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The use of protonated *Sargassum muticum* as biosorbent for cadmium removal in a fixed-bed column

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Abstract

The protonated *Sargassum muticum* seaweed was studied as a possible biosorbent for cadmium removal in a fixed-bed column. The experiments were conducted in order to determine the effect of flow rate (0.42, 5, 10 and 20 mL min^{-1}) and bed height (0.6 and 15.3 cm for the lowest flow rate or 7.4, 13 and 16.6 cm for the others) on breakthrough curves behaviour. The determined breakthrough and exhaustion times increased with the diminution in flow rate and with the increase in bed height. The maximum cadmium uptake capacity, obtained from the area below adsorbed cadmium concentration versus time curves, was found to remain practically constant with bed depth and flow rate. The bed depth service time (BDST) model was applied to analyse experimental data, determining the characteristic process parameters. The optimal lowest sorbent usage rate was evaluated at 2 min contact time and the minimum bed height values necessaries to prevent the effluent solution concentration from exceeding 0.02 mg L^{-1} at zero time were 5.3, 6.9 and 7.5 cm for flow rates of 5, 10 and 20 mL min^{-1}, respectively. Several empirical models proposed in the literature (Bohart–Adams, Yan, Belter and Chu models) were investigated in order to obtain the best fit of column data, describing in a simple manner the breakthrough curves. A correlation between model parameters and the variables implied in the process was attempted.

Keywords: *Sargassum muticum*; Fixed-bed column; Cadmium; Biosorption; Modelling

1. Introduction

The presence and persistence of certain heavy metals in the environment due to industrial pollution is one of the most important sources of contamination throughout the world. Although the conventional techniques, such as precipitation or ion exchange, have been extensively used, in the last decade an alternative technology called biosorption has been developed. Biosorption is more economical and provides a greater metal removal capacity, overall at very low metal concentration [1], where traditional technologies became expensive and ineffective.

Among the different biological substrates tested in biosorption studies, algal biomass has received much attention due to the cost saving, low sensitivity to environmental and impurity factors, the possible contaminant recovery from the biomaterial and its elevated adsorption capacity. This is the case of *Sargassum muticum*, which constitute a renewable, ubiquitous natural marine resource, available in large quantities in littoral zones and therefore, an inexpensive sorbent material. Moreover, this alga is considered an invasive species in European waters, so its obliteration is very important in order to avoid the hazard to environment and aquaculture industry.

Most of the earlier investigations on algal biosorption were restricted to batch equilibrium studies [2–7]. Therefore, the data are not applicable to most treatment systems where contact time is not sufficient for the attainment of equilibrium, and then continuous sorption studies are needed (e.g. in fixed-bed columns).

A previous paper by the authors [8] provided information about the possible algae treatments to solve the problems associated to native seaweed, such as mass loss or low biomass stability, which can produce a blockage in the column. Based on this earlier study and taking into account the possibility of biomass reutilization, we selected an acid algal treatment that results in a great increase in adsorption capacity, biomass stabilization and attrition characteristics compared with native biomass. However, although the acid treatment has not showed the best characteristics between the other tested in the mentioned previous paper [8],

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Nomenclature

a	Yan empirical parameter
BDST	bed depth service time
C_{Cd}	effluent cadmium concentration (mg L^{-1})
C_i	feed or initial cadmium concentration (mg L^{-1})
D	bed height (cm)
D_{min}	minimum bed height (cm)
dC/dt	slope of the breakthrough curves from t_b to t_e (mg L^{-1} h^{-1})
EBCT	empty bed contact time (min)
erf(x)	error function of x
F	flow rate (mL min^{-1})
k	rate constant (L mg^{-1} h^{-1})
m_s	dry weight of biomass (g)
N_0	sorption capacity of the bed (mg L^{-1})
$Q_{Cd,max}$	maximum cadmium uptake capacity (mg g^{-1})
Q_{max}	maximum cadmium uptake capacity from Yan model (mg g^{-1})
t	time (h)
t_b	breakthrough point (h)
t_e	bed exhaustion time (h)
$t_{0.5}$	time at which the exit cadmium concentration is half the inlet (h)

Greek symbols

Δt	sorption zone (h)
ν	linear velocity (cm h^{-1})
σ	standard deviation

the state of the algae will influence the selection of the appropriate desorbing agent for sorption–desorption studies. Therefore, as an example, an acid wash allows the release of metal adsorbed and the regeneration of the algae just in one step.

In order to describe the fixed-bed column behaviour and to scale up it for industrial applications, an accurate model has to be used [9–11]. Due to the system complexity, the calculations, which may include axial dispersion, sorption kinetics, film distribution resistance and intraparticle diffusion resistance, are normally very tedious and not simple, implying the resolution of a series of non-linear partial differential equations. If the objective is to explain the breakthrough performance of a biosorption column, more simple semiempirical models can be used [12–15], avoiding the complicate mathematical equations solution.

The present work reports the study of cadmium biosorption in a fixed-bed column by the protonated algae *S. muticum*. The advantages of this column design for practical applications are frequently cited in literature [1,13]: effective use of reactor volume and concentration gradient, which allows a great utilization of the sorbent capacity and results in a better quality of the effluent. The effect of design parameters was completely studied and the use of several empirical models was proposed to adequately describe the obtained breakthrough curves.

2. Materials and methods

2.1. Biomass

Samples of the brown marine alga *S. muticum* were collected from the coast of A Coruña (Galicia, NW Spain). The alga was washed with tap and deionised water to eliminate impurities, oven dried at 60 °C overnight, crushed with an analytical mill, sieved (size fraction of 0.5–1 mm) and stored in polyethylene bottles until its use.

