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## Equilibrium of Cu(II) and Ni(II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: Competitiveness and selectivity

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### ABSTRACT

The study focuses on the equilibrium of dynamic biosorption in single and binary systems containing Cu(II) and Ni(II) ions using *Sargassum filipendula* (a marine alga). The experiments were performed in fixed-bed columns with both single-component and bi-component metal solutions (using different molar concentrations). Experimental data were fitted with different equilibrium models such as Langmuir, Langmuir with inhibition, Jain and Snowyink and Langmuir–Freundlich equations. The biosorption of pure metal ions in solution presented adequate capacities both for Cu(II) and Ni(II). In binary solutions the preferential sorption of Cu(II) over Ni(II) was demonstrated by the displacement of Ni(II) (marked overshoot on the breakthrough curves).

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### 1. Introduction

Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals. Biosorption has retained a great attention for the last decades as an alternative to conventional processes (such as precipitation, ion exchange and complexing resins, membrane processes, solvent extraction etc.) for the removal of metal ions from dilute solutions. An efficient biosorbent requires a series of properties to be combined: (a) low cost, (b) large availability, (c) high efficiency and affinity (in terms of both equilibrium and kinetics), (d) sufficient stability (mechanical and chemical), (e) possible recycling. Vijayaraghavan et al. (2005) showed the high efficiency of biomass, its cost-effectiveness and reusability after several sorption/desorption cycles. Brazil profits from a great diversity and abundance of biomass that can be applied to metal recovery: agriculture wastes, biopolymers, bacterial biomass, fungal biomass and algal biomass, for example. Brazilian coasts are offering a number of different algal biomass that could be used for metal biosorption, especially brown algae.

The capacity of brown marine algae to remove several metal species is due to the presence of a series of biochemical constituents on their cell wall. These cell walls are mainly composed of three types of biopolymers: alginate (heteropolymer constituted of guluronic acid and mannuronic acidic residues), fucoidan

(heteropolymer constituted of sulfated esters of fucose and glucuronic acid moieties), and cellulose (Kratochvil and Volesky, 2000; Davis et al., 2003). The algal biomass bears functional groups such as: amino, carboxyl, hydroxyl and sulfate groups. In the case of alginate, divalent cations bind to the biopolymer through interactions with carboxylic groups with a spatial arrangement that corresponds to the so-called egg-box mechanism: the divalent cation interacts on each side with different chains of the biopolymer contributing to the strength of the biopolymer–metal composite material (Morris et al., 1980; Rees, 1981). This interaction of alginate with divalent cations can be used for the ionotropic gelation of the biopolymer (Davis et al., 2003).

Though most of the studies on biosorption deal with batch systems because this experimental design is much simple to manage, using fixed-bed columns for the investigation of both equilibrium and kinetic performance allows to approach more efficiently the systems used in industry (resin column, for example). The saturation of the column is controlled by parameters such as time, space and column length (Volesky, 2001) while in the batch mode, the experiments only vary with time (Sanchez et al., 1999).

Industrial effluents generally consist of a complex mixture of ions competing with each other for binding on the same functional groups sites (in most cases). Thus, it is essential to determine the selectivity of the biosorbent for ions present in the solution. The biosorption isotherms describe the distribution of the solute (metal ions) between aqueous and sorbent phases. Several equations can be used to model sorption isotherms in function of the

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## Nomenclature

$q_j$	$j$ metal ion biosorption capacity ( $\text{mmol g}^{-1}$ )	$C_j^*$	concentration of ion in non adsorbed solution at equilibrium, ( $\text{mmol L}^{-1}$ )
$C_{\text{out},j} _{z=L}$	concentration of $j$ metal ion at the column output ( $\text{mmol L}^{-1}$ )	$q_m$	maximum amount adsorbed of ion per adsorbent unit to form a complete monolayer in surface ( $q = q_m$ ), ( $\text{mmol g}^{-1}$ )
$C_j^0$	initial concentration of $j$ metal ion in the feed ( $\text{mmol L}^{-1}$ )	$b_j$	constant related to the adsorption energy, ( $\text{L mmol}^{-1}$ )
$\dot{Q}$	volumetric flow of metal solution ( $\text{cm}^3 \text{min}^{-1}$ ); $t =$ time (min) and $m_s =$ biosorbent material dry mass (g).	$t$	time
$q_j^*$	quantity of metal ion adsorbed by adsorbent unit mass at equilibrium, ( $\text{mmol g}^{-1}$ )	$m_s$	biosorbent material

type of adsorbent (Guibal et al., 2001; Pagnanelli et al., 2002; Hammaini et al., 2003; Ma and Tobin, 2003; Fagundes-Klen et al., 2007; Kumar et al., 2008; Chen et al., 2008; Boujelben et al., 2009; Luna et al., 2010; Vieira et al., 2010). The models used for the description of metal sorption from mono-component solutions cannot be used for the modeling of sorption in binary systems since in general the sorption of one metal is influenced by the presence of the second metal. The conventional models neglect this competitor effect on the equilibrium. There is a need to interpret the derived isotherm parameters considering the sorption data of the primary and secondary metal, and total metal for the same binary system (Kumar et al., 2008). The dynamic biosorption of metal ions helps to interpret the competitor mechanism through the study of the shape of the breakthrough curves in dynamic system.

This study investigates the dynamic biosorption of Cu(II) and Ni(II) in fixed-bed columns using the marine alga *Sargassum filipendula*. These two metals are frequently found in industrial wastewater (for example in plating industry). The breakthrough curves are established in both single and binary systems. At saturation of the column, the sorption capacity can be calculated and used for modeling isotherm curves. The discussion of data helps to understand the competitive effect and to evaluate the selectivity of the biosorbent.

## 2. Methods

### 2.1. Marine alga *S. filipendula*

The marine alga *S. filipendula* was collected on the North Coast of São Paulo State, in the city of São Sebastião, Brazil. The alga was washed with distilled water and dried at 60 °C for 24 h prior to being stored. Biomass was grinded and separated by dynamic sieving with a mean diameter of 0.855 mm.

### 2.2. Metal solutions

Cu(II) and Ni(II) solutions were prepared from nitrate salts of nickel ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and copper ( $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ). The concentration of metal ions was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a JY 2000 spectrometer (Jobin–Yvon, Longjumeau, France).

### 2.3. Dynamic column testing

An acrylic-made cylindrical column (internal diameter: 11 mm; height: 110 mm) was packed with the biomass. The amount of alga was set to 3.0 g (average diameter of biomass particles: 0.855 mm). The column was fed upward with a flow rate set to  $5 \text{ mL min}^{-1}$  (i.e., superficial velocity:  $3.2 \text{ m h}^{-1}$ ). Experiments were performed at room temperature (i.e.,  $21 \pm 2$  °C). The pH of the feed solution was controlled to 4.5 using 0.5 M nitric acid solution.

