Communication to the Editor

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

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Calculations of the diffusivity of Cu^{2+} in calcium alginate gel beads using the shrinking core model were checked by us. Corrected results are reported here. Diffusivity was still found to increase with increasing alginate concentration, but at a lower rate than reported in the cited paper. The diffusivity increased by a factor of 2 over the range of alginate concentrations studied rather than 10. The original data is included with sample calculations.
Key words: copper • biosorption • biopolymers • diffusion • alginate gel

INTRODUCTION

The accompanying article by Jang, "Diffusivity of Cu^{2+} in calcium alginate," recalculated some of our results presented in an article by the same title and suggested that the two models compared gave essentially identical results.[2] Because Jang did not have the original numerical data and used a graph to extract the experimental data, his calculations are slightly off. We recalculated our results and found that our numerical solution to the shrinking core model (SCM) contained an error. Our recalculations indicate that the increase in the diffusivity resulting from the increase in the polymer concentration did show a trend, but the increase should be approximately a factor of 2, not 10, as we previously reported (Fig. 1). Although diffusivities calculated from those two models are not as far apart as we previously thought, the SCM still indicated a trend in the data that was not expected. The numerical error does not change our claim that the linear absorption model has obvious advantages over the SCM. The former provides more insight into the diffusion processes in the bead and the treatment is more rigorous.

The SCM diffusivity data, reported graphically in Figure 2 of our original article, should be replaced by the diffusivities in the last row of Table II of this communication.

CALCULATIONS

Calculation of diffusivity of copper^{2+} in calcium alginate gel beads using the SCM relies on solving for D in the equation.

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

where

X_t = the extent of reaction, $[C_i - C_t]/[C_i - C_\infty]$, at time t
C_t = concentration of free metal in solution at time t (mol/m^3)
C_i = initial concentration of free metal in solution (mol/m^3)
C_∞ = concentration of free metal in solution at equilibrium (mol/m^3)
C^0 = average Cu^{2+} binding site density of the alginate gel (mol/m^3)
D = biopolymer diffusion coefficient (m^2/s)
R = radius of the bead (m)

The average Cu^{2+} binding site density of the alginate gel, C^0, is calculated according to the equation

$$\frac{(C_i - C_\infty)V}{N \cdot \frac{4}{3}\pi R^3} \quad (2)$$

where

N = number of beads in the reactor
V = volume of solution in the reactor (m^3)

To implement this model the slope of a plot of $F(X_t) = 1 - 3 \cdot (1 - X_t)^{2/3} + 2 \cdot (1 - X_t)$ vs. $\int_0^t C \, dt$ is determined. The term $\int_0^t C \, dt$ was evaluated graphically using the trapezoid rule. The slope, in units of mM^{-1} min^{-1}, was converted to units of M^{-1} s^{-1} by dividing by 0.06 (M/mM × s/min). Diffusivity, D, is then calculated from the slope of the above plot: $D = [\text{slope}] \cdot C_0 \cdot R^2/6$.

SAMPLE CALCULATION

Data found in the appendix were used to calculate D for diffusion of Cu^{2+} in beads formed from the 5% alginate solution. First, $F(X)$ was plotted against $\int_0^t C \, dt$ (Table I) to obtain a linear slope of 0.0327 M^{-1} s^{-1}. Second, the average binding site density of the spheres (0.00631 mol/L) was calculated from the reactor fluid volume (0.5 L), the radius of the beads, R, and the initial and final concentrations of Cu^{2+} (Table II). Finally, D was calculated (1.86×10^{-5} cm^2/s) from the expression $D = [\text{slope}] \cdot C^0 \cdot R^2/6$.

For each data set, except for the 2% alginate beads, all points were used in the least squares regression calculations (nine data points for 3%, 4%, and 5% alginate beads); for

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Table I. Calculations for SCM Model (actual data).