This raw biomass were acid-treated in order to transform the alga into its fully protonated form by soaking and shaking it in a 0.2 mol L^{-1} HNO_3 (Merck p.a.) solution in a rotary shaker (175 rpm) for 4 h, at a biomass concentration of 10 g L^{-1}. Afterwards, the material was rinsed thoroughly with deionised water until pH 4.5 was attained. Following filtration, treated biomass was dried in an oven at 60 °C overnight.

2.2. Column experiments

The experiments were carried out in glass columns of 40 cm length and 1 cm internal diameter, each filled with different quantities of dried protonated *S. muticum*. A porous sheet (pore size 0) was attached at the bottom of the column in order to support the algal bed and to ensure uniform inlet flow and a good liquid distribution into the column. The top of the bed was closed by a 10 cm height layer glass beads (1 mm in diameter), which avoid the loss of biomass and also ensure a closely packed arrangement (Fig. 1).

A 50 mg L^{-1} cadmium solution, prepared by dissolving accurately weighed samples of $Cd(NO_3)_2 \cdot 4H_2O$ (Merck p.a.) in deionised water, was fed through the bed in up-flow mode at the desired flow rate with a peristaltic pump (Watson Marlow) connected at the bottom of the column. Samples were collected periodically and filtered through a 0.45 μm pore size cellulose nitrate filter, in order to separate the dissolved fraction from possible suspension material that could influence the cadmium

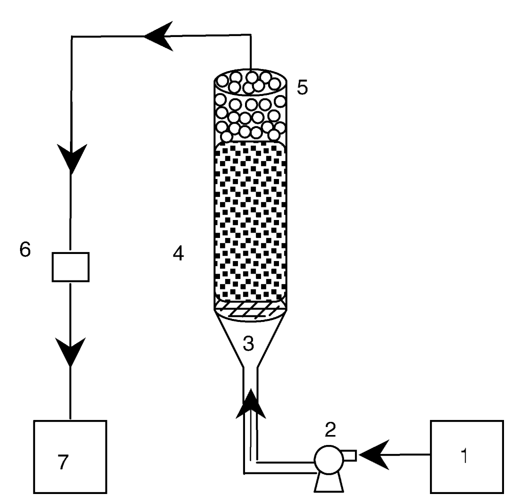

Fig. 1. Schematic diagram of experimental set up: (1) Reservoir tank with Cd^{2+} solution, (2) peristaltic pump, (3) porous sheet, (4) column, (5) glass beads, (6) cellulose nitrate filter and (7) effluent storage.

measurements. The filtrate was analysed for the remaining cadmium ion concentration by differential pulse anodic stripping voltammetry (DPASV) using a 757 VA Computrace (Metrohm) with a conventional system of three electrodes: hanging mercury drop electrode as working electrode, a Pt auxiliary electrode and 3 mol L^{-1} Ag/AgCl as reference electrode. Data presented constitute average values from at least two replicates.

Operation of the column was stopped when the effluent metal concentration reached a constant value. The pH of the effluent showed a slight diminution as the cadmium was sorbed. It was periodically recorded founding values between 3.5 (at the initial times) and 4.5 (at the final times). As the metal solution is contacted with the protonated biomass, an exchange between cadmium sorbed and proton released take place and therefore a pH decrease can be observed. When the bed was exhausted no more protons were liberate and then the pH tend to a constant value.

The effect of flow rate and bed depth on the biosorption of cadmium in the fixed-bed column was investigated. It was compared the effect of four different flow rates: 0.42, 5, 10 and 20 mL min^{-1} over an algal bed of several heights (0.6 and 15.3 cm for the lowest flow rate or 7.4, 13 and 16.6 cm for the others).

3. Theory: modelling and analysis of column data

The performance of packed bed is described through the concept of the breakthrough curve. Both, the time until the sorbed species are detected in the column effluent (breakthrough point), at a given concentration, and the shape of the concentration–time profile or breakthrough curve, are very important characteristics for operation, dynamic response and process design of a biosorption column because they directly affect the feasibility and economics of the sorption phenomena. Experimental determination of these parameters is very dependent on column operating conditions [1].

The efficiency in the overall use of the alga in the column is indicated by the length of the transfer zone, which is reflected on the step character of the breakthrough curve. Moreover, the adsorption capacity of the column depends on the position of the breakthrough point along the time axis; e.g. a broad leading edge indicates a poor utilization of the column capacity. Therefore, the breakthrough curves obtained in the present experiments need to be examined quantitatively.

The breakthrough point (t_b) was defined as the time when the effluent concentration of cadmium reached a value of 0.02 mg L^{-1} (breakthrough concentration), which is around 10 times lower than the recommended limits for industrial discharges in European Union (83/513/EEC directive); nevertheless, the quality objectives fixed in this directive indicated that the concentration of dissolved cadmium in territorial waters, internal coastal waters, etc., that will be measured sufficiently close to the point of discharge, must not exceed 0.0025 mg L^{-1}. The bed exhaustion time (t_e) was selected as the time when the effluent concentration achieved a constant value around 45 mg L^{-1} although the bed was not fully saturated, except for the flow rate of 0.42 and 5 mL min^{-1} at the highest bed depth, where only a 40 mg L^{-1} effluent concentration was reached. The time period from t_b to t_e (Δt) represents the sorption zone and therefore, constitutes an index of the rate of mass transfer.

The results obtained for the flow rate of 0.42 mL min^{-1} are shown in Table 1, although they were not considered in the discussions or model calculations (data not shown). Such decision is justified by both, the different quantity of biomass used at this flow rate, with respect to the others employed in this work (no comparison possible), and the probable column blockage with a high bed depth.

