

Hydrogen peroxide *on-site* electrogeneration combined with UV process for degradation of pharmaceutical products in water

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A wide variety of pharmaceuticals end up contaminating waters used as sources of public water supply. Advanced treatment technologies, such as hydrogen peroxide (H₂O₂) and UV radiation, can easily be applied in potabilization treatment plants (PTP) and have shown a capacity to degrade these pharmaceuticals. However, some limitations hinder the application of combined H₂O₂/UV systems in PTP, which requires special chemical care and increases the cost of the process. This study aimed to evaluate the degradation of a pharmaceutical mixture consisting of atenolol (ATN), prednisone (PRED), and sulfamethoxazole (SMX) using an *on-site* H₂O₂ (E-H₂O₂) electrogeneration system combined with UV-C radiation. The combined E-H₂O₂/UV-C system demonstrated superior degradation and mineralization of the pharmaceuticals compared to the E-H₂O₂ and UV-C processes that were applied alone. The proposed system is presented as an alternative for treating water with multiple contaminants, providing safer drinking water to the population.

Introduction

Pharmaceuticals are present in the environment, and their mixture can cause synergistic effects, necessitating more advanced water and wastewater treatment [1]. Therefore, this study selected atenolol (ATN), prednisone (PRED), and sulfamethoxazole (SMX) due to their widespread occurrence in surface water samples [2-3]. Advanced oxidation technologies, such as UV combined with hydrogen peroxide (H₂O₂), have been identified as effective methods for water decontamination. However, the intensive production of H₂O₂ by the anthraquinone process and its limitations in transportation, storage, and handling which incur additional costs and risks, make the *on-site* generation of this oxidant an interesting alternative [4]. The combination of *on-site* H₂O₂ generation and UV treatment has gained prominence due to several advantages. This method is considered safer and more economical since it does not require the transportation, handling, and external addition of H₂O₂ [4-5].

Synthetic or low ionic charge solutions often require the addition of a supporting electrolyte, typically a salt, to increase conductivity in electrochemical processes. However, using these salts can lead to secondary contamination, rendering the process unsuitable for potabilization [6]. Solid electrolytes are being studied as an alternative to enable the electrosynthesis process in the treatment of drinking water [7]. In this study, *on-site* electrosynthesis of H₂O₂ (E-H₂O₂) using a solid electrolyte, combined or not with a UV process, was investigated as a strategy to degrade a mixture of three pharmaceuticals in a drinking water system. This proposal aims to improve advanced techniques for multicontaminant degradation.

Material and Methods

The electrochemical reactor consists of an Electro MP cell connected to the UV-C reactor. The MP cell was assembled with a DIACHEM[®] anode, a perforated graphite plate (Grafites Sulamericana), and a commercial gas diffusion electrode (GDE) as cathode, both with an active area of 100 cm². The anodic and cathodic chambers were separated by a cation exchange membrane (HDX 100), to prevent decomposition of H₂O₂ at the anode. Air was continuously supplied to a gas chamber by an air compressor, with the airflow regulated by an air rotameter. In addition, an ion exchange resin (AMBERLITETM IRC120 H) was selected as the solid electrolyte and introduced into the cathodic chamber to increase the conductivity of the influent solution that contains 5 mg L⁻¹ of ATN, PRED, and SMX as it flows through the resin.

In the anodic chamber, 1 L of 0.035 M Na₂SO₄ solution was also used, circulated at a flow rate of 2 L min⁻¹. UV irradiation was provided by a UV-C lamp (13 W, Philips TUV PL-S).

The maximum *on-site* production of H₂O₂ at a neutral initial pH was previously evaluated and the operating conditions selected were a current density of 30 mA cm⁻², a constant affluent flow of 50 L h⁻¹, and an air flow of 5 L min⁻¹ during a process time of 120 min. Samples were analyzed using an HPLC system to monitor the pharmaceutical degradation and determine the generated carboxylic acids. Shimadzu equipment (TOC-LCPH) was used to determine the pharmaceutical mineralization. Phytotoxicity tests were conducted using onions (*Allium cepa*) as the test organism.

