



Peracetic acid treatment for removing steroid hormones in a pilot-scale wastewater installation

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ARTICLE INFO

Editor: Sadao Araki

Keywords:

Endocrine disruptors
Steroid hormones
Peracetic acid
Advanced oxidation processes (AOPs)
Wastewater treatment
Environmental protection

ABSTRACT

The global water scarcity challenge urges sustainable solutions such as wastewater reuse, which is crucial to alleviate pressure on dwindling freshwater sources. However, this approach must address the presence of emerging pollutants (EPs), demanding specific treatment processes to ensure water safety and environmental protection. Peracetic acid (PAA) has garnered global interest due to its high oxidation potential and production of low-toxicity byproducts, making it a promising alternative for wastewater decontamination. This study aimed to assess PAA efficacy in removing three EPs: estrone (E1), 17 β -estradiol (E2), and 17 α -ethinylestradiol (EE2). Conducted in a pilot-scale wastewater treatment facility using real wastewater, the study explored six operational conditions, with varying PAA concentrations (5 mg/L to 15 mg/L) and hydraulic retention times (HRT) of 5, 10, and 15 min. Control parameters were monitored throughout the study. The condition with 15 mg/L PAA and 15 min HRT was the most efficient achieving over 85 % removal efficiency for all three compounds. The condition with 15 mg/L PAA and 10 min HRT was less efficient, achieving 70 % removal for E1 and 60 % and 44 % for E2 and EE2, respectively. A Spearman correlation matrix identified temperature and *E. coli* as strongly correlated with EPs removal, potentially influencing PAA decay. Overall, PAA demonstrated effective removal of target EPs under real wastewater conditions, underscoring its viability as a sustainable alternative for enhancing wastewater treatment processes, contributing to environmental protection and public health. Future studies could explore the long-term efficiency of PAA application and its scalability.

1. Introduction

In the last decade, water resource management has encountered significant challenges. On one hand, global water scarcity, driven by climate change and rapid urbanization, has led to a decline in available water bodies [1,2]. Consequently, climate change is expected to alter the spatial and temporal distribution of water availability, compromising the achievement of Sustainable Development Goals (SDGs) [2,3]. On the other hand, the continuous inflow of emerging pollutants (EPs) into water bodies, primarily through wastewater discharges [4], with limited dilution potential, results in an escalation of their concentrations [5]. EPs encompass a wide range of substances, including pharmaceutical

and personal care products (PPCPs), pesticides, industrial chemicals, surfactants and perfluoroalkyl and polyfluoroalkyl substances (PFASs) [4]. The primary concern regarding the presence of EPs in the environment is their high toxicity combined with their bioavailability and the potential to bioaccumulate in different environmental matrices [6]. Awareness of these issues has increased due to advancements in analytical techniques, allowing detection at trace levels, ranging from ng/L to μ g/L [7].

Among EPs, endocrine-disrupting compounds are a key group of contaminants, with steroid hormones such as 17 α -ethinylestradiol (EE2), 17 β -estradiol (E2) and estrone (E1) being the primary representatives [8,9]. Both E2 and E1 are naturally produced hormones, by

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<https://doi.org/10.1016/j.jwpe.2024.106453>

Received 25 June 2024; Received in revised form 17 October 2024; Accepted 29 October 2024

Available online 6 November 2024

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humans and animals, while EE2 is a synthetic hormone commonly used in oral contraceptives and in hormone replacement therapies [10]. The physicochemical properties and their structures are presented in the supplementary material (Table S1), where they share the same base structure, a tetracyclic framework with three cyclohexane rings, a phenolic ring, and one cyclopentane ring [11]. Their major differences lie in the C₁₇ position: E1 has a ketone group, E2 has a hydroxyl group (β position), and EE2 has a hydroxyl group and an ethinyl group (α position).

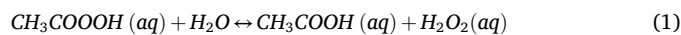
These compounds are excreted through urine and faeces, and within the context of human production and consumption, they primarily enter the environment through wastewater treatment plants (WWTPs) [9]. Indeed, as reported by Adeel et al., [12], by the year 2017, considering the world population of around 7 billion people, approximately 30,000 kg per year of natural steroid estrogens are discharged into the environment, with an additional 700 kg per year originating from birth control pills containing the synthetic steroid hormone EE2 [8,12]. These compounds are detected at exceedingly low concentrations (in the range of ng/L), raising significant concern. Even at minute levels, the literature describes potential hazardous effects on aquatic biota, with the most reported impacts in mammals being alterations to normal reproductive functions [9,10,13,14]. A recent global five-year review and analysis of the risk posed by steroid hormones to various aquatic environments determined the risk quotient of these three compounds in descending order as EE2 > E2 > E1 [10]. Due to the risk posed by these compounds, they were included in the 2015 and 2018 Watch List [15,16], and recently mentioned in the proposal for amending the EU water legislation [17], as priority substances for monitoring in surface water, aiming to define environmental quality standards for each.

Conventional WWTPs indeed constitute one of the principal sources of these compounds entering the environment. However, these infrastructures were not originally designed to specifically address the removal of such compounds [18]. Consequently, these compounds pass through all treatment stages without significant reduction and are finally discharged into the environment [12,19,20]. Recently, the European Parliament and Council proposed a directive concerning urban wastewater treatment, which includes specific objectives for monitoring and treating EPs [21]. For instance, all urban wastewater treatment plants serving 150,000 p.e. and above should provide quaternary treatment, as these facilities represent a significant contribution of EPs discharges in the environment. Thus, monitoring EPs is mandatory to verify compliance with the quaternary treatment's reduction targets, with a minimum removal efficiency of 80 % of the influent load [21].

