Research Article

Boron removal from aqueous solutions using alginate gel beads in fixed-bed systems

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Abstract

BACKGROUND: A column sorption study was carried out using calcium alginate gel beads as adsorbent for the removal of boron from aqueous solutions. The breakthrough curve was obtained as a function of pH, initial concentration of boron, feed flow rate, adsorbent mass and column diameter. The breakthrough capacity values and adsorption percentage of calcium alginate gel for boron were calculated. Column data obtained at different conditions were described using the Adams–Bohart model and bed-depth service time (BDST), derived from the Adams–Bohart equation to predict breakthrough curves and to determine the characteristic column parameters required for process design.

RESULTS: The maximum adsorption percentage of boron on calcium alginate gel beads using an initial concentration of boron of 50 mg L^{-1} at pH 11 and room temperature (20$\pm$1°C) was calculated to be 55.14%.

CONCLUSION: The results indicated that calcium alginate can be used in a continuous packed-bed column for boron adsorption. The optimal conditions for boron adsorption were obtained at high pH, higher initial boron concentration, increased column depth and lower flow velocity.
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Keywords: sorption; boron; alginate; removal

INTRODUCTION

The increase in our knowledge of boron science in recent years has been of great importance both commercially and environmentally. Boron enters the hydrosphere naturally through the erosion of rocks, but its presence in water is increasingly attributed to pollution caused by industrial growth. Boron is an essential trace element for plant growth and human health but in excessive quantities it can affect human reproduction and lead to diseases of the nervous system. Boron has many industrial applications, particularly in the manufacturing of glass, detergents, ceramics and catalysts, but it is also used for its preservative and refrigerant properties. In all of these uses, boron is mainly released into the environment through industrial wastewater discharge. In recent years, boron has been identified as an essential element in chemical processes. In the natural environment, it is found mainly as boric acid or borates. In aqueous solutions at a boron concentration below 270 mg L^{-1}, boric acid is very weak and acts as a Lewis acid, as shown below:

$$B(HO)_3 + 2H_2O \leftrightarrow B(HO)_4^- + H_3O^+; \ pK_a = 9.23 \tag{1}$$
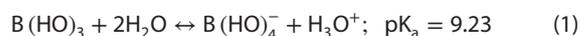
where the acid dissociation constant is pKa = 9.23.[1] The relative concentration of the tetrahydroxyborate anion increases with increasing pH and becomes the dominant species at pH 9.2. However, at higher concentrations and with increasing pH, especially above pH 11, polynuclear ions such as

$[B_3O_3(OH)_5]^{2-}$ and $[B_4O_5(OH)_4]^{2-}$ form.[2] Formation of these species is a direct result of boron's tendency to form complexes with electron-donor species including oxygen, which attaches to the boron itself.[3]

Boron's electrophilicity and tendency to form esters through condensation with compounds bearing hydroxyl groups, including B-OH, make it particularly suitable for widespread industrial use. The increased presence of boron in the natural environment has led to the creation of guidelines that establish recommended limits for boron content in water used for irrigation and human consumption. According to the World Health Organization (WHO),[4] the guideline value for boron concentration in drinking water is 2.4 mg L^{-1}. Alongside this, the need for new sources of drinking water has led to the development of desalination processes for obtaining potable water from seawater. The boron content of seawater is approximately 5 mg L^{-1}, and after desalting

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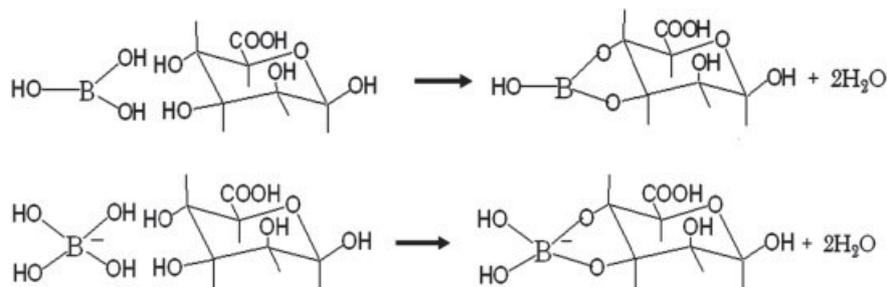
Figure 1. Possible interactions of boric acid and tetrahydroxyborate with diol groups of alginate.

