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Advanced catalytic oxidation coupled to biological systems to treat pesticide-contaminated water: A review on technological trends and future challenges

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ABSTRACT

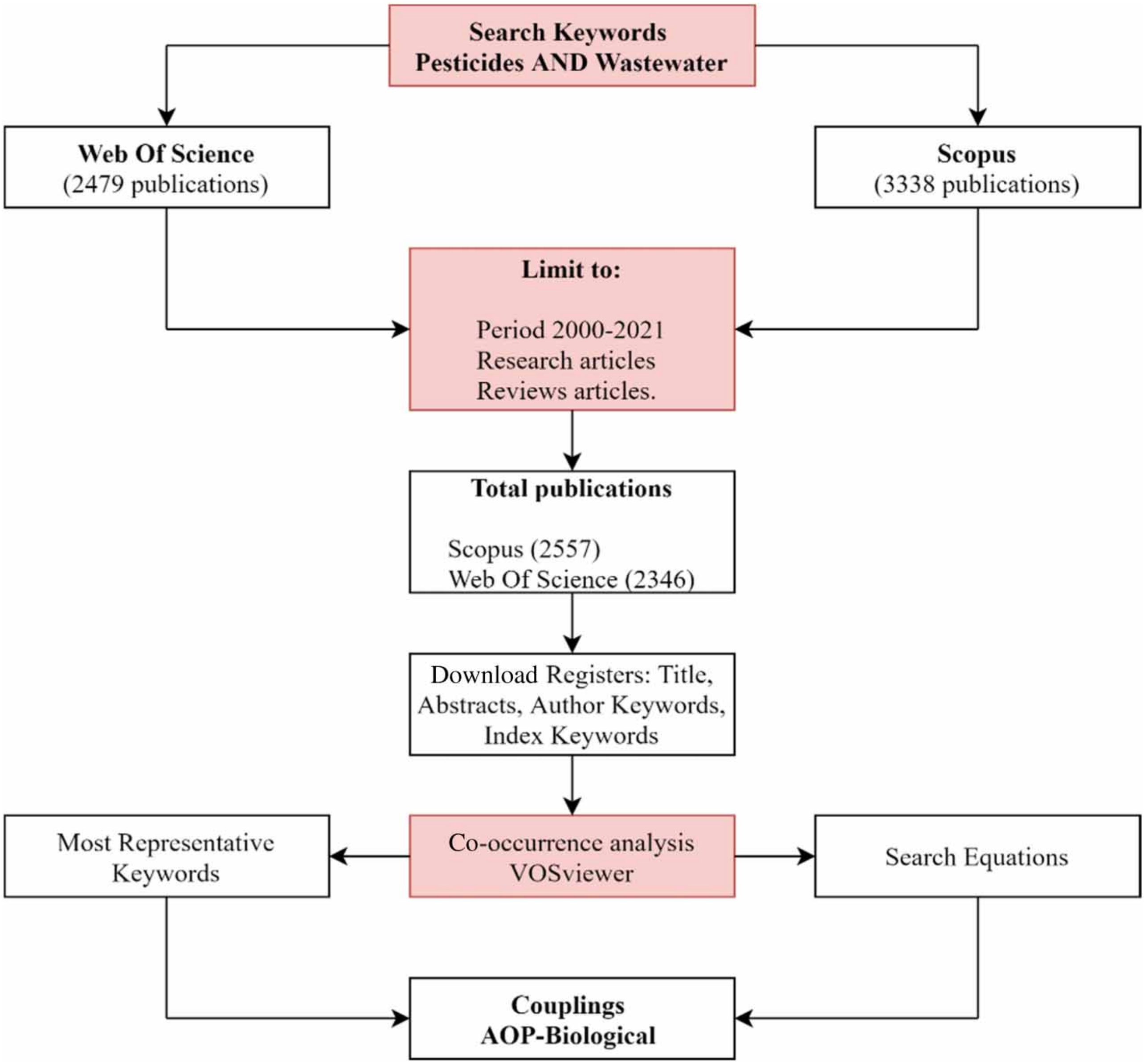
This article had the one and only objective of consolidating the couplings of advanced oxidation processes and biological systems in the decontamination of wastewater with pesticide content reported in the Scopus and Web of Science databases, through a critical analysis of which have been the most used, what methodologies have been implemented to develop them, identifying the objectives of each work, determining the success of the research and where the main niches of knowledge are, which can lead to the generation of new scientific knowledge as well as future trends. A co-occurrence analysis was carried out through the VOSViewer software to determine the most associated key words with the treatment configurations described above. Fenton and Photo-Fenton processes, heterogeneous photocatalysis TiO_2/UV, electrocatalysis, ozonization and a particular case of hydrodynamic cavitation-ozone as main advanced oxidation processes, together with advanced biological processes such as sequential batch bioreactor (SBR), membrane bioreactor (MBR), mobile bed biofilm reactor (MBBR); biodegradability and toxicity tests with bacterial strains and surface wetlands, whose treatment philosophy is activated sludge. The main future trends are the reuse of treated wastewater, the analysis and control of costs towards the efficient use of resources and the primary study of the byproducts generated in advanced oxidation to improve the efficiencies in the coupling.

