Chemical equilibrium of ion exchange in the binary mixture Cu²⁺ and Ca²⁺ in calcium alginate

M. G. C. da Silva[1] · R. L. S. Canevesi[2] · R. A. Welter[1] · M. G. A. Vieira[1] · E. A. da Silva[2]

Abstract Biopolymer alginate is capable of triggering interchain interactions in the presence of divalent and trivalent cations. Calcium alginate particles obtained by the emulsification method have been used in ion-exchange packed bed tests to remove synthetic copper effluents. Adsorption equilibrium data were obtained from single and binary component systems, which were subsequently subject to mathematical modeling. In the case of the modeling system with binary components, where the calcium was considered as a second ion, there was no significant improvement for the models analyzed, in counterpoise to the isotherm models applied to the single component system. The ideal law of mass action and the law of mass action which presupposed that both phases were non-ideal showed similar results. This process was found to be effective and feasible for industrial applications used in heavy metal removal processes.

List of symbols

a_i^α	Activity of the compound i in phase α
A	Debye Huckel constant
a_{Cu}	Freundlich constant considering the presence of copper in the binary mixture (L/meq)
a_{Cu-Ca}	Freundlich constant considering the copper and calcium binary mixture (L/meq)
b	Parameter associated with the bioadsorbent adsorption capacity (L/meq)
B	Number of empty sites
B_0	Total number of available sites
B_{ji}	Bromley parameter involving the cation i and the anion j
$B-Cu$	Active sites connected to copper ions
$B-Ca$	Active sites connected to calcium ions
$B-Cu-Ca$	Active sites connected to copper and calcium ions
C	Metal solution concentration in equilibrium state (meq/L)
$CEC_{available}$	Available cation exchange capacity (meq/g)
CEC_{Total}	Total cation exchange capacity (meq/g)
F_i	Sum of interaction parameters
F_{obj}	Objective function
I	Ionic length (molal)
K_{Cu}^{Ca}	Thermodynamic equilibrium constant of the ion exchange reaction between copper and calcium
K_d	Parameter associated with the free energy of biosorption (mg/L)
K_{Ca}	Langmuir model competition
K_{Ca-Cu}	Langmuir competition model
K_{Cu}	Langmuir competition model
K_{Cu-Ca}	Langmuir competition model
k_{Cu}	Langmuir power and Lang–Freundlich models
k_{Ca}	Langmuir power and Lang–Freundlich models
L	Bed height covered by ionic solution (eq. ad. and des.) (cm)
m_i	Molality of component i (molal)

✉ M. G. A. Vieira
melissagav@feq.unicamp.br

1 Department of Processes and Product Design, School of Chemical Engineering, University of Campinas, UNICAMP, Av. Albert Einstein, 500, Cidade Universitária "Zeferino Vaz", Campinas, SP 13083-852, Brazil

2 State University of West Paraná, Rua da Faculdade 645, Jardim La Salle, Toledo, PR 85903-000, Brazil

n	Parameter associated with the effect of the concentration of metal ions on the adsorption capacity
n_i	Freundlich constant of component i considering a binary mixture
q	Amount adsorbed (meq/g)
q_{max}	Maximum amount adsorbed (meq/g)
qi	Amount of component i adsorbed
r	Ratio between the amount of adsorbed and desorbed ions of alginate particles
t	Time (min)
V	Power flow system in porous bed (mL/min)
y_i	Fraction of component i in solid phase
Z	Bed height (equation of ratio between ad. and des.) (cm)
z_i	Ionic charge of component i
z_{ji}	Arithmetic average between cation i and anion j

Greek

α'_{11}	Parameter of Freundlich model for Copper ion
α'_{12}	Parameter of Freundlich model for Calcium ion
$\gamma_i^{(\alpha)}$	Coefficient of fugacity
γ_i^{α}	Activity coefficient of component i in phase α
θ	Parameter fitted for each model used according to the objective function F_{obj}, used
Λ_{ij}	Wilson parameter involving cation i and anion j

Superscripts

A	Solid phase—alginate
α	Phase
R	Solid phase—resin (alginate)
S	Aqueous phase—solution
$*$	Equilibrium

Subscripts

i	Cation
j	Anion
n	Number of components
m	Number referring to the total test concentration
f	Copper fraction at a given total concentration

1 Introduction

Heavy metals, as well as copper, are present in the effluents released by several industries, such as mining and electrotyping, among others. Before these effluents are discharged into the receiving bodies, they need to be reduced because of their high toxicity, in keeping with the increasingly stricter laws which provide for their disposal. To meet this need, several methods for the reduction of heavy metals of industrial effluents have been studied.

Among these methods, the adsorption and/or ion-exchange method has low operating costs, insomuch as it reduces the volume of chemical and/or biological sludges, not to mention the high detoxification efficiency of its much diluted effluents (Vieira et al. 2008; Volesky and Kratochvil 1998). The use of biopolymers, such as the alginic acid, has emerged as a viable option due to its satisfactory capacity of removing several metal species, besides allowing the regeneration of exchangers (Bertagnolli et al. 2014; Papageorgiou et al. 2008; Mutlu et al. 1997).

The alginic acid, found in brown algae and some bacteria, has high affinity for divalent and trivalent cations. The presence of such types of cations leads to the gelification of the polymer chains, which are typically formed from α-L-guluronic acid and β-D-mannuronic acid. The fractionation of each one of the acids present in the alginate polymer chains depends on several factors, such as the conditions under which the starting material was developed and the material from which it was extracted. The fractional variation of each of the alginic acids in the alginate directly influences the capacity of removing metals, Moreover, a great content of α-L-guluronic acids, which is connected to the trans conformation of its organic chain, increases the removal capacity, meanwhile great contents of β-D-mannuronic acids typically reduce the removal capacity due to the cis conformation it entails (Davis et al. 2003). The use of alginate with other materials, such as activated carbon, has also shown good results with respect to the removal of metals (Park et al. 2007).

The preparation of calcium alginate particles also interferes with their physical properties, such as the porosity, volume of water, sphericity and elasticity; and the particles obtained by the emulsification method have dense and homogeneous internal structure, in addition to small pores (Fundueanu et al. 1999; Poncelet et al. 1999). However, other methods may be employed, such as dripping (Díaz et al. 2007; Papageorgiou et al. 2006) and atomization (Tu et al. 2005).

The use of the alginate as an ion exchanger essentially depends on the distribution of the equilibrium between the phases. The representation of equilibrium data can be ascertained using ion-exchange isotherms, or even adsorption isotherms (Papageorgiou et al. 2006; Pieroni and Dranoff 1963; Lai et al. 2008).

The use of ion-exchange isotherms takes into account the concentration of different interfering ions in the mixture, i.e., it considers the effect of the counter ions originally present in the alginate structure. Such effect does not take place when the adsorption isotherms are used (Sag et al. 1998), in which only the adsorbed ions are considered for the modeling. (Lin and Juang 2005) used both concepts to treat the removal of heavy metals from aqueous solutions using resins Chelex 100 and Amberlite IRC 748 as

the ion exchangers. With regard to the adsorption, they applied the Langmuir model in the ion-exchange process, in keeping with the law of mass action. Both models showed responses considerably close to the experimental conditions, although the model connected to the law of mass action more satisfactorily represented the actual behavior. However, although the former models present a less satisfactory result due to the simplicity of the adsorption models, they are largely used, including in ion-exchange systems.