The area below the adsorbed metal concentration versus time plots, obtained through numerical integration, can be used to find the quantity of cadmium retained in the column. Dividing this value by the mass of alga in the bed (m_s), the maximum uptake capacity of the biomass ($Q_{Cd,max}$) was obtained, as it is shown

Table 1
Column data and parameters obtained for variable bed depths and flow rates in fixed-bed column during the removal of cadmium (50 mg L^{-1}) by protonated *S. muticum* biomass

$Q_{Cd,max}$ (mg g^{-1})	D (cm)	Bed volume (cm^3)	m_s (g)	dC/dt (mg L^{-1} h^{-1})	t_b (h)	t_e (h)
0.42 mL min^{-1}						
102	0.6	0.47	0.25	n.d.	n.d.	50
69	15.3	12.0	7.4	0.1	247	600
5 mL min^{-1}						
89	7.4	5.8	3.4	0.8	2.5	60
88	13	10.2	5.9	0.5	9.0	85
94	16.6	13.0	7.7	0.4	13.5	95
10 mL min^{-1}						
83	7.4	5.8	3.4	2.1	0.25	20
95	13	10.2	5.9	1.0	2.2	43
96	16.6	13.0	7.7	0.8	3.8	57
20 mL min^{-1}						
85	7.4	5.8	3.4	4.2	0.03	10
94	13	10.2	5.9	2.3	1.6	19
108	16.6	13.0	7.7	2.0	3.0	23

The cadmium concentration at the breakthrough point is 0.02 mg L^{-1}.

in the following equation:

$$Q_{\mathrm{Cd,max}} = \frac{0.06 \cdot F}{m_{\mathrm{s}}} \int_{t=0}^{t=t_{\mathrm{e}}} (C_{\mathrm{i}} - C_{\mathrm{Cd}}) \cdot \mathrm{d}t \tag{1}$$

where F is the flow rate (mL min^{-1}), C_i the feed cadmium concentration and C_{Cd} is the effluent cadmium concentration (mg L^{-1}). The numerical parameter was included for unit concordance (t is expressed in hours).

According to Bohart–Adams model, which was first based on reaction kinetics for the adsorption of chlorine on charcoal, the relationship between C_{Cd}/C_i and t in a flowing system is given by [16]:

$$\ln\left(\frac{C_{\mathrm{i}}}{C_{\mathrm{Cd}}} - 1\right) = \ln\left[\exp\left(\frac{N_0 k D}{\nu}\right) - 1\right] - kC_{\mathrm{i}}t \tag{2}$$

where N_0 is the sorption capacity of the bed (mg L^{-1}), k the rate constant (L mg^{-1} h^{-1}), ν the linear velocity, calculated by dividing the flow rate by the column section area (cm h^{-1}) and D is the bed height (cm). Since the exponential term in this equation is much larger than unity, the expression can be rearranged and reordered, obtaining the following:

$$t = \left(\frac{N_0}{C_{\mathrm{i}}\nu}\right) \times D - \frac{\ln[(C_{\mathrm{i}}/C_{\mathrm{Cd}}) - 1]}{kC_{\mathrm{i}}} \tag{3}$$

Based on this equation, the bed depth service time (BDST) model is used to predict the relationship between service time and bed height in terms of process concentrations and adsorption parameters [17,18]. This relation has the form of a straight line, where the adsorptive capacity (N_0) can be evaluated from the slope, which represents the time required for the adsorption zone to travel a unit length through the adsorbent. Besides, the rate constant (k), which characterizes the net effect of mass transfer in the fluid and in the solid phase [16], can be evaluated from the intercept.

By letting $t = 0$ and solving for D in the above equation, the minimum bed depth (D_{min}) is obtained. This parameter reflects the shortest possible bed length needed to obtain the breakthrough concentration at $t = 0$.

Moreover, Eq. (3) can be expressed in a form that allows to fit the breakthrough curves:

$$\frac{C_{\mathrm{Cd}}}{C_{\mathrm{i}}} = \frac{1}{1 + \exp[(N_0 k D/\nu) - kC_{\mathrm{i}}t]} \tag{4}$$

Eq. (4) is able to describe acceptably well the sigmoid shape of the breakthrough curves; however, when the variable t is zero, the relation C_{Cd}/C_i is not zero and equal to a constant value, contrary to real conditions.

In the range of low effluent concentrations, Eq. (4) was rearranged considering that C_{Cd}/C_i is much lower than unity; e.g. for $C_{Cd} < 0.15C_i$, and then, the following equation is applied under this condition:

$$\frac{C_{\mathrm{Cd}}}{C_{\mathrm{i}}} = \frac{1}{\exp[(N_0 k D/\nu) - kC_{\mathrm{i}}t]} \tag{5}$$

The great significance of the Bohart–Adams model is based on its simplicity; the basic assumptions in its deduction is that intraparticle diffusion and external mass resistance are negligible, and that adsorption kinetics is controlled by the surface chemical reaction between the solute and the adsorbent. Although these postulations are usually not validate in real systems, it is easy to make some simplifications from this model that lead to the equations showed above. These simple equations are able to describe the breakthrough curves with accuracy in most of the cases, and at the same time, they provide important system parameters like the rate constant, the uptake capacity, etc., that can be used to predict the service time of the column for the scale up of the experiments.

Based on statistical analysis of experimental data, Yan et al. [19] proposed after some simplifications, the following non-linear regression representation based on Bohart–Adams model:

$$\frac{C_{\mathrm{Cd}}}{C_{\mathrm{i}}} = 1 - \frac{1}{1 + ((0.06 \cdot C_{\mathrm{i}} F/Q_{\mathrm{max}} m_{\mathrm{s}}) \times t)^a} \tag{6}$$

where a is an empirical parameter that decides the slope of the regression function.