The challenge of EPs removal has been addressed by the scientific community through the development of various technologies to improve wastewater treatment [18,22]. Among these efforts, treatment technologies based on advanced oxidation processes (AOPs) have been promising in the complete/partial mineralization of EPs by the production of reactive species, such as hydroxyl radicals ([•]OH), hydroperoxyl radicals (HO₂[•]), sulphate radicals (SO₄^{•-}) and superoxide anion radicals (O₂^{•-}) [23–25]. For full reuse purposes, addressing not only EPs monitoring but also pathogenic contamination is mandatory to ensure safe treated water storage and distribution, without the risk of bacterial regrowth [26]. AOPs provide a dual benefit by combining disinfection and EPs elimination into a single water treatment stage [24]. However, not all AOPs, such as UV and O₃, provide a residual concentration suitable for storage and safe reuse. This characteristic must be considered when evaluating other applications [27,28], making peracetic acid (PAA) an interesting alternative.

PAA is an organic peroxyacid that is commonly used as a sanitiser, surface disinfectant, and oxidizer [29]. It has gained attention in the water sector, as a promising substitute for conventional disinfectants such as chlorinated disinfectants, allowing wastewater reuse. This is due to PAA's high oxidation potential (Table S2), its high microbial inactivation [27,30], and its low-toxicity disinfection by-products (DBPs) [31–35]. Other notable characteristics include low pH dependence, easy

technical implementation and operation due to a similar application as chlorine already present in most wastewater treatment plants (WWTP), and the presence of residual concentration [24,25,27,36]. PAA is commonly commercialised as an equilibrium mixture of PAA, H₂O₂, acetic acid, and water (Eq. (1)) [37], with the typical molar ratio between PAA and H₂O₂ ranging from 0.1 to 3.0 [38].



Although H₂O₂ has oxidative properties and can produce [•]OH, the O-OH energy bound in PAA is lower than H₂O₂ and its peroxy bonds are longer, making it easily broken and leading to the rapid formation of [•]OH radicals [24,35,36]. Consequently, higher doses of H₂O₂ are necessary to achieve oxidation levels equivalent to those of PAA [24]. Due to its oxidative properties, the direct application of PAA has been tested for the elimination of EPs, including antibiotics [39,40] and steroid hormones [33,34]. Previous studies on the removal of E2 and EE2 using PAA showed that high removal rates were attained, above 80 % for each compound in laboratory conditions with real wastewater, though without control parameters variability and the daily variability observed in a real wastewater quality [33,34]. No further research studies using PAA for the direct removal of E1, E2 and EE2 in real conditions have been published, indicating a knowledge gap in the literature.

The application of PAA for the elimination of EPs is gaining increasing attention in the scientific community. However, the effect of direct PAA application on the removal of EPs in real wastewater conditions is still not well understood. Therefore, the main goal of this study was to evaluate the elimination capacity of PAA for three steroid hormones, E1, E2 and EE2, in a pilot-scale installation in a real WWTP in the Mediterranean area. It aims to assess various operational conditions, including different PAA concentrations and hydraulic retention times, to determine optimal conditions for maximum removal efficiency. Additionally, this research explores the relation of wastewater characteristics, such as temperature and *Escherichia coli* (*E. coli*) content, on PAA performance, providing insights into potential improvements for real-world wastewater treatment applications.

2. Materials and methods

2.1. Chemicals, standards and stock solutions

The estrogen analytical standards, E1 and E2 were obtained from Dr. Ehrenstorfer (Germany) and EE2 from Sigma-Aldrich (Germany) (highest purity available, ≥ 95 %). Deuterium-labelled internal standards (IS) estrone-d4 (d4-E1), 17β-estradiol-d5 (d5-E2) and 17α-ethinylestradiol-d4 (d4-EE2) were from Sigma-Aldrich (Denmark). The PAA solution was purchased from Evonik Operations GmbH, PAA OxyPure® BIO (Germany), consisting of a mixture of 15 % PAA, 24 % H₂O₂ and 16 % acetic acid.

The stock solution containing E1, E2 and EE2 was prepared in 2 L of distilled water with 10 % MeOH (>99.9 %, Honeywell Riedel-de Haën, Germany), reaching a concentration of 5 mg/L after 5 min of exposure to ultrasounds in an ultrasound chamber (JULABO, USR3 model) to ensure full compounds dissolution. The 2 L solution was fully diluted in the 5 m³ mixing tank, to ensure an initial concentration of 2 μg/L. Previous batch studies developed by Maurício, Semedo et al., [34] and Maurício, Jorge et al., [33], who studied the removal of steroid hormones by PAA, using initial concentrations in the μg/L range supported the possibility of attaining feasible removal efficiencies. In an effort to attain quantifiable final concentrations to assess the removal efficiency attained by using PAA and to approximate initial concentrations of the existing ones in wastewater, the selected concentration was 2 μg/L. Additionally, the study by Pešoutová et al., [41] used similar initial concentrations of E1, E2 and EE2 to spike a pilot-scale installation of several different advanced oxidation processes. [33,34,41] Such concentrations ensure the presence of the steroid hormones mixture in the pilot installation and to account for the variability of wastewater concerning these

compounds. By employing a higher concentration of EPs, the analysis of PAA performance becomes more feasible.

2.2. Pilot-scale installation

The pilot-scale installation presented in Fig. 1 comprised a 5 m³ cylindrical tank equipped with a vertical mixer (TIMSA, model TA) powered by a 0.75 kW electric motor and a vertical coaxial reducer (600 mm diameter, 100 rpm speed). The setup was assembled downstream of the secondary clarifiers, as previously described by Dias et al., [30] and Sousa et al., [27]. The system was installed within a conventional Portuguese domestic WWTP designed to handle a daily flow rate exceeding 50,000 m³, after the secondary treatment before the final discharge [27,30]. The installation was fed by a submersible pump with adjustable flow rates ranging from 20 to 60 m³/h, as detailed by Dias et al., [30] and Sousa et al., [27].

