Diffusivity of Cu^{2+} in Calcium Alginate Gel Beads

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A linear absorption model (LAM) is used to describe the process of metal binding to spherically shaped biopolymer particles. The LAM was solved using a numerical algorithm which calculates diffusivities of metal ions in biopolymer gels. It assumes attainment of rapid metal–biopolymer binding equilibrium accompanied by rate limiting diffusion of the metal ions through the gel. The model was tested using batch experiments in which copper (Cu^{2+}) binding with calcium alginate beads was investigated. Biopolymer density in the beads was varied between 2% and 5%. The diffusion coefficient of Cu^{2+} calculated from the LAM ranged from 1.19×10^{-9} to 1.48×10^{-9} m^2 s^{-1} (average $1.31 \pm 0.21 \times 10^{-9}$ m^2 s^{-1}), independent of biopolymer density. The LAM has theoretical advantages over the shrinking core model (shell progressive model). The latter calculated an unreasonable exponential increase in the diffusion coefficient as density of alginate polymer in the bead increased.
Key words: biopolymers • metal binding • polymer–metal binding • calcium alginate beads • copper binding

INTRODUCTION

The potential for using biopolymers as safe, cost-effective materials for removing heavy metals from dilute aqueous solutions has long been recognized.[3,18,20] Biopolymers are selective, efficient, and inexpensive, and thus highly competitive with ion exchange resins and activated carbon. Thermodynamic parameters, in the form of stability constants and binding capacities, have been reported in the literature for a wide variety of both metal ions and biopolymers.[12,13] Calcium alginate has been one of the most extensively investigated biopolymers for binding heavy metals from dilute aqueous solutions.[3,5,16,17] Alginates form a family of gel salts produced from naturally occurring alginic acids. These acids are copolymers comprised of linear, unbranched chains of 1,4-linked β-D-manuronic and α-L-guluronic acid residues.[8,15,17] The biopolymer's chains display varying lengths and proportions and sequences of acid units depending on the source from which it was extracted. As might be expected, different alginates exhibit different physical and chemical properties. Jang et al.[4] determined that the binding capacity (K_1) of algin (Keltone grade sodium alginate) was about 0.123 g Cu^{2+}/g algin, and the conditional stability constant (K_c) was 1.56×10^4 L/mol.

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Using calcium aginate biosorbents on a practical scale requires knowledge of not only the thermodynamic parameters but also the kinetics of polymer–metal binding. This knowledge is important for selecting optimum operating conditions for full-scale metal removal from aqueous solutions. For example, flow rates and hydraulic residence times in reactors are both important parameters calculated from kinetic data.

The overall rate of binding (diffusion plus reaction) depends primarily on diffusivity.[2,11] Previous investigators[3,5] have calculated the diffusivities of heavy metals in biopolymers using the shrinking core model (SCM). This model, first developed by Yagi and Kunii,[21] was applied to fluid–particle chemical reactions by Levenspiel.[6] Later, based on concepts presented by Helfferich,[2] it was modified by Rao and Gupta[11] and applied to sorption of heavy metals in ion exchange resins. The model is based on the observation that when examining a cross section of a partly reacted solid particle, one often finds an unreacted core of material surrounded by an outer layer of reacted material. The dynamic picture is one of metal ions diffusing through a transformed shell material to a core of unreacted material that is progressively shrinking. Such a picture, though obviously simplified, permits an exact mathematical solution for kinetics of the ion exchange process. The SCM is described by the following equation (detailed derivation can be found in Rao and Gupta[11]):

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = \frac{6D}{R^2 C^0} \int_0^t C \, dt \qquad (1)$$

To implement this model, the slope of a plot of $F(X) = 1 - 3 \cdot (1 - X)^{2/3} + 2 \cdot (1 - X)$ vs. $\int C \, dt$ is calculated, where $X = [C_0 - C]/[C_0 - C_\infty]$. Diffusivity D is calculated from the slope of the above plot as $D = [\text{slope}] \cdot C^0 \cdot R^2/6$. Here C^0 is calculated from the total amount of copper bound over the course of an experiment and the total volume of alginate beads used (mol/m^3).

