Heavy metal sorption by calcium alginate beads from *Laminaria digitata*

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Abstract

Alginate with a high M/G ratio, extracted from *Laminaria digitata*, was evaluated for Cu^{2+}, Cd^{2+} and Pb^{2+} sorption in acidic solutions, in the form of calcium cross-linked beads. The high M/G ratio of alginate extracted from this algal species is most likely the determining factor for the increased adsorption capacity of the investigated metals, indicating that the mannuronic acid is responsible for the ion exchange mechanism. The data obtained from the batch experiments have been interpreted with Langmuir, Freundlich and Sips models. The Sips equation provided the best fit with the experimental results, indicating sorption sites heterogeneity for the material. The pH was found to have a significant effect on the process, with sorption capacity reaching a maximum at pH 4.5, indicating a competition mechanism between H^+ and metal ions.

Kinetic experiments were performed at the optimum pH. For the interpretation of the kinetic experiments the Linear Adsorption Model was employed and diffusion coefficients were determined. The model fits the experimental data at higher concentrations, where the adsorbed quantity remains almost constant. Finally, a simplified expression of the batch kinetic adsorption model was employed. The model, predicts adequately, not only the diffusivity values, but also the concentration profiles inside the spherical particles.

1. Introduction

Heavy metal solutions are widely used in industrial activities such as metal finishing, electroplating, painting, dying, photography, surface treatment, printed circuit board manufacture, etc. Most of the heavy metal ions are well-known toxic and carcinogenic agents, while metal residues in the environment pose a threat not only for human health, but also have serious detrimental effects for the aquatic ecosystem [1]. The presence of heavy metals in the aquatic environment has forced international environmental agencies to introduce strict regulations with regard to metal discharge, especially from industrial activities.

Various methods have been suggested and applied for the removal of toxic metals from aqueous solution, such as chemical precipitation, evaporation, ion-exchange, adsorption, cementation, electrolysis and reverse osmosis. Due to the specific nature of industrial effluents (low pH, variety of cations and anions, oil emulsions, particles, etc.) the effective removal of metal ions has proven to be a very difficult and costly process [2]. Although adsorption is the most effective and widely used method [3], commercial chelating resins, one of the mostly utilized sorbents, are still an expensive material and most are non-biodegradable. Hence, research is focused on the preparation of novel, cheap and more effective sorbents. A very promising material, that offers such advantages, is alginate, a natural anionic polymer.

Alginate is a linear copolymer of a-L-guluronate (G) and a-D-mannuronate (M), which constitutes 10–40% of the dry weight of all species of brown algae [4]. Depending on the algal species used for the extraction of alginic acid its molecular weight as well as its M/G ratio presents great variations. The capability of this copolymer to form stable biodegradable gels in the presence of divalent cations has been known and studied extensively since the seventies [5,6]. These gelation properties can be attributed to the simultaneous binding of the divalent cations such as Ca^{2+} to different chains of a-L-guluronate blocks (G-blocks) [7]. As a result of their configuration, these chains form electronegative

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cavities, capable of holding the cations via ionic interactions, resulting in cross-linking of the chains into a structure resembling an "egg box" [5].

Due to its ability to form stable structures, cross-linked alginate has been used for the immobilization of biological material for various purposes, including the immobilisation of material with metal binding properties, such as algae, for the removal of heavy metal from wastewater [8–12]. However, although the predominant role of alginate present in algae on the uptake of heavy metals has already been demonstrated (alginate contains carboxyl groups capable of binding with heavy metal cations) very few studies have been conducted on the potential use of alginate itself as a sorbent for heavy metal removal from aqueous solutions [13–18].

The aim of this work is to study the heavy metal sorption capacity of alginate extracted from *Laminaria digitata*, in the form of calcium beads prepared via the dripping technique. Morphological characteristics and behaviour of the beads in aqueous solution are also discussed. The uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from dilute solutions was studied using batch experiments. The influence of pH on the uptake was reported, and a study on sorption kinetics is also presented. Additionally, diffusion coefficients and metal concentration profiles were determined using different batch kinetic models.

2. Materials and methods

2.1. Reagents and instrumentation

All reagents were of analytical grade and were used without further purification. Sodium alginate was supplied by CEVA France and extracted from *L. digitata*. Stock and test solutions were prepared using $CuSO_4 \cdot 5H_2O$, $3CdSO_4 \cdot 8H_2O$ and $Pb(NO_3)_2$ for metal sorption experiments.

All experiments were performed in a Julabo SW22 shaking bath and metal concentrations were determined by Flame Atomic Absorption Spectrometry (FAAS) (GBC Avanta Σ).

