Treatment of Effluent from The Pharmaceutical Industry by Advanced Oxidation Processes: Removal of Organic Load and Acute Toxicity

ORAL/POSTER

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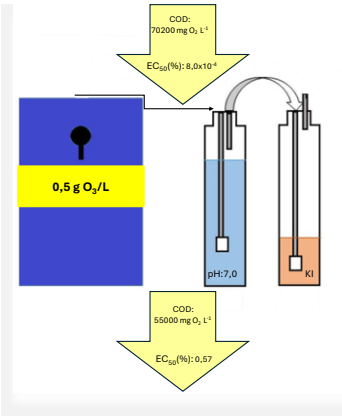

Treating industrial effluents is crucial for compliance with regulations, but some effluents contain recalcitrant substances, posing challenges for conventional treatment methods. Advanced Oxidative Processes (AOP), such as Fenton's reagent, ozonation, and photoperoxidation, offer promising alternatives. This study evaluated these techniques for treating effluent from the pharmaceutical industry, focusing on reducing organic load and toxicity. All processes partially removed organic load and reduced acute toxicity. Ozonation at 500 mg O_3/L and pH 7 was the most effective, reducing BOD5 by 37.8% and toxicity by 96.8% — further testing combined ozonation with coagulation, significantly reducing COD and acute toxicity. Subsequent tests with a higher organic load showed promising COD, BOD, TOC, and acute toxicity reductions.

Introduction

Treating industrial effluents is a crucial step in the production process. Conventional treatment techniques are optimized to comply with current legislation. However, some effluents have recalcitrant substances in their composition, which can cause high toxicity, making it difficult to meet legal requirements. Alternative treatment techniques must be used for these cases, including Advanced Oxidative Processes (AOP), which is emerging as a technically and economically viable alternative. The objective of this work was the evaluation of three advanced oxidative processes: Fenton's reagent ($H^+/Fe^{2+}/H_2O_2$), ozonation (O_3), and peroxidation assisted by ultraviolet radiation (UV/H_2O_2) in the treatment of an effluent generated by a pharmaceutical industry, mainly aimed at reducing the organic load and reducing the toxicity of the effluent.

Material and Methods

The raw pharmaceutical effluent was characterized by Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), alkalinity, pH, and acute toxicity. The same parameters were analyzed after applying the three processes.

In all processes, 1000 mL of sample was used. In the Fenton reaction, the effluent was adjusted to pH 3 (H_2SO_4), 5,000 mg of H_2O_2 and 114 mg of $FeCl_2$ were added, and 150 minutes of testing. After total oxidant consumption, the pH was adjusted to 7.0.

In the ozonization process, a borosilicate glass tubular reactor was used and operated in a batch regime. A model O3R generator (Philizon) generated ozone from atmospheric air and was applied with a sintered glass diffuser. Ozone concentration was monitored with a potassium iodide (KI) solution [1]. Five different concentrations between 500 and 5,000 mg L^{-1} of ozone were evaluated. Acute toxicity tests were carried out with neonatal Daphnia similis microcrustaceans, which were exposed to diluted aqueous solutions of the sample or standard, distributed in 4 replicates. The organisms were kept at 20 °C in the dark and without nutrients. After 48 hours, the immobility of the microorganisms in the samples and the control (cultivation water) was observed [2].

Results and Discussion

Analyzing the results obtained in the tests, it is possible to affirm that all three techniques evaluated partially removed the organic load and reduced the effluent's acute toxicity.

The most efficient process was ozonation 500 mg L^{-1} de ozônio on pH 7.0, which showed BOD_5 removal of 37.8% and acute toxicity of 96.8% and was chosen to continue the effluent treatability tests. The lower doses of oxidant likely caused the oxidation of the molecules present in the effluent matrix, so the intermediate compounds generated were less toxic than those generated when there was a higher

oxidant concentration. Cases in which the intermediate products of drug oxidation are more harmful than the parent compounds are not rare in the literature. Tay & Madehi studied the ozonization of ofloxacin, an antibiotic from the fluoroquinolone class, and found that this reaction can generate more toxic by-products than ofloxacin [3].

In this second phase, it was decided to include a treatment step, a physicochemical process of coagulation with Aluminium sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$), before optimizing the ozonation reaction parameters due to the high organic load (initial COD of 70,200 $mgO_2\ L^{-1}$), which resulted in a reduction in COD to 58,457 $mgO_2\ L^{-1}$. When optimizing the parameters of the ozonization process, it was observed that the best results were obtained at pH 7 and 500 mg L^{-1} of ozone, COD of 55,000 mgO_2/L. The optimized condition showed a toxicity reduction of 99.85% about EC50 (0.57%).

The test was carried out with a new effluent with a higher organic load, where the initial values of COD (147,500 $mgO_2\ L^{-1}$), BOD (83,200 $mgO_2\ L^{-1}$), TOC (41,125 mgC L^{-1}), and Acute Toxicity - EC_{50} (1.3 x 10^{-3}%), and the results of reduction in parameter values were 17%, 29%, 32%, and 99.5%, respectively.

It would be interesting to develop an analytical procedure to determine the various antibiotics in the effluent and the degradation by-products generated in the ozonation process. Individual toxicological and ecotoxicological studies, with each drug present in the effluent, would also help determine the compound or compounds with more significant toxicity. This would allow greater care during the generation of the effluent in the production of these drugs, even resulting in a possible segregation of effluent streams at specific periods.

Table 1 – Concentration of Chemical Oxygen Demand ($mgO_2\ L^{-1}$), Biochemical Oxygen Demand ($mgO_2\ L^{-1}$), Total Organic Carbon (mgC L^{-1}), and Toxicity Acute *Daphnia similis* (%) and percentage of removal (%) of each parameter in relation to the raw effluent in effluents treated by the three processes.

		Fenton		O_3		UV/H_2O_2	
	Inicial	**final**	**Reduction (%)**	**final**	**Reduction (%)**	**final**	**Reduction (%)**
COD (mgO_2/L)	70,200	65,090	7.3	54,710	22.1	66,430	5.4
BOD (mgO_2/L)	55,500	36,500	34.2	34,500	37.8	40,600	26.8
TOC (mgC/L)	20,455	19,010	7.1	16,040	21.6	19,420	14.3
Acute Toxicity (EC50%)(%)	$8.8\ 10^{-4}$	0.026	96.5	0.028	96.8	0.027	96.7

Conclusions

Considering the results obtained in the present treatability study of this type of wastewater, it is concluded that ozonation is a very effective process for reducing toxicity and organic load. To increase the process efficiency, it would be interesting to have a prior reduction in the organic load of the effluent, either through a treatment step before ozonization, such as a biological process. An improvement could also be made in the production process aiming to generate an effluent with a lower organic load or even a possible segregation of some flow of effluents with a high organic load or toxicity to be treated individually.

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