Samples were regularly collected using an automatic sampler for determining outlet concentrations of Cu(II) and/or Ni(II) by ICP-AES. Metal concentrations were varied changing the molar fractions of Cu(II) and Ni(II) (respecting the following Cu(II)/Ni(II) ratios: 1/3, 1/1 and 3/1). The total concentration of metals in feed solutions was varied between 0.3 and  $4.0 \text{ mmol L}^{-1}$ . The breakthrough curves, representing the relative concentration  $C(t)/C_0$ , were plotted versus time for different experimental conditions.

### 2.4. Column biosorption capacity

The amount of metal ion removed in the process was calculated on the basis of experimental breakthrough curves using Eq. (1):

$$q_j = \frac{C_j^0 \dot{Q}}{1000 m_s} \int_0^t (1 - C_{\text{out},j}|_{z=L}/C_j^0) dt \quad (1)$$

The integral part of Eq. (1) (right side) was solved by numerical integration using ORIGIN 7.0 software.

### 2.5. Mass transfer zone (MTZ)

Vieira et al. (2010) applied a simplified method for calculating the MTZ length. Firstly, the time equivalent to the active capacity of the column ( $t_u$ ) and the saturation time ( $t_t$ ) were calculated. The breaking point is defined as the operating time that corresponds to an outlet metal concentration higher than 5% of feed concentration. The time equivalent to the active capacity of the bed ( $t_u$ ) until the breaking point time ( $t_b$ ) can be calculated by Eq. (2). Similarly, the time ( $t_t$ ) required for reaching the saturation of the biosorbent in the whole bed can be calculated by Eq. (3).

$$t_u = \int_0^{t_b} (1 - C_{\text{out},j}|_{z=L}/C_j^0) dt \quad (2)$$

$$t_t = \int_0^t (1 - C_{\text{out},j}|_{z=L}/C_j^0) dt \quad (3)$$

The dimensionless time  $\tau = t_u/t_t$  corresponds to the fraction of the active column height, and the total column height is given by Eq. (4).

$$H_u = \tau \cdot H_t \quad (4)$$

The MTZ corresponding to the difference between the total ( $H_t$ ) and the active ( $H_u$ ) length of the bed is given by Eq. (5):

$$\text{MTZ} = (1 - \tau) \cdot H_t \quad (5)$$

### 2.6. Models of equilibrium

Table 1 shows the equilibrium models used in this paper for simulating experimental data. A SIMPLEX optimization method (Nelder and Mead, 1965) was applied for the calculation of the

**Table 1**  
Equilibrium models used to adjust experimental data.

<i>Mono-component</i>		
Langmuir	$q_j^* = \frac{q_m b_j C_j}{1 + b_j C_j}$	(6)
Langmuir	$q_1^* = \frac{q_m C_1 b_1}{1 + b_1 C_1 + b_2 C_2}$	(7)
Langmuir with inhibition	$q_1^* = \frac{q_m C_1 b_1 (1 + (K/b_1) C_2)}{1 + b_1 C_1 + b_2 C_2 + 2K C_1 C_2}$	(8)
<i>Bicomponent</i>		
Langmuir–Freundlich	$q_1^* = \frac{q_m b_1 (C_1)^{k_1}}{1 + b_1 (C_1)^{k_1} + b_2 (C_2)^{k_2}}$	(9)
Jain and Snowyink	$q_1^* = \frac{(q_{m1} - q_{m2}) b_1 C_1}{1 + b_1 C_1} + \frac{q_{m2} b_1 C_1}{1 + b_1 C_1 + b_2 C_2}$	(10a)
	$q_2^* = \frac{q_{m2} b_2 C_2}{1 + b_1 C_1 + b_2 C_2}$	(10b)

parameters for mono-component and bi-component sorption isotherms through the determination of the minimum of the objective function given by Eq. (11):

$$F_{\text{OBJ}} = \sum_{j=1}^N \left( \frac{q_{1j}^{\text{Exp}} - q_{1j}^{\text{Mod}}}{q_{1j}^{\text{Exp}}} \right)^2 + \sum_{j=1}^N \left( \frac{q_{2j}^{\text{Exp}} - q_{2j}^{\text{Mod}}}{q_{2j}^{\text{Exp}}} \right)^2 \quad (11)$$

where  $q_j^{\text{Exp}}$  is the “jth” species equilibrium concentration in biosorbent which is determined experimentally;  $q_j^{\text{Mod}}$  the calculated amount of “jth” species by the adsorption isotherm model;  $N$  is the number of experimental data. Indexes 1 and 2 are related to the ions species Cu(II) and Ni(II), respectively.

Fagundes-Klen et al. (2007) applied a model originally developed by Bailey and Ollis (1986) to represent the biosorption equilibrium from bi-component solutions. The original model was developed to describe the non-competitive inhibition during enzymatic kinetic studies. This model is represented by Eq. (7).

For the Langmuir model with inhibition (Eq. (8)), the parameter  $K$  is correlated with the equilibrium constants using the expressions:  $K = K_1 K_{12}$  and  $K = K_2 K_{21}$ . Parameters  $q_m$ ,  $b_1$  and  $b_2$  have the same meaning as in the Langmuir isotherm, while the parameter  $K$  values concern the formation of the complex  $[B M_1 M_2]$ .

By adding the constants ( $k_1$ ,  $k_2$ ) as exponents to the numerator and denominator of Langmuir isotherm (Eq. (7)), obtained the Langmuir–Freundlich type isotherm that can be applied to biosorption from bi-component solutions (Eq. (9)).

