

Article

Advanced Oxidation Processes Based on Sulfate Radicals for Wastewater Treatment: Research Trends

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Abstract: In this work, the recent trends in the application of the sulfate radical-based advanced oxidation processes (SR-AOPs) for the treatment of wastewater polluted with emerging contaminants (ECs) and pathogenic load were systematically studied due to the high oxidizing power ascribed to these technologies. Additionally, because of the economic benefits and the synergies presented in terms of efficiency in ECs degradation and pathogen inactivation, the combination of the referred to AOPs and conventional treatments, including biological processes, was covered. Finally, the barriers and limitations related to the implementation of SR-AOPs were described, highlighting the still scarce full-scale implementation and the high operating-costs associated, especially when solar energy cannot be used in the oxidation systems.

Keywords: alternative technology; natural resource; emerging contaminant; pathogen; conventional system



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1. Introduction

In the last decades, the increase in population, industrial production and agricultural practices have caused a rise in the consumption and subsequent pollution of water [1–7]. The pollutants contained in wastewater (WW) are a group of heterogeneous substances [8]. Besides pathogens, bacteria and genes resistant to antibiotics [9], the main pollutants include organic compounds such as pharmaceuticals, personal care products, perfluorinated compounds, pesticides, surfactants, flame retardants, dyes and a wide variety of industrial additives and synthetic chemical compounds [5,10–14]. Among these pollutants, the group of emerging contaminants (ECs) stands out due to their bioaccumulable, persistent and toxic character, along with their carcinogenic and mutagenic potential, posing a risk to human health and the environment [15–18], and constituting a concern of great interest nowadays [19]. Additionally, several ECs are not yet included in the legislation of many countries, or there is no legal regulation determining the maximum allowable levels of these substances in the environment [20–23].

On the other hand, it is important to note that the WW conventional treatments cannot fully degrade ECs [6,24–26], since they were not initially designed to eliminate this group of pollutants [14]. Furthermore, for the particular case of biological processes, their operation can be affected by the toxicity of pollutants to be treated, leading to the inhibition of the microorganisms responsible for the treatment [11]. Additionally, conventional disinfection treatments with chlorine or other halogens were found to generate disinfection by-products, which can exhibit a mutagenic and carcinogenic character [3,25]. Therefore, effluents from domestic WW treatment plants (WWTPs), or WW with comparable physicochemical and biological characteristics, are considered as potential contributors of ECs to natural environments [27–29]. In this regard, the implementation of innovative and efficient treatment technologies is required to make this type of effluents suitable for discharge or reuse [6]. This is where advanced oxidation processes (AOPs) play a key role.

AOPs are considered as promising and environmentally friendly oxidation technologies [30,31] that are based on the generation of powerful radicals, such as hydroxyl radicals ($\text{HO}\bullet$) [26,32] and sulfate radicals ($\text{SO}_4\bullet^-$). These radicals can oxidize toxic organic components and pathogens contained in WW [5,12,33] that cannot be degraded in conventional WWTPs [6,26]. Thus, the implementation of AOPs allows for the regeneration and reuse of WW, being an alternative to reduce water stress in some regions of the world [14,34,35], particularly in those where the scarcity of this natural resource is recurrent.

There are several AOPs based on electrochemical, sonochemical, photochemical and chemical reactions, being the sulfate radical-based advanced oxidation processes (SR-AOPs), such as the combination of persulfate (PS) with ultraviolet radiation (UV), iron (Fe) and cobalt (Co) (i.e., the PS/UV, PS/Fe and the PS/Co systems), the processes that stand out among other AOPs [7,8,33,36,37]. In fact, according to the reports in the literature, the referred processes have been shown to be promising technologies for the degradation of ECs due to the high efficiencies obtained. As a matter of fact, Gao et al. [38] achieved a metoprolol (MTP) degradation of 91.1% through the implementation of the PS/Fe system. In turn, Yu et al. [39] reported a methylene blue removal of 99.9% by applying Elbaite to catalyze peroxymonosulfate (PMS) in WW purification. Likewise, Dibene et al. [40] found a paracetamol (PCT) elimination higher than 90%; particularly, 94.2% of the pollutant of interest was degraded by the heat-activated peroxydisulfate (PDS). It is important to note that the set of results indicated above was achieved under optimal operating conditions of the SR-AOP applied.

On the other hand, a number of studies report the efficiency of AOPs based on $\text{HO}\bullet$ and $\text{SO}_4\bullet^-$ for degrading pollutants contained in water. The SR-AOPs are the oxidation technologies showing the best results in terms of pollutant removal and mineralization [41,42]. Shad et al. [41] studied the degradation of sulfadimethoxine (SDM) by the combination of UV radiation and hydrogen peroxide (H_2O_2) as the oxidizing agent. The results obtained were compared to the ones achieved by the UV/PMS process and it was found that SDM total degradation was obtained in 12 and 7 min when the UV/ H_2O_2 process and the UV/PMS system were used, respectively. Similarly, Wang et al. [42] found that the total degradation of thiamphenicol was achieved in 75 min of treatment by applying the UV/ H_2O_2 system, while the same results were obtained by the UV/PS process in 45 min of reaction time.

However, even though SR-AOPs have several disadvantages ascribed to them, the coupling of SR-AOPs and conventional processes is recommended for effective WW treatment [16,43]. In fact, from the literature review, there is growing attention on coupling AOPs based on $\text{SO}_4\bullet^-$ and bioremediation systems [10,19].

Given this scenario, this work presents the progress on the AOPs application for the degradation of a vast range of ECs and bacteria resistant to antibiotics in WW, focusing on the AOPs based on $\text{SO}_4\bullet^-$. The fundamental reactions involved and the parameters affecting the efficiency of the referred to AOPs are presented, as well as the applications of this group of oxidation technologies. In addition, the main barriers and limitations related to the implementation of SR-AOPs, particularly when the systems are combined with conventional processes, are covered. For this purpose, the databases and the search string used, along with the methodology followed for this systematic study, are also described. SR-AOPs are found to stand out over other AOPs for overcoming the problem of WW pollution.