Key words: advanced oxidation, bibliometric analysis, biological processes, coupling, pesticides, wastewater

HIGHLIGHTS

- The most successful couplings are related to advanced biological processes.
- Identifying by-products in advanced oxidation is key to the biological process.
- The treatment costs are central aspects of the processes on an industrial scale.

GRAPHICAL ABSTRACT



LIST OF ACRONYMS

WWPC	Wastewaters with pesticide content.
SBR	Sequential Batch Bioreactor.
IBR	Immobilized Mass Biological Reactor.
MBR	Membrane Bioreactor.
MBBR	Mobile Bed Biofilm Reactor.
HRT	Hydraulic Retention Time.
VSS	Volatile Suspended Solids
TOC	Total Organic Carbon.
DOC	Dissolved Organic Carbon.
COD	Chemical Oxygen Demand.
OD	Dissolved Oxygen
BOD_5	Biological Oxygen Demand at 5 days

UASB	Up-flow Anaerobic Sludge Blanket
CPC	Compound Parabolic Collector
WWTP	Wastewater Treatment Plant
OECD	Organization for Economic Cooperation and Development

INTRODUCTION

For decades, a wide range of agrochemicals to increase agricultural productivity has been a common technique worldwide (Zhang & Yang 2021; Zhou & Li 2021). Their use has increased in the last two decades as a result of global population growth and problems of low land yields, as well as the emergence of new pests or recrudescence of existing pests (Jayaraj *et al.* 2016) due to climate change (Sun *et al.* 2018). It has led to an increasing concentration of pesticides in surface water bodies (Matheus *et al.* 2020; Yu *et al.* 2021).

Water resource is affected due to the different means of transport of these pesticides, such as direct application to water bodies (Schreiner *et al.* 2021), landslides (Butkovskyi *et al.* 2021), or washing of spraying equipment (Becerra *et al.* 2020a; Manasa & Mehta 2020), which generate wastewaters with pesticide content (WWPC), and trigger a series of effects on the environment, human health and living organisms (Van Lexmond *et al.* 2015; Elfikrie *et al.* 2020; Malakootian *et al.* 2020). The main characteristics of these pollutants are related to high toxicity, slow degradation processes, high COD concentrations, and low removal in conventional biological treatments (Ignatowicz 2020; Ge *et al.* 2021; Sarker *et al.* 2021; Yu *et al.* 2021).

Advanced oxidation processes (AOPs) have recently gained momentum, improving the prospects for treating wastewater with high pollutant loads (Delgado Nina & Santander Pacoricona 2017; Li *et al.* 2021). They have been recognized as efficient alternatives for the removal of pesticides to acceptable levels (Affam & Chaudhuri 2019; Vagi & Petsas 2020; Vela *et al.* 2018), decreased toxicity levels (Vela *et al.* 2019), and improvements in effluent biodegradability (Ballesteros Martín *et al.* 2010). However, AOPs as the sole treatment process require considerable energy and chemical reagent costs (Oller *et al.* 2011; Paździor *et al.* 2019).

AOP-Biological couplings emerge as an alternative to reduce the limitations in advanced oxidation and enhance the results (Gernjak *et al.* 2006). The configuration consists of converting the toxic waste liquid in the AOP into another with more biodegradable and suitable characteristics for its subsequent degradation in biological reactors (Vela *et al.* 2019), as validated by several studies (Lafi & Al-Qodah 2006; Berberidou *et al.* 2017).

