

Effect of Cu(II), Cd(II) and Zn(II) on Pb(II) biosorption by algae *Gelidium*-derived materials

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Abstract

Biosorption of Pb(II), Cu(II), Cd(II) and Zn(II) from binary metal solutions onto the algae *Gelidium sesquipedale*, an algal industrial waste and a waste-based composite material was investigated at pH 5.3, in a batch system. Binary Pb(II)/Cu(II), Pb(II)/Cd(II) and Pb(II)/Zn(II) solutions have been tested. For the same equilibrium concentrations of both metal ions (1 mmol l^{-1}), approximately 66, 85 and 86% of the total uptake capacity of the biosorbents is taken by lead ions in the systems Pb(II)/Cu(II), Pb(II)/Cd(II) and Pb(II)/Zn(II), respectively. Two-metal results were fitted to a discrete and a continuous model, showing the inhibition of the primary metal biosorption by the co-cation. The model parameters suggest that Cd(II) and Zn(II) have the same decreasing effect on the Pb(II) uptake capacity. The uptake of Pb(II) was highly sensitive to the presence of Cu(II). From the discrete model it was possible to obtain the Langmuir affinity constant for Pb(II) biosorption. The presence of the co-cations decreases the apparent affinity of Pb(II). The experimental results were successfully fitted by the continuous model, at different pH values, for each biosorbent. The following sequence for the equilibrium affinity constants was found: $\text{Pb} > \text{Cu} > \text{Cd} \approx \text{Zn}$.

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1. Introduction

An algal waste, from agar extraction industry, and a composite material (algal waste immobilized with PAN—polyacrylonitrile), as well algae *Gelidium*, which is the raw material for agar extraction, have been used to remove metal ions from solution in batch [1] and continuous systems [2,3]. Their ability to uptake metal ions has been attributed to the carboxylic groups present in the biomass structure [4]. Proton competition with metal ions has been described by discrete and continuous models, considering homogeneous and heterogeneous distribution of the carboxylic groups, respectively [1]. As industrial effluents can contain several metals, it is useful to study the simultaneous sorption of two or more metal ions to quantify multimetal competitive interactions. Several works have been published about two-metal biosorption. Chong and Volesky

[5] studied the equilibrium of the metal systems (Cu + Zn), (Cu + Cd) and (Zn + Cd) using *Ascophyllum nodosum* seaweed biomass crosslinked with formaldehyde, and concluded that the uptake of Zn decreased drastically when Cu or Cd was present. Pagnanelli et al. [6] tested the biosorption of binary systems (Cu + Cd; Cu + Pb and Cu + Zn) by *Sphaerotilus* biomass at different pH values, and concluded that copper uptake was strongly influenced by increasing lead concentrations in solution, while it was less affected by the presence of cadmium. Cadmium uptake is strongly influenced by copper, while lead is weakly sensitive to the presence of copper. The biosorption performance of binary systems (Cr + Cd, Cr + Cu and Cu + Cd) onto peat biomass was studied by Ma and Tobin [7]. These investigators found out that copper and chromium have the same competition effect and that the presence of these cations highly decreases the cadmium uptake capacity. In order to describe the metal adsorption in the presence of other metal ions, several models have been developed, as the classical multi-component Langmuir or Langmuir–Freundlich models [5,6]. Some of those models consider a homogeneous distribution of binding sites. Because the algal biomass adsorbent has an heterogeneous

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distribution of different active sites [4], this work presents a multi-component equilibrium model (NICA model), which takes into account the competition of metal ions and protons for an heterogeneous Sips distribution of binding sites [8,9].

The objective of this work was to study the equilibrium uptake of binary systems (Pb + Cu, Pb + Cd and Pb + Zn) by algae *Gelidium* and algal waste in two different forms.

2. Materials and methods

2.1. Biosorbents preparation

An algal waste from the agar extraction industry and the same waste granulated by an organic polymer (polyacrylonitrile) were the adsorbents used in this study, as well as the algae *Gelidium*, the raw material for agar extraction. The characteristics and preparation of the three materials were presented in a previous work [10].

2.2. Preparation of metal solutions

Pb(II), Cu(II), Cd(II) and Zn(II) solutions were prepared by dissolving anhydrous lead(II) chloride (Sigma–Aldrich, 98%), copper(II) chloride dehydrate (Riedel-de Haën, 99%), anhydrous cadmium(II) chloride (Sigma–Aldrich, 99%) and anhydrous zinc(II) chloride (Merck, 98%) in distilled water. pH was controlled by adding 0.01 M HCl or 0.01 M NaOH solutions.

2.3. Sorption equilibrium studies

The experiments were conducted in duplicate, using 100 ml Erlenmeyer flasks, at constant values of pH = 5.3 and temperature ($T = 20\text{ }^{\circ}\text{C}$). Metal solutions contained combinations of either (Pb/Cu), (Pb/Zn) or (Pb/Cd) in the concentration range of 0–300 mg l^{-1} of each metal. A given weight of adsorbent (0.2 g of algae *Gelidium* and algal waste; 0.1 g of composite material) was suspended in 100 ml of a two-metal solution and stirred at 100 rpm; the pH was adjusted and controlled by adding NaOH and HCl diluted 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 metals.

2.4. Analytical procedure

The concentration of residual Pb(II), Cu(II), Cd(II) and Zn(II) in the supernatants has been determined by atomic absorption spectrometry (GBC 932 Plus Atomic Absorption Spectrometer). The amount of each metal adsorbed per gram of biosorbent was calculated as:

$$q = \frac{V(C_i - C_f)}{W} \quad (1)$$

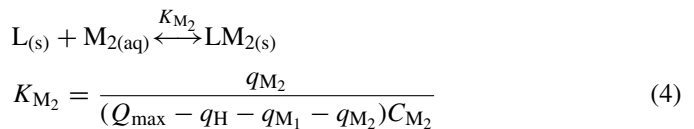
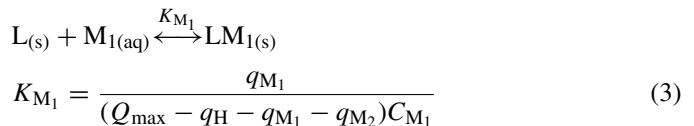
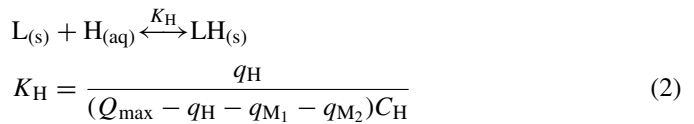
where q is the metal uptake (mmol metal g^{-1} of the biosorbent), C_i and C_f the initial and final metal concentrations in solution

(mmol l^{-1}), V the volume of solution (l), and W the dry weight of the added biosorbent (g).

