A Bayesian Approach to Experimental Design for Tetracycline Adsorption in a Fixed-Bed Column: A Comparison between Activated Carbon and Modified Activated Carbon

Letícia Reggiane de Carvalho Costa[a], Júlia Toffoli de Oliveira[a], Gustavo Dall Agnol[a], Liliana Amaral Féris[a,*]

[a]*Federal University of Rio Grande do Sul, Department of Chemical Engineering, 2777 Ramiro Barcelos Street, Postal Code: 90035-007, Porto Alegre – RS, Brazil*

Abstract

In this study, the efficiency and applicability of fixed-bed columns were evaluated for tetracycline (TC) adsorption on granular activated carbon (GAC) and modified granular activated carbon (GAC-Cu). An experimental design using the Box-Benking (BOX) method was employed to optimize column operation, considering three independent variables: initial pollutant concentration (20, 50, and 80 mg/L), bed height (1, 2, and 3 cm), and feed flow rate (3, 6, and 10 mL/min). Response factors included saturation time (t_{sat}) and maximum adsorption capacity (q_{max}). To simulate breakthrough curves, six models (Thomas, Yoon-Nelson, Yan, Clark, Gompertz, and Log-Gompertz) were applied under optimal conditions. Parameter estimation and model selection were performed using Bayesian techniques, incorporating experimental qmax values and five statistical metrics (R^2 and R^2_{ajstd}; AIC, AIC_C, and BIC). The results demonstrate that both GAC and GAC-Cu exhibit high efficiency in TC removal, achieving 95% removal under optimal operational conditions (C_{0TC} = 80 mg/L, Q = 6 mL/min, and Z = 1 cm). For CAG, these conditions resulted in a saturation time (t_{sat}) of 23 minutes and a maximum adsorption capacity (q_{max}) of 2.08 mg/g, while for GAC-Cu, a significantly higher adsorption bed capacity of 6.87 mg/g was observed in 107 minutes. These findings suggest that the modification of GAC enhances its adsorption capacity for TC, making it three times more effective than unmodified GAC. Additionally, the saturation time indicates the efficiency of the process in treating high TC concentrations with minimal solid mass, highlighting its feasibility for implementation on a larger scale. Applying the Bayesian technique, it was observed that, for GAC and CAG-Cu respectively, the Yan and Clark models were the best predictors of the breakthrough curve behavior, elucidating the mechanisms of the column. Moreover, the Log-Gompertz model was useful for the scale-up of the process. Finally, this work contributes valuable information for the development and implementation of environmentally sustainable and effective water treatment strategies.

Keywords: tetracycline; fixed-bed column; mathematical modeling; parameter estimation; Bayesian technique.

1. Introduction

Since the discovery of antibiotics in 1929, the pharmaceutical sector has experienced significant growth, leading to the widespread presence of pharmaceuticals and their byproducts in various aqueous matrices, posing environmental threats [1]. Tetracycline (TC), commonly used in human and veterinary medicine, can persist in the environment, alter microflora characteristics, and pose toxicity risks to aquatic organisms and human health [2].

Various treatment techniques have been employed to address tetracycline contamination in water and wastewater [3–7], with fixed-bed column adsorption offering advantages such as simplicity, high removal efficiency, and scalability [8,9].

Mathematical models for breakthrough curves play a crucial role in designing and optimizing these columns, aiding in data description, prediction, and sizing [8]. Through Bayesian inference and its statistical metrics, parameters can be estimated and the most suitable model selected, enabling accurate estimation of adsorption operation in fixed-bed columns by extracting information on mass balance and process kinetics [10].

Therefore, the main objective of this work is to apply a Bayesian technique for the estimation of the parameters and selection of the breakthrough curve models for TC adsorption in fixed-bed columns using GAC and modified GAC, assessing the potential scale-up of the process.

2. Experimental Procedure

2.1 Materials

Tetracycline (CAS 60-54-8) was obtained from the Sigma-Aldrich company (St Louis, MO, USA) in an analytical purity >98%. Granular activated carbon (CAS 7440-44-0), with a granulometric fraction between 1.00 and 1.40 mm, was supplied by Êxodo Científica (Sumaré, SP, Brazil), and the modified GAC was prepared following the proposed methodology by Costa and Féris [11], with copper sulfate through an aqueous solution containing $CuSO_4$ (2% w/v) at 298K for 24h. After this time, the material was filtered and the solid was dried for 4–6 hours at 373K.