2. Materials and Methods

2.1. Databases

Scopus (Elsevier, Amsterdam, The Netherlands) and Web of Science (Clarivate Analytics, London, UK) are two of the most relevant databases where peer reviewed scientific works are compiled [20]. However, several studies evidence that using Scopus is the best option in a systematic literature review, since it is considered the largest scientific database in the world [44]. This fact motivated the utilization of Scopus as the scientific database

chosen for obtaining both research and review studies regarding the implementation of AOPs in the treatment of WW polluted with ECs.

On the other hand, when consulting Web of Science by using the same search string, which is described below, several publications have been found since 1998, while by utilizing Scopus database, 1990 was reported as the first year when papers on the field started to be published. In addition, for the research area related to “environmental sciences”, a total of 2428 and 2992 publications were observed in Web of Science and Scopus, respectively. This fact ratifies the interest in conducting the research trend analysis focusing on Scopus database results.

2.2. Search Strategy

Based on the information collected in Scopus, the search was performed by using [TITLE-ABS-KEY (“wastewater” and “advanced oxidation”)] as the search string, which yielded 4707 documents obtained in an observation window of about 30 years (from 1990, the year in which the first publication was reported, until 2021), considering 28 February as the cut-off date.

Figure 1 illustrates the works published related to advanced oxidation and WW in a period of time between 1990 and 2020. The studies reported for 2021 were not included in the figure in order to visualize the upward trend in the interest within the scientific community in relation to the use of advanced oxidation in WW treatment. It is important to note that the year 2021 has not ended yet at the time of this research being conducted and there are still studies to be published corresponding to the referred year.

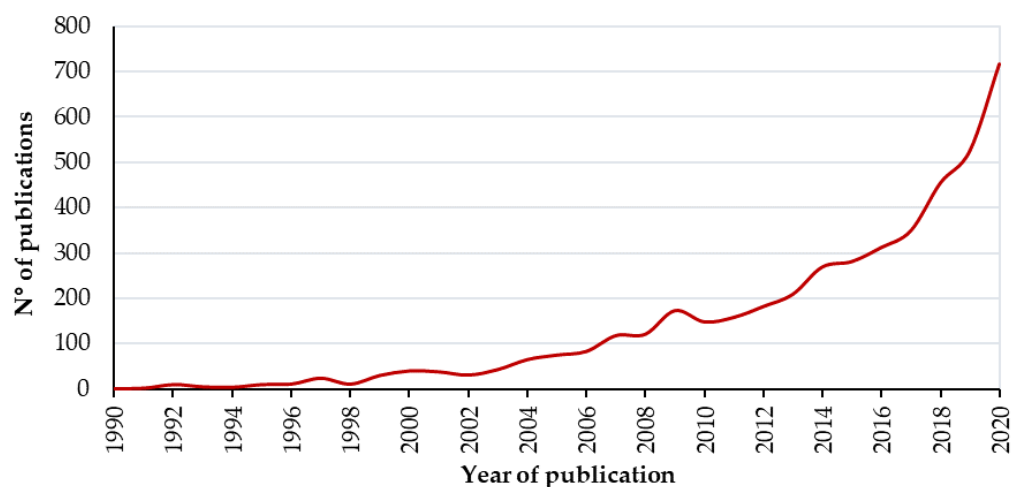


Figure 1. Evolution of the number of works published between 1990 and 2020. Source: Scopus database.

On the other hand, VOSviewer[®] software (Leiden University, Leiden, The Netherlands) was used in order to gather information related to the subject of interest, especially concerning the relationships among the countries around the world. Figure 2 shows the relationships between countries (scientific communities) of the studies published in the literature.

It is important to clarify that the number of publications distributed throughout the years from 1990 to 2020, and the relationships obtained among countries related to advanced oxidation and WW, would change if the search string was modified. The obtained results would also be different from the ones reported here due to the continuous updating of the database used.

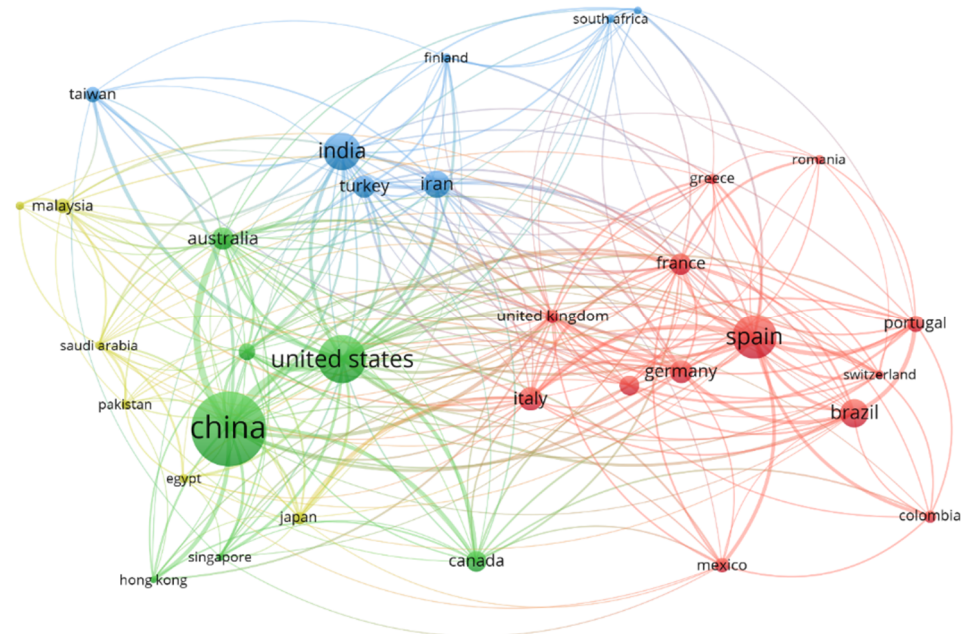


Figure 2. Bibliometric map of global collaboration network among countries between 1990 and 2021. Source: VOSviewer® software.

