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# Prediction of the copper (II) ions dynamic removal from a medium by using mathematical models with analytical solution

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## Abstract

A copper (II) ions biosorption by *Sargassum* sp. biomass was studied in a fixed bed column at 30 °C and pH 3.5. The experimental curves were obtained for the following feed concentrations −2.08, 4.16, 6.42 and 12.72 mmol/L of the copper ions. The mathematical models developed by Thomas and Bohart–Adams were used for description of ions sorption process in the column. The models principle hypothesis is that the mass transfer controlling stage of the process is the adsorption kinetics between sorbate and adsorbent. The phenomena such as intraparticle diffusion, a mass transfer external resistance and axial dispersion effects were out of considerations. Some of the models parameters were experimentally determined ($\rho_B$, $\varepsilon$, $u_0$, $C_0$) and the others were evaluated on the bases of the experimental data ($k_{a1}$, $k_{a2}$). The unique fitting parameter in all models was the adsorption kinetic constant. The identification procedure was based on the least square statistical method. Simulation results show that the models describe well a copper ions sorption process in a fixed bed column. The used models can be considered as useful tools for adsorption process design and optimization in fixed bed column by using algae biomass of *Sargassum* sp. as an adsorbent.
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*Keywords:* Bohart–Adams; Thomas; Fixed bed; Breakthrough curve

## 1. Introduction

Heavy metals such as lead, copper, cadmium and zinc are one of the most toxic pollutants presented in the residual industrial waters. In addition, heavy metals can be accumulated in the whole food chain because of their solubility and mobility which presents a serious risk for human health. The copper, for example, in low quantities is essential for live and human health, but when its concentration is superior then a critical one, copper ion acts as a toxic compound on the environment and humans.

For human beings copper may cause serious problems such as anemia, kidney and stomach ache and stomach intestinal distress [1–3]. Principal copper sources in industrial waste waters are electroplating, metal cleaning plating baths, mining, fertilizers, pulp and paper, and petroleum industries. The copper ions concentration in these waters may reach values as much as 1000 mg/L [3,4].

Various technologies have been applied for reduction of pollutants' levels in industrial effluents prior entering rivers and lakes. The conventional methods for wastewater treatment include chemical precipitation, adsorption, ion exchange, membrane purification and reverse osmosis [5]. However, these methods have shown some disadvantages such as high cost, continuous treatment with chemical substances, and sometimes these methods are not able to meet the Environmental Protection Agency requirements for concentration levels of metal ions in industrial effluents [3,6].

One of the most promising alternatives for treatment of wastewater containing heavy metals appears to be the biosorption process, where living organisms such as fungi, bacteria and marine algae are used as an adsorbent. A major advantage of using these organisms is that they can be obtained as a residue from the bio-industries or as an algae biomass existing in nature [7]. The efficiency of the biosorption process on heavy metals

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**Nomenclature**

| | |
|---|---|
| $A_0$ | frequency factor of the Ahrrenius equation |
| $b$ | Langmuir isotherm parameter (L/mmol) |
| $C$ | concentration of copper (II) ions in the bulk fluid phase (mmol/L) |
| $C_e$ | concentration of copper (II) ions in the bulk fluid phase in equilibrium (mmol/L) |
| $C_0$ | feed concentration of copper (II) ions in the bulk fluid phase (mmol/L) |
| $C_{OUT}$ | concentration of copper (II) in the column outlet (mmol/L) |
| $C_i^{EXP}$ | experimental effluent concentration of copper ions (mmol/L) |
| $C_i^{MOD}$ | model effluent concentration of copper (II) ions (mmol/L) |
| $E_a$ | activation energy (KJ/mol) |
| $I_0$ | Bessel function |
| $k_{a1}$ | adsorption kinetic constant of the Thomas model (L/mmol min) |
| $k_{a2}$ | adsorption kinetic constant of the Bohart–Adams model (L/mmol min) |
| $k_d$ | desorption kinetic constant of the Thomas model (min$^{-1}$) |
| $m$ | experiments number |
| $m_s$ | biomass dry weight (g) |
| $\bar{q}$ | average concentration of copper (II) ions adsorbed in the algae (mmol/g) |
| $q_e$ | average concentration of copper (II) ions adsorbed in the algae in equilibrium (mmol/g) |
| $q_{max}$ | Langmuir isotherm parameter (mmol/g) |
| $Q$ | volumetric flow rate (cm$^3$/min) |
| $R$ | ideal gas constant (=8.314 J/mol K) |
| $t$ | time (min) |
| $t_f$ | minimum residence time (min) |
| $T$ | absolute temperature (K) |
| $u_0$ | fluid phase interstitial velocity (cm/min) |
| $V_L$ | fixed bed volume (cm$^3$) |
| $V_V$ | void bed (cm$^3$) |
| $z$ | bed height (cm) |