The ion-exchange process can be applied in different reactor configurations, such as finite bath, fixed bed or fluidized bed, although the removal capacity of metal ions in the batch and continuous processes may be different (Silva et al. 2002; Ko et al. 2001; Yoshida et al. 1994; Weber and Wang 1987). According to (Preetha and Viruthagiri 2007), who analyzed the removal capacity of chromium alginate coming from the algae *Rhizopus arrhizus*, the batch system removed up to 1.00 meq$_{chrome}$/g$_{alginate}$, while in the fixed bed system the maximum capacity reached 3.45 meq$_{chrome}$/g$_{alginate}$. The equilibrium data obtained for the batch reactor system does not effectively represent the equilibrium that takes place when using columns, which is the reason why the models applied need to be fitted in keeping with the experimental data obtained with the use of columns. A major factor that triggers this change of behavior in the two systems is that the concentration decreases over time in batch systems, while the feeding is constant in continuous systems (Ko et al. 2001).

In this paper, calcium alginate particles were characterized and used in ion-exchange fixed bed tests to remove copper. Furthermore, other tests were performed to obtain the system's equilibrium data; and the mathematical modeling considered single and binary component systems.

2 Mathematical modeling

2.1 Adsorption isotherms for single component systems

Several models can be used to represent the equilibrium data of adsorption processes; with the Langmuir and Freundlich models being the most largely used and serving as basis to create several other models.

The Langmuir isotherm model, represented by Eq. (1), considers the following: all monolayers undergo chemisorption, all sites present the same activation energy, and molecules do not interact among themselves and with the neighboring sites that adsorb them.

$$q* = \frac{q_{max}bC*}{1 + bC*} \tag{1}$$

The Freundlich model, represented by Eq. (2), is an empirical model that considers that the energy of the adsorbent material's active sites is heterogeneous and that the adsorption process is reversible.

$$q* = k_d C*^n \tag{2}$$

The Redlich–Peterson model was successfully used to represent the equilibrium data of the adsorption of organic compounds on activated carbon (Quintelas et al. 2008; Chern and Chien 2001). It is an empirical model that presents three adjustable parameters, as shown in Eq. (3). The parameter n of this equation has values in the range of [0, 1] with the Langmuir model being used to represent it when $n = 1$. When the concentration values are low, the model can be described by the Henry's law, while at high concentrations its behavior resembles the Freundlich model.

$$q* = \frac{q_{max}bC*}{1 + bC*^n} \tag{3}$$

The Toth model more accurately correlates the heterogeneous adsorbents, being also employed in processes including multicomponent gas adsorption. However, it can also be used for liquids (Quintelas et al. 2008; Chern and Chien 2001; Cooney 1999; Hindarso et al. 2001). This model is described by Eq. (4) where parameter n has values in the range of [0, 1], while the Langmuir equation accounts for equation when $n = 1$.

$$q* = \frac{q_{max}C*b^{1/n}}{\left(1 + bC*^n\right)^{1/n}} \tag{4}$$

The Radke–Prausnitz model is typically used for the adsorption of organic compounds in aqueous solutions. It is represented by Eq. (5) and, when n equals to 1, the Langmuir model describes it. Its behavior at low concentrations is described by the Henry's Law model, while the Freundlich model is used for high concentrations.

$$q* = \frac{q_{max}C*b}{\left(1 + bC*\right)^n} \tag{5}$$

2.2 Adsorption isotherms for binary systems

Considering the presence of the Cu^{2+} and Ca^{2+} ions in a binary system in which both metals can be found in the adsorbent sites, the kinetic of the adsorption of these metals can be represented by Eqs. (6) and (7):

$$B + Cu \leftrightarrow B - Cu \tag{6}$$

$$B + Ca \leftrightarrow B - Ca \tag{7}$$

The equilibrium of the active sites resulting from Eq. (8) considers that the sites are occupied by only one cation, or that the site is empty and unavailable for adsorption:

$$[B_0] = [B - Ca] + [B - Cu] + [B] \tag{8}$$

In this case, the Langmuir model, referred to as 3-parameter Langmuir, can be described by Eq. (9):

$$q^*_{Cu} = \frac{q_{max} C^*_{Cu} b_{Cu}}{1 + b_{Ca} C^*_{Ca} + b_{Cu} C^*_{Cu}} \tag{9}$$

Another model used by (Bailey and Ollis 1986) considers that there is a competition between the ions and that one site occupied by a cation can adsorb a second different cation. In this case, in addition to the reactions (6) and (7), the reactions (10) and (11) take place, as follows:

$$B - Cu + Ca \leftrightarrow B - Cu - Ca \tag{10}$$
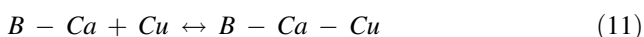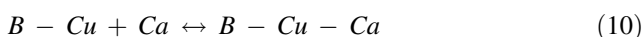
$$B - Ca + Cu \leftrightarrow B - Ca - Cu \tag{11}$$

Therefore, the equilibrium of the sites is given by Eq. (12):

$$[B_0] = [B - Ca] + [B - Cu] + [B - Ca - Cu] + [B] \tag{12}$$

Thus, the Langmuir equation can be rewritten as Langmuir isotherm with inhibition, as shown by Eq. (13):

$$q^*_{Cu} = \frac{q_{max} C_{Cu} b_{Cu} [1 + (K/b_{Cu}) C^*_{Ca}]}{1 + b_{Ca} C^*_{Ca} + b_{Cu} C^*_{Cu} + 2K C^*_{Ca} C^*_{Cu}} \tag{13}$$

Where K is a parameter represented by the constants of reactions (10) and (11) and equivalent to: $K = K_{Ca} K_{Ca-Cu}$ and $K = K_{Cu} K_{Cu-Ca}$, respectively, and where the high levels of K indicate the favoring of formation of the complex $[B-Cu-Ca]$.