The PAA solution was dosed into the system via a 12 L/h capacity Grundfos metering pump (Model DME12-6AR-PP/E/E-F-311F, Denmark), operating at 6 bar pressure and utilizing a single-phase power supply at 220 V (Dias, Sousa et al., 2023). The stock solution containing the three studied compounds (E1, E2 and EE2), was pumped through a metering pump Dosatron DOSETec PS PVDF-PTFE (Germany) with

adjustable flow rates ranging from 8 to 25 L/h, operating at 4 bar pressure, before the PAA injection, as shown in Fig. 2.

2.3. Control parameters

In addition to evaluating the removal efficiency of E1, E2, and EE2 at varying concentrations of PAA and hydraulic retention time (HRT), an analysis of wastewater characteristics was conducted. The parameters monitored included *E. coli*, total suspended solids (TSS), turbidity, pH, temperature and chemical oxygen demand (COD). TSS measurements followed the protocol outlined in the *Standard Methods for the Examination of Water and Wastewater* [42]. The parameters COD and *E. coli* were determined following ISO 6060:1989 [43] and ISO 9308-2:2012 [44], respectively, as detailed by Dias et al., [30] and Sousa et al., [27]. Temperature and pH were measured using single equipment with a temperature probe and through a potentiometric method with a WTW inoLab pH/ION 735 m. Turbidity was measured with a portable turbidimeter 0–1000 NTU HANNA Fast Tracker HI98703 (Portugal), by a nephelometric method.



Fig. 1. Pilot-scale installation set-up.

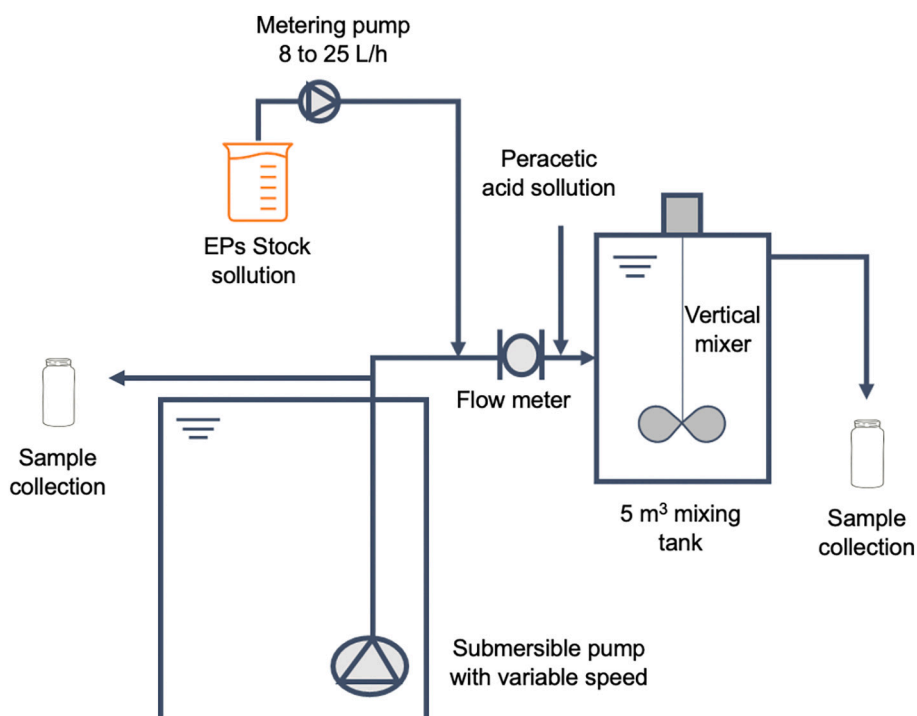


Fig. 2. Pilot installation flow diagram and sample collection, adapted from Sousa et al. [27].

2.4. Operation conditions and sample collection

The operational conditions for analysing EPs included two sampling points, and the study was conducted during both dry and wet seasons. The first sampling point was before the introduction of the stock solution and the subsequent injection of PAA. This initial sampling point aimed to provide information on the actual concentrations of steroid hormones present in the wastewater, crucial for evaluating the effectiveness of PAA treatment. The second sampling point was located after the mixing tank, as shown in Fig. 2. For the sample collection after PAA injection, 100 mg/L sodium thiosulfate was added to each 1 L schott flask to inhibit the PAA effect after collection. To evaluate the performance of PAA, three different PAA concentrations (C) in combination with three different contact times (T) were tested. The conditions tested were as follows:

- Concentration of 15 mg PAA/L with contact times of 15, 10, and 5 min, identified as C15T15, C15T10, and C15T5, respectively.
- The concentration of 10 mg PAA/L with contact times of 15 and 10 min, identified as C10T15 and C10T10.
- Concentration of 5 mg PAA/L with a contact time of 10 min, identified as C5T10.

The operational conditions were based on studies by Maurício, Jorge, et al., [33] and Maurício, Semedo, et al., [34] which demonstrated that increasing contact time of PAA led to greater removal efficiency of E2 and EE2. However, extending the contact time would require larger contact tank volumes, making this treatment impractical for rapid implementation in existing wastewater treatment plants. Additionally, higher PAA concentrations than those tested result in higher residual PAA levels in the effluent, potentially causing toxic effects on the receiving aquatic environment, as highlighted in the study by Domínguez-Henao et al., [32] The results on PAA disinfection performance published by Dias et al., [30], using 5 mg/L PAA over 10 min only reached Class D (not sufficient quality for the majority of reuse uses foreseen in the Regulation). As a possibility of PAA application would be for its dual effect purpose, no further conditions were tested with 5 mg/L

of PAA.

