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Breakthrough Curve Model Evaluation for the Sorption of Perfluorooctanoic Acid in a Fixed Bed Column

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Abstract – Solid-liquid adsorption has been demonstrated as an effective technology in eradicating contaminants of environmental concern; however, studies on proper model evaluation are scanty. On the other hand, proper system modeling is imperative to correlate adsorption dynamic data for effective process design, particularly in fixed-bed adsorption studies. As such, this study focuses on the sorption of perfluorooctanoic acid on chitosan-carbon nanotube hydrogel beads from aqueous solution in a fixed-bed adsorption column. The traditional and fractal-like Thomas, Bohart-Adams, and Yoon-Nelson breakthrough curve models were employed to fit adsorption experimental data. Breakthrough curve models were statistically evaluated using the Akaike information criterion (AIC) as the first case for the present system. Native model evaluation parameters, i.e., R^2 and adjusted R^2, did not give conclusive results on the preferred model. On the other hand, the AIC explicitly indicated that the traditional Thomas, Bohart-Adams, and Yoon-Nelson models were the preferred models to navigate the system with minimal error compared to the fractal-like models. From the present study's findings, it is evident that a model with more parameters does not automatically qualify it to produce a better fit. Therefore, the AIC can be employed to evaluate competing models with minimal biasness.

***Keywords*:** Breakthrough curve; Akaike-weight; Thomas model; Bohart-Adams model; Yoon-Nelson model.

1. Introduction

The environmental occurrence of toxic chemicals as a result of anthropogenic activities has posed a serious health risk to both human and aquatic life [1, 2]. The continuous discharge of toxic compounds into water-receiving bodies has significantly affected the availability of freshwater resources, particularly in developing countries without stringent environmental bylaws. Perfluoroalkyl carboxylic acids are one of the highly detected emerging contaminants of environmental concern [1]. These contaminants belong to the class of organic aliphatic carboxylic acids, particularly fluoroalkyl substances (PFAS) characterized by an alkyl group that is fully fluorinated ($C_nF_{2n-1}COOH$). Amongst the class of PFAS, perfluorooctanoic acid (PFOA) compounds have the highest environmental detection frequency factor [3]. This is ascribed to the PFOA strong carbon-fluorine bond (530 kJ/mol), which makes it chemically stable and extremely difficult to degrade in the environment [4], resulting in its occurrence in water treatment plants' effluent streams. It is worth noting that PFOA is characterized by peculiar thermodynamic properties such as hydrophobicity, oleophobicity, and high thermal stability [2, 5]. These properties have resulted in the industrial application of PFOA as an anti-staining product for carpets and upholstery, as well as a fire-extinguishing agent [6]. The available literature [2, 3, 5] suggest that human exposure to PFOA can lead to bioaccumulation in the human body, resulting in severe health problems such as thyroid hormone disorder, compromised immune system, and worst, low birth weight in infants. As such, there is an urgent need to develop technologies aimed at the complete eradication of PFOA from drinking water.

Hitherto, researchers are still developing cost-effective and environmentally green technologies for the effective removal of PFOA from aqueous streams. Due to the chemical stability of the C-F bond in PFOA, this compound is not easily biodegraded by currently existing wastewater treatment plants in the African context due to its high detection frequency factor in water bodies [7]. This has resulted in the application of emerging technologies such as plasma, sonolysis, and electron beams, which have been demonstrated to be highly effective for the removal of PFOA from aqueous streams [5, 8, 9]. However, these technologies are reported as not economically viable since they require high energy usage on a large scale [5]. On the other hand, solid-liquid adsorption has been demonstrated to be a promising technology in eradicating emerging contaminants of environmental concern, which has led to the development of chitosan-based adsorbents [10]. Chitosan is

derived from chitin, characterized as the most abundant biopolymer after cellulose, found in a range of eukaryotic species [11]. The appetite for the development of chitosan-based adsorbents is attributed to the presence of amino and hydroxyl functional groups within the chitosan structure, which are essential for the chelating of target contaminants.

Despite the development of novelty adsorbents, studies on adsorption column dynamics are scanty. As such, this study focuses on the application of traditional, fractal-like, and modified breakthrough curve models for the sorption of PFOA on chitosan-carbon nanotube (CCNT) hydrogel beads as the first case. The primary aim of the present work is the application of the Akaike information criterion (AIC) as a statistical parameter for competing adsorption breakthrough curve model evaluation.