2.2. Alginate extraction and characterisation

L. digitata was collected from coastal areas around France and sodium alginate was extracted by lixiviation with HCl according to the method described by McHugh [19], 1987. The M/G ratio of the sodium alginate obtained was 1.5–1.7 (60–63% mannuronate).

2.3. Alginate beads preparation

Solutions of 2% w/v of sodium alginate were prepared by mixing the fine sodium alginate powder with distilled water while stirring. 0.1 L of the alginate solution was added dropwise into 0.5 L of 50 mmol L^{-1} CaCl$_2$ solution under gentle stirring at 25 °C. Ca-alginate gel spheres were formed upon contact with the cross-linker solution and were left overnight to stabilise. The excess of cross-linker solution was removed by filtration and washing several times with distilled water. Finally, the beads were left to dry at room temperature.

2.4. Metal binding batch experiments

The metal salts were dissolved in distilled water and stock solutions of different concentrations of single metal solutions were prepared. Samples of ≈0.1 g alginate beads were contacted with 100 mL of metal solution in 200-mL Erlenmeyer flasks under shaking at 190 rpm, at 25 °C. Known amounts of 0.5 M HNO$_3$ were added till the pH measured on a Metrohm 744 pH meter was stabilised at the desired value (2.5, 3.5 or 4.5). The samples were then left shaking overnight for complete equilibration and the metal content of the final solution was determined. The initial metal concentrations ranged from 5 to 500 ppm.

2.5. Sorption kinetics experiments

Stock metal solution was prepared and the pH was adjusted to 4.5 by addition of a known quantity of 0.5 M HNO$_3$. Samples of ≈0.1 g alginate beads were contacted as described above for different contact times. The beads were then removed from the solution by filtering and metal concentrations were determined.

3. Results and discussion

3.1. Alginate beads characterisation

The beads prepared by the dripping method were examined and tested in terms of size, surface structure, porosity, density, water regain and water loss. Density and porosity were determined by means of a mercury porosimeter (Quantachrome Autoscan 60). The pressure was varied from 0 to 50,000 psi at scanning mode. The values for surface tension and density of mercury were obtained form literature [20]. Their density was found to be 1.8–1.9 g mL^{-1}, while the porosity analysis showed no pores for the material. A small and broad peak at about 70 μm was observed (about 1/5 of the particle radius) which can be attributed either to interparticle space or to surface roughness. The particle size distribution, determined by means of a sieving system, ranged from 0.4 to 0.8 mm exhibiting a maximum value at 0.7 mm. The surface of the beads was examined using SEM (Fig. 1). Weight measurements after drying show that the wet beads contain of 95.58% w/w water. When left in H$_2$O to swell the beads regained 2.34% w/w of water.

3.2. Batch metal uptake experiments

3.2.1. Experimental results

The sorption isotherms for the metals examined in this work are shown in Fig. 2. There are pronounced differences between sorption capacities of the alginate beads with respect to the different metals examined, following the order: $Pb^{2+} > Cu^{2+} > Cd^{2+}$. This behaviour has also been reported by other authors [21,22]. Haug [21] 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 $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+} > Mg^{2+}$. The preferential binding of larger ions can be attributed to stereochemical effects such as
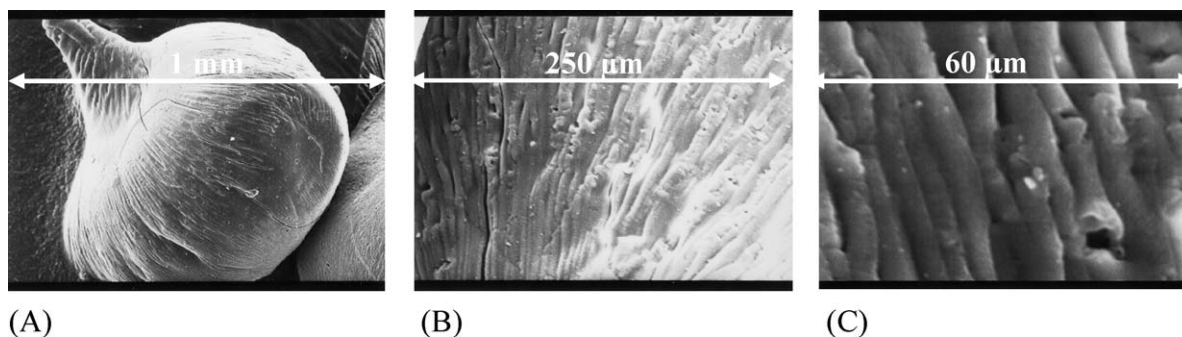
Fig. 1. SEM photographs of dry Ca-alginate beads. A: 1 mm, B: 250 μm, C: 60 μm.

the coordination of the oxygen atoms surrounding the metal ion.