2.5. Sample preparation and analytical methods

2.5.1. Sample preparation

The quantification of steroid hormones in treated wastewater samples (before and after PAA dosage) required pretreatment and pre-concentration steps before analysis. Each 500 mL sample collected was filtered using GF3 grade glass microfiber filters, \varnothing 47 mm (CHM by CHMLAB group). The sample pre-concentration step was performed using the solid-phase extraction (SPE) technique. SPE was performed in a manual workstation (SUPELCO) using Oasis HLB 200 mg (6 cc) cartridges from Waters (Ireland). SPE cartridges were first conditioned with 8 mL of MeOH and 8 mL of ultrapure water. After conditioning, the analytes were eluted with 6 mL of MeOH, at around 2 mL/min rate [45,46]. The extracts were then evaporated to dryness with a gentle nitrogen stream coupled with a column heating block Supertherm (Omega) 230 Vac/6 A, 30–200C (Mikrolab Aarhus, Denmark), at 40 °C. The extracts were reconstituted with 500 μ L of MeOH, subjected to 15 min of ultrasound and centrifuged (Ole Dich APS, type 157, Denmark) for 6 min at 6000 rpm. Finally, 135 μ L of the sample supernatant was transferred into an HPLC vial and mixed with 15 μ L of internal standard solution.

2.5.2. Chromatographic conditions

The injection volume was set to 10 μ L of the mixtures and each sample was analysed in duplicate in a high-performance liquid chromatograph (HPLC) Agilent 1290 (Waldbronn, Germany) coupled with a tandem mass spectrometer (MS/MS) Sciex Qtrap 5500 (Framingham, MA, USA). The chromatographic separation was conducted with a 250 μ L/min solvent flow in a Synergi Polar-RP column (150 \times 2 mm, 4 μ m particle size) from Phenomenex (Torrance, CA, USA), thermostated at 20 °C. E1 was separated using a mixture of water (eluent A) and methanol (eluent B) that both contained 0.2 % v/v formic acid). E2 and EE2 were separated using a mixture of water (eluent A) and methanol (eluent B) that both contained 0.02 % ammonium hydroxide. The multi-step linear gradient for each method is presented in Table 1. The mass

Table 1
Multi-step linear gradient for each compound method.

Time (min)	E1		Time (min)	E2 and EE2	
	Eluent A (%)	Eluent B (%)		Eluent A (%)	Eluent B (%)
0–1	100	0	0–1	100	0
1–2.5	50	50	1–2	35	65
2.5–8.5	20	80	2–6.5	10	90
8.5–9	0	100	6.5–7	0	100
9–14	0	100	7–9	0	100
14–14.5	100	0	9–10	100	0
14.5–19.5	100	0	10–14	100	0

spectrometer was adjusted to 400 °C with a capillary voltage of 5500 V with electrospray ionization in positive mode (ESI(+)) for E1, and 4500 V negative mode (ESI(-)) for E2 and EE2.

The quantification of each compound concentration was determined using an analytical standard calibration with 9 points. The instrumental limits of quantification (LOQ), instrumental limits of detection (LOD) and method limits are presented in Table 2. The HPLC- MS/MS operation parameters are provided in Table S3 of the supplementary material.

2.6. Statistical analysis

Statistical analysis was conducted using GraphPad Prism 9 software, employing nonparametric tests due to the sample size and non-normal distribution of data. Initially, a Kruskal-Wallis test was conducted to assess differences between conditions (through multiple comparisons), with a significance level set at 5 % ($p \leq 0.05$). To further examine the effects of *E. coli* levels, TSS, turbidity, pH, temperature and COD on the removal of E1, E2 and EE2, a multivariate analysis was performed using Principal Component Analysis (PCA), considering E1, E2 and EE2 as dependent variables. Variables were standardized, and principal components (PCs) were selected based on percent of total explained variance (75 %). Scores close to ± 1.0 indicate a strong association between a variable and the principal component. Also, a Spearman correlation matrix was performed for each tested condition. A two-tailed p -value was used, with a confidence interval set at 95 %. The Spearman r correlation results were classified as follows: $0.5 < r < 0.7$: moderate correlation (positive or negative); $r \geq 0.7$: strong correlation (positive or negative).

3. Results and discussion

3.1. Steroid hormone removal efficiency

The efficacy of PAA as an oxidizing agent for the targeted EPs was assessed through a comparative analysis of data under various test conditions. This evaluation involved discerning PAA's reactivity and selectivity towards each compound, as well as considering the influence of control parameters on the elimination process. According to Table 3, in the exploratory data analysis, condition C15T15 presented the highest median value for E1, E2 and EE2, with a removal efficiency above 85 %. Similar results were obtained by Maurício et al. [33] in the Jar Test for E2, where 15 mg/L of PAA and 15 min contact time achieved above 80

Table 2
Instrumental and method limits.

	E1	E2	EE2
Instrumental limits			
LOQ (ng/mL)	3	5	10
LOD (ng/mL)	2	3	5
Method limits			
LOD (ng/L)	2	3	5

% removal efficiency. However, under the same conditions for EE2, lower efficiencies of around 50 % had been previously obtained [34]. Nevertheless, in the present study, the removal efficiency was much lower for 10 mg/L PAA than the 15 mg/L condition.

Comparing other conditions with the same PAA concentration, as shown in Fig. 3, no statistical differences were revealed between conditions C15T15 and C15T10 for E1 and E2. However, the p -value for E2 is 0.598, suggesting some variability in the data, which is verified by the results presented in Table 3, for the C15T10 condition, with a decrease in removal efficiency. For EE2, significant differences were observed (p -value of 0.0083), C15T10 presented almost 50 % less removal efficiency than C15T15. Additionally, within the same PAA concentration of 15 mg/L C15T15 was significantly higher, approximately 50 %, than C15T5 for E1, E2 and EE2 with p -values of 0.0137, 0.0002 and 0.0075. Within the 10 mg/L PAA conditions, removal efficiency for C10T10 was slightly higher than C10T15, but the differences were not statistically significant. Overall, the results of this study show for the first time that the direct application of PAA can remove steroid hormones in a real wastewater treatment context.