	Cu^{2+} (mM)	X	$F(X)$	$\int_0^t C\,dt$ (mM − min)
		2% Alginate beads		
0	1.066	0.000	0.000	0.0
10	1.004	0.222	0.019	10.3
22	0.987	0.278	0.030	22.3
30	0.971	0.333	0.044	30.1
40	0.945	0.417	0.073	39.7
70	0.903	0.556	0.142	67.4
100	0.874	0.653	0.213	94.1
179	0.840	0.764	0.327	161.8
240	0.823	0.819	0.403	212.5
295	0.819	0.833	0.425	257.7
782	0.769	1.000	1.000	644.3
		3% Alginate beads		
0	1.050	0.000	0.000	0.0
10	0.982	0.160	0.009	10.2
20	0.935	0.270	0.028	19.7
30	0.914	0.320	0.040	29.0
40	0.897	0.360	0.052	38.0
70	0.854	0.460	0.091	64.3
100	0.807	0.570	0.151	89.2
160	0.769	0.660	0.219	136.5
310	0.709	0.800	0.375	247.4
1038	0.624	1.000	1.000	732.9
		4% Alginate beads		
0	1.086	0.000	0.000	0.0
10	0.975	0.203	0.015	10.3
20	0.928	0.289	0.032	19.8
30	0.894	0.352	0.050	28.9
40	0.872	0.391	0.063	37.8
70	0.804	0.516	0.119	62.9
100	0.766	0.586	0.162	86.4
165	0.706	0.695	0.252	134.3
310	0.629	0.836	0.430	231.0
1065	0.539	1.000	1.000	672.0
		5% Alginate beads		
0	1.057	0.000	0.000	0.0
A 10	0.941	0.176	0.011	10.0
20	0.876	0.275	0.029	19.1
30	0.832	0.340	0.046	27.6
40	0.794	0.399	0.066	35.7
70	0.724	0.503	0.112	58.5
100	0.668	0.588	0.164	79.4
170	0.595	0.699	0.255	123.6
300	0.530	0.797	0.371	196.7
1050	0.396	1.000	1.000	453.9

the 2% alginate beads only the first nine points were used. In addition, the regression lines were forced through zero Y intercept.

Table II. Calculation of diffusivities of Cu^{2+} in alginate beads from SCM model (actual data).

	2% Alginate	3% Alginate	4% Alginate	5% Alginate
Number of beads	105	104	103	100
Radius of beads (cm)	0.21	0.214	0.225	0.233
Cu(II) initial (mM)	1.07	1.05	1.09	1.06
Cu(II) final (mM)	0.769	0.624	0.539	0.396
Binding site density (M, $\times 10^2$)	3.69	4.99	5.61	6.31
Slope (1/mM − min, $\times 10^3$)	1.97	1.54	1.86	1.94
Slope (1/M − s)	32.88	25.64	30.98	32.32
Diffusivity (cm^2/s, $\times 10^5$)	0.89	0.98	1.47	1.84

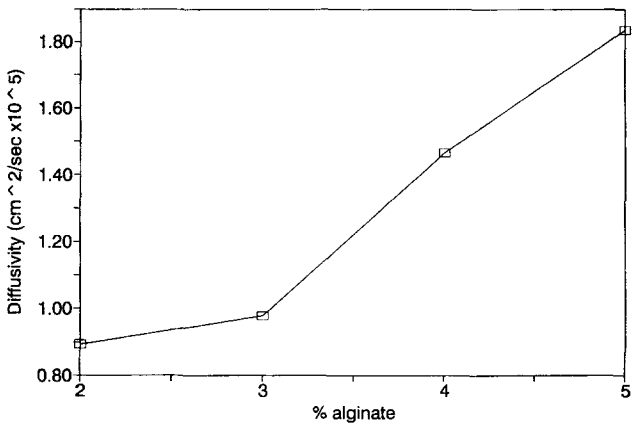

Figure 1. Diffusivity of copper(II) as a function of alginate concentration.

References

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