Journal of Molecular Liquids 208 (2015) 114–121

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Breakthrough curve modeling of liquid-phase adsorption of fluoride ions on aluminum-doped bone char using micro-columns: Effectiveness of data fitting approaches

C.K. Rojas-Mayorga [a], A. Bonilla-Petriciolet [a,*], F.J. Sánchez-Ruiz [a], J. Moreno-Pérez [a], H.E. Reynel-Ávila [a], I.A. Aguayo-Villarreal [a], D.I. Mendoza-Castillo [a,b]

[a] Instituto Tecnológico de Aguascalientes, Aguascalientes 20256, Mexico
[b] Consejo Nacional de Ciencia y Tecnología, Cátedras CONACYT, México D.F. 03940, Mexico

ARTICLE INFO

Available online xxxx

Keywords:
Packed-bed columns
Fluoride
Aluminum-modified bone char
Breakthrough curve modeling
Liquid-phase adsorption

ABSTRACT

A comparative numerical analysis of three approaches for the breakthrough curve modeling has been performed using the experimental data of packed-bed fluoride adsorption on a novel aluminum-doped bone char using micro-columns. The performance of traditional Thomas and Yan breakthrough equations, a mass transfer model for a mobile fluid flowing through a porous media, and an artificial neural network with the optimal brain surgeon approach have been studied and discussed in the data fitting of asymmetric fluoride breakthrough curves. Results of this study highlighted the relative merits of tested breakthrough curve models for the non-linear adsorption data analysis involved in water defluoridation using a new adsorbent. In particular, the application of artificial neural networks is reliable for fitting highly non-linear adsorption patterns of priority water pollutants.

1. Introduction

Adsorption processes can be performed using batch and continuous type configurations [1,2]. Both operation modes offer different advantages but the dynamic adsorption systems are preferred for large-scale applications in water treatment due to their flexibility and easy operation [1,3]. The liquid-phase adsorption at continuous flow conditions is recognized as a non-linear and multivariable process that can be analyzed by the breakthrough curve. Specifically, the breakthrough curve describes the adsorption column dynamics and provides relevant information and key parameters for the design, operation and optimization of the separation system [4–6]. For example, the sharpness of the breakthrough curves is an indicator of the effectiveness of the adsorption process [4]. The characteristics of breakthrough curves depend on the bed configuration, feed flow, adsorbate concentration, pH, temperature, adsorbent mass, and other relevant variables [1,5–8]. Therefore, it is expected that the adsorption pattern may vary significantly for each adsorbent–adsorbate system in packed-bed columns.

Results reported in the literature indicate that the breakthrough curves obtained in the adsorption of water pollutants usually show an asymmetric sigmoidal profile even for mono-component solutions (i.e., solutions with only one adsorbate/pollutant). The modeling of these breakthrough curves for liquid-phase adsorption is fundamental for water treatment design in real-life applications [8]. The principal objective of the breakthrough data modeling stage is the correlation and prediction of adsorption behavior based on the parameters obtained from experimental studies. However, the fitting of adsorption patterns in packed-bed columns is more difficult than the modeling in batch processes because the concentration profiles in the adsorbent and liquid phases for dynamic systems are determined by the mass transfer phenomena, adsorption kinetics and thermodynamics [4]. The breakthrough curve modeling is considered as a challenging mathematical problem, which implies non-linear data regressions for the determination of model parameters using an error function. Depending on the model complexity, the application of other computational strategies is often necessary in breakthrough curve fitting, e.g., the use of numerical methods for solving partial differential equations.

To date, several models have been proposed for the correlation of breakthrough curve data obtained in dynamic adsorption processes. These models include the Thomas [9], Bohart-Adams [10], Yon-Nelson [11], Clark [12], Yan [13] and other empirical or semi-empirical breakthrough equations [2,4]. These models are usually analytical equations that require a low computational time for data processing and are popular for the correlation of adsorption data in water treatment due to their simple form and acceptable-fitting performance. Alternatively, a variety of mass transfer models can be applied for data fitting of adsorption results at dynamic conditions [2,14]. This type of models shows different degrees of mathematical complexity depending on the transport phenomena considered for the adsorption analysis [2]. Besides the

* Corresponding author.
E-mail address: petriciolet@hotmail.com (A. Bonilla-Petriciolet).

http://dx.doi.org/10.1016/j.molliq.2015.04.045
0167-7322/

analytical and mass transfer models, the breakthrough curves can be also modeled using computationally intelligent data processing algorithms such as artificial neural networks [6–8,15,16]. These strategies are considered as effective empirical approaches for non-linear data analysis [17].

Herein, it is convenient to highlight that the desirable characteristics for the breakthrough curve models include a suitable mathematical complexity, a capability for providing an acceptable accuracy in the correlation and estimation of adsorption patterns at different operating conditions, and the model should be useful for assessing the effect of operating variables on the adsorption column dynamics [2]. Depending on the type of breakthrough model, some of these desirable characteristics can be fulfilled. However, the numerical performance of available models cannot be determined a priori based on the fact that they may show limitations for data analysis depending on the adsorption system under study and its experimental conditions. In fact, some studies have reported the performance of different approaches for breakthrough curve modeling but using concentration patterns with symmetric behavior [18]. In order to improve the performance of breakthrough models and to develop reliable approaches for adsorption data processing, it is important to identify and to compare the relative advantages of available models in the analysis of dynamic processes for the removal of priority water pollutants involving highly asymmetric adsorption profiles.