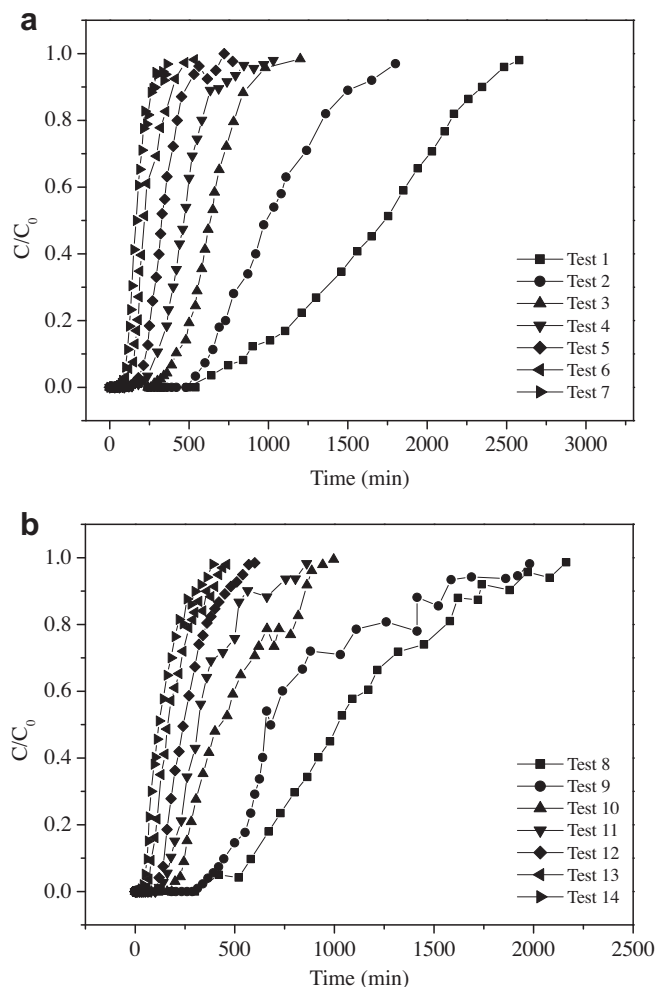
Jain and Snoeyink (1973) proposed an adsorption model for binary mixtures based on the hypothesis that part of the adsorption occurs with no competition when  $q_{m,1} \neq q_{m,2}$  (Kumar et al., 2008). For  $q_{m,1} > q_{m,2}$ , the number of sites with no competition is given by the difference ( $q_{m,1} - q_{m,2}$ ). The mathematical representation is given by Eqs. (10a) and (10b) in Table 2.

The first term on the right of Eq. (10a) in Table 2 is the Langmuir isotherm expression for the number of chemical molecules  $M_1$ , which can be adsorbed with no competition ( $q_{m,1} - q_{m,2}$ ). The second term represents the number of chemical molecules  $M_1$  that are adsorbed on the surface associated to  $q_{m,2}$  with  $M_2$  competition, based on the Langmuir competitive adsorption model. The number of  $M_2$  molecules adsorbed on the surface associated to  $q_{m,2}$  with  $M_1$  competition can be calculated by Eq. (10b) (Hashim and Chu, 2004).

### 3. Results and discussion

#### 3.1. Mono-component solutions

Based on the experimental data of the breakthrough curves for copper (Fig. 1a) and nickel (Fig. 1b), obtained for the different feed concentrations, the sorption capacities (for the different metal ions) were calculated until breaking ( $q_u$ ) and saturation ( $q_t$ ) sorption capacities of the column, together with the length of the mass



**Fig. 1.** Experimental breakthrough curves obtained for sorption of Cu(II) (a) and Ni(II) (b) from mono-component solutions – effect of metal concentration (according to Table 2).

**Table 2**

Sorption capacities of Cu(II) and Ni(II) obtained from breakthrough curves and MTZ values for mono-component systems.

Metal	Test	$C_0$ (mmol L <sup>-1</sup> )	$q_u$ (mmol g <sup>-1</sup> )	$q_t$ (mmol g <sup>-1</sup> )	MTZ (cm)
Cu(II)	1	0.29	0.32	0.80	6.65
	2	0.50	0.46	0.87	5.13
	3	0.97	0.58	1.05	4.88
	4	1.51	0.68	1.22	4.90
	5	2.12	0.69	1.24	4.86
	6	3.00	0.58	1.25	5.85
	7	4.18	0.59	1.21	5.66
Ni(II)	8	0.30	0.21	0.56	6.86
	9	0.50	0.32	0.72	6.10
	10	1.08	0.41	0.88	5.92
	11	1.50	0.42	0.91	5.90
	12	2.15	0.46	0.97	5.81
	13	3.00	0.35	0.98	7.04
	14	4.01	0.32	1.00	7.44

transfer zone (MTZ) (Table 2). The lower the MTZ length, the closer the system is to ideality (step function). This means that short MTZ represent systems with high removal efficiency.

Fig. 1 shows the influence of metal concentration on the shape of breakthrough curves for mono-component solutions. When the metal concentration in the feed increases the slope of the breakthrough curve also increases. At high metal concentration the

concentration gradient between the surface of the biosorbent (and also the core of the particle) and the solution is increased; this improves the driving force for mass transfer and reduces the resistance to film diffusion, and to intraparticle diffusion. For low metal concentrations (i.e., in the range 0.3–0.5 mmol L<sup>-1</sup>), the shape of the breakthrough curves is significantly different to those obtained with higher metal concentrations, for both Cu(II) and Ni(II). The resistance to diffusion is thus mainly active for 0.5 mol L<sup>-1</sup> (and below) concentrations of metal ions. This is confirmed by the comparison of MTZs (Table 2). When the concentration of metal ions in the feed increases the MTZ decreases up to a limit value above which the MTZ tends to increase again. For both Cu(II) and Ni(II) the optimum concentration is in the range 1–2 mmol metal L<sup>-1</sup>. In the column adsorption process, the increased flow results in reduced resistance to film diffusion. This leads to a reduced mass transfer zone (MTZ) as observed by Vijayaraghavan et al. (2005). At low concentration gradient the driving force is not sufficient to enhance mass transfer (limitations due to the resistance to film diffusion and intraparticle diffusion) and the MTZ is enlarged. At high metal concentration, the residence time in the column (under selected experimental conditions) is not sufficient for achieving the complete removal of the metal in short MTZs and the length of the MTZ progressively increases. The MTZ is slightly lower for Cu(II) (i.e., close to 4.0) than for Ni(II) (i.e., close to 5.8). This is a first indication that the biosorbent has a greater affinity for Cu(II) than for Ni(II).

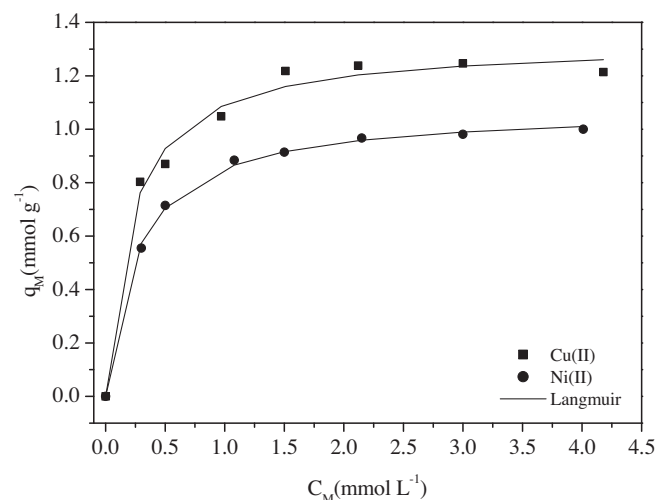


Fig. 2. Sorption isotherms for Cu(II) and Ni(II) recovery from mono-component solutions using acidified *Sargassum filipendula* (derived from breakthrough curves).

