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HIGHLIGHTS

• A model based on Thomas equation and ANNs has been proposed to predict breakthrough curves.
• This model has been used to predict fluoride adsorption breakthrough curves using bone char.
• This modeling approach is useful for process systems engineering of fixed-bed columns.

GRAPHICAL ABSTRACT

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ABSTRACT

This study introduces a hybrid model based on the Thomas equation and artificial neural networks (ANNs) for the modeling of unsymmetrical breakthrough curves obtained from the fluoride adsorption on bone char. Experimental results of kinetics, isotherms and breakthrough curves of fluoride adsorption on two commercial bone chars have been used for analyzing the capabilities and limitations of this hybrid ANN model. Performance of this hybrid model has been studied and compared with respect to the results of traditional linear regression of the Thomas breakthrough equation at different operating conditions of packed-bed adsorption columns. Results showed that an improvement in the modeling capabilities of Thomas model can be obtained using ANNs. Specifically, the hybrid ANNs–Thomas model showed determination coefficients higher than 0.9 and its average mean square errors are lower, up to 86%, than those obtained with the linear modeling approach. In fact, the present study illustrates that the improper handling of the Thomas model using traditional regression approach may lead to imprecise values of design parameters and erroneous conclusions of adsorption performance. On the other hand, the hybrid ANNs–Thomas model is useful for determining reasonable and accurate design parameters of packed-bed adsorption columns. This modeling approach can be useful for the process system engineering of dynamic adsorption systems involved in the field of water treatment and purification.

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1. Introduction

Fluoride pollution in water resources for human consumption is considered a significant environmental problem in several developing countries of America, Africa and Asia [1,2]. Water pollution by fluoride is caused by both natural factors (e.g., geochemical composition of water wells) and anthropogenic sources (e.g., the use of fertilizers and semiconductors). In particular, water consumption with fluoride concentrations higher than 1.5 mg/L is toxic for human beings and, therefore, this fluoride concentration limit has been established as the guideline value by the WHO for drinking water [3]. Traditional symptoms of a chronic exposure to fluoride are the dental and skeletal fluorosis. However, studies reported in literature have documented different lesions in other organs of human being such as the endocrine glands, liver and
thyroid [4]. Therefore, water defluoridation is fundamental to meet environmental regulations for water quality, to prevent public health risks and to reduce the prevalence of dental and skeletal fluorosis and other fluoride-related diseases in endemic areas.

Adsorption process is considered the most effective and rentable method for fluoride removal from water and it offers advantages with respect to results obtained with other water treatment and purification technologies such as the electrodialysis, membrane processes and chemical precipitation [4,5]. Literature on adsorption process indicates that a wide variety of natural and synthetic adsorbents has been tested and applied for the removal of fluoride ions from aqueous solution [5–21]. These adsorbents include several types of activated carbons [7–9], polymers [10], clays [11], industrial wastes [12], biomasses [13–15] and others materials [16–21]. In particular, the modification of surface chemistry of adsorbents using multivalent metallic species (e.g., lanthanum, magnesium, zirconium) appears to be a promising approach for developing novel materials for water defluoridation [14,22,23].

In the case of commercial options available in the worldwide market, the activated alumina [4,24] and the bone char [25–27] are the most used and effective adsorbents for fluoride removal from water.

Water defluoridation systems based on the adsorption process generally use the configuration of packed-bed columns [10,24,28–32]. This separation system is very flexible and easy in terms of design and operation; and it offers several advantages such as there is an effective contact between the adsorbent and the fluid to be treated, the adsorption rates are favored due to the adsorbent is continuously in contact with a fresh solution, a large-scale water treatment is feasible in a reduced time, the adsorbent regeneration can be performed in the same column, and the equipment and supplies required for the column operation are not expensive. Overall, this treatment system shows a high degree of stability and reliability at a wide range of operating conditions and it can practically meet strict regulations of water quality [33].

Performance of packed-bed adsorption columns are characterized via the breakthrough curve, i.e., the effluent concentration profile versus time (for a constant flow rate) or volume of treated effluent. The quantitative characterization of the performance of the packed-bed adsorption columns involves the modeling and prediction of this breakthrough curve. Note that this modeling stage is fundamental for the design and optimization of this separation system. In fact, extensive studies in pilot plant scale can be avoided if the breakthrough curves for adsorption columns can be reliably predicted using laboratory measurements [33].

The reliable modeling of breakthrough curves requires the application of proper numerical procedures. The modeling approaches used for data fitting of breakthrough curves include theoretical (e.g., mass transfer and kinetic models), empirical and semi-empirical equations. Note that the modeling of packed-bed adsorption processes using a theoretical and rigorous model usually requires the application of numerical methods, which may show convergence problems due to poor initialization and non-linearity of the problem to be solved. Alternatively, several simple breakthrough equations have proposed for data correlation of dynamic adsorption experiments. For example, these equations include Bohart–Adams model [34], Thomas model [35], Yoon–Nelson model [36], Clark model [37] and the error-function model [38]. However, these models are suitable for the data correlation of symmetrical breakthrough curves but they may be inadequate and fail to describe the performance of packed-bed columns with a complex adsorption process (i.e., unsymmetrical breakthrough curves). It is convenient to remark that the modeling of breakthrough curves is challenging due to the nonlinearity of equations used for describing the equilibrium, kinetics and mass transport phenomena involved in dynamic adsorption processes [39]. In fact, some authors have recognized that the development of breakthrough models for describing accurately the performance of packed-bed columns is a difficult task [40].

