Degradation of the Drug Prednisone in Aqueous Solution by Combined Ozonation and Photolysis (O_3/UV)	POSTER Ph.D. Student: Y Journal: JECE

P.R.A. Mendes[1,2], K.C.Santos[1], L.F. Santos[1], P.C. Oliveira [1], L.F.F.Faria[1]. (1) Lorena School of Engineering, University of São Paulo (EEL-USP), Estrada municipal do Campinho, s/n, Campinho, Lorena/SP, Brazil, (2) email: paulo_ricardo_am@yahoo.com.br

Pharmaceuticals are substances that can negatively impact the environment when improperly discarded. The O_3/UV treatment process is an alternative for treating these compounds. This study evaluated the effectiveness of O_3/UV on synthetic prednisone effluent by assessing the reduction of total organic carbon (TOC). A central composite design (CCD) was used to optimize the O_3/UV treatment process. Its was investigated the influence of two control variables: O_3 (9 to 13 mg.min^{-1}) and UV radiation (3.25x10^{-6} to 8.69x10^{-6} einstein.s^{-1}), with TOC as the response variable. Among the runs, experiment 2 (O_3=12.42 mg.min^{-1}; UV Rad=4.05x10^{-6} einstein.s^{-1}) provided the highest TOC reduction (40.97%). Based on statistical analysis, the optimal condition (O_3=13 mg.min^{-1}; UV Rad.=3.25x10^{-6} einstein.s^{-1}) was determined, resulting in a theoretical TOC reduction of 48.34%, experimentally validated with a real TOC reduction of 46.61 ± 2.51%.

Introduction

Among emerging contaminants, pharmaceuticals originate from various anthropogenic activities such as therapeutic drugs, agricultural, industrial, and hospital effluents. Their presence in the environment can pose significant threats to public health [1]. Prednisone, the focus of this study, was one of the most commonly used medications during the COVID-19 pandemic, leading to increased contamination of aquatic environments [2].
Considering this, the advanced treatment process that combines ozonation with photolysis (O_3/UV), also known as photo-assisted ozonation, emerges as an alternative for degrading recalcitrant substances, either through direct reactions with O_3 or indirect reactions involving radicals generated from O_3, such as hydroxyl radicals [3]. Thus, this study presents the results of prednisone degradation in synthetic effluent, focusing on reducing the organic matter present in the reaction medium, using the Design of Experiment, specifically the Central Composite Design (CCD).

Material and Methods

Prednisone, of HPLC grade, and other analytical reagents of analytical grade were used in the preparation and assays of photo-assisted ozonation. The synthetic effluent utilized in the experiments was prepared with prednisone (60 mg.L^{-1}) and an initial pH of 10.14, adjusted using diluted solutions of H_2SO_4 and NaOH. Batch assays were conducted in a quartz annular photochemical reactor, with Osram Puritec HNS G23 lamps ranging from 5 to 13 W and emitting UV radiation at 253.9 nm. The lamps were either internally and/or externally coupled to the photoreactor, with a reaction time of 60 minutes and a uniform radiation field was assumed.
The reactor was connected to a mixing tank where the medium was recirculated at a rate of 1.5 L.min^{-1}, from which samples were withdrawn. The total volume of the reaction medium was 1000 mL, with a useful volume of 70 mL in the irradiated reactor. All experiments were conducted at room temperature.
Ozone (O_3) was generated using Ozone Life® equipment, through high-voltage electrical discharge (corona effect), fed with 99% oxygen at a pressure of 2 kgf.cm^{-2} and an inlet flow rate of 0.25 L.min^{-1}.
These experiments were conducted according to a central composite design (CCD) experimental plan, with 4 corner points, 4 axial points, and triplicates at the central point. The control variables were ozone mass flow rate (9 to 13 mg.min^{-1}) and UV radiation (3.25×10^{-6} to 8.69×10^{-6} einstein.s^{-1}). The response variable chosen was the percentage reduction of total organic carbon (TOC).
TOC was analyzed through controlled combustion at 680°C with a platinum catalyst, using a Shimadzu brand TOC-VCPN analyzer, as established in the Standard Methods of Examination of Water and Wastewater.

