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PERFORMANCE OF ADVANCED OXIDATION PROCESSES IN ESTROGEN REMOVAL: A SYSTEMATIC REVIEW

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Abstract

The presence of estrogens such as estrone (E1), 17β-estradiol (E2), estriol (E3) and 17α-ethinylestradiol (EE2) in the aquatic environments, even in low concentrations, is an ambient concern that needs an appropriate degradation process in wastewater treatment plants. In this study, a systematic review was carried out to identify the most suitable advanced oxidation processes to remove E1, E2, E3 and EE2 from aqueous effluents. A performance parameter (γ) relating electrical consumption, treated volume and, both initial and final estrogen concentrations was proposed. The initial concentration of estrogen, the kind of water (residual or synthetic) and the pH of the system were the more relevant variables to remove those estrogens. Ozonation was the best treatment for estrogen removal due to the lower γ values as 2.95 10^2, 6.91 10^3 and 2.38 10^3 kWh g^{-1} for E1, E2 and EE2, respectively in wastewater and 9.40 10^{-2} kWh g^{-1} (E1) and 8.50 10^{-2} kWh g^{-1} (EE2) in synthetic water, all of them with removal higher than 99%. The operational cost estimated of ozonation was USD$ 23.1/1000 m^3 for E1 and E2 treatment in wastewater.

Keywords: Advanced oxidation process; wastewater treatment; estrogens, ozonation; systematic review.

Nomenclature

CECc	Contaminants of emerging concern	$KMnO_4$	Potassium permanganate
WWTP	Wastewater treatment plants	HPLC	High performance liquid chromatography
AOP	Advanced oxidation process	MS/MS	Mass spectrometry
E1	Estrone	GC-MS	Gas Chromatography/Mass Spectrometry
E2	17β-estradiol	H_2O_2	Hydrogen peroxide
E3	Estriol	O_3	Ozone/Ozonation
EE2	17-α-ethinylestradiol	UV	Photolysis
γ	Performance parameter	Fe	Iron
EED	Electrical consumption of the AOP in kWh	TiO_2	Titanium dioxide
V	Volume treated in liters	TAML	Full-functional peroxidase enzyme replicas
C_{Ao}	Initial estrogen concentration	Zn	Zinc
C_A	Estrogen concentration	CNT	Carbon nanotube
σ	Initial estrogen concentration in g L-1.	BDD	Boron-doped diamond anode
$HO^{\cdot}$	Hydroxyl radicals	E	Pump electrical consumption in kWh
g L^{-1}	Gram litre $^{-1}$	ΔP	System differential pressure in psi
mg L^{-1}	Miligram litre $^{-1}$	Q	Volumetric flow in gpm
µg L^{-1}	Microgram litre $^{-1}$	t	Treatment time in hours of operation/year
ng L^{-1}	Nanogram litre $^{-1}$	η	Pump efficiency
gpm	Gallons per minute	psi	Pound per square inch
kWh	Kilowatt hour		

Introduction

For decades, there have been environmental problems in water bodies due to pollution generated by effluents from human and industrial activity. Traces of pharmaceuticals, pesticides and other substances have been found in wastewater, rivers and other surface water sources, causing damage not only to the environment but also to the health of humans, fauna and flora (Martinez de Yuso Ariza 2012).

Substances that are found in the environment and whose discharge limits are not regulated, but which have the potential to adversely affect health or the environment, even at very low concentrations (on the order of ng L^{-1}), have been termed *contaminants of emerging concern* (*CECs*). *CECs* have been found mainly in bodies of water and have been spread in the environment through discharges of domestic and industrial wastewater, wastewater treatment plants (WWTP), hospital effluents, agricultural activities, among others. Although *CECs* are found in very low concentrations in the environment (of the order of ppt), their increasing production represents an unquestionable threat (Patiño et al. 2014). Currently, it has been found that the most common *CECs* are pesticides, drugs for human and animal use (analgesics, antibiotics, etc.), licit drugs, personal care products (perfumes, sunscreens, etc.), surfactants, steroid hormones, among others (Janet Gil et al. 2012).

Steroid hormones are present in bodies of water because the human body produces them naturally through the female and male reproductive organs (estrogens, progesterone, testosterone, etc.), but they are also present in synthetic hormones as a constituent part of birth control pills. It is important to highlight those estrogens and androgens are introduced into the environment mainly through WWTP effluents, where they are not fully eliminated and, if a person consumes them, they can act as endocrine disruptors (chemical substances outside the body capable of altering the hormonal balance). Estrogens constitute a group of abundant steroid compounds because they are constantly excreted by women. Therefore, studies are being conducted to achieve their degradation/removal, especially for natural estrogens such as estrone (E1), 17β-estradiol (E2) and estriol (E3), and for the synthetic estrogen 17-α-ethinylestradiol (EE2) (Janet Gil et al. 2012).

There is high interest in testing degradation or mineralization techniques on effluents containing steroid hormones, including biological or physicochemical processes. For the degradation of *CECs*, advanced oxidation processes (*AOPs*) have been tested mainly because they achieve higher reaction rates compared to biological treatments, obtaining higher removal percentages. In addition, *AOPs* can remove persistent substances in water after biological treatments have been applied. *AOPs* take advantage of the capacity to generate hydroxyl radicals ($HO^{\bullet}$), strong oxidizing agents used for the complete degradation or mineralization of different organic compounds (producing CO_2 or organic acids) that act non-selectively and have high reaction rates (Valenzuela Larrea 2019). In the particular case of steroid hormones, *AOPs* such as ozonation mediated with H_2O_2 or UV radiation, ultrasound, photo-Fenton, electrochemical oxidation, among others, have been reported for the treatment of water contaminated with E1, E2, E3 and EE2 (Silva et al. 2012; Miklos et al. 2018).

The growing number of studies using *AOPs* for the degradation of steroid hormones present in effluents and the large number of *AOP´s* combinations tested propose an enormous challenge to identify the best treatment alternative, especially if it is necessary to analyze indicators related to the performance obtained, electricity consumption, chemical inputs required, operating conditions and operating costs (Miklos et al. 2018). In this sense, the use of performance indicators is very useful to establish the feasibility of applying *AOPs* on a real scale.

In the present study, a systematic review was carried out to identify the most recommended *AOPs* to degrade/remove steroid hormones E1, E2, E3 and EE2 from aqueous effluents. For this purpose, a performance parameter was proposed that relates the electrical consumption, the volume treated and both the initial and final estrogen concentrations. By using this performance parameter, the most relevant *AOPs* were compared and the operating conditions with the highest incidence in the degradation of the mentioned estrogens were determined.

Materials and methods

Database

Scopus database was used because it is one of the main tools for compiling peer-reviewed scientific reports, with access to more than 25,000 specialized journals and a little more than 77 million records (including articles, conference papers, reviews, books, etc.). In addition, the data from *Scopus* were exported to *Microsoft Excel®* and then, they were analyzed with the *VOSviewer* software.

Search strategy

Search equations were established to find papers related to research on the removal of *CECs* (E1, E2, E3 and EE2) using *AOPs*. For this purpose, a logbook was prepared in which all the search equations reviewed were reported with the respective number of documents retrieved. Two search scenarios were evaluated, both aimed at collecting articles concerning estrogen treatment in wastewater. To connect and associate keywords in the same study, the Boolean operators "*AND*" and "*OR*" were used. Additionally, quotation marks were used to improve search precision and the asterisk was used to search for all forms of a keyword. The first study was restricted to the search for documents (articles, conference papers, reviews and books) published from 2010 to 2020, while the second study was limited only to articles published during the same period. It should be noted that there were no restrictions in terms of the language of the documents collected.

The keywords "*estrogens*", "*wastewater*" and "*advanced oxidation processes*" were used, and after making several combinations the final search equations for each study were determined. This process is shown in Tables 1 and 2. The search equations used in this study are shown below:

First study:

(TITLE-ABS-KEY ((domestic AND water) AND estrogen) OR
TITLE-ABS-KEY ((urban AND water) AND estrogen) OR
TITLE-ABS-KEY (municipal AND water) AND estrogen) AND
TITLE-ABS-KEY ("advanced oxidation process") OR
TITLE-ABS-KEY ("advanced treatment") OR
TITLE-ABS-KEY (remo*)) AND
PUBYEAR > 2009

Second study:

(TITLE-ABS-KEY (("wastewater treatment" AND estr*) OR (sewage AND estr*)) AND
TITLE-ABS-KEY ("advanced oxidation process" OR "advanced treatment")) AND
DOCTYPE (ar) AND
PUBYEAR > 2009

VOSviewer1.6.15 software was used to identify connections between topics related to the treatment of estrogens in wastewater. Additionally, the duplicity of singular and plural keywords found in the bibliometric networks were eliminated by combining the corresponding nodes.