3. Theory

3.1. Discrete model

Heavy metals biosorption is described as a process of ion exchange with protons and complexation of metal ions on the adsorbent active sites [11]. For an homogeneous adsorbent (only one kind of active sites), the following reactions can be considered [12]:



where Q_{\max} represents the maximum amount of active sites (mmol g^{-1}); q_H , q_{M_1} and q_{M_2} are the equilibrium uptake capacities for hydrogen and metal ions M_1 and M_2 (mmol g^{-1}); C_H , C_{M_1} and C_{M_2} are the equilibrium solution concentrations of hydrogen and metal ions M_1 and M_2 (mmol l^{-1}); K_H is the protonation apparent equilibrium constant (l mmol^{-1}); K_{M_1} and K_{M_2} are the apparent equilibrium constants for metal ions M_1 and M_2 (l mmol^{-1}).

Combining Eqs. (2)–(4) we get the equilibrium relationship between the equilibrium uptake capacity, the equilibrium concentration of the metal ions and the hydrogen ion concentration, which is expressed by the following expression:

$$q_{M_1} = \frac{Q_{\max} K_{M_1} C_{M_1}}{1 + K_H C_H + K_{M_1} C_{M_1} + K_{M_2} C_{M_2}} \quad (5)$$

Dividing Eq. (5) by $(1 + K_H C_H + K_{M_2} C_{M_2})$, the Langmuir equation is obtained:

$$\begin{aligned} q_{M_1} &= \frac{Q_{\max} K_L [M_1] C_{M_1}}{1 + K_L [M_1] C_{M_1}}, \\ K_L [M_1] &= \frac{K_{M_1}}{1 + K_H C_H + K_{M_2} C_{M_2}} \end{aligned} \quad (6)$$

where $K_L [M_1]$ is the Langmuir constant that depends on the pH and on M_2 concentration. A similar equation is obtained for M_2 . The total metal uptake ($M_1 + M_2$) can be calculated as:

$$q_T = q_{M_1} + q_{M_2} = \frac{Q_{\max} (K_{M_1} C_{M_1} + K_{M_2} C_{M_2})}{1 + K_H C_H + K_{M_1} C_{M_1} + K_{M_2} C_{M_2}} \quad (7)$$

3.2. Continuous model

As a starting point for the derivation of the NICA (Non-Ideal Competition Adsorption) model, Koopal et al. [13] postulated that the extended Henderson-Hasselbalch [14] or Hill [15] equations could be used to describe the local competitive binding of species X , assuming one type of active sites:

$$\theta_{i,X} = \frac{(K_{i,X}^{\text{int}} C_X)^{n_X}}{1 + \sum_X (K_{i,X}^{\text{int}} C_X)^{n_X}} \quad (8)$$

where $\theta_{i,X}$ is the fraction of sites occupied by species X , $K_{i,X}^{\text{int}}$ is the intrinsic affinity of species X for sites i and C_X is the concentration of species X in solution, n_{M_i} is thought to reflect the overall non-ideality due to lateral interactions and/or stoichiometric effects.

For heterogeneous ligands with a continuous distribution of affinities and assuming competition between metal ions and protons, the total fraction of bound metal is obtained by a multiple integral equation:

$$\theta_{T,X} = \int \dots \int_{\Delta K_{i,X}^{\text{int}}} \theta_{i,X}(K_{i,X}^{\text{int}}, C_X) f_i(\log K_{i,X}^{\text{int}}) d(\log K_{i,X}^{\text{int}}) \quad (9)$$

where $f_i(\log K_{i,X}^{\text{int}})$ is the distribution function of the affinity constant, $\theta_{i,X}(K_{i,X}^{\text{int}}, C_X)$ is the local adsorption isotherm, and $\Delta \log K_{i,X}^{\text{int}}$ is the range of $\log K_{i,X}^{\text{int}}$ considered.

This equation can be solved analytically, assuming that the local adsorption isotherm is given by Eq. (8) and $f(\log K_{i,X}^{\text{int}})$ is a Quasi-Gaussian distribution [8], represented by the following equation:

$$f(\log K_{i,X}^{\text{int}}) = \frac{\ln(10) \sin(m_H \pi)}{(\pi [(K_{i,X}^{\text{int}}/K'_X)^{-m_H} + 2 \cos(m_H \pi) + (K_{i,X}^{\text{int}}/K'_X)^{m_H}])} \quad (10)$$

The final result is the basic NICA equation:

$$\theta_{T,X} = \frac{(K'_X C_X)^{n_X}}{\sum_X (K'_X C_X)^{n_X}} \times \frac{[\sum_X (K'_X C_X)^{n_X}]^p}{1 + [\sum_X (K'_X C_X)^{n_X}]^p} \quad (11)$$

where K'_X is the average value of the affinity constants distribution for species X . The effect of the intrinsic heterogeneity of the carboxylic group (p) can be isolated from the non-ideal behaviour of species X (n_X), $m_X = n_X \times p$ (apparent heterogeneity of the binding). The total bound amount, q_X , is given by:

$$q_X = Q_{\text{max}}(\theta_{T,X}) \left(\frac{n_X}{n_H} \right) \quad (12)$$

where the factor n_X/n_H is added to give thermodynamic consistency and has some other advantages. Assuming that metal ions adsorb only on carboxylic groups ($\text{pH} < 7.0$), the total metal uptake ($M_1 + M_2$) can be expressed as:

$$q_T = \frac{Q_{\text{max}}}{n_H} \{n_{M_1} (K_{M_1} C_{M_1})^{n_{M_1}} + n_{M_2} (K_{M_2} C_{M_2})^{n_{M_2}}\} \times \frac{\{(K'_H C_H)^{n_H} + (K'_{M_1} C_{M_1})^{n_{M_1}} + (K'_{M_2} C_{M_2})^{n_{M_2}}\}^{p-1}}{1 + \{(K'_H C_H)^{n_H} + (K'_{M_1} C_{M_1})^{n_{M_1}} + (K'_{M_2} C_{M_2})^{n_{M_2}}\}^p} \quad (13)$$

3.3. Parameters estimation

The experimental data obtained from equilibrium studies with three independent variables (C_H , C_{M_1} and C_{M_2}) were fitted to mathematical models using the Excel Solver (Quasi-Newton algorithm). The objective function (F_{obj}) to minimize for optimal regression is:

$$F_{\text{obj}} = \sum_{i=1}^n (q_{i,M_1}^{\text{exp}} - q_{i,M_1}^{\text{teo}})^2 + \sum_{i=1}^n (q_{i,M_2}^{\text{exp}} - q_{i,M_2}^{\text{teo}})^2 + \sum_{i=1}^n (q_{i,T}^{\text{exp}} - q_{i,T}^{\text{teo}})^2 \quad (14)$$

where q_{i,M_1}^{exp} , q_{i,M_2}^{exp} and $q_{i,T}^{\text{exp}}$ are the experimental metal biosorption uptakes (M_1 , M_2 , and total), q_{i,M_1}^{teo} , q_{i,M_2}^{teo} and $q_{i,T}^{\text{teo}}$ are the equilibrium metal uptakes, calculated by the model, i is the experimental sample number and n is the number of samples.