The power langmuir isotherm (Sánchez et al. 1999; Chong and Volesky 1995) is a modified Langmuir model which combines two new parameters to the model described by Eq. (14):

$$q^*_{Cu} = \frac{q_{max} C^*_{Cu} b_{Cu}}{1 + b_{Ca} \left(C^*_{Ca}\right)^{k_{Ca}} + b_{Cu} \left(C^*_{Cu}\right)^{k_{Cu}}} \tag{14}$$

Freundlich is another model used (Eq. 15), which considers that there is physisorption in infinite layers, and that the energy of the active sites is heterogeneous. In this case, the equation describing this model for binary mixtures is represented by:

$$q^*_{Cu} = \frac{a_{Cu} \left(C^*_{Cu}\right)^{n_{Cu} + \alpha'_{11}}}{\left(C^*_{Cu}\right)^{\alpha'_{11}} + a_{Cu-Ca} \left(C^*_{Ca}\right)^{\alpha'_{12}}} \tag{15}$$

According to (Ruthven 1984), it is possible to correlate the Langmuir and Freundlich models using Eq. (16), which refers to the Langmuir–Freundlich model:

$$q^*_{Cu} = \frac{q_{max} b_{Cu} \left(C^*_{Cu}\right)^{k_{Cu}}}{1 + b_{Ca} \left(C^*_{Ca}\right)^{k_{Ca}} + b_{Cu} \left(C^*_{Cu}\right)^{k_{Cu}}} \tag{16}$$

In this case, at low concentrations, the behavior described by the Freundlich model stands as an alternative, and in higher concentrations the behavior described by the equation is emphasized by the Langmuir model.

Jain and Snoeyink (1973), based on the Langmuir model, developed a model that considers that part of the adsorption occurs without competition. In this case, Eq. (17) shows the amount of calcium adsorbed in the alginate, and Eq. (18) shows the amount of copper adsorbed.

$$q^*_{Ca} = \frac{q_{Cu} b_{Ca} C^*_{Ca}}{1 + b_{Ca} C^*_{Ca} + b_{Cu} C^*_{Cu}} + \frac{(q_{Ca} - q_{Cu}) b_{Ca} C^*_{Ca}}{1 + b_{Ca} C^*_{Ca}} \tag{17}$$

$$q^*_{Cu} = \frac{q_{Cu} C^*_{Cu} b_{Cu}}{1 + b_{Ca} C^*_{Ca} + b_{Cu} C^*_{Cu}} \tag{18}$$

The first term of the Eq. (17) represents the competitive adsorption of ions Ca^{2+}, based on the Langmuir competitive adsorption model. The second term on the right side of the Eq. (17) represents the single-component Langmuir isotherm model. In this case there is no competition between species, the term $(q_{Ca} - q_{Cu})$ represents the amount of available sites that can be occupied exclusively by the chemical species Ca^{2+}. The number of ions of the Cu^{2+} species that adsorbs on the sites $B-Cu$ upon the competition of the Ca^{2+} species can be calculated by Eq. (18).

2.3 Ideal law of mass action

Considering the binary system Cu^{2+} and Ca^{2+} involved in the ion-exchange reaction shown by Eq. (19):

$$Cu_S^{+2} + Ca_{Al}^{+2} \leftrightarrow Cu_{Al}^{+2} + Ca_S^{+2} \tag{19}$$
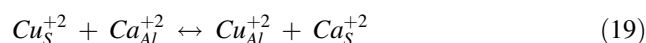
For the case in which the reagents and products are ions, the reaction constant is given by Eq. (20):

$$K_{Cu}^{Ca} = \left(\frac{a_{R_{Ca}}}{a_{S_{Ca}}}\right)^{z_{Cu}} \left(\frac{a_{S_{Cu}}}{a_{R_{Cu}}}\right)^{z_{Ca}} \tag{20}$$

In this equation, the ionic activities are correlated, taking into account the non-ideality of both phases involved.

However, considering the simplification proposed by Klein and Tondeur (1967) that both phases behave ideally, the activity coefficients are equal to 1 and, on account of this, the Eq. (16) is rewritten by Eq. (21):

$$K_{Cu}^{Ca} = \left(\frac{q_{Ca}}{C_{Ca}}\right)^{z_{Cu}} \left(\frac{C_{Cu}}{q_{Cu}}\right)^{z_{Ca}} \tag{21}$$

2.4 Law of Mass Action

Because it is an ionic solution, considering the ideal solution is not recommended, as in these systems the atomic charges of these species interact due to the coulombic forces. In this case, the Henry's Law should be used to calculate the activity coefficients that results in significant errors (Sanlder 1999). Therefore, when the Law of Mass Action is used in such systems, the non-ideality of both phases in the calculation of ions should be considered. Therefore, in this case, the standard states should be specified for both phases.

Liquid phase hypothetical ideal solution of component j for solvent, system temperature and pressure and at the concentration of 1 molal (Prausnitz et al. 1999):

$$a_j^S = \left(\gamma_j^S m_j \right) \tag{22}$$

where: $\gamma_j^S \to 1$ when $m_j \to 0$.

Solid phase considers the pure component's standard state:

$$a_j^A = \left(\gamma_j^R y_j \right). \tag{23}$$

where: $\gamma_j^R \to 1$ when $y_j \to 1$.

Equation (24) is obtained applying Eqs. (22) and (23) to Eq. (20), as follows:

$$K_{Ca}^{Cu} = \left(\frac{y_{Cu} \gamma_{Cu}^A}{m_{Cu} \gamma_{Cu}^S} \right)^{z_{Ca}} \left(\frac{m_{Ca} \gamma_{Ca}^S}{y_{Ca} \gamma_{Ca}^A} \right)^{z_{Cu}} \tag{24}$$

However, in this case, the specification of the models to calculate the activity coefficients for both phases is necessary.

Activity: coefficient for the aqueous phase In this study, the (Bromley 1973) was applied. It considers the interaction of ions due to coulombic forces and is described by Eq. (25):

$$\log \gamma_i^S = -\frac{A z_i^2 \sqrt{I}}{1 + \sqrt{I}} + F_i \tag{25}$$

The ionic length, I, is given by Eq. (26), and the term F is described by Eq. (27), the latter referring to the sum of the interaction parameters.

$$I = \sum_i m_i z_i^2 \tag{26}$$

$$F_i = \sum_j B_{ji} z_{ji}^2 m_i \tag{27}$$

The arithmetic average of the charges of the ions found in the salt composition, z_{ji}, is given by Eq. (28) and Bromley parameter for salt, B_{ji}, is given by Eq. (29).

$$z_{ji} = \frac{z_j + z_i}{2} \tag{28}$$

$$B_{ji} = -\frac{(0.06 + 0.6B)|z_j z_i|}{\left(1 + \frac{1.5}{|z_j z_i|} I \right)^2} + B \tag{29}$$

Activity coefficient for solid phase as there are no specific models for calculating the activity coefficient for the solid phase, the models developed for the liquid phase, such as Wilson, were used.

Wilson Model is given by Eq. (30), standing as a simple method used by several authors (Petrus and Warchol 2005; Petrus and Warchol 2003; Allen and Addison 1989; Smith and Woodburn 1978) for calculating the activity coefficient of ions in resins, and can be used to n components, being adjusted to $n.(n-1)$ binary pairs.

$$\ln \gamma_i^A = 1 - \sum_{j=1}^n y_j \Lambda_{ij} - \sum_{j=1}^n \left[y_j \Lambda_{ji} / \sum_{k=1}^n y_k \Lambda_{ji} \right] \tag{30}$$

where for $i = j$, $\Lambda ij = 1$.

