Application Of Photo-Assisted Ozonation (O_3/UV) In The Treatment Of Synthetic Prednisone Effluent

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Emerging contaminants, even at low concentrations in aquatic environments, can pose risks to human health. Thus, advanced treatment processes, such as O_3/UV, can be used as an alternative to the conventional treatment of these compounds. This present study evaluated the behavior of the O_3/UV process using a synthetic prednisone effluent, aided by a complete 2^3 factorial design with triplicates at the central point. The control variables were ozone mass flow rate (7 to 11 $mg.min^{-1}$), UV radiation (5.99×10^{-7} to 3.39×10^{-6} $einstein.s^{-1}$), and pH (5 to 9), and the evaluated response was the reduction of total organic carbon (TOC). Among the experiments conducted, the one in which all control variables were employed at their maximum levels (pH: 9; UV radiation: 3.39×10^{-6} $einstein.s^{-1}$; O_3: 11 $mg.min^{-1}$) showed the highest TOC reduction (42.16%). Statistical analysis indicates that, for greater reductions in TOC, it would be necessary to increase the values of the control variables.

Introduction

Several recalcitrant organic substances, such as medications, pesticides, and endocrine disruptors, are present in water sources around the world. These substances, even at low concentrations, can cause serious negative impacts on human health and the ecosystem [1]. Prednisone, the focus of this study, was one of the most used medications during the COVID-19 pandemic, leading to increased contamination of aquatic environments [2].
Among advanced treatment technologies, ozonation stands out as an efficient alternative for degrading these substances, given its high oxidizing power. When decomposed, it can generate the hydroxyl radical, which enhances organic matter degradation [1-3].
Therefore, the study of technologies aiming to improve the efficiency of organic substance degradation is necessary. This study evaluated the effectiveness of photo-assisted ozonation process in a synthetic effluent containing prednisone, with the aim of removing the present organic matter.

Material and Methods

HPLC-grade Prednisone and other analytical-grade reagents were used in the preparation and assays of photo-assisted ozonation.
Synthetic effluents were prepared with a prednisone concentration of 60 $mg.L^{-1}$ and the pH was manually adjusted using dilute H_2SO_4 and NaOH solutions, according to the experimental condition. Batch assays were conducted in a quartz annular photochemical reactor, with externally coupled Osram Puritec HNS G23 lamps emitting UV radiation at 253.9 nm, with a reaction time of 60 minutes. A uniform radiation field was assumed.
The reactor was connected to a mixing tank through which the medium was recirculated (1.5 $L.min^{-1}$), from which samples were withdrawn.
The total volume of the reaction medium was 1000 mL, and the usable volume of the photoirradiated reactor was 70 mL. All experiments were conducted at room temperature. Ozone (O_3) was generated in an Ozonio Life® ozonizer, by high-voltage electrical discharge (corona effect), fed by a 99% oxygen cylinder, at a pressure of 2 $kgf.cm^{-2}$ and a gas inlet flow rate of 0.25 $L.min^{-1}$.
The experiments were conducted according to a complete factorial experimental design 2^3 with triplicates at the central point. The control variables were ozone mass flow rate (7 to 11 $mg.min^{-1}$), UV radiation (5.99×10^{-7} to 3.39×10^{-6} $einstein.s^{-1}$), and pH (5 to 9). The chosen response variable was the percentage reduction of total organic carbon (TOC), which was analyzed by controlled combustion at 680°C on a platinum catalyst in a Shimadzu analyzer, model TOC-VCPN, as established in the Standard Methods of Examination of Water and Wastewater.

Results and Discussion

The conditions indicated in the experimental matrix shown in Table 1 were used to evaluate the action of the ozonation on predinisone.
Experiment 8 achieved the highest TOC reduction (42.16%) by employing all control variables at their maximum levels (pH: 9; UV radiation: 3.39×10^{-6} $einstein.s^{-1}$; ozone mass flow rate: 11 $mg.min^{-1}$).
To assess the level of influence of these control variables on the response variable TOC, the results were treated using Statistica® software. Subsequently, the Pareto diagram and main effects plots were obtained, presented in Figures 1 and 2.
The Pareto Diagram (Figure 1) showed that all individual control variables and their respective third-order interaction showed statistical significance regarding the reduction of TOC, as they presented calculated t-values higher than the tabulated value (3.1824). This is likely because, under alkaline

conditions and UV radiation, ozone can generate hydroxyl radicals that have a higher oxidation potential than molecular ozone, leading to more efficient degradation of organic matter [1-2].