Wastewater treatments with pesticides contents in AOP-Biological couplings are studied using a bibliometric co-occurrence analysis with the VOSViewer software in the most important databases of scientific literature: Web of Science (WoS) and Scopus (Garrido-Cardenas *et al.* 2020). The research aims to analyze the articles found from a critical point of view, consolidate the different configurations applied in the removal of pesticides in aqueous matrices, highlight the relevance of the topic studied, and specify future trends in research. Figure 1 details the summary of the methodology described above and its relation to the main findings.

MATERIALS AND METHODS

The search for information is carried out in the WoS and Scopus databases with the keywords 'pesticides' and 'wastewater', the purpose of which is to identify information related to WWPC, specifically their treatment.

In the case of WoS, an advanced search by topic is carried out with Boolean operations (TS = (pesticide AND wastewater)). In the case of Scopus, an advanced search is carried out with the TITLE-ABS-KEY(pesticides AND wastewater) filter, allowing the words of interest to be located in the title, abstract, or keywords of the indexed articles. The search period for both databases is 2000–2021, limited to research articles and review articles. The results are consolidated taking into account the last search on 24 June 2021.

Results obtained in the general search in the databases are the input to perform the bibliometric analysis of co-occurrence by author keywords in the VOSViewer software, taking into account that it is a powerful study to identify topics, themes and research methods central or peripheral to a field and how they have changed over time, as well as an in-depth analysis that allows representing future trends in research as a guide for researchers in the scientific field studied (Bastos De Sousa 2021; Ismail *et al.* 2021; Mao *et al.* 2021).

The aim of the bibliometric analysis in this research is to determine the most suitable keywords for the query in the databases and to create a search equation that allows finding the precise information on the couplings of advanced oxidation processes and biological processes in the treatment of WWPC. The search is then refined in detail for each particular coupling found.