Bibliometric review

The evolution of scientific publications was analyzed, as well as the distribution of publications by areas of knowledge and keywords. Both the evolution of publications and their distribution by topic were identified using the *Scopus* database tools, while keyword analysis was performed in the *VOSviewer* software.

Compilation of relevant articles

The quartile of the journal, the specific pollutant studied and the oxidation technique were used as inclusion criteria for a first selection and classification of the information. Only articles issued in journals ranked in the Q1 and Q2 quartile that were focused on steroid estrogen treatment (E1, E2, E3 and EE2) using *AOPs* were included. Articles that did not meet these criteria were discarded.

Subsequently, a more rigorous analysis of the relevance of each study was made, where the articles were classified considering the initial concentration of the contaminant, the quantification techniques used, and the type of water treated (real or synthetic). Figure 1 shows the flowchart of the process developed to carry out the systematic review.

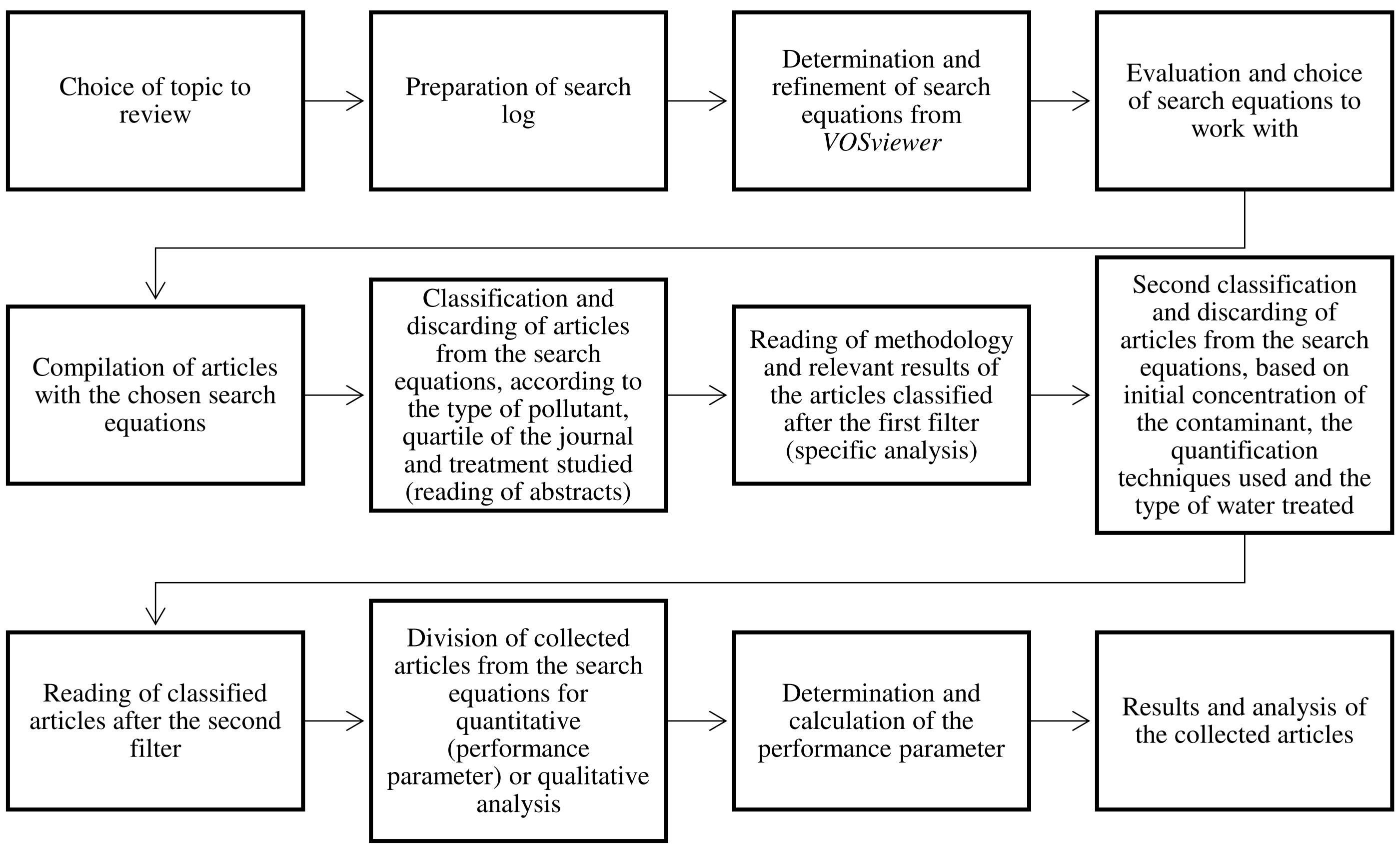

Fig. 1 Flowchart for the elaboration of a systematic review.

Performance parameter (γ)

For comparison between the different studies, the performance parameter γ was defined, which relates the yield or removal of *CECs*, the electrical consumption of the treatment, the initial concentration of estrogen and the volume treated (Equation 1) (Sarkar et al. 2014). The γ parameter was used to quantitatively compare the performance of the *AOPs* techniques applied in the different studies and to establish the most appropriate technique for treatment. However, several articles do not include the data necessary to calculate γ. Thus, those studies were compared using a qualitative analysis.

$$\gamma = \frac{EED}{V \cdot \sigma \cdot log\left(\frac{C_{Ao}}{C_A}\right)} \quad (1)$$

where EED is the electrical consumption of the AOP in kWh, V is the volume treated in liters, $log\frac{C_{Ao}}{C_A}$ is the normalized pollutant removal, and σ is the initial estrogen concentration in g L^{-1}. It should be noted that, in the studies analyzed, mass removal was determined from Equation 2.

$$\%remotion\ EC = \frac{C_{A0}-C_A}{C_{A0}} \times 100 \qquad (2)$$

where C_{A0} and C_A are the initial and final concentrations in µg L^{-1} of contaminant, respectively.

Results and discussion

Search equation refinement

For the first study, 943 documents were initially collected, which were reduced to 659 by restricting the results to publications made between 2010 and 2020. By changing the Boolean operator "OR" to "AND" the search was reduced to 22 retrieved documents; this ensured that the search equation included terms related to estrogens in wastewater and advanced oxidation treatments (see Table 1). However, to increase the results obtained, the term "OR Remo*" was included. This allowed the collection of 152 documents that included and related the last-mentioned term to estrogens in wastewater (see Table 1).

Table 1. Documents collected with preliminary search equations from study 1.

Step	Keywords used	Number of documents retrieved
1	(Domestic water treatment AND estrogen) OR (Urban water treatment AND estrogen) OR (Municipal water treatment AND estrogen) OR (Domestic water treatment AND Advanced oxidation process) OR (Urban water treatment AND Advanced oxidation process) OR (Municipal water treatment AND Advanced oxidation process)	943
2	Limit to documents from 2010 to 2020	659
3	(Domestic water treatment AND estrogen) OR (Urban water treatment AND estrogen) OR (Municipal water treatment AND estrogen) AND (Advanced oxidation process) OR (Advanced treatment) Limit to documents from 2010 to 2020	22
4	(Domestic water treatment AND estrogen) OR (Urban water treatment AND estrogen) OR (Municipal water treatment AND estrogen) AND (Advanced oxidation process) OR (Advanced treatment) OR (Remo*) Limit to documents from 2010 to 2020	152

Checking the bibliometric network of the initial search equation in *VOSviewer*, it was determined that the keywords "*sewage*", "*wastewater*" and "*estrogen*" were interconnected. Therefore, a new search involving this combination was chosen. Thus, 1762 documents were initially collected (between the years 2010 and 2020) during the development of the search equation for the second study. By restricting the search to articles and changing the Boolean operator "*OR*" to "*AND*", the search was reduced to 15 documents. Subsequently, and thanks to the visualization and analysis of the first study by the *VOSviewer* software, the keyword "*advanced treatment*" was included, which increased the collection to 42 articles. Additionally, the keyword "*estrogen*" was substituted for the truncated term "*estr** in the search equation to obtain results that related all its possible forms to the other phrases in the search equation. This increased the collection to 74 articles (Table 2).