A series of experiments presented in this article show that the apparent suitability of the SCM to describe heavy metal sorption in alginate beads breaks down under closer inspection. The SCM calculated diffusivities of copper ions in a series of increasingly dense calcium alginate gels are not plausible.

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Instead of the SCM, this article presents a useful application of a linear absorption model (LAM), developed by Crank,[1] to describe this process. Major assumptions in this model are that rapid binding occurs between diffusing material and polymer, and that a dynamic equilibrium is established at every point throughout the bead. For these assumptions the differential equation of diffusion with reaction was solved using an infinite series approximation. In our judgment, the linear absorption model (LAM) is more realistic and generates more reasonable copper ion diffusion coefficients for experiments employing different density alginate beads.

EXPERIMENTAL

Beads of calcium alginate were exposed to solutions containing initial concentrations of 0.01 *M* KCl, 0.001 *M* Ca^{2+}, and 0.001 *M* Cu^{2+}. Experiments were run at a constant temperature of 25°C and employed calcium alginate beads prepared from 2%, 3%, 4%, and 5% sodium alginate solutions.

Sodium alginate solutions were prepared by dissolving the appropriate weight of the powder (Sigma low-viscosity form of *Microcystis pyrifera*) in demineralized water and diluting to 100 mL. Calcium chloride (1.0 *M*) was prepared by dissolving 147.0 g of the dihydrate (Baker analyzed) in demineralized water and diluting to 1 L. Cupric chloride solution (0.50 *M*) was prepared by dissolving 3.41 g of the hydrate in demineralized water and diluting to 100 mL. Calcium alginate beads were prepared by dripping sodium alginate into a 1-L beaker of slowly stirred calcium chloride (0.05 *M*) at room temperature. Calcium alginate first formed as a thin film around the sodium alginate droplet, holding it in a spherical shape. Stable calcium alginate beads formed on stirring for 24 h. A known volume, hence weight, of sodium alginate solution was used for each run. Diameters of 10 beads from a representative sample of each preparation were measured under a dissecting microscope. This information was used to calculate the bead volume and shrinkage which occurred during bead formation. Each preparation was rinsed a minimum of five times with 100 mL of demineralized water. Experiments used 105 ± 2 beads with radii of 0.208 ± 0.002 cm.

An experiment consisted of first equilibrating the beads for 6 h in a water-jacketed beaker containing 500 mL of an equilibration solution. This allowed the beads to come to equilibrium in terms of both osmotic pressure and calcium ion distribution. The equilibration solutions consisted of 0.01 *M* KCl and 0.001 *M* $CaCl_2$. Temperature was controlled to 0.1°C. To initiate the experiment 1 mL of 0.5 *M* cupric chloride was rapidly added to the beaker with stirring to give an initial Cu^{2+} concentration of 0.001 *M*; stirring at a constant rate was continued throughout the experiment. A 1.0-mL sample, diluted to 10.0 mL with 5% HCl, was taken before addition of the cupric chloride; additional samples were removed at appropriate times during the course of the reaction. A total of 10 samples were taken for each experiment. They were subsequently analyzed by atomic absorption spectroscopy for copper and calcium.

THEORETICAL BACKGROUND

Linear Absorption Model

A major assumption of the LAM is that the reaction or exchange rate is much faster than the rate of diffusion. If this condition is met, it is reasonable to say that the concentration of bound metal (S) is proportional to the concentration of free metal diffusing (C_b). A local equilibrium between free metal ion concentration and immobilized metal ion concentration exists at each point along the bead's radius:

$$S = K \cdot C_b \tag{2}$$

When the process being described is diffusion of a species along with reaction on internal surfaces or sites, the equation is referred to as a linear adsorption isotherm.[1] Equation (2) indicates that the concentration of bound metal is a linear function of the concentration of free metal. The constant K should not be confused with the equilibrium constant K_{eq} for the metal binding reaction.