In order to determine the errors associated with the parameters, the matrix inverse approach [16] has been used. Defining the non-linear function as:

$$y_i = f(x_i; a_0, a_1, \dots, a_m) + e_i \quad (15)$$

where y_i is a measured value of the dependent variable, $f(x_i; a_0, a_1, \dots, a_m)$ is a function of the independent variable x_i and a non-linear function of the parameters a_0, a_1, \dots, a_m and e_i is a random error.

The diagonal and off-diagonal terms of the matrix $[[Z]^T [Z]]^{-1}$ give, respectively, the variances and the covariances of the a 's. $[Z]$ is the matrix of the partial derivatives of the function for all experimental points, defined as:

$$[Z] = \begin{bmatrix} \frac{\partial f_1}{\partial a_0} & \frac{\partial f_1}{\partial a_1} & \dots & \frac{\partial f_1}{\partial a_m} \\ \frac{\partial f_2}{\partial a_0} & \frac{\partial f_2}{\partial a_1} & \dots & \frac{\partial f_2}{\partial a_m} \\ \vdots & \vdots & \dots & \vdots \\ \frac{\partial f_n}{\partial a_0} & \frac{\partial f_n}{\partial a_1} & \dots & \frac{\partial f_n}{\partial a_m} \end{bmatrix} \quad (16)$$

where n is the number of experimental data points, m is the number of parameters of the function and $\partial f_i/\partial a_k$ is the partial derivative of the function with respect to the k th parameter evaluated at the i th data point.

The matrix inverse of the product of the matrix $[Z]$ by its transpose $[Z]^T$ results:

Table 1
Adjustable parameters for the multi-component discrete equilibrium model (Eq. (7)) (value \pm standard deviation)

Biosorbent	System	Metal	Discrete model			R_2	S_R^2 (mmol g ⁻¹) ²
			Q_{\max} (mmol g ⁻¹)	pK_M	pK_H		
<i>Gelidium</i>	Pb ²⁺ /Cu ²⁺	Pb ²⁺	0.40	3.63 \pm 0.05	4.21	0.912	1.1 \times 10 ⁻³
		Cu ²⁺	\pm 0.01	3.23 \pm 0.05	\pm 0.06		
	Pb ²⁺ /Cd ²⁺	Pb ²⁺	0.28	3.98 \pm 0.05	4.05	0.926	4.3 \times 10 ⁻⁴
		Cd ²⁺	\pm 0.01	3.16 \pm 0.04	\pm 0.05		
Pb ²⁺ /Zn ²⁺	Pb ²⁺	0.29	3.89 \pm 0.05	3.88	0.915	3.9 \times 10 ⁻⁴	
	Zn ²⁺	\pm 0.01	2.89 \pm 0.04	\pm 0.06			
Algal waste	Pb ²⁺ /Cu ²⁺	Pb ²⁺	0.24	3.83 \pm 0.07	4.59	0.884	6.5 \times 10 ⁻³
		Cu ²⁺	\pm 0.01	3.36 \pm 0.07	\pm 0.08		
	Pb ²⁺ /Cd ²⁺	Pb ²⁺	0.20	3.99 \pm 0.06	4.35	0.911	2.8 \times 10 ⁻⁴
		Cd ²⁺	\pm 0.01	3.12 \pm 0.04	\pm 0.06		
Pb ²⁺ /Zn ²⁺	Pb ²⁺	0.20	3.97 \pm 0.06	4.26	0.900	2.5 \times 10 ⁻⁴	
	Zn ²⁺	\pm 0.01	2.84 \pm 0.05	\pm 0.08			
Composite material	Pb ²⁺ /Cu ²⁺	Pb ²⁺	0.15	4.2 \pm 0.2	4.9	0.771	7.5 \times 10 ⁻⁴
		Cu ²⁺	\pm 0.01	3.9 \pm 0.2	\pm 0.2		
	Pb ²⁺ /Cd ²⁺	Pb ²⁺	0.098	4.50 \pm 0.05	4.58	0.924	6.0 \times 10 ⁻⁵
		Cd ²⁺	\pm 0.002	3.42 \pm 0.04	\pm 0.05		
Pb ²⁺ /Zn ²⁺	Pb ²⁺	0.098	4.50 \pm 0.06	4.58	0.919	5.4 \times 10 ⁻⁵	
	Zn ²⁺	\pm 0.002	3.42 \pm 0.05	\pm 0.07			

$$[[Z]^T[Z]]^{-1} = \begin{bmatrix} z_{11} & z_{12} & \cdots & z_{1m} \\ z_{21} & z_{22} & \cdots & z_{2m} \\ z_{31} & z_{32} & \cdots & z_{3m} \\ \vdots & \vdots & \cdots & \vdots \\ z_{m1} & z_{m2} & \cdots & z_{mm} \end{bmatrix} \quad (17)$$

$$\text{var}(a_{k-1}) = z_{kk}^{-1} S_R^2, \quad k = 1, m \quad (18)$$

where the square residual is

$$S_R^2 = \frac{\sum_{i=1}^n (q_{i,T}^{\text{exp}} - q_{i,T}^{\text{teo}})^2}{n - m} \quad (19)$$

For the first two parameters we get:

$$\text{var}(a_0) = z_{11}^{-1} S_R^2 \quad (20)$$

If the diagonal elements of $[[Z]^T[Z]]^{-1}$ are designed as z_{kk}^{-1} , then the variance of the parameters is defined as:

Table 2
Adjustable parameters for the multi-component continuous equilibrium model (Eq. (3)), using the experimental data of each metal ion in the binary system (value \pm standard deviation)