Results and Discussion

At the end of the E-H₂O₂ process (Fig. 1(a)), the degradation of ATN, PRED, and SMX reached 90%, 75%, and 83%, respectively. Compared with the UV-C process (Fig. 1(b)), ATN achieved a higher degradation by E-H₂O₂, unlike PRED and SMX, which achieved a higher degradation by UV-C in the first few min of the process. The percentage of degradation in the UV-C system reached 99% and 70% for PRED and SMX, respectively. While for ATN the degradation was lower, reaching the highest percentage reduction of 45% in 120 min. These results are consistent with those reported by other authors because PRED and SMX are readily photodegraded compounds [8]. However, photodegradation is generally associated with the formation of more toxic by-products [9-10]. In the combined E-H₂O₂/UV-C system (Fig. 1(c)), there was an increase in the degradation of multicontaminants, especially PRED and SMX, in the first few min of the process compared to the tests with UV-C or E-H₂O₂ alone. In 15 min, 82%, 97%, and 81% degradation were obtained for ATN, PRED, and SMX, respectively.

In terms of mineralization, 33% was observed in 120 min using the E-H₂O₂ process and 39% of mineralization was found in 15 min using the combined process, while no mineralization was observed using UV-C. In the electrochemical processes used in this study, part of the reduction in the contaminants concentration may be related to an adsorption process due to the use of ion exchange resin as a solid electrolyte. In addition, the pharmaceuticals can desorb from the resin at certain times, which is why there is a slight increase in the concentration of compounds and TOC at some points, given that the resin was not replaced between experiments. It should also be noted that the electrogenerated H₂O₂ can be transported to the

surface of the resin where the contaminants are adsorbed, resulting in their degradation near the surface layer. Another hypothesis for the increase in TOC is the loss of carbon coverage on the cathode surface due to possible degradation of the GDE [11].

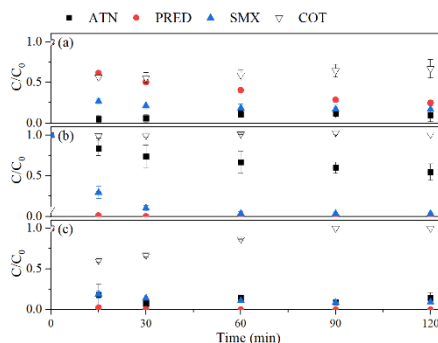


Figure 1. Effect of (a) *on-site* electrogeneration of H₂O₂ (E-H₂O₂) and (b) direct photolysis (UV-C) and (c) combined system (E-H₂O₂/UV-C) on degradation and mineralization of several pharmaceutical products. Fixed conditions for E-H₂O₂ and E-H₂O₂/UV-C applied electric current: 30 mA cm⁻²; affluent flow rate: 50 L h⁻¹; air flow rate: 5 L min⁻¹.

The assessment of carboxylic acids produced during the pharmaceutical degradation indicates that the E-H₂O₂/UV-C process only produces short-chain acids, suggesting a greater tendency towards mineralization. Toxicity was evaluated in *A. cepa*, and the UV-C process was found to be toxic, possibly due to the formation of more toxic by-products. However, the other treatments did not exhibit any toxicity when compared to the control. Therefore, the combined system exhibited higher degradation and mineralization of the three studied pharmaceuticals compared to the other treatments.

Conclusions

Comparing the UV-C, E-H₂O₂, and E-H₂O₂/UV-C processes, the latter achieved higher degradation and mineralization of ATN, PRED, and SMX in 15 min, suggesting the formation of lower chain biodegradable by-products and the exhibited no phytotoxicity in *A. cepa*. This highlights the potential use of this technology in potabilization treatment plants to remove pharmaceutical products.

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