*Greek letters*

| | |
|---|---|
| $\varepsilon$ | column void fraction |
| $\eta, \xi$ | integration variables of the Thomas model |
| $\rho_B$ | bed density (g/L) |

fixed bed column is the most advantageous. Its mode of operation is simple, it is possible to reach high removal efficiency, and can be easily scaled up from a laboratory to an industrial application. The operation with fixed bed column is effective, because mass transfer into it is favorable by concentration driving force established in the column which is the same one for the adsorption process allowing more adsorbent efficiency, which reflects on effluent quality [5].

Most separation and purification processes, based on the sorption technology, involve continuous flow operations. In this operating mode, the saturated solid sorbent zone gradually extends throughout the column where the sorbate is adsorbed. The adsorption experimental data show a typical S-shaped curve where the slope is a result of three factors: the equilibrium sorption isotherm relationship, mass transfer effects throughout the sorbent in the column, and the influence of axial mixing, which determines deviation from the ideal plug-flow behavior [14].

The design and fixed bed column optimization involve the mathematical models, which are used for description and prediction of the experimental data (breakthrough curves) giving opportunity to scale up the biosorption process [15].

Recently, the computer development technology in relation with effective modern numerical methods has been given more possibilities for development of adequate and robust models which are used for prediction of fixed bed column dynamics and behavior [16]. As the results of this development, various researchers [7,14,17] have presented complex mathematical models which in order to predict fixed bed column dynamic behavior for heavy metal removal required the solution of a set of partial differential equations.

A serious disadvantage of these models, based on the mass transfer effects, is that they require extraordinary efforts to determine many model parameters [16]. In addition, if the goal of the modeling is to predict the adsorption fixed bed column height with high level of exactness, the use of more simple models which necessitate numerical solutions seems to be more effective giving immediate benefits [5]. Recently, different researchers [8,9,18] have successfully used models with analytical solutions, such as Thomas and Bohart–Adams models for representation of the heavy metals removal dynamics in fixed bed column.

The main considerations of Bohart–Adams model are that the intraparticle diffusion and external resistance for mass transfer are negligible and the adsorption kinetics is controlled by chemical reaction on the surface between the adsorbent and sorbate [15]. The same considerations are valid for the Tomas model.

The most important aim of this work was to evaluate the efficiency of Thomas and Bohart–Adams models analytical solutions describing the copper (II) ions removal dynamics in fixed bed column by using the *Sargassum* sp. marine algae biomass as an adsorbent.

## 2. Materials and methods

### 2.1. Biomass

The utilized biomass in this study was marine algae of *Sargassum* sp. The biomass was washed with chlorinated water and

removal from industrial effluents has been studied by numerous researchers [3,8–10].

Some studies on heavy metals biosorption in batch operation system may be found elsewhere [3,11–13]. However, for wastewater treatment of huge quantities, practical application of the biosorption process in fixed bed columns in a continuous operation mode seems to be more useful. There are other reactor types such as well mixed reactors or fluidized bed columns which can be applied, but nevertheless an adsorption process in

was rinsed with distilled water. Further, it was dried in oven at 60 °C for 24 h. To be obtained dry weight biomass, it was dried in the oven at 105 °C for 24 h.

The performed experiments in this study have utilized the non-chemically treated biomass. To guarantee the more homogenous biosorbent, a particular biomass form was used. The dried algae were triturated by a domestic liquifier. The particular biomass was separated with a particular sieve. The algae fraction taken from the "mesh" sieves 8 and 9 corresponded to a diameter of 2.2 mm, and was separated and stored in plastic bags to be preserved at room temperature.