Biosorbent	System	Metal	Continuous model		R^2	S_R^2 (mmol g ⁻¹) ²
			pK'_M	n_M		
<i>Gelidium</i>	Pb ²⁺ /Cu ²⁺	Pb ²⁺	3.8 \pm 0.1	0.64 \pm 0.03	0.940	7.5 \times 10 ⁻⁴
		Cu ²⁺	3.1 \pm 0.1	0.79 \pm 0.03		
	Pb ²⁺ /Cd ²⁺	Pb ²⁺	3.8 \pm 0.1	0.64 \pm 0.03	0.924	4.5 \times 10 ⁻⁴
		Cd ²⁺	3.1 \pm 0.1	0.50 \pm 0.03		
Pb ²⁺ /Zn ²⁺	Pb ²⁺	3.8 \pm 0.1	0.64 \pm 0.03	0.919	5.4 \times 10 ⁻⁴	
	Zn ²⁺	2.9 \pm 0.1	0.46 \pm 0.05			
Algal waste	Pb ²⁺ /Cu ²⁺	Pb ²⁺	3.9 \pm 0.1	0.72 \pm 0.04	0.919	4.1 \times 10 ⁻⁴
		Cu ²⁺	3.5 \pm 0.1	0.73 \pm 0.04		
	Pb ²⁺ /Cd ²⁺	Pb ²⁺	4.1 \pm 0.1	0.67 \pm 0.04	0.896	3.3 \times 10 ⁻⁴
		Cd ²⁺	3.2 \pm 0.1	0.59 \pm 0.04		
Pb ²⁺ /Zn ²⁺	Pb ²⁺	4.2 \pm 0.1	0.65 \pm 0.05	0.886	4.0 \times 10 ⁻⁴	
	Zn ²⁺	2.9 \pm 0.1	0.63 \pm 0.08			
Composite material	Pb ²⁺ /Cu ²⁺	Pb ²⁺	4.0 \pm 0.1	0.79 \pm 0.08	0.869	3.3 \times 10 ⁻⁴
		Cu ²⁺	3.3 \pm 0.1	1.0 \pm 0.09		
	Pb ²⁺ /Cd ²⁺	Pb ²⁺	4.3 \pm 0.1	0.69 \pm 0.04	0.920	6.5 \times 10 ⁻⁵
		Cd ²⁺	3.0 \pm 0.1	0.63 \pm 0.04		
Pb ²⁺ /Zn ²⁺	Pb ²⁺	4.1 \pm 0.1	0.73 \pm 0.04	0.938	4.3 \times 10 ⁻⁵	
	Zn ²⁺	3.0 \pm 0.1	0.65 \pm 0.05			

$Q_{\max} = 0.36 \pm 0.01$, 0.23 ± 0.05 and 0.16 ± 0.01 mmol g⁻¹; $pK'_H = 5.0 \pm 0.1$, 5.3 ± 0.3 and 4.4 ± 0.1 ; $m_H = 0.43 \pm 0.01$, 0.37 ± 0.03 and 0.33 ± 0.04 and $p = 0.88 \pm 0.08$, 0.69 ± 0.09 and 0.43 ± 0.09 , respectively for algae *Gelidium*, algal waste and composite material.

Table 3

Adjustable parameters for the multi-component continuous equilibrium model (Eq. (3)), using all the experimental data for all metal ions (value ± standard deviation)

Biosorbent	Metal	Continuous model		$\frac{n_M}{n_H}$	m_M	R^2	S_R^2 (mmol g ⁻¹) ²
		pK'_M	n_M				
<i>Gelidium</i>	Cu ²⁺	3.1 ± 0.1	0.78 ± 0.03	1.7	0.71	0.944	5.4 × 10 ⁻⁴
	Pb ²⁺	3.7 ± 0.1	0.64 ± 0.03	1.4	0.57		
	Cd ²⁺	2.9 ± 0.1	0.53 ± 0.05	1.1	0.48		
	Zn ²⁺	2.7 ± 0.3	0.53 ± 0.09	1.1	0.48		
Algal waste	Cu ²⁺	3.5 ± 0.1	0.74 ± 0.04	1.3	0.49	0.928	2.9 × 10 ⁻⁴
	Pb ²⁺	4.2 ± 0.1	0.66 ± 0.04	1.2	0.44		
	Cd ²⁺	3.2 ± 0.1	0.63 ± 0.05	1.1	0.42		
	Zn ²⁺	2.9 ± 0.3	0.70 ± 0.09	1.3	0.46		
Composite material	Cu ²⁺	3.3 ± 0.1	1.0 ± 0.1	1.3	0.44	0.885	2.0 × 10 ⁻⁴
	Pb ²⁺	4.0 ± 0.1	0.75 ± 0.08	1.0	0.33		
	Cd ²⁺	2.9 ± 0.1	0.7 ± 0.1	0.9	0.30		
	Zn ²⁺	2.8 ± 0.3	0.8 ± 0.1	1.1	0.35		

$Q_{max} = 0.36 \pm 0.01$, 0.23 ± 0.05 and 0.16 ± 0.01 mmol g⁻¹; $pK'_H = 5.0 \pm 0.1$, 5.3 ± 0.3 and 4.4 ± 0.1 ; $m_H = 0.43 \pm 0.01$, 0.37 ± 0.03 and 0.33 ± 0.04 and $p = 0.88 \pm 0.08$, 0.69 ± 0.09 and 0.43 ± 0.09 , respectively for algae *Gelidium*, algal waste and composite material.

$$\text{var}(a_1) = z_{22}^{-1} S_R^2 \tag{21}$$

The regression coefficient (R^2) of the non-linear regression can be calculated as:

$$R^2 = 1 - \frac{S_R^2}{S_{y/y}^2} \tag{22}$$

where $S_{y/y}^2$ corresponds to the variance of the experimental data points ($q_{i,T}^{\text{exp}}$) relatively to the mean value (\bar{q}_T), given by the following expression:

$$S_{y/y}^2 = \frac{\sum_{i=1}^n (q_{i,T}^{\text{exp}} - \bar{q}_T)^2}{n - m} \tag{23}$$