Based on the fact that accurate and simple breakthrough models are required for the proper design of adsorption process, in this study we propose a hybrid neural network approach for the modeling of unsymmetrical adsorption breakthrough curves. Specifically, artificial neural networks (ANNs) are used to improve the modeling capabilities of traditional breakthrough equations for adsorption systems involving priority water pollutants. Literature indicates that ANNs have been widely used to model complex relationships between inputs and outputs or to find patterns in selected data [41]. For the case of dynamic adsorption systems, some studies have reported the application of ANNs as a black-box model (i.e., an empirical model that relies on measurements only) for data fitting of breakthrough curves [33,42,43]. In this study, a hybrid approach based on the combination of Thomas breakthrough equation [35] and ANNs (i.e., a gray-box model) has been used to model the performance of packed-bed adsorption columns for the fluoride removal from water using bone char. This modeling approach has been used for data analysis in other science fields [44,45] and, to the best of our knowledge, this is the first application of ANNs to improve the performance of traditional breakthrough equations in adsorption research. Capabilities and limitations of this approach for modeling dynamic adsorption processes are discussed and analyzed. Our results show that an improvement in the modeling capabilities of Thomas model can be obtained using ANNs. Finally, the proposed approach can be useful for the process system engineering of dynamic adsorption systems involved in the field of water treatment and purification.

2. Methodology

2.1. Bone chars used in adsorption experiments

Fluoride adsorption experiments were performed using two commercial bone chars: BCM from Carbones Mexicanos (Mexico) and BCB (Brimac 216) from Brimac Carbon Services (United Kingdom). Table 1 provides the general specifications of these adsorbents provided by the supplier. Physicochemical properties and textural parameters of these adsorbents were determined in this study. Specifically, the elemental composition of bone chars was determined with a LECO CHNS-932 elemental analyzer and the oxygen content with a LECO VTF-900. Textural parameters were calculated from the nitrogen adsorption isotherms at 77 K, which were obtained with a Micromeritics TriStar II 3020. Organic functional groups were identified by FT-IR spectroscopy using a Thermo Nicolet 6700 spectrophotometer and the diffraction patterns of these adsorbents were recorded in a Bruker D8 Advance diffractometer equipped with a Cu Kα X-ray source operated at 40 kV and 40 mA. A single Göbel mirror configuration was used.
to monochromatise and focus the X-rays on the samples attaining highly efficient parallel beam geometry. Step scanning, with a step size of 0.02° 2θ and a scan step time of 5 s, was used for collecting the diffraction data. Additionally, the physical morphology of bone chars was observed using a FE-SEM system (Quanta FEG 650, FEI) equipped with an EDX analyzer (Ametek-EDAX). Adsorbent particles were dispersed on a graphite adhesive tab placed on an aluminium stub and no further coating was required. A semi-quantitative analysis of the inorganic elements was obtained by EDX and an average of three punctual analyses on the bone char surface at 20 μm was reported.

2.2. Fluoride adsorption experiments in packed-bed columns using bone chars

Dynamic adsorption experiments were performed in a Pyrex glass column with 2.5 cm of internal diameter and 13 cm of length. This column was packed with 27.69 g (i.e., 7.5 cm of packing height) of each commercial boner char (particle size: 20–35 mesh fraction) and the bed porosity ranged from 25% to 30% for both adsorbents in all adsorption experiments. Fluoride breakthrough curves were obtained using each bone char and different feed fluoride concentrations (9–40 mg/L) and feed flow rates (3.3 and 6.6 mL/min). Note that these pollutant concentrations have been selected by considering that the groundwater extracted in several regions of Mexico and other countries may show fluoride concentrations up to more than 30 mg/L [2,5,9].

On the other hand, the range of feed flow rates corresponds to ≈1.5–3.0 min of residence time, which are common conditions for the operation of packed-bed adsorption columns [46,47]. Our experience in adsorption process used dynamic conditions indicated that residence times higher than 3 min do not improve significantly the performance of removal process due to limitations caused by mass transfer phenomena. Fluoride solutions were prepared using analytical grade sodium fluoride (NaF) and deionized water. All adsorption experiments were performed at pH 7 and 30 °C using a peristaltic pump and an upflow operation mode, which was used to avoid an excessive head-loss and channeling.

Several effluent samples were collected from the packed-bed column at regular time intervals and the fluoride concentration in all samples was determined to obtain the breakthrough curve. Fluoride concentrations were quantified using a fluoride ion selective electrode (Denver Instruments, UP-25) and TISAB buffer (Hach) [33]. Concentrations were measured using a fluoride ion selective electrode equipped with an EDX analyzer (Ametek-EDAX). Adsorbent particles were dispersed on a graphite adhesive tab placed on an aluminium stub and no further coating was required. A semi-quantitative analysis of the inorganic elements was obtained by EDX and an average of three punctual analyses on the bone char surface at 20 μm was reported.