The integration of the breakthrough curves allowed determining the sorption capacities according to Eq. (1). The best conditions were observed for 2.12 and 2.15 mmol L<sup>-1</sup> concentrations for copper (Fig. 1a) and nickel (Fig. 1b), respectively. Under these

Table 3

Evaluation of Langmuir parameters for the sorption of Cu(II) and Ni(II) from mono-component solutions using *Sargassum filipendula* biomass.

Langmuir Model					
Cu(II)			Ni(II)		
$q_m$ (mmol g <sup>-1</sup> )	$b_j$ (L mmol <sup>-1</sup> )	$R^2$	$q_m$ (mmol g <sup>-1</sup> )	$b_j$ (L mmol <sup>-1</sup> )	$R^2$
1.324 ± 0.0351	4.673 ± 0.707	0.989	1.07028 ± 0.0163	4.0654 ± 0.332	0.998

Table 4

Cu(II) and Ni(II) adsorption capacities of different adsorbents for mono-component systems.

Metal	Adsorbent	pH	Metal uptake (mmol g <sup>-1</sup> )	References	
Cu(II)	<i>Laminaria japonica</i>	4.5	1.59	Fourest and Volesky (1997)	
	<i>Fucus vesiculosus</i>	4.5	1.18		
	<i>Sargassum vulgare</i>	4.5	0.93	Davis et al. (2000)	
	<i>Sargassum filipendula</i>	4.5	0.89		
	<i>Sargassum fluitans</i>	4.5	0.80		
	<i>Sargassum</i> sp.	3.5	1.08	da Silva et al. (2002)	
	<i>Cymodocea nodosa</i>	4.5	0.81	Sanchez et al. (1999)	
	<i>Sargassum</i> sp.	5.0	0.99	Sheng et al. (2007)	
	<i>Padina</i> spp.	4.5–5.0	0.80	Jalali et al. (2002)	
	<i>Undaria pinnatifida</i>	4.0	0.62	Chen et al. (2008)	
	<i>Sargassum filipendula</i>	5.0	0.60	Volesky (2003)	
	<i>Trametes versicolor</i>	5.51	0.63	Sahan et al. (2010)	
	Chitosan coated PVC	4.5–5.0	1.38	Popuri et al. (2009)	
	<i>Sargassum filipendula</i>	4.5	1.32	This work	
	<i>Sargassum fluitans</i>	3.5	0.75	Holan and Volesky (1994)	
	Ni(II)	<i>Ascophyllum nodosum</i>	3.5	0.68	
		<i>Sargassum natans</i>	3.5	0.41	
<i>Fucus vesiculosus</i>		3.5	0.39		
<i>Sargassum vulgare</i>		3.5	0.09		
<i>Sargassum wightii</i>		4.5	0.32	Vijayaraghavan et al. (2005)	
<i>Undaria pinnatifida</i>		4.7	0.42	Chen et al. (2008)	
Bofe bentonite clay		5.3	0.032	Vieira et al. (2010)	
<i>Cystoseria indica</i> ,		6.0	0.81	Pahlavanzadeh et al. (2010)	
<i>Nizmuddinia zanardini</i>		6.0	0.89		
<i>Sargassum glaucescens</i>		6.0	0.94		
<i>Padina australis</i>		6.0	0.45		
<i>Sargassum filipendula</i>		4.5	1.07	This work	

**Table 5**  
Sorption capacities of Cu(II) and Ni(II) obtained from breakthrough curves for bi-component systems.

Test	$C_{\text{Total}}$ (mmol L <sup>-1</sup> )	$X_{\text{Cu}}$	$X_{\text{Ni}}$	$C_{\text{Cu}}$ (mmol L <sup>-1</sup> )	$C_{\text{Ni}}$ (mmol L <sup>-1</sup> )	$q_{\text{Cu}}$ (mmol g <sup>-1</sup> )	$q_{\text{Ni}}$ (mmol g <sup>-1</sup> )	$q_t$ (mmol g <sup>-1</sup> )
15	4.08	0.47	0.53	1.92	2.16	1.03	0.21	1.24
16	3.11	0.45	0.55	1.40	1.71	0.95	0.23	1.18
17	2.11	0.49	0.51	1.03	1.08	1.00	0.14	1.14
18	1.45	0.49	0.51	0.71	0.74	0.85	0.15	1.00
19	1.02	0.48	0.52	0.49	0.53	0.76	0.12	0.88
20	0.48	0.5	0.5	0.24	0.24	0.74	0.004	0.75
21	2.98	0.74	0.26	2.21	0.77	1.12	0.10	1.22
22	3.06	0.24	0.76	0.73	2.33	0.76	0.21	0.97
23	1.93	0.25	0.75	0.48	1.45	0.74	0.40	1.14
24	1.96	0.76	0.24	1.49	0.47	1.07	0.09	1.16
25	1.44	0.24	0.76	0.35	1.09	0.63	0.34	0.97
26	1.47	0.75	0.25	1.10	0.37	1.10	0.08	1.18
27	0.95	0.74	0.26	0.70	0.25	0.99	0.08	1.07
28	1.02	0.23	0.77	0.24	0.79	0.56	0.20	0.76
29	0.5	0.25	0.75	0.13	0.38	0.58	0.11	0.69
30	0.49	0.74	0.26	0.36	0.13	0.76	0.038	0.80

conditions, sorption capacities reached 0.69 and 0.46 mmol g<sup>-1</sup> and MTZ 4.86 and 5.81 cm for nickel and copper (Table 2), respectively.

The maximum adsorption capacity ( $q_m$ ), the Langmuir adsorption constant ( $b$ ) and the correlation coefficient ( $R^2$ ) obtained by the least squares method for this model are reported in Table 3. Fig. 2 shows that the Langmuir equation correctly fits experimental data for both Cu(II) and Ni(II). The isotherm is characterized by a “favorable” profile: high sorption capacities are adsorbed at low residual concentration (i.e., steep initial slope). The equilibrium constant  $b_j$  is analogous to a partition coefficient and describes the affinity of the solute for the biosorbent. Its value is increased with the interaction force and depends on the temperature. The affinity coefficient is slightly higher for Cu(II) (i.e., 4.7 L mmol<sup>-1</sup>) than for Ni(II) (i.e., 4.1 L mmol<sup>-1</sup>); this result confirms that *S. filipendula* has a slightly higher affinity for Cu(II). The maximum sorption capacities obtained by the Langmuir equation (i.e., 1.3 and 1.1 mmol metal g<sup>-1</sup> for Cu(II) and Ni(II), respectively) are consistent with experimental values reported in Table 2.