3 Materials and methods

3.1 Obtaining calcium alginate particles

The particles were obtained by the emulsification method (Mofidi et al. 2000). We prepared an emulsion by pouring an aqueous solution of sodium alginate (Sigma Aldrich) in canola oil, kept under continuous stirring by a naval-propeller impeller (Fisatom, 712). After 10 min of contact between the phases, an aqueous solution was added, having the same characteristics: 4 g of calcium chloride ($CaCl_2 \cdot 2H_2O$, Synth), 30 mL of Ethanol (CH_3CH_2OH, Synth), 2 mL of Acetic Acid (CH_3COOH, Ecibra) and 30 mL of distilled water. After the addition of this solution, the system was kept under stirring for 15 min. The entire procedure for obtaining particles was performed at 60 °C. Then, the particles were filtered and washed with distilled water. After the procedure described by Mofidi et al. (2000), the particles were also washed with acetone (C_3H_6O, Vetec) to remove most of the oil adhered to the interstices of the particles' surface and washed again with distilled water.

Particle size distribution Using energy dispersive spectroscopy (EDS), the particles were analyzed according to their shape and size distribution.

Total moisture The particles were subjected to drying at 40 °C for 12 h in the preliminary drying, and for 2 h in the consecutive drying. This was performed until the constancy of the kinetics of drying was achieved.

pH$_{ZPC}$ (Zero point charge) The pH value in which the particles' surface charges are equal to zero was induced. The method (Kummert and Stumm 1980) refers to the potentiometric titration considering the law of mass action. The titration was performed using acetic acid solution 0.1 M (CH$_3$COOH, Synth), and an alkaline solution of ammonium hydroxide 0.1 M (NH$_4$OH, Synth).

Total cation exchange capacity (CEC$_{Total}$) the amount of calcium in alginate particles was achieved by means of a digestion process induced using 2 g of hydrated calcium alginate particles and 50 mL of sulfuric acid (H$_2$SO$_4$, Synth), keeping them under stirring state for 90 min for the complete dissolution of particles. To assess the reliability of the results, the same procedure was used for an aliquot of 1 mL of a standard calcium solution (Merck) in 50 mL of sulfuric acid. The analysis of both samples was performed in triplicate, and the reading of the final concentration was performed by atomic absorption spectroscopy (Perkin Elmer).

3.2 Speciation

This research analyzed the behavior of the ions in the solution, at a given concentration, due to pH variation, using the plug in hydra of the application make equilibrium diagrams using sophisticated algorithms (Medusa), both developed by the Royal Institute of Technology—Sweden. With this method, an optimal pH was achieved, which also entailed correction in the solutions with nitric acid (HNO$_3$, Synth) and ammonium nitrate (NH$_4$OH, Synth).

3.3 Equilibrium study

Copper Nitrate salts (Cu(NO$_3$)$_2$·3H$_2$O, Vetec) and Calcium Nitrate (Ca(NO$_3$)$_2$·4H$_2$O, Vetec) were used dissolved in distilled water. The solutions prepared contained different total and partial concentrations, as shown in Table 1.

The Bed Tests were performed in order to obtain the equilibrium data, and all tests were performed until its saturation.

A fixed mass of 19.24 g of hydrated calcium alginate particles was used in each test for packing the bed of 13.3 cm height and 1.4 cm diameter. A fixed flow of 3 mL/min and 25 °C was adopted, and the total amount of Copper ions retained by the ion exchanger was obtained by the Eq. (31), meanwhile the amount of calcium ions that has not been exchanged was obtained by Eq. (32).

$$q_{eq(m,f)}^{Cu} = \frac{C_{0(m,f)}^{Cu} V}{1000 \cdot m_{Al}} \int_0^t \left(1 - \frac{C|_{Z=L(m,f)}^{Cu}}{C_{0(m,f)}^{Cu}}\right) dt \quad (31)$$

$$q_{eq(m,f)}^{Ca} = q_{eq(m,f=1,0)}^{Cu} - q_{eq(m,f)}^{Cu} \quad (32)$$

Table 1 Power solutions

Solution concentration (meq/L)	Cu^{+2}	Ca^{+2}
3.147	1.0	0.0
3.147	0.9	0.1
3.147	0.8	0.2
3.147	0.6	0.4
3.147	0.4	0.6
3.147	0.2	0.8
6.295	1.0	0.0
6.295	0.9	0.1
6.295	0.8	0.2
6.295	0.6	0.4
6.295	0.4	0.6
6.295	0.2	0.8
9.442	1.0	0.0
9.442	0.9	0.1
9.442	0.8	0.2
9.442	0.6	0.4
9.442	0.4	0.6
9.442	0.2	0.8

With regard to the tests involving 100 % Copper solutions as for their total concentration, the amount adsorbed was considered the maximum amount available for the exchange of each total concentration, which was ascertained by Eq. (31). This assessment did not consider the CEC_{Total} value, as it concerns all calcium ions in the alginate, and not only the ions connected to the active sites available for ion exchange.

The experimental equilibrium data was modeled as shown in item 2, applying Eq. (33) to process the results obtained by the monocomponent isotherm models, and Eq. (34) to all other models applied.

$$F_{obj} = \sum_{j=1}^{n\_exp} \left[\left((y_A^B)_j^{EXP} - (y_A^B(\theta))_j^{MOD}\right)^2\right] \quad (33)$$

$$F_{obj} = \sum_{j=1}^{n\_exp} \left[\begin{array}{c} \left((y_{Ca}^{Cu})_j^{EXP} - (y_{Ca}^{Cu}(\theta))_j^{MOD}\right)^2 + \\ \left((y_{Cu}^{Cu})_j^{EXP} - (y_{Cu}^{Cu}(\theta))_j^{MOD}\right)^2 \end{array} \right] \quad (34)$$

The ratio between the amount of ions of Cu^{2+} absorbed and ions of Ca^{2+} desorbed on the bed's outlet was calculated by Eq. (35) in order to assess which the predominant process: adsorption or ion exchange.

$$r = \frac{C^{Cu^{2+}}\big|_{Z=L} + C^{Ca^{2+}}\big|_{Z=L}}{C_0} \quad (35)$$

In this case, CEC_{Total} was not applied, i.e., not all alginate sites would be available for ion exchange.

Concentration of ions the amount of copper and calcium ions in the solution before and after the ion exchange process was obtained using the atomic absorption spectroscopy.

4 Results and discussion

4.1 Calcium alginate particles

According to the EDS result, the particles had average diameters of 1083 μm, sphericity as shown in Fig. 1a and the particle size distribution shown in Fig. 1b. The particles yielded a value of CEC_{Total} of 12.893 meq/g, total moisture of 95 %, and the change of surface charge as pH function, as shown in Fig. 2, where the pH_{ZPC} value was around 6.0.

4.2 pH

Considering the pH_{ZPC} test results, in Fig. 2a, and that of the speciation study, it may be concluded that, for the mixture Cu^{2+}–Ca^{2+}, the optimal pH value is 4.5, which is

a value in which the particles surface's charge is not zero, but around 0.001. Furthermore, there is no Copper precipitation, which is the limiting factor for the choice. As ascertained in the speciation study, using the Hydra plug-in, the ion Ca^{2+} did not bring on significant change in the pH value due to the concentration variation, although the Cu^{2+} species showed considerable variation, as shown in Fig. 2b. However, for the concentrations tested, as shown in Table 2, at a pH of 4.5, only the ionic form Cu^{2+} can be considered in the solution content.