2.2. Fluoride adsorption experiments in packed-bed columns using bone chars

2.3. Analysis and modeling of the breakthrough curves of fluoride adsorption on bone char

2.3.1. Calculation of design parameters of breakthrough curves

Design parameters of the packed-bed columns were calculated from the experimental data of the fluoride breakthrough curves using both bone chars. Specifically, the mass transfer zone (MTZ) was calculated for different operating conditions of packed-bed columns using the next expression

\[
MTZ = L \left( \frac{t_b - t_0}{t_e} \right)
\]

where \( t_b \) is the breakthrough time, \( t_e \) is the exhaustion time and \( L \) is the bed height in cm. For this analysis, \( t_0 \) was defined as the time when \( [F^-]/[F]^0 = 0.05 \), while \( t_e \) corresponds to \( [F^-]/[F]^0 = 0.95 \), where \( [F^-] \) is the effluent fluoride concentration and \( [F]^0 \) is the feed fluoride concentration both in mg/L, respectively. The overall adsorption zone (\( \Delta t \)) was also determined using

\[
\Delta t = t_e - t_0
\]

On the other hand, the retardation factor (\( r_f \)) was used to determine the rate at which the pollutant moves within the packed-bed column [46]. This parameter has been obtained from the treated volume per void volume that gives \( [F^-]/[F]^0 = 0.5 \) or, equivalently, the operating time (\( t_{50S} \)) of the packed-bed column when the effluent concentration has reached 50% of the influent concentration, then

\[
r_f = \frac{V_{sox}}{A \varepsilon}
\]

where \( \varepsilon \) is the void volume of the packed-bed column, \( A \) is the cross sectional area of the column and \( L \) is the bed height of the column, respectively. Retardation factors were estimated for all operating conditions used in fluoride adsorption experiments.

Finally, the bed adsorption capacity (\( q_{bed} \)) and the maximum adsorption capacity obtained from fluoride adsorption isotherms (\( q_{e, max} \)) were used for the estimation of the filter material usage rate (\( F_q \))

\[
F_q = \frac{q_{bed}}{q_{e, max}}
\]

where \( q_{bed} \) and \( q_{e, max} \) are given in mg/g and are obtained at the same conditions of temperature and pH. Note that \( q_{bed} \) can be calculated via the integration of the experimental data \( \frac{t}{t} \) versus \( t \), or using a specific breakthrough equation (e.g., Thomas model). All these design parameters were used for characterizing the performance of both bone chars in fluoride adsorption columns at different operating conditions.

2.3.2. Data fitting of fluoride breakthrough curves using Thomas model

Thomas model [35] was used for modeling the fluoride adsorption breakthrough curves using commercial bone chars. This breakthrough model is based on Langmuir-type adsorption-desorption and assumes isothermal and isobaric operating conditions, a constant column void fraction, and the radial and axial dispersion are negligible in the packed bed column. For the case of fluoride adsorption, this model is given by

\[
\frac{[F^-]}{[F]^0} = \frac{1}{1 + \exp \left( \frac{q_{bed}W_{bed} - [F^-]_{V_{eff}}}{q_{e, max}W_{bed}} \right)}
\]

where \( V_{eff} \) is the treated volume of fluoride solution in L, \( Q \) is the feed flow rate in L/h, \( W_{bed} \) is the amount of bone char packed in the columns and is given in g, \( q_{bed} \) is the adsorption capacity of the packed-bed column estimated by the model given in mg/g and \( k_{th} \) is the Thomas rate constant reported in L/h mg, respectively.

Parameters \( k_{th} \) and \( q_{bed} \) can be obtained from a linear regression approach using the following linearized form of Thomas model

\[
\ln \left( \frac{[F^-]}{[F]^0} - 1 \right) = \frac{k_{th}W_{bed}}{Q} - \frac{k_{th}W_{bed}[F^-]V_{eff}}{Q}
\]

A plot of \( \ln \left( \frac{[F^-]}{[F]^0} - 1 \right) \) versus \( t \) at the given operating conditions (i.e., feed flow rate, temperature and pH) is used for this linear
regression. Excel Solver® has been used for performing the linear regression of Thomas model using the fluoride breakthrough curves of tested bone chars.

2.3.3. A gray-box model using ANNs and Thomas equation for data fitting of breakthrough curves

As stated, the linear regression approach is extensively used for determining the parameters of Thomas model and other traditional breakthrough equations. However, this approach may fail to fit the experimental adsorption data of unsymmetrical breakthrough curves. In fact, our experience and results of other studies on adsorption processes for water treatment indicate that the experimental breakthrough curves obtained for the removal of fluorides and other priority pollutants (e.g., heavy metals, dyes) are commonly unsymmetrical, e.g., [42,43,46,47]. Based on this fact, we have used a hybrid approach for modeling the breakthrough curves using ANNs and Thomas equation. Herein, it is important to remark that some authors have used ANNs for modeling adsorption breakthrough curves [33,39,43]. For example, Cavas et al. [43] have reported the comparison of the results obtained with the Thomas model and those results from the application of ANNs for modeling breakthrough curves. However, no attempts have been performed to combine both ANNs and breakthrough equations for modeling the experimental data of dynamic adsorption systems.

