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Modeling of fixed-bed adsorption of fluoride on bone char using a hybrid neural network approach

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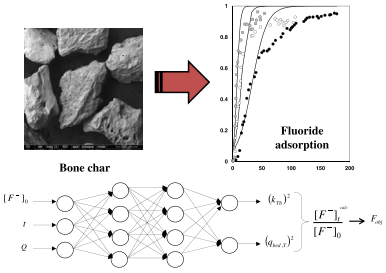
HIGHLIGHTS

- 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.

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

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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]. However, these promising adsorbents are not still commercially available. 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

Table 1
Supplier specifications of commercial bone chars used in packed-bed adsorption columns for fluoride removal from water.

Property[a]	Bone char	
	Carbones Mexicanos (BCM)	Brimac 216 (BCB)
Carbon content	10–15%	9–11%
Tricalcium phosphate	80–85%	70–76%
Specific surface area	104 m^2/g	129 m^2/g
Humidity	<4%	<5%

[a] Adsorbent specifications provided by the supplier.