Yan model has a relative importance because it normally describes the complete breakthrough curves with great accuracy; however, it is difficult to relate the empirical parameter "a" with the experimental conditions, so the scale up of the system is not possible.

The simple empirical model proposed by Belter (Eq. (7)) and two subsequent modifications by Chu (Eq. (8)) are also used to fit the breakthrough curves [14]:

$$\frac{C_{\mathrm{Cd}}}{C_{\mathrm{i}}} = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{t - t_{0.5}}{\sqrt{2} \cdot \sigma \cdot t_{0.5}}\right)\right] \tag{7}$$

$$\frac{C_{\mathrm{Cd}}}{C_{\mathrm{i}}} = \frac{1}{2}\left[1 + \mathrm{erf}\left(\frac{(t - t_{0.5}) \cdot \exp(\pm\sigma(t/t_{0.5}))}{\sqrt{2} \cdot \sigma \cdot t_{0.5}}\right)\right] \tag{8}$$

where erf(x) is the error function of x, $t_{0.5}$ the time at which the effluent concentration is half the inlet concentration and σ represents the standard deviation, which is a measure of the slope of the breakthrough curve.

In order to fit column data, the error function was transformed using a Maclaurin expansion for small values of x [20].

According to Belter, Eq. (7) is capable of modelling only symmetric curves employing two parameters, σ and $t_{0.5}$, empirically correlated with the process variables (flow rate, bed height, etc.). On the other hand, the equations proposed by Chu (Eq. (8) with sign + or −) are capable of modelling both, symmetric and asymmetric curves with no additional parameters. However, the use of these simple models to design or optimize fixed-bed biosorption columns make necessary to empirically correlate the model parameters with the process variables.

One of the advantages of the equations proposed by Chu is that they are able to fit breakthrough curves obtained from systems, where either mass transfer limitation or flow non-idealities exist. Moreover, the mechanism influencing the shape of the curves may be deduced from the relationships between σ^2 the linear velocity (ν) and column height (D).

4. Results and discussion

4.1. Effect of bed height

The breakthrough curves for cadmium biosorption were obtained for different bed heights at four constant flow rates (compare data a–c in Fig. 2). It can be observed that the breakthrough and the exhaustion times increased with the rise in bed height for all the flow rates studied (Table 1). This may be due to an increase in the surface area of the algae as the quantity of biomass packed in the column grows, and then, as the number of available sorption sites is greater. However, the increase in the quantity of biomass deposited in the column also resulted in a broadened mass transfer zone, which makes breakthrough curves less steeper. This more gradual character of the curves as the bed height is increased implies that the bed was more difficult to be completely exhausted, as it has been showed in the literature [21,22]; the decrease in the slope of the curves from t_b to t_e (dC/dt) with increasing bed height clearly reflects this fact (Table 1).

The breakthrough curves showed no "tail" towards saturation time when the algae mass inside the column is low. Moreover, as the quantity of biomass is increased a slower approach of C_{Cd}/C_i towards the saturation of the bed can be observed. The broad tailing edge of breakthrough curves could be a consequence of the rate limiting intraparticle diffusion mechanism or flow non-idealities [16], which may occur when an excessive quantity of algae is presented in the column.

The maximum metal uptake capacity determined from Eq. (1), was found to remain constant with bed depth for a flow rate of 5 mL min^{-1}. At the flow rates of 10 and 20 mL min^{-1} the smallest bed height showed a lower cadmium uptake capacity, which was increased with the quantity of biomass presented in the column. This fact could be attributed to the limited availability of adsorption sites: at flow rates as high as 10 or 20 mL min^{-1}, probably there is not enough residence time for all the metal to be sorbed when the quantity of biomass is low, so an increase in the algae mass leads to a higher adsorption sites availability and therefore, a rise in biosorption capacity is observed.

The obtained values are very similar to the maximum adsorption capacity determined from Langmuir isotherm model (95 mg g^{-1}) in previous batch studies at the equilibrium concentration of 50 mg L^{-1} [23].

The application of the BDST theory allowed to attain the relationship between bed depth and breakthrough time as it is shown in Fig. 3a. These plots showed a good linearity with regression