ANNs are black-box (i.e., empirical) computational models inspired by the biological neural networks. ANNs have the capabilities for predicting the performance of complex and non-linear problems and for finding patterns in data analysis relying only on measurements (inputs and outputs) [41]. A neural network consists of input, hidden and output layers, which are constituted by an interconnected group of artificial neurons. These artificial neurons are interconnected to each other via connection weights, which represent the relative strength of an input neuron in contributing to the output neuron, see Fig. 1. Formally, the net input $Y_\text{ij}$ of the neuron $j$ in the layer $i$ is given by

$$Y_\text{ij} = \sum_{k=1}^{m} w_{ik} V_{i,k} + \theta_\text{ij}$$  \hspace{1cm} (7)

$$V_\text{ij} = g(Y_\text{ij})$$  \hspace{1cm} (8)

where $w_{ik}$ is the connection weight, $V_{i,k}$ is the neuron input and $\theta_\text{ij}$ is the neuron bias. An activation function $g(Y_\text{ij})$ is used to calculate the neuron output $V_\text{ij}$ given the set of neuron inputs. The most common activation function is the sigmoid function, which has been used in this study for the neurons of hidden layers; while an identity function (i.e., $V_\text{ij} = Y_\text{ij}$) was used in the output layer. A training process is used to determine suitable values of $w$ and $\theta$ for each neuron of the ANNs model. Note that this training is performed using input data and target output values obtained from the system to be studied. So, we have used the classical backpropagation algorithm for ANNs training, which is a first order gradient descent method.

In this study, a hybrid model using a feed-forward ANNs architecture and Thomas breakthrough equation has been proposed for data fitting of fluoride breakthrough curves, see Fig. 2. In particular, this hybrid model imposes non-negativity constraints for the values of parameters of Thomas model: $k_\text{Th}$ and $q_{\text{bed,T}}$. The handling of these constraints has been performed using the procedure proposed by Dena-Aguilar [45]. Before the ANNs training process, the values of input neurons were normalized. Parameters of Thomas model, which were used to calculate the values of $\frac{F^-}{C_0}$, were considered as the targets of the ANNs model subject to the non-negativity restrictions: $k_\text{Th} > 0$ and $q_{\text{bed,T}} > 0$. These restrictions have been considered for the hybrid model because both parameters of Thomas equation have a physical and theoretical meaning. Without these restrictions, the hybrid model may find negative values for these model parameters thus losing its physical significance.

The training of the hybrid model was performed via the minimization of the following objective function

$$F_{\text{obj}} = \frac{1}{2} \sum_{m=1}^{n} \sum_{j=1}^{m_{\text{dat}}} \left( \frac{[F^-]_{\text{exp}} - [F^-]_{\text{calc}}}{[F^-]_0} \right)_{m,j}^2$$  \hspace{1cm} (9)

subject to:

$$k_\text{Th} > 0$$

$$q_{\text{bed,T}} > 0$$

![Fig. 1. Illustration of a neuron in an ANN model.](image)

![Fig. 2. Artificial neural network architecture used for modeling the fluoride adsorption breakthrough curves using bone char.](image)
where \( n_{\text{dat}} \) is the number of experimental data used for the training of hybrid model, \( n_n \) is the number of output neurons and superscripts \( \text{calc} \) and \( \text{exp} \) indicate the calculated and experimental values, respectively. Fortran\textsuperscript{9} programs were used for data modeling of fluoride breakthrough curves using this hybrid model based on ANNs and Thomas equation.

For ANNs training, the input data include the feed fluoride concentration \( \left[ F^- \right]_0 \), the operation time of packed bed column \( t \) and the feed flow \( Q \) obtained from fluoride breakthrough curves. Note that previous studies have used these input variables for the modeling of breakthrough curves using black-box ANNs models \([33,39,43]\) because they have a statistical influence on the performance of dynamic adsorption process. Additionally, this set of input variables is uncorrelated, which is in agreement to the basis of the principal component analysis approach. The architecture of hybrid ANN model was determined based on preliminary calculations using a trial and error procedure where the combination of input variables, the number of hidden layers and neurons were changed until finding a proper ANN architecture. Several ANN models were analyzed and they included different configurations of the input variables, i.e.: \( t-Q, t-\left[ F^- \right]_0, \left[ F^- \right]_0-Q \) and \( t-Q-\left[ F^- \right]_0 \), where the hybrid ANN model with three input variables offered the best performance. On the other hand, the results of sensitivity analysis indicated the following trend for the most influential variables: \( t > \left[ F^- \right]_0 > Q \). Therefore, the ANNs architecture used for modeling the fluoride adsorption breakthrough curves consisted of an input layer with three neurons \( t-Q-\left[ F^- \right]_0 \), two hidden layers with 18 neurons for each layer, and one output layer, see Fig. 2. It is convenient to remark that our calculations indicated that high number of hidden neurons (i.e., >18) caused overfitting of the model. Finally, the results obtained from the linear regression approach and those obtained from the hybrid model have been compared and analyzed using statistical criterions and design parameter calculations of packed-bed columns.

3. Results and discussion

3.1. Breakthrough curves of fluoride adsorption using commercial bone chars

Experimental data of fluoride breakthrough curves for both bone chars at different operating conditions of packed-bed columns are reported in Fig. 3. As expected, the characteristics and shape of fluoride breakthrough curves depend on the operating conditions of adsorption columns (i.e., feed flow rate, fluoride initial concentration and adsorbent type). However, it is clear that all the fluoride breakthrough curves of both adsorbents show a common S-shape but they are unsymmetrical. Note that all breakthrough curves obtained for the commercial bone chars showed a

![Fig. 3. Fluoride breakthrough curves using packed-bed adsorption columns and commercial bone chars. BCB: (a) 3.3 and (b) 6.6 mL/min; BCM: (c) 3.3 and (d) 6.6 mL/min.](image-url)
slow approach of \( [F^-]_t/[F^-]_0 \rightarrow 1.0 \), which is a common characteristic of adsorption processes in a liquid phase where the diffusion phenomena are the rate-limiting mass transport process [40].