As depicted in Fig. 2, the adsorption capacity with respect to Pb^{2+} is 1.79 mmol g^{-1} (372.38 mg g^{-1}) while for Cu^{2+} and Cd^{2+} it reaches a value of 1.38 mmol g^{-1} (87.39 mg g^{-1}) and 1.16 mmol g^{-1} (129.95 mg g^{-1}), respectively. The alginate beads metal adsorption capacity is significantly higher than that of commercially available sorbents, such as activated carbons, bentonite, etc. with maximum uptake capacity ranging between 0.05 and 0.15 mmol$_{metal}$ g^{-1} Additionally, the values obtained in this study are higher than the corresponding uptake reported for alginate beads in previous studies: 75–80 mg g^{-1} for Cu^{2+}, 230 mg g^{-1} for Pb^{2+} and 40 mg g^{-1} for Cd^{2+} [18,23,24].

The pH of the initial solution was found to have a significant effect on the sorption capacity of the alginate beads. It is known that the carboxyl group tends to be ionised at pH values over 4. As pH reaches lower values, the competition between H^+ and M^{2+} species in the solution, results in decreased metal uptake [25]. However, as metal affinity increases, the effect of pH on the uptake capacity gets less significant as can be seen in Fig. 2. For the metals under study, the optimum pH for adsorption was found to be 4.5.

3.2.2. Sorption isotherm equations

Several sorption equilibrium models are available for sorption data analysis. In this work, three isotherm models, namely, the Langmuir, the Freundlich and Sips (also known as Langmuir–Freundlich model), were employed to study the adsorption process. In all cases, the Levenberg-Marquardt method was used in order to determine the fitting parameters (Table 1).

The Langmuir isotherm is described by the following equation:

$$Q = \frac{q_m bC}{1 + bC} \qquad (1)$$

where b and q_m, are related to the affinity and maximum sorption, respectively. The model, assumes a monolayer adsorption process on a homogeneous surface and would be most applicable in cases where all binding sites exhibit uniform behaviour towards the sorbate. The Ca-alginate, however, contains two different types of binding sites, which are related to different configurations of the polymeric chains. The G-block carboxyl groups participating in the egg box structure are less readily available to the metal ions, while the M-block carboxyl groups can easily interact with the sorbate [26]. Additionally, interactions of metal ions with the hydroxylic oxygens present [22] may also introduce heterogeneity onto the surface, in violation of the basic assumption of the Langmuir isotherm.

Unlike the Langmuir, the Freundlich model is usually applied in a strictly empirical sense, it can be of theoretical interest in terms of adsorption onto an energetically heterogeneous surface [27,28]. According to the Freundlich model the adsorbed mass per mass of adsorbent can be expressed by a power law function of the solute concentration as follows:

$$Q = kC^{1/n} \qquad (2)$$

where k can be related to the amount sorbed and n can be considered as a measure of sorption intensity.

Both models are widely used for the interpretation of adsorption data, however none of them in their simple form include the effect of pH, thus they cannot predict changes in proton binding [29]. Taking the abovementioned into account, the simple sorp-

Table 1
Parameter data for Cu^{2+}, Cd^{2+} and Pb^{2+} sorption isotherm equations (pH 4.5)