Table 2. Documents collected with preliminary search equations from Study 2.

Step	Keywords used	Number of documents retrieved
1	("Wastewater treatment" AND estrogen) OR (sewage AND estrogen) OR ("wastewater treatment" AND "advanced oxidation process") OR (sewage AND "advanced oxidation process") AND (remo*) AND Limit to documents from 2010 to 2020	1762
2	("Wastewater treatment" AND estrogen) OR (sewage AND estrogen) AND ("Advanced oxidation process") AND (remo*) AND Limit to documents from 2010 to 2020 AND Limit to journal research articles	15
3	("Wastewater treatment" AND estrogen) OR (sewage AND estrogen) AND ("Advanced oxidation process" OR "advanced treatment") AND (remo*) AND Limit to documents from 2010 to 2020 AND Limit to journal research articles	42
4	("Wastewater treatment" AND estr*) OR (sewage AND estr*) AND ("Advanced oxidation process" OR "advanced treatment") AND (remo*) AND Limit to documents from 2010 to 2020 AND Limit to journal research articles	74

Bibliometric network of estrogen degradation by *AOPs*

A total of 226 papers were found in the *Scopus* database published between 2010 and 2020 from the above search equations (first and second study). Figure 2 shows the connections between the authors' keywords of the publications related to *AOPs* for the degradation of estrogens present in wastewater during the analysis period. Here, 4 clusters were observed and easily identified by colors.

The most representative nodes of the network (with at least five occurrences) corresponded to the keywords: "*advanced oxidation process*", "*estrogens*", "*endocrine disrupting chemicals*" and "*wastewater*". The above confirms that research related to estrogen treatment in wastewater in the last decade is being focused on *AOPs*. Additionally, the ozonation node is the only *AOP* found in the bibliometric network, demonstrating that it is the most studied treatment in water treatment plants.

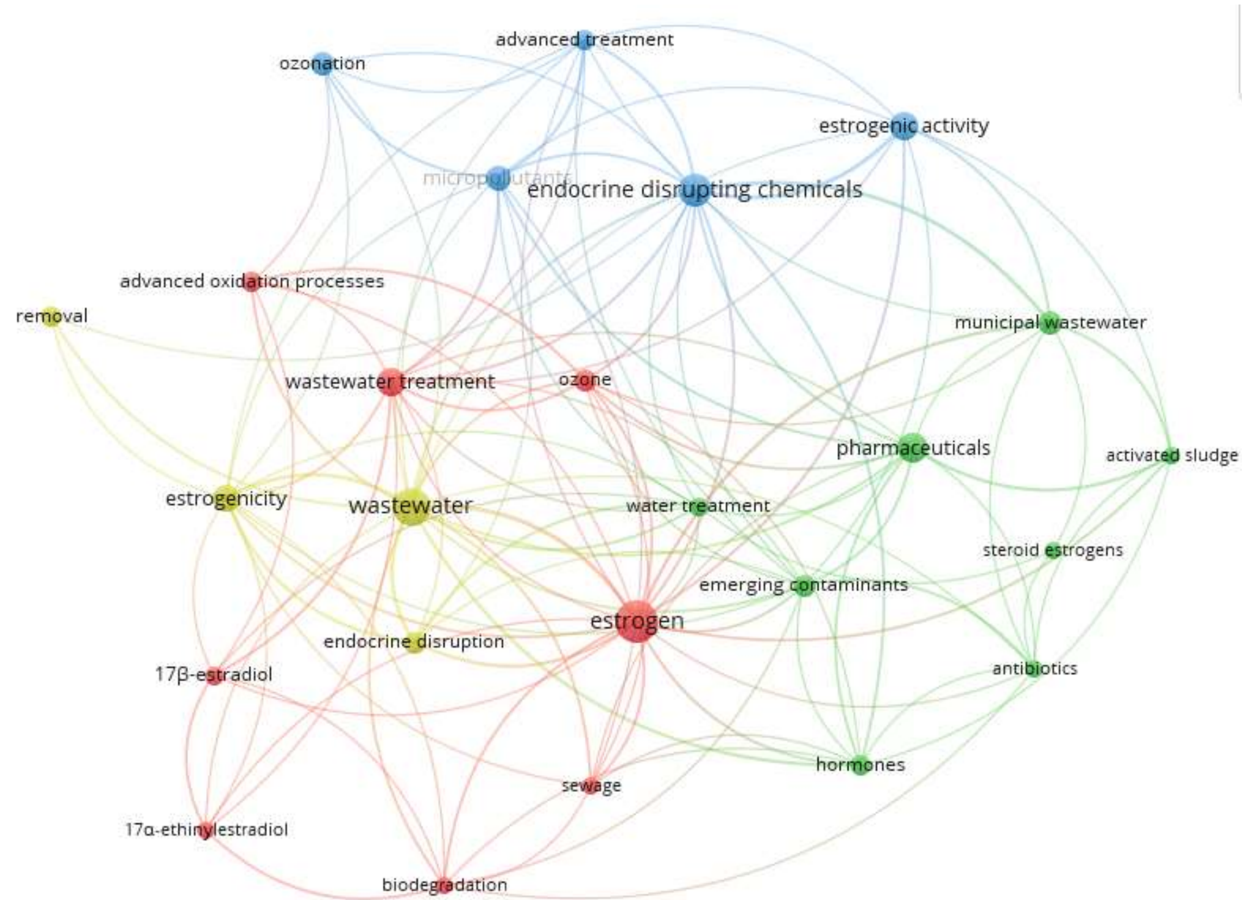

Fig. 2 Bibliometric network of studies related to estrogen degradation by *AOPs*. Note: minimum number of occurrences of 5.

Bibliometric indicators of estrogen degradation by *AOPs*

In the last 10 years, there has been an increase in the publication of research articles related to wastewater treatment with *AOPs* for the removal of *CECs* (Fig. 3); this indicates that there is a high interest in the scientific community to search for an alternative to remove them from water bodies. It is important to highlight that the use of *AOPs* has increased due to the low average removal rates of *CECs*, between 10 and 50% over long periods (> 5 days), obtained commonly by using biological treatments.

Analyzing the distribution of scientific publications in the last 10 years (by using *Scopus* tools), it was determined that the field with the highest academic productivity (in terms of published articles) was environmental sciences, followed by chemistry and chemical engineering. The results showed that research has focused on these fields and on an *AOP* that achieves the best performance in the removal of *CECs* in aqueous effluents.