The result achieved in this study is among the highest values cited in literature (Table 4). *S. filipendula* is an efficient biosorbent for Cu(II) and Ni(II).

### 3.2. Bi-component solutions

Sixteen binary mixture sorption experiments were conducted in fixed-bed columns varying the molar fraction between Cu(II) and Ni(II) (Table 5 and Fig. 3a–g). These results were used for evaluating the amounts of the different metal ions that were sorbed on the biomass at saturation (Table 5). The breakthrough curves for bi-component solutions (Fig. 3a–g) show substantial differences with the shape of the curves obtained from mono-component tests (Fig. 1a and b). This is obviously due to the competition effect of the metals to be bound on a limited number of identical binding sites. There is a drastic difference in the behavior of Cu(II) and Ni(II) biosorption profiles. While for Cu(II) biosorption the breakthrough curves shows the conventional sigmoid trend, the breakthrough curves for Ni(II) are characterized by the presence of an overshoot (the outlet concentration of the metal exceeds the inlet concentration). This overshoot clearly demonstrates that the binding of Cu(II) displaces Ni(II) ions that were previously adsorbed on the biomass.

The overshoots for a variety of metals and biomasses have been reported in the literature for the biosorption of base metals on *Sargassum* biomass (Figueira et al., 2000; Kratochvil and Volesky,

2000; Naja and Volesky, 2006), anaerobic biomass (Hawari and Mulligan, 2006) but also for the biosorption of platinum group metals on biopolymers (Chassary et al., 2005).

The sorption capacities for the two metals (and the cumulative sorption capacity Cu(II) + Ni(II), in molar units) have been calculated at equilibrium. The values are reported on Table 5. The molar ratio  $q_{\text{Cu}}/q_{\text{Ni}}$  can be calculated and compared to the molar ratio [Cu(II)]/[Ni(II)] in the feed solution. Except for the cases corresponding to low total concentrations (tests 28–30) the molar ratio on the sorbent can be linearly correlated to the molar ratio in the feed solution, according to the relationship:

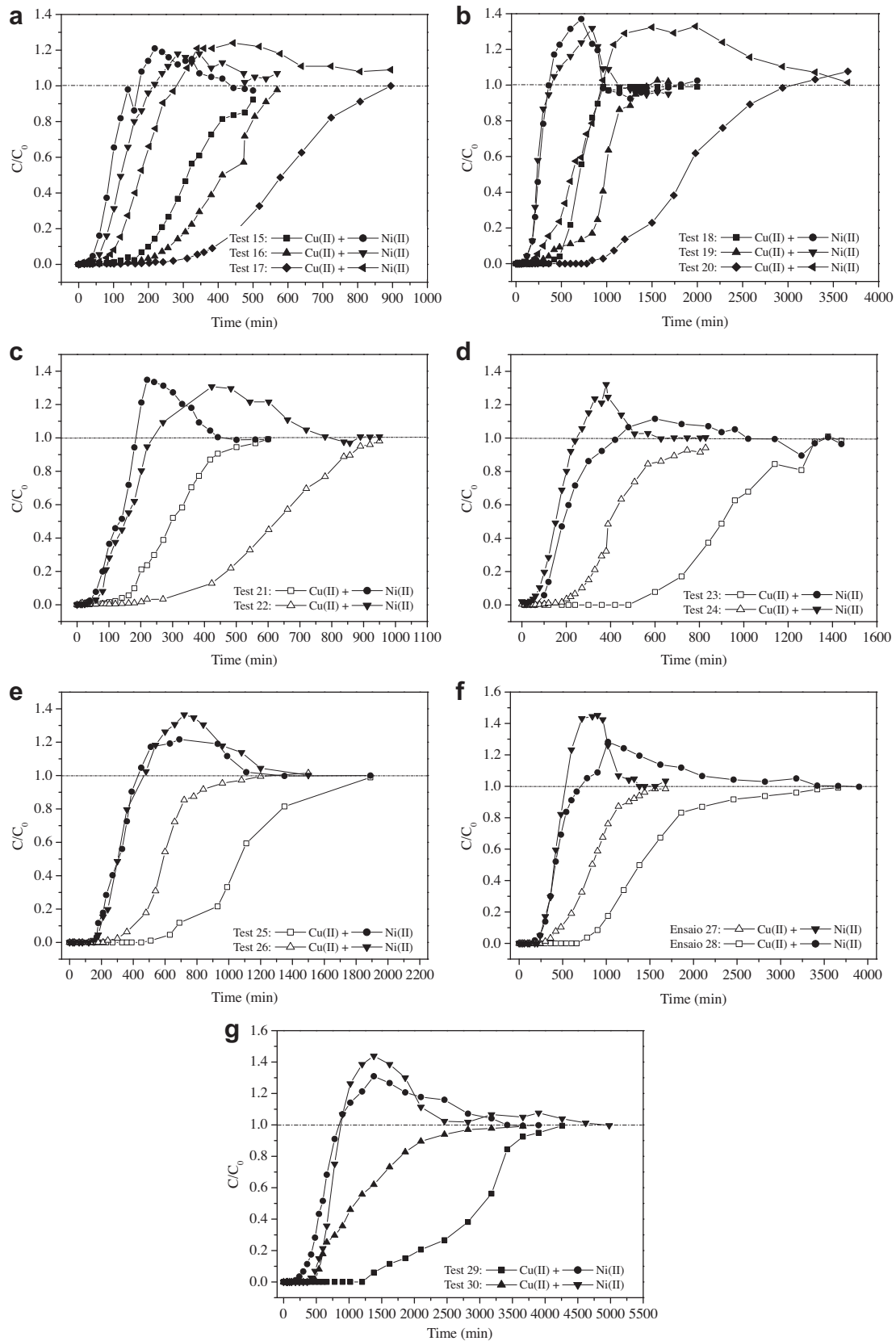
$$Q_{\text{Cu}}/q_{\text{Ni}} = 3.7[\text{Cu(II)}]/[\text{Ni(II)}] + 1.85(R^2 : 0.955) \quad (12)$$

This means that the biosorbent has a preference at equilibrium for Cu(II) over Ni(II). This is consistent with previous conclusions on single-component solutions.

