Assessment of Advanced Oxidative Processes in the Degradation of Estrone (E1) in Sanitary Sewage

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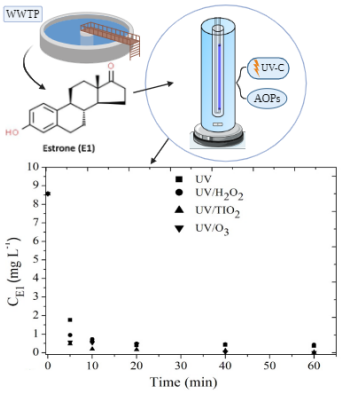

The increasing presence of the hormone estrone (E1) in effluents from wastewater treatment plants (WWTPs) poses both environmental and public health concerns. This study quantified E1 in samples of effluent treated by a municipal WWTP in Paraná, Brazil, and evaluated the effectiveness of different Advanced Oxidative Processes (AOPs) in its degradation. UV/O_3 treatment emerged as the most efficient, significantly improving various physicochemical and microbiological parameters. The AOPs, especially UV/TiO_2 and UV/O_3 processes, demonstrated efficiency in degrading E1 without the formation of more toxic byproducts compared to the initial sample. The findings underscore the importance of effective treatments in WWTPs to prevent environmental contamination by estrogens.

Introduction

The presence of the hormone estrone (E1) in effluents from wastewater treatment plants (WWTPs) is a growing concern due to its potential environmental and public health implications. This compound originates from pharmaceuticals, personal care products, and industrial activities [1]. Considering this context, the search for effective removal methods has become necessary. Advanced oxidative processes (AOPs) have gained prominence [2], as they involve the generation of highly reactive species such as hydroxyl radicals capable of oxidizing and degrading a wide range of persistent compounds, including E1, into less toxic products [3]. In this regard, the present study aimed to (i) quantify E1 in samples of effluent treated by a WWTP; (ii) evaluate the kinetics of different AOPs in E1 degradation; and (iii) compare the toxicity of effluents before and after AOP treatment.

Material and Methods

Samples of the treated effluent were collected from a WWTP located in the Southwest of Paraná, Brazil (2160 m^3 d^{-1}). The treatment system used is activated sludge. Physicochemical and microbiological characterization of the samples was carried out, both before and after the AOPs, according to the Standard Methods [4]. The AOPs evaluated in the degradation of E1 were UV, UV/H_2O_2, UV/TiO_2, and UV/O_3. The reactions were conducted in a batch reactor described by Bohrer [5]. The pH of the samples was not altered. Predetermined concentrations of TiO_2 (1 g L^{-1}), H_2O_2 (1.8 g L^{-1}), and ozone (800 mg h^{-1}) were added [5]. To identify and quantify E1, HPLC-UV analyses were performed, following the methodology described by Bohrer [5]. Six sample points were collected during a 1 hour reaction. By fitting the experimental data to the pseudo-first-order kinetic model, the kinetic constant (k) was calculated. To assess ecotoxicological effects, immobility/mortality tests were conducted with the bioindicator *Artemia salina* L. [6, 7], and evasion tests were conducted with *Eisenia fetida* [8].

Results and Discussion

Physicochemical and microbiological characteristics

The UV/O_3 treatment proved to be the most efficient, resulting in a significant improvement in all monitored parameters, meeting environmental standards [9, 10, 11]. Turbidity was reduced by 58.33%, and color removal reached 47.97%. Additionally, a reduction of 66.42% in chemical oxygen demand (COD) and 70.28% in biochemical oxygen demand (BOD_5) was achieved. Similarly, it exhibited high efficacy in reducing total phosphorus concentrations by 88.27% and total nitrogen concentrations by 70.85%. Furthermore, the AOPs showed high efficiency in the inactivation of thermotolerant coliforms (>99%).

Quantification of E1 in the effluent

E1 was identified in all effluent samples at a significantly elevated concentration (4.120 µg L^{-1}).

This concentration can be attributed to the fact that E1 is an important decomposition product of E2 and EE2 [12]. This result is consistent with those of Pessoa et al. [13]. Effluents from municipal WWTPs emerge as a significant source of contamination by estrogen hormones in water bodies.

Degradation of E1 by AOPs

The concentration of E1 decreased exponentially throughout the reaction (as shown in the Graphical Illustration), demonstrating that the pseudo-first-order kinetic model was appropriately fitted to the experimental data in all AOPs. Higher degradation efficiency of E1 was observed in the UV/TiO_2 (99.79%) and UV/O_3 (100%) processes. The UV/TiO_2 process exhibited the highest kinetic constant (k) in E1 degradation (0.57 min^{-1}). Although slightly lower, the UV/O_3 process also showed a significant kinetic constant (0.50 min^{-1}). Therefore, the increasing order in the degradation rate of E1 was: $k_{UV/TiO2} > k_{UV/O3} > k_{UV/H2O2} > k_{UV}$.

The utilization of oxidants (H_2O_2 and O_3) and photocatalysts (TiO_2) enhances the efficiency of E1 degradation by generating reactive species. Hydroxyl radicals generated during the AOPs attack the phenolic groups, which are the most significant functional groups of estrogen hormones like E1, resulting in their effective degradation [5]. The results of this study are consistent with those of Pešoutová, Stříteský, and Hlavínek [14], where efficiencies exceeding 98% were observed in the removal of E1 in samples of municipal WWTP effluent treated by biological processes subjected to AOPs.

Ecotoxicity assessment

The bioindicator *Artemia salina* demonstrated that the WWTP effluent was statistically different ($p<0.05$) from the negative controls. However, for the AOP samples, it was observed that as the exposure concentration was reduced, toxicity decreased. The AOPs showed statistical equivalence ($p<0.05$) to the WWTP effluent at a concentration of 100%, indicating that these processes did not generate byproducts with higher toxic potential for the evaluated organism. In the evasion test with *Eisenia fetida*, the WWTP effluent demonstrated an evasion behavior similar to the response observed in the positive control. However, for the AOPs, no toxicity was observed. Similar results were observed in the degradation of estrogens by AOPs [15], where there was a decrease in the toxic effects of the WWTP effluent compared to the initial sample.

Conclusions

A high concentration of E1 in the WWTP effluent was evidenced, demonstrating its low removal by conventional treatment. Through AOPs, E1 was effectively degraded in real effluent samples, with a 100% removal in the UV/O_3 process. Additionally, the physical-chemical and microbiological quality of the effluent was improved, reducing the toxicity of the samples compared to the initial sample. This highlights the importance of effective treatments in WWTPs to prevent the entry of estrogens into the environment.

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