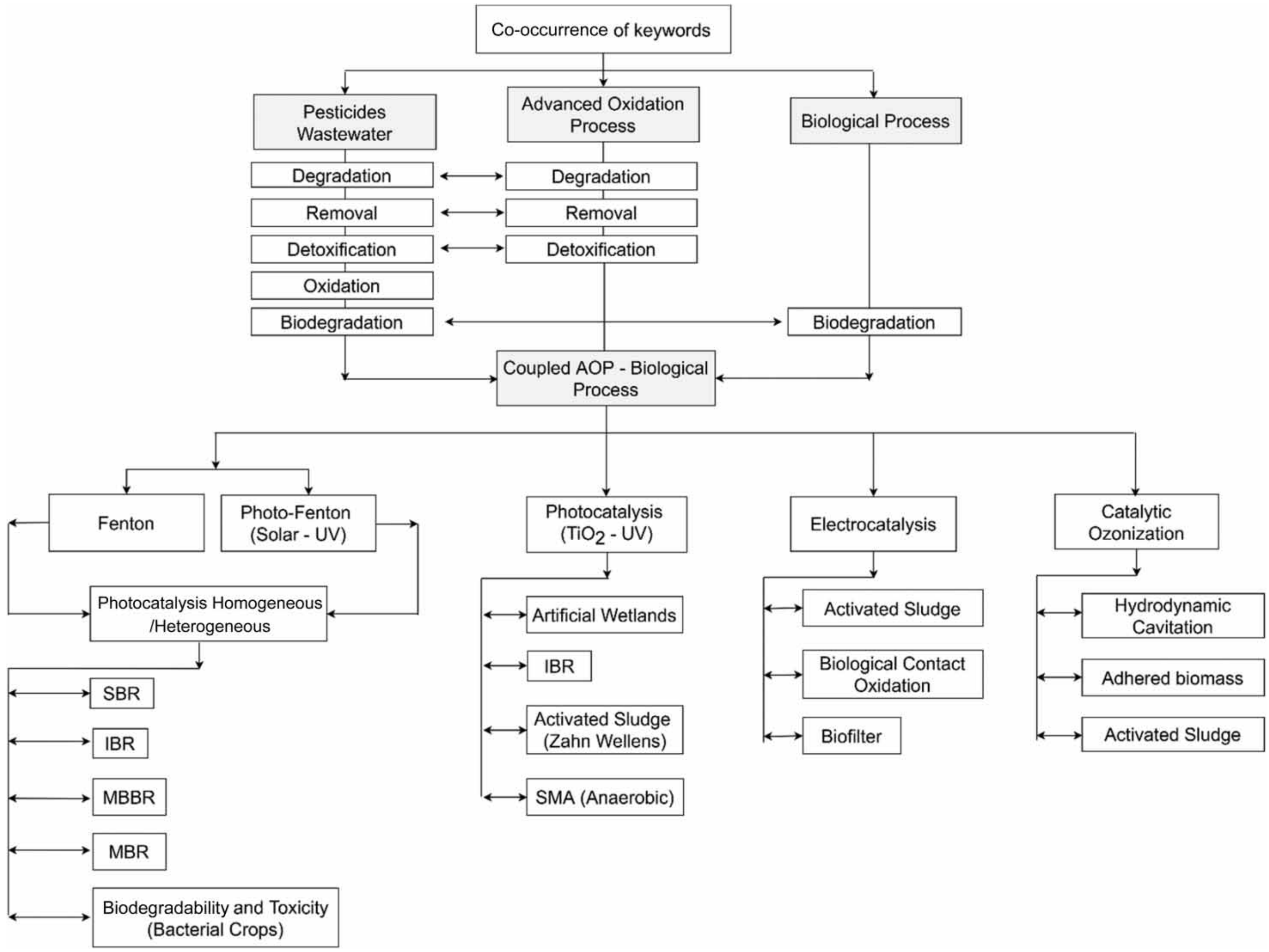


Figure 1 | Summary of AOP-Biological results and their relation to keywords correlation.

RESULTS AND DISCUSSION

Web of Science and Scopus publications

The search in WoS and Scopus databases provides the number of papers published chronologically in the period between 2000 and 2021 to date, which are related to wastewater and pesticides, which indicates, according to Figure 2, that since 2016 the interest in this field of research has had exponential growth, covering by 2020 a total of related publications of 319 and 305 articles in WoS and Scopus, respectively, and by the end of this year, 2021, the same trend line would be expected.

This indicates that it is a topical and relevant topic, which is consistent with the fact that in recent years pesticides have been prioritized as hazardous substances (Lefrancq *et al.* 2017; Rasheed *et al.* 2019; Kumar *et al.* 2021) and have been classified as contaminants of emerging concern (CECs) (Gomes *et al.* 2018; Servadio *et al.* 2021), micropollutants (MPs) (Munz *et al.* 2017; Kiefer *et al.* 2019) and persistent organic pollutants (POPs) (Wagner *et al.* 2021).

The above classification establishes that pesticides are chemical, synthetic, and toxic substances of great concern that affect human health and the environment, with high chemical resistance and difficult degradation, and although they end up in aquatic environments in low concentrations, they generate acute and chronic impacts on ecosystems (Kodavanti *et al.* 2014; Chavoshani *et al.* 2020; Llamas-Dios *et al.* 2021). Hence, their removal from different environmental matrices is indispensable, especially from water sources (Mekonen *et al.* 2016).

Bibliometric analysis

Records downloaded from the databases must be processed in VOSViewer to perform the bibliometric analysis of the information. This software requires the following inputs for the analysis:

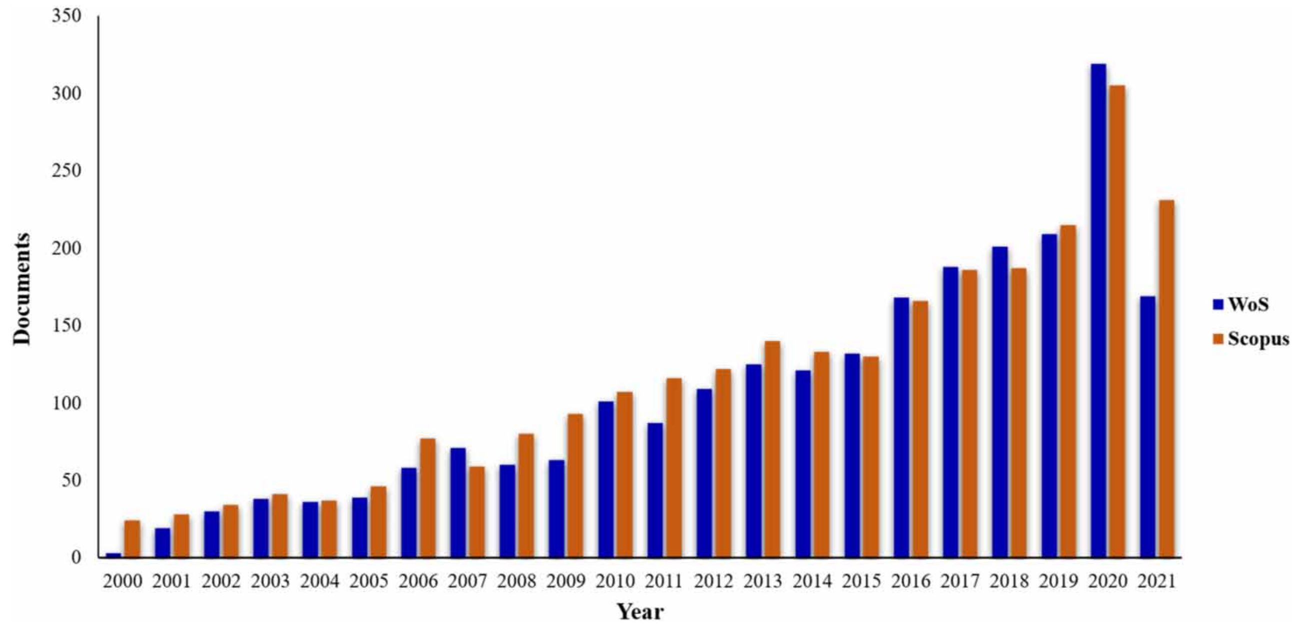


Figure 2 | Analysis of WoS and Scopus publications – Keywords pesticides and wastewater.

- Type of analysis: co-occurrence.
- Unit of analysis: author keywords.
- The minimum number of occurrences of keywords: 20.

With the information processed and the previous inputs defined, the map shown in Figure 3 is formed with the 51 keywords with the highest frequency and occurrence in the researches consulted by title, abstract, and keywords.

The co-occurrence analysis allows grouping the most frequent words in clusters, which are identified by a different color, and in the case of the map represented in Figure 3, there are five: red, green, blue, yellow, and purple. The size of the cluster is defined by the importance of the keyword around the whole network and in each cluster; the thickness of the lines between two clusters is related to the number of interactions established between them (Garrido-Cardenas *et al.* 2020).

By performing analysis in each cluster, the most important keywords in line with the research process can be identified, as follows:

- Cluster 1 (Yellow). It is represented by the keywords with which the information was extracted from the databases analyzed. Likewise, following the colored lines, there is a direct relationship with the characteristics of pesticides such as emerging pollutants, endocrine disruptors, their presence in underground and surface water bodies, and the evaluation of associated risks, the latter being related to the toxic characteristics and their effect on the environment.
- Cluster 2 (Red). It is represented by the keywords pesticides and wastewater treatment, which prioritizes one of the research objectives related to the treatment of WWPC. This is followed by a link to advanced oxidation treatment processes such as ozonation, Fenton and photo-Fenton, photocatalysis, and the resulting degradation processes. Processes involving activated sludge are also prioritized. This cluster represents the relevance of focusing the review on couplings between AOPs and biological processes in decontamination.
- Cluster 3 (Blue). It is represented by keywords associated with biodegradation, bioremediation, and adsorption, which are related to biological processes. Likewise, removal mechanisms and water quality are established, which correspond to the elimination of pesticides in aqueous matrices.
- Cluster 4 (Purple). This is directly related to the toxic characteristics and classification of pesticides as organic pollutants and their treatment by advanced oxidation. In this cluster, the importance of AOPs in the treatment of wastewater with recalcitrant and difficult to degrade characteristics, such as WWPC, can be highlighted.
- Cluster 5 (Green). It is related to the classification of pesticide micropollutants and how they can impact the different environmental matrices of soil and water.