For multi-component isotherm, different models were used to fit binary experimental data: the Langmuir Model (Figure AMa, in Additional Material Section), the Langmuir with inhibition equation (Li, Figure AMb), the Jain and Snowyink model (J&S, Figure AMc) and the Langmuir–Freundlich equation (LF, Figure AMd). The Figure AM shows that the lower data dispersion occurred for the Langmuir with inhibition and the Langmuir–Freundlich models. This is confirmed by the comparison of the values of the objective function (i.e., 1.30 and 1.27, Table 6 for Li and LF equations, respectively).

Regardless of the model used, the affinity coefficient (or analogous parameter) ( $b_j$ ) of Cu(II) for *S. filipendula* biomass is greater than that of Ni(II). For the Langmuir model with inhibition (Li), the constant  $k$  is related to the ratio between the constants of formation of the complex  $BM_{\text{Cu}}M_{\text{Ni}}$  and the constant of consumption. The value of the constant  $k$  (i.e., 0.75 (L mmol<sup>-1</sup>)<sup>2</sup>) is lower than the values of  $b_{\text{Cu}}$  (i.e., 5.83) and higher than the value of  $b_{\text{Ni}}$  (i.e., 0.32). This means that the formation of the  $BM_{\text{Cu}}$  complex is more favorable than the formation of the  $BM_{\text{Ni}}M_{\text{Cu}}$  and  $BM_{\text{Ni}}$  complexes.

The Jain and Snowyink model supposes that a given part of the adsorption is not competitive. In the present case, the fraction of copper ion adsorbed with no competition (from nickel) is defined by the difference ( $q_{m,\text{Cu}} - q_{m,\text{Ni}}$ ) (i.e., 1.08 mmol g<sup>-1</sup>), while the fraction of metal adsorbed under the control of competition effect is given by  $q_{m,\text{Ni}} = 0.73$ . The values of these model's parameters show that copper ion have higher affinity for adsorbent material sites than nickel ions, since about 60% of sorption capacity occurs with no competition. This means that about 60% of sites are exclusively accessible to copper ions, while the copper and nickel ions



**Fig. 3.** Experimental breakthrough curves for the sorption of Cu(II) and Ni(II) from bi-component solutions using *Sargassum filipendula* (varying the molar ratio of metals – according to Table 5).

compete for the remaining sites. Fagundes-Klen et al. (2007) studied competitive biosorption of Zn(II) and Cd(II) by marine alga

*S. filipendula* and observed that 41% of the sites in the alga absorb Zn(II) without competition.

**Table 6**  
Model parameters for equilibrium sorption in bi-component solutions.

Langmuir	$b_{Cu} = 1.77 \text{ L mmol}^{-1}$ $b_{Ni} = 0.23 \text{ L mmol}^{-1}$ $q_m = 1.73 \text{ mmol g}^{-1}$ Objective function = 2.41
Langmuir with inhibition	$b_{Cu} = 5.83 \text{ mmol}^{-1}$ $b_{Ni} = 0.32 \text{ L mmol}^{-1}$ $k = 0.75 \text{ (L mmol}^{-1})^2$ $q_m = 1.22 \text{ mmol g}^{-1}$ Objective function = 1.30
Jain & Snowyink	$q_{m,Cu} = 1.81 \text{ mmol g}^{-1}$ $q_{m,Ni} = 0.73 \text{ mmol g}^{-1}$ $b_{Cu} = 2.16 \text{ L mmol}^{-1}$ $b_{Ni} = 0.60 \text{ L mmol}^{-1}$ Objective function = 2.32
Langmuir–Freundlich	$b_{Cu} = 0.39 \text{ L mmol}^{-1}$ $b_{Ni} = 0.81 \text{ L mmol}^{-1}$ $k_{Cu} = 0.80 \text{ (dimensionless)}$ $k_{Ni} = 0.13 \text{ (dimensionless)}$ $q_m = 2.22 \text{ mmol g}^{-1}$ Objective function = 1.27

### 3.3. Competitive effect and selectivity

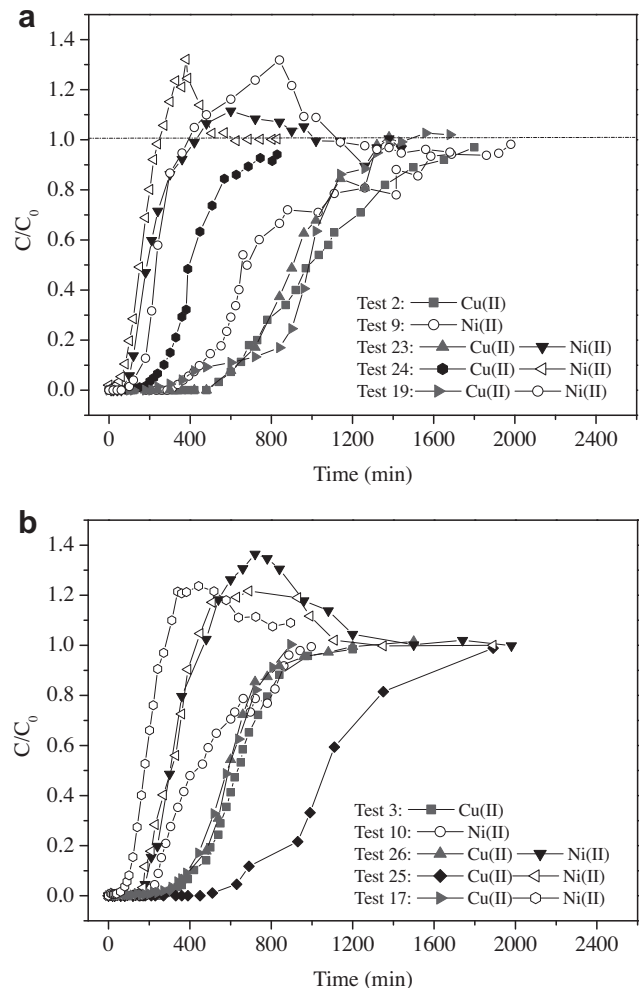
In order to analyze the competitive effect and selectivity of the biomass for metal ions, the breakthrough curves obtained in tests 2, 9, 20, 21 and 25 are shown in Fig. 4a and those of tests 3, 10, 19, 23 and 24 in Fig. 4b. The shape of the breakthrough curves for Cu(II) is hardly changed in the presence of Ni(II), while the presence of Cu(II) in Ni(II) solutions significantly reduced the sorption capacity for nickel. Nickel previously sorbed is released from loaded biomass and the breakthrough curve is characterized by an overshoot.