The functional groups of E1, E2 and EE2 suggest high reactivity and selectivity by PAA, primarily due to the phenolic group and the presence of aromatic rings with alkene group [31]. These functional groups make these compounds electron-rich, enhancing their elimination by PAA through the mechanism of transferring electrophilic single oxygen to an electron-rich site [31]. Similar characteristics are highlighted by Rizzo et al. [18], who classified E1, E2 and EE2 as class A in abatement (%) due to their electron-rich moieties and a fast reaction with ozone. For instance, Mathon et al., [47] tested a full-scale ozone installation for micropollutant removal and achieved high removal rates for E1, E2 and EE2, namely 93–96 %, 88 % and 87 %, respectively.

Dong et al., [48] also achieved comparable results for EE2, using 10 mg O₃/L and 15 min of contact time. Although ozone is classified as a strong oxidant, PAA achieved similar efficiency while offering a solution with lower implementation and operational costs, lower risk of toxic by-products and a residual concentration for storage and safe reuse purposes [27,29,30,32,49]. In reference to Section 1, it should be noted the possible reactivity contribution of H₂O₂, as it is a component of the commercially available PAA solution and a decomposition product of PAA. Despite the oxidation mechanism being similar, the weaker O-OH bond energy in PAA compared to H₂O₂ (Table S2) enhances PAA's reactivity towards organic compounds [31].

Regarding comparison with the application of chlorine for disinfection, a recent study by Cochran et al., [50] concluded that chlorine disinfection reduced the estrogenic activity of E1, E2 and EE2 in treated wastewater by 4–6 orders of magnitude under controlled laboratory conditions [51] Molé et al., [51], achieved a reduction of over 99 % in the concentration of E2 during a bench-scale study that tested the chlorine disinfection conditions of a real wastewater treatment plant (WWTP). In contrast, a UV-disinfection simulation system in the same study resulted in only a 12 % reduction in E2 concentration, demonstrating significantly lower efficiency [51]. However, in the study developed by Cochran et al., [50], the chlorination process drastically increased cytotoxicity due to the formation of DBPs [50]. This finding supports the need to substitute chlorinated disinfectants with alternatives, such as PAA that is known to produce fewer harmful by-products, though further studies on this subject must be addressed [24,29,52,53].

3.2. Effect of wastewater characteristics and operation conditions on the removal efficiency

The best performance of PAA in removing the target steroid hormones is represented in Fig. 4. However, EPs removal from wastewater is influenced by diverse characteristics of wastewater, such as TSS, temperature, pH, dissolved organic matter and turbidity [24,25,31,52,54,55]. The wastewater quality control parameters for each tested condition are presented in supplementary material,

Table 3
Median values and quartiles of E1, E2 and EE2 removal efficiency (n = 6).

Compound	Value	Tested conditions					
		C15T15	C15T10	C15T5	C10T15	C10T10	C5T10
E1	Median	87.1	70.7	41.1	33.6	58.2	41.1
	Q3	91.0	73.7	48.9	35.2	61.2	48.0
	Q1	83.0	70.6	33.2	29.2	51.0	33.6
	IQR	8.02	3.02	15.7	6.01	10.2	14.5
E2	Median	86.4	59.9	40.8	43.2	62.5	55.5
	Q3	88.00	64.2	43.4	45.6	66.2	62.9
	Q1	82.3	53.6	40.1	37.9	59.6	50.6
	IQR	5.70	10.60	3.40	7.70	6.60	12.1
EE2	Median	89.7	44.1	47.1	45.6	59.9	49.3
	Q3	91.5	55.3	48.0	45.9	62.4	53.9
	Q1	86.9	35.9	42.0	44.4	56.6	46.0
	IQR	4.53	19.3	6.08	1.51	5.86	7.90

Q1 - 1st quartile.
Q3 - 3rd quartile.
IQR - Interquartile range.

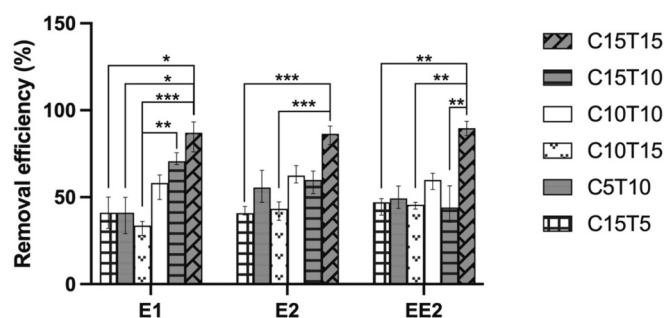


Fig. 3. Estrogens removal efficiency (%), median values and interquartile range error bar. Statistical significance identified as *** p-value <0.001; ** p-value 0.001–0.01; * p-value 0.01–0.05.

Table S4.

Additionally, the disinfection itself is a PAA consumption process due to the direct elimination of microorganisms [29,56]. Therefore, parameters that affect PAA decay may explain its inefficiency in removing the target EPs. The major results on PCA analysis and principal components (PCs) correlation with each control parameter, regarding the removal of the target EPs are presented in supplementary material, Table S5. As it is shown, 59.01 % of the total accumulated variance regarding E1, E2 and EE2 removal was explained by the three first PCs (PC1, PC2 and PC3). PCA individual results of each EPs had the same results. The most representative component was PC1, which contributed with 23.75 % of the variance, and revealed high positive correlation (>0.7) with temperature and a week/medium negative correlation (> -0.7) with HRT, PAA concentration and COD. The Fig. 5 shows graphically the correlation between the control parameters and the two more relevant PCs, where the parameter temperature was more relevant to PC1 and pH to PC2. The correlation matrix between all tested parameters and the removal of each target EPs, E1, E2 and EE2, for each tested