This result is consistent with the value obtained by (Papageorgiou et al. 2006). (Veglio et al. 2002) evaluated the removal capacity of copper for alginate at different pH values, and at a pH amounting to 3.80, 4.60 and 4.84, obtaining, respectively, the following amounts of adsorbed metal: 0.448, 0.426 and 0.396 meq/g. At lower pH values, such as 2.27, the amount removed was 0.103 meq/g.

Table 2 Maximum amount of exchangeable ions in the presence of 100 % Cu^{2+}

C_0 (meq/L)	q_{max} (meq/g)
3.147	4.560
6.294	6.600
9.442	7.728

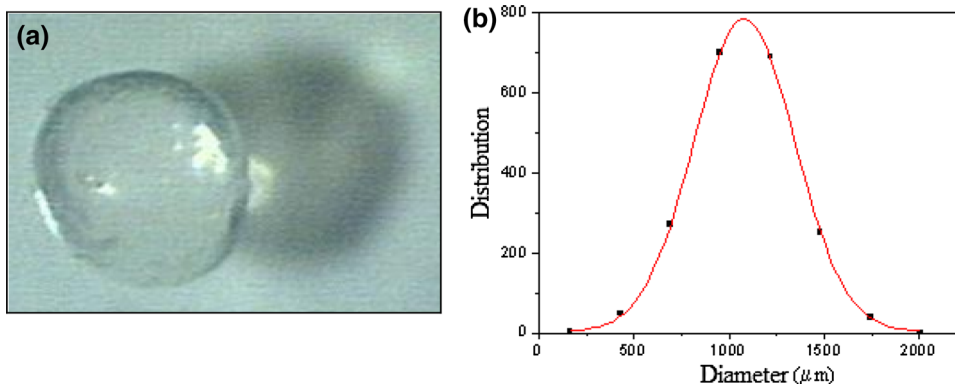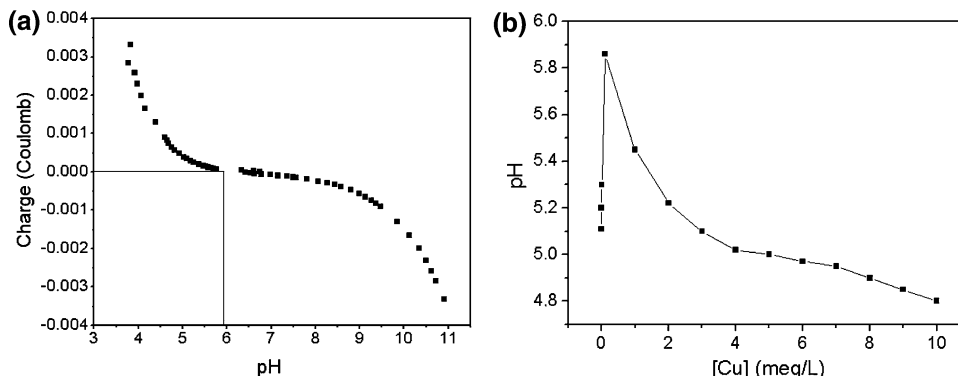**Fig. 1 a** Calcium alginate particle, **b** particle size distribution

Fig. 2 a pH_{ZPC}, **b** pH values for which, at different copper concentrations, have only the ionic species Cu^{2+} in the solution

According to (Ngah and Fatinathan 2008), Cu^{2+} is found at pH values ranging from 1.0 to 6.0. With pH values equal to 7.0, the formation of $Cu(OH)_2$ and the precipitation of Cu^{2+} can be found.

4.3 Equilibrium study

Equation (35) was used to ascertain the amount of ions of Cu^{2+} which were adsorbed or exchanged for ions of Ca^{2+} in the active sites of calcium alginate particles, which can be observed in Fig. 3a. In keeping with this result, the predominant process is the ion exchange, insofar as the ratio between adsorbed copper ion and desorbed calcium ions is nearly 1, i.e., the sum of output levels of both ions involved is about the same as the inlet concentration, C_0. Values below 1 indicate adsorption or, as assumed in the Baley and Ollis' model (Bailey and Ollis 1986), which considers that a site occupied by a given ion can be occupied by a second ion, this behavior points to a competitive adsorption in which the adsorbent charges interact with more than one ion, due to a deficit of charges, and can

observed for the concentration of 6.295 meq/L for a fraction of Cu^{2+} of 0.2.

The amount of exchangeable ions, q_{max}, for each total concentration is shown in Table 2, which shows non-linearity with respect to initial concentrations, indicating the behavior of an isotherm close to equilibrium.

Figure 3b shows the isotherm of the copper adsorption by calcium alginate, where, at the concentration of 7.554 meq/L, the onset of a plateau region takes place, indicating the saturation of the sites available for alginate exchange, and the following after 8.498 and 9.442 meq/L show an amount of adsorbed copper around 7.73 meq/g.

According to the behavior described for each of the concentrations tested, calcium found in the process can be pointed out as an agent interfering with the process. This can be seen, for example, for a copper concentration of 4 meq/L, where two points can be discerned: the total concentration is 6.294 meq/L and contains 60 % of copper, and an adsorbed amount of 5.25 meq/g, the second presents a total concentration of 9.442 meq/L which contains 40 % of copper, and an adsorbed amount of 4.75 meq/g.
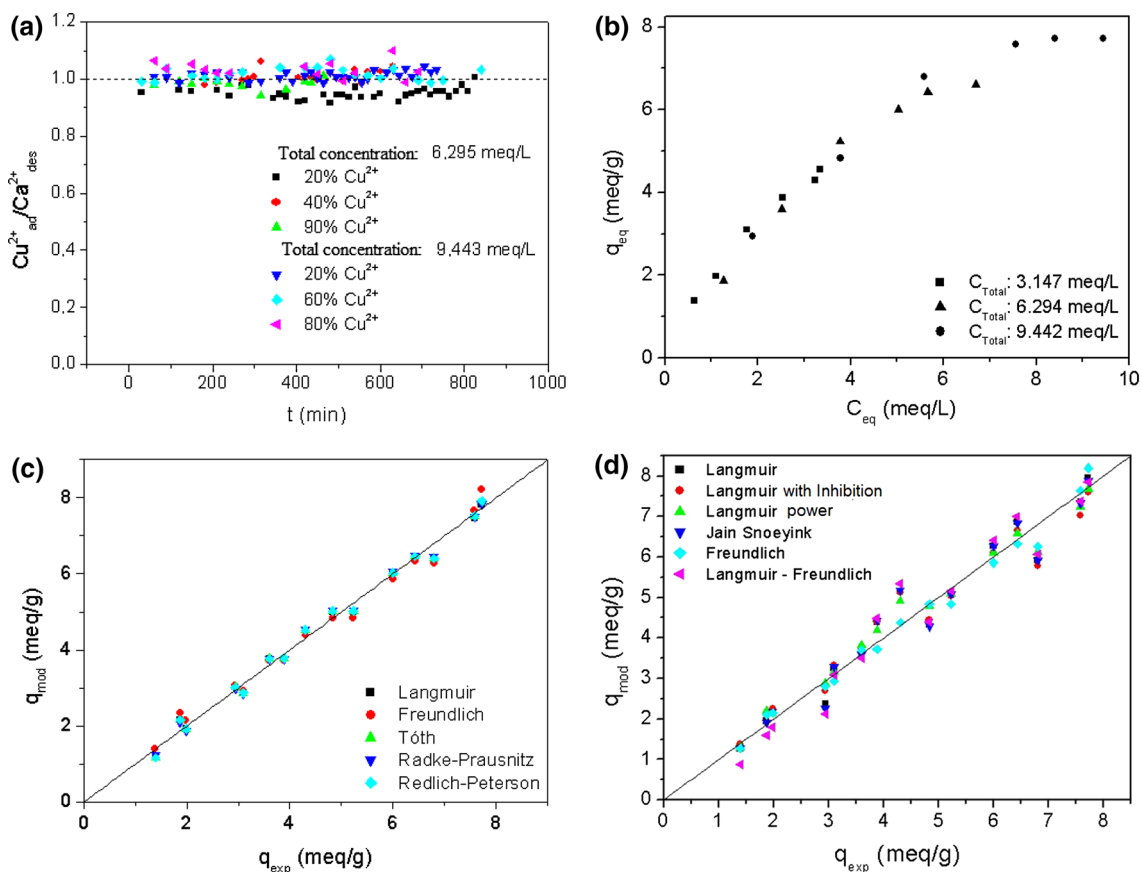