In monocomponent solutions (with a metal concentration close to  $0.5 \text{ mmol L}^{-1}$ ) the biosorption capacities were  $0.87$  and  $0.72 \text{ mmol g}^{-1}$  for Cu(II) and Ni(II) ions, respectively. Under the binary condition ( $0.49 \text{ mmol Cu(II) L}^{-1} + 0.53 \text{ mmol Ni(II) L}^{-1}$ ), the biosorption capacities decreased to  $0.75$  and  $0.12 \text{ mmol g}^{-1}$  for Cu(II) and Ni(II), respectively. A reduction of approximately 12% was observed in the sorption capacity for Cu(II), in the presence of Ni(II), while the presence of equimolar concentration of Cu(II) reduced by 84% the sorption capacity of Ni(II). In the presence of an excess of Ni(II) (i.e.,  $0.48 \text{ mmol Cu(II) L}^{-1} + 1.45 \text{ mmol Ni(II) L}^{-1}$ ), the sorption capacity for Cu(II) was  $0.74 \text{ mmol g}^{-1}$ , this means a 15% reduction compared to the sorption capacity in mono-component solutions. On the reciprocal, Ni(II) sorption capacity (i.e.,  $0.085 \text{ mmol Ni g}^{-1}$ ) decreased by 79% in the presence of a large excess of Cu(II) ( $0.47 \text{ mmol Ni(II) L}^{-1} + 1.49 \text{ mmol Cu(II) L}^{-1}$ ). The same trends were basically obtained when increasing the total metal concentration. For concentrations of Cu(II) ( $0.97 \text{ mmol Cu(II) L}^{-1}$ ) and Ni(II) ( $1.08 \text{ mmol Ni(II) L}^{-1}$ ) the sorption capacities increase up to  $1.05 \text{ mmol Cu g}^{-1}$  and  $0.88 \text{ mmol Ni g}^{-1}$ , respectively.

When adding small amounts of competitor ions the sorption capacity for Cu(II) remained almost unchanged (i.e.,  $1.10 \text{ mmol Cu g}^{-1}$  for a solution containing  $1.10 \text{ mmol Cu(II) L}^{-1}$  and  $0.37 \text{ mmol Ni(II) L}^{-1}$ ) while for Ni(II) a reduction of approximately 61% of the sorption capacity was observed when a small amount of Cu(II) was added (i.e.,  $0.34 \text{ mmol Ni g}^{-1}$  for a solution containing  $1.10 \text{ mmol Ni(II) L}^{-1}$  and  $0.34 \text{ mmol Cu(II) L}^{-1}$ ).

In the presence of the competitor ion at the same molar concentration, Cu(II) sorption decreases by approximately 5% (i.e.,  $1.00 \text{ mmol Cu g}^{-1}$ ), while Ni(II) decreased again by approximately 84% (down to  $0.14 \text{ mmol Ni g}^{-1}$ ).

While the biosorption capacity for Cu(II) is hardly influenced by the presence of Ni(II), the presence of Cu(II), even at minor concentration, significantly reduces the sorption capacity for Ni(II). It is also interesting to observe that the cumulative sorption capacity



**Fig. 4.** Comparison of the breakthrough curves obtained in mono- and bi-component solutions for different metal concentrations (according Tables 2 and 5).

(Table 4) reaches, under optimum conditions (Cu(II) + Ni(II) concentration higher than  $3 \text{ mmol metal g}^{-1}$ ), values (i.e.,  $1.24 \text{ mmol Cu} + \text{Ni g}^{-1}$ ) of the same order as those obtained with Cu(II) in mono-component solutions (i.e.,  $1.25 \text{ mmol Cu g}^{-1}$ , Table 2) and with the Langmuir model (i.e.,  $1.32 \text{ mmol Cu g}^{-1}$ , Table 3).

The effect of the presence of copper or cadmium on the removal of lead in *Sargassum* sp. algae was quantitatively demonstrated by Sheng et al. (2007). This shows the decrease of Pb(II) biosorption in the presence of an increasing concentration of Cu(II) or Cd(II). Cu(II) exerted a greater inhibitory effect on Pb(II) removal than Cd(II). Pb(II) showed the highest inhibitory effect on the biosorption of other metal ions, followed by Cu(II) and Cd(II).

The carboxylic groups are generally the most abundant acidic functional groups in brown algae (Davis et al., 2003). The adsorption capacity of the algae is directly related to the presence of these sites on the alginate polymer, which represent up to 40% of the dry weight of dried seaweed.

The basic mechanism involved in the heavy metal ions sorption from dilute solutions using biosorbents such as alginate is considered to be ion exchange due to the electrostatic interactions between the metal cations and the anionic carboxyl groups existing in the matrix of the polysaccharide. Copper, with greater affinity for the carboxylic group, will be preferentially sorbed over nickel.

Haug (1961) suggested a competition mechanism between metal ions and protons for organic binding sites. Based on the amount of protons released, the affinity of alginic acid to metal ions follows

the order Pb(II) > Cu(II) > Cd(II) > Ba(II) > Sr(II) > Ca(II) > Co(II) > Ni(II) > Mn(II) > Mg(II). Haug (1961) interpreted the preferential binding of heavier ions to stereochemical effects, since larger ions might better fit a binding site with two distant functional groups. The preferential binding of larger ions can be attributed to stereochemical effects such as the coordination of the oxygen atoms surrounding the metal ion (Papageorgiou et al., 2006).

#### 4. Conclusion

*S. filipendula* is an efficient biosorbent for nickel and copper, when they are individually in solution. However, in bi-component solutions, the biomass has a marked preference for Cu(II) over Ni(II). In the presence of nickel, both the maximum sorption capacities for Cu(II) and the shape of the breakthrough curves are almost unchanged. On the opposite hand the presence of copper significantly reduced the sorption capacity of nickel. This is confirmed by the presence of an overshoot for Ni(II) concentration at the outlet of the column: copper sorption induces a displacement of nickel initially adsorbed.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2010.12.049.