Consider the case of a sphere of radius R in a solution of volume V with uniform initial concentration of solute C_0. Assuming that diffusion is only in the radial direction, the diffusion equation in spherical coordinates takes the form

$$\frac{\partial C_b}{\partial t} = D\left(\frac{\partial^2 C_b}{\partial r^2} + \frac{2}{r}\frac{\partial C_b}{\partial r}\right) - \frac{\partial S}{\partial t} \tag{3}$$

with the initial condition

$$C_b = 0 \qquad r < R \qquad t = 0 \tag{4}$$

and boundary condition

$$C_b = C_0 \qquad r = R \qquad t = 0 \tag{5}$$

An additional boundary condition is obtained from the fact that the rate at which solute leaves the solution is equal to that at which it enters the spherical bead (area = $4\pi R^2$):

$$V\frac{\partial C}{\partial t} = -4\pi R^2 D\frac{\partial C}{\partial r} \qquad r = R \tag{6}$$

It is also assumed that the solution is well stirred and the concentration of solute in the solution is only time dependent.

Equation (3) was solved using an infinite series approximation. The following equations describing temporal and spatial changes in the metal ion concentration were derived:

Free metal concentration in solution:

$$C(t_i, D) = \frac{\alpha C_0}{1+\alpha}\left[1 + 6(1+\alpha)\sum_{n=1}^{\infty}\frac{\exp\left(-\frac{D}{1+K}\frac{S_n^2}{R^2}t_i\right)}{9 + 9\alpha + \alpha^2 S_n^2}\right] \tag{7}$$

Free metal concentration within the bead ($0 < r \leq R$):

$$C_b(t_i, D) = \frac{\alpha C_0}{1 + \alpha}\left[1 + 6(1 + \alpha)\sum_{n=1}^{\infty} \times \frac{\exp\left(-\frac{D}{1 + K}\frac{S_n^2}{R^2}t_i\right)}{9 + 9\alpha + \alpha^2 S_n^2}\frac{R}{r}\frac{\sin\left(S_n\frac{r}{R}\right)}{\sin S_n}\right] \quad (8)$$

Because r appears in the denominator of Equation (8), the metal concentration in the center of the bead ($r = 0$) is calculated separately:

$$C_b(t_i, D)|_{r=0} = \lim_{r\to 0} C_b(t_i, D) = \frac{\alpha C_0}{1 + \alpha}\left[1 + 6 \times (1 + \alpha)\sum_{n=1}^{\infty} \frac{\exp\left(-\frac{D}{1 + K}\frac{S_n^2}{R^2}t_i\right)}{9 + 9\alpha + \alpha^2 S_n^2}\frac{S_n}{\sin S_n}\right] \quad (9)$$

where in Equations (7)–(9),

$$\alpha = \frac{C_\infty}{C_0 - C_\infty} \quad (10)$$

also,

$$\alpha = \frac{V/N}{4/3\pi R^3(1 + K)} \quad (11)$$

from which K is calculated as

$$K = \frac{V/N}{4/3\pi R^3 \alpha} - 1 \quad (12)$$

The S_n are the roots of Equation (13). For the purpose of further calculations 200 positive roots of this equation were calculated:

$$1 - \frac{S_n}{\tan S_n} = -\frac{\alpha}{3}S_n^2 \quad (13)$$

The above substitutions are the same as those used by Crank[1] in solving the mathematical model.

Evaluation of Diffusion Coefficient

Experimental data are obtained in the form of $C(t_i)$, where t is the time at which solution sample i ($i = 1, 2, 3, \ldots m$) is collected. Using this data in combination with Equation (7) derived above for $C(t_i, D)$, a "best fit" diffusion coefficient D can be calculated using a least squares procedure. The number of summation terms in Equation (7) was limited to N_1, a number sufficient to satisfy the required accuracy.