In particular, the feed flow rate \( Q \) is a crucial parameter for the operation of packed-bed adsorption columns. This operating parameter has a direct impact on the mass transfer phenomena involved in the adsorption process under dynamic conditions. Fig. 3 also shows the effect of feed flow rate on the performance of both commercial bone chars for the fluoride removal from aqueous solution in the fixed-bed columns. It is clear that there is a reduction in the values of both \( t_b \) and \( t_e \) with the increment of the feed flow rate because the contact time between the adsorbent and the fluid to be treated is not enough for reaching the adsorption equilibrium thus limiting the diffusion and mass transfer of fluoride ions into the adsorbent. On the other hand, the feed fluoride concentration also influences the performance of adsorption columns using both bone chars. The adsorption columns operated at the lowest feed fluoride concentration (i.e., 9 mg/L) exhibited higher operating times than those obtained for the columns receiving feed fluoride concentrations of 20 or 40 mg/L. Note that the change of concentration gradient affects the adsorbent performance in packed bed columns [33] and, consequently, the saturation rate and the breakthrough time depends on the pollutant feed concentration. As expected, the breakthrough time of adsorption columns increased with a decrement in the feed fluoride concentration. In summary, the exhaustion of fluoride adsorption columns using both bone chars is faster if a high feed fluoride concentration and/or high feed flow rate are used, see Fig. 3. The service time of bone char packed columns used for fluoride removal decreased with both feed flow rate and inlet fluoride concentration. In particular, the fluoride breakthrough curves of BCM required the longest operating time to reach the breakthrough and exhaustion points than those breakthrough curves of BCB at the same operating conditions. Experimental operating times of adsorption columns for the exhaustion of BCB ranged from 12.7 to 58.3 h, and from 12.4 to 178.0 h for the BCM at tested experimental conditions. Therefore, characteristics, shape and position of the breakthrough curves indicate that the capacity of adsorption columns is different for each adsorbent and more fluoride ions can be removed using BCM in comparison to the packed-bed columns using BCB.

With illustrative purposes, Figs. 4 and 5 show the fluoride adsorption kinetics and isotherms obtained at batch conditions for both bone chars at 30 °C and pH 7. Results of fluoride adsorption kinetics have been modeled using both pseudo first- and second-order kinetic models, see Table 2. It is clear that the pseudo-second order model offers the best correlation for the fluoride adsorption rates on the commercial bone chars BCB and BCM. On the other hand, fluoride adsorption isotherms of Fig. 5 were fitted to Langmuir, Freundlich and Sips models and results of data correlation are reported in Table 3. Both Langmuir and Sips are suitable for the correlation of fluoride adsorption isotherms on commercial bone chars. Based on this fact, we have used the Langmuir model.

**Table 2**

<table>
<thead>
<tr>
<th>Bone char</th>
<th>([F^-]_0 ) (mg/L)</th>
<th>Results of kinetic data of fluoride adsorption on bone char</th>
<th>Pseudo second-order model[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_1) (h(^{-1}))</td>
<td>(q_e) (mg/g)</td>
</tr>
<tr>
<td>BCB</td>
<td>9</td>
<td>0.218</td>
<td>0.936</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.514</td>
<td>1.872</td>
</tr>
<tr>
<td>BCM</td>
<td>9</td>
<td>0.218</td>
<td>0.939</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.243</td>
<td>2.763</td>
</tr>
</tbody>
</table>

\[ a \ q_t = q_e(1 - e^{-k_1t}). \]

\[ b \ q_t = \frac{q_e k_2 t}{1 + \frac{k_2 t}{q_e}}. \]
isotherm model for determining the monolayer fluoride adsorption capacities \(q_{\text{max}}\): BCM: \(q_{\text{max}} = 4.51\) mg/g and BCB: \(q_{\text{max}} = 3.62\) mg/g, respectively. Results of fluoride breakthrough curves are consistent with the batch adsorption results and the monolayer adsorption capacities obtained from Langmuir model, which indicate that BCM has the greatest fluoride adsorption capacity in both static and dynamic conditions. Note that these maximum adsorption capacities from Langmuir model has been used for the calculation of the filter material usage rate \(q_{\text{F}}\) during the analysis of design parameters of bone char packed-bed columns (see Table 4).

### 3.2. Results of data modeling of breakthrough curves for fluoride adsorption using bone chars

Results of the linear regression of Thomas model for both bone chars are given in Fig. 6, while Table 4 provides the model parameters. Herein, it is convenient to note that the fluoride adsorption kinetics and isotherms confirmed that the assumptions of Thomas model are satisfied and, consequently, this model is valid for presenting and analyzing the fluoride breakthrough results. In general, the linear approach of Thomas model gave a suitable fit for data modeling of the fluoride adsorption experiments using BCB and the best correlation results are obtained for adsorption experiments performed at the lowest feed flow rate. However, the Thomas model gave a poor fit of some breakthrough curves obtained for BCM especially at higher feed flow rate, see Fig. 6. These results suggest that although the linear regression method is the traditional and widely used approach for modeling breakthrough data with Thomas equation, it may not be adequate in describing and predicting the experimental data of unsymmetrical breakthrough curves. Note that the calculated values of \(k_{\text{Th}}\) and \(q_{\text{bed,T}}\) may vary significantly for each operating condition used for adsorption columns, see Table 4. Specifically, the values of \(k_{\text{Th}}\) ranged from 0.0088 to 0.0198 L/h mg for BCB and from 0.0024 to 0.0132 L/h mg for BCM, while the calculated values of \(q_{\text{bed,T}}\) ranged from 0.47 to 2.47 mg/g and from 2.26 to 5.00 mg/g for these bone chars, respectively.