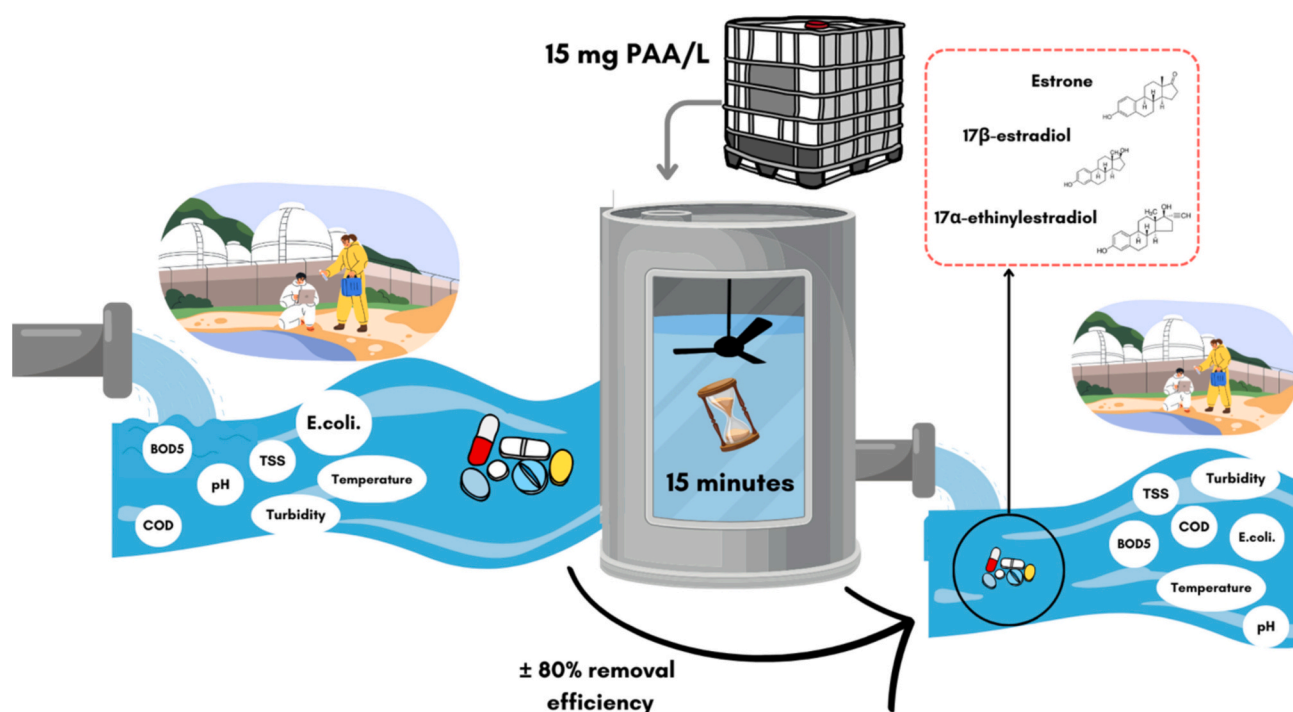


Fig. 4. Operational condition with higher steroid hormone removal efficiency.

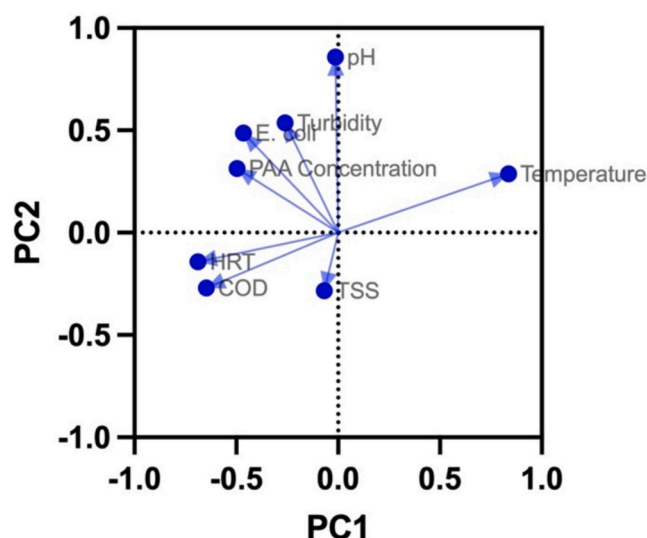


Fig. 5. PC1 and PC2 correlation with control parameters regarding E1, E2 and EE2 removal.

condition, is presented in the supplementary material, Table S6, where the r values and the corresponding p -values are detailed.

During the present study, the wastewater temperature varied considerably between conditions (Fig. S1). Within condition C15T15, the temperature varied between 19 °C and 22 °C, while in condition C15T10 temperature varied between 20 °C and 24 °C. In all the remaining conditions, the wastewater temperature consistently remained above 25 °C. The thermal decomposition of PAA follows a first-order reaction, where the decay rate increases with rising temperature [24,57]. Amerian et al., [55], who studied the dependence of PAA decay on temperature in secondary wastewater effluent, found that raising the temperature from 10 °C to 30 °C led to higher PAA decay rates. Pederson et al., [58] observed similar behaviour in PAA decay with increasing temperature. Additionally, the large activation energy required for PAA decay in secondary wastewater effluent samples indicates its sensitivity to temperature fluctuations compared to primary wastewater effluent [55]. Regarding the removal of E1, E2 and EE2, in condition C15T15, temperature showed a moderate negative correlation with both E2 and EE2 (−0.6). Additionally, conditions C10T15, C5T10 and C15T5 showed strong negative correlations with E1 (−0.77, −0.83 and −0.74 respectively), and condition C5T10 showed moderate negative correlations with E2 and EE2 (−0.6). However, all these correlations were not statistically significant (p -values >0.05). A positive correlation between the target EPs and temperature was identified in condition C15T10 for both E2 and EE2 (0.79), but it was not statistically significant. In condition C10T10 a significant ($p = 0.022$) positive correlation was found for E1 (0.92). Also, temperature was the parameter with stronger correlation with PC1 regarding the removal of all target compounds, with a 0.8 correlation factor, enhancing its strong influence in the process. Therefore, although temperature affects PAA decay and may have influenced some conditions regarding EPs removal, condition C10T10, which was influenced by increasing wastewater temperature, seems to have a measurable positive effect on E1 removal, although the median removal efficiency was 58.2 %. Nonetheless, to overcome temperature fluctuations and reduce the variability in PAA efficiency, PAA dosage should be adjusted to maintain the expected performance [55].