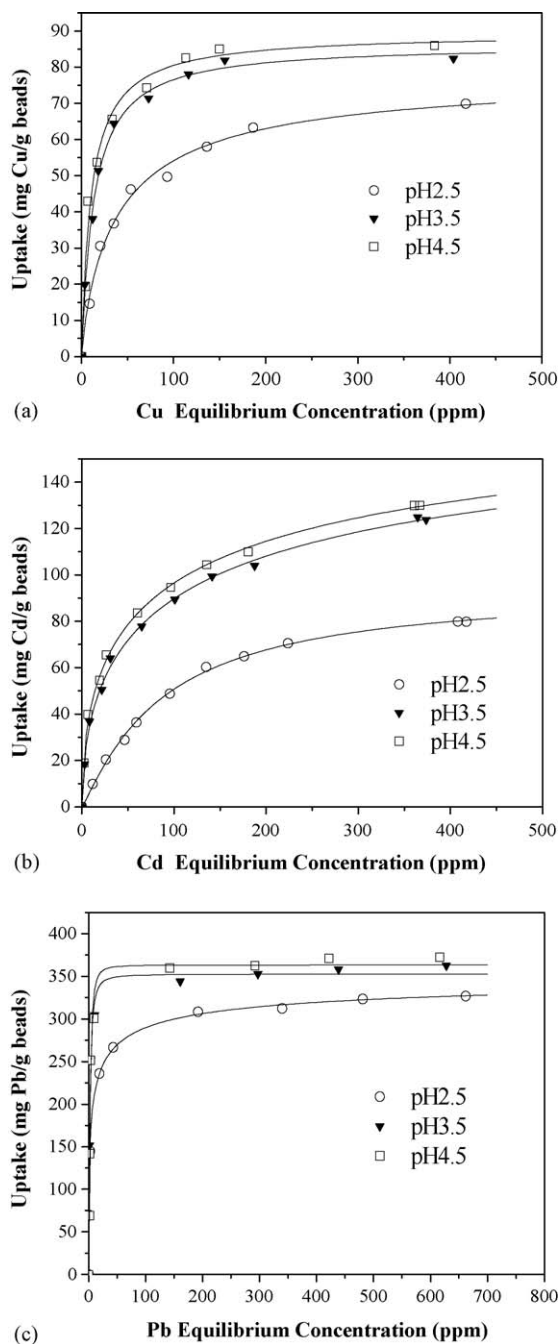|	Langmuir	Freundlich	Sips
Cd^{2+}	$q_m = 130.77$, $b = 0.038$, $R^2 = 0.96$	$k = 23.72$, $n = 3.41$, $R^2 = 0.98$	$q_m = 198.43$, $b = 0.009$, $n = 1.90$, $R^2 = 0.99$
Cu^{2+}	$q_m = 88.95$, $b = 0.096$, $R^2 = 0.96$	$k = 28.40$, $n = 4.80$, $R^2 = 0.83$	$q_m = 89.56$, $b = 0.094$, $n = 1.03$, $R^2 = 0.96$
Pb^{2+}	$q_m = 374.67$, $b = 0.328$, $R^2 = 0.92$	$k = 162.37$, $n = 7.10$, $R^2 = 0.74$	$q_m = 373.67$, $b = 0.331$, $n = 1.00$, $R^2 = 0.92$

Fig. 2. Sorption isotherms and sips simulation curves for (a) Cu^{2+}, (b) Cd^{2+} and (c) Pb^{2+} at pH 2.5, 3.5 and 4.5.

tion models will be in good agreement with the experimental data only in cases where proton binding plays a less important role in the equilibrium.

Alternatively, the Sips isotherm model (Eq. (3)) can be considered as a combination of Langmuir and Freundlich equations

$$Q = \frac{q_m(bC)^{1/n}}{1 + (bC)^{1/n}} \qquad (3)$$

where q_m is the total number of binding sites, b the median association constant and $1/n$ is the heterogeneity factor. Values for $1/n \ll 1$ indicate heterogeneous adsorbents, while values closer

to or even 1.0 indicate a material with relatively homogenous binding sites. In this case the, the Sips model is reduced to the Langmuir equation.

In this work, the Freundlich model proves to be incapable to describe the sorption process for all metals studied. In contrast, Langmuir model exhibits excellent fit for both Cu^{2+} and Pb^{2+}. This implies that, for these metals, the ion exchange reaction with the available binding sites is almost quantitative, therefore cation exchange with protons can be considered insignificant. The deviations observed between Cd^{2+} adsorption isotherm and Langmuir simulation data can be attributed to the increased competition between the metal ion and the Ca^{2+} and/or H^+ cations. Moreover, b parameter values (affinity index) in the Langmuir simulation agree with the experimental results following the order $b_{Pb} > b_{Cu} > b_{Cd}$, while b_{Pb} and b_{Cd} values having a difference of almost an order of magnitude.

On the other hand, the Sips model provides the best fit with the experimental results, for all metals studied in this work. The calculated values for b parameter follow the same order as in the Langmuir simulation, while the obtained heterogeneity index $(1/n)$ ranges between 0.5 for Cd^{2+} (increased heterogeneity) and about 1.0 for Cu^{2+} and Pb^{2+} (almost homogeneous sorbent). Thus, for the last case, the Sips equation is reduced to the Langmuir model, indicating the preferential binding of metals on all sites of sorbent, which act as a homogenous surface.

In addition, a relation between heterogeneity and affinity factors is expected. It can be assumed that in the case of Cd^{2+} (in which the affinity is small) the metal ions can "distinguish" the different kinds of binding sites (M-block carboxyl, G-block carboxyls and hydroxyls) having different adsorption enthalpy. On the other hand as the affinity increases (Cu^{2+} and Pb^{2+}), the metal ions are easily adsorbed on all the sites available on the beads. The obtained results of binding strength are in agreement with the data reported by other authors [30].