On the other hand, results of data fitting of fluoride dynamic adsorption experiments using the hybrid model (i.e., ANNs–Thomas model) are also reported in Table 4. Specifically, the 75% of the experimental data of two bone chars were used for the training stage of this hybrid model: 186 and 198 experimental data for BCB and BCM bone chars, respectively; while the 25% remaining data (i.e., 62 and 66 experimental points) were used as the verification and test sets. We have used two approaches for determining the parameters of the hybrid model: (a) all fluoride breakthrough curves of each bone char has been simultaneously used for the training of the ANNs–Thomas model, and (b) each individual breakthrough curve has been used alone for the training of the ANNs–Thomas model. The same ANNs architecture given in Fig. 2 has been used for both variations of the ANNs–Thomas model. As expected, both modeling approaches provide different results for the modeling of packed bed adsorption columns, see Table 4. In particular, the hybrid model based on all breakthrough curves for ANNs training offers the flexibility of reliably predicting the performance of packed-bed adsorption columns at different operating conditions using constant and unique values of both \(k_{\text{Th}}\) and \(q_{\text{bed,T}}\) for Thomas equation. In contrast, the modeling of each individual breakthrough curve using the hybrid model provides specific values for the parameters of Thomas model, see results reported in Table 4. However, the calculated values of Thomas model by this hybrid approach showed a less variability than those obtained from the application of the linear regression approach specially for the parameter \(q_{\text{bed,T}}\). In general, the kinetic coefficients \(k_{\text{Th}}\) calculated by all models increased with the inlet fluoride concentration and the feed flow rate suggesting that the driving force of fluoride mass transfer in the liquid film is also increased. Similar trends have been observed for parameters of Thomas model in other studies on the removal of water pollutants using packed-bed adsorption columns [43].

For comparing tested models, we have calculated the average Mean Square Error (MSE) between experimental and predicted breakthrough curves of fluoride adsorption using each bone char

<table>
<thead>
<tr>
<th>Model</th>
<th>Bone char</th>
<th>BCB</th>
<th>BCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>[ q_e = \frac{K_L q_{\text{max}}}{1 + \frac{C_0}{K_L}} ]</td>
<td>0.027</td>
<td>0.129</td>
</tr>
<tr>
<td></td>
<td>[ q_e ]</td>
<td>3.64</td>
<td>4.510</td>
</tr>
<tr>
<td></td>
<td>[ K_L ]</td>
<td>0.935</td>
<td>0.943</td>
</tr>
<tr>
<td></td>
<td>[ q_{\text{max}} ]</td>
<td>0.090</td>
<td>0.166</td>
</tr>
</tbody>
</table>

| Freundlich | \[ q_e = \frac{K_T q_{\text{max}}}{1 + \frac{C_0}{K_T}} \] | 0.114 | 0.519 |
|            | \[ q_e \] | 1.267 | 1.461 |
|            | \[ K_T \] | 0.856 | 0.847 |
|            | \[ q_{\text{max}} \] | 0.175 | 0.268 |

| Sips       | \[ q_e = \frac{K_P q_{\text{max}}}{1 + \frac{C_0}{K_P}} \] | 1.815 | 2.525 |
|            | \[ q_e \] | 0.026 | 0.232 |
|            | \[ K_P \] | 1.579 | 1.941 |
|            | \[ q_{\text{max}} \] | 0.995 | 0.970 |
|            | \[ q_{\text{max}} \] | 0.008 | 0.076 |
MSE values of the different modeling approaches are reported in Table 4. In general, the ANNs–Thomas models provided a better fit (i.e., lowest values of MSE) of the experimental fluoride breakthrough curves than that obtained with the linear regression of Thomas model. However, it is convenient to remark that the major deviations between predicted and experimental breakthrough curves were observed at early operating times of adsorption columns (i.e., the beginning of column operation) for all tested models. For illustration, Fig. 3 shows the performance and comparison of the results obtained from the hybrid model, using all fluoride breakthrough curves for ANNs training, in the data modeling of adsorption columns for fluoride removal using both bone chars. Overall, the performance of the hybrid ANNs model is worse in the zone \( [F^-]_t/[F^-]_0 < 0.1 \) of the fluoride breakthrough curve while this model provides satisfactory predictions for fluoride adsorption in the region \( 0.1 < [F^-]_t/[F^-]_0 < 1.0 \) (i.e., \( R^2 > 0.9 \)). It is convenient to remark that the failures of Thomas model for representing adequately the initial part of the breakthrough curve (i.e., \( t \to 0 \)) has been documented in other studies [49]. However, there is a significant improvement on the modeling capabilities of the ANNs–Thomas model in comparison to results obtained with the traditional Thomas model for this zone of the breakthrough curve. For further studies, it is convenient to study the application of this hybrid ANNs approach using other more flexible breakthrough equations such as the Yan model [49].