For the least squares procedure, the sum of the squares of the residuals, F, in Equation (14),

$$F = \sum_{i=1}^{m}[C(t_i) - C(t_i, D)]^2 \quad (14)$$

is minimized by setting the first derivative equal to zero.

$$\frac{\partial F}{\partial D} = \sum_{i=1}^{m}\left\{2[C(t_i) - C(t_i, D)]\left(-\frac{\partial C(t_i, D)}{\partial D}\right)\right\} = 0 \quad (15)$$

To simplify the presentation, the following three equations are substituted for constants in Equation (7):

$$f_{1n} = \frac{1}{9 + 9\alpha + \alpha^2 S_n^2} \quad (16)$$

$$f_{2n} = \frac{S_n^2}{(1 + K)R^2} \quad (17)$$

$$A = \frac{\alpha}{1 + \alpha}C_0 \quad (18)$$

Making these substitutions and solving for Equation (15) results in the equation

$$\sum_{i=0}^{m}\left\{t_i\left[C(t_i) - A(1 + 6(1 + \alpha))\sum_{n=1}^{N_1} f_{1n}e^{-f_{2n}Dt_i}\right] \cdot \sum_{n=1}^{N_1} f_{1n}f_{2n}e^{-f_{2n}Dt_i}\right\} = 0 \quad (19)$$

Newton's method was used to numerically solve for D in this nonlinear equation. Using this procedure, Equation (20) was iterated to obtain a converging value for D_n:

$$D_{n+1} = D_n - \frac{g(D_n)}{g'_D(D_n)} \quad (20)$$

In Equation (20), $g(D_n)$ is the left part of Equation (19) and $g'(D_n)$ is the first derivative of $g(D_n)$ with respect to D. The convergence criterion was $|D_{n+1} - D_n| \leq \epsilon_1$, where ϵ_1 was arbitrarily set to 10^{-8}.

In using Newton's method, the initial root of Equation (20), D_0, should be relatively close to the true value of D to avoid converging on secondary roots. It was found by setting $n = 1$ in Equation (7) and solving explicitly for an approximate D using the same least squares procedure [see Equation (21)]:

$$D_0 = \frac{\sum_{i=0}^{m}\ln\left[\frac{C(t_i) - A}{6\alpha(1 + \alpha)f_{11}}\right]t_i}{\sum_{i=0}^{m} f_{21}t_i^2} \quad (21)$$

Substituting D_0 into the iteration equation (20) permits calculation of the diffusion coefficient D. This value for D is accepted as the diffusivity of the metal ion in the polymer.

Equation (7) was used to calculate hypothetical solution metal concentrations, $C(t_i, D)$, for each time t_i using the best fit D determined above. This procedure gave us paired data consisting of experimental and theoretical bulk solution metal ion concentrations at sequential times.

RESULTS

The data collected during the experiments were interpreted using two models: (1) shrinking core model (SCM) and (2) linear absorption model (LAM).

Figure 1 shows the variation in Cu^{2+} ion concentration in solution for different density calcium alginate beads when all other experimental conditions remained the same. The temperature of the solution was maintained at 25°C and the initial Cu^{2+} concentrations were nearly identical. The curves

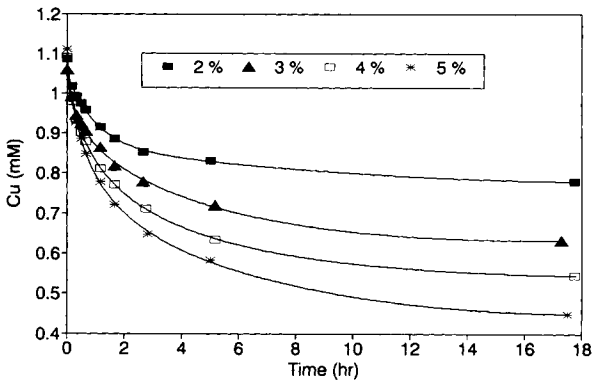

Figure 1. Variation of Cu^{2+} concentration in solution during the course of an experiment for different density alginate beads.

clearly show that more Cu^{2+} was absorbed by the beads of higher density. Absorption of Cu^{2+} by the beads in the initial 100 min was very fast and the process approached equilibrium after that.