The variations in metal affinity–binding strength can be interpreted using the classification of metal ions according to Nieboer and Richardson [30] who suggested that metal ions are separated into three categories: *class A* (oxygen-seeking), *class B* (nitrogen/sulphur-seeking) and *borderline* (or intermediate) metal ions.

In the proposed system, metal interactions with ligands are determined by three parameters: metal ion charge z, radius r, and electronegativity X_m. The values of the abovementioned factors, obtained from the literature, are: 2, 138 (pm units) and 1.90 (Pauling scale) for Cu^{2+} respectively, 2, 148 and 1.68 for Cd^{2+} and for Pb^{2+} 2, 147 and 2.33 respectively. These parameters are used to calculate of z^2/r and $X_m^2 r$ (for Cu^{2+} 0.0290 and 498, respectively, for Cd^{2+} 0.0270 and 422, respectively, and for Pb^{2+} 0.0272 and 798, respectively). The factor z^2/r can be considered as an indicator of the ion charge density and it is related to electrostatic bonding strength, while $X_m^2 r$ represents the valence orbital energy and it is a measure of the strength of covalent bonding relative to ionic bonding.

It can be easily deduced that while the value of the ion charge density is similar for all metals, the strength of covalent bonding follows the sequence $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The obtained results from adsorption isotherms are in agreement with the

hard-soft-acid-base theory [31], in which the hardness of an acid is associated with increased proton binding. According to this theory, "hard" acids prefer to bind with "hard" bases while "soft" acids with "soft" bases and Pb^{2+} and Cu^{2+} are referred as intermediate acids (borderline section) whereas Cd^{2+} as "soft" acid. Consequently, the increased metal affinity–binding factor of Pb^{2+} and Cu^{2+} in relation with Cd^{2+} ions can be attributed to their preference for binding with the "hard" carboxyl base.

The mechanism of divalent metal sorption on alginate beads is dominated by ion exchange involving mainly the carboxyl groups present in the alginate molecule, with hydroxyl groups playing a secondary role. Due to the differences in conformation of polyguluronic and polymannuronic blocks, all carboxyl groups are not readily available, resulting in differences in the sorption capacity, with respect to different metals. Metals with low bonding strength (e.g.Cd^{2+}) are mainly bound by polymannuronic chain carboxyls and are greatly influenced by changes in pH, while metals with higher bonding strength such as Pb^{2+}, show greater affinity, they are not affected by cation exchange with protons in the solution and are adsorbed homogenously by all available carboxyl groups both in polyguluronate and polymannuronate bocks.

Based on the findings presented, the *L. digitata* Ca-alginate beads show excellent performance in heavy metal sorption. The materials' metal sorption capacity is comparable to and in many cases higher than other types of sorbents [18,23,24,32] proving it to be a promising material for the treatment of wastewater, containing heavy metals. To use a material in a specific environmental application, apart from the sorption capacity, several other parameters, such as sorption/desorption rate, particle stability, etc., must be determined, in order to define the most advantageous design and the optimal operating conditions for the intended process (e.g. column dimensions, flow rate, regeneration time and flow, etc.). Therefore the kinetics of adsorption was also studied, and the effective diffusion coefficients were resolved.

3.3. Kinetics experiments

3.3.1. Experimental results

The results obtained from the kinetic studies on Cu^{2+}, Cd^{2+} and Pb^{2+} sorption by Ca-alginate beads are shown in Fig. 3. It can be seen that, in all cases, the adsorbed quantity increases rapidly at the beginning of the experiment, reaching a limiting value at longer exposure times.

The rate of metal uptake is influenced by factors affecting mass transfer from the bulk solution to the binding sites. Thus a kinetic experiment can be considered as a combination of different processes-steps. These include bulk transport of metal ions in the solution phase, film transport through a hydrodynamic boundary layer around the sorbent surface, diffusion of the sorbate inside the particles, etc. The equilibrium time of a certain sorbent–sorbate system depends mainly on temperature, diffusion coefficient and particle size of the sorbent.