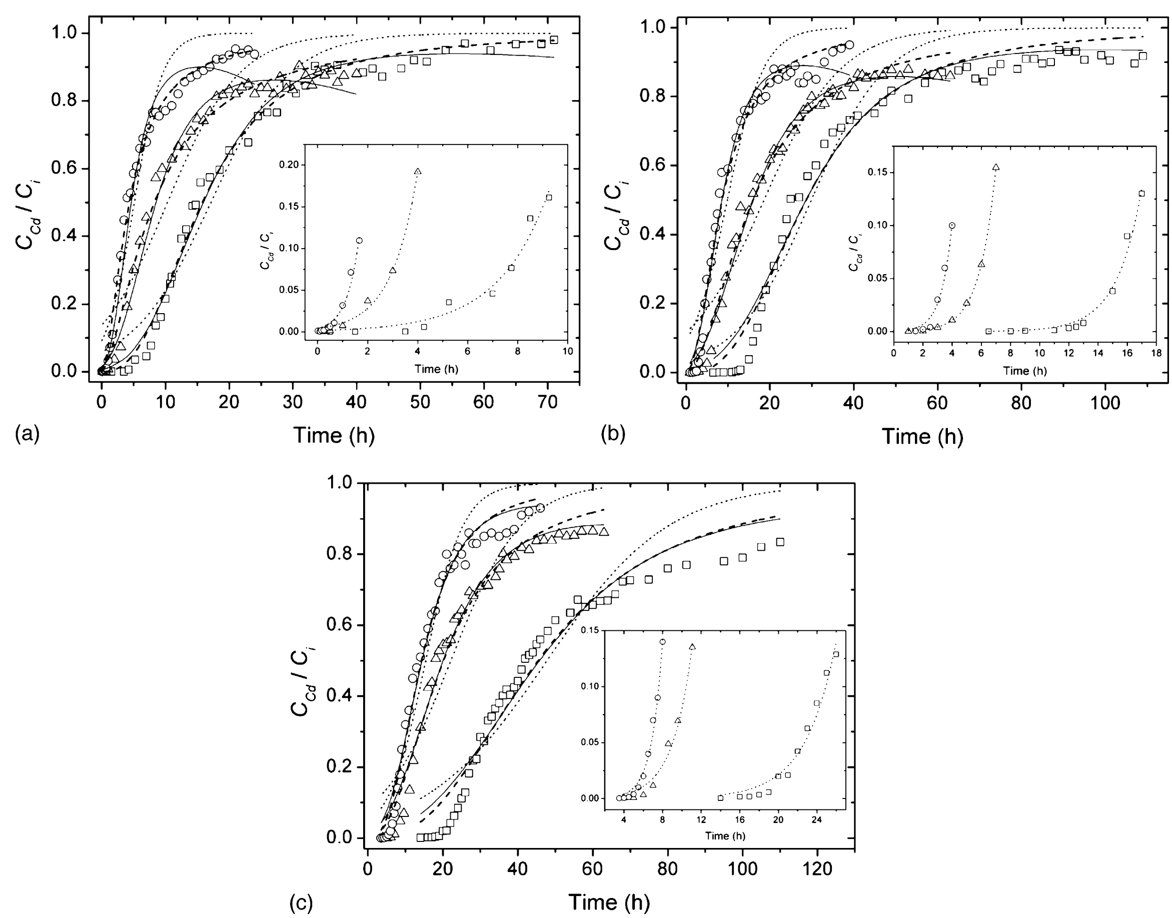

Fig. 2. Comparison of the experimental and model fit breakthrough curves for cadmium biosorption (50 mg L^{-1}) by protonated *S. muticum* biomass at different bed depths: (a) 7.4 cm, (b) 13 cm, (c) 16.6 cm and flow rates: 5 mL min^{-1} (squares), 10 mL min^{-1} (triangles) and 20 mL min^{-1} (circles), according to: Bohart–Adams (dotted lines), Yan (dashed lines) and Chu (solid lines) models. The insets represent the fits to Bohart–Adams model but only applied to the first part of the breakthrough data (for C_{Cd}/C_i values between 0 and 0.15).

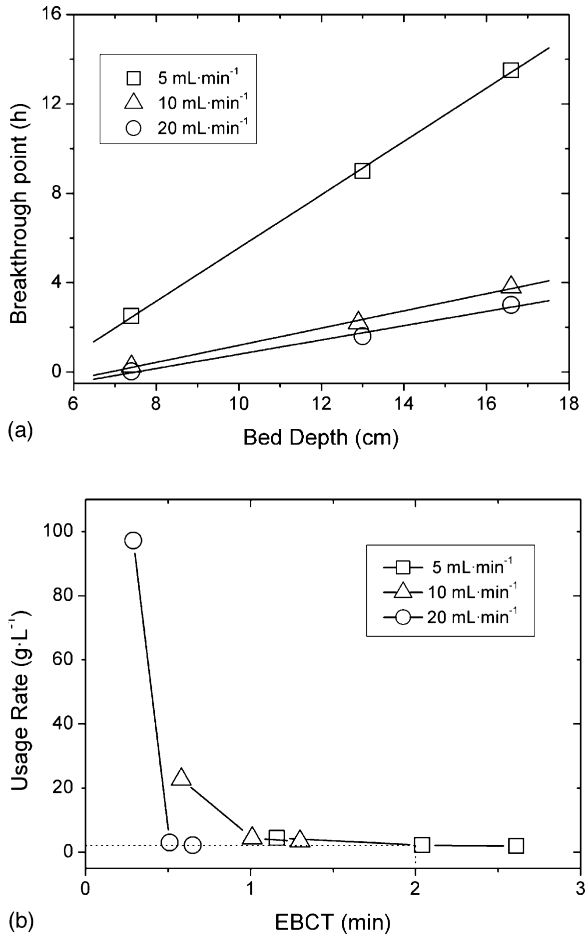

Fig. 3. (a) BDST curves at breakthrough point for different flow rates: $5\,\mathrm{mL\,min^{-1}}$ (squares), $10\,\mathrm{mL\,min^{-1}}$ (triangles) and $20\,\mathrm{mL\,min^{-1}}$ (circles). (b) Effect of sorption column liquid residence time on specific usage of protonated *S. muticum* biomass at different flow rates: $5\,\mathrm{mL\,min^{-1}}$ (squares), $10\,\mathrm{mL\,min^{-1}}$ (triangles) and $20\,\mathrm{mL\,min^{-1}}$ (circles).

coefficients higher than 0.99 for the three flow rates tested, indicating the validity of the model. The bed sorption capacity and the sorption rate constant of the BDST plots, evaluated from the slope and intercept of Eq. (3), respectively, are shown in Table 2. These parameters are both reflected in the sorbent usage rate factor, which is determined dividing the mass of alga in the column by the volume of water treated up to the breakthrough time. The obtained values are shown in Fig. 3b as a function of the bed contact time (EBCT), which represents the flow rate in the column (bed volume/*F*) [24]. From this plot, the optimal lowest sorbent usage rate was evaluated at 2 min contact time. This indicates that the ideal contact time in the column should not be less than 2 min in order to maintain the lowest usage rate (around $2.2\,\mathrm{g\,L^{-1}}$). This value is very close to the dosage employed in batch systems, so the same dose of adsorbent can be used both in column and in batch systems from the same volume treated.