Fig. 3 **a** Ratio between adsorption of Cu^{2+} and desorption of Ca^{2+}, **b** adsorption isotherm of Cu^{2+} ions in calcium alginate, **c** relationship between q_{eq} obtained by single component system models, q_{mod}, and

through experimental data, q_{exp} **d** Relationship between q_{eq} obtained by binary system models, q_{mod}, and through experimental data, q_{exp}

Table 3 Amount of Cu^{2+} adsorbed by different adsorbents

Adsorbents	Reference	Cu^{2+} (meq/g)
Macrophyte *Eichhornia crassipes*	Mishra and Tripathi (2008)	5.52
Macrophyte *Salvinia cucullata*	Silva et al. (2012)	0.586
Macrophyte *Salvinia natans*	Lima et al. (2012)	0.602
Macrophyte *Pistia stratoites*	Mishra and Tripathi (2008)	1.75
Macrophyte *Spirodela polyrrhiza*	Mishra and Tripathi (2008)	0.37
Amberlite IR-120	Lee et al. (2006)	3.30
Seaweed biomass	Sheng et al. (2004)	2.52
Alga *Sargassum vulgare*	Davis et al. (2003)	1.86
Alga *Sargassum filipendula*	Kleinübing (2009)	1.64
Natural rice husk	Vieira et al. (2012)	0.074
Alginate particles extracted from *Laminaria digitata*	Papageorgiou et al. (2008)	3.00
Natural chitosan	Vieira (2008)	4.00
Sericin powder	Silva (2013)	0.494

Table 4 Parameters obtained for single-component isotherms models

Model	Parameters	F_{obj}	R^2
Langmuir	q_{max} (meq/g) = 14.5402	0.06983	0.9904
	b (L/meq) = 0.1397		
Freundlich	K (meq/g) = 2.0203	1.05498	0.9828
	n = 0.6589		
Toth	q_{max} (meq/g) = 14.9706	0.5718	0.9905
	b (L/meq) = 0.1337		
	n = 0.9999		
Radke–Prausnitz	q_{max} (meq/g) = 40.5551	0.54961	0.9910
	b (L/meq) = 4.67768		
	n = 2.1396		
Redlich–Peterson	q_{max} (meq/g) = 14.9515	0.5718	0.9905
	b (L/meq) = 0.1240		
	n = 0.9999		

This behavior is consistent with the results obtained by (Chen et al. 2007) researching the removal of Lead using calcium alginate, who found out that the amount of Lead removed from a solution free from Sodium and Calcium ions is 2.24 and 4.98 meq/g, respectively higher than in solutions containing Na^+ and Ca^{2+} ions due to ionic competition. Table 3 shows the amount of Copper removed by different adsorbents tested by different authors.

The adsorption isotherm models shown in Item 2.1, which only consider the ion removed by alginate, which is Copper, showed a satisfactory adjustment as shown in Fig. 3c, as it is possible to observe by the value of F_{obj} and R^2, shown in Table 4.

For the Langmuir model in which the value of q_{max} is the maximum amount of available sites, this parameter, although above the CEC_{Total} value, which is 12.893 meq/g, showed no significant discrepancy. For all other models the

parameter q_{max} does not represent the total number of sites available, but an adjustable parameter of the models.

According to (Papageorgiou et al. 2008) using calcium alginate particles to remove copper and cadmium, the Sips model proved to be more satisfactory to fit the data compared to the Langmuir and Freundlich model, due to the heterogeneity of the adsorbent surface. (Lai et al. 2008) successfully used the Freundlich model to describe the metal removal process using calcium alginate. The Langmuir, Freundlich, Redlich–Peterson, Radke–Prausnitz and Toth models were evaluated by (Limons 2008), which removed metals using aquatic macrophyte, and all models, except Freundlich, had R^2 above 0.90.

The treatment of equilibrium data, considering binary adsorption isotherms, shown in item 3.2, allowed a satisfactory fitting of the experimental data, as shown in Fig. 3d.

Table 5 shows the parameters obtained for each model, as well as F_{obj} and the value of R2. The Langmuir–Freundlich model presented the most discrepant result, while the best fitting was given by the Freundlich model. The value obtained for the b parameter is associated with the preference of the metal species with the sites, and the difference between b_{Cu} and b_{Ca} increases in proportion with the separation.

Comparing Isotherm models for single component and binary systems, both satisfactory results showed can be observed. Although the Isotherm models for single component systems disregarded the presence of Calcium, a good fitting is due to the greater affinity of alginate for Copper, which can be adsorbed even in the presence of Calcium, as shown in Fig. 3b.