In the present study, experimental conditions allow good mixing of solutes and sorbents in the system so the kinetic limitations due to bulk transport and film resistance are assumed to be neg-
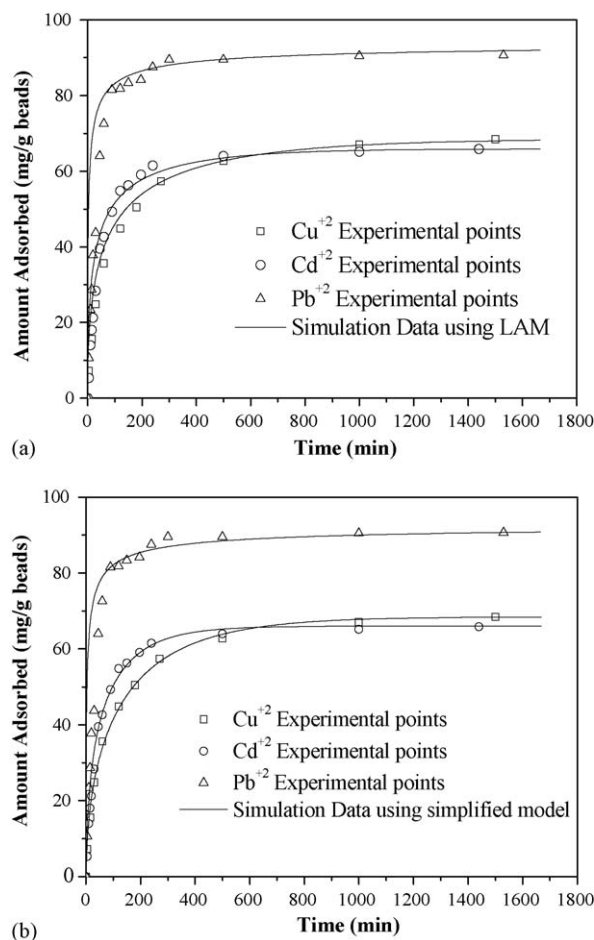

Fig. 3. (a) Kinetics data and simulation using LAM and (b) kinetics simulation using the proposed model—initial metal concentration $100\,\mathrm{mg\,L^{-1}}$.

ligible. Therefore, the kinetics of the process is governed only by the diffusion of metal ions towards the interior of particle sorbents.

3.3.2. Batch kinetic model

For the quantitative description of the biosorption process dynamics, a mathematical model is introduced making the following assumptions [33]:

1. The particle-to-liquid mass transfer resistance has been eliminated by stirring.
2. The intraparticle diffusion inside the alginate beads is one-dimensional and the shape of the beads spherical.

Based on these assumptions, the mass conservation equation for metal ions, (assuming constant diffusivity), is the following [34]:

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho \frac{\partial q}{\partial t} = D_{\mathrm{eff}} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \right) \qquad (4)$$

where q is the amount adsorbed (mmol M/g alginate), r the radial distance, D_{eff} the effective intraparticle diffusion coefficient, ε_p the porosity, c is the metal concentration inside the

particle (mmol M/cm^3 of free volume) and ρ is the density of the particles.

For a step change in solution concentration at time zero, the initial and boundary conditions are

$$t = 0, \qquad c = 0 \text{ for } 0 \le r \le r_c, \quad C = C_0 \text{ for the bulk phase} \tag{5}$$

$$t \ge 0, \qquad r = r_c, \qquad c_r = C \tag{6}$$

$$\left(\frac{\partial c}{\partial t}\right)_{r=0} = 0 \text{ for all } t \tag{7}$$

$$-V_f \frac{\partial C}{\partial t} = \frac{3V_s}{r_c}\left(\frac{\partial c}{\partial r}\right)_{r_c} D_{\text{eff}} \tag{8}$$

where C represents the bulk fluid metal concentration (mmol L^{-1}), C_0 the initial values of C at zero time, V_f the volume of bulk solution, V_s the volume of the beads and r_c is the particle radius.

3.3.3. Linear adsorption model (LAM)

From the adsorption kinetics experiments, the effective diffusion coefficient can be determined using the Linear Adsorption Model (LAM) with sorption taking place in a well-stirred solution of initial concentration C_0 and finite volume V. The model also presumes that the diffusion of solute inside the particle is the limiting step of the sorption process, while the film resistance on the surface of the particle is negligible.

Therefore the equation describing the system is

$$q = KC \tag{9}$$

And Eq. (8) is transformed to

$$\frac{\partial c}{\partial t} = \frac{D_{\text{eff}}}{\varepsilon_p + \rho K}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)\right) \tag{10}$$

Supposing that the particle radius is r_c, the volume of the solution is V and the concentration of solute in the solution is uniform and initially C_0, the total amount of solute m_t in the sphere after time t is expressed as a fraction of the corresponding quantity after infinite time by the relation (analytical expression):

$$\frac{m_t}{m_0} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp(-D_{\text{eff}}q_n^2 t/r_c)}{9 + 9\alpha + q_n^2\alpha^2} \tag{11}$$

where q_n are given by the roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n} \tag{12}$$

And α and K are given by

$$\alpha = \frac{C_\infty}{C_0 - C_\infty} \quad \text{and} \quad K = \frac{V_1}{V_s\alpha} - 1 \tag{13}$$

The effective diffusion coefficients (Table 2) were calculated using a least squares method (Fig. 3). The D_{eff} values obtained in this work are of the same order of magnitude of those obtained by other authors that used LAM [35,36] to evaluate diffusion coefficients of metal ions sorption on calcium alginate beads.