the resulting water still has high boron content, making it unsuitable for human consumption and, in certain cases, even for use in irrigation. It is therefore unsurprising that recent years have seen numerous efforts to develop new processes for removing boron from water, including reverse osmosis membranes,[5] ionic exchange resins,[6] anion exchange membranes,[7] electrocoagulation and chemical coagulation.[8] Many of these methods are effective, but the high cost involved makes them difficult to apply at the industrial level. Another removal technique that deserves special attention is adsorption. The adsorption process has become particularly important in this field due to the low cost of the adsorbents used to separate/recover boron from water, many of which are waste materials from a range of industrial processes. Studies using Sepiolite,[9] Siral-30 and Pural,[10] bentonite,[11] red mud,[12] ash,[13] and impregnate carbon[14] have been carried out for this purpose. However, the use of biopolymers for boron adsorption has received little attention in the last decade. The literature describes the possible use of cotton cellulose[15] or chitosan modified with N-methylglucamine,[16] sugars,[17] polyols,[18] and calcium alginate gel beads.[19] However, although all of these studies discuss adsorption capacity or adsorption rate, none describes a continuous examination of the industrial application of the adsorbent. Consequently, this paper evaluates the use of calcium alginate gel beads in fixed-bed systems under several experimental conditions as a potential adsorbent for industrial-scale removal of boron from wastewater. Calcium alginate was chosen as the adsorbent because it is a polymer rich in hydroxyl groups. Alginates are linear unbranched polymers containing β-(1→4)-linked D-mannuronic acid (**M**) and α-(1→4)-linked L-guluronic acid (**G**) residues. The pKa values for mannuronic and guluronic acid are 3.38 and 3.65, respectively. Alginate gelation takes place when divalent cations (usually Ca^{2+}) interact ionically with blocks of guluronic acid residues, resulting in the formation of a three-dimensional network which is usually described by an 'egg-box' model.[20] The presence of OH^- groups enables the formation of complexes by reaction of boron compounds (Fig. 1). Obtaining a model to accurately describe the dynamic behaviour of the adsorption process in a fixed-bed system is inherently difficult. Although several models based on fundamental mass-transport mechanisms – including external film, and pore and surface diffusion – have been proposed, their application involves the use of complex numerical methods to solve a number of differential equations. To make the process easier, various simple mathematical models have been proposed for predicting the dynamic behaviour of the column, including the Adams–Bohart model and the bed-depth service time (BDST) design model,[21] which is derived from the Adams–Bohart equation. These simplified models are used in this study to optimize boron sorption on calcium alginate gel beads.

EXPERIMENTAL
Materials
Sodium alginate was supplied by Panreac as a power material. Boron solutions were prepared from boric acid (supplied by Merck) in demineralized water. The pH of each solution was adjusted using concentrated solutions of HCl and NaOH. HCl, NaOH and calcium nitrates were supplied by Panreac.

Synthesis of calcium alginate gel beads
For bead production, a solution of sodium alginate at 2% w/w was prepared. This solution was shaken at 800 rpm for a minimum of 5 h until completely homogenized. Next, the stirring speed was lowered to approximately 50 rpm to allow air to be dissipated and prevent the formation of air bubbles, which affect the manufacturing process. The viscous solution was then pumped and distributed drop-wise through a thin nozzle (diameter 0.6 mm) into a 0.05 mol L^{-1} calcium nitrate solution under continuous agitation. The alginate drops coagulated in the calcium nitrate solution and formed perfectly spherical beads with an average diameter of 2 ± 0.2 mm.

Sorption studies in batch and column systems
The effect of initial pH on boron sorption by calcium alginate gel beads was examined in a batch system. Beads containing 0.7 g of alginate were contacted with 100 mL of the boron solution (50 mg L^{-1}) in flasks at the desired pH. The flasks were agitated on a shaker at 50 rpm and room temperature ($20 \pm 1°C$) for 78 h, which is more than ample time for sorption equilibrium. Samples were then filtered through 1.2 μm filtration membranes and the boron content was analysed by the Azomethine-H method in a spectrophotometer (Varian UV-visible).[22] At the same time, the calcium release from the beads during the adsorption process was analysed by atomic absorption in a fast sequential atomic absorption spectrometer (Varian AA240FS).