### 2.2. Copper solution

The copper solutions were prepared by dissolving sulfate copper salt ($Cu(SO_4) \cdot 5H_2O$) (Merck®) in distilled water.

### 2.3. Preparation and operation with the biosorption column

The experiments were performed for continuous operation in a stainless steel column with 2.8 cm i.d. and 50 cm height. The bed height used in the study was 30.6 cm. The biomass was inserted into the column and after that the column was filled up with distilled water for 12 h. This hydration was necessary because of the used biomass ability to absorb huge amount of water expanding the bed volume. Further, the biomass was separated from the water used for hydration and once again was distributed into the column, where the column height was fixed at 30.6 cm. The biosorbent was distilled water washed for the last time by using continuous flow for 12 h. Fig. 1 illustrates the experimental module.

A feed solution containing copper (II) ions was pumped into the column bottom by peristaltic pump, with the flow rate 6 cm³/min. The values of total copper ions concentration in the solution were as follows: 2.08, 4.16, 6.42 and 12.72 mmol/L.

The feed solution and the fixed bed column temperature were maintained at 30 °C with a thermostatic bath. The feed solution pH was maintained constant at pH = 3.5.

The column effluent samples containing metal ions of interests were taken at predefined time intervals and were analyzed by using atomic absorption spectrophotometer (Varian SpectrAA-10 plus).
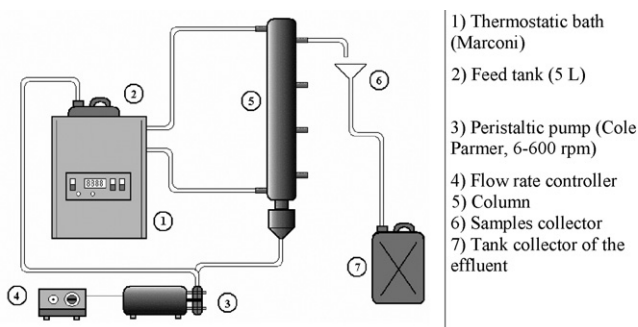


1) Thermostatic bath (Marconi)

2) Feed tank (5 L)

3) Peristaltic pump (Cole Parmer, 6-600 rpm)

4) Flow rate controller
5) Column
6) Samples collector
7) Tank collector of the effluent

Fig. 1. Scheme of the biosorption experimental equipment with fixed bed column.

### 2.4. Calculous of the biosorption column efficiency

The copper ion quantity removed from the marine algae biomass of *Sargassum* sp. was calculated through the obtained experimental curves by applying the following equation:

$$q_e = \frac{C_0 Q}{1000 m_s} \int_0^t \left( 1 - \frac{C_{OUT}}{C_0} \right) dt - \frac{V_L \varepsilon C_0}{m_s} \tag{1}$$

The integral term of the Eq. (1) was solved numerically by using trapezium principal method and applying curve experimental data.

In relation with $q_e$ and $C_0$ four experimental points were generated utilizing four curves and using Eq. (1). The Langmuir isotherm constants values were estimated on the bases of these four points and applying a nonlinear identification procedure.

### 2.5. Bed porosity determination

The bed porosity ($\varepsilon$) was determined on the bases of the empty volume measures (distilled water volume necessary to fill up the bed). At the end of each experiment, the copper solution was drained out from the column. The solution drainage was performed for at least 24 h. The peristaltic pump was feeding the (drained) column by using a recipient vessel with the known volume of distilled water. The water volume necessary to fill up the column bed was determined from the difference between the initial recipient vessel volume and the final one after the procedure of bed fulfillness.

The bed porosity was calculated on the bases of the following equation:

$$\varepsilon = \frac{V_V}{V_L} \tag{2}$$

These experimental data were already published by Silva et al. [19]. The authors has represented the biosorption of copper ions in fixed bed by mathematical models with numeric solution.

## 3. Mathematical modeling

The mathematical modeling has a key role in the scale up procedure from laboratory experiments through pilot plant to industrial scale. The adequate models can help to analyze and to explain experimental data, to identify mechanisms relevant to the process, to predict changes due to different operating conditions, and to optimize the overall productivity of the process [7].