2.2 Fixed-bed Adsorption Experiments

Fixed-bed experiments were conducted using a borosilicate glass column with dimensions of 12 mm internal diameter and 20 cm total length (Figure 1). The TC solution was pumped upward through the column using a peristaltic pump in a controlled flow mode. Distilled water was used to rinse and equilibrate the column before each operation.

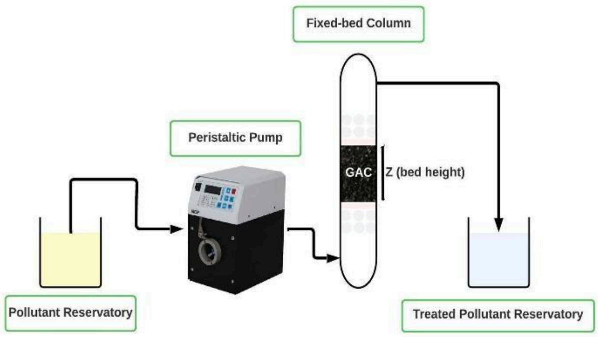

Fig. 1. Scheme of the adsorption fixed-bed column system.

The number of experiments was optimized using experimental planning, through the Box-Behnken (BOX) design, using the STATISTICA 7.0® software. The matrix of the experimental design containing 3 factors, these being: initial TC concentration (C_{0TC} - x_1), volumetric flow rate (Q - x_2) and height of the bed (Z - x_3); in 3 levels and 1 block, covering a total of 15 experiments. Two response factors were selected: the saturation time (t_{sat}) and the adsorbent maximum adsorption capacity (q_{max}).

All experiments were conducted at 298 K, at natural pH (~7,0), using distilled water for TC dilution from the stock solution. The breakthrough curves were obtained by continuously monitoring the pollutant concentration over the process time. The final TC concentration of all samples was determined by a UV-Vis spectrophotometer at a wavelength of 357 nm [12].

2.3 Breakthrough Curves and Modeling

Mathematical models such as Thomas, Yoon-Nelson, Clark, Yan, Gompertz and Log-Gompertz were used to simulate breakthrough curves, facilitating potential process scaling-up, using a Bayesian technique. For this, the Markov Chain Monte Carlo method (MCMC) applying the Metropolis-Hastings (MH) algorithm was used for the estimation of the parameters, and the selection of the models was made through five statistical metrics: coefficient of determination (R^2), adjusted coefficient of determination (R^2_{ajstd}), Akaike criterion (AIC), correct Akaike criterion (AIC_C) and information criterion Bayesian (BIC) [13].

3. Results and Discussion

3.1 Experimental Design of the Fixed-bed column

For the definition of the best experimental conditions for the removal of TC took into account the efficiency of the process, which is based on the shortest saturation time and the highest amount of the resulting maximum adsorption capacity. Table 1 shows the best results of the response variables for the matrix of the experimental design applied in the present work and Figure 2 shows the breakthrough curves obtained for the TC adsorption.

	Independent variables			***Response***	
	C_{0TC}	Q	Z	t_{sat} (min)	q_{max} (mg/g)
a	80	6	1	23	2.08
b	mg/L	mL/min	cm	107	6.87

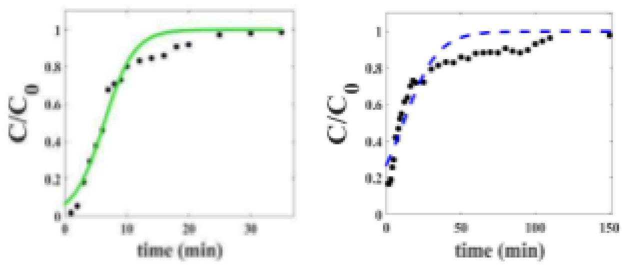

Table 1. Matrix of experimental design and responses for adsorption of TC for (a) GAC and (b) GAC-Cu.

Fig. 2. Breakthrough curves of TC adsorption for (a) GAC and (b) GAC-Cu.

The results suggest that modifying the type of solid used in the column for TC removal enhances the efficiency of GAC materials under these operational conditions. Additionally, these findings indicate a significant improvement in adsorbent capacity, approximately 230.29% higher compared to unmodified GAC, achieved simply by impregnating the solid. Figure 2 demonstrates that the values estimated by the Bayesian technique in this study accurately align with all experimental conditions, effectively predicting breakthrough curve behavior. Figure 2a notably depicts a sigmoidal (S) curve, ideal for breakthrough curves according to Giles [14], indicating favorable adsorption kinetics. Conversely, Figure 2b, representing unmodified GAC, shows both S-shaped and L-shaped curves, implying less optimal behavior. This highlights the positive impact of adsorbent modification, resulting in improved breakthrough curve characteristics and longer residence times.