Based on the data presented in Figure 1, the diffusion coefficients were calculated using SCM and LAM and displayed as a function of alginate bead density in Figure 2. The SCM calculated diffusion coefficients increased exponentially with increasing density of alginate in the beads. The LAM calculated diffusion coefficients were nearly constant over the range of alginate densities examined.

Figure 5 indicates that Cu^{2+} absorbed is a function of both initial solution calcium concentration and concentration of alginic acid in the beads. This implies that exchange of Cu^{2+} for calcium in alginate beads is not complete; an equilibrium situation exists.

DISCUSSION

Both the SCM and LAM take diffusion and chemical reaction into account. However, there are some critical differences in the assumptions they make.

The assumptions in the SCM are that within the bead:

1. Chemical reaction rate far exceeds the metal ion diffusion rate.
2. The concentration of freely diffusing metal ions approaches zero at the surface of the shrinking core where total and irreversible reaction takes place.
3. The outer reacted (chelated) shell is inert to the diffusing metal ions (Cu^{2+}).
4. The shrinkage of the unreacted core is much slower than the mass transfer of metal ions toward the core.

In the LAM, it is assumed that within the bead:

1. The chemical reaction rate far exceeds the metal ion diffusion rate.
2. Absorption is linear, that is, the concentration of the immobilized metal ions at every point in the bead is directly proportional to that of the freely diffusing metal ions.
3. Some unoccupied reaction sites in the biopolymer matrix are always available for immobilization of the diffusing metal ions.

The SCM assumes that metal ions are rapidly and totally consumed at the core–shell interface, while the LAM assumes that equilibrium develops between bound and unbound species at every point in the bead. The significance of this is that, in the SCM, the shell is inert to ions diffusing toward the unreacted zone, a characteristic not shared with the LAM. The LAM free metal ion concentration gradient is due to a combination of diffusion and equilibrium while the SCM gradient is a consequence of diffusion alone. The equilibrium assumption in the LAM model states that the concentration of bound metal ions is a linear function of the concentration of free metal ions in the interstitial solution. Both models display continuous but dissimilar metal ion concentration gradients.

Figure 3 shows simulated profiles of Cu^{2+} ion concentration along the radius of a bead at various times during the course of an experiment. To compare the two models, the variations in free Cu^{2+} concentration along the radius of a bead at one arbitrary time during the middle

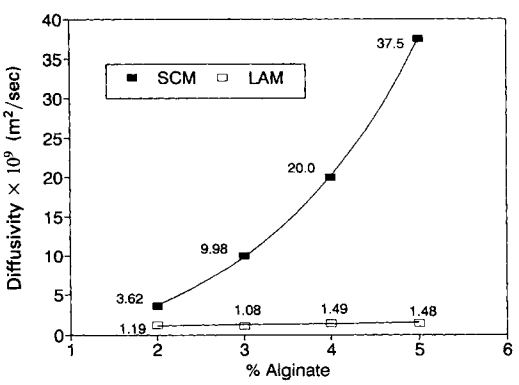

Figure 2. Variation in the diffusion coefficient of Cu^{2+} as a function of alginate density in the beads, calculated from the SCM and LAM.

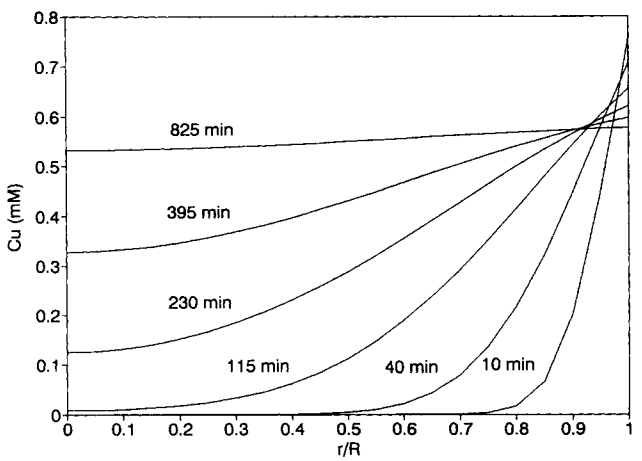

Figure 3. Profiles of the Cu^{2+} concentration along the radius of a bead at different times during the course of an experiment, calculated from the LAM.

of an experiment (115 min) are plotted in Figure 4. The difference in profiles are evident.