2. Materials and Methods

2.1. Materials

All materials used in this study were of analytical grade, and they were used without any modification. PFOA and multiwall carbon nanotubes were supplied by Lasec Laboratories in Durban, South Africa. Sodium hydroxide (NaOH) pellets, methanol (CH_3OH), sulfuric acid (H_2SO_4), and chitosan powder from shrimp shells were supplied by Sigma-Aldrich, South Africa. Shalom Laboratories, South Africa, supplied glacial acetic acid ($C_2H_4O_2$).

2.2. Fixed-bed adsorption studies

The adsorbent used in the present study was synthesized by adopting the procedure presented in our previous work, the reader may refer to Khumalo, et al. [10]. Herein, adsorption breakthrough curve studies for the uptake of PFOA on CCNT hydrogel beads were investigated by conducting a set of experiments at a feed flow rate of 1 ml/min, adsorbate concentration of 15 mg/L, and bed height of 35 cm. A fixed amount of CCNT hydrogel beads was placed in a glass column with a height of 60 cm and an internal diameter of 1.5 cm, as depicted in Fig. 1. The bottom of the column consisted of a glass sieve to support the adsorbent. The bottom and top of the column were filled with glass beads to compact the CCNT hydrogel beads bed and minimize dead volume as well as channeling. An aqueous solution of the feed was placed in a glass beaker and pumped at a volumetric flow rate of 1 ml/min using a peristaltic pump. Samples were collected using a glass beaker at a specific time interval, which was then filtered using a 0.45 µm syringe filter and transferred into a 10 mL sample tube. The filtered samples were centrifuged at 5000 rpm for 10 minutes; thereafter, a supernatant solution of the centrifuged sample was analyzed for the residual PFOA concentration using a high-pressure liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). Adsorption column experiments were conducted in duplicates for data validation. Samples were collected until the saturation state was reached.

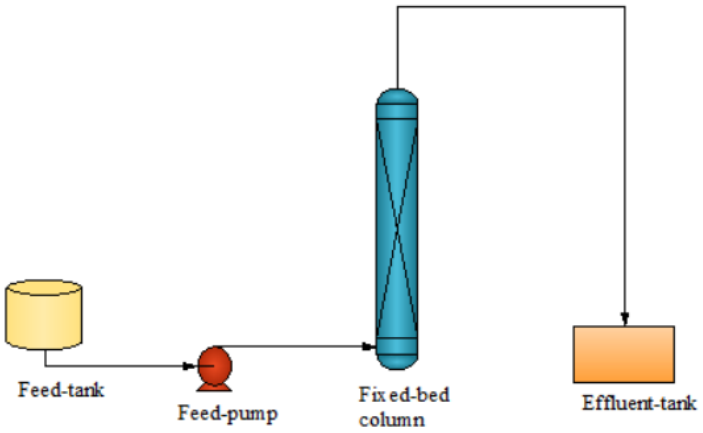

Fig. 1: Fixed column adsorption experimental set-up.

2.3. Breakthrough models in a fixed-bed column

Herein, traditional, and fractal-like versions of the Thomas, Bohart-Adams, and Yoon-Nelson breakthrough curve models were applied to correlate adsorption dynamic data.

Thomas model

$$\frac{c_i}{c_{0i}} = \frac{1}{1 + exp\left[k_T c_0 \left(\frac{q_0 m}{v c_0} - t\right)\right]} \tag{1}$$

Bohart-Adams model

$$\frac{c_i}{c_{0i}} = \frac{1}{1 + exp\left[k_{BA} c_0 \left(\frac{N_0 L}{u c_0} - t\right)\right]} \tag{2}$$

Yoon-Nelson model

$$\frac{c_i}{c_{0i}} = \frac{1}{1 + exp(k_{YN}\tau - k_{YN}t)} \tag{3}$$

Fractal-like Thomas model

$$\frac{c_i}{c_{0i}} = \frac{1}{1 + exp\left(\frac{k_{T,0} t^{-h} q_0 m}{v} - \frac{k_{T,0} c_0}{1-h} t^{1-h}\right)} \tag{4}$$

Fractal-like Bohart-Adams model

$$\frac{c_i}{c_{0i}} = \frac{1}{1 + exp\left(\frac{k_{BA,0} t^{-h} N_0 L}{u} - \frac{k_{BA,0} c_0}{1-h} t^{1-h}\right)} \tag{5}$$

Fractal-like Yoon-Nelson model

$$\frac{c_i}{c_{0i}} = \frac{1}{1 + exp\left(\frac{k_{BA,0} t^{-h} N_0 L}{u} - \frac{k_{BA,0} c_0}{1-h} t^{1-h}\right)} \tag{6}$$