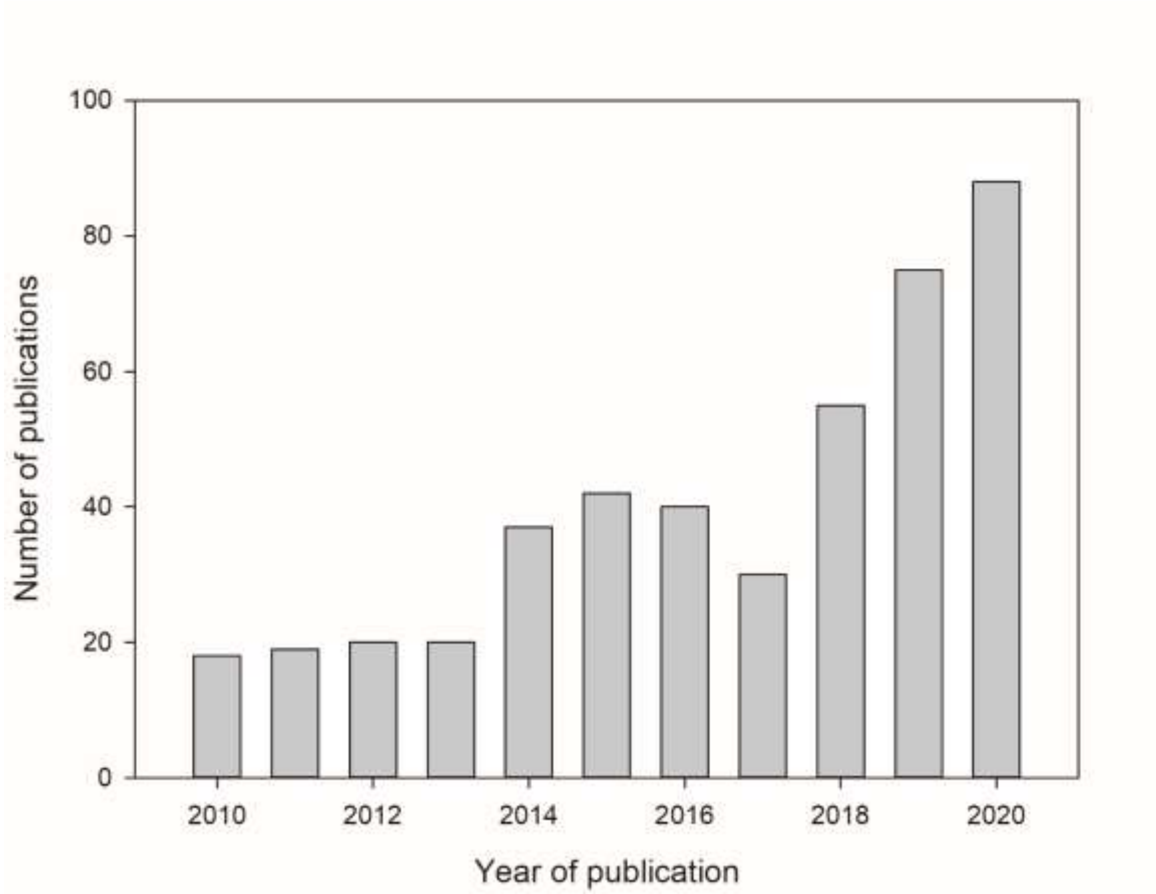

Fig. 3 Evolution of studies related to water treatments with *AOPs* between 2010 and 2020. Source: *Scopus*.

Compilation of relevant articles of estrogen degradation by AOPs

Tables 3 and 4 show the most cited articles with the two refined search equations.

Table 3: Most cited documents for the first study.

Author	Title	Year	Journal	Citations/year	No. total of citations
Moreira, N et al.	Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO_2 with LEDs: Micropollutants, antibiotic resistance genes and estrogenic activity	2016	Water Research (Q1)	24.0	96
Zhang, W et al.	Effect of water composition on TiO_2 photocatalytic removal of endocrine disrupting compounds (EDCs) and estrogenic activity from secondary effluent	2012	Journal of Hazardous Materials (Q1)	7.6	61
Roudbari, A et al.	Hormones removal from municipal wastewater using ultrasound	2018	AMB Express (Q2)	4.5	9
Zhang, W et al.	Performance evaluation and application of surface-molecular-imprinted polymer-modified TiO_2 nanotubes for the removal of estrogenic chemicals from secondary effluents	2013	Environmental Science and Pollution Research (Q1)	3.9	27

Table 4: Most cited documents for the second study.

Author	Title	Year	Journal	Citations/ year	No. total of citations
Margot, J et al.	Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	2013	Science of the total environmental (Q1)	54.6	382
Schaar, H et al.	Micropollutant removal during biological wastewater treatment and a subsequent ozonation step	2010	Environmental Pollution (Q1)	7.5	75
Ouarda, Y et al.	Synthetic hospital wastewater treatment by coupling submerged membrane bioreactor and electrochemical advanced oxidation process: Kinetic study and toxicity assessment	2018	Chemosphere (Q1)	7.5	15
Sarkar, S et al.	Degradation of estrone in water and wastewater by various advanced oxidation processes	2014	Journal of Hazardous Materials (Q1)	6.7	40
Almomani, F et al.	Potential use of solar photocatalytic oxidation in removing emerging pharmaceuticals from wastewater: A pilot plant study	2018	Solar Energy (Q1)	5.5	11

Article analysis of estrogen degradation by *AOPs*

AOPs have been commonly employed in the removal of pollutants in wastewater as they have different ways to carry out the destruction of organic molecules and obtain high performance in the process. Generally, *AOPs* are techniques that work individually and are highly efficient in estrogen removal (greater than 90%) (Pešoutová et al. 2014; Moreira et al. 2016; Zhu et al. 2020).

All *AOPs* are carried out in two phases, the *in situ* formation of reactive oxidant species and the reaction of oxidants with the target pollutants (Miklos et al. 2018). Therefore, many factors can affect the removal performance of contaminants, in this case estrogens, depending on each treatment and even the type of water to be treated.

A list of articles related to the chosen search equations was found. However, with the implementation of certain criteria such as type of pollutant, type of treated water and quartile of the journal, this list was further reduced and refined. The present study focused only on the removal of E1, E2, E3 and EE2 present in wastewater or synthetic water. Therefore, articles involving different contaminants, whether antibiotics, any other *CECs*, or even other known estrogens, were discarded.

Articles that did not use *AOPs* and that were not conducted in wastewater or synthetic water were also discarded. The articles that passed all filters (23 of 226 studies) were subjected to an exhaustive reading to obtain the necessary information for the calculation of the performance parameter. Nevertheless, several of them did not have sufficient information to determine the performance parameter. Therefore, for those documents, it was decided to carry out a qualitative analysis, in which the main advantages and disadvantages of the mentioned *AOPs* were highlighted.

Qualitative analysis

It was determined that the most influential parameters in the performance of the treatment were: the initial concentration of estrogen, the characteristics of each *AOP* (O_3 concentration in the supplied gas, catalyst concentration, oxidizing agent dose, and ultrasound frequency) and, additionally, the type of water (wastewater or synthetic) and its pH. These criteria were chosen based on the frequency with which they were studied in all articles analyzed.

Influence of initial estrogen concentration

In wastewater, estrogens are generally found in concentrations of the order of ng L^{-1}. However, depending on the quantification limits of analytical techniques, several studies have opted to add a mixture (spike) of estrogenic hormones to the effluent to increase the estrogen concentration to the order of µg L^{-1} (Frontistis et al. 2011; Ma et al. 2014; Pešoutová et al. 2014; Cunha et al. 2019). This turns out to be a useful alternative for the development of *AOPs* in wastewater samples, because it allows the detection of contaminants before and after treatment, even at low concentrations, to evaluate the removal percentages. Ma et al. (2014) investigated the influence of initial concentration on E2 degradation with ultrasound and ultrasound mediated by $KMnO_4$ to promote the reaction in the ultrasonic process. The authors found that increasing the initial E2 concentration (71-333 µg L^{-1}) increased the probability of $HO^{\bullet}$ attack on the contaminant and, consequently, the reaction rate.

Deng et al. (2015) studied the degradation of E1, E2 and EE2 using ultrasound and ultrasound/$KMnO_4$, and showed that the removal of contaminants decreased by about 10% when the initial estrogen concentration was increased from 100 to 500 µg L^{-1}. The authors attributed this behavior to the fact that at low contaminant concentrations there is preferential contact of $HO^{\bullet}$ radicals with estrogens in the water. Thus, the initial concentration of estrogen cannot be taken as the only parameter that affects the degradation process. Consequently, additional criteria must be considered such as the influence of the type of water to be treated and its pH, as well as the characteristics of the degradation technique used. These characteristics may vary from one study to another, even when working in the same initial concentration range. However, sometimes it is necessary to concentrate the solutions to be analyzed, to be detected in the quantification method selected in the research (HPLC-MS/MS and GC-MS).

Influence of water type

Contaminant removal analysis was performed in wastewater and synthetic water. The latter allows the solution to be prepared at the desired concentration, which is advantageous for the quantification and removal of estrogens. However, many studies that worked with this type of water only prepared the solution with one or two contaminants (either E1, E2, E3 or EE2). Several authors used only E1 or E2 solutions, which are natural hormones and are more prone to removal (Zhang et al. 2012; Jiang et al. 2013; Ma et al. 2014; Sarkar et al. 2014; Zhu et al. 2020).