### 3.3. Analysis of design parameters of breakthrough curves for fluoride adsorption using bone chars

Design parameters of packed-bed columns were calculated using the model parameters obtained from the Thomas equation and the hybrid models and these results are reported in Table 5. In particular, we have analyzed the effect of the modeling approach on the calculation of design parameters of packed-bed columns. Based on the fact that tested models showed the major uncertainty for predicting the performance of fluoride breakthrough curves at low values of column operating time \( t \), the breakthrough time \( t_b \) of packed columns has been determined from the experimental data of fluoride breakthrough curves and the exhaustion time \( t_e \) was calculated from Thomas equation applying the condition \( [F^-]_t/[F^-]_0 = 0.95 \) in Eq. (5), where

\[
t_e = \frac{q_{bed}W_{bed}}{Q[F^-]_0} + \frac{\ln(19)}{k_m[F^-]_0}
\]
Calculated values of $t_e$ were used for the determination of MTZ, $\Delta t$ and $r_f$ for the different operating conditions of fluoride adsorption columns using both bone chars (see Table 5). Note that Thomas equation has also been used for the calculation of retardation factors replacing $[F]/[F]_0 = 0.5$ in Eq. (5) and rearranging, then $r_f$ is given by

$$r_f = \frac{q_{bed,T} P_{ads}}{\left[ F \right]_0}$$  \hspace{1cm} (12)

The time ($t_{50\%}$) used for the calculation of retardation factors has been also obtained from Thomas equation using

$$t_{50\%} = \frac{q_{bed,W_{bed}}}{Q \left[ F \right]_0}$$  \hspace{1cm} (13)

For both adsorbents, the calculated values of MTZ increased with the flow rate of fluoride solution at given feed fluoride concentration, while $r_f$ decreased with an increment of both feed flow rate and inlet fluoride concentration. These trends have been observed for all modeling approaches used in adsorption data analysis. As stated in literature [40], the ideal breakthrough curve is a step function where there should be an instantaneous increment of the effluent pollutant concentration from zero to the feed pollutant concentration when the maximum adsorption capacity of the column is reached. Therefore, a short MTZ and a low value of $\Delta t$ (i.e., $t_o - t_M < 0$) are desirable for optimizing the performance of dynamic adsorption process. On the other hand, the calculated values of $r_f$ are higher for BCM than those obtained for BCB indicating that fluoride ions are adsorbed more effectively in the first adsorbent, as expected, the retardation factors calculated using Eq. (4) while the results from linear regression of Thomas model are used, we overpredicted the filter material usage rates and incorrect estimations are obtained (i.e., $F_p > 1$ or $q_{bed,T} > q_{max}$); see Table 5 especially for BCM adsorbent. Therefore, the estimated values of the design parameters may be not representative of the true adsorption process and any decision based on these values would be in error, thus potentially leading to ineffective process design decisions. In fact, these results highlight some of the limitations of the use of linearized Thomas equation for breakthrough data modeling and, consequently, for adsorption process design. As stated in other studies, e.g. [47], Thomas model is reliable to predict the performance of breakthrough curves and to estimate the maximum pollutant uptake by the adsorbent at dynamic operation conditions. However, this study shows that the improper handling of this model may lead to imprecise values of design parameters and erroneous conclusions of adsorption performance. On the other hand, ANNs–Thomas models provide reasonable values of $F_p$ for the different operating conditions of fluoride breakthrough curves and these calculated ratios of filter material usage are consistent with calculations performed in other studies, e.g. [47]. As stated, the hybrid model trained using all breakthrough curves predicted constant values of $F_p$ for both bone chars, i.e., 0.35 for BCM and 0.47 for BCB. In turn, the values of $F_p$ calculated from the other hybrid model varied from 0.31 to 0.47 and from 0.37 to 0.58 for BCB and BCM, respectively. In summary, the design parameters calculated by linear regression and ANNs–Thomas models showed significant deviations. These deviations are caused by the characteristics of the modeling approach used for adsorption data analysis. However, ANNs–Thomas hybrid models provide reasonable and accurate values of column design parameters.

### 3.4. Comparison of performance of commercial bone chars and the fluoride removal mechanism

Finally, the differences in the adsorption performance of tested bone chars are mainly related to its chemical composition. Results of elemental composition and the inorganic constituents identified by EDX in both bone chars are reported in Table 6. In this case, it is important to highlight the difference that exists in the percentage of carbon, hydrogen and oxygen between these two adsorbents. Specifically, BCM showed the highest content of oxygen and hydrogen and, probably, this adsorbent may have a higher quantity of