Where c_i and c_{oi} are the concentration of species i in the liquid phase at time t in mg.L^{-1} and the concentration of species i in the feed in mg.L^{-1}, respectively; k_T, and k_{BA} are the rate coefficients measured in cm^3.mg^{-1}.min^{-1} for the Thomas and Bohart-Adams models, respectively; k_{YN} rate constant for the Yoon-Nelson model measured in min^{-1}; $k_{T,0}$, and $k_{BA,0}$ are the fractal-like Thomas and Bohart-Adams rate constants, respectively, measured in cm^3.mg^{-1}.min^{h-1}; $k_{YN,0}$ is the fractal-like Yoon-Nelson rate constant measured in min^{h-1}; τ is the operating time required to reach 50% breakthrough measured in min; m is the amount of adsorbent in the column measured in g; q_0 (mg.g^{-1}) is the solid loading per unit mass of adsorbent; and v (cm^3.min^{-1}) is the volumetric flow rate; N_0 (mg.cm^{-3}) is the adsorption capacity of the adsorbent per unit volume of the bed; L is the height of the bed in cm; and u is the superficial velocity measured in cm.min^{-1}.

2.4. Model evaluation

The coefficient of determination R^2, adjusted R^2, Akaike information criterion (AIC), and the F-test were employed in evaluating the goodness of fit for the tested Thomas, Bohart-Adams, and Yoon-Nelson breakthrough curve models. All regression calculations were computed in Microsoft Excel version 2024.

$$R^2 = \left(\frac{\sum_i^n \left(c_{i_{exp}} - \bar{c}_{i_{exp}}\right)^2 - \sum_i^n \left(c_{i_{exp}} - c_{i_{model}}\right)^2}{\sum_i^n \left(c_{i_{exp}} - \bar{c}_{i_{exp}}\right)^2}\right) \tag{7}$$

$$\text{adj.}R^2 = 1 - \left[\frac{(1-R^2)(n-1)}{n-p-1}\right] \quad (8)$$

$$AIC = n \ln\left(\frac{RSS}{n}\right) + 2p + \frac{2p(p+1)}{n-p-1} \quad (9)$$

$$W_i = \frac{exp(-0.5\,\Delta\,AIC_i)}{\sum_{i=1}^{n} exp(-0.5\,\Delta\,AIC_i)} \quad (10)$$

$$F = \frac{(RSS_1 - RSS_2)/(df_1 - df_2)}{RSS_2/df_2} \quad (11)$$

Where p is the number of model parameters; n is the number of data set points; c_{iexp} is the experimentally measured relative concentration of species i; $\bar{c}_{i_{exp}}$ is the average of all measured experimental values of relative concentration; and $c_{i_{model}}$ is the predicted value by the fitted model [10]. RSS is the residual sum of squares, df is the degree of freedom with the subscripts 1 and 2 corresponding to the simple and complex models, respectively.

3. Results and Discussion

Experimental data for the sorption of PFOA on CCNT hydrogel beads was fitted in three commonly reported breakthrough curve models in literature i.e., the Thomas model, Bohart-Adams model, and Yoon-Nelson model. The traditional and fractal-like versions of the aforementioned models were statistically evaluated to determine the preferred breakthrough curve model to fit PFOA adsorption data as presented in Table 1. Most studies in solid-liquid adsorption employ a naive approach to compare models by applying R^2 and/or adjusted R^2. These parameters are a measure of the goodness of fit, in most cases, the best fit is selected based on the high value of R^2 or adjusted R^2. However, these parameters neglect the complexity of the model. Portet [12] reported that these model selection criteria select the model that maximizes the values of R^2 and adjusted R^2, and the model with the highest parameters is often favoured.

Table 1: Statistical parameters of traditional and fractal-like breakthrough curve models.

Statistical Parameter	**Thomas model**		**Bohart-Adams model**		**Yoon-Nelson model**	
	Traditional	Fractal-like	Traditional	Fractal-like	Traditional	Fractal-like
R^2	0.9975	0.9975	0.9974	0.9973	0.9975	0.9975
Adj.R^2	0.9972	0.9970	0.9972	0.9967	0.9972	0.9970
AIC	-144.35	-141.77	-144.35	-142.55	-144.35	-144.33
W_{PFOA}	0.2131	0.0587	0.2131	0.0890	0.2131	0.2130
F-test	0.9963		0.9899		0.9977	
p-value	0.4969		0.4915		0.4980	

It is worth noting that, in selecting the best model, it is imperative that the principle of parsimony is applied. Parsimony's principle states that a model should be as simple as possible, a good model should give a proper balance between underfitting and overfitting [12]. In order words, few model parameters result in high biasness in estimating model parameters and an underfit model which fails to identify all factors of importance. On the other hand, too many model parameters result in a

high variance in parameter estimators and an overfit model that risks identifying spurious factors as important, and that cannot be generalized beyond the observed sample data. As such, for the present work, AIC was employed as a model selection criterion. This criterion accounts for both the goodness of fit and the parsimony principle. From the results presented in Table 1, R^2 and adjusted R^2 values of more than 0.99 were recorded for all breakthrough curve models investigated for the sorption of PFOA in CCNT hydrogel beads. From the reported R^2 and adjusted R^2 results in Table 1 and breakthrough curves model fit in Figure 2, one cannot explicitly conclude on the preferred model that best fits the experimental data.