3. Results and Discussion

3.1. Study Selection and Preliminary Approaches

From the total number of publications (4707) obtained using the Scopus database, 94.2% of the works are written in English. Other works written in Chinese, Spanish and Portuguese were also included, exceeding 20 publications per language. Regarding the distribution of publications by countries, 95 countries were found to have made at least one publication on the subject of interest. In addition, according to the type of document, research articles predominate with 76.6%, followed by documents such as reviews of the state-of-the-art, conferences and book chapters, with a weight of 10.7%, 7.7% and 3.6%, respectively, with respect to the total number of works found.

Figure 1 presents the scientific documents on WW and advanced oxidation that have been published since 1990. A continuous growth has been observed, especially since 2004, exceeding 50 documents per year. The maximum number of publications corresponds to 2020 (a total of 716 documents for the consultation date). Hence, it can be observed that there is a growing interest in the subject at an international level. The demand for research on AOPs is notable [10], probably due to the need to achieve an efficient degradation of pollutants of emerging concern and pathogenic load contained in WW [12] before being discharged to the environment.

A total of 17 countries have exceeded 100 publications on WW and advanced oxidation, including China (979 documents), the United States (528 publications) and Spain, with 478 documents. Figure 2 illustrates the relationships among countries (minimum 30 relationships) concerning the scientific production on the topic of interest throughout the selected observation window. It is highlighted that each node illustrated in the figure refers to a country. The node size is proportional to the number of scientific works published in the country. On the other hand, the thickness of each line represents the collaboration number conducted with the connecting country. The countries with the largest number of scientific publications were found to be the ones that have carried out the largest number of collaborative research with other countries. Four scientific communities were also observed. The main community is illustrated in the green color and is led by China. In this community, the United States also plays a relevant role. The second community, represented in the red color, is formed by Latin American and European countries, where Spain occupies the central position, even though Brazil, Italy, Germany and France are equally important. The

third group, which is illustrated in blue, consists mainly of India, Iran and Turkey. Finally, Malaysia and Japan predominate in the fourth group that is depicted in the yellow color.

When the scientific communities in the last decade (2010–2020) are considered (Figure S1 from Supplementary Material), the main scientific groups continue to be dominated by China and the United States, followed by Spain, as the representative countries of the first and second community, respectively. The third community is still led by India; however, Iran and Turkey are not part of this community, heading the community represented by Malaysia. Furthermore, within the last decade, a new scientific community is included and represented by Canada, Mexico and Colombia.

Compared to the United States and the European Union standards in terms of water quality and regulation, the Chinese legislation concerning WW discharge is not very restrictive and there are several gaps to be filled [20]. Therefore, the Chinese government is making efforts to increase its capacity to treat WW and innovate in this topic [45], which is reflected in the number of scientific publications in the field of knowledge of interest. In turn, in the United States, an increase in the number of publications focusing on WW recovery has been reported due to the potential use of WW in the energy field [46], among other sectors. Concerning the European Union, and considering the importance associated with WW reuse, several changes in the regulation have also occurred, leading to a rise in this research area, especially in countries where water is scarce, such as Spain [20], which ranks third with regards to the number of scientific contributions on WW and advanced oxidation.

According to the latest reports found in the literature regarding AOPs and WW, it can be observed that there is a notable interest within the scientific community in processes based on $SO_4^{\bullet-}$, as well as in the integration of SR-AOPs with conventional systems, mainly biological ones. On the other hand, it was found that several efforts worldwide are focused on the application of sustainable AOPs based on $SO_4^{\bullet-}$, such as the ones that benefit the use of solar energy, given the advantages in terms of operating costs. The aforementioned aspects are described below in a more detailed way.

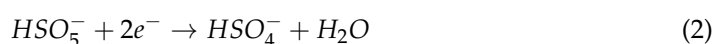
3.2. Advanced Oxidation Processes Based on $SO_4^{\bullet-}$

SR-AOPs have generated an increasing interest in the field of WW treatment due to their versatility, high oxidation potential and efficiency in the disinfection and degradation of persistent environmental pollutants and pathogenic load [7,46–49].

In order to understand the referred to AOPs, the fundamentals of the process, as well as the main factors affecting their degradation efficiency and the choices of application for treating WW polluted with ECs and pathogens, are covered.

3.2.1. Fundamentals

$SO_4^{\bullet-}$ can be generated from a primary oxidant such as PS, including PDS (Equation (1)) and PMS (Equation (2)) [7,31] once these chemical species have been activated, since they are not highly reactive.



Several activation techniques have been reported in the literature; PMS and PDS can be activated catalytically with energy or other oxidants [3,32]. The primary purpose of the PDS and PMS activation is to break the (hydro)peroxide (O-O) bond by homolytic or heterolytic cleavage [31]. The main activators of these oxidation processes are: different forms of energy (photochemical, sonochemical (US) and thermal activation), transition metals (e.g., Co, manganese (Mn), Fe, silver (Ag) and copper (Cu), among others), activated carbon (AC) catalysts and other oxidants, such as ozone (O_3) and H_2O_2 [33,48,50]. In Figure 3, the fundamentals related to the SR-AOPs are outlined.