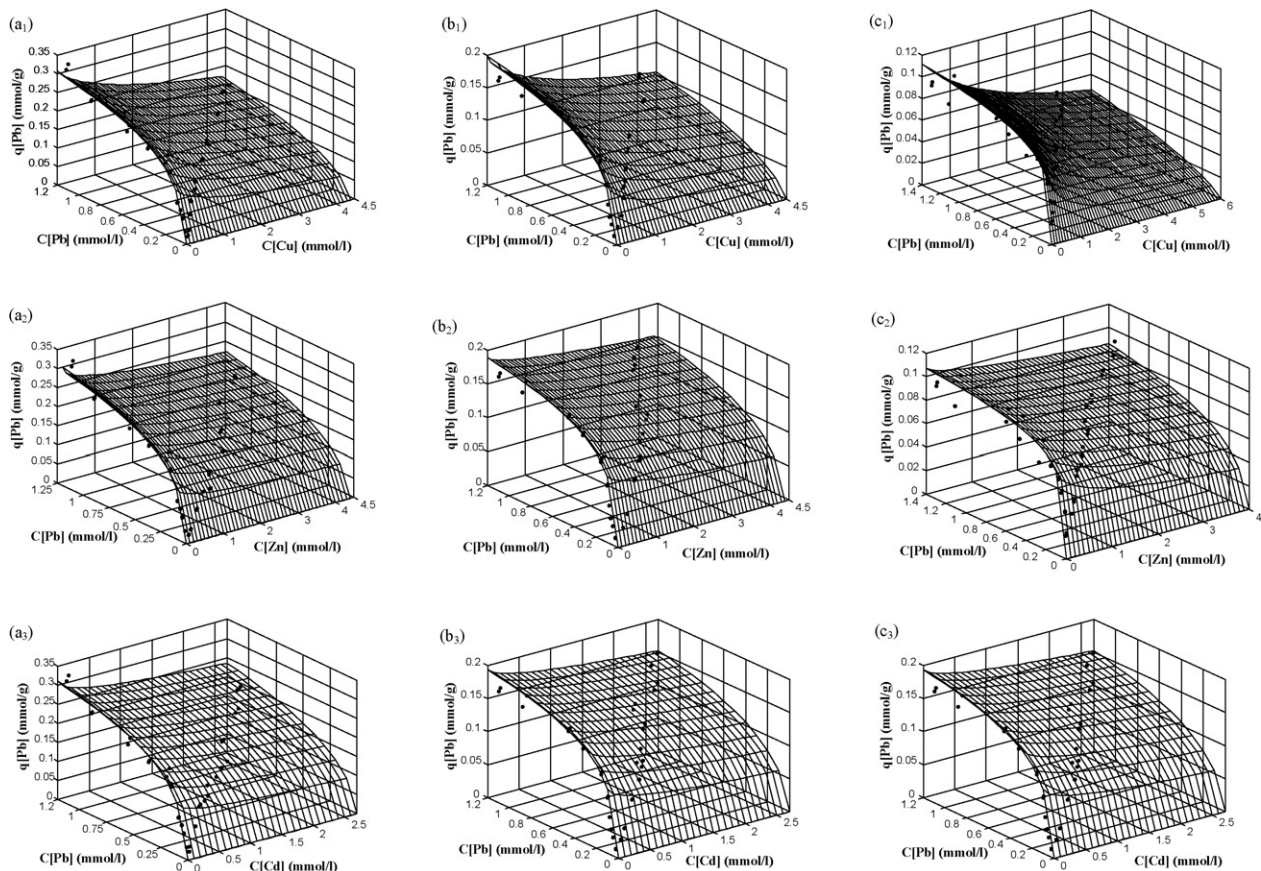


Fig. 1. Two-metal sorption isotherm surfaces. Lead uptake as a function of the equilibrium concentration of two metals at pH 5.3 and 20 °C. (a_i) Algae *Gelidium*, (b_i) algal waste and (c_i) composite material: $i = 1$ —Pb(II)/Cu(II); $i = 2$ —Pb(II)/Zn(II); $i = 3$ —Pb(II)/Cd(II).

4. Results and discussion

4.1. Model parameters

Biosorption equilibrium for Pb(II)/Cu(II), Pb(II)/Zn(II) and Pb(II)/Cd(II) aqueous solutions has been studied at pH 5.3 and 20 °C for the same initial concentrations of both metal ions (mg l^{-1}). In order to quantify the co-cation effect, the experimental data were fitted to a discrete (Eq. (7)) and a continuous model (Eq. (3)). The discrete model parameters were also determined using the single-metal experimental data at different pH [4]. The parameters are presented in Table 1. To fit the continuous model to the experimental data, the parameters Q_{max} , pK'_H and m_H were obtained from potentiometric titrations, and the p parameter was obtained from the single metal adsorption experiment [4]. The model gives the pK'_M and n_M values for each metal ion in each binary system are presented in Table 2.

The same parameters were also determined using all the experimental data (single-metal and two-metal systems) for each

biosorbent. In this case, the model gives only one value of pK'_M and n_M for each metal and respective biosorbent (Table 3).

The statistical parameters presented in Tables 1 and 2 shows that both models, discrete and continuous, describe well the experimental data. Comparing the two models by the test- F for a 95% confidence level, we concluded that, although for some two-metal systems one model is better than the other, no significant statistical difference exists between the two models when considering all the binary systems. So, as the discrete model is simpler, it can be used in the mathematical mass transfer modelling, both in batch and continuous systems.

pK'_M values obtained from the discrete (Table 1) and continuous (Table 2) models, are similar suggesting that both models are capable of predicting experimental data as it was statistically demonstrated by using the test- F .

Tables 2 and 3 show that the values of pK'_M and n_M are very similar, concluding that the affinity constant of the metal ions to the biosorbents remains constant in each system, independent of the co-cation.

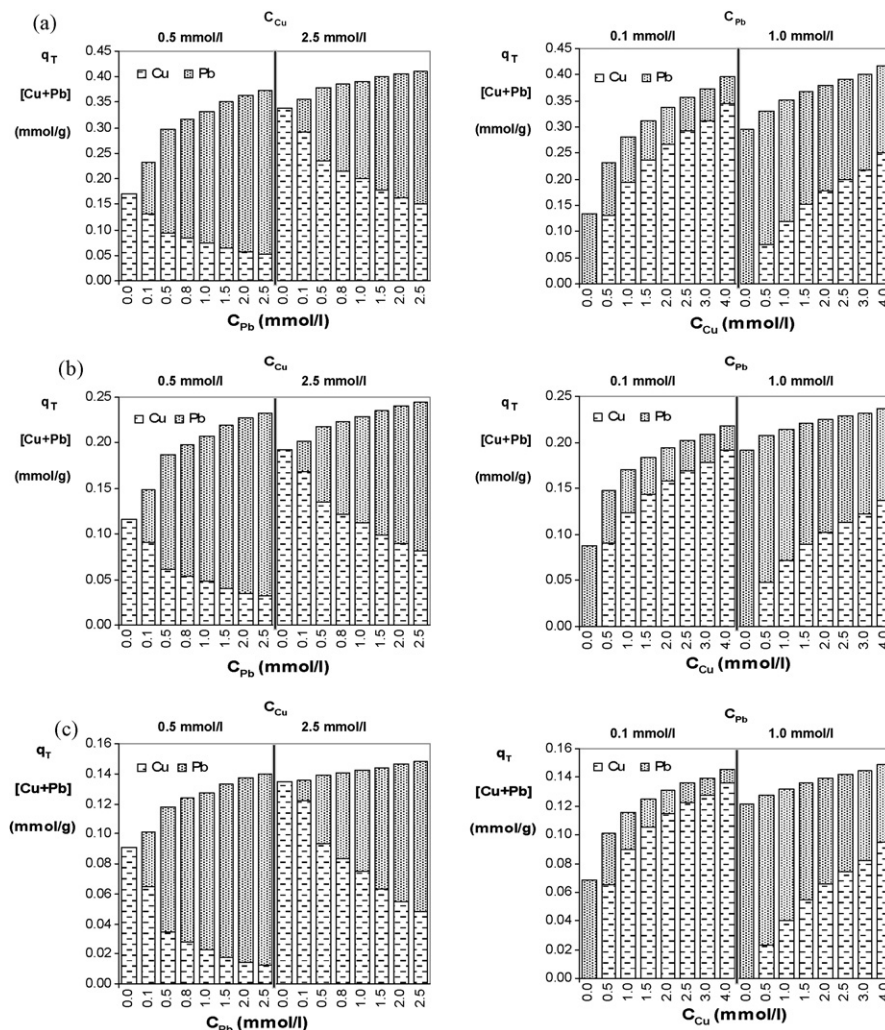


Fig. 2. Iso-concentration cuts of the Pb(II)/Cu(II) sorption isotherm surface. Total metal uptake from the two-metal solution vs. equilibrium concentration of one metal, for constant concentration of the other metal. (a) Algae *Gelidium*, (b) algal waste and (c) composite material.