In this study were applied mathematical models with analytical solutions developed by Thomas [20] and Bohart–Adams [21] to represent the copper (II) ions biosorption dynamics in fixed bed column by using marine algae biomass of *Sargassum* sp.

### 3.1. Thomas model

The Tomas model has considered the following assumptions:

- negligible axial and radial dispersion in the fixed bed column;
- the adsorption is described by a pseudo second-order reaction rate principle which reduces a Langmuir isotherm at equilibrium;
- constant column void fraction;
- constant physical properties of the biomass (solid phase) and the fluid phase;
- isothermal and isobaric process conditions;
- the intraparticle diffusion and external resistance during the mass transfer processes are considered to be negligible.

On the bases of these assumptions, the mass balance of copper ion concentration distribution and utilization in the fluid phase is described by

$$\frac{\partial C(t,z)}{\partial t} + \frac{\rho_B}{\varepsilon}\frac{\partial \bar{q}(t,z)}{\partial t} + u_0\frac{\partial C(t,z)}{\partial z} = 0 \tag{3}$$

The term $\partial \bar{q}(t,z)/\partial t$ of the Eq. (3) represents the local adsorption rate between the fluid and solid phases. The Thomas model assumes that the adsorption process can be described by a pseudo second-order reaction rate expression:

$$\frac{\partial \bar{q}(t,z)}{\partial t} = k_{a1}(q_{max} - \bar{q}(t,z))C - k_d\bar{q}(t,z) \tag{4}$$

At equilibrium ($\partial \bar{q}(t,z)/\partial t = 0$), the Eq. (4) results in Langmuir isotherm form:

$$\bar{q} = q_e = \frac{q_{max}C_e(k_{a1}/k_d)}{1 + C_e(k_{a1}/k_d)} = \frac{q_{max}C_e b}{1 + C_e b} \tag{5}$$

The Langmuir constant and the ratio between adsorption kinetic constant and desorption one is ($b = k_{a1}/k_d$), hence, the Eq. (4) can be rewritten as follows:

$$\frac{\partial \bar{q}(t,z)}{\partial t} = k_{a1}(q_{max} - \bar{q}(t,z))C - \frac{k_{a1}}{b}\bar{q}(t,z) \tag{6}$$

The initial condition of the fluid phase concentration is as follows:

$$C(0,z) = 0 \tag{7}$$

The initial condition for the model of average concentration of the adsorbed copper (II) ions in the algae ($\bar{q}$) can be written as follows:

$$\bar{q}(0,z) = 0 \tag{8}$$

The boundary condition is written as suggested by Amundson [22]:

$$C(t,0) = \begin{cases} 0, & t = 0 \\ C_0, & t > 0 \end{cases} \tag{9}$$

The analytical solution of Eqs. (3) and (6), where the initial conditions were given by Eqs. (7) and (8), and the boundary condition was given by Eq. (9) (Thomas[20]), is obtained as follows:

$$\frac{C_{OUT}}{C_0} = \frac{I_0(2\sqrt{ABxy}) + \varphi(\alpha y, \beta x)}{I_0(2\sqrt{ABxy}) + \varphi(Bx, Ay) + \varphi(\alpha y, \beta x)} \tag{10}$$

where

$$\varphi(Bx, Ay) = \int_0^x B\,e^{B\xi}I_0(2\sqrt{AB\eta(x-\xi)})\,d\xi \tag{11}$$

$$\varphi(\alpha x, \beta y) = \int_0^y B\,e^{B\eta}I_0(2\sqrt{\alpha\beta x(y-\eta)})\,d\eta \tag{12}$$

and

$$x = \frac{z}{u_0} \tag{13}$$

$$y = \frac{1}{\omega}(t - x) \tag{14}$$

The variable $t$ represents the process time (min) and $\eta$, $\xi$ are integration variables and where

$$A = \frac{\omega k_{a1}}{b}, \qquad B = \omega k_{a1}C_0, \qquad \omega = \frac{\rho_B q_{max}}{\varepsilon C_0} \tag{15}$$

$$\alpha = \omega k_{a1}C_0 + \omega\left(\frac{k_{a1}}{b}\right), \qquad \beta = \frac{\omega k_{a1}(k_{a1}/b)C_0}{k_{a1}C_0 + (k_{a1}/b)} \tag{16}$$

The parameters units of $A$, $B$, $\alpha$ and $\beta$ are [min$^{-1}$] and $\omega$ are a dimensionless constants.