Other researchers have also observed similar breakthrough curves for TC on activated carbon in fixed-bed columns, displaying both S-shaped and L-shaped behaviors. The S-shaped curve suggests cooperative adsorption, where molecules adsorb vertically and facilitate additional adsorption as more solute accumulates [14]. Conventional models, leading to deviations in curve predictions, do not always predict this cooperative behavior accurately. However, the Gompertz and Log-Gompertz models can better account for curve asymmetry. Conversely, L-shaped curves indicate decreased chances of solute adsorption as the column becomes saturated, resulting in longer residence times [15–17].

Figure 3 shows the adjustment of the curves to all models applied for best experiment, applying the value of q_{max} as a random variable and deterministically for Thomas and Yan models.

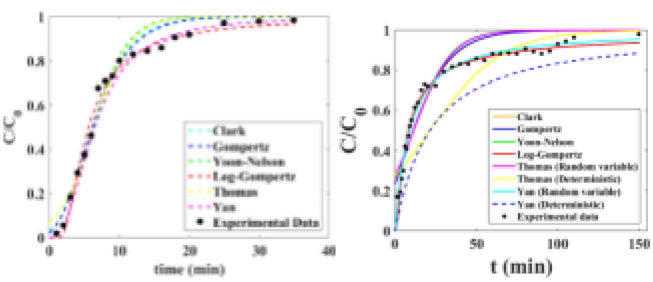

Fig. 3. Adjustment for the breakthrough curves to all models applied at the present work while (a) GAC and (b) GAC-Cu.

The model that best suits the experimental data, taking into consideration the mechanisms of the adsorption process, is the Yan model (Figure 3a) as well. However, when leaving the parameter deterministic, with its experimentally obtained value, satisfying the physics of the process, the model that best fits the data is the Clark model, thus, being able to change the selected model as well as the elucidation of the mechanisms involved in the process. Comparing the results for the unmodified GAC (Figure 3b), it can be seen that the model selected for the mechanisms of the adsorption process was altered (Yan to Clark) and if q_{max} was estimated along with the other parameters, the model that would better adjust the experimental data would continue to be Yan's model. In both of them, the Log-Gompertz model the best for practical purposes.

The same behavior was also found by Juela et al. [15], especially at the beginning of the breakthrough curves obtained by the authors.

Conclusion

The study highlights the significance of precise operational parameters and comprehensive statistical analysis in optimizing TC removal through adsorption processes. The optimal conditions achieved 95% TC removal, with GAC-Cu demonstrating a maximum adsorption capacity three times higher than GAC. Bayesian analysis accurately predicted breakthrough curves, and the Log-Gompertz model was deemed practical for both scenarios.

Acknowledgements

The authors thank the Coordination for the Improvement of Higher Education Personnel (CAPES), Brazilian Government, and the Gaucho Researcher Program – PqG, 21/2551-0002148-9) for the support in the development of this research.