For the study of sorption in continuous systems, columns of different diameters (1.2 and 1.6 cm) were filled with different amounts of the sorbent (0.39, 0.50, 1.44 and 3.5 g) to obtain different column depths (12, 15 and 18 cm) and fed with boron solutions (pH 6 and 11) at different flow rates (0.17 and 0.91 mL min^{-1}). Samples were regularly collected and analysed. Randomly, some breakthrough curves were duplicated, proving that experiments are reproducible (within an error lower than 7% in the breakthrough volume and with a similar breakthrough slope). Table 1 shows the different experimental conditions used for the column study.

Empirical modelling of breakthrough curves
The performance of packed beds is described through the concept of the breakthrough curve. Breakthrough curves are usually

Table 1. The effect of the operational parameters

									Adsorption parameters
Columnno.	C_0 (mg L^{-1})	pH	m (g)	Z (cm)	Ø (cm)	Q (mL min^{-1})	q_{total} (mg)	q_{eq} (mg g^{-1})	Boron removal (%)
pH									
I	59	**6**	0.50	15	1.6	0.91	1.53	3.03	24.18
II	59	**11**	0.50	15	1.6	0.91	4.93	9.86	38.01
Initial concentration of boron, C_0 (mg L^{-1})									
III	**10**	11	1.44	18	1.6	0.91	0.59	0.36	42.10
IV	**25**	11	1.44	18	1.6	0.91	2.99	2.07	43.56
V	**50**	11	1.44	18	1.6	0.91	5.29	3.88	55.14
Alginate mass, m (g)									
VI	59	11	**0.39**	12	1.6	0.91	3.89	9.96	30.74
II	59	11	**0.50**	15	1.6	0.91	4.93	9.86	38.01
Flow rate, Q (mL min^{-1})									
VII	10	11	3.50	18	2.6	**0.17**	1.59	0.45	32.44
VIII	10	11	3.50	18	2.6	**0.91**	1.51	0.45	29.90
Diameter, Ø (cm)									
III	10	11	1.44	18	**1.6**	0.91	0.59	0.36	42.10
VIII	10	11	3.50	18	**2.6**	0.91	1.51	0.45	29.90

expressed in terms of the ratio of effluent boron concentration to inlet boron concentration (C/C_0) as a function of time or effluent volume for a given bed height.[23] Effluent volume (V_{eff}) can be calculated as follows:

$$V_{eff} = Q\, t_{total} \qquad (2)$$

where t_{total} and Q are the total flow time (min) and volumetric flow rate (mL min^{-1}), respectively. The area under the breakthrough curve (A), obtained by integrating the adsorbed concentration (C_{ad}; mg L^{-1}) versus t (min) plot, can be used to determine the total adsorbed boron quantity (maximum column capacity). The total adsorbed boron quantity (q_{total}; mg) in the column for a given feed concentration and flow rate is calculated as follows:

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad}\, dt \qquad (3)$$

The total amount of boron fed to the column (m_{total}; g) is calculated from the following equation:

$$m_{total} = \frac{C_i Q t_{total}}{1000} \qquad (4)$$

The total percentage removal of boron is determined from the ratio of total adsorbed quantity of boron (q_{total}) to the total amount of boron passing through the column (m_{total}):

$$Total\, removal\,\% = \frac{q_{total}}{m_{total}} 100 \qquad (5)$$

The sorption capacity of the column is defined as the total amount of boron sorbed (q_{total}) per gram of sorbent ($m_{sorbent}$) at the end of the total flow time:

$$q_e = \frac{q_{total}}{m_{sorbent}} \qquad (6)$$

The fundamental equation describing the relationship between C/C_0 and t in a continuous system was established by Bohart and Adams[23] in 1920 and, although it was originally applied to a gas–solid system, it has been widely used to describe and

quantify other systems. This model assumes that the sorption rate is proportional to the residual capacity of the solid and the retained species concentration and is used to describe the initial part of the breakthrough curve:[24,25]

$$\frac{C_t}{C_0} = \frac{\exp\left[kC_0 t\right]}{\exp\left[kN_0 Z/v\right] - 1 + \exp\left[kC_0 t\right]} \qquad (7)$$