According to previous literature, the organic matter content is a relevant parameter for the contribution to PAA decay [24,29], which is commonly evaluated through COD indicator in wastewater effluents [52]. Increasing concentration of organic content has a direct correlation with PAA decay. In this study, the average COD effluent was 31.4 mg/L (Fig. S2), and there was no significant fluctuation of COD during the assay. According to Ragazzo et al., [59], supported by Koivunen and

Heinonen-Tanski [60], COD values between 27 and 89 mg/L in secondary wastewater effluents do not interfere with PAA efficiency. The correlation matrix presented in Table S4, shows that only in condition C15T10, COD exhibited a moderate to strong negative correlation with E1, E2 and EE2, with the r values of −0.65, −0.72 and −0.78, respectively. However, these correlations were not statistically significant. Furthermore, the PCA analysis indicates a weak/medium negative correlation (−0.66) between COD and PC1, in relation to the removal of E1, E2 and EE2. Regarding the *E. coli* content in the secondary effluent wastewater (before the pilot installation), conditions C10T15 and C10T10 presented values consistently above the average, 2.6×10^4 MPN/100 mL (Fig. S3). The correlation matrix of condition C10T10 showed a strong negative correlation with E1 (−0.71) though not statistically significant. On the other hand, despite the *E. coli* content being above average, it showed a moderate positive correlation with E1 (0.66, significance >0.05) and a significant strong positive correlation with E2 (0.94; $p = 0.017$). Condition C15T15 had the highest *E. coli* content of 7.3×10^4 MPN/100 mL and also the highest removal efficiency of the target EPs. According to the correlation matrix, E2 and EE2 presented a strong negative correlation with *E. coli* content (−0.81 and −0.77, respectively) despite the positive results on removal efficiency. Condition C5T10 was influenced by the lowest *E. coli* content throughout the study, below 1.0×10^4 MPN/100 mL, and the correlation matrix showed a medium to strong positive correlation with all studied EPs, but these were not statistically significant ($p > 0.05$). Finally, in condition C15T5, a slight increase in *E. coli* is observed in the secondary effluent (Fig. S3), with strong positive correlations with E1 removal and strong negative correlations with E2, though these were not statistically significant ($p > 0.05$). These correlations between *E. coli* and the target EPs may suggest competitive behaviour, where PAA reacts more easily with one of them.

Both TSS and turbidity are wastewater parameters commonly referred to as liable to compromise PAA efficiency [54,55]. In this study, the secondary wastewater flowing into the pilot-scale installation exhibited a low concentration of TSS, averaging 5.2 mg/L (Fig. S4), and an average turbidity of 1.1 NTU (Fig. S5). In condition C10T15, the average TSS concentration was the highest among all tested condition (Table S5), at approximately 10 mg/L. According to Amerian et al., [55], 10 mg/L of TSS increases the PAA demand on about 0.034 mg/L. Such increment on PAA demand could eventually explain the difference in the target EPs removal on the previous section, when comparing C10T15 and C10T10 condition. However, other variables could lead to this result, as wastewater contains other EPs that may have higher reactivity with PAA, such as compounds with sulphur moieties group, namely antibiotics as amoxicillin and sulfamethoxazole [31], commonly detected in wastewater [61]. Even though, according to the findings of Domínguez Henao et al., [54], TSS concentrations of 5 mg/L and 40 mg/L did not affect initial PAA concentrations. However, TSS concentrations exceeding 40 mg/L exhibited an increasing impact on PAA decay. Similar results were described by Amerian et al., [55]. Therefore, it was not expected that the TSS concentration in this study would have an effect on PAA decay and consequently on the removal of the target EPs. However, condition C15T10 showed a significant ($p < 0.05$) strong negative correlation with E2 and EE2, −0.89 and −0.94, respectively. Also, condition C15T5 showed a significant ($p < 0.05$) strong negative correlation between TSS and E1, −0.99. This suggests that a deeper understanding of the effects of TSS should be addressed in the future studies, by testing the removal efficiency under different TSS concentrations.

Regarding turbidity, from a disinfection perspective, Zhang et al. [62] findings pointed out that turbidity varying from 1 to 10 NTU did not affect disinfection performance, thus the PAA performance was not affected. Drawing on the results of the current study, it was likewise anticipated that this parameter would not adversely affect the removal of individual EPs, as indicated in the correlation matrix by the absence of significant correlations.

Concerning the effect of pH on PAA performance and consequently,

on the removal efficiency of these compounds, high rates of the decomposition of PAA are observed above the pKa (8.2), where the equilibrium is reached in its dissociated form CH_3CO_3^- [52] and PAA reacts both through spontaneous decomposition and hydrolysis producing acetic acid and H_2O_2 [24,63]. During the present study, secondary effluent wastewater (before the pilot installation) pH varied between 6.3 and 7.4, with an average value of 6.8 (Fig. S6), which are usual values for wastewater and below the pKa of PAA, where only spontaneous decomposition is expected [35]. Therefore, it was not expected that the PAA performance would be affected by pH in this range of values, and consequently, EPs removal would also not be affected, as corroborated by Domínguez Henao et al., [52] and supported by Yuan et al., [64] and Pedersen et al., [58]. Additionally, PCA analysis indicates a weak correlation between PC1 and pH on the removal of both E1, E2 and EE2. However, a strong positive correlation between pH and PC2 was observed (0.88). Moreover, the correlation matrices for each condition do not show significant correlations between pH and the removal of E1, E2 and EE2, though strong positive correlations were identified (Table S6).

