Application of Neural Networks to Data Generated in the Treatment of Industrial Wastewaters containing Ciprofloxacin

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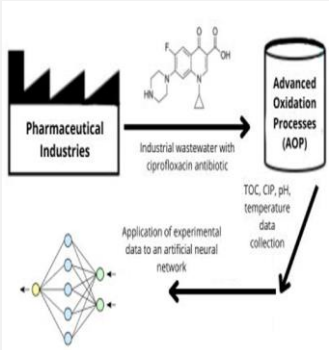

AOP are quite complex systems, making the phenomenological modeling of these processes difficult. Therefore, the use of empirical techniques, such as artificial neural networks (ANN), can be an interesting alternative. So, in this present work, the ANN technique was applied to model the degradation of the antibiotic ciprofloxacin (CIP), via ozonation process. Two models were developed for predicting the total organic carbon content ([TOC]) and the ciprofloxacin concentration ([CIP]). The obtained models were able to represent, satisfactorily, the CIP degradation, presenting, for example, values of the coefficient of determination (R^2), for the validation step, equals to 0.9994 and 0.9984, respectively, and did not present overfitting problems.

Introduction

Pollutants from pharmaceutical industries have attracted increasing concern. These compounds are biologically active substances, such as the antibiotic ciprofloxacin [1]. Therefore, it is necessary to develop effective methods for treating pharmaceutical wastewaters. In this context, several systems have been studied, highlighting the so-called advanced oxidative processes (AOP), such as ozonation [2].

The ozonation process is characterized by the use of ozone (O_3) as the oxidizing agent, in order to degrade the target pollutants. Ozonation involves a complex mechanism of chemical reactions, in addition to the mass transfer of O_3 from the gas phase to the aqueous phase [3].

However, understanding ozonation process is important for achieving more favorable conditions. In this context, the development of mathematical models is an essential tool for this. As ozonation process is complex, the application of empirical modeling techniques, such as artificial neural networks (ANN), appears as a possible solution to this problem [4].

Parise (2022) applied the ANN for modeling the CIP degradation by ozonation process, however, the obtained model presented some overfitting problems [5]. In this present work, the experimental database used by Parise (2022) was expanded, with the proposition of adjusted non-linear functions (empirical models) to adequately describe the behavior of total organic carbon ([TOC]) and [CIP] concentrations, as a function of the reaction time, in each experimental condition. Then, two ANN models were developed in order to predict the [TOC] and [CIP] values.

Material and Methods

In this work, experimental data, previously obtained by Baptistucci (2012), were used, studying the CIP degradation, applying the ozonation process operating isothermally (25 ºC) and in a batch regime. The experiments were carried out adopting the following controlled variables: initial pH (pH_0), ozone concentration in the gaseous feed stream in the reactor ($[O_3]_0$), the initial total organic carbon concentration ($[TOC]_0$) and the initial CIP concentration ($[CIP]_0$). During the tests, samples were analyzed for [TOC] and [CIP] determinations, along the reaction time (30 minutes) [6].

This present work was carried out in three steps: (i) statistical treatment of experimental data; (ii) proposition of empirical models (non-linear functions) to expand the original database, using the TableCurve 2D® software, expanding the database from 133 to until 1800 experimental points and (iii) development of ANN models, using the MATLAB® software, applying the Neural Network Toolbox.

In order to obtain the ANN models, three main steps were performed: training, testing and validation. The experimental database was divided into training (70%), testing (15%) and validation (15%) sets. Two ANN models with the same topology were proposed, presenting: an input layer, a hidden layer and an output layer. The so-called Models 1 and 2 were developed in order to predict [TOC] and [CIP] values (output variables), respectively. The two models presented 4 input variables, namely: reaction time (t); pH_0 and $[O_3]_0$, these three applied in both, in addition to $[TOC]_0$ and $[CIP]_0$ adopted in Models 1 and 2, respectively. The number of neurons in the hidden layer was minimized, maintaining a satisfactory predictive capacity of the models.

Results and Discussion

In Figure 1, it can be observed the behavior between the ANN predicted and experimental values, for Models 1 (a) and 2 (b), for the training, testing and validation steps, already considering the optimized number of neurons in the hidden layers: 8 and 7, for Models 1 and 2, respectively. Considering the data presented in Figure 1, the following values of the determination coefficients (R^2) were obtained: 0.9993 and 0.9946 (training); 0.9996 and 0.9997 (testing) and, finally, 0.9994 and 0.9984 (validation), for Models 1 and 2, respectively. In general, it can be observed that the two models presented results in good agreement with the experimental values.

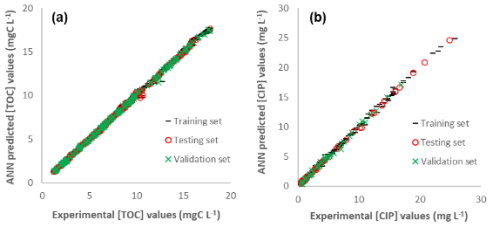

Figure 1. Comparison between ANN predicted and experimental values for Models 1 (a) and 2 (b) in training, testing and validation steps.

Furthermore, the models obtained were simulated, under different conditions, with the aim of evaluating their behavior. In Figure 2, for example, it can be observed simulations of Models 1 and 2, under the following conditions: (a) $[TOC]_0$ = 11 mgC/L; $[O_3]_0$ = 17.1 mg/L; pH_0 = 7 and (b) $[CIP]_0$ = 15.6 mg/L; $[O_3]_0$ = 17.1 mg/L; pH_0 = 7.

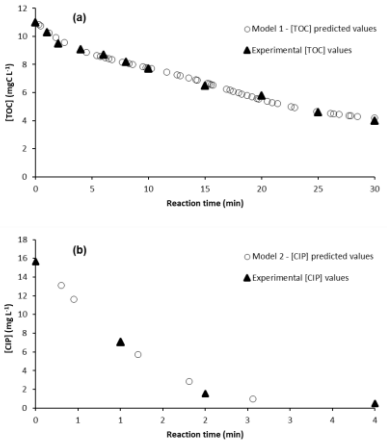

Figure 2. Simulations of the ANN models for [TOC] and [CIP], including experimental results, along the reaction time, considering the following experimental conditions: (a) $[TOC]_0$ = 11 mgC/L; $[O_3]_0$ = 17.1 mg/L; pH_0 = 7; (b) $[CIP]_0$ = 15.6 mg/L; $[O_3]_0$ = 17.1 mg/L; pH_0 = 7.

As seen in Figure 2, the obtained models were able to satisfactorily represent the non-linear behavior of CIP degradation by the ozonation process, without presenting overfitting problems.

Conclusions

The developed models showed good agreement with the experimental data, evidenced by the high R^2 values obtained during the training, validation and testing steps. The models were able to satisfactorily predict the total organic carbon and ciprofloxacin concentrations. Furthermore, according to the simulations carried out, it was also possible to observe that the proposed models did not present overfitting problems. The developed ANN models can be applied to carry out further simulations, with the aim of determining more favorable operational conditions for the degradation of ciprofloxacin by ozonation.

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