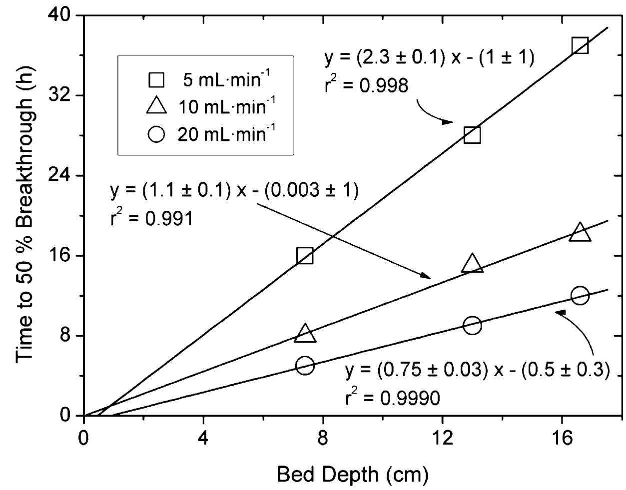

Fig. 4. BDST curves at 50% breakthrough curve ($C_{\mathrm{Cd}} = 0.5C_{\mathrm{i}}$) for different flow rates: $5\,\mathrm{mL\,min^{-1}}$ (squares), $10\,\mathrm{mL\,min^{-1}}$ (triangles) and $20\,\mathrm{mL\,min^{-1}}$ (circles).

Fig. 4 shows the straight lines obtained from the BDST model at 50% breakthrough curve, when the logarithmic term in Eq. (3) reduces to zero. Therefore, an additional confirmation of the validity of this model is obtained because the straight lines pass near the origin as model predicts under this condition.

Each minimum bed height value (D_{min}) necessary to prevent the effluent solution concentration from exceeding $0.02\,\mathrm{mg\,L^{-1}}$ at zero time was determined reorganizing Eq. (3). The obtained values were 5.3, 6.9 and 7.5 cm for flow rates of 5, 10 and $20\,\mathrm{mL\,min^{-1}}$, respectively.

It is important to note that an assumption inherent in the BDST theory is the symmetry of the breakthrough curves that is known to be not true in practice, evidencing the limitations of this simple model (e.g. it is not accurate in predicting the effects of changes in breakthrough concentration). Because of this, although the BDST theory predicts that the slope should be proportional to the inverse of linear velocity, it was not obtained in practice, overall at low breakthrough concentration values.

4.2. Effect of flow rate

The effect of flow rates from 5 to $20\,\mathrm{mL\,min^{-1}}$ on breakthrough curves can be observed in Fig. 2. As expected, an increase in flow rate produces a diminution in breakthrough and exhaustion times, and as a consequence, the curves become steeper with a shorter mass transfer zone.

Table 2
Bed depth service time (BDST) equations (slope and intercept) and the corresponding constants (Eq. (3))

F ($\mathrm{mL\,min^{-1}}$)	ν ($\mathrm{cm\,h^{-1}}$)	Slope	Intercept	r^2	k ($\mathrm{L\,mg^{-1}\,h^{-1}}$)	N_0 ($\mathrm{mg\,cm^{-3}}$)
5	382	1.19 ± 0.02	−6.4 ± 0.3	0.9998	0.025	23
10	764	0.38 ± 0.02	−2.6 ± 0.3	0.998	0.060	15
20	1528	0.32 ± 0.03	−2.4 ± 0.4	0.996	0.065	24

The flow rate was not found to influence the maximum cadmium uptake capacity of the columns ($Q_{\mathrm{Cd,max}}$) for the three bed depths studied. Only a little increase with the augment in flow rate was found at the highest bed depth (from 94 to 108 mg g^{-1}). It was attributed to the different geometries of the breakthrough curves that provided some errors in the area calculations, generally when the slopes of the curves are high.

As it was described above for the influence of bed height, if the flow rate is sufficiently high, the limited number of active binding sites present at the lowest bed depths could be not enough to uptake all the metal in solution; therefore at the lowest bed depth (7.4 cm), when the flow rate is increased from 5 to 10 or 20 mL $\min^{-1}$, a little diminution in the adsorption capacity was detected (Table 1).

4.3. *Model of column data*

The design and optimization of a fixed-bed sorption column involves the employment of mathematical models, which must be used to describe and predict the experimental breakthrough curves, in order to possible scale up of the process. A complete model must consider the equilibrium and mass transfer phenomena inside the sorbent particles and the fluid flow conditions in the column [9,11].

Since the sorption process is a non-steady state operation, model derivation requires solving a series of non-linear partial differential equations that complicate in excess the mathematical problem. Moreover, the parameters involved, such as kinetic constants, diffusion coefficients, axial and radial dispersion coefficients, etc., are difficult to be experimentally measured.

A series of simplifications applied by different authors may reduce the system complexity and make the model equations easily solvable [25–27]; nevertheless, the calculations are normally very time consuming and powerful computer programs are needed. Furthermore, model parameters are usually determined by fitting the model to experimental breakthrough curves, so no predictions are employed.

Because of this, some empirical models proposed in the literature have been investigated in order to obtain the best breakthrough curve fit of our data, describing in a simple manner the behaviour of a biosorption column [13–15]. One must be aware that some of these models lack of theoretical rigour and may, therefore, be inadequate and inaccurate for extrapolation.