where N_0 is the volumetric sorption capacity (mg L^{-1}), and is equal to $q(C_0)(1-\epsilon)\rho/\epsilon$, where ρ represents the volumetric mass (mg L^{-1}) and ϵ is the column voidage, which varied between 0.77 and 0.83 with the beads used in this study. The average column voidage value was used for calculations. The parameter k is the kinetic constant (L mg^{-1} min^{-1}) and v represents the linear flow velocity (cm min^{-1}) ($v = U_0/\epsilon$), U_0 is the superficial flow velocity (cm min^{-1}) ($U_0 = Q/S$), Q is the flow rate (cm^3 min^{-1}) and S is the cross-section area of the column (cm^2). The advantages of this model are its simplicity and its reasonable accuracy in predicting breakthrough under various conditions.

The linearized form of the Bohart and Adams model can be expressed as follows:

$$\ln\left[\frac{C_0}{C_t} - 1\right] = \ln\left[\exp\left(\frac{kN_o Z}{v}\right) - 1\right] - kC_0 t \qquad (8)$$

where t is the service time of the breakthrough curve (min), N_0 is the volumetric sorption capacity (g L^{-1}), k is the kinetic constant (L mg^{-1} min^{-1}), Z is the depth of the bed (cm), C_0 (mg L^{-1}) is the initial boron concentration, C_t (mg L^{-1}) is the effluent boron concentration and v is the linear flow rate (cm min^{-1}).

Hutchins[26] (1973) proposed a linear relationship between the service time and the weight of the adsorbent. As the exponential term is usually much larger than unity, the unity term in the brackets on the right-hand side of Equation (4) is often neglected, leaving:

$$\ln\left[\frac{C_0}{C_t} - 1\right] = \frac{kN_o Z}{v} - kC_0 t \qquad (9)$$

Solving the above equation for t,

$$t = \frac{N_o}{C_0 \upsilon} Z - \frac{1}{C_0 k} \ln \left(\frac{C_0}{C_t} - 1 \right) \qquad (10)$$

Equation (10) is the bed depth service time (BDST). According to this equation, the service time, t, and the bed depth, Z, can be correlated with the following process parameters: the initial solute concentration, the solution flow rate, the sorption capacity and the sorption rate constant.

Setting $t = 0$ and solving Equation (10) for Z yields

$$Z_0 = \frac{\upsilon}{k N_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \qquad (11)$$

where Z_0, the critical bed depth, is the theoretical depth of sorbent required to prevent the sorbate concentration from exceeding the limit concentration C_b, defined as a limit concentration or a fixed percentage of the inlet concentration, generally 5%. The breakthrough point is the time required to reach this 5% concentration, while the exhaustion point is defined as the time at which the outlet concentration reaches 100% of the inlet concentration.

Another important parameter is the coefficient s_0, which is defined using the Hutchins equation. It represents the time required for the adsorption wave front to pass through the critical bed depth and is obtained from the following expression:

$$s_0 = \frac{1}{k C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \qquad (12)$$

The coefficient s is the slope of Equation (6). It represents the time required to exhaust a unit length of the column under the selected experimental conditions and with the limited outlet concentration:

$$s = \frac{N_o}{C_0 \upsilon} \qquad (13)$$

The experimental curves were mathematically modelled through the Bohart–Adams model, Equation (8), using the Macro Solver from Microsoft Excel. From the theoretical breakthrough curves and according to Equation (9), the value of k can be obtained from the slope of the plot $\ln[C_0/C_t - 1]$ versus breakthrough time t, and the parameter N_0 from the intersection with the axis at time $t = 0$.