It must be noted, that the Linear Adsorption Model, while for the cases of Cu^{2+} and Cd^{2+} kinetic data shows rather good regression, it fails to do so in the case of Pb^{2+}. This can be attributed to the fact that the Pb^{2+} isotherm cannot be expressed by linear adsorption, in contrast with the isotherms for Cu^{2+} and Cd^{2+} at the corresponding experimental conditions. In general, the Linear Adsorption Model fails to predict the exact kinetic behaviour of a system when it follows the Langmuir isotherm, especially at low concentrations, where the slope of the isotherm increases dramatically. Nevertheless, due to its simplicity, the LAM has been widely used as a rough approximation for the calculation of diffusion coefficients in such systems as it provides an analytical expression.

3.3.4. Simplified batch kinetic model

Eq. (4) refers to a general batch kinetic model, where the change in bulk metal concentration is attributed to both adsorption inside the particles and accumulation in the free volume of the particles (pores), as both phases-liquid and adsorbed-exist into the material. However, for the interpretation of the data, a simple model for non-porous solids was employed, based on the porosity measurements for the particles studied. Assuming also that the mass resistance is negligible due to proper stirring, the equation describing the adsorption on non-porous spherical adsorbents is the following:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{\text{eff}}^M \frac{\partial q}{\partial r}\right) \tag{14}$$

The initial and boundary conditions for the proposed model assuming a Langmuir-type adsorption isotherm are as follows:

$$t = 0, \qquad C = C_0, \qquad r = r_c, \qquad q_0 = \frac{q_s b C_0}{1 + b C_0} \tag{15}$$

Table 2
Diffusion coefficients calculated using linear adsorption model and the proposed simplified model for the different metal ions

| | K_c (g/g) | $\bar{K}_c$ (g/g) | LAM | Proposed model | | |
| | | | D_{eff} (cm^2/s) | D_{eff}^M (cm^2/s) | D_{eff} (cm^2/s) | |
					Using K_c	Using $\bar{K}_c$
Cu^{2+}	3914	2431	1.42×10^{-5}	7.8×10^{-9}	3.0×10^{-5}	1.9×10^{-5}
Cd^{2+}	4936	3112	1.90×10^{-5}	9.2×10^{-9}	4.5×10^{-5}	2.8×10^{-5}
Pb^{2+}	118535	24262	2.35×10^{-5}	0.7×10^{-9}	8.3×10^{-5}	1.7×10^{-5}

$$t \leq 0, \quad 0 \leq r < r_c \quad q(r,t) = 0 \tag{16}$$

$$\text{For all } t, \quad \left(\frac{\partial q}{\partial t}\right)_{r=0} = 0 \tag{17}$$

$$t \geq 0, \quad C = f(t), \quad q(r_c, t) = q(t) = \frac{q_s b C(t)}{1 + b C(t)} \tag{18}$$

As adsorption proceeds, the concentration of the bulk solution decreases exponentially to a limiting value. The partial differential equation describing the diffusion in non-porous spherical particles is solved by the implicit finite difference method [37] using the MATLAB software package. To test the applicability of the mathematical model, the simulation data are regressed, using least square fitting, with the experimental data obtained from kinetic experiments – adsorbed quantity at certain time and remaining solution concentration – and is shown in Fig. 3. Additionally, the model is capable of predicting the concentration profiles inside the spherical beads in relation to equilibration time (Fig. 4). The predicted curves are in agreement with the results presented in other studies [38].

