Enhancing Tetracycline Mineralization: Integrated Optimization Strategy with Ozonation and Hydrogen Peroxide

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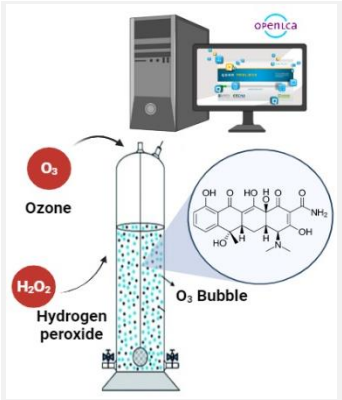
L. R. de C. Costa[1], *G. Dall Agnol[1], F. O. V. da Cunha[1], L. A. Féris[1]. (1) Federal University of Rio Grande do Sul, Department of Chemical Engineering, Ramiro Barcelos Street, 2777, Porto Alegre,RS, Brazil, leticiaregicar@hotmail.com.*



Antibiotics pose a growing concern as environmental contaminants. Tetracycline (TC) stands out due to its persistent presence in water and soil, challenging traditional treatment methods. The study investigated the optimization of TC mineralization through a combined ozone and hydrogen peroxide (H_2O_2) system. Operational variables such as pH, contact time, and ozone dosage were assessed alongside the presence of H_2O_2 in three TC solutions. QSAR in-silico was applied to assess TC ecotoxicity pre-ozonation, and openLCA to evaluate process environmental impacts. The toxicity of TC indicates risks to aquatic life, emphasizing the need for monitoring. LCA highlights electricity's as major environmental impact. Results indicated that the addition of H_2O_2 and changes on operational variables were crucial for enhancing TC mineralization. The inclusion of 0.8% H_2O_2 resulted in approximately 80.1% mineralization, while introducing 2% H_2O_2 allowed a significant reduction in ozone dosage. These findings underscore the potential as an effective resource in the mineralization of emerging contaminants.

Introduction

Antibiotics, such as tetracycline (TC), are widely used in human and veterinary medicine, but their presence in the environment poses a threat to public health [1]. Conventional water treatment methods show limitations in the complete removal of TC, driving the search for alternatives [2]. Although ozone processes hold promise for treating persistent pollutants, they face challenges such as high operational costs and the formation of undesirable by-products [3]. To overcome these limitations, ozone processes combined with hydrogen peroxide (H_2O_2) have been considered. H_2O_2 acts as an additional oxidizing agent, reducing the amount of ozone required [4].

In this context, the present study investigates the effectiveness of combined ozone and H_2O_2 treatment in the TC mineralization and its impact on operational parameters such as pH, ozone dosage, and reaction time.

Material and Methods

Preparation of Tetracycline Solutions

Three TC solutions were used: i) a TC solution (20 mg/L); ii) a TC solution (20 mg/L) with a ratio of 20 mL of 35% H_2O_2 (2% v/v) to 980 mL of distilled water; iii) a TC solution (20 mg/L) with a ratio of 8 mL of 35% H_2O_2 to 992 mL of distilled water (0.8% v/v).

Eco-toxicity assessment and Life-Cycle Analysis (LCA)

An in-silico approach using QSAR was employed to assess the ecotoxicity of TC before the ozonation process. The analysis was conducted using the OECD Toolbox, Version 4.3.1, employing the integral model. LCA was calculated in openLCA 2.0 software using ReCiPe 2016 midpoint method, considering complete removal of TC and functional unit of one lab batch volume.

Ozone Reactor and Treatment Design

The experimental setup used in this study includes an oxygen concentrator, an ozone generator, a liquid/gas contact reactor, and a gas washing bottle. The average ozone dosage produced is 1.3 ± 0.05 gO_3/h. The ozonation process was conducted using a $3^{(3-1)}$ factorial design. The variables and their interactions were analyzed using analysis of variance (ANOVA) with a confidence level of 95%. The experimental design totaled 11 experiments, where the main response factors were the degradation and the mineralization capacity of TC. Table 1 presents the matrix of the experimental design applied.

Table 1. Experimental design matrix for TC synthetic solutions.

	Level		
Independent variables	-1	0	+1
x_1: pH	3	6.5	9
x_2: time (min)	10	20	45
x_3: gas flow (L/min)	0.3	0.6	0.9

After the experiments, TC concentration was measured using high-performance liquid chromatography (HPLC), while matrix mineralization was assessed through total organic carbon (TOC) concentration.

Results and Discussion

Pre-treatment toxicity assessment of TC and LCA analysis

Table 2 presents data on the aquatic ecotoxicity of TC, based on QSAR analyses.

Table 2. Information on aquatic ecotoxicity caused by TC.