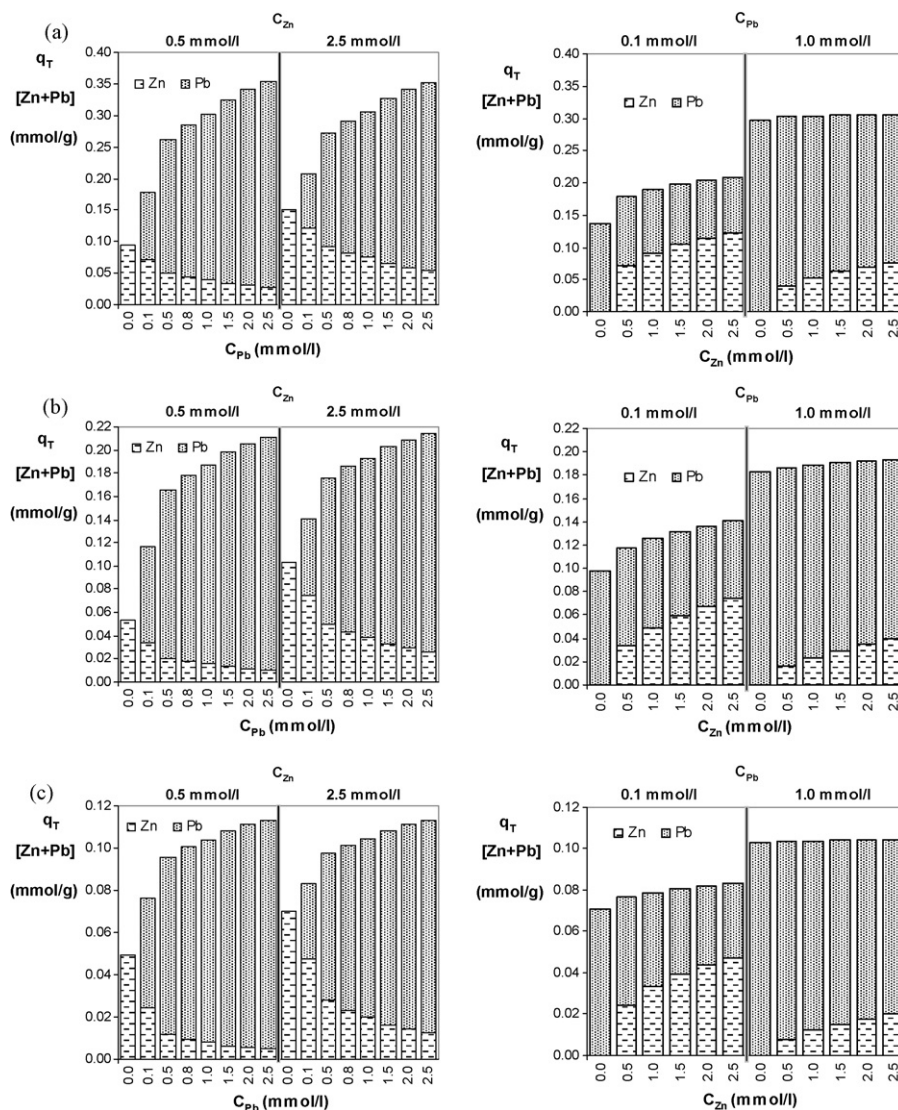


Fig. 3. Iso-concentration cuts of the Pb(II)/Zn(II) sorption isotherm surface. Total metal uptake from the two-metal solution vs. equilibrium concentration of one metal, for constant concentration of the other metal. (a) Algae *Gelidium*, (b) algal waste and (c) composite material.

The values of n_M/n_H (Table 3) are generally greater than one, which indicates that the maximum binding for species i is higher than for protons, reflecting some degree of cooperativity [17].

The ratio n_H/n_M has a particularly strong influence on the exchange ratio (r_{ex}) of the ion exchange process, since it is linearly related to it [17]. r_{ex} can change inside the range $0 < r_{ex} < n_H/n_M$, the greatest value being found for small p (high heterogeneity), low metal concentration and low pH. This is true when most sites are occupied by protons or other ions as potassium, sodium, calcium and magnesium and the binding reaction approaches a “normal” ion exchange reaction. Under these conditions, the ratio n_H/n_M represents some kind of reaction stoichiometry [17]. As shown in Table 3, $n_H/n_M \cong 1$ indicates a stoichiometry exchange.

The narrowest binding constant distribution was obtained for copper ions (high m_M value), suggesting that copper binds to homogeneous active sites on the biosorbent surface.

4.2. “Iso-concentration” cuts of the isotherms surfaces

The three-dimensional (3-D) sorption isotherm plot is the most appropriate way to represent the biosorption equilibrium of a two-metal system. The metal uptake in this case can be either the uptake of one metal or the total uptake of both metals. Fig. 1 shows the Pb(II) uptake as a function of Pb(II), Cu(II), Cd(II) and Zn(II) equilibrium concentrations. Surfaces were constructed with the continuous model, and the parameters indicated in Table 2, using MATLAB.

While 3-D isotherm surfaces represent the two-metal equilibrium results, the cuts through the 3-D diagrams—iso-concentration graphs (Figs. 2–4) represent the total metal uptake vs. the equilibrium concentration of M_1 for a constant equilibrium concentration of M_2 . Moreover, to better evaluate the effect of the presence of the secondary metal (co-cation) (M_2) on the uptake capacity of the primary metal (M_1), the uptake percentage of lead ion as a function of the concentration