The above is not an accurate approximation for a large-scale study as there are more organic contaminants in the wastewater that may decrease the removal of the target steroid hormones. Pešoutová et al. (2014) studied estrogen ozonation and found that the quality of the wastewater can affect the performance of the oxidation reactions since the water sometimes contains carbonates and bicarbonates that are radical scavengers. Similarly, during electrochemical treatment with carbon nanotubes in wastewater, it was shown that the presence of other organic compounds decreased the efficiency of electron transfer between the estrogens and the anode nanotube filter (Cunha et al. 2019).

Some researchers evaluated the effect of the pH on estrogen degradation in synthetic water. Ma et al. (2014) showed that for the degradation of E2 by ultrasound, the solution should be alkaline (pH=10.9), whereas it should be acidified (pH=2.5) in case of using ultrasound/$KMnO_4$. The authors determined that alkalinization accelerates the removal efficiency due to the dissociation potential of E2 and mentioned that at a pH of 10.9 (close to the pKa of E2 =10.7), E2 readily dissociates to its anionic form. Therefore, the negatively charged is more hydrophilic than the uncharged state and estrogen can be degraded more easily.

On the other hand, Mills et al. (2015) achieved >90% removal of E1, E2 and EE2 at alkaline conditions (pH=9.0) using the Fenton treatment with high concentrations of H_2O_2 (150 mg L^{-1}). PH conditions vary greatly from one technique to another. However, if research is to be carried out to real scale any AOP it is suggested to work at regulatory wastewater discharge conditions (pH between 6.0 and 9.0) to avoid the additional reagent cost.

Influence of the characteristics of each *AOP*

Factors such as O_3 concentration in ozonation, catalyst loading in catalytic processes, wavelength and frequency in ultrasound or photolysis, together with their respective combinations, are important parameters in the performance of the *AOP* used. For this reason, the choice of these criteria is key as they have a direct impact on the removal and cost of treatment.

Margot et al. (2013) and Pešoutová et al. (2014) determined that E1 is the most reactive estrogen to O_3, obtaining removals of up to 99% with initial concentrations of 1.65 10^3 and 1.34 10^2 ng L^{-1}, respectively. Similarly, they also reported >98% removals for E2, E3 and EE2. This may be because O_3 reacts rapidly with compounds containing an activated aromatic group, double bonds or amino groups in their structure, as is the case of the estrogens studied, which allows the oxidation reaction to occur more easily. The removal of compounds that do not have these characteristics depends, to a greater extent, on the operational conditions of the treatment, such as the concentration of O_3 in the supplied gas and the pH of the water to be treated (Schaar et al. 2010; Margot et al. 2013). Table 5 shows the removal reported in each article studied.

Ozonation is commonly employed in the degradation of steroid hormones and other contaminants; Sun et al. (2017) demonstrated that it is a technique that requires a high concentration of O_3 (up to 40 mg L^{-1}) in the supplied gas to obtain high removals (>95%) when the estrogen concentration is very low (between 0.24 and 4.68 ng L^{-1}). Filby et al. (2010) achieved removals between 64% and 76% for E1, E2 and EE2 with an O_3 concentration of 1.0 mg L^{-1} in the supplied gas and compared them with a previous study that obtained removals between 90% and 100% for the same pollutants, but with an O_3 concentration in the gas between 5-15 mg L^{-1}. For this reason, they attributed the low removals obtained to the low O_3 concentration they used. However, according to Margot et al. (2013b) using high concentrations of O_3 (in this case 5.7 mg L^{-1}) for estrogen removal is not advantageous because of the increased cost of treatment and the formation of toxic and carcinogenic by-products such as bromates, nitroamines and formaldehyde. The latter was determined by increasing the bromate concentration in the treated solution (up to 3.7 µg L^{-1}) after ozonation was performed. Moreover, Jiang et al. (2013) identified the presence of different by-products in E2 ozonation (2-hydroxy-estradiol, semiquinones, oxalic and malonic acid), which may have toxic effects in water, using an initial concentration of 10 µg L^{-1} of E2.

Table 5. *CECs'* percentage of removal reported by the authors.

WASTEWATER				
Author	**Title**	**Treatment**	**Initial concentration (ng/L)**	**Percentage of removal (%)**
Moreira N.-2016[1]	Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO2 with LEDs: Micropollutants, antibiotic resistance genes and estrogenic activity	O_3	63 **(E2)** 3981 **(EE2)**	99.9 **(E2)** 99.9**(EE2)**
		UV Catálisis		30 **(E2)** 8 **(EE2)**
		UV Catálisis/ O_3		99.9 **(E2)** 99.9**(EE2)**
Margot, J.-2013[1]	Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	O_3	134 **(E1)** 14**(E2)**	90 **(E1)** 61 **(E2)**
Schaar, H.-2010[1]	Micropollutant removal during biological wastewater treatment and a subsequent ozonation step	O_3	1.6 **(E1)** 7.4 **(EE2)**	99.9 **(E1)** 99.9 **(EE2)**
Almomani, F.-2018	Potential use of solar photocatalytic oxidation in removing emerging pharmaceuticals from wastewater: A pilot plant study	O_3	$1\ 10^6$ **(E1)** $1.1\ 10^6$ **(EE2)**	99.9 **(E1)** 99.9 **(EE2)**
		UV/Fe		36 **(E1)** 65 **(EE2)**
		UV/TiO_2		99.9 **(E1)** 99.9 **(EE2)**
		Foto-Fenton		84.4 **(E1)** 83.6 **(EE2)**
		Foto-Fenton/O_3		99.9 **(E1)** 99.9 **(EE2)**
Ouarda,Y 2018	Synthetic hospital wastewater treatment by coupling submerged membrane bioreactor and electrochemical advanced oxidation process: Kinetic study and toxicity assessment	Electroquímica	$1\ 10^4$ **(E2)**	99.9 **(E2)**

Table 5. (Continued)

Author	Title	Treatment	Initial concentration (ng/L)	Percentage of removal (%)
Zhu, N.-2020	Bismuth impregnated biochar for efficient estrone degradation: The synergistic effect between biochar and Bi/Bi2O3 for a high photocatalytic performance	UV/Catálisis	2.6 10^6 **(E1)**	99.5 **(E1)**
Zhang W.-2012[1]	Effect of water composition on TiO 2 photocatalytic removal of endocrine disrupting compounds (EDCs) and estrogenic activity from secondary effluent	UV/Catálisis	26.4 **(E1)** 13.8 **(E2)** 12.7 **(E3)**	99.2 **(E1)** 99.2 **(E2)** 98.7 **(E3)**
Ma, X.Y.-2019	The treatability of trace organic pollutants in WWTP effluent and associated biotoxicity reduction by advanced treatment processes for effluent quality improvement	UV	2.8 **(E1)**	>90 **(E1)**
		UV/TiO_2	3.2 **(E1)**	>90 **(E1)**
		O_3	0.8 **(E1)**	>90 **(E1)**
Bennett, J.L.-2018	Advanced oxidation processes for treatment of 17β-Estradiol and its metabolites in aquaculture wastewater	UV	1 10^4 **(E1)** 1 10^4 **(E2)** 1 10^4 **(E3)**	>90 **(E1)** >90 **(E2)** >90 **(E3)**
		UV/H_2O_2		>90 **(E1)** >90 **(E2)** >90 **(E3)**

Table 5. (Continued)