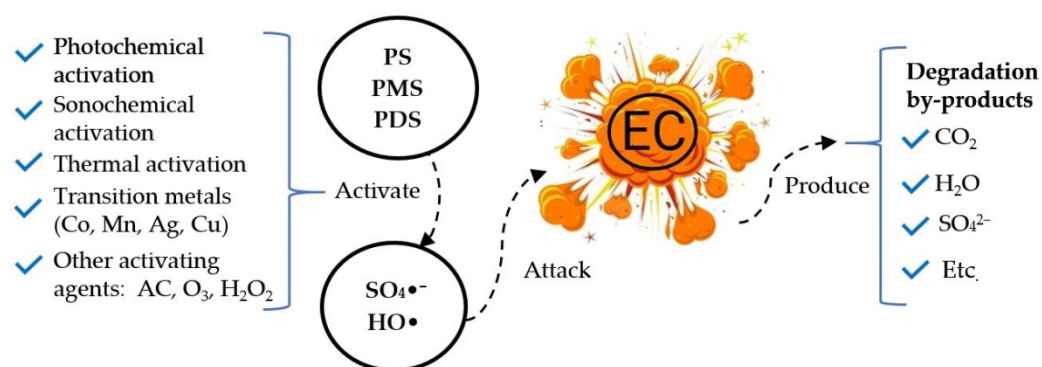
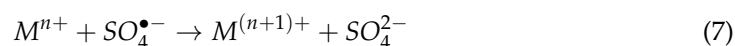
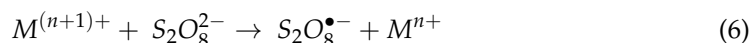
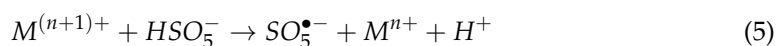
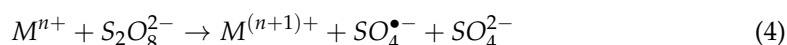
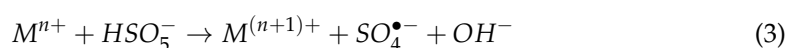
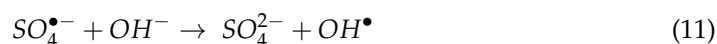
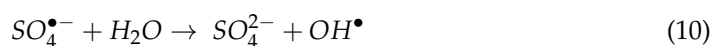
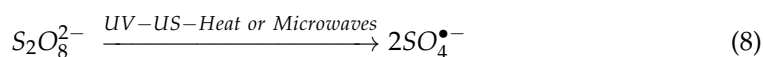


Figure 3. Advanced oxidation processes based on sulfate radicals ($\text{SO}_4\bullet^-$).

When a transition metal with a lower valence is used as an activating agent, the O-O bonds of PS anions can break, and $\text{SO}_4\bullet^-$ are generated (Equations (3) and (4)). However, $\text{SO}_5\bullet^-$ and $\text{S}_2\text{O}_8\bullet^-$ are produced when transition metals with a higher oxidation state are used to activate PMS and PDS (Equations (5) and (6), respectively), which are of lower reactivity in comparison to $\text{SO}_4\bullet^-$ [7]. Furthermore, according to Equation (7), the excess of transition metals within the solution can scavenge $\text{SO}_4\bullet^-$. Therefore, the relationship between the transition metal and PS is a key factor that must be optimized to avoid the extinction of $\text{SO}_4\bullet^-$ [51].



Another way of activating PDS and PMS is by means of energy such as heat, UV radiation, US and microwaves (Equations (8) and (9), respectively). It is noteworthy that, in the former case, two moles of $\text{SO}_4\bullet^-$ are produced for each mole of PDS involved in the activation [7,52]. Additionally, $\text{SO}_4\bullet^-$ can be transformed into $\text{HO}\bullet$ in the aqueous solution according to Equation (10). This reaction is significantly dependent on the pH of the water to be treated, since a further conversion and, subsequently, a higher number of $\text{HO}\bullet$ are produced at basic pH values (Equation 11) [52,53].



Current studies related to the activation of PS are mainly based on the use of transition metals and heterogeneous metal-based catalysts [39], since they are cheaper and simpler than treatments requiring energy [54]. Recently, new low-cost catalysts have been sought, due to their abundance and non-toxic and environmentally friendly character. These catalysts can activate PS without the need for additional energy resources such as heat, UV radiation and US [55].

3.2.2. Parameters Influencing the Efficiency of the Process

Several parameters, such as the concentrations of PS and the pollutant of interest, as well as the pH and the temperature of the water to be treated, have an influence on the efficiency of the covered AOPs [38]. Other factors of interest that affect the oxidation process are the presence of anions, cations and organic matter, which are typically found in wastewater. Generally, low levels of pollutants and high PS concentrations favor the efficiency of the AOPs based on $\text{SO}_4^{\bullet-}$. In turn, low and high pH and temperature values are involved in the increase in the system oxidation potential [38].

As mentioned previously, the generation of $\text{SO}_4^{\bullet-}$ mainly depends on the activation of PMS and PDS oxidants; therefore, the efficiency of the process is influenced to a great extent by the concentration of the referenced oxidants. Different authors have found that the increase in the concentration of PMS and PDS generates a positive effect on the degradation efficiency [7,33]. Nevertheless, this occurs up to a point of inhibition, the so-called optimal dose, from which the removal efficiency of the target compound decreases [52]. In this regard, for high concentrations of PS, a decrease in the rate of elimination of the toxic substance of interest is observed, which is mainly ascribed to the secondary reactions and the self-combination of radicals [47]. Sun et al. [33] evaluated the effect of the initial concentration of PMS activated by FeCo_2O_4 /rectorite to treat atrazine (ATZ) and found that the pollutant degradation rate improved remarkably when the dose of PMS was increased from 0.3 mM to 0.7 mM. Likewise, Gao et al. [38] evaluated the PS/Fe process to remove metoprolol (MTP) and found that the degradation of MTP increased from 40.2% to 96.3% as the concentration of PS rose from 0.5 mM to 3 mM, respectively, revealing that a higher concentration of PS favored the degradation of MTP. These improvements could be attributed to the greater decomposition of PS to produce a higher number of $\text{SO}_4^{\bullet-}$. Nonetheless, in both cases, as the PS concentration increased over 0.7 mM and 4 mM, respectively, the degradation of ATZ and MTP remained almost unmodified. This fact is probably due to the side reactions between $\text{SO}_4^{\bullet-}$ and the excess of PS to produce $\text{SO}_5^{\bullet-}$, which have a lower oxidation capacity, along with the self-combination of $\text{SO}_4^{\bullet-}$ [33,38].