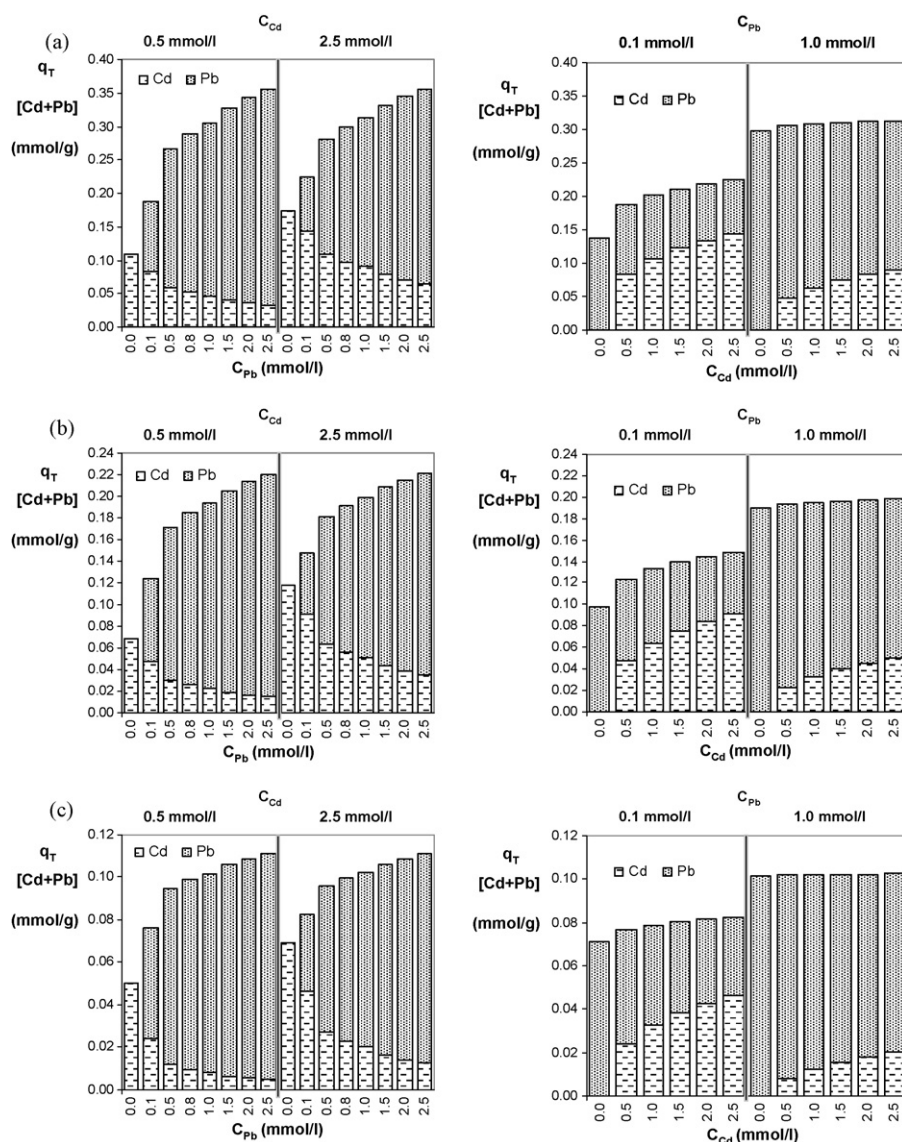


Fig. 4. Iso-concentration cuts of the Pb(II)/Cd(II) sorption isotherm surface. Total metal uptake from the two-metal solution vs. equilibrium concentration of one metal, for constant concentration of the other metal. (a) Algae *Gelidium*, (b) algal waste and (c) composite material.

of the co-cation at pH 5.3 was represented in Fig. 5. The resulting curves are well described by the Langmuir model. The parameter K_L (Eq. (6)), which represents the apparent affinity of the metal ion towards the binding sites, is plotted as a function of the co-cation concentration for pH 5.3 in Fig. 6.

4.2.1. Pb(II)/Cu(II)

For a given C_{Cu} , as C_{Pb} increases, the uptake capacity of lead also increases for the three biosorbents (Fig. 2(a–c)). However, this increase becomes gradually smaller at higher concentrations of copper, possibly due to the saturation of the active sites.

The equilibrium models for a binary biosorption system indicate that the presence of one metal always lowers the binding capacity of the other metal, which means that competition to the binding sites occurs between the two metals and protons. When

compared to the one-metal biosorption process, the total metal uptake is always higher when the biomass is exposed to a binary solution.

For equal equilibrium concentrations of lead and copper, the biosorbents present a preference for sorbing Pb over Cu. The same contribution of both metals for the total binding capacity is obtained when $C_{Cu} \cong 2.5C_{Pb}$ at equilibrium.

4.2.2. Pb(II)/Zn(II)

Increasing C_{Pb} or C_{Zn} and keeping constant the concentration of the other metal, the total and individual metal uptake increases (Fig. 3(a–c)), except for $C_{Pb} = 1.0 \text{ mmol l}^{-1}$, where increasing C_{Zn} , the total uptake capacity remains constant.

At equilibrium, C_{Zn} should be 10, 20 and 15 times higher than C_{Pb} to bind the same fraction of metal, respectively for algae, algal waste and composite material.

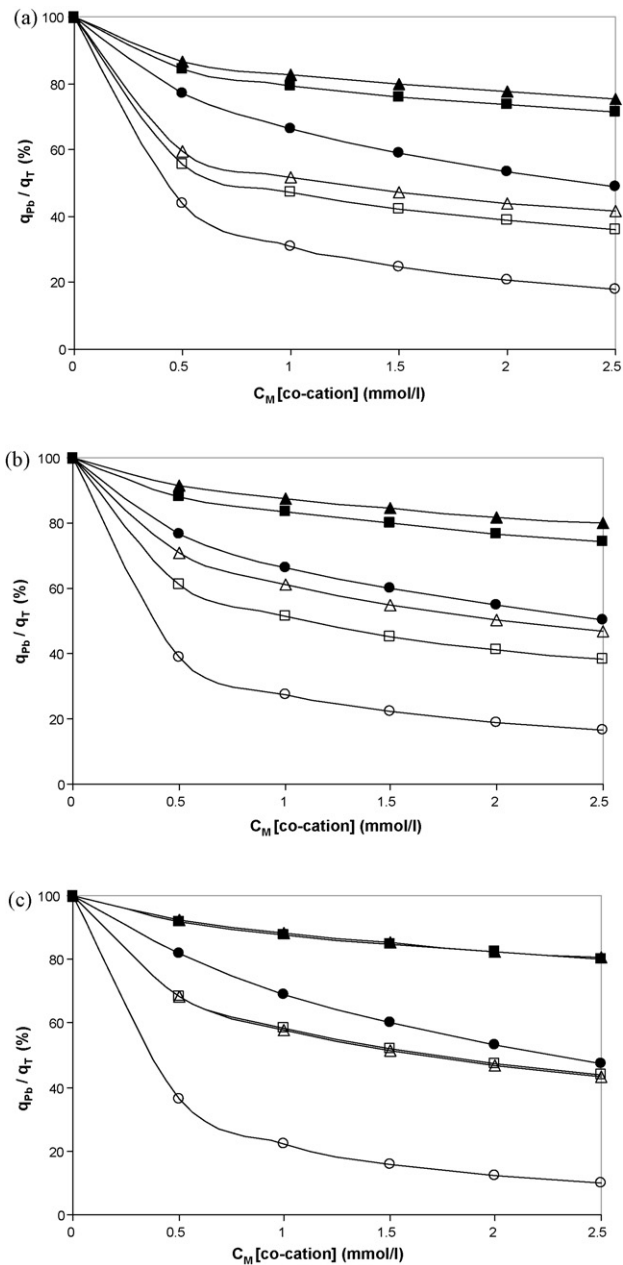


Fig. 5. Effects of the co-cation (M_2) on the uptake of the primary metal (M_1). Curves: (Δ) $C_{M1} = 0.1$ mmol l⁻¹, M_2 : Zn; (\blacktriangle) $C_{M1} = 1.0$ mmol l⁻¹, M_2 : Zn; (\square) $C_{M1} = 0.1$ mmol l⁻¹, M_2 : Cd; (\blacksquare) $C_{M1} = 1.0$ mmol l⁻¹, M_2 : Cd; (\circ) $C_{M1} = 0.1$ mmol l⁻¹, M_2 : Cu; (\bullet) $C_{M1} = 1.0$ mmol l⁻¹, M_2 : Cu. (a) *Algae Gelidium*, (b) algal waste and (c) composite material.