<table>
<thead>
<tr>
<th>Bone char</th>
<th>Flow rate (L/h)</th>
<th>$[F]_0$ (mg/L)</th>
<th>Results of fluoride breakthrough data modeling for</th>
<th>ANNs–Thomas model using all breakthrough curves</th>
<th>ANNs–Thomas model using individual breakthrough curves</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCB</td>
<td>0.198</td>
<td>9</td>
<td>$\Delta t$ (h)</td>
<td>MTZ (cm)</td>
<td>$t_M$ (h)</td>
</tr>
<tr>
<td>0.198</td>
<td>9</td>
<td>37.00</td>
<td>6.47</td>
<td>404.1</td>
<td>0.37</td>
</tr>
<tr>
<td>0.198</td>
<td>20</td>
<td>30.00</td>
<td>6.62</td>
<td>337.7</td>
<td>0.06</td>
</tr>
<tr>
<td>0.198</td>
<td>40</td>
<td>12.17</td>
<td>6.88</td>
<td>21.7</td>
<td>0.44</td>
</tr>
<tr>
<td>0.198</td>
<td>9</td>
<td>13.29</td>
<td>6.76</td>
<td>136.7</td>
<td>0.55</td>
</tr>
<tr>
<td>0.396</td>
<td>9</td>
<td>2.96</td>
<td>6.27</td>
<td>32.1</td>
<td>0.13</td>
</tr>
<tr>
<td>0.396</td>
<td>20</td>
<td>83.5</td>
<td>7.31</td>
<td>938.9</td>
<td>0.69</td>
</tr>
<tr>
<td>0.396</td>
<td>40</td>
<td>92.19</td>
<td>7.18</td>
<td>683.6</td>
<td>1.11</td>
</tr>
<tr>
<td>0.396</td>
<td>9</td>
<td>26.11</td>
<td>7.09</td>
<td>447.1</td>
<td>0.73</td>
</tr>
<tr>
<td>0.396</td>
<td>20</td>
<td>39.63</td>
<td>7.00</td>
<td>334.3</td>
<td>1.08</td>
</tr>
<tr>
<td>0.396</td>
<td>40</td>
<td>8.83</td>
<td>6.95</td>
<td>154.5</td>
<td>0.50</td>
</tr>
</tbody>
</table>
hydroxyl groups than that of BCB. These hydroxyl groups are involved in the fluoride removal according to the reaction [50]

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2F^- \rightarrow \text{Ca}_{10}(\text{PO}_4)_6F_2 + 2\text{OH}^-$$  \hspace{1cm} (14)

where \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\) is the chemical structure of hydroxyapatite, which is the principal component of bone chars according to results reported in the literature [50–52]. Our results corroborated that Ca and P are the principal inorganic elements identified in BCM and BCB according to EDX analysis, see Table 6 and Fig. 7. Also, the diffraction patterns of the crystalline form of hydroxyapatite were observed in the X-ray results of both BCM and BCB (Fig. 8a). In general, the diffraction patterns of these adsorbents are very similar to those reported for other bone chars obtained from swine [53] and bovine bones [51]. On the other hand, some characteristics peaks of hydroxyapatite were identified in the FT-IR spectrum of BCM and BCB at 1030 and 600 cm\(^{-1}\), which can be assigned to vibrations of stretching and bending of phosphate [54], see Fig. 8b. Additionally, other peaks were identified and the signal around 3400 cm\(^{-1}\) can be attributable to the existence of hydroxyl groups and the peaks at 1460 cm\(^{-1}\) can be assigned to C–O stretching vibrations of carboxyl groups [25]. Finally, the particles of BCM and BCB have an irregular form and few pores are observed on the char surface (see Fig. 7). This morphology is associated with the low specific surface of these adsorbents, which was 104 and 129 m\(^2\)/g for BCM and BCB, respectively. These characterization results are similar to those obtained for other commercial bone chars reported in the literature such as the bone chars from Carvão Ativado do Brasil and Barnebey Sutcliffe Corporation [25].

### Table 6

Results of ultimate analysis and principal elements identified by EDX in the commercial bone chars used for the fluoride removal from water.

<table>
<thead>
<tr>
<th>Element (w%)</th>
<th>BCM</th>
<th>BCB</th>
<th>Element (w%)</th>
<th>BCM</th>
<th>BCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6.1</td>
<td>7.3</td>
<td>Mg</td>
<td>1.26</td>
<td>1.155</td>
</tr>
<tr>
<td>H</td>
<td>0.5</td>
<td>0.1</td>
<td>P</td>
<td>16.64</td>
<td>15.48</td>
</tr>
<tr>
<td>N</td>
<td>0.8</td>
<td>0.7</td>
<td>Ca</td>
<td>30.72</td>
<td>37.78</td>
</tr>
<tr>
<td>S</td>
<td>0.0</td>
<td>0.0</td>
<td>O</td>
<td>10.3</td>
<td>6.9</td>
</tr>
</tbody>
</table>

* Average of three determinations.

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**Fig. 7.** SEM images and EDX results of the adsorbents: BCM and BCB.
4. Conclusions

A hybrid neural network approach has been proposed for data modeling of asymmetric experimental breakthrough curves of the fluoride removal from water using packed-bed adsorption columns and bone chars. Specifically, it is a gray-box model obtained from the combination of artificial neural networks and Thomas breakthrough equation. Capabilities and limitations of this hybrid model has been compared and analyzed with respect to the performance of traditional linear regression of Thomas model. Results showed that the breakthrough data modeling using the linear regression of Thomas model may overestimate design parameters of adsorption columns causing erroneous conclusions for design and operation policy of adsorption processes. On the other, the hybrid model is useful for fitting and predicting satisfactorily the fluoride breakthrough curves. This hybrid model can predict properly the fluoride breakthrough curves at different operating conditions using a unique set of values of parameters $k_D$ and $q_{bed,T}$ of Thomas equation. In summary, the proposed modeling approach can be useful for process engineering of dynamic adsorption systems involved in the water and wastewater treatment.

Acknowledgements

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Fig. 8. (a) XRD patterns and (b) FT-IR spectra of BCM (black line) and BCB (gray line).
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