Akaike [13] and Bozdogan [14] demonstrated that choosing a model with the lowest expected information loss is asymptotically equivalent to choosing a model with the lowest AIC value. As such models with the smaller AIC values are to be preferred. When studying Table 1, the traditional Thomas, Bohart-Adams, and Yoon-Nelson models recorded the least value of AIC (i.e., -144.35) compared to the fractal-like models. Furthermore, the traditional breakthrough curve models recorded the highest Akaike weight of 0.2131 when compared to the fractal-like breakthrough curve models suggesting that the traditional Thomas, Bohart-Adams, and Yoon-Nelson models were the preferred models to fit breakthrough curve experimental data. It is worth noting that, the Akaike weight can be interpreted as the probability that the model *i* is the best model, given the data and the set of candidate models.

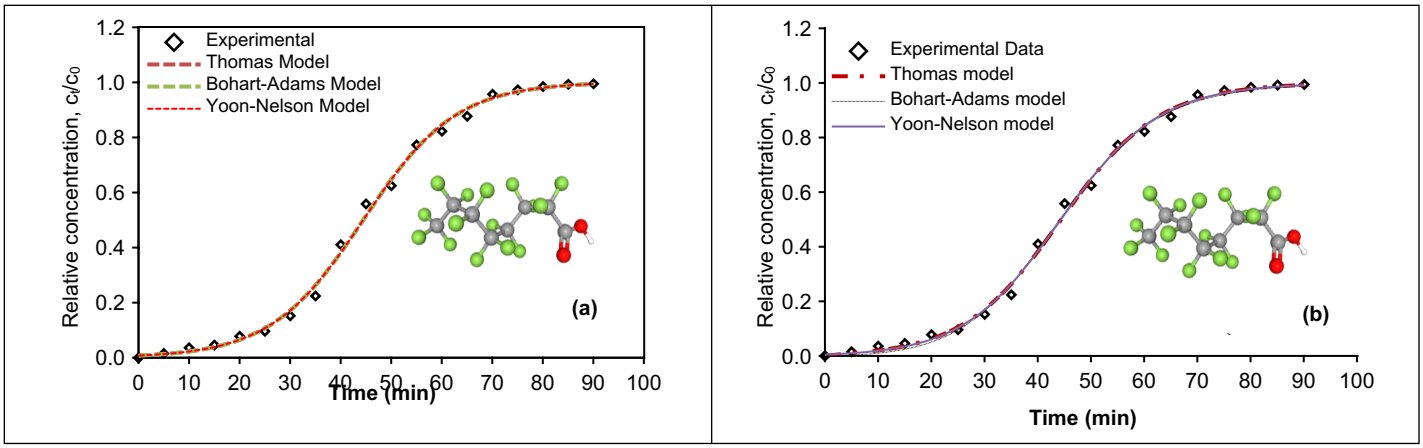

Fig. 2: Experimental and predicted traditional **(a)** and fractal-like **(b)** breakthrough curves for the sorption of PFOA.

Furthermore, the goodness of fit for the models studied was further tested by applying the F-test. Results for the F-test (Table 1), recorded p-values greater than 0.05 for the uptake of PFOA on CCNT hydrogel beads rejecting the fractal-like Thomas, Bohart-Adams, and Yoon-Nelson breakthrough curve models. The findings of the present study on the uptake of PFOA are congruent with the work reported by Hu and coworkers [15], where they reported that a model with more parameters does not necessarily mean a better fit.

4. Conclusion

Based on the model evaluation results presented in Table 1, it can be inferred that breakthrough experimental data for PFOA were well-fitted in the traditional Thomas, Bohart-Adams, and Yoon-Nelson breakthrough curve models when compared with the fractal-like breakthrough curve models. The statistical error results obtained when comparing the traditional breakthrough models with the fractal-like models suggest that a model with more parameters does not automatically qualify it to produce a better fit. Furthermore, from the results obtained, it can be concluded that the application of R^2 and adjusted R^2 alone can never be enough in evaluating models with different parameters without accounting for the biasness and complexity of the model.

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