In AOPs, the solution pH is an important parameter, since it influences the action of the oxidants and catalysts, as well as the degradation of pollutants [52]. In the case of SR-AOPs, several studies evaluated the effect of a wide pH range in the applicability of this kind of AOPs [16,38], as PMS and PDS are relatively stable compounds throughout the pH scale. It has been reported that PMS can be hydrolyzed in acidic media, although below a pH of 1 [7]. Gao et al. [38] also analyzed the influence of the solution pH in the PS/Fe process, finding that the maximum degradation efficiency of MTP was 99.5%, which was achieved at a pH value of 3. Additionally, the authors observed that almost 88.7% of MTP was degraded in the first 5 min of oxidation. When the water pH increased from 5 to 9, the removal of MTP was slightly reduced from 95.9% to 83.8%, respectively. These results confirmed that acidic conditions improved the degradation of MTP due to the generation of a high amount of $\text{SO}_4^{\bullet-}$. However, a significant inhibition of MTP elimination was observed at a pH of 11, suggesting that the degradation of the pollutant of interest is hampered in basic conditions. Similarly, Dibene et al. [40] assessed the pH range to be between 3 and 9 during the removal of PCT at a constant pollutant concentration of 0.661 mM and a temperature of 70 °C. The authors observed that the investigated pH range had an insignificant effect on the degradation of PCT, as a drastic decrease in the water pH was observed during the first minutes of treatment, regardless of the initial pH solution, reaching values close to 2.65 pH units.

Another important factor influencing the efficiency of the process is the temperature of the solution. The activation of PS by means of thermal energy was studied by several researchers, demonstrating that pollutant degradation is favored under higher activation temperatures [56]. As a matter of fact, Cheken et al. [50] evaluated the removal of 10 pharmaceuticals at room temperature (20 °C) and found a degradation percentage lower than 8% in 5 h of reaction. The elimination of the pollutant of interest started to be significant as the solution temperature increased. The referenced researchers observed that, as the

applied temperature was higher, the rate constant of the pollutant disappearance kinetics was also increased. The highest efficiencies were achieved for the highest evaluated temperature (75 °C). Similar results were found by Dibene et al. [40] during PCT degradation by heat-activated PDS-based AOPs. The PCT removal rate was observed to increase linearly with temperature, which can be attributed to the rise in the number of $\text{SO}_4\bullet^-$ generated as the water temperature was increased due to the rise in the PDS decomposition rate. A high amount of $\text{SO}_4\bullet^-$ enhanced the PCT degradation.

WW has a very complex matrix, since the presence of high loads of organic and inorganic matter is generally found, which can generate side reactions and by-products during the application of the SR-AOPs, modifying the general efficiency of the referred to oxidation processes [7,57]. Natural organic matter (NOM) is made up of humic substances that react with a large amount of active radicals and exhibit an inhibitory effect, resulting in a decrease in the oxidation performance of the system [52]. Indeed, Ma et al. [57] found that NOM inhibited the degradation of a mixture of benzene, toluene, ethylbenzene and xylene (BTEX) in the thermally-activated PS process. The referenced authors also found that the inhibitory effects became greater as the concentration of NOM increased.

On the other hand, the anions contained in WW may generate an inhibitory effect on the SR-AOPs efficiency. Nevertheless, an exception to this phenomenon is constituted by the chloride anion (Cl^-), which has also been found to exert a positive influence on PS by activating this reactant [38,52]. Gao et al. [38] evaluated the effect of anions on the degradation of MTP by PS/Fe and observed that the removal efficiency of MTP decreased from 91.1% without the addition of anions within the solution to 79.5%, 72.3% and 14.7% with the addition of SO_4^{2-} , NO_3^- and HCO_3^- , respectively, under optimal operating conditions and the addition of 0.33 g/L of anions. The authors also found that 0.33 g/L of Cl^- accelerated the degradation of MTP. This positive effect was ascribed to the production of reactive chlorine radicals, including $\text{Cl}\bullet$ and $\text{Cl}_2\bullet^-$, which would increase the total amount of radical species within the bulk. The result was the degradation improvement of the target pollutant. In turn, Sun et al. [33] investigated the influence of common inorganic ions such as NO_3^- , Cl^- , HCO_3^- and H_2PO_4^- during ATZ treatment by using FeCo_2O_4 /rectorite to activate PMS. Sun et al. reported a significant inhibition on the elimination of ATZ when HCO_3^- and H_2PO_4^- were added within the reaction solution. However, almost no differences were observed with the addition of NO_3^- and only a slight inhibition of the ATZ degradation was detected in the presence of 20 mM of Cl^- .

3.2.3. Application of the Process

SR-AOPs have been used in the treatment of different WW to degrade organic pollutants, including pharmaceuticals [58–62], herbicides [33,37], dyes [39] and a number of additives used in the manufacture of plastics [32,55]. Likewise, they have been used for the disinfection of WW with the presence of *Escherichia coli* and *Enterococcus faecalis* [8,36]. High degradation and inactivation efficiencies have been obtained from these applications, therefore AOPs based on $\text{SO}_4\bullet^-$ constitute promising oxidation technologies in the degradation of EC and pathogens resistant to antibiotics. Table 1 presents a summary of some recent works related to the implementation of SR-AOPs for the treatment of WW with the presence of EC and pathogenic load.

Table 1. Advanced oxidation processes (AOPs) based on sulfate radicals ($\text{SO}_4^{\bullet-}$).