The integrals of the Thomas model (Eqs. (11) and (12)) were solved by using subroutine QDAG coded in FORTRAN. This subroutine integrates a function using a globally adaptive scheme based on Gauss–Kronrod rules.

### 3.2. Bohart–Adams' model

Bohart–Adams [21] have developed one of the simplest models for the rupture curve representation. The model was proposed to describe the sorption dynamics of gaseous chlorine in fixed bed columns utilizing charcoal as an adsorbent. The Bohart–Adams model can be considered as a simple form of the Thomas model. When the isotherm is highly favorable, the Thomas model is reduced to the Bohart–Adams one. The difference between models is in the adsorption kinetics, where Thomas has considered that the adsorption description has been in accordance with the principle of the second order reversible reaction. Bohart–Adams have considered the adsorption as an irreversible second order reaction. The adsorption kinetics according to the Bohart–Adams models is written as follows:

$$\frac{\partial \bar{q}(t,z)}{\partial t} = k_{a2}(q_e - \bar{q}(t,z))C \tag{17}$$

The rate equation of the Bohart–Adams model in equilibrium ($\partial \bar{q}(t,z)/\partial t = 0$) is reduced to an isotherm rectangular, which is $q_e = \bar{q}$.

The analytical solution of the Bohart–Adams model (see Eqs. (3) and (17) with the given initial Eqs. (7) and (8) and boundary conditions Eq. (9)) is obtained in the form of Eq. (18). The applied method for search of the analytical solution has been

presented by Amundson [22].

$$\frac{C_{\text{OUT}}}{C_0} = \begin{cases} 0, & t < t_{\text{f}} \\ \dfrac{1}{(e^A + e^{-B} - 1)e^B}, & t > t_{\text{f}} \end{cases} \qquad (18)$$

where

$$A = \frac{z\beta}{u_0}, \qquad B = \frac{(-tu_0 + z)\beta}{\alpha u_0}, \qquad \alpha = \frac{\rho_{\text{B}} q_{\text{e}}}{C_0 \varepsilon} \qquad (19)$$

$$\beta = k_{\text{a}2} C_0 \alpha, \qquad t_{\text{f}} = \frac{z}{u_0} \qquad (20)$$

Three groups of parameters have to be distinguished in the Thomas and Bohart–Adams models. Experimentally determined parameters, such as ($\rho_{\text{B}}$, $\varepsilon$, $u_0$, $C_0$) are included in the first group. The second group of parameters ($q_{\text{max}}$, $b$) include Langmuir isotherm constants which were determined on the bases of dynamic equilibrium data obtained in the column. The third group included the model parameters ($k_{\text{a}1}$, $k_{\text{a}2}$) which values were estimated in the non-linear identification procedure by using the experimental data and least square statistical method.

The parameters values of the Thomas model ($k_{\text{a}1}$) and Bohart–Adams model ($k_{\text{a}2}$) were obtained during the search of a minimum of the following objective function:

$$F_{\text{OBJ}} = \sum_{j=1}^{n_1} (C_j^{\text{EXP}} - C_j^{\text{MOD}})^2 + \sum_{j=1}^{n_2} (C_j^{\text{EXP}} - C_j^{\text{MOD}})^2 + \cdots$$
$$+ \sum_{j=1}^{n_{\text{m}}} (C_j^{\text{EXP}} - C_j^{\text{MOD}})^2 \qquad (21)$$

where $m$ is the number of independent experimental sets ($m = 4$), and $n_j$ is the number of experimental data referred to set $j$ and all concentrations are considered in position $z = L$.

To search the objective function minimum, the safeguarded quadratic interpolation method was applied which was coded in FORTRAN language. This method was used to find a minimum point of an unvaried function.

## 4. Results and discussion

This work evaluated the ability of the Bohart–Adams and Thomas models to predict the copper (II) ions removal dynamics in a fixed bed column by utilizing the biomass from marine algae *Sargassum* sp. as an adsorbent.