RESULTS AND DISCUSSION

Effect of initial pH-calcium release

The pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the interaction between the boron species in solution, the adsorptive sites of the adsorbent and the species present in the solution. In the low pH region most of the carboxylic acid groups in the alginate were in the form of –COOH, as the pKa of alginate is approximately 3.2. At this pH boron exits in a neutral form, showing no interaction with the adsorbent. Figure 2 shows that when working at acidic pH there is increased release of calcium ions into the solution. At acidic pH, the high concentration of protons in the solution causes an ion exchange between the protons and the calcium ions in the beads. The concentration of boric acid in the solution is much lower than the concentration of protons, so the flow of protons into the adsorbent prevents the
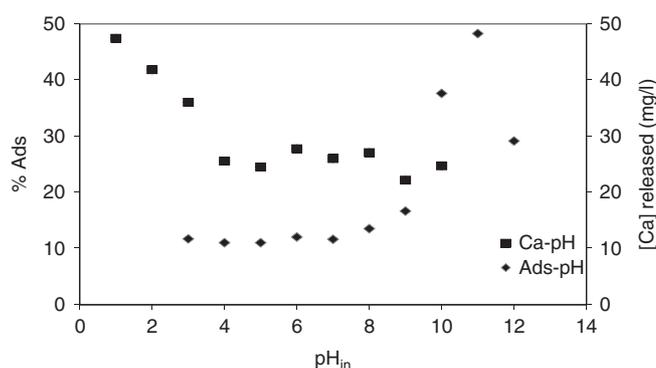

Figure 2. Influence of pH on the percentage adsorption by calcium alginate gel beads and in the calcium released to the solution during the process of adsorption (room temperate (20 ± 1°C); initial concentration of boron, 50 mg L^{-1}; alginate mass, 0.7 g).

adsorption of boron by the beads. From pH 4–5 calcium release remains practically constant. Calcium is released into the solution by diffusion, due to the difference in concentration of calcium ions between the interior of the beads and the calcium present in the solution. When the pH of the medium increases the carboxylic acid groups of the alginate are ionised. In the case of calcium alginate, the negative surface density is partially neutralized by the presence of calcium ions in the beads but it is interesting to note that the surface charge density increases as the solution's pH increases. At pH 6 and 8, boron exits predominantly in the neutral boric acid form. As the pH increases the concentration of protons in the solution decreases, allowing the boron to access the adsorbent more easily where it reacts with the hydroxyl groups in the alginate beads to form boron esters. At pH 9 and above the negatively charged form (borate) increases and the interaction between boron and the adsorbent increases (Fig. 2). The hydroxide groups in the solution are not attracted to the adsorbent, allowing the boron to be more easily adsorbed. Figure 2 shows that the maximum adsorption is produced at pH 11. Above pH 11, negatively charged polynuclear species can form and the negatively charged bead surface increases. Charge repulsion prevents the negatively charged borate species from interacting with the adsorbent, reducing the adsorption rate.

The column experiments were conducted at bed depth of 1.6 cm with a flow rate of 0.9 mL min^{-1}, initial concentration 10 mg L^{-1} at pH 6 and 11. The breakthrough curve C/C_0 versus V_{eff} at pH 6 and 11 is shown in Fig. 3. When pH was increased from 6 to 11, the breakthrough volume increased from 7.45 to 14.25 mL. Boron uptake at influent pH 6 and 11 was 3.03 and 9.87 mg g^{-1}, respectively, under these experimental conditions.

Effect of inlet boron concentration

The sorption breakthrough curves obtained by changing the inlet boron concentration from 10 to 50 mg L^{-1} at flow rate 0.91 mL min^{-1}, pH 11, column diameter 1.6 cm, column depth 18 cm and with 1.44 g of adsorbent are given in Fig. 4. The breakthrough curves became steeper and breakthrough volume decreased when boron concentration was increased from 10 to 50 mg mL^{-1}, as higher boron concentration leads to a higher boron loading rate which decreases the adsorption zone length due to the weaker driving force or lower mass-transfer flux from the bulk solution to the particle surface. The main effect is an increase in adsorption capacity with increasing boron concentration as shown in Table 1.
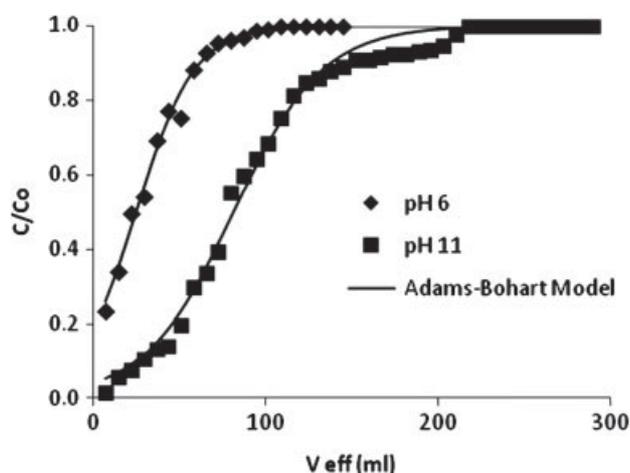
Figure 3. Comparison of the experimental data and predicted breakthrough curves obtained at different pH according to the Adams–Bohart model (room temperature (20±1°C); initial boron concentration 59 mg L^{-1}; flow velocity 0.91 mL min^{-1}; adsorbent mass 0.5 g; column depth 15 cm).
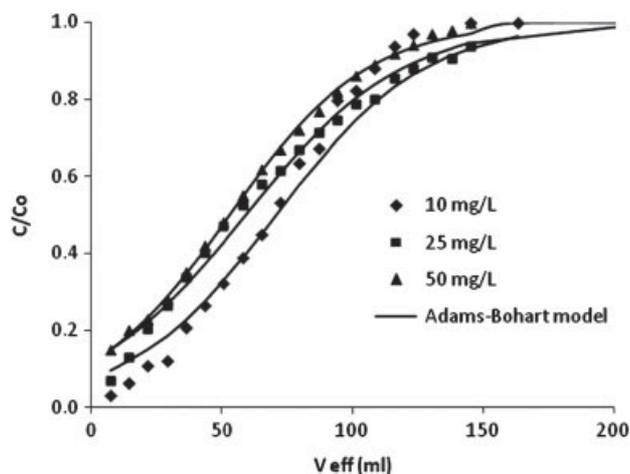