Results and Discussion

The results obtained from the photo-assisted ozonation for the prednisone model effluent following the CCD proposal are shown in Table 1, where it was observed that experiment 2, which used an ozone mass flow rate of 12.42 mg.min^{-1} and UV radiation with a photon flux of 4.05×10^{-6} einstein.s^{-1}, provided the best result for TOC reduction (40.97%).
To assess the level of influence of the studied variables on TOC reduction (%), the obtained results were statistically evaluated at a confidence level of 95% using Statistica® software. From this analysis, the Pareto chart and the response surface were obtained, as shown in Figures 1 and 2, respectively.

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

Exp	UV radiation ($.10^6$ einstein.s^{-1})	O_3 ($mg.min^{-1}$)	TOC (%)
1	4.05 (-1)	9.58 (-1)	15.90
2	**4.05 (-1)**	**12.42 (+1)**	**40.97**
3	7.89 (+1)	9.58 (-1)	23.37
4	7.89 (+1)	12.42 (+1)	30.06
5	3.25 (-1,41)	11.00 (0)	25.97
6	8.69 (+1,41)	11.00 (0)	24.68
7	5.97 (0)	9.00 (-1,41)	17.84
8	5.97 (0)	13.00 (+1,41)	37.58
9	5.97 (0)	11.00 (0)	25.28
10	5.97 (0)	11.00 (0)	27.00
11	5.97 (0)	11.00 (0)	26.98

(1) The values in parentheses represent the respective levels of the experimental design: (-1) low, (0) central point, (+1) high, and axial points (-1.41 and +1.41).

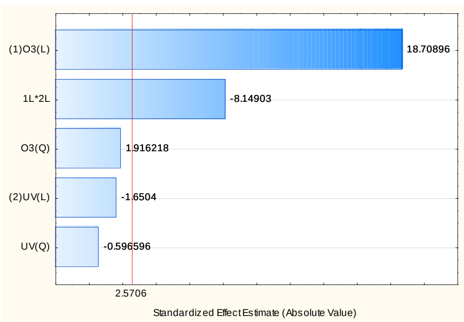

Figure 1. Pareto chart for TOC reduction.

From the Pareto chart revealed that the ozone flow rate variable and its interaction with UV radiation showed statistical significance regarding TOC reduction, where the calculated t-values were higher than the tabulated ones (2.5706). This was experimentally proven, as assays conducted at higher ozone levels showed greater reductions in TOC. This suggests that the presence of ozone in the reaction medium is crucial to enhance the generation of hydroxyl radicals, which is facilitated by the alkaline pH of the reaction medium. On the other hand, the interaction between the control variables showed that the combination of ozone and UV radiation did not significantly increase TOC reduction, as higher photon rates were not efficient when combined with high ozone flow rates. This can be explained by the higher availability of photons in the reaction medium, which may lead to the generation of other less reactive oxidative species. This behavior is observed in Figure 2, which indicates the optimal treatment region (TOC reduction > 60%) at lower radiation levels and higher ozone levels.

With the assistance of the Desirability function in Statistica® software along with the proposed model (Equation 1), the optimal conditions of the studied O_3/UV process were obtained, in which the theoretical response for TOC reduction was 48.34% while using 13.0 $mg.min^{-1}$ of O_3 and 3.25×10^{-6} einstein.s^{-1} of UV.

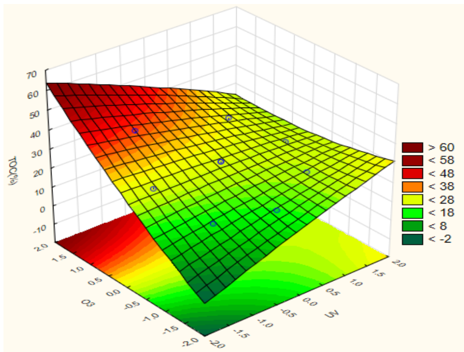

Figure 2. Response surface for TOC reduction.

$$TOC\ (\%) = 26.42 - 0.66\times UV + 7.46\times O_3 - 0.28\times UV^2 - 0.91\times(O_3)^2 - 4.60\times UV\times O_3 \quad (1)$$

In order to validate this proposed optimal condition, duplicate experiments were conducted and the average reduction in TOC found was 46.61±2.51%, confirming that the proposed mathematical model accurately represents the process under study.

Conclusions

The response surface methodology proved to be a useful tool for determining the optimal region of the O_3/UV photo-assisted ozonation process for the chosen control variables (O_3 and UV radiation), aiming at the degradation of prednisone. The application of the O_3/UV process as a treatment technique for this corticosteroid demonstrated the ability to remove approximately half of the organic load present in the reaction medium (reduction of 46.61 ± 2.51% in TOC).

Acknowledgments

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