The proposed model, assumes there is always Langmuir type equilibrium between the bulk solution and the amount of adsorbent on a thin layer of the bead surface. The sorption inside the spherical bead is determined only by the effective diffusivity of the metals while in the center of the particle the gradient is zero.
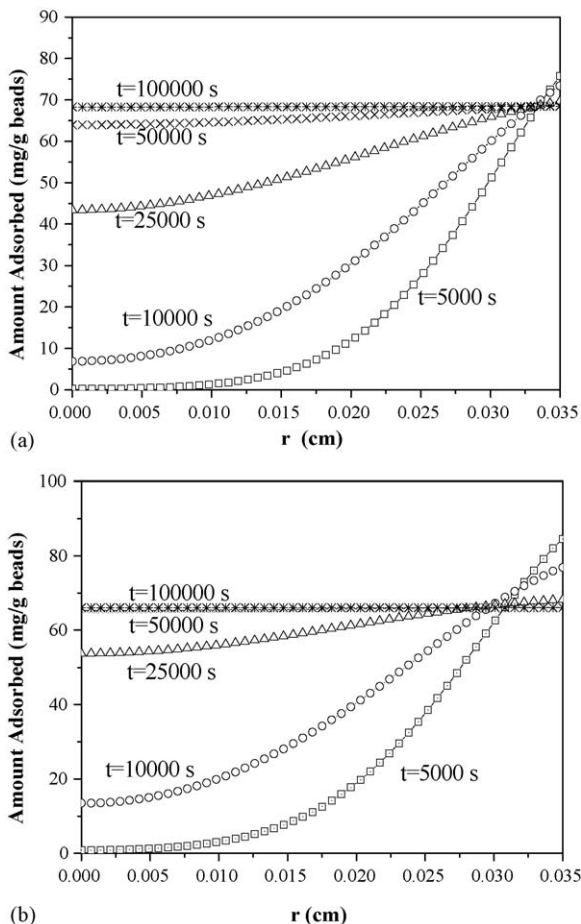

(a)

(b)

Fig. 4. Concentration profiles inside the beads obtained from the simplified model for (a) copper and (b) cadmium.

The proposed model fits the experimental data better than the LAM for the whole range of concentrations. The small deviations observed in the case of Pb^{2+}, can be attributed to the fact that due to its high adsorption capacity, there is a significant reduction in the remaining bulk solution concentration. This, leads to an error in the calculation of the adsorbed quantity of the first thin layer of the beads surface and consequently causes the deviations between simulation and experimental results.

In order to test the validity of the proposed simplified model was tested for the prediction of the kinetic behaviour, assuming linear adsorption through the equation: $q = K_c C$. In this case the diffusion coefficient obtained, D_{eff}^M, are related to the effective diffusivity (D_{eff}) derived by the LAM, with the expression:

$$D_{eff}^M = \frac{D_{eff}}{1 + K_c} \tag{19}$$

where K_c is the linear equilibrium adsorption constant (mass metal ion/volume of beads)/(mass metal ions/volume of bulk solution). It must be noted that in a Langmuir isotherm, the K_c parameter is different at every point of the sorption process. Therefore, during a kinetic experiment, the adsorption constant changes as the bulk metal solution decreases leading to an error in the estimated diffusivity values. In our opinion it is better to use the mean value of the constant, $\bar{K}_c$ as given be the equation in the case of a Langmuir isotherm:

$$\bar{K}_c = \frac{q_s}{C_{fin} - C_{init}} \ln \frac{1 + b C_{fin}}{1 + b C_{init}} \tag{20}$$

The simulation data obtained are in agreement with the results derived from the LAM (Table 2).

In general the simplified model for non-porous spheres, in contrast to the LAM, mathematically fits the experimental results for the whole concentration range. The kinetics model we propose can be used either for non-porous adsorbents or in cases where the mass transfer is determined by the diffusivity e.g. "intra-crystalline" or intra-particle diffusion, where both the film resistance and the macro-pore diffusion are negligible. Furthermore it can be extended to other similar systems, providing a useful tool for determining parameters such as the diffusion coefficient, needed for the incorporation of the material in a packed bed column. Additional studies on equilibrium (multicomponent sorption) and dynamic properties (effect of concentration on diffusivities, flow through experiments) are currently under way.

4. Conclusions

Equilibrium sorption experiments showed that the sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by alginate beads from *L. digitata* were greater than commercial alginate beads and other sorbents. The increased sorption capacity was attributed in the higher M/G ratio of the alginate under study. The maximum adsorption capacities follow the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The results, which are in agreement with previous studies, were interpreted using the hard-soft-acid-base theory. The sorption isotherm equations were best described with the Sips model equation suggesting surface heterogeneity of the material espe-

cially for metals with lower affinity for the sorbent. There is a competitive mechanism between H^+ and metal ions that results in increased sorption with increasing pH. Metals with increased affinity for the material such as Pb^{2+} are less affected by the changes in pH suggesting a competition mechanism between the metal ions in multimetal solutions. A simplified kinetic model was applied for the interpretation of the adsorption kinetics which predicts not only the diffusivities but also the concentration profiles inside the spherical particles. A further study of the material will focus on its performance in a packed bed column and issues of metal species competition in multi metal solutions will also be addressed in later works.

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