When compared to diffusion coefficients in water, diffusion coefficients in calcium alginate gels have been reported to decrease for large molecules such as proteins and polysaccharides and remain nearly constant for smaller molecules like ethanol and glucose.[8,18,19]

Westrin and Axelsson[22] present a good discussion of diffusion coefficients in gels. In general, a solute exhibits an effective diffusion coefficient in a gel polymer which is smaller than its diffusion coefficient in water. The polymer first reduces the volume available for the solute to move in; this is termed the exclusion effect. Second, the inpenetrable part of the polymer increases the path length for movement of the solute; this is termed the obstruction effect. The predictive value of these concepts is limited but is useful in visualizing the process.

Jang et al.[3] measured the diffusion coefficient for Cu^{2+} in 3.2% calcium alginate gel and found it to be in the range of 1.0×10^{-9}–1.4×10^{-9} m^2 s^{-1}. The diffusion coefficient for Cu^{2+} in water has been measured by Marcinkowsky and Phillips[7] using radioactive tracers and by Quickenden and Jiang[10] using a rotating disk electrode. Both investigators measured diffusion coefficient in the range of 0.62×10^{-9}–0.75×10^{-9} m^2 s^{-1}. The results consistently show that diffusion coefficients of small species in calcium alginate are close to those in water.

The two models calculate significantly different diffusivities from our experimental data. Calculations using the LAM (Fig. 2), indicate a diffusion coefficient in the range of 1.19×10^{-9}–1.48×10^{-9} m^2 s^{-1} over a series of bead densities ranging from 2% to 5%. This is in good agreement with Jang's result for 3.2% algin beads and also consistent with the view that polymer gel does not significantly affect diffusivities of small diffusing species. The diffusion coefficients calculated using the SCM exponentially increase from 3.62×10^{-9} up to 37.5×10^{-9} m^2 s^{-1} over the same range of bead densities. This behavior is not easily explainable and is in clear disagreement with the values calculated from the LAM.

A discussion about the SCM constant C^0 is warranted at this time. Here C^0 is defined as the average density of Cu^{2+} binding sites in the alginate gel bead. In the original implementation of the model,[11] where irreversible total reaction is assumed, it is defined as the initial concentration of desorbing ion in the bead (e.g., calcium). Actually, the driving force for diffusion at any time t is the remaining *available* calcium. If, as in our case, not all the calcium desorbs (see Fig. 5), C^0 can be thought of as the initial concentration of *available* calcium, i.e., the difference between initial and final concentrations of calcium in the beads.

Unfortunately, this presents a dilemma in rationalizing one of the basic assumptions of the SCM. If, as in our case, complete reaction does not take place at the shell–core interface, then the shell is not inert to Cu^{2+} ions and diffusion is not the only process occurring within the shell.

Implicit in the assumptions for both the SCM and LAM is that binding sites are uniformly distributed throughout the bead. Evidence exists to the contrary.[9,14] The biopolymer is more concentrated toward the outside of the bead. If diffusion is assumed to be independent of biopolymer concentration, as our calculations using the LAM suggest, then reaction would be initially faster in the actual bead than either model implies.

It has already been noted that other assumptions made in the SCM may not be realistic.[6] In particular, the assumption that reaction occurs entirely at a sharp interface between reacted and unreacted zones is probably not accurate. Our measurements confirm these doubts. When comparing the diffusivities calculated from the LAM and SCM with literature observations, it is evident that the SCM provides unrealistic values and therefore should be rejected in this application. Instead, the LAM, which generates diffusivities which are consistent with expectations, should be used.