AOP	Pollutant	Operating Conditions	Pollutant Removal	Reference
PS/Fe	<i>Enterococcus faecalis</i> (<i>E. faecalis</i>) and carbamazepine (CBZ)	Time: 12 min, [<i>E. faecalis</i>]: 1×10^7 CFU/mL, [CBZ]: 10 μM , [PS]: 1 mM, Zero valent iron: 0.2 g/L, ácido acético: 10 mM, initial pH: 5.5	<i>E. faecalis</i> (73.8 \pm 2.3)%, CBZ 42.3%	[8]
	Clofibric acid (CFA)	Time: 30 min, [CFA]: 0.01 mM, [PS]: 270 mg/L, [Fe]: 56 mg/L, initial pH: 7	72.0%	[37]
	Metoprolol (MTP)	Time: 30 min, [MTP]: 0.05 Mm, [PS]: 2.0 Mm, [Fe]: 0.33 g/L, pH was not modified	91.1%	[38]
PS/Fe–Electrochemical, electrocoagulation	Dyeing WW	Time: 120 min, initial pH: 6, applied voltage: 3 V, [PS]: 500 mg/L; [Ferrous ion]: 100 mg/L	93.5% chemical organic demand (COD)	[47]
PS/heat	Paracetamol (PCT)	Time: 120 min, [PCT]: 0.33 Mm, [PDS]: 5 mM, T: 68 $^\circ\text{C}$, pH: 6	94.2%	[40]
PS/AC	Metronidazole (MTZ)	Time: 2.8 min, [MTZ]: 0.58 mM, PS/MTZ = 20/1, [PS]: 11.6 mM, Q_L : 2.40 cm^3/min , initial pH: 3.9, h_{bed} : 3.5 cm	93.0%	[60]
PS/UV/Cu ⁰ -Cu ₂ O	Sulfamerazine (SMZ)	Time: 30 min, [SMZ]: 50 mg/L, [catalyst]: 0.2 g/L, [PS]: 0.8 g/L, UV wavelength: 365 nm, initial pH: 7.0, T: 25 $^\circ\text{C}$	99.9% SMZ, 30% TOC	[62]
PMS/Elbaite	Methylene blue (MB)	Time: 40 min, [MB]: 5 mg/L, [PMS/elbaite]: 1.0 g/L, [PMS]: 0.50 g/L, initial pH: 2.9, T: 25 $^\circ\text{C}$	99.9%	[39]
PS/MnOx@OMC	Phenol	Time: 30 min, [phenol]: 20 mg/L, [catalyst]: 0.1 g/L, [PS]: 1 mM; initial pH: 8	98%	[32]
PMS/FeCo ₂ O ₄ /rectorite	Atrazine (ATZ)	Time: 20 min, [ATZ]: 10 ppm, [PMS]: 0.5 mM, [catalysts]: 0.3 g/L, T: 298 K, initial pH: 7.0	90.44%	[33]
PMS/FeCo-BDC	Phenanthrene (PHE)	Time: 30 min, [PMS]: 0.2 mM, [PHE]: 1.0 mg/L, [catalysts]: 50 mg/L, initial pH, T = 25 $^\circ\text{C}$	99.0%	[63]
PMS/ UVA-LED	<i>Escherichia coli</i> (<i>E. coli</i>)	Time: 60 min, [<i>E. coli</i>]: 20 mL (about 1×10^6 CFU/mL), wavelength UVA-LED: 365 nm, [PMS]: 1.0 mg/L, initial pH: 7	58.7%	[36]
PMS/ZSM-5-(C@Fe)	Ciprofloxacin (CIP)	Time: 20 min, PMS: CIP: 40:1, [CIP]: 20 mg/L, [catalyst]: 4 g/L, T = 25 $^\circ\text{C}$, pH was not modified	99.9% CIP, 41.8% COD	[58]
PDS/CuO@AC	Textile WW	Time: 60 min, [PDS]: 7 mM, [catalyst]: 1 g/L, initial pH: 7.0	61% total organic carbon (TOC), 72% COD, 95% color	[48]
PDS/Goethite	Bisphenol A (BPA)	Time: 240 min, [goethite]: 0.5 g/L, [BPA]: 0.1 mM, [PS]: 1.0 Mm, initial pH: 4.5	61.4%	[55]
PDS/CeO ₂ /visible light	Ciprofloxacin (CIP)	Time: 240 min, Reaction condition: Visible light, [catalyst]: 0.375 g/L, [CIP]: 10 ppm, initial pH: 7	92%	[59]
PDS/clinoptilolite + heat	2-Methoxyphenol (MOP)	Time: 20 min, T: 80 $^\circ\text{C}$, [MOP]: 200 mg/L, [modified zeolite]: 1.0 g/L, [PS]: 1.2 g/L	99.2%	[64]

There is a vast number of studies in the literature that indicate the advantages of SR-AOPs in comparison to other AOPs, due to better decontamination prospects having been reported compared to those AOPs based exclusively on HO^\bullet . Among the benefits, the following can be named: the formation of radicals in a wider pH range of water

(from 2 to 8 pH units) [16,33,54], a longer shelf-life of $\text{SO}_4\bullet^-$ compared to $\text{HO}\bullet$ (20 ns for $\text{HO}\bullet$ vs. 30–40 μs for $\text{SO}_4\bullet^-$) [16,37,48,50], a high selectivity for the removal of pollutants [8,31,33,37,54], a larger redox potential at a circumneutral pH (1.8–2.7 V for $\text{HO}\bullet$ vs. 2.5–3.1 V for $\text{SO}_4\bullet^-$) [8,32,33,48,50,54,63] and the generation of $\text{SO}_4\bullet^-$ along with $\text{HO}\bullet$ in PMS [54]. Additionally, PDS is an easily available reactant [64]. For this reason, SR-AOPs can be utilized when specific functional groups contained in the pollutant structure must be oxidized [32,33,48,50,54,63].

Among the reported disadvantages, SR-AOPs can be involved in the rise of total dissolved solids in water because of the formation of sulfate anions (SO_4^{2-}). Additionally, a water pH decrease can occur, which implies an additional adjustment [15] before the treated effluent is discharged to the environment. However, according to Duan et al. [31], the application of these oxidation technologies on a real scale is still scarce despite the large number of publications.