Author	Title	Treatment	Initial concentration (ng/L)	Percentage of removal (%)
Pešoutová, R.-2014	A pilot scale comparison of advanced oxidation processes for estrogenic hormone removal from municipal wastewater effluent	O_3	$1.65\ 10^{3}$**(E1)** $2.01\ 10^{3}$ **(E2)** $2.0\ 10^{3}$ **(E3)** $2.5\ 10^{3}$ **(EE2)**	99.8 **(E1)** 99.7 **(E2)** 99.9 **(E3)** 99.7 **(EE2)**
		O_3/H_2O_2	$1.79\ 10^{3}$**(E1)** $1.72\ 10^{3}$ **(E2)** $2.06\ 10^{3}$ **(E3)** $2.15\ 10^{3}$**(EE2)**	99.4 **(E1)** 98.2 **(E2)** 98.7 **(E3)** 99.6 **(EE2)**
		O_3/UV	$2.13\ 10^{3}$**(E1)** $2.64\ 10^{3}$ **(E2)** $2.10\ 10^{3}$ **(E3)** $2.97\ 10^{3}$ **(EE2)**	99.4 **(E1)** 98.2 **(E2)** 98.7 **(E3)** 99.6 **(EE2)**
		O_3/UV/H_2O_2	$1.95\ 10^{3}$ **(E1)** $2.88\ 10^{3}$ **(E2)** $2.52\ 10^{3}$ **(E3)** $3.59\ 10^{3}$ **(EE2)**	99.4 **(E1)** 98.2 **(E2)** 98.7 **(E3)** 99.6 **(EE2)**
Filby, A.L.-2010	Effects of advanced treatments of wastewater effluents on estrogenic and reproductive health impacts in fish	O_3	1.74 **(E1)** 0.15 **(E2)** 0.28 **(EE2)**	74 **(E1)** 77 **(E2)** 64 **(EE2)**
Cunha,G.D.S 2019	Insights into estrogenic activity removal using carbon nanotube electrochemical filter	Electroquímica	$1\ 10^{7}$ **(E2)** $1.1\ 10^{7}$ **(EE2)**	96 **(E2)** 95 **(EE2)**
Sun, J 2017	Comparison of different advanced treatment processes in removing endocrine disruption effects from municipal wastewater secondary effluent	O_3	3.95 **(E1)** 4.68 **(E2)** 0.24 **(E3)**	95.7 **(E1)** 99.9 **(E2)** 99.9 **(E3)**

Table 5. (Continued)

Author	Title	Treatment	Initial concentration (ng/L)	Percentage of removal (%)
Mills,M 2015	Removal of ecotoxicity of 17α-ethinylestradiol using TAML/peroxide water treatment	TAML / H_2O_2	-	>90 **(E1)** >90 **(E2)** >90 **(EE2)**
		SYNTHETIC WATER		
Jiang, L.-2013	Degradation of 17β-estradiol in aqueous solution by ozonation in the presence of manganese (II) and oxalic acid	O_3	$1\ 10^4$ **(E2)**	60 **(E2)**
		O_3/Catálisis	$1\ 10^4$ **(E2)**	95 **(E2)**
Zhang,W.- 2013	Performance evaluation and application of surface-molecular-imprinted polymer-modified TiO2 nanotubes for the removal of estrogenic chemicals from secondary effluents	UV/Catálisis	100 **(E2)**	99.9 **(E2)**
Sarkar, S.-2014	Degradation of estrone in water and wastewater by various advanced oxidation processes	O_3 O_3/H_2O_2 $UV/O_3/H_2O_2$ UV UV/H_2O_2	$5\ 10^6$ **(E1)**	99 **(E1)** 99 **(E1)** 99 **(E1)** 99 **(E1)** 99.4 **(E1)**
Deng, J.-2015	Competitive degradation of steroid estrogens by potassium permanganate combined with ultrasound	Ultrasonido	$1.3\ 10^4$ **(E1)** $1.7\ 10^4$ **(E2)** $2.5\ 10^4$ **(EE2)**	37 **(E1)** 31 **(E2)** 30 **(EE2)**
		Ultrasonido/ Catálisis		47 **(E1)** 49 **(E2)** 48 **(EE2)**
		Catálisis		68 **(E1)** 72 **(E2)** 70 **(EE2)**
		Ultrasonido/ $KMnO_4$		37 **(E1)** 31 **(E2)** 30 **(EE2)**

Table 5. (Continued)

Author	Title	Treatment	Initial concentration (ng/L)	Percentage of removal (%)
Roudbari, A.-2018	Hormones removal from municipal wastewater using ultrasound	Ultrasonido	485 **(E1)** 580 **(E2)**	94 **(E1)** 94 **(E2)**
Bennett, J.L.-2018	Advanced oxidation processes for treatment of 17β-Estradiol and its metabolites in aquaculture wastewater	UV	$1\ 10^4$ **(E1)** $1\ 10^4$ **(E2)** $1\ 10^4$ **(E3)**	>90 **(E1)** >60 **(E2)** >50 **(E3)**
		UV/H_2O_2		>90 **(E1)** >60 **(E2)** >50 **(E3)**
Engelhardt,T 2020	Development of a novel high throughput photo-catalyst screening procedure: UV-A degradation of 17ff-ethinylestradiol with doped TiO2-based photo-catalysts	UV/TiO_2	$1.5\ 10^4$ **(EE2)**	60 **(EE2)**
		$UV/TiO_2/Zn$		>80 **(EE2)**
Ma,X 2015	Simultaneous degradation of estrone, 17β-estradiol and 17α-ethinyl estradiol in an aqueous UV/H2o2 system	UV/H_2O_2	$5\ 10^4$ **(E1)** $5\ 10^4$ **(E2)** $5\ 10^4$ **(EE2)**	99.9 **(E1)** 88.7 **(E2)** 91.5 **(EE2)**
Cunha,G.D.S 2019	Insights into estrogenic activity removal using carbon nanotube electrochemical filter	Electroquímica	$1\ 10^7$ **(E2)** $1.1\ 10^7$ **(EE2)**	99 **(E2)** 98 **(EE2)**
Frontistis,Z 2011	BDD anodic oxidation as tertiary wastewater treatment for the removal of emerging micro-pollutants, pathogens and organic matter	Electroquímica con electrodos de DDB	$1\ 10^5$ **(E2)** $1\ 10^5$ **(EE2)**	100 **(E2)** 100 **(EE2)**
Mills,M 2015	Removal of ecotoxicity of 17α-ethinylestradiol using TAML/peroxide water treatment	TAML / H_2O_2	$1\ 10^7$ **(EE2)**	100 **(EE2)**
Ma, X.Y.-2014	Parameters on 17β-Estradiol degradation by Ultrasound in an aqueous system	Ultrasonidos	$3.33\ 10^5$ **(E2)**	22 **(E2)**
		Ultrasonidos/ $KMnO_4$		98 **(E2)**
		$KMnO_4$		75 **(E2)**

Acronyms:
Estrone (**E1**), 17β-Estradiol (**E2**), Estriol (**E3**) and 17α-Etinylestradiol (**EE2**).

Some authors have combined ozonation with other *AOPs* to decrease the O_3 concentration in the feed. For example, Almomani et al. (2018) performed experiments with various combinations of *AOPs*, based on catalytic (O_3 + Fe or TiO_2 or Fe + H_2O_2), photolytic (UV+O_3) and photocatalytic (O_3+UV+ Fe or TiO_2) ozonation. Furthermore, they determined that UV light promotes the conversion of O_3 to H_2O_2, due to its reaction with water, and that H_2O_2 generates $HO^{\bullet}$ through its photodegradation. Likewise, Moreira et al. (Moreira et al. 2016) demonstrated that photocatalytic ozonation with TiO_2 was able to completely remove EE2. The complete removal through this combination of *AOPs* can be attributed to a synergistic effect between the treatments, due to the ability of O_3 to accept electrons from the TiO_2 and generate more $HO^{\bullet}$ which ensures that oxidation reactions of organic compounds present are favored. Nevertheless, it must be considered that producing UV light with low and medium pressure lamps will also generate an additional cost.

Sarkar et al. (2014) and Pešoutová et al. (2014) demonstrated that with the use of peroxone (O_3 + H_2O_2), an estrogen removals greater than 98% were achieved, where the elimination rate of estrogens increased to more than 99% when the H_2O_2 concentration in the solution was increased from 20 to 60 mg L^{-1}. H_2O_2 is commonly used as a catalyst in ozone catalytic and ozone-photocatalytic treatments, but although estrogen removal is comparable to other combinations of *AOPs* involving O_3 (greater than 99%), H_2O_2 in excess can act as an inhibitor of the process (Pešoutová et al. 2014). In addition, H_2O_2 has low absorptivity. Therefore, it can generate a limitation in the yield of $HO^{\bullet}$ during the reaction (Sarkar et al. 2014).
Other treatments that are used independently are electrochemical, UV photolysis and ultrasound. The first technique generally presents high yields (90%) in the removal of estrogens thanks to the correct choice of anode material. For example, Cunha et al. (2019) used a carbon nanotube (CNT) electrochemical filter for the removal of E2 and EE2 and obtained removals greater than 95% after reaching the steady state (300 min) with an applied cell voltage of 2.5 V (anode potential of ~ 0.8 V vs. Ag/AgCl). The above, according to the authors, is the result of the oxidative capacity of the CNT anode with increasing current density, due to a higher electro-generation of oxidizing species, such as $HO^{\bullet}$. Frontistis et al. (2011) worked with a boron-doped diamond anode (BDD) and achieved 100% removal of E2 and EE2 in 7 min, with a current density of 2.6 mA cm^{-2}. These results showed the potential of electrochemical oxidation with BDD to serve as a tertiary wastewater treatment. It is worth noting that both studies used different initial concentrations of E2 and EE2, because they concentrated the wastewater. Frontistis et al. (2011) evaluated the solution with a concentration of 0.1 g L^{-1} and Cunha et al. (2019) worked it with 0.01 g L^{-1}.