Endpoint	Value (mg/L)	Specie, duration, database
LC50	>20÷<40	Daphnia magna; 48 h; ECOTOX
NOEC	340	
LOEC	0.01 – 10	Daphnia magna; 21 d ECOTOX

In a 48-hour exposure, the TC concentration between >20÷<40 mg/L resulted in 50% mortality in *Daphnia magna* (LC50). Concentrations below 340 mg/L did not cause observable adverse effects (NOEC). The adverse effect (LOEC), including mortality and other alterations, was observed in the range of 0.01 to 10 mg/L within 21 days. These data emphasize the importance of monitoring and controlling TC concentrations to protect aquatic life.

The LCA results showed electricity to produce ozone has main influence in global warming potential impact, higher than 80%. The environmental impact of H_2O_2 and electricity can be observed in freshwater and human ecotoxicity. Further study considering mineralization results is recommended.

Statistical Analysis of the Model and Interactions

The model's adequacy was confirmed through ANOVA, with R^2 values above 0.849, indicating a strong correlation between the data and effective predictability of the process efficiency. The p-values were all below 0.05, affirming the significance of regression.

The Pareto chart (Fig. 1) illustrated the standardized influences of independent variables.

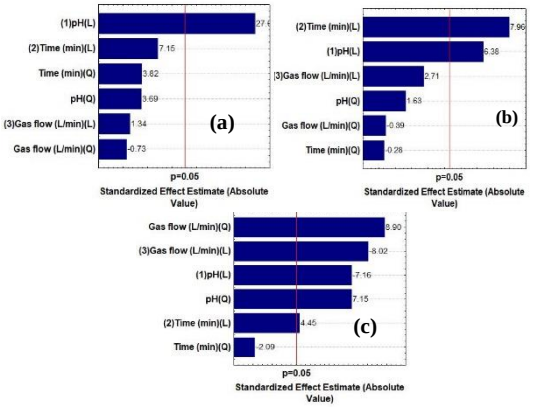


Figure 1. Pareto chart of main and interaction effects from the experimental design: a) 20 mg/L TC; b) 20 mg/L TC + 0.8%; and c) 20 mg/L TC + 2%.

It was demonstrated that pH had a significant effect on the response in all solutions, followed by time (Fig. 1b) and flow rate (Fig. 1c), with the latter only affecting the TC solution containing 2% of H_2O_2. Furthermore, increasing peroxide concentration (Fig. 2c) paralleled enhanced interaction between process variables, potentially influencing system reactivity due to greater oxidative species availability [5].

Synergistic effects of H_2O_2 presence and ozone

Figure 2 illustrates the mineralization capacity, considering the optimal condition obtained from the experimental design for each solution.

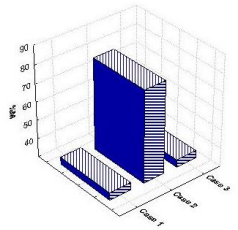


Figure 2. Mineralization capacity of TC considering - Case 1: 20 mg/L TC (pH 9 and O_3 dosage 5.85 g/L); Case 2: 20 mg/L TC + 0.8% (pH 9 and O_3 dosage 5.85 g/L); and Case 3: 20 mg/L TC + 20% (pH 3 and O_3 dosage 3.91 g/L).

The combination of ozone and H_2O_2 exhibits different behaviors in acidic and alkaline environments: in alkaline environments, H_2O_2 acts as a potent oxidizing agent, whereas in acidic environments, it complements the action of ozone in a controlled manner [6].

Comparing the studied cases, it was observed that the presence of H_2O_2 facilitated a vigorous oxidation of TC in the contaminated matrix (Case 2), resulting in a mineralization of 80.1%. On the other hand, in acidic conditions (Case 3), H_2O_2 acted more gently, complementing the action of ozone in a controlled manner. Additionally, there was an optimization of the process with a reduction of 33.2% in the ozone dosage, from 5.85 to 3.91 g/L. This reduction in the amount of ozone required to achieve the desired treatment goals can lead to significant energy savings and cost reductions associated with the ozonation process [7].

Conclusions

In summary, the addition of H_2O_2 to ozonation can be advantageous in water treatment applications. At a concentration of 0.8% H_2O_2, a mineralization of 80.1% of the matrix with TC was achieved, with a strong influence of the pH. The toxicity assessment of TC and the LCA analysis underscore the importance of understanding the environmental implications of processes. This analysis resulted that electricity has the main influence on global warming potential impact. Regarding toxicity, adverse effects were observed in the range of 0.01 to 10 mg/L. However, conducting pilot studies and feasibility assessments is crucial to determine the optimal conditions to maximize benefits and mitigate risks.

Acknowledgments

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