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Biologically activated carbon (BAC) combined with a Solar Fenton-based process to treat municipal wastewater containing gestodene (GES)

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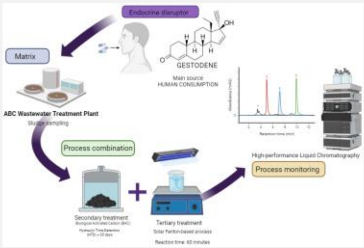

In this study, gestodene (GES) was degraded by the combination of biological activated carbon (BAC) and homogeneous photocatalysis. Real municipal wastewater samples were sampled from a wastewater treatment plant (WWTP) located in ABC, São Paulo, Brazil, before biological treatment. The sludge was applied to the BAC treatment as a secondary process. Advanced oxidation processes were conducted with synthetic and treated sludge under solar-driven and Fenton-based processes. The irradiation experiments were conducted using a UVA lamp (solar reflector) to photoactivate the oxidizing precursors. Progestin concentrations were monitored, highlighting the efficiency of each treatment. Solar-Fenton/S_2O_8 and solar/S_2O_8 were the best processes, removing over 85% of the target hormone. This investigation motivates the optimization of solar-Fenton/S_2O_8 to degrade progestins in a complex matrix.

Introduction

The fate and behavior of endocrine disruptors (EDCs) in aquatic environments have been considered a worldwide concern. Among synthetic steroids, progestins have attracted attention due to their widespread use in contraceptive pills and their harmful effects on different organisms [1,2]. Gestodene (GES) has been found in WWTP samples at around 0.85 ng L^{-1} [3].

Considering the low removal of EDCs by conventional treatment technologies, the evaluation of advanced oxidative processes (AOP) is an alternative. The application of combined processes such as biological+AOP [4] or gamma radiation and photocatalytic processes [5], has also been investigated to intensify waste remediation.

In this sense, the present study aims to investigate the best solar-driven and Fenton-based process to degrade GES in a synthetic solution. Furthermore, the removal of estrogenic activity is the main objective for the viability of the process.

Material and Methods

Reagents. Gestodene (GES, $C_{21}H_{28}O_2$, ≥ 98.0%) was purchased from Zhejiang Xianju Pharmaceutical Co. Ltd. H_2O_2 (35% w/w solution), H_2SO_4 (97%) and $FeSO_4{\cdot}7H_2O$ were supplied by LabSynth, while $Na_2S_2O_8$ (PS, ≥ 98.0%) was supplied by Sigma-Aldrich. All the components required for the YES bioassay were research-grade biochemicals suitable for cell culture (supplied by Sigma-Aldrich. Methanol (HPLC grade) and acetic acid (LabSynth) were used to prepare the mobile phases used in liquid chromatography. Deionized water (18.2 MΩ cm) was obtained from a Milli-Q Direct-Q system (Millipore).

Case study. The São Paulo Metropolitan Region, with 39 municipalities, is the sixth-largest urban agglomeration in the world and the largest in South America. It contributes more than 30% of Brazil's Gross Domestic Product (GDP). The wastewater treatment plant selected for this study is located in ABC (-23.6116688, -46.5865216). Using refrigerated automatic samplers (Etsus 2000) after primary treatment of the composite type, samples were collected at 24-hour intervals and analyzed for physicochemical characterization.

Analytical methods. GES concentrations were monitored by ultra-fast liquid chromatography (UFLC) using Shimadzu equipment (LC 20AD) equipped with a UV-visible detector (SPD 20A) and C18 column (ACE, 250 mm × 4.60 mm, 5 µm). An isocratic method was applied using 70% methanol and 30% water containing 1% v/v acetic acid as the mobile phase [8]. GES was detected at 244 nm. The sample injection volume, oven temperature, and flow rate were 20 µL, 40 °C, and 1.0 mL min^{-1}, respectively. The calibration curves were obtained by diluting the stock solutions to obtain GES standards from 0.05 to 20.0 mg L^{-1}.

Photocatalytic degradation. The photodegradation tests were performed using a mercury iodide lamp (Master HPI-T Plus, Philips Co.), providing 4.3 mW cm^{-2} in the 300-400 nm range. The sludge and the synthetic solution with GES (1.18 ± 0.21 mg L^{-1}) were introduced into the reaction vessel under magnetic stirring for 30 min. **Table 1** shows the experimental conditions for each treatment applied.

Table 1. Experimental conditions applied to the degradation of gestodene (GES).

Treatment	$[H_2O_2]$ (mg L^{-1})	$[S_2O_8]$ (mg L^{-1})	$[Fe^{+2}]$ (mg L^{-1})
Solar/H_2O_2 [6]	1.8	none	none
Solar/S_2O_8 [6]	none	12.0	none
Fenton [7]	4.3	none	5
Solar-Fenton [7]	4.3	none	5
Solar-Fenton-S_2O_8 [7]	4.3	12.0	5

The initial pH of the solution in the Fenton-based process was adjusted using H_2SO_4 from 7 to 3. Samples were withdrawn periodically, immediately quenched with 100 µL of MeOH, and then analyzed by ultra-fast liquid chromatography (UFLC), as described elsewhere [8].

Results and Discussion

Table 2 shows the physicochemical characterization, according to the Standard Methods for the Examination of Water and Wastewater [9]. **Table 3** presents the effect of the Fenton-based process and homogenous catalysis on the degradation of GES. The ranking order of GES degradation efficiency ranking order was established as solar-Fenton < solar/H_2O_2 < Fenton < solar/S_2O_8 < solar -Fenton/S_2O_8. De Jesus *et al.* (2022) [8] evaluated the feasibility of a radiolytic process to treat a mixture of progestins, including GES. The best operating condition of the process (doses of 10 kGy) achieved complete removal of GES.

Table 2. Physicochemical parameters of wastewater collected at ABC WWTP.

pH	DO* (mg O_2 L^{-1})	Conductivity (µS cm^{-1})	COD (mg L^{-1})	Alkalinity (mg L^{-1})
7.12 ± 0.4	0.3 ± 0.4	2078.1 ± 1293.8	200.6 ± 89.3	160.0 ± 59.9

DO* = dissolved oxygen.

Table 3. Removal efficiency (%), k_{obs}, and R^2 obtained for solar-driven treatments in synthetic solutions. $[GES]_0$ = 1.18 ± 0.21 mg L^{-1}. Runs carried out in duplicate.

GESTODENE			
Treatment	Removal (%)	k_{obs} (min^{-1})	R^2
Solar/H_2O_2	31.8 ± 0.3	0.0280	0.8597
Solar/S_2O_8	96.7 ± 0.1	0.1285	0.9618
Fenton	33.7 ± 1.5	0.0180	0.8620
Solar-Fenton	21.8 ± 1.7	0.0100	0.8400
Solar-Fenton/S_2O_8	100.0 ± 0.2	0.5852	0.9106

Conclusions

In this study, the degradation of gestodene was evaluated through different solar-driven and Fenton-based processes, to investigate the effect of the water matrix and the feasibility of each process. According to the results, some experimental conditions stood out concerning the others, considering the high removal of the hormone, as Solar-Fenton/S_2O_8. This first screening will contribute to the choice of a combination of processes focused on optimizing the removal of progestins in complex aqueous mixtures and ecotoxicological assessment.

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