As for UV photolysis, low degradation yields are generally obtained when carried out alone. Almomani et al. (2018) reported removals of only 8.6 and 10.7% for E2 and EE2, respectively. However, the authors reported better results when adding catalysts to the process (TiO_2, el MnO_2 and Fe^{+}), obtaining removals of 90% working with UV/Fe/H_2O_2 (photo-Fenton) and 99% using UV/TiO_2. The improved results are a product of the generation of more $HO^{\bullet}$ by the presence of catalysts. Zhang et al. (2012) also performed their investigation with UV/ TiO_2 and reported removals greater than 99% for E1, E2 and E3. Similarly, (Ma et al. (2019) obtained >90% removals for E1 in wastewater. The high contaminant removals using UV/ TiO_2, compared to the photo-Fenton process, are because the generation of $HO^{\bullet}$ in the system was continuous throughout the irradiation process, so the oxidation potential remained constant. In contrast, the oxidation potential of the photo-Fenton process decreased with the consumption of H_2O_2 in solution (Almomani et al. 2018).

Few records (3 articles) were found regarding estrogen removal by ultrasound. Roudbari and Rezakazemi (2018) investigated wastewater treatment with E1 and E2 and examined the effect of power (70 and 110 W) of ultrasound at frequencies of 30, 45 and 60 kHz. The authors achieved removals between 85 and 95% at both high power (110 W) and frequency (60 kHz) conditions. The authors also found that the individual effect of these variables on the reduction of pollutants was significant. The increase in frequency generated induced cavitation in the system, thus increasing the number of cavitation bubbles and the number of $HO^{\bullet}$ in solution. Moreover, according to sonochemical theory, when the ultrasound power is above the cavitation threshold, energy is released more easily. For this reason, the higher the frequency and power, the better the removal of contaminants.

The above may justify the low removal percentages of other studies, which were carried out at a frequency of 20 kHz (Ma et al. 2014; Deng et al. 2015). Ma et al. (2014) and Deng et al. (2015) obtained removals of 19% and 30% of E2 after 180 and 120 min, respectively. Both studies complemented their work by adding a $KMnO_4$, and higher removals were obtained in a shorter time than when working with ultrasound alone. Ma et al. (2014) highlighted that, better removals of estrogen were achieved by increasing the amount of $KMnO_4$ in the process.

In summary and from a purely qualitative perspective, without knowing the relevant performance indicators of the process, the most recommended methods for estrogen degradation are ozonation and electrochemical treatment with BDD anode; the removal percentages were 99.9% and 100%, respectively (Schaar et al. 2010; Frontistis et al. 2011; Moreira et al. 2016; Almomani et al. 2018). On the other hand, the combination of *AOPs* guaranteed high removals, as is the case of photocatalytic ozonation with UV/TiO_2/O_3, which according to Almomani et al. (2018), removed E1 and EE2 in their totality. However, to maintain the oxidation potential at high levels, O_3 must be constantly supplied to the wastewater, which may affect the economic feasibility of combined treatments with O_3.

Quantitative analysis

The values of γ are given for a specific pollutant and *AOP* as they are related to the following variables: treatment time, initial pollutant concentration range, percentage of degradation, volume of treated water and electrical energy used directly (UV lamp operation, O_3 generation, energy sources, among others) or indirectly in the process (only for H_2O_2 demand). In this sense, γ values were calculated for the different *AOPs* used in the investigations that reported or allowed estimation of the variables mentioned above. The results were grouped according to the estrogen treated. Additionally, the conditions of the treated water (pH, turbidity, among others), the presence of other organic contaminants and the catalyst dosage can have a significant influence on the performance parameter. Therefore, for this section, it was necessary to classify the investigations by type of treated water: synthetic or wastewater.

Synthetic water

In general, most of the treatments using synthetic water presented much lower γ values compared to those obtained in wastewater (Table 6). This can be attributed to the difference in the initial concentrations of the contaminants worked in both systems (differences between 3 to 6 orders of magnitude) and to the absence of organic contaminants, inorganic ions and dissolved organic matter in synthetic water matrices, which normally act as $HO^{\bullet}$ consumers. However, ultrasound-based treatments required large energy consumptions ($\gamma > 1.10\ 10^3$ kWh g^{-1}) and failed to obtain removals above 94% for E1, E2 and EE2 (Deng et al. 2015; Roudbari and Rezakazemi 2018).

Thus, it was found that the lowest value of γ calculated for the degradation of E1 and EE2 in synthetic water was presented in the solar photo-Fenton treatment, with $\gamma < 3.35\ 10^{-4}$ kWh g^{-1}, since Almomani et al. (2018) employed H_2O_2 concentrations that represented a low electrical consumption (0.054 Wh L^{-1}) for a water volume of 200 L. In addition, the UV radiation was generated by solar energy. Thus, the power consumption of the system associated with photolysis should not be considered. The second best AOP used for E1 and EE2 degradation was ozonation, with electrical consumptions of $9.40\ 10^{-2}$ and $8.50\ 10^{-2}$ kWh g^{-1}, respectively, because total contaminant removals were achieved with exposure times of only 30 min (Almomani et al. 2018).

On the other hand, it was identified that the AOP with the lowest electrical consumption used for E2 degradation corresponds to the electrochemical treatment with BDD electrodes or a mixture of metal oxides composed of: Ti/IrO2/RuO2 (MOM), with a value of $\gamma < 5.33$ kWh g^{-1} where complete degradations of the pollutant were obtained in a time of 120 min and a current density of 96.0 mA cm^{-2} (Ouarda et al. 2018). The calculated γ results demonstrate that initial contaminant concentrations play a key role in the power consumption of *AOPs* as degradation is favored in water systems containing higher amounts of contaminants (Table 6).

Table 6. Calculated γ values.

Author	Title	Treatment	γ (kWh g^{-1})
Moreira N.-2016*	Photocatalytic ozonation of urban wastewater and surface water using immobilized TiO2 with LEDs: Micropollutants, antibiotic resistance genes and estrogenic activity	O_3	2.44 10^{6} (E2) 3.68 10^{4} (EE2)
		UV catálisis	1.58 10^{7} (E2) 1.07 10^{6} (EE2)
		UV catálisis/ O_3	1.02 10^{5} (E2) 8.08 10^{4} (EE2)
Jiang, L.-2013	Degradation of 17β-estradiol in aqueous solution by ozonation in the presence of manganese (II) and oxalic acid	O_3 catálisis	2.31 10^{3} (E2)
Margot, J.-2013*	Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?	O_3	2.95 10^{2} (E1) 6.91 10^{3} (E2)
Schaar, H.-2010*	Micropollutant removal during biological wastewater treatment and a subsequent ozonation step	O_3	1.10 10^{4} (E1) 2.38 10^{3} (EE2)
Ouarda, Y 2018	Synthetic hospital wastewater treatment by coupling submerged membrane bioreactor and electrochemical advanced oxidation process: Kinetic study and toxicity assessment.	Electroquímica	5.33 (E2)
Almomani, F.-2018	Potential use of solar photocatalytic oxidation in removing emerging pharmaceuticals from wastewater: A pilot plant study	O_3	9.40 10^{-2} (E1) 8.50 10^{-2} (EE2)
		Foto-Fenton	3.35 10^{-4} (E1) 3.13 10^{-4} (EE2)
		Foto-Fenton/O3	18.1 (E1) 16.4 (EE2)
Zhang, W.- 2013	Performance evaluation and application of surface-molecular-imprinted polymer-modified TiO2 nanotubes for the removal of estrogenic chemicals from secondary effluents	UV/catálisis	8.08 10^{4} (E2)
Sarkar, S.-2014	Degradation of estrone in water and wastewater by various advanced oxidation processes	O_3	53.3 (E1)
		O_3/H_2O_2	67.7 (E1)
		$UV/O_3/H_2O_2$	68.9 (E1)
		UV	2.20 (E1)
		UV/H_2O_2	21.0 (E1)
Zhu, N.-2020	Bismuth impregnated biochar for efficient estrone degradation: The synergistic effect between biochar and Bi/Bi2O3 for a high photocatalytic performance	UV	839 (E1)
Zhang W.-2012*	Effect of water composition on TiO_2 photocatalytic removal of endocrine disrupting compounds (EDCs) and estrogenic activity from secondary effluent	UV/catálisis	4.68 10^{3} (E1) 9.07 10^{3} (E2) 1.09 10^{4} (E3)