Four experimental sets of copper (II) ions biosorption were performed in fixed bed column. The feed concentrations of the copper (II) ions were chosen as follows – 2.08, 4.16, 6.42 and 12.72 mmol/L, where experimental conditions like flow rate, porosity, bed height and density were maintained constant during the all sets of experiments. Their values are shown in Table 1.

The Langmuir isotherm constants were obtained on the bases of the equilibrium data from the experimental sets on the copper (II) ions removal performed in the fixed bed column. The Langmuir isotherm constants values estimated by using non linear parameters identification procedure were as follows: $q_{\text{max}} = 7.14$ mmol/g and $b = 1.22$ L/mmol. Recently, some publications [7,8,18] have pointed out that the Langmuir isotherm

Table 1
Operating conditions and bed properties values Parameters

| | |
|---|---|
| $Q$ (cm$^3$/min) | 6.00 |
| $\varepsilon$ | 0.90 |
| $z$ (cm) | 30.6 |
| $\rho_{\text{B}}$ (g/L) | 41.56 |

constants can be determined on the bases of equilibrium data obtained in a continuous system.

Table 2 shows comparison of the capacity values of copper (II) ions removal obtained either experimentally (see Eq. (1), or mathematically using Langmuir model. Analyzing the obtained low values, it was obvious that the Langmuir isotherm can be used adequately for description of the equilibrium relation between concentrations of copper (II) ions in solution and in the solid phase.

A representation of the copper (II) ions adsorption dynamics in fixed bed column by using both Thomas and Bohart–Adams models require to determine adsorption kinetic rate constants values ($k_{\text{a}1}$, $k_{\text{a}2}$) [16], as well the Langmuir isotherm constants. The adsorption kinetic rate constants can be estimated by solving simultaneously the system differential equations (see Eq. (6) for Thomas model, Eq. (17) for the Bohart–Adams one, Eq. (3) for mass conservation, Eq. (9) for the boundary condition, and Eqs. (7) and (8) for the initial conditions).

The biosorption rate constant ($k_{\text{a}}$) is expressed as a function of temperature in accordance with the Arrhenius equation [5]:

$$k = A_0 e^{-E_{\text{a}}/RT} \qquad (22)$$

To obtain the rupture curves, the temperature was maintained constant at 30 °C. The unique adsorption rate kinetic constant ($k_{\text{a}}$) value was estimated for both models Thomas and Bohart–Adams, independently from the copper (II) ions concentration in the column feed. Lodeiro and Goel [15,18] demonstrated an application of the Bohart–Adams model for representation of the adsorption/biosorption dynamics in the fixed bed columns and estimating ($k_{\text{a}2}$, $q_{\text{max}}$) parameters by using rupture curve experimental data. In particular, the parameters identification were done for the initial part of the rupture curve (until to rupture point). In the original model of Bohart–Adams, the removal capacity of adsorbate by the adsorbent is considered to be constant, and this is independent from the concentration of the liquid phase. However, for the majority of cases this fact is not observed. The results in Table 2 have shown that the quantity of removed copper has increased signifi-

Table 2
Experimental and calculated (Langmuir) data of copper (II) uptake capacity ($q_{\text{max}} = 7.14$ mmol/g; $K = 1.22$ L/mmol)

| $C_0$ (mmol/L) | $q_{\text{e}}$ (mmol/L) (experimental data) | $q_{\text{e}}$ (mmol/L) (Langmuir isotherm data) | Deviation (%)[a] |
|---|---|---|---|
| 2.08 | 5.12 | 5.12 | 0.00 |
| 4.16 | 5.82 | 5.96 | 2.35 |
| 6.42 | 6.66 | 6.32 | 5.38 |
| 12.72 | 6.56 | 6.70 | 2.09 |

[a] Deviation $= 100|q_{\text{e}}^{\text{exp}} - q_{\text{e}}^{\text{mod}}|/q_{\text{e}}^{\text{exp}}$.