The theory of Ideal Law of Mass Action was used to represent the equilibrium data, as shown by Eq. (17). The Law of Mass Action considers the non-ideality of both phases, as show in Eq. (20), which in this case is the

Table 5 Parameters obtained for the isotherm models of the binary system: Cu^{2+} and Ca^{2+}

Model	Parameters	F_{obj}	R^2
Langmuir	b_{Cu} (meq/L) = 0.23385	6.7441	0.9231
	b_{Ca} (meq/L) = 0.11603		
	q_{max} (meq/g) = 12.4330		
Langmuir with inhibition	b_{Cu} (meq/L) = 0.26130	8.8361	0.9175
	b_{Ca} (meq/L) = 0.12272		
	K (meq/L)^2 = 111.072		
	q_{max} (meq/g) = 11.5700		
Langmuir power	b_{Cu} (meq/L) = 0.21871	5.3493	0.9418
	b_{Ca} (meq/L) = 0.10033		
	k_{Cu} = 1.00790		
	k_{Ca} = 0.633558		
	q_{max} (meq/g) = 12.3994		
Freundlich	a_{Cu} = 0.000242408	6.9263	0.9833
	a_{Cu-Ca} = 0.000100224		
	α'_{11} = 4.98376		
	α'_{12} = 4.51418		
	α'_{21} = 5.5428		
	n_{Cu} = −0.217961		
Langmuir–Freundlich	b_{Cu} (L/meq) = 0.281287	5.6056	0.8972
	b_{Ca} (L/meq) = 0.227979		
	k_{Cu} = 1.35106		
	k_{Ca} = 0.893793		
	q_{max} (meq/g) = 9.76056		
Jain Snoeyink	q_{Cu} (meq/g) = 12.1394	6.5702	0.9172

activity coefficient of the solid phase obtained by the Wilson model, as shown in Eq. (26), and the ions in solution are described by Bromley model. The parameters, according to (Bromley 1973), were used to calculate the activity coefficient, as follows:

$Ca(NO_3)_2$: 0.0410 $Cu(NO_3)_2$: 0.0797

The total amount of available sites, $CEC_{available}$, considered in this model refers to the amount of copper adsorbed, while its fraction would be equal to 1, for the respective total concentration, as shown by Eqs. 31 and 32. Table 6 shows these values.

The parameters fitted in the Law of Mass Action were: K_{eq} and the Wilson model parameters. According to Fig. 4, which refers to the total concentrations evaluated, there was no significant difference between the behaviors of the models, both of them successfully fitted to the experimental data.

The parameters analyzed in each model, as well as the values of F_{obj} and R^2, are shown in Table 7. The Law of Mass Action, which considers the non-ideality of the phases, was found to present the best fitting. Nonetheless, although it brought on the smallest K-eq-, the fitting obtained by the Ideal Law of Mass Action was also satisfactory. Comparing these results with those obtained by the Adsorption models, all of them revealed similar behavior,

Table 6 Available cation exchange capacity ($CEC_{available}$)

Essay	$CEC_{available}$ (meq/g)
CEC_{Total}: 3.147 meq/L	4.56
x_{Cu}: 1.00 x_{Ca}: 0.00	
CEC_{Total}: 6.294 meq/L	6.60
x_{Cu}: 1.00 x_{Ca}: 0.00	
CEC_{Total}: 9.442 meq/L	7.73
x_{Cu}: 1.00 x_{Ca}: 0.00	

however. Moreover, the Law of Mass Action allowed predicting multicomponent systems using the parameters obtained for the respective binary pairs.

The activity coefficients of Calcium and Copper ions in the solid phase were calculated by Wilson model, as in Fig. 5a. According to Wilson model, the behavior of both metals behavior is close to satisfactory. The activity coefficient of the liquid phase calculated by the Bromley model is shown in Fig. 5b. For any concentrations and compositions evaluated, the coefficient in this study remained constant, although their behavior was not satisfactory. The value remained constant because of its two divalent ions.

Considering that the total amount of available sites is equal to the amount of calcium in the alginate, i.e.,
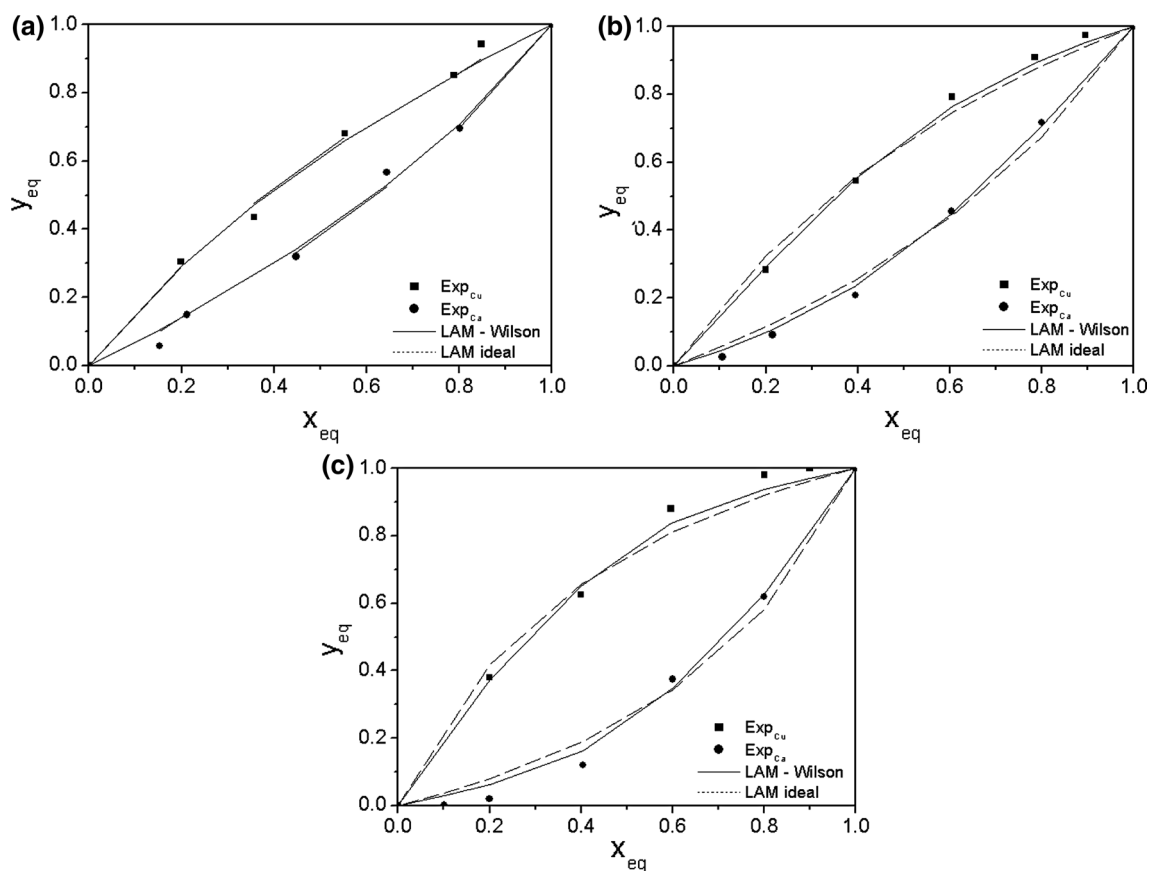
Fig. 4 Mass Action Law considering $CEC_{available}$—solution concentration: **a** 3.147 meq/L, **b** 6.294, 9.442 meq/L