4.3.1. *The Bohart–Adams model*

Fig. 2 shows that the Bohart–Adams model did not appear to fit the data of breakthrough curves well, as it is demonstrated by the low regression coefficients determined (between 0.85 and 0.96). As a general rule in this case, the model overestimates the effluent cadmium concentration at initial and final times. The parameters obtained from the adjusted of Bohart–Adams equation to all data points (not shown) were discarded due to the bad model adjustment, which provided a great associated error in their calculations.

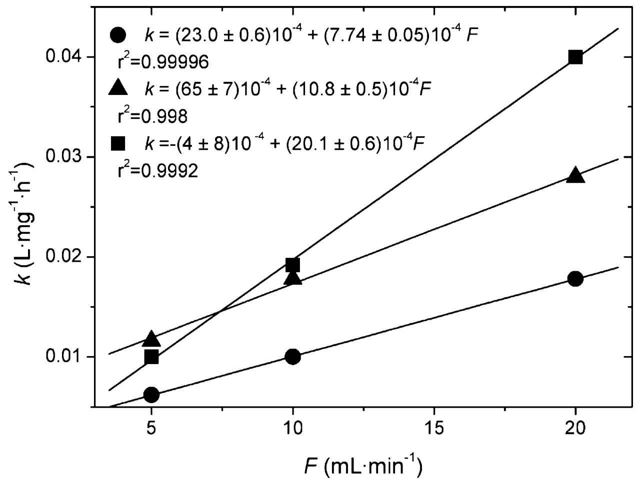

Fig. 5. Variation of parameter k, determined from simplified Bohart–Adams model (Eq. (5)), with the flow rate at different bed depths: 7.4 cm (solid squares), 13 cm (solid triangles) and 16.6 cm (solid circles).

However, if we consider the simplification of this model for low effluent concentrations ($C_{\mathrm{Cd}} < 0.15C_{\mathrm{i}}$) applying Eq. (5), a considerable improvement in curve fits is attained. This simplified model was able to fit experimental curves with great accuracy, describing the data tendency with precision for all the flow rates and bed depths studied (insets of Fig. 2). The model parameters determined from Eq. (5), N_0 and k, are shown in Table 3. N_0 values show no apparent tendency with changes in flow rate or in the quantity of biomass; in contrast, the kinetic rate constant presents a clear linear dependency on flow rate or on its equivalent expressed as linear velocity (v), at the three bed depths studied (Fig. 5). This implies that, for low operation times, the rate constant is mainly determined by the mass transfer in the fluid, which typically varies with flow rate, and not by the mass transfer in the solid, which is independent of velocity.

Eq. (4) was also used to fit experimental curves when $C_{\mathrm{Cd}} > 0.15C_{\mathrm{i}}$, obtaining not very good adjustment; however, a significant improvement was achieved with respect to the full data fit using Eq. (5) (fits not shown).

The use of this simplification of the Bohart–Adams model is of special interest overall at low operation times, where it

Table 3
Parameters obtained from the non-linear fit of breakthrough data ($0 < C_{\mathrm{Cd}}/C_{\mathrm{i}} < 0.15$) to Bohart–Adams model (Eq. (5))

F	7.4 cm			13 cm			16.6 cm		
	k	N_0	r^2	k	N_0	r^2	k	N_0	r^2
5	0.01	33.04	0.97	0.0116	30.14	0.98	0.0062	37.48	0.97
10	0.0192	29.57	0.994	0.0178	26.77	0.9998	0.01	34.52	0.98
20	0.04	28.39	0.97	0.028	32.32	0.98	0.0178	47.05	0.99

Table 4
Parameters obtained from the non-linear fit of breakthrough data to Yan model (Eq. (6))

F (mL min^{-1})	7.4 cm			13 cm			16.6 cm		
	Q_{max} (mg g^{-1})	a	r^2	Q_{max} (mg g^{-1})	a	r^2	Q_{max} (mg g^{-1})	a	r^2
5	71.82	2.54	0.992	71.50	2.7	0.98	88.44	2.6	0.96
10	75.45	1.58	0.990	80.00	1.86	0.990	78.70	2.21	0.98
20	78.91	1.72	0.996	86.00	2.01	0.98	111.43	2.7	0.98

Table 5
Parameters obtained from the non-linear fit of breakthrough data to Chu model (Eq. (8) with negative sign in the exponential term)

F	7.4 cm			13 cm			16.6 cm		
	$t_{0.5}$ (h)	σ	r^2	$t_{0.5}$ (h)	σ	r^2	$t_{0.5}$ (h)	σ	r^2
5	15.9	0.399	0.990	28.6	0.402	0.97	45.8	0.41	0.95
10	8.5	0.462	0.990	16.0	0.464	0.990	20.0	0.445	0.98
20	4.6	0.431	0.98	8.5	0.439	0.98	14.4	0.40	0.98

is able to describe with great accuracy the initial part of the breakthrough curves (the most important for process applications) under different flow rates and bed heights, which greatly simplify scale up design.

4.3.2. The Yan model

Yan model allowed us to describe with great precision the tendency of experimental curves in the whole range of effluent concentration, opposite to Bohart–Adams model fit (Fig. 2). The parameters obtained by non-linear fit of the data, Q_{max} and a, are listed in Table 4.

The inconvenient of this model is that the maximum cadmium adsorption capacity, Q_{max}, and the measurement of curve slope, a, shows no apparent tendency with the flow rate and bed depth variables. Then, it is not possible to correlate these parameters with any variable implied in the process and therefore, only a very good description of the breakthrough curves is attained.