References

[1] M. Gavrilescu, K. Demnerová, J. Aamand, S. Agathos, F. Fava, Emerging pollutants in the environment: Present and future challenges in biomonitoring, ecological risks and bioremediation, N. Biotechnol. 32 (2015) 147–156. https://doi.org/10.1016/j.nbt.2014.01.001.
[2] R. Daghrir, P. Drogui, Tetracycline antibiotics in the environment: A review, Environ. Chem. Lett. 11 (2013) 209–227. https://doi.org/10.1007/s10311-013-0404-8.
[3] S. Heidari, M. Haghighi, M. Shabani, Ultrasound assisted dispersion of Bi2Sn2O7-C3N4 nanophotocatalyst over various amount of zeolite Y for enhanced solar-light photocatalytic degradation of tetracycline in aqueous solution, Ultrason. Sonochem. 43 (2018) 61–72. https://doi.org/10.1016/j.ultsonch.2018.01.001.
[4] T. Ikhlef-Taguelmimt, A. Hamiche, I. Yahiaoui, T. Bendellali, H. Lebik-Elhadi, H. Ait-Amar, F. Aissani-Benissad, Tetracycline hydrochloride degradation by heterogeneous photocatalysis using TiO2(P25) immobilized in biopolymer (chitosan) under UV irradiation, Water Sci. Technol. 82 (2020) 1570–1578. https://doi.org/10.2166/wst.2020.432.
[5] B. Kakavandi, N. Bahari, R. Rezaei Kalantary, E. Dehghani Fard, Enhanced sono-photocatalysis of tetracycline antibiotic using TiO_2 decorated on magnetic activated carbon (MAC@T) coupled with US and UV: A new hybrid system, Ultrason. Sonochem. 55 (2019) 75–85. https://doi.org/10.1016/j.ultsonch.2019.02.026.
[6] Y. Zhang, J. Zhou, J. Chen, X. Feng, W. Cai, Rapid degradation of tetracycline hydrochloride by heterogeneous photocatalysis coupling persulfate oxidation with MIL-53(Fe) under visible light irradiation, J. Hazard. Mater. 392 (2020) 122315. https://doi.org/10.1016/j.jhazmat.2020.122315.
[7] C. Liu, H. Dai, C. Tan, Q. Pan, F. Hu, X. Peng, Photo-Fenton degradation of tetracycline over Z-scheme Fe-g-C3N4/Bi2WO6 heterojunctions: Mechanism insight, degradation pathways and DFT calculation, Appl. Catal. B Environ. 310 (2022) 121326. https://doi.org/10.1016/j.apcatb.2022.121326.
[8] M. Suzuki, Adsorption engineering, 1st ed., Elsevier Science Publishers B. V., Amsterdam, The Netherlands, 1990. https://doi.org/10.1016/0923-1137(91)90043-n.
[9] T.A. Saleh, K.O. Sulaiman, S.A. AL-Hammadi, H. Dafalla, G.I. Danmaliki, Adsorptive desulfurization of thiophene, benzothiophene and dibenzothiophene over activated carbon manganese oxide nanocomposite: with column system evaluation, J. Clean. Prod. 154 (2017) 401–412. https://doi.org/10.1016/j.jclepro.2017.03.169.
[10] M.A. Pasqualette, D.C. Estumano, F.C. Hamilton, M.J. Colaço, A.J.K. Leiroz, H.R.B. Orlande, R.N. Carvalho, G.S. Dulikravich, Bayesian estimate of pre-mixed and diffusive rate of heat release phases in marine diesel engines, J. Brazilian Soc. Mech. Sci. Eng. 39 (2017) 1835–1844. https://doi.org/10.1007/s40430-016-0649-9.
[11] L.R. de C. Costa, L.A. Féris, Use of functionalized adsorbents for tetracycline removal in wastewater: adsorption mechanism and comparison with activated carbon, J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 55 (2020) 1604–1614. https://doi.org/10.1080/10934529.2020.1827654.
[12] APHA, Standard methods for the examination of water and wastewater, 21st edition, (2017). https://doi.org/10.1016/0048-9697(94)90332-8.
[13] J.T. de Oliveira, K.G.P. Nunes, D. Cardoso Estumano, L.A. Féris, Applying the Bayesian Technique, Statistical Analysis, and the Maximum Adsorption Capacity in a Deterministic Way for Caffeine Removal by Adsorption: Kinetic and Isotherm Modeling, Ind. Eng. Chem. Res. (2023). https://doi.org/10.1021/acs.iecr.3c02619.
[14] C.H. Giles, A.P. D'Silva, I.A. Easton, A general treatment and classification of the solute adsorption isotherm part. II. Experimental interpretation, J. Colloid Interface Sci. 47 (1974) 766–778. https://doi.org/10.1016/0021-9797(74)90253-7.
[15] D. Juela, M. Vera, C. Cruzat, X. Alvarez, E. Vanegas, Mathematical modeling and numerical simulation of sulfamethoxazole adsorption onto sugarcane bagasse in a fixed-bed column, Chemosphere 280 (2021) 130687. https://doi.org/10.1016/j.chemosphere.2021.130687.
[16] K.H. Chu, Fitting the Gompertz equation to asymmetric breakthrough curves, J. Environ. Chem. Eng. 8 (2020) 103713. https://doi.org/10.1016/j.jece.2020.103713.
[17] Q. Hu, Y. Xie, Z. Zhang, Modification of breakthrough models in a continuous-flow fixed-bed column: Mathematical characteristics of breakthrough curves and rate profiles, Sep. Purif. Technol. 238 (2020). https://doi.org/10.1016/j.seppur.2019.116399.