Degradation of Pharmaceutically Active Compound Using an Advanced Oxidative Process such as Photo-Assisted Peroxidation

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L.F. Santos[1,3]*, K.G. Ferreira* [1]*, C.D. Meneghatti*[2]*, P.R.A.Mendes* [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) National Institute for Space Research – INPE, Av. dos Astronautas, 1758 - Jd. Granja - SJC/SP - Brazil (3) email: professorlucrecio@usp.br*

Conventional effluent treatment is ineffective in degradation of recalcitrant organic substances such as pharmaceuticals. Thus, advanced processes, notably photo-assisted peroxidation (H_2O_2/UV), can be used to improve treatment efficiency. The present work evaluated the ability of the H_2O_2/UV process to mineralize the organic matter of a model prednisone effluent. An experimental design of the complete factorial type 2^2 with triplicate at the central point was employed. The control variables were H_2O_2 concentration (3.52 to 10.55 mM) and UV radiation (5.99×10^{-7} to 11.1×10^{-6} einstein.s^{-1}). The reduction in total organic carbon (TOC) was used as the response variable. Among the experiments conducted, the greatest TOC reduction (10.80%) was obtained at the maximum levels of both control variables (H_2O_2 = 10.55 mM and UV radiation = 1.11×10^{-6} einstein.s^{-1}). According to statistical analysis, to obtain better TOC results, higher levels of H_2O_2 and UV radiation should be investigated.

Introduction

Conventional treatment processes can be ineffective when of recalcitrant substances, such as pharmaceuticals, are present in the effluent. Therefore, it is necessary to implement specific treatments, employing advanced alternative technologies [1-3].

The degradation of prednisone, by advanced oxidative processes (AOP), almost always involves several intermediate reaction steps, which may form different by-products that may be more toxic or less toxic than the original drug. Therefore, it is important to find a more optimized form of degradation, which allows the disintegration of the active drug into elementary substances of no or reduced toxicity, enabling safer disposal in the environment [1-4].

Thus, this work evaluated the efficiency of the photo-assisted peroxidation treatment process to reduce the total organic load of a prednisone model effluent.

Material and Methods

HPLC grade prednisone and other analytical grade reagents were used to prepare the solutions and conduct the photo-assisted peroxidation tests.

The synthetic effluent consisted of an aqueous solution of prednisone at 60 mg.L^{-1} and pH 8.0. The tests were carried out in batches in an annular quartz photochemical reactor equipped with externally coupled Osram Puritec HNS G23 lamps emitting UV radiation at 253.9nm. A uniform radiation field was assumed.

This reactor was connected to a mixing tank, where the medium was recirculated (1 L.min^{-1}), from which the samples were taken. The total volume of the reaction medium was 500 mL and the useful volume of the photoirradiated reactor was 70mL. The tests were carried out at room temperature (25ºC). These experiments were carried out according to a 2^2 complete factorial experimental design with triplicates at the central point. The control variables were H_2O_2 concentration (3.52 to 10.55 mM), UV radiation (5.99×10^{-7} to 1.11×10^{-6} einstein.s^{-1}) and the reduction in total organic carbon (TOC) was evaluated as a response.

TOC was analyzed by controlled combustion at 680°C with platinum catalyst, using a Shimadzu Analyzer, Model TOC-VCPN, as established in the Standard Methods of Examination of Water and Wastewater.

Results and Discussion

The experiments were carried out according to the matrix indicated by the experimental design, and the results obtained are shown in Table 1.

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

Exp.	H_2O_2 (mM)	UV radiation (10^7 einstein.s^{-1})	TOC Red. (%)
1	3.52 (-1)[(1)]	5.99 (-1)	1.10
2	10.55 (+1)	5.99 (-1)	5.92
3	3.52 (-1)	11.1 (+1)	3.13
4	**10.55 (+1)**	**11.1 (+1)**	**10.80**
5	7.03 (0)	8.53 (0)	6.48
6	7.03 (0)	8.53 (0)	6.21
7	7.03 (0)	8.53 (0)	6.57

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

Among the experiments carried out, it was observed that condition 4, in which both control variables were used at the highest level (10.55 mM H_2O_2 and 1.11×10^{-7} einstein.s^{-1}), was found to be the highest TOC reduction (10.81%).

To assess the level of influence of the control variables on the TOC response variable, the results were analyzed using the Statistica® software, with a confidence level of 95%. The analysis generated a Pareto diagram and main effects plots, shown in Figures 1 and 2, respectively.

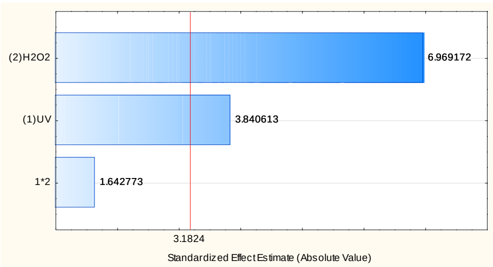

Figure 1. Pareto diagram for TOC reduction.

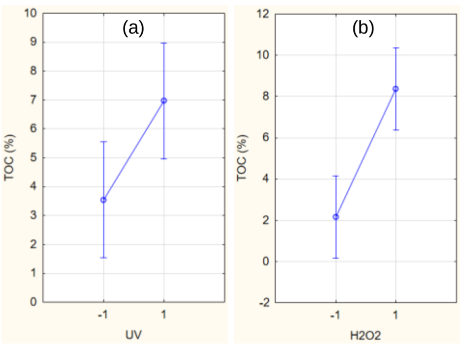

Figure 2. Main effects for the control variables (a) UV radiation and (b) H_2O_2.

Analyzing the Pareto Diagram, it is possible to observe that both control variables individually showed statistical significance in terms of TOC reduction, as they presented calculated t values higher than the tabulated value (3.1824).

Higher concentrations of H_2O_2 in the reaction medium led to greater degradation of organic matter. This is because increased H_2O_2 availability, in conjunction with UV radiation, generates more hydroxyl radicals, which are highly effective oxidizing agents. The main effects plot (Figure 2) confirms this trend.

Based on these statistical analyses, it was possible to obtain a mathematical model that could represent the experimental procedure (Equation 1).

$$TOC(\%) = 5.756 + 1.713\times UV + 3{,}108\times[H_2O_2] \quad (1)$$

The present model was validated by analysis of variance (ANOVA), as shown in Table 2, where the p values for both control variables were significant, that is, less than 0.05, indicating that this model accurately reflects the experimental data.

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

	SS	df	MS	F	p
(1)UV	11.73063	1	11.73063	14.75031	0.031137
(2)H_2O_2	38.62623	1	38.62623	48.56935	0.006062
1*2	2.14623	1	2.14623	2.69870	0.198973
Pure error	2.38584	3	0.79528		
Total	54.88891	6			

Therefore, despite the low TOC reduction values, the exploratory planning indicated that higher concentrations of H_2O_2 and photon rates are necessary to achieve better degradations of the organic matter present in the model effluent studied.

Conclusions

According to the results obtained, the treatment of the prednisone model solution by photo-assisted peroxidation proved to be more effective when greater amounts of H_2O_2 and UV radiation were used, as shown in experiment 4, where the greatest reduction in TOC was found (10.81 %). Therefore, to obtain better TOC reduction results, which directly implies greater biodegradability of the studied effluent, higher concentrations of H_2O_2 and UV radiation rates must be used in search of an optimized condition of the chosen treatment process.

Acknowledgments

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