Table 3
Rate constants of Thomas and Bohart–Adams models and objective function values

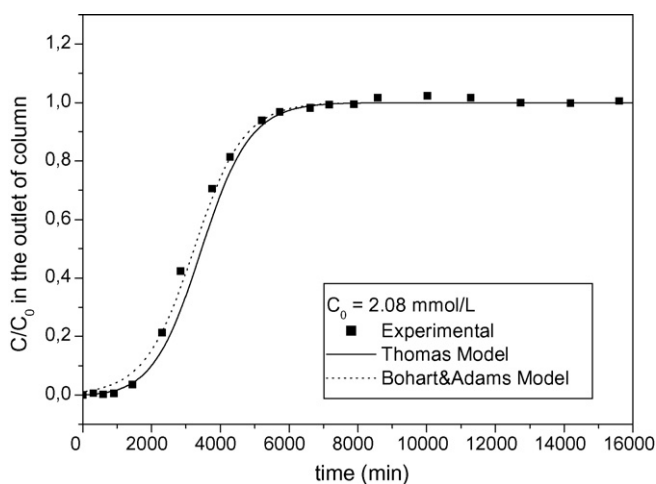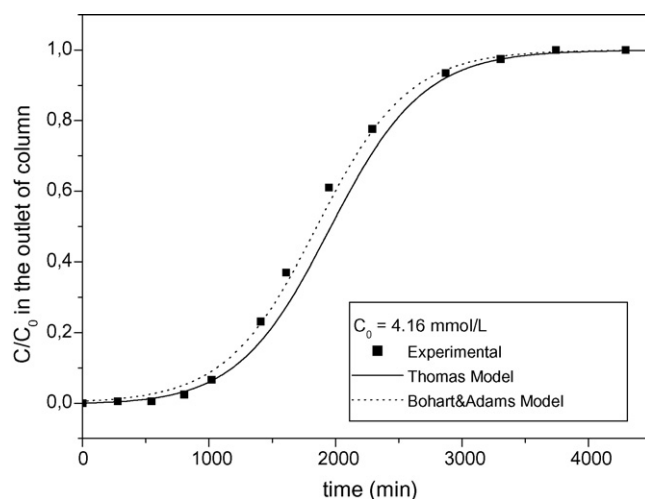| Thomas model | |
|---|---|
| $k_{a1}$ (L/mmol min) | 0.0006 |
| $F_{OBJ}$ | 0.1157 |
| Bohart–Adams model | |
| $k_{a2}$ (L/mmol min) | 0.0006 |
| $F_{OBJ}$ | 0.0770 |

cantly with the increasing of the copper concentration in the fluid phase. Hence, to apply the Bohart–Adams model for description of experimental data of rupture curve, the value of $q_e$ of the Eq. (17) was calculated by using the Langmuir isotherm model for each feed concentration.

Table 3 presents the rate constants values of Thomas and Bohart–Adams models estimated by using non linear parametrical identification procedure and experimental data of the rupture curve. All of the rupture curve experimental points were taken into consideration during the identification process. Table 3 presents the objective function (see Eq. (21)) values for both models, as well. By using the adsorption kinetic constant of Thomas model, desorption constant value $k_d = 0.0005$ was calculated.

Rupture curve values obtained both, experimentally and calculated by using Thomas and Bohart–Adams models are presented in Figs. 2–5. The influence of the copper (II) feed column concentration on the shape of the rupture curve was significant. For majority of the feed concentrations, a major rupture curve inclination and smaller saturation time were observed. Copper (II) ions feed concentration values were 2.08, 4.16, 6.42 and 12.72 mmol/L, and saturation times were 7000, 4500, 3000 and 1500 min, respectively.

In our case, the driving force of the adsorption process was the difference between the concentration of sorbate on the adsorbent surface and in the solution. For high feed concentrations differences, elevated column adsorption capacity was obtained (see Table 2) which is in accordance with the theory.

The models have predicted very well the initial part of the rupture curve. This result is extremely important for the prac-



Fig. 3. Experimental and calculated breakthrough curves for $C_0 = 4.16$ mmol/L.
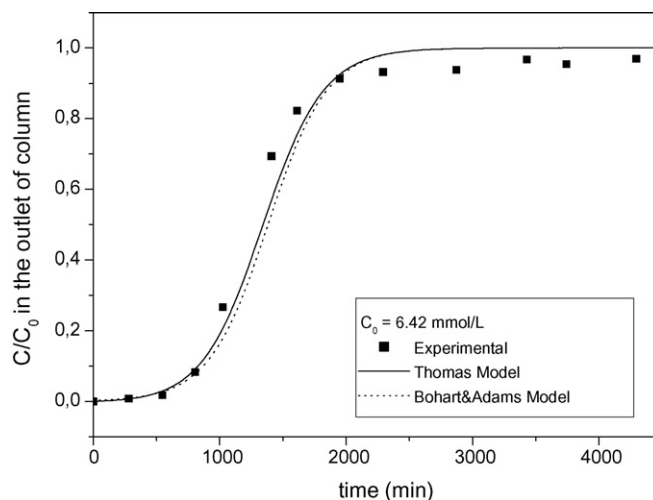