Table 6. (Continued)

Author	Title	Treatment	γ (kWh g-1)
Deng, J.-2015	Competitive degradation of steroid estrogens by potassium permanganate combined with ultrasound	Ultrasonido	$1.60\ 10^3$ (E1) $1.53\ 10^3$ (E2)
		Ultrasonido/ catálisis	$1.16\ 10^3$ (E1) 840 (EE2)
Roudbari, A.-2018	Hormones removal from municipal wastewater using ultrasound	Ultrasonido	$8.15\ 10^4$ (E1) $7.06\ 10^4$ (E2)

*Treatments used in wastewater.

Wastewater

The *AOPs* used for estrogen degradation in wastewater were ozonation, UV catalysis/O_3 and UV catalysis. It was evidenced that the treatment with the lowest electrical consumption required to remove E1, E2 and EE2 was ozonation, obtaining γ values of $2.95\ 10^2$; $6.9\ 10^3$ and $2.4\ 10^3$ kWh g^{-1}, respectively (Schaar et al. 2010; Margot et al. 2013; Moreira et al. 2016). This is because estrogens can be completely degraded during exposure times of ≤ 60 min by reaction with O_3 in wastewater (Schaar et al. 2010; Margot et al. 2013), whereas UV energy-based processes tend to exhibit high exposure times (180 min), due to the effect of wastewater conditions (turbidity) on the UV incidence in solution and the photosensitivity of the pollutants to be degraded. Thus, increases in the radiation time and therefore in the power consumption of the technique are generated ($\gamma > 4.68\ 10^3$ kWh g^{-1} and $\gamma > 9.07\ 10^3$ kWh g^{-1} for E1 and E2, respectively) (Zhang et al. 2012; Moreira et al. 2016). In addition, the range of initial estrogen concentrations in all studies using wastewater was in the order of ng L^{-1} and the average pH was 7.1. Thus, the incidence of these variables on the value of γ was practically negligible.

Influence of the initial pH

The initial pH of the water is an important parameter in the efficiency of degradation of estrogens and organic pollutants by *AOPs* as it conditions the generation of the $HO^{\bullet}$. Almomani et al. (2018) and Roudbari and Rezakazemi (2018) demonstrated that alkaline conditions favor the generation of $HO^{\bullet}$ in water, thereby increasing the oxidation potential of the system and enhancing the degradation of contaminants. As mentioned in the qualitative analysis, the dissociation constant (pKa) of estrogens is > 10. Thus, in conditions of pH > 8 they are in their dissociated form. Consequently, their degradation is facilitated due to the weakening of the intermolecular forces of their molecules (Bennett et al. 2018; Zhu et al. 2020). However, for the study, results and operating conditions that evaluated degradation at initial pH between 6.0 and 9.0 were selected, since it is not feasible to make pH modifications to water entering a full-scale treatment system.

Operational costs of wastewater *AOPs*

Degrading estrogens involves significant operational costs due to the electricity consumption required. In this study, an estimate of these was made, considering an approximate value of USD$ 0.1/kWh for the cost of electricity, values of γ determined for wastewater treatment and initial estrogen concentrations of 80 and 30 ng L^{-1}, for E1 and E2, respectively. In the case of the ozonation treatment studied by Margot et al. (2013) an average cost of US$ 23.1/1000 m^3 was estimated for the degradation of E1 and E2. Similarly, for the catalytic UV treatment performed by Zhang et al. (2012), a cost of more than USD $64.7/1000 m^3 was determined for the same pollutants and at the same conditions. It follows from the above that the lower the value of γ the lower the operational cost of the *AOP* (See Table 7).

Table 7. Estimated operational costs for AOPs used for wastewater

Author	Treatment	*CECs*	Operating Cost* ($USD\$/1000\ m^3$)
	O_3		7,358.6
Moreira N.-2016	UV Catálisis	E2 Y EE2	48,470.0
	UV Catálisis/ O3		386.8
Margot, J.-2013	O_3	E1 y E2	23.1
Schaar, H.-2010	O_3	E1 y EE2	90.4
Zhang W.-2012	UV/Catálisis	E1, E2 y E3	151.9

*A cost of USD$ 0.1 per kWh and initial concentrations of 80, 30, 80 and 10 ng L^{-1} were considered for E1, E2, E3 and EE2, respectively.

However, *AOPs* are generally used as tertiary wastewater treatments, so the value of primary and secondary treatment (USD$ 43.0/1000 m^3) should be included in the total operational costs (USD$ 66.1/1000 m^3) (Turton et al. 2018). Consequently, degrading estrogens in wastewater with *AOPs* is expensive, because the price of operating a WWTP (filtration with biological treatment and chlorination) is in the order of USD$ 56.0/1000 m^3 (Turton et al. 2018); but, unlike conventional treatments, *AOPs* guarantee the removal of *CECs* and mitigate their effects on the environment.

It should be noted that the electrical consumption of the pumping system was not considered in this review for the calculation of γ. Nevertheless, it be noted that determining the electrical cost of wastewater treatment involves including the use of a pumping system, which increases the cost of treatment. For example, based on Equation 3, an estimated electricity consumption for a WWTP pump of 1.39 10^5 kWh (USD$ 13.8/1000 m^3), operating 8400 h/year, was determined. It consider a 20 psi differential pressure, 50% pumping efficiency and a system with a capacity of 950 gpm (Margot et al. 2013).

$$E = 4.35\ 10^{-4}\ \frac{\Delta P\ .\ Q\ .\ t}{\eta} \qquad (3)$$

where E is the pump electrical consumption in kWh, ΔP is the system differential pressure in psi, Q is the WWTP volumetric flow in gpm, t is the treatment time in hours of operation/year, and η is the pump efficiency.

Among the *AOPs* studied, the most recommended treatment for degrading estrogens in wastewater was the conventional ozonation, since it obtained the lowest γ values at real conditions and in synthetic water, being surpassed only by treatments based on solar UV energy. However, it should be kept in mind that the implementation of techniques that use the sun as an energy source, on a real scale, are limited by the environmental conditions of the sites and the area available for the installation of solar panels.

Conclusions

An increase in the number of publications related to estrogen removal (E1, E2, E3 and EE1) was evident between 2010 and 2020. The ratio of documents per year was even more pronounced as of 2017, reflecting a greater interest in finding a suitable process for handling these *CECs*. The bibliometric network made it possible to establish the most representative keywords of the selected search equations, where ozonation was identified as the most studied *AOP*.

The variables with the greatest impact on the research collected were the initial estrogen concentration, the type of water, the pH of the system and the variables of each *AOP*. It was determined that the increase in the initial concentration of estrogen in the water facilitates the degradation process. In addition, basic pH conditions favor contaminant removal. Variables such as O_3 concentration in the supplied gas, catalyst concentration, UV light power, current density and ultrasonic frequency were relevant for each *AOP*. Finally, ozonation was identified as the most suitable AOP for estrogen treatment, both in synthetic water and wastewater, because it achieved removals above 99% with the lowest γ values (9.40 10^{-2} and 8.50 10^{-2} kWh g^{-1} for E1 and EE2 in synthetic water, respectively, and 2.95 10^2, 6.91

10^3 and 2.38 10^3 kWh g^{-1} for E1, E2 and EE2 in wastewater, respectively) and the lowest operational costs in wastewater (USD$ 23.1/1000 m^3 for E1 and E2).

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Author Contributions

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