4.3.3. The Belter and Chu models

The equation proposed by Belter and the subsequent Chu's modification (positive sign) were not able to fit the experimental breakthrough curves in a non-linear analysis. Nevertheless, the other model equation employed by Chu (Eq. (8) with the negative sign in exponential term) showed a good fit to most of the obtained column data. It must be pointed out that, particularly at the highest bed depth, this model overestimates the metal effluent concentration at low C_{Cd}/C_i relations, although considerably less than with Bohart–Adams model. Moreover, at the lowest bed depth, this equation is not able to follow the breakthrough curves tendency at the final times underestimating the experimental values. Even so, the obtained regression coefficients are high (Table 5).

The model parameters $t_{0.5}$ and σ were determined by fitting Eq. (8) to the experimental column data. The relationship between this two parameters and the linear velocity are shown in Fig. 6. The high regression coefficients obtained confirm that $t_{0.5}$ is inversely proportional to ν. Several correlations between the standard deviation and bed depth or linear velocity were tested, founding a clear linear dependency of σ^2 with $\nu^{1/2}/D$ at 7.4 and 13 cm bed depth. On the contrary, such dependency is lost for the highest bed depth and no new relation was found, probably due to the inaccuracy of the model fit at this bed height.

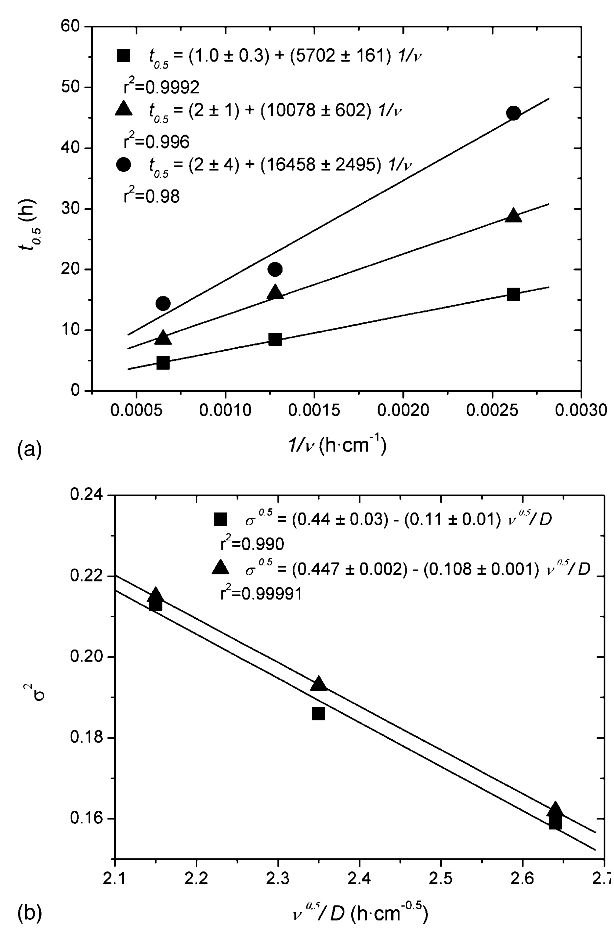

Fig. 6. Variation of the parameters obtained from the fit of all column data to Chu model at 7.4 cm (solid squares), 13 cm (solid triangles) and 16.6 cm (solid circles) bed depths. (a) Variation of $t_{0.5}$ with $1/\nu$. (b) Variation of σ^2 with $\nu^{1/2}/D$.

From the established relations for σ^2, the mechanism of the cadmium biosorption in the column can be deduced [14]. Therefore, at the lowest bed heights used, the controlling mechanism is the mass transfer of metal from solution to the biomass.

So that, the linear relations obtained can be used to estimate the changes in $t_{0.5}$ and σ parameters with flow rates, other than used in these column studies. However, it must be taken into account that these empirical dependencies lack of physical significance and are only valid under the same conditions employed to obtain the breakthrough curves, because they can change with variables like column dimensions or algae packed. Nevertheless, this shortcoming is also present when simplified mechanistic models are used.

To summarize it can be said that the Chu model is able to describe the complete breakthrough curve, suggesting that the features of the dynamics of sorption columns have been taken into account by the mathematical form of the model equation.

5. Conclusions

The maximum metal uptake capacity, determined from the area below adsorbed cadmium concentration versus time curves, was found to remain constant with flow rate and with bed depth (if the quantity of biomass is high enough). Moreover, the breakthrough and the exhaustion times increased with the rise in bed height and with the diminution in the flow rate.

The best fit of the breakthrough curves, obtained under different experimental conditions tested, was achieved with the Yan model. However, it was not possible to correlate the model parameters with any variable implied in the process, restricting its usefulness.

The Chu model was also able to follow with accuracy the column data tendency under most of the conditions tested, although not as well as Yan model. The model parameters were correlated with the linear velocity and bed depth, so the obtained linear regressions may be use under the same conditions to estimate the time at which the exit concentration is half the inlet and the slope of the breakthrough data, characterising the future curves.

The Bohart–Adams model was not able to fit with precision full breakthrough curves. Nevertheless, the simplification of this model for low effluent concentrations described data tendency with a great precision, and then a linear relation between the rate constant and the flow rate for the different bed depths tested was found.

The bed depth service time model was used to predict the relationship between service time and bed height, which is essential in column process design. The bed sorption capacity and the sorption rate constant can be calculated from these plots. Moreover, this simple model allowed us to obtain the ideal solution–biomass contact time in the column (2 min) and the minimum bed height values necessaries to prevent the effluent solution concentration from exceeding 0.02 mg L^{-1} at zero time (5.3, 6.9 and 7.5 cm for flow rates of 5, 10 and 20 mL min^{-1}, respectively). So that, employing this model we can predict, under the same process conditions (column dimensions, algae packed, etc.) very important design parameters from simple experiments.

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