Fig. 4. Experimental and calculated breakthrough curves for $C_0 = 6.42$ mmol/L.



Fig. 2. Experimental and calculated breakthrough curves for $C_0 = 2.08$ mmol/L.
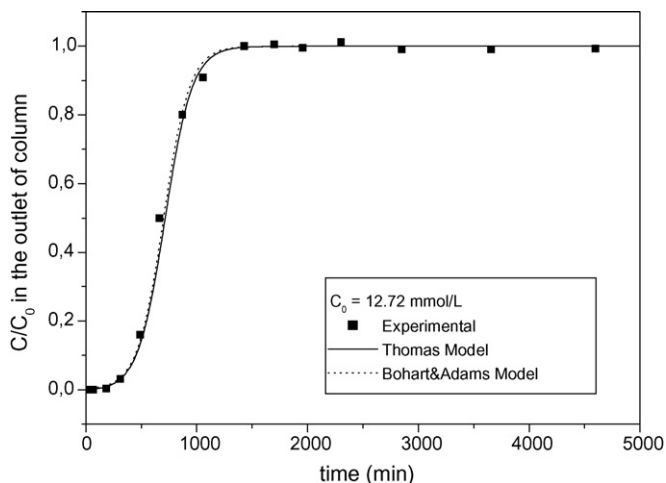


Fig. 5. Experimental and calculated breakthrough curves for $C_0 = 12.72$ mmol/L.

tice because the initial part of the rupture curve determines the useful dynamic capacity of the fixed bed column [16]. Nevertheless, the model predicted curves and experimental ones did not match perfectly in the second part of the rupture. The possible explanation of this deviation may be found in the hydrodynamic phenomena such as axial dispersion and related with these velocity gradients into the column. It has to be noted, that these effects are out of consideration in our study because of the Thomas and Bohart–Adams models assumptions.

The adequacy of the Thomas and Bohart–Adams models to experimental data can be explained by the fact that the models have considered internal and external diffusion as not controlling adsorption process stages. In the particular case of the Tomas model, the kinetics of adsorption/desorption process follows the Langmuir isotherm. On the other hand, the adsorption process is not controlled by a chemical reaction, but more often is controlled by interphase mass transfer processes [5,20,23]. This fact can initiate some errors when the Thomas and Bohart–Adams are used for the representation of the adsorption process dynamics [5], where mass transfer effects are significant.

According to Lodeiro [15], for majority of cases, these simple models are able to describe rupture curve precisely, and at the same time, give values of the important kinetic constant such as ($k_a$).

## 5. Conclusions

In this work was studied the ability of the Thomas and Bohart–Adams mathematical models to represent the copper (II) ions removal dynamics in fixed bed column by using algae biomass of *Sargassum* sp. at temperature $30\,^\circ$C and pH = 3.5.

The principles conclusions of the study are as follows:

- the adsorption process of copper (II) ions in fixed bed column by using marine algae of *Sargassum* sp. was strongly dependent from the copper(II) ions column feed concentration;
- the used models predicted very well the initial part of the experimental curve which has given the good idea about the fixed bed column efficiency. However, it was observed a small deviation between experimental curve and models prediction in the area of the ascended part of the curve, but nevertheless the authors are confident about the predictive power of the used models;
- The Thomas and the Bohart–Adams models have demonstrated flexibility and have represented well the copper (II) ions biosorption dynamics in the simple way, where in the fixed bed column the marine algae biomass of *Sargassum* sp. was used as an adsorbent. Moreover, the obtained values of equation rate constants of the Tomas and Bohart–Adams models can be used for adsorption column design which is applied for this particular system and working conditions.

## Acknowledgements

## References

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