Figure 4. Comparison of the experimental data and predicted breakthrough curves obtained at different inlet boron concentrations according to the Adams–Bohart model (room temperature (20±1°C); pH 11; adsorbent mass, 1.44 g; flow rate, 0.91 mL min^{-1}; column depth, 18 cm).

Table 2 shows the standard Adams–Bohart and Hutchins coefficients of the BDST model calculated from Equations (8–10). The kinetic parameter k varies continuously with the concentration; when the inlet concentration increases a decrease of parameter k is observed. As expected, increasing the inlet concentration increases the volumetric capacity of the sorbent in the column from 1.12 to 4.24 g L^{-1}. The volumetric sorption capacity, N_0 (kg m^{-3}), is equal to $q(C_0)(1-\epsilon)\rho/\epsilon$, so N_0 is directly proportional to $q(C_0)$. When the adsorption capacity increases, the volumetric sorption increases. At higher concentrations the availability of boron species for the adsorption sites increases, leading to higher boron uptake. Boron concentration at column exhaustion increases with the initial concentration, reaching 0.36, 2.07, and 3.88 mg g^{-1} for concentrations of 10, 25, and 50 mg L^{-1}, respectively.

The critical bed length of the column increases from 10 to 25 mg L^{-1}, after which it stabilizes. The time required to exhaust a unit length of sorbent in the column (s) under the test conditions decreases continuously with increasing initial concentration. However, in the range of concentration used in this study the time required for the adsorption wave front to pass through the critical bed depth (s_0) remains constant.

Influence of column depth (sorbent amount) on breakthrough curves

Increasing the column depth is expected to affect the volume of the solution corresponding to an outlet concentration that is 50% of the inlet concentration. With a short column depth, the breakthrough point occurs at lower volume; increasing the depth of the column increases the contact time between the sorbent and the sorbate. As shown in Table 1, boron uptakes at different bed depths (12 and 15 cm) were 9.96 and 9.86 mg g^{-1}, respectively. The effect of column depth on the column parameters is shown in Table 2. Boron adsorption decreased with a longer bed, and the same tendency was observed for the volumetric capacity (N_0). Moreover, the breakthrough curves for the longer beds tended to be more gradual, as shown in Fig. 5; this means that a longer bed was more difficult to completely exhaust. Bed depth was found to increase breakthrough volume, which is seemingly due to the increase in the number of binding sites, which broadens the mass transfer zone. This increases the critical bed depth, Z_0, which represents the theoretical depth of the sorbent necessary to prevent the sorbate concentration from exceeding the limit concentration C_b. Increasing the depth of the bed also increases the surface area of the adsorbent, providing more binding sites for adsorption, which could lead to an increase in the rate of adsorption. In our case, the value of the parameter k obtained from the Adams–Bohart model, which is directly related to rate of adsorption, decreased from 0.7 to 0.6 (L mg^{-1} min^{-1}), respectively, when the adsorbent depth was increased from 12 to 15 cm. This result can be attributed to the fact that the calcium alginate gel beads are non-rigid, and can therefore produce packing in the initial part of the column. This packing may reduce the contact surface between the solution and the adsorbent in the initial part of the column, which contrasts with the use of rigid adsorbents and leads to increased diffusion problems in this part of the column and a consequent decrease in adsorption rate.