In this study, a comparative numerical analysis of three approaches for breakthrough curve modeling has been performed using the experimental data of packed-bed fluoride adsorption on a novel aluminum-doped bone char. Specifically, the performance of traditional Thomas and Yan breakthrough equations, the mass transfer model for a mobile fluid flowing through a porous media, and an artificial neural network approach have been studied and discussed in the data fitting of asymmetric fluoride breakthrough curves obtained with micro-columns. To the best of the authors' knowledge, a systematic study of the capabilities and limitations of breakthrough models for the correlation and prediction of adsorption patterns in packed beds for water defluoridation has not been reported. In summary, the results of this study highlight the relative merits of tested breakthrough curve modeling strategies for the adsorption data analysis involved in water defluoridation using a new bone char.

2. Methodology

2.1. Synthesis of aluminum-doped bone char used in fluoride adsorption with packed-bed columns

Packed-bed adsorption experiments for fluoride removal from water were performed using an aluminum-doped bone char. This novel adsorbent was obtained via metal surface modification of bone char using an aqueous solution of aluminum sulfate. First, the bone char was obtained from the pyrolysis of bovine bones using the optimum synthesis conditions reported by Rojas-Mayorga et al. [19]. These conditions involved a pyrolysis process with N_2 at 700 °C during 2 h of residence time. In a second stage, the surface modification of bone char was performed with an aluminum sulfate solution 0.1 M. The adsorbent was mixed with this metallic solution at 50 °C during 6 h. The samples of aluminum-doped bone char were washed using deionized water, dried and stored for dynamic adsorption experiments. The physicochemical properties of the modified adsorbent were determined using the results from FTIR, XPS and XRD analyses. Diffraction pattern of bone char was obtained using an X-ray diffractometer Bruker D8-Advance with a mirror Göebel that has a tube with cooper anode RX and radiation Cu Kα ($\lambda = 1.5406$ Å). Functional groups of the adsorbent were identified via FTIR spectroscopy using a Bruker IFS 66/S spectrophotometer and all samples were analyzed using spectroscopic grade KBr. XPS studies were performed with a Prevac photoelectron spectrometer equipped with a hemispherical analyzer (VG SCIENTA R3000). Finally, the textural properties of metal-modified bone char were determined via N_2 adsorption–desorption isotherm at 77 K using a N_2 Gsorb-6 equipment.

2.2. Determination of breakthrough curves for fluoride adsorption on aluminum-doped bone char using packed-bed micro-columns

Fluoride adsorption experiments were performed in packed-bed micro-columns with 5.4 cm of length and 1.8 cm of internal diameter. These columns were packed with 10.35 g of metal-doped bone char with a particle size of 20–35 mesh fractions. Dynamic adsorption experiments were performed at pH 7 and 30 °C using different fluoride feed concentrations from 10 to 100 mg/L and feed flow rates of 0.18 and 0.36 L/h. All adsorption micro-columns were operated at up flow operating mode using a peristaltic pump. The mean bed porosity (ε) in all adsorption columns was 30%. For the determination of experimental fluoride breakthrough curves, several samples were collected from the adsorption column outlet at regular time intervals (i.e., 10 min) and the fluoride concentrations were quantified. Adsorbate concentrations were determined using a fluoride ion selective electrode and TISAB chemical reagent [21] where linear calibration curves were used. All experiments were performed twice, including the fluoride measurements, and the mean results were used for adsorption calculations.

Analysis of fluoride breakthrough curves implied the determination of the breakthrough time (t_b in h), the bed adsorption capacity (q_{bed} in mg/g), the retardation factor (r_f) and the degree of bed utilization (R_q in %). These parameters were calculated using

$$t_{b=}t_{oper} \text{ where } 0.2\cdot[F^-]_{feed} \tag{1}$$

$$q_{bed} = \int_{t=0}^{t=t_{oper}} \left(\frac{[F^-]_{feed}-[F^-]_{outlet}}{m_{bed}}\right) Q dt \tag{2}$$

$$r_f = \frac{V_{50\%}}{AL\varepsilon} \tag{3}$$

$$R_q = \frac{q_{bed}}{q_{batch}} \tag{4}$$

1. Train a reasonably large network to minimum error
2. Compute H^{-1}
3. Find the q that gives the smallest saliency, Eq. (16). If this candidate error increase is lower than the error function used in training process, then the qth weight should be deleted, and continue with step 4 of this algorithm; otherwise step 5 applies.
4. Use the q from step 3 to update all weights using Eq. (15). Go to step 2.
5. No more weights can be deleted without large increase in the error function of training process. At this point it may be desirable to retrain the network.

Fig. 1. Algorithm reported by Hassibi et al. [22 for the optimal brain surgeon procedure in artificial neural network models.