Table 7 Parameters for the Law of Mass Action for the binary system Cu-Ca

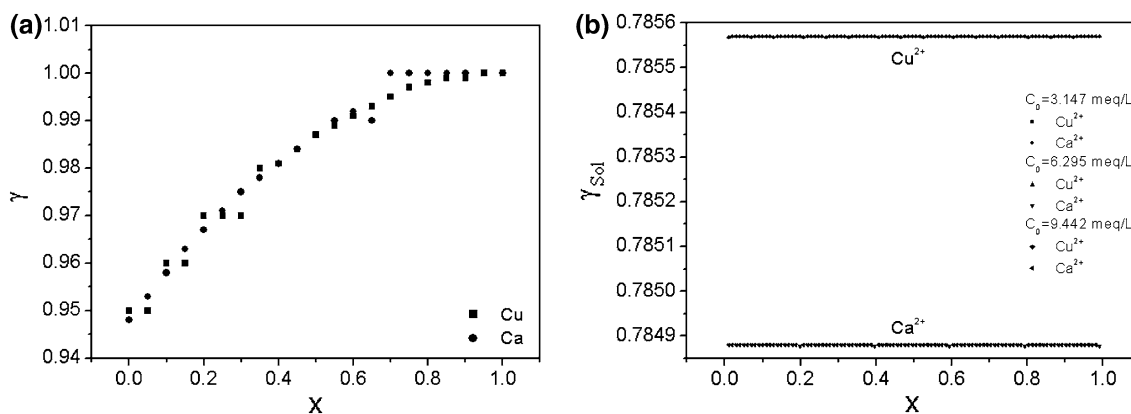| Model	Parameter obtained	F_{obj}	R^2
Wilson	$W_{Cu,Ca} = 0.63382\ W_{Ca-Cu} = 1.11398\ K_{eq} = 0.705756$	0.0607	0.9941
LAM—satisfactory	$K_{eq} = 0.476270$	0.1007	0.9899

Fig. 5 Coefficient of activity of copper and calcium ions in the: **a** solid phase, **b** liquid phase

CEC_{Total}, then the ion exchange isotherms, as shown in Fig. 4, have the behavior shown in Fig. 6a–c, in which the Copper and Calcium curves do not touch, which is opposed to the behavior described by the Las of Mass Action. By means of these Figures, it can be concluded that alginate has a higher affinity for Calcium than for Copper, which is
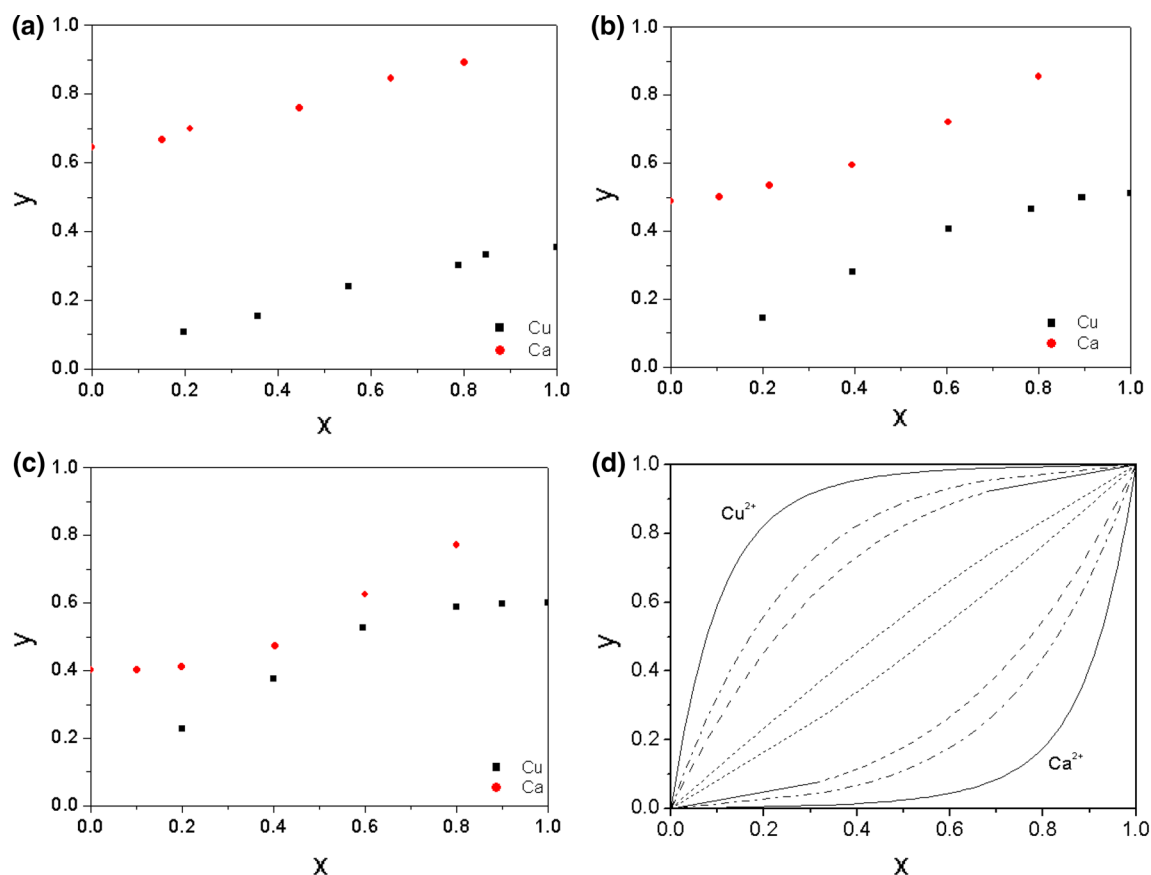
Fig. 6 Mass action law considering CEC_{Total}—solution concentration: **a** 3.147 meq/L, **b** 6.294, 9.442 meq/L, **d** ideal mass action law applied to: C_0: 20 meq/L(*continuous line*), C_0: 12 meq/L (*dashed dotted line*), C_0: 8 meq/L (*dashed line*), C_0: 2 meq/L (*dotted line*)

not consistent with the experimental result obtained by other authors (Papageorgiou et al. 2006).

Another way to assess the Law of Mass Action is to compare the equilibrium curves with different values of C_0. In such case, the parameters obtained for this system applying the Law of Mass Action were used to ascertain the Fig. 6d, in which there are different values of C_0. In such figure, for $x = 1$, y should always be equal to 1, which is not consistent with the results shown above.

5 Conclusions

Ca-alginate particles used in ion exchange fixed bed for the removal of Cu^{2+} showed high q_{max} (12.4330 meq/g).

The Isotherms for the single component system showed satisfactory results, due to the fact that the affinity for Cu^{2+} was potentially higher than for Ca^{2+}.

The isotherms for the binary system fitted well the experimental data. Although the presence of the second ion (Ca^{2+}) was considered, there was no significant improvement of these models compared to the Isotherms models for the single system.

The Ideal and Non-Ideal Law of Mass Action showed similar results. The $CEC_{available}$ resulted in a satisfactory equilibrium curve, unlike the CEC_{Total}, which presented an ion exchange isotherm ($x = 1$, $y \neq 1$).

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