Other parameters such as inorganic nitrogen species (ammonia, nitrate and nitrite), reduced iron and orthophosphate, as well as organic substances such as glucose, cellulose, butyric acid, oleic acid, casein, and peptone, have minimal impact on the effectiveness according to Domínguez-Henao et al. [52]. Regarding the effect of salinity, Liu et al., [65], reported PAA decay in an aquaculture system attributing it to salinity. However, the concentrations tested within the study of Liu et al., [65], was of 10 and 30 g/L (1 and 3 % NaCl), such concentration would compromise the biological wastewater treatment within the WWTP [66]. As no saline intrusion phenomena were reported, the effect of salinity was neglected within this study.

3.3. PAA future prospects

As mentioned in previous sections, PAA has been gaining global attention due to its oxidative and reactive potential, especially concerning its disinfection performance [24,67]. It is estimated that the global PAA market will grow from USD 1.0 million in 2023, to USD 1.4 million by 2028 at a compound annual growth rate (CAGR) of 7.4 % [68]. Additionally, previous literature already reports the growing competitive cost of PAA, most likely due to its expansion into different applications, especially in the water sector [24,36,67]. Besides the promising application of PAA for EPs removal shown in the present work, PAA-based AOPs have been suggested as an effective emerging technology for water decontamination and disinfection [24]. These technologies enhance PAA's capacity to produce hydroxyl radicals by activating its molecules. Due to its low energy O—O bond, as previously discussed, is easily broken and therefore activated [24,67]. This activation process increases PAA's production of hydroxyl radicals, making it a stronger oxidant [67]. Within PAA-based AOPs, UV radiation serves as the activation process, leading to the homolytic cleavage of the O—O bond in PAA, generating acetoxyl and hydroxyl radicals. This process, coupled with PAA (UV/PAA), has been widely described as highly efficient for disinfection purposes [69] and also for EPs removal [67,70–72]. Hu et al., [72] tested a UV/PAA process to remove steroid hormones such as E1, E2 and EE2, achieving approximately 90 % removal efficiency with an initial EPs concentration of 50 $\mu\text{g/L}$ each, HRT of 30 min, and PAA dosage of 30 mg/L. Additionally, the estrogenic activity was reduced by 94 %. Overall, efficiencies are under close conditions to the ones reported here. One of the most attractive aspects of UV/PAA is its compatibility with existing WWTPs that already utilize UV disinfection [24]. However, the energy cost associated with UV treatment, due to its dependence on wastewater quality and the operational constraints of lamp fragility [73], has led to the need for the development of new effective and eco-friendly activation methods for PAA [67]. Current results show the potential of directly using PAA, without the need for UV activation. However, other advanced

wastewater treatment technologies are consolidated in the market, such as ozonation or membranes with higher EPs removal rates, although they encompass higher operational and implementation cost [18]. PAA must consolidate as an eco-friendly alternative to these costly solutions.

4. Conclusions

The findings of this study highlight the efficacy of PAA in removing steroid hormones within a real wastewater treatment system, affirming its potential as a cost-effective treatment option worth further exploration for wastewater reuse, aligned with the foreseen objectives of the European Parliament and Council proposal for the urban wastewater treatment directive. The condition with a concentration of 15 mg/L PAA and HRT of 15 min (C15T15) attained the highest removal efficiency for the three target compounds, above 85 %. The remaining conditions also demonstrated removal efficiency, though with lower percentages. Moreover, the achieved removal in each condition is expected to eliminate the estrogenic activity posed by these compounds, as they reach the ng/L range. The correlation analyses between removal efficiency and control parameters showed that increasing wastewater temperature and *E. coli* content might have influenced the removal efficiency of the target EPs. Due to this wastewater variability, further research in real wastewater treatment plants should test higher PAA dosages to mitigate its decay. Also, since coupling PAA with other treatment technologies, such as UV, has proven to increase removal efficiency, this could serve as an alternative approach to consolidate technologies such as ozonation or membranes, mitigating the impact of wastewater variability while maintaining the same PAA operational conditions.

Despite fluctuations in quality parameters inherent to real wastewater, the treatment system effectively removed E1, E2 and EE2. Therefore, for long-term considerations, scaling up implementation to a full-scale system and investigating PAA's dual role in eliminating EPs and disinfecting pathogens with the study of different operational conditions are recommended topics for further research on wastewater reuse. The integration of PAA into wastewater treatment practices promises not only to enhance the removal efficiency of hazardous compounds but also to contribute to broader environmental protection and public health goals. This study provides a foundation for future advancements in sustainable wastewater treatment technologies, advocating for the continued exploration and implementation of PAA in real-world applications.

CRedit authorship contribution statement

Rita Dias: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Diogo Sousa:** Investigation. **Pedro N. Carvalho:** Writing – review & editing, Supervision, Resources. **Vaidotas Kisielius:** Writing – review & editing, Investigation. **Mário Diniz:** Writing – review & editing. **Rita Maurício:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was funded by Fundação para a Ciência e a Tecnologia (FCT, Portugal), through the strategic projects UIDB/04292/2020 (<https://doi.org/10.54499/UIDB/04292/2020>) and UIDP/04292/2020 (<https://doi.org/10.54499/UIDP/04292/2020>) granted to MARE - Marine and Environmental Sciences Centre, and the project LA/P/0069/2020 (<https://doi.org/10.54499/LA/P/0069/2020>) granted to the Associate Laboratory ARNET - Aquatic Research Network and through a

PhD grant by FCT for Rita Dias (SFRH/BD/148793/2019). The projects UIDP/04378/2020 and UIDB/04378/2020 of the Research Unit on Applied Molecular Biosciences - UCIBIO and the project LA/P/0140/2020 of the Associate Laboratory Institute for Health and Bioeconomy - i4HB are also acknowledged. Steroid hormone analysis was supported by project MULTISOURCE (<https://doi.org/10.3030/101003527>), which received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101003527.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2024.106453>.

Data availability

Data will be made available on request.

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