The biosorbents exhibited a net preference for Pb over Zn, in such a manner that increasing the concentration of Zn, the uptake of Pb remains approximately constant for each C_{Pb} . On the other hand, it can be verified that increasing C_{Pb} , the uptake capacity of Zn rapidly decreases to small values.

However, when comparing the systems Pb/Cu and Pb/Zn, the binding of Pb is more influenced by Cu than by Zn, suggesting that the competition between Cu and Pb is stronger than between Pb and Zn. These results are in agreement with the pK'_M values: $Pb > Cu > Zn$.

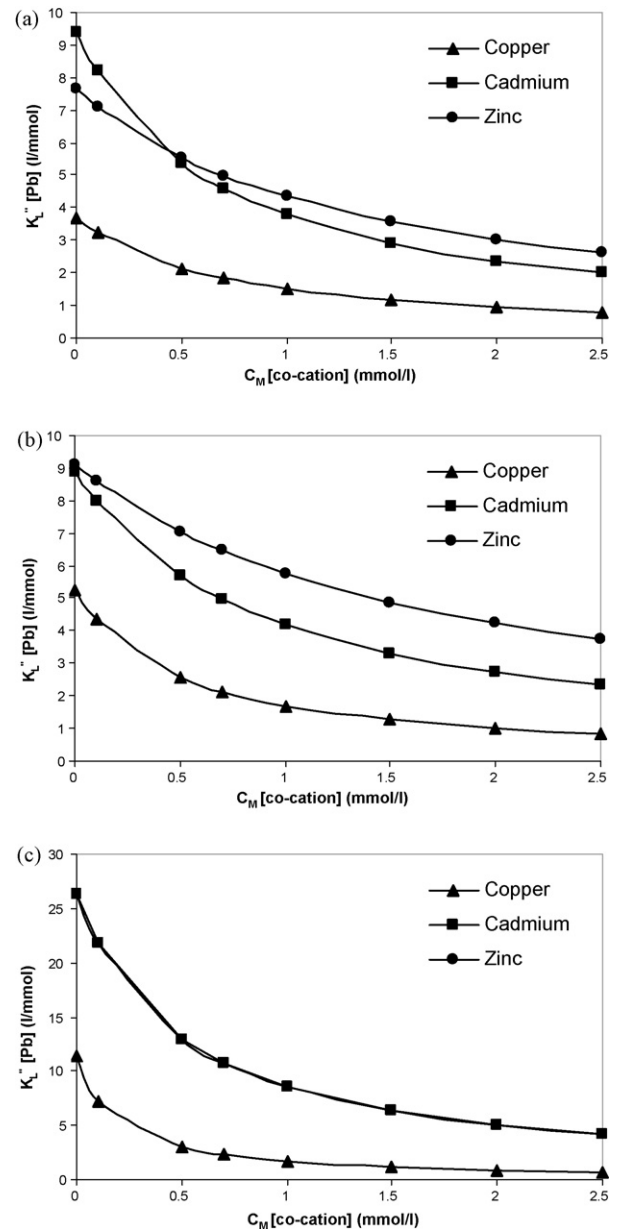


Fig. 6. Effects of co-cation concentration on the Langmuir K_L value (Eq. (6)) for the primary metal (Pb). (a) *Algae Gelidium*, (b) algal waste and (c) composite material.

4.2.3. Pb(II)/Cd(II)

As indicated by Fig. 4(a–c), Pb or Cd inhibits the uptake capacity of the other metal. The presence of Pb contributes to the increase of the total metal ion binding, by competing more effectively for sites occupied by protons or by occupying additional free sites. For high concentrations, the total uptake capacity remains almost constant, but Cd uptake is strongly dependent on the Pb growing concentration in solution.

The interference of Cd and Zn on Pb biosorption is similar, resulting in the following sequence of affinities to the binding sites: $Pb > Cu > Cd \approx Zn$. This sequence is in agreement with the values of the affinity constants of the metal ions to the binding sites.

4.3. Effect of the co-cation on the biosorption capacity and Langmuir constant

Values of “low” (0.1 mmol l^{-1} Pb or 0.5 mmol l^{-1} Cu, Cd and Zn) and “high” (1.0 mmol l^{-1} Pb or 2.5 mmol l^{-1} Cu, Cd and Zn) concentrations were arbitrarily chosen to evaluate the metal preference by the biosorbents.

Fig. 5 shows that, for “high” and “low” equilibrium concentrations, Pb uptake decreases in a similar way, in the presence of Cd and Zn ions, for the three biosorbents. This means that the competition between Cd and Pb ions is approximately the same as between Zn and Pb. Comparing the inhibition of Cd, Zn and Cu on Pb binding, we verify that Cu presents a higher influence, decreasing the uptake capacity of Pb by more than 50% for $C_{\text{Cu}} = 0.5 \text{ mmol l}^{-1}$. The values of K_L for lead present approximately the same trend in the presence of Cd and Zn (Figs. 6(a–c)). For $C_{\text{Cu}} = 0.5 \text{ mmol l}^{-1}$, K_L , decreases from 3.7, 5.3 and 11.3 to 2.1, 2.6 and 3.0, respectively for algae, algal waste and composite material. Different values of K_L for each biosorbent when the co-cation concentration is zero are observed in Fig. 6, principally for composite material, because the model regression was performed for each two-metal system individually and for composite material was obtained the poor less regression.

5. Conclusions

The marine algae *Gelidium*, an algal waste and an algal-derived composite material as the ability to remove Cu(II), Cd(II), Zn(II) and Pb(II) from two-metal solutions. Discrete and continuous models fitted well the experimental data from two-metal and one-metal biosorption systems. However, the continuous heterogeneous equilibrium model gives better predictions of the metal uptake by the biosorbent.

Lead ions revealed higher affinity to the carboxylic groups in the biosorbent surface, than copper, cadmium and zinc ions. The presence of co-cations decreases the Pb(II) uptake, due to the competition for the same binding sites. The presence of cadmium and zinc leads to a similar decreasing effect in the Pb(II) binding capacity. The strongest competition was found between copper and lead ions.

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