Table 1. Experimental matrix and results obtained from the photo-assisted ozonation process.

Exp	pH	UV Rad. (.10^7)	O_3	Red. TOC (%)
1	5.00 (-1)(1)	5.99 (-1)	7.0 (-1)	7.64
2	9.00 (+1)	5.99 (-1)	7.0 (-1)	18.51
3	5.00 (-1)	33.9 (+1)	7.0 (-1)	13.99
4	9.00 (+1)	33.9 (+1)	7.0 (-1)	21.64
5	5.00 (-1)	5.99 (-1)	11.0 (+1)	10.05
6	9.00 (+1)	5.99 (-1)	11.0 (+1)	19.68
7	5.00 (-1)	33.9 (+1)	11.0 (+1)	13.90
8	**9.00 (+1)**	**33.9 (+1)**	**11.0 (+1)**	**42.16**
9	7.00 (0)	21.0 (0)	9.00 (0)	20.52
10	7.00 (0)	21.0 (0)	9.00 (0)	22.44
11	7.00 (0)	21.0 (0)	9.00 (0)	20.06

(1) The values within parentheses represent the levels of the experimental design: (-1) low, (0) centrer, and (+1) high.

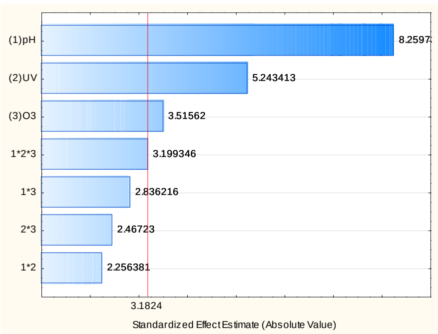

Figure 1. Pareto Diagram for TOC reduction.

The main effects of the studied control variables (pH, UV radiation, and ozone), shown in Figure 2, demonstrated that higher pH values, UV radiation rates, and ozone mass flow rates lead to increased organic matter degradation.

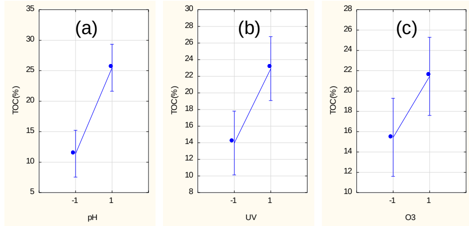

Figure 2. Main effects plot for control variables (a) pH, (b) UV radiation, and (c) ozone

The statistical analysis yielded a mathematical model that represents the experimental procedure (Equation 1).

$$TOC(\%) = 19.14 + 7.05\times pH + 4.47\times UV + 3.00\times O_3 + 2.73\times pH\times UV\times O_3 \quad (1)$$

Statistical validation of the model was performed using analysis of variance (ANOVA), as detailed in Table 2. Significant p-values (less than 0.05) for the control variables confirm the model's validity.

Table 2. ANOVA for TOC reduction in the photo-assisted ozonation process.

	SS	df	MS	F	p
(1)pH	397.76	1	397.76	68.22	0.0037
(2)UV	160.30	1	160.30	27.49	0.0135
(3)O_3	72.06	1	72.06	12.36	0.0390
1*2	29.68	1	29.68	5.09	0.1093
1*3	46.90	1	46.90	8.04	0.0659
2*3	35.49	1	35.49	6.09	0.0903
1*2*3	59.68	1	59.68	10.24	0.0494
Pure error	17.49	3	5.83		
Total	819.36	10			

Despite achieving reductions in TOC, the exploratory planning suggests that higher values of O_3 and photon flux (light intensity), in an alkaline medium would lead to more significant degradation results of the organic matter present in the studied synthetic effluent.

Conclusions

According to the results obtained, the treatment of the prednisone model solution by photo-assisted ozonation proved to be more effective when higher amounts of O_3 and UV radiation, in the presence of alkaline pH (9), were employed, as shown by experiment 8, where the highest TOC reduction was found (42.16%). For optimizing the results, higher rates of O_3 mass flow and UV radiation, within the alkaline pH range, should be used.

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