CONCLUSIONS

Two numerical algorithms, the LAM and the SCM, used for calculating Cu^{2+} ion diffusion coefficients from experimental calcium alginate gel bead data, were described and compared. From the results it is seen that the LAM is

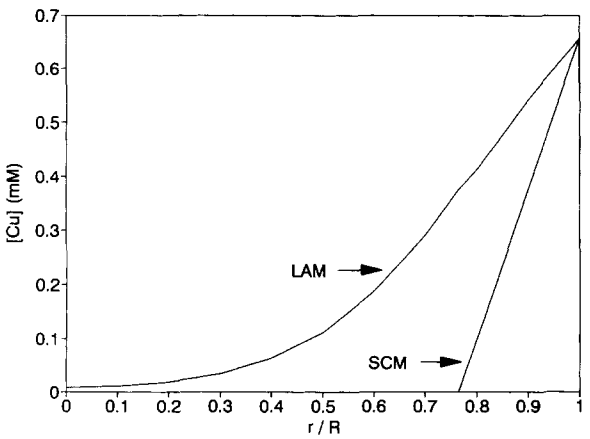

Figure 4. Profiles of the Cu^{2+} concentration along the radius of a bead after 115 min, calculated from the SCM and LAM.

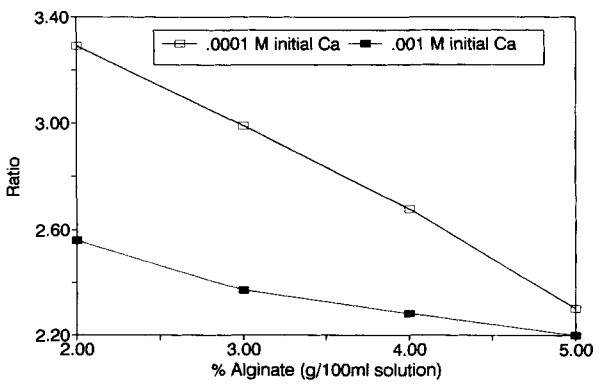

Figure 5. Ratio of mass of Cu^{2+} absorbed to total mass of alginate as a function of alginate density in the beads.

preferable to the SCM for the copper–calcium alginate gel system studied in this lab. When the density of calcium alginate in the gel is increased, nearly constant diffusion coefficients are calculated with the LAM; the SCM, on the other hand, predicts exponentially increasing diffusion coefficients.

The major contributions of this article are (1) application of the LAM to successfully interpret the experimental data of Cu^{2+} binding in alginate biopolymer beads and (2) the measured diffusion coefficients which remain nearly constant under a useful range of alginate gel densities. Diffusion coefficients for Cu^{2+} ions in calcium alginate gels are in good agreement with results from other investigators and range from 1.19×10^{-9} to 1.48×10^{-9} m^2 s^{-1} over a series of bead alginate densities ranging from 2% to 5%.

The model provides credible diffusion coefficients for use in process calculations. Although the model was applied here only to interpret data from Cu^{2+} binding to spherically shaped polymer beads, its application is not necessarily limited to this situation. It is expected that the model will behave correctly everywhere the SCM has been used, e.g., behavior of metal ions in ion exchange resins.

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NOMENCLATURE

C	concentration of free metal in solution (mol/m^3)
C_b	concentration of free metal within bead (mol/m^3)
C_0	initial concentration of free metal in solution (mol/m^3)
C^0	average Cu^{2+} binding site density of alginate gel (mol/m^3)
C_∞	concentration of free metal in solution at equilibrium (mol/m^3)
D	biopolymer diffusion coefficient (m^2 s^{-1})
i	sample number
K	proportionality constant
N	number of beads in reactor
N_1	number of roots in Equation (13)
r	distance from center of bead (m)
R	radius of bead (m)
S	concentration of bound metal (mol/m^3)
S_n	roots of Equation (13)
t	time (s)
V	volume of solution (m^3)
α, A, f_{1n}, f_{2n}	constants

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