Cheken et al. [50] evaluated the removal of 10 pharmaceuticals in WW using thermally-activated PS by means of pilot-scale solar powered equipment. They achieved a reduction of up to 95% of the target pollutants after 1.5 h, at 200 μM of PS, 65 °C and a solution volume of 800 L. On the other hand, Fernandes et al. [65] studied the degradation potential at a pilot-scale of 16 volatile organic compounds (VOCs) by AOPs based on $\text{HO}\bullet$ and $\text{SO}_4\bullet^-$. The PDS-based and PMS-based AOPs with oxidant doses of 436 and 70 g at 60 °C were found to reach the highest degradation percentages of the studied compounds, with total removal efficiencies of 98.6% and 95.6% of VOCs, respectively.

3.3. Combination of Conventional Systems and SR-AOPs

From the review of recent publications, it can be seen that great attention is shown by several researchers [10,19,34,66] to the combination of AOPs with conventional treatments, mainly biological ones, because of the economic benefits and the greater efficiency in the degradation of ECs and in the inactivation of antibiotic-resistant bacterial load. Furthermore, the most studied biological processes to be integrated with AOPs have been found to be membrane bioreactors (MBRs) and activated sludge systems [19,67], which have been used as pre- or post-treatment, according to the characterization of the WW effluents.

Concerning the integration of treatment systems, the position that AOPs should occupy with regard to the biological treatment (i.e., whether the AOP should be applied before or after the biological process) has been widely discussed for more than one decade [37]. Nevertheless, when WW effluents contain recalcitrant compounds, the application of AOPs as pre-treatments is generally needed in order to increase the biodegradability of the effluent that will be subsequently treated in a biological process [10]. Moreover, if inhibitory compounds are contained in WW, a pre-treatment is required to eliminate the toxic chemicals that limit the metabolism of the communities of microorganisms operating within the biological reactor [10,68]. In turn, when WW contains non-toxic pollutants that persist after a biological treatment, the implementation of an AOP is required as a post-treatment in order to polish the effluent, achieving the advantage that no chemical products or degradation energy are wasted in biodegradable compounds that can be transformed by the action of microorganisms [66]. Finally, in the study conducted by Paździor et al. [66] at an industrial level using untreated effluents from textile factories located in Poland, the combination of processes (biodegradation + AOP + biodegradation) was evidenced to be a promising treatment system due to the greater efficiency of the coupled treatment and the lower operating costs associated.

In Figure 4, a flow chart is presented where the aspects to be considered when selecting an AOP as a pre- or post-treatment in biological processes are highlighted.

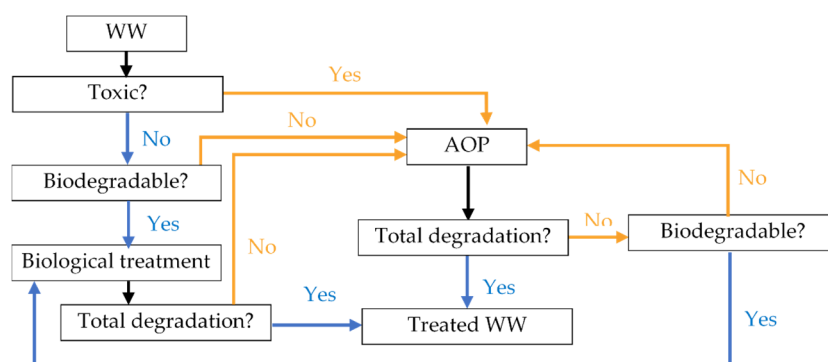


Figure 4. Combination of advanced oxidation technologies and bioremediation processes. WW: Wastewater, AOP: Advanced oxidation processes. Source: Adapted from [7].

On the other hand, the integration of AOPs with MBRs has been of recent interest given the high efficiencies reported for the treatment of different types of WW [19,69]. In this regard, Sathya et al. [70] indicated that the combination of AOPs before the membrane filtration process is advisable to improve the useful life of the membrane. In turn, Guo et al. [71] applied a solar photo-thermochemical system that involves PDS as oxidant and a Xenon lamp as the source of solar light, in order to degrade the organic matter contained in the tested water and reduce the fouling of the ultrafiltration membrane. The authors found that the pretreatment with solar-activated PDS at 70 °C, 0.4 Mm of PDS, a light intensity of 1 kW/m² and a reaction time of 2 h significantly minimized the membrane fouling, resulting in a reduction in the transmembrane pressure of ~69.6%. Furthermore, Pramanik et al. [72] assessed the effect of the ferric coagulation process combined with PS as a pretreatment of a direct osmosis process to mitigate the membrane fouling during the treatment of municipal WW effluents. The aforementioned authors found that the flow of water without pretreatment was reduced by 30% due to the membrane fouling in comparison to the water flow obtained using a concentration of 1 mM of PS and 5 mg/L of FeCl₃ 6H₂O with a rapid stirring for 1 min at 200 rpm, followed by a gentle stirring for 20 min at 50 rpm and then being directly applied for membrane filtration. Additionally, the UV/PS process has been studied in WW tertiary treatment using an ultrafiltration membrane, being highlighted in the work conducted by Qu et al. [73]. The referenced authors found that the use of UV radiation coupled to PS, as a pretreatment, only reduced the water flow by 23% and improved the fouling reversibility during the secondary effluent filtration. The pretreatment was carried out at a contact time of 30 min, a UV dose of 2.36 × 10³ mJ/cm² and a PS concentration of 0.1 mM.