For this experimentation the value of U_0 (cm min^{-1}) is the same for the two columns (12 and 15 cm depth) that give the same value of v. The initial concentration used for the two columns was 59 mg L^{-1}; based on these values, the value of s depends only on N_0, and an increase in N_0 leads to an increase in s, which is consistent with the experimental results.

Influence of superficial flow velocity on breakthrough curves

Figure 6 shows the effect of the superficial velocity on boron sorption breakthrough curves. As indicated in Table 1, at the lowest flow rate of 0.17 mL min^{-1}, relatively higher uptake was observed for boron sorption to immobilized calcium alginate gel beads. A much sharper breakthrough curve was obtained at lower flow rates. This behaviour is explained by the fact that boron sorption by calcium alginate gel beads is affected by insufficient solute residence time in the column, the diffusion of the solute into the pores of the biosorbent and the limited number of active sites and hydroxyl groups in the calcium alginate for sorption. The dependence of the rate parameter k on the flow velocity indicates that the external and intraparticle diffusion are rate-controlling.
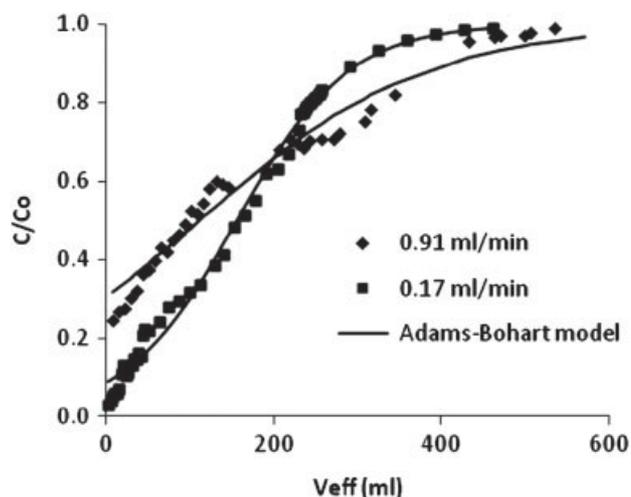
Table 2. Influence of experimental conditions on the parameters of the Adams–Bohart and Hutchins models

Operational parameters	Bohart–Adams		Hutchins			
	$k \times 10^{-3}$ (L mg^{-1} min^{-1})	N_0 (mg L^{-1})	Z_0 (cm)	s (min cm^{-1})	s_0 (min)	R^2
pH						
6	0.63	49.88	26.27	0.24	80.01	1
11	0.62	97.55	13.78	0.46	80.01	1
Initial concentration of boron						
10	3.68	10.99	20.50	0.31	80.01	1
25	1.23	22.04	24.94	0.31	80.01	1
50	0.70	47.62	24.82	0.27	80.01	1
Alginate mass						
0.39	0.65	110.42	11.48	0.55	80.01	1
0.50	0.62	97.55	13.78	0.46	80.01	1
Flow rate						
0.17	0.23	11.50	21.84	0.02	1177.7	1
0.91	0.67	10.49	44.66	0.11	439.46	1
Diameter						
1.6	3.6	10.99	20.50	0.31	80.01	1
2.6	0.67	10.49	44.66	0.11	439.46	1
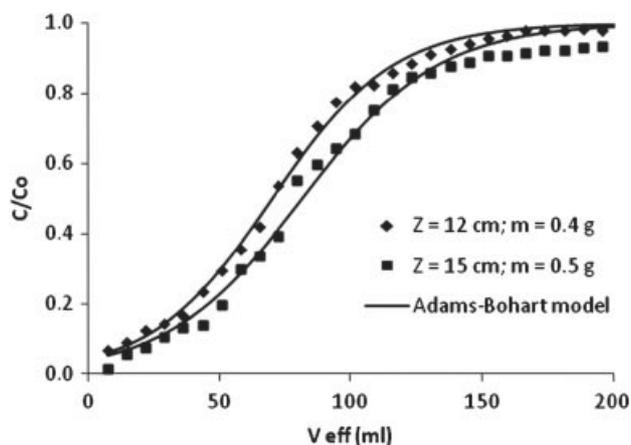
Figure 5. Comparison of the experimental data and predicted breakthrough curves obtained at different depths of the column according to the Adams–Bohart model (room temperature (20±1°C); pH 11; initial boron concentration 59 mg L^{-1}; flow rate 0.91 mL min^{-1}).