#### References

- Bailey, J.E., Ollis, D.F., 1986. *Biochemical Engineering Fundamentals*. McGraw Hill, New York.
- Boujelben, N., Bouzid, J., Elouear, Z., 2009. Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: study in single and binary systems. *J. Hazard. Mater.* 163, 376–382.
- Chassary, P., Vincent, T., Sanchez Marcano, J., Macaskie, L.E., Guibal, E., 2005. Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives. *Hydrometallurgy* 76, 131–147.
- Chen, Z., Ma, W., Han, M., 2008. Biosorption of nickel and copper onto treated alga (*Undaria pinnatifida*): application of isotherm and kinetic models. *J. Hazard. Mater.* 155, 327–333.
- da Silva, E.A., Cossich, E.S., Tavares, C.R.G., Filho, L.C., Guirardello, R., 2002. Modeling of copper(II) biosorption by marine alga *Sargassum* sp. In fixed-bed column. *Process Biochem.* 38, 791–799.
- Davis, T.A., Volesky, B., Vieira, R.H.S.F., 2000. *Sargassum* seaweed as biosorbent for heavy metals. *Water Res.* 34, 4270–4278.
- Davis, T.A., Volesky, B., Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* 37, 4311–4330.
- Fagundes-Klen, M.R., Ferri, P., Martins, T.D., Tavares, C.R.G., Silva, E.A., 2007. Equilibrium study of the binary mixture of cadmium-zinc ions biosorption by the *Sargassum filipendula* species using adsorption isotherms models and neural network. *Biochem. Eng. J.* 34, 136–146.
- Fourest, E., Volesky, B., 1997. Alginate properties and heavy metal biosorption by marine algae. *Appl. Biochem. Biotechnol.* 67 (3), 215–226.
- Figureira, M.M., Volesky, B., Ciminelli, V.S.T., Roddick, F.A., 2000. Biosorption of metals in brown seaweed biomass. *Water Res.* 34, 196–204.
- Guibal, E., Offenberger Sweeney, N., Zikan, M.C., Vincent, T., Tobin, J.M., 2001. Competitive sorption of platinum and palladium on chitosan derivatives. *Int. J. Biol. Macromol.* 28, 401–408.
- Hammami, A., González, F., Ballester, A., Blázquez, M.L., Muñoz, J.A., 2003. Simultaneous uptake of metals by activated sludge. *Miner. Eng.* 16, 723–729.
- Hashim, M.A., Chu, K.H., 2004. Biosorption of cadmium by brown, green, and red seaweeds. *Chem. Eng. J.* 97, 249–255.
- Haug, A., 1961. The affinity of some divalent metals to different types of alginates. *Acta Chem. Scand.* 15, 1794–1795.
- Hawari, A.H., Mulligan, C.N., 2006. Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. *Bioresour. Technol.* 97, 692–700.
- Holan, Z.R., Volesky, B., 1994. Biosorption of lead and nickel by biomass of marine algae. *Biotechnol. Bioeng.* 43, 1001–1009.
- Jain, J.S., d Snoeyink, V.L., 1973. Adsorption from biosolute systems on active carbon. *J. Water Pollut. Control Fed.* 45, 2463–2479.
- Jalali, R., Ghafourian, H., Asel, Y., Davarnapah, S.J., Sepehr, S., 2002. Removal and recovery of lead using non-living biomass of marine algae. *J. Hazard. Mater.* 92 (3), 253–262.
- Kratochvil, D., Volesky, B., 2000. Multicomponent biosorption in fixed beds. *Water Res.* 34, 3186–3196.
- Kumar, D., Singh, A., Gaur, J.P., 2008. Mono-component versus binary isotherm models for Cu(II) and Pb(II) sorption from binary metal solution by the green alga *Pithophora oedogonia*. *Bioresour. Technol.* 99, 8280–8287.
- Luna, A.S., Costa, A.L.H., da Costa, A.C., Henriques, C.A., 2010. Competitive biosorption of cadmium(II) and zinc(II) ions from binary systems by *Sargassum filipendula*. *Bioresour. Technol.* 101, 5104–5111.
- Ma, W., Tobin, J.M., 2003. Development of multimetal binding model and application to binary metal biosorption onto peat biomass. *Water Res.* 37, 3967–3977.
- Morris, E.R., Rees, D.A., Thom, D., 1980. Characterisation of alginate composition and block-structure by circular dichroism. *Carbohydr. Res.* 81, 305–314.
- Naja, G., Volesky, B., 2006. Multi-metal biosorption in a fixed-bed flow-through column. *Colloids Surf.* 281, 194–201.
- Nelder, J.A., Mead, R., 1965. A Simplex method for function minimization. *Computer J.* 7, 308–313.
- Pagnanelli, F., Esposito, A., Veglio, F., 2002. Multi-metallic modelling for biosorption of binary systems. *Water Res.* 36, 4095–4105.
- Pahlavanzadeh, H., Keshtkar, A.R., Safdari, J., Abadi, Z., 2010. Biosorption of nickel(II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies. *J. Hazard. Mater.* 175, 304–310.
- Papageorgiou, S.K., Katsaros, F.K., Kouvelos, E.P., Nolan, J.W., Le Deit, H., Kanellopoulos, N.K., 2006. Heavy metal sorption by calcium alginate beads from *Laminaria digitata*. *J. Hazard. Mater.* 137, 1765–1772.
- Popuri, S.R., Vijaya, Y., Boddu, V.M., Abburi, K., 2009. Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. *Bioresour. Technol.* 100 (1), 194–199.
- Rees, D.A., 1981. Polysaccharide shapes and their interactions - some recent advances. *Pure Appl. Chem.* 53, 1–14.
- Sahan, T., Ceylan, H., Sahiner, N., Aktas, N., 2010. Optimization of removal conditions of copper ions from aqueous solutions by *Trametes versicolor*. *Bioresour. Technol.* 101 (12), 4520–4526.
- Sanchez, A., Ballester, A., Blázquez, M.L., González, F., Muñoz, J., Hammami, A., 1999. Biosorption of copper and zinc by *Cymodocea nodosa*. *FEMS Microbiol. Rev.* 23, 527–536.
- Sheng, P.X., Ting, Y.-P., Chen, J.P., 2007. Biosorption of heavy metal ions (Pb, Cu, and Cd) from aqueous solutions by the marine alga *Sargassum* sp. In single- and multiple-metal systems. *Ind. Eng. Chem. Res.* 46, 2438–2444.
- Vieira, M.G.A., Neto, A.F.A., Gimenes, M.L., da Silva, M.G.C., 2010. Sorption kinetics and equilibrium for the removal of nickel ions from aqueous phase on calcined Bofe bentonite clay. *J. Hazard. Mater.* 177, 362–371.
- Vijayaraghavan, K., Jegan, J., Palanivelu, K., Velan, M., 2005. Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column. *Chemosphere* 60, 419–426.
- Volesky, B., 2001. Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy* 59, 203–216.
- Volesky, B., 2003. Biosorption process simulation tools. *Hydrometallurgy* 71, 179–190.