In turn, the work conducted by Xie et al. [40] reported the viability of a PS system activated by iron (PS/Fe) for the removal of clofibric acid (CFA), achieving the total elimination of the pollutant of interest in 30 min of treatment, with a PS dose of 270 mg/L, which was activated with 56 mg/L of Fe. Additionally, less than 3% ammonia and ~15% of the dissolved organic carbon degradation, which was primarily attributed to the glucose oxidation by HO•, were removed. These results indicated the excellent selective oxidation capacity of the CFA-targeted Fe-PS system. On the other hand, Dibene et al. [40] investigated PCT degradation by heat-activated PDS and its relevance as a pre-treatment of a biological activated sludge system. These authors found a PCT elimination of 94.2% at 68 °C, a pH value of 6, a PCT concentration of 0.33 mM and a PDS level of 5 mM, during 240 min of oxidation. Under these conditions, the BOD₅/COD ratio increased from 0.008 to 0.34 after 10 h of treatment, leading to a significant improvement in biodegradability, and favoring the subsequent biological treatment.

Finally, although the advantages related to the combination of advanced oxidation technologies and bioremediation techniques have been investigated, there are still gaps linked to the coupling of both types of treatments, mainly related to the lack of studies

aiming at evaluating the efficiency of the coupled system at a real scale, since most of the studies reported in the literature have been focused on a laboratory scale [10,68].

3.4. Barriers and Limitations Acribed to SR-AOPs Implementation

Even though the benefits of AOPs are widely recognized for their ability to mineralize organic pollutants to carbon dioxide (CO₂) and water (H₂O) [30,31], the application of AOPs has significant limitations. Among the main barriers detected, the scarce implementation of these advanced processes at a full scale in comparison to the available research and laboratory-scale tests is highlighted [7]. Moreover, when incomplete mineralization occurs, degradation or transformation by-products can be formed, which could cause more detrimental effects to the environment than the initial compounds [11,74,75]. Cai et al. [76] found that the elimination of Orange II dye through a heterogeneous photodegradation using ZnFe₂O₄/PS enhanced by visible (VIS) radiation led to the generation of transformation products with higher toxicity compared to the toxicity associated with the original compound for a treatment time of 60 min using a dose of 0.5 g/L of ZnFe₂O₄, 1.0 g/L of PS and 150 W of radiation. These authors found a pollutant removal of 95%; however, the percentage of inhibition of oxygen uptake rates increased from 16.5% to a maximum of 30.1% in 30 min, which implies that more toxic compounds were produced during the oxidation process. In order to overcome this limitation, the extension of the reaction time was proposed. It was found that toxic by-products were no longer generated with a treatment time of 300 min. Likewise, Gao et al. [38] detected by-products with carcinogenic potential during the first 30 min of MTP degradation using the PS/Fe system with a concentration of 0.05 mM MTP, 2.0 mM PS and 0.33 g/L Fe, without the adjustment of the pH solution.

Finally, one of the greatest difficulties reported is related to the high costs ascribed to energy and reagent consumptions that are required in the performance of SR-AOPs [4,74,76,77]. Fernandes et al. [65] carried out a basic economic evaluation of the chemical and energy costs of the O₃/H₂O₂ system and the AOPs based on PDS and PMS activated by heat for the removal of VOCs. The O₃/H₂O₂ oxidation process was evidenced to have a lower cost (0.01 US \$/L) than the PDS-based AOPs (3.55 US \$/L) and the PMS-based AOPs (1.30 US \$/L) that achieve a VOCs elimination higher than 95%. The high costs ascribed to the PS-based AOPs were due to the oxidant price, taking Polish prices as the reference values. The difference among the tested AOPs is considerable. This gives a clear idea that SR-AOPs are not economically viable. In fact, oxidation processes based on PS have higher operating costs compared to the costs associated with conventional biological processes [78].

In order to overcome the limitations linked to the operating costs related to the implementation of SR-AOPs, a large amount of research has been focused on increasing AOPs sustainability, based on aspects such as the reduction in energy requirements, the minimization of waste and, consequently, the achievement of the so-called circular economy [10]. Among these works, the ones focused on the efficiency of solar energy-based AOPs stand out, since they allow the production of radicals in a more sustainable way [50,56]. Indeed, Chekem et al. [50] carried out a study based on the PS/solar energy process for the elimination of piroxicam, caffeine, bezafibrate, atenolol, diclofenac, ibuprofen, niflumic acid, tramadol, carbamazepine, trimethoprim and sulfamethoxazole in WW [50]. A reduction of up to 95% was found at 2 h of treatment, under a concentration of 200 µM of PS and 65 °C, utilizing a pilot-scale solar reactor.

Under this scenario, SR-AOPs and their combination with other WW treatment processes, both conventional and alternative ones, become attractive and highly promising technologies for the decontamination of WW containing ECs and pathogens resistant to antibiotics, and natural radiation is required for their operation.

4. Conclusions

The presence of ECs and bacterial load in the environment and, mainly, in WW effluents cannot be ignored due to the adverse effects caused to humans and natural

ecosystems. Therefore, the implementation of stricter monitoring, control and regulation procedures is required for their subsequent elimination in WW.

Based on the analysis of secondary information, which constituted the fundamental basis of this systematic study, it is possible to conclude that there is a marked interest in the investigation of AOPs to be implemented in the treatment of WW polluted with ECs and pathogens, and SR-AOPs have been proven to be one of the most studied processes in recent years, due to their high oxidation potential and decontamination prospects; however, the research is still limited to the laboratory scale. Therefore, further research focused on the application of this kind of AOPs on a real scale is required in order to achieve results closer to reality.

On the other hand, one of the main disadvantages ascribed to the implementation of SR-AOPs for WW treatment is that these treatment systems have been identified as expensive technologies. Additionally, these oxidation processes can be involved in the generation of more persistent and toxic degradation by-products in comparison to the original compounds to be treated. In this regard, a vast number of studies aiming at improving the sustainability of these AOPs has been reported, focused on the use of SR-AOPs with low energy requirements and reduced waste generation, leading to the contribution of the principles by which the circular economy is governed.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13172445/s1>, Figure S1: Bibliometric map of global collaboration network among countries during 2010–2020. Source: VOSviewer®software.

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