Figure 6. Comparison of the experimental data and predicted breakthrough curves obtained at different flow rates according to the Adams–Bohart model (room temperature (20±1°C); pH 11; initial boron concentration, 10 mg L^{-1}; mass adsorbent, 3.5 g; column depth, 18 cm; column diameter, 2.6 cm).

Influence of column diameter on breakthrough curves

Experiments were performed with different column diameters. Figure 7 shows two breakthrough curves obtained with the same column depth (2.6–18 cm, and 1.6–18 cm) and the same superficial flow velocity. The change in column diameter did not alter the breakthrough curves at BV_0 for the same column depth, as can be seen in Fig. 7, and the curves intersected at the breakthrough point (BV_0). The breakthrough point was defined as the point at which the effluent concentration was equal to $0.05C_0$. Increasing the column diameter for the same column depth increases the mass of the sorbent. As a result, the resistance to diffusion may limit the overall mass transfer and the adsorption efficiency. The kinetic parameter k decreases as the column diameter is increased, perhaps due to insufficient contact time and to dispersion effects. This finding is consistent with the previous results on the effect of the alginate mass. Although the larger amount of adsorbent in the wider column increases the dynamic adsorption capacity, the parameter N_0 decreases. For the same column depth, increasing

the column diameter also increases the critical bed depth Z_0; consequently, a greater height is needed to prevent the sorbate concentration from exceeding the limit concentration C_b, and the time required to exhaust a unit length of the column (s) increases. Moreover, the slope of the breakthrough curve clearly shows that the column of diameter 1.6 cm was more efficient than the column of diameter 2.6 cm.

CONCLUSIONS

The biosorption of boron from aqueous solution on alginate gel beads was investigated in a continuous packed-bed column. The influence of several parameters on breakthrough curves such as pH, inlet boron concentration, column depth, flow rates and diameter of the column at room temperature (20±1°C) was studied. The
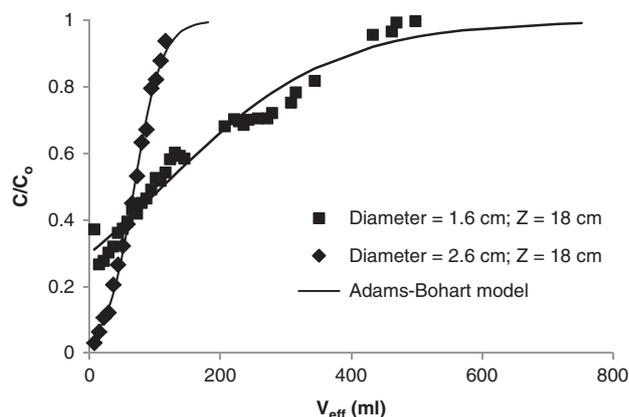
Figure 7. Comparison of the experimental and predicted breakthrough curves obtained at different diameters of the column according to the Adams–Bohart model (room temperature (20±1°C); pH 11). ■: Column diameter, 1.6 cm; flow rate, 0.91 mL min^{-1}; adsorbent mass, 1.44 g. ◆: Column diameter, 2.6 cm; flow rate, 0.91 mL min^{-1}; adsorbent mass, 3.50 g.

results showed that the removal yield of boron is dependent on all the above parameters. The best conditions for boron adsorption were obtained at high pH (the optimum value being pH 11), higher initial boron concentration, increased column depth and lower flow velocity.

The Adams–Bohart and Hutchins models were applied to experimental data from dynamic studies performed on a fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The breakthrough curve is well described by the Adams–Bohart model for all of the experimental conditions analysed in this study.

With this study we have demonstrated that calcium alginate can be use as adsorbent for the removal of boron from aqueous solutions in fixed-bed systems and its application to industrial scale is possible.

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