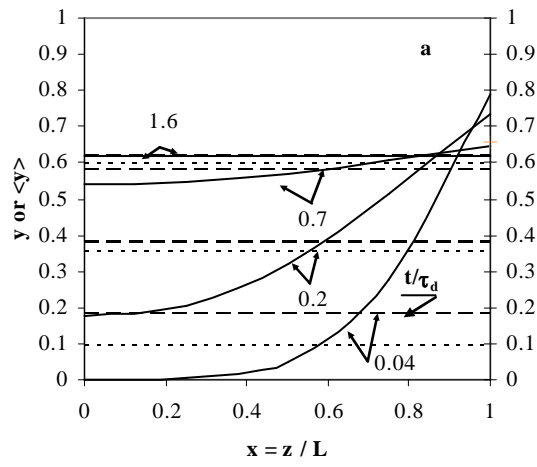956   **(a)**

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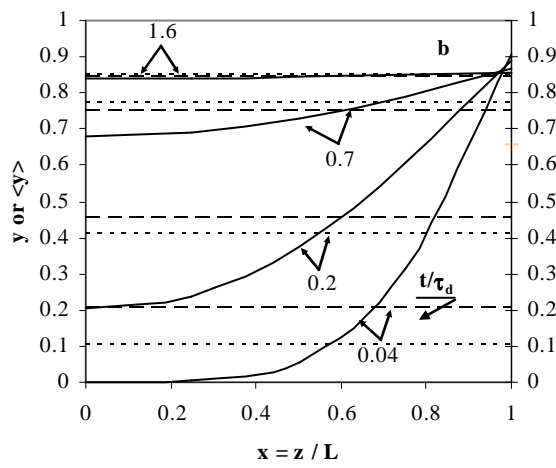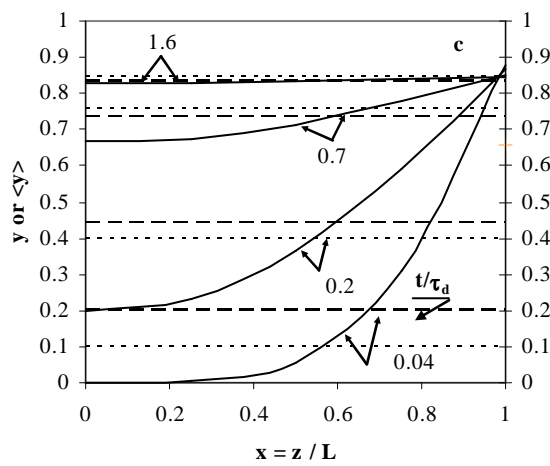
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966   **Figure 6.**

967   **(a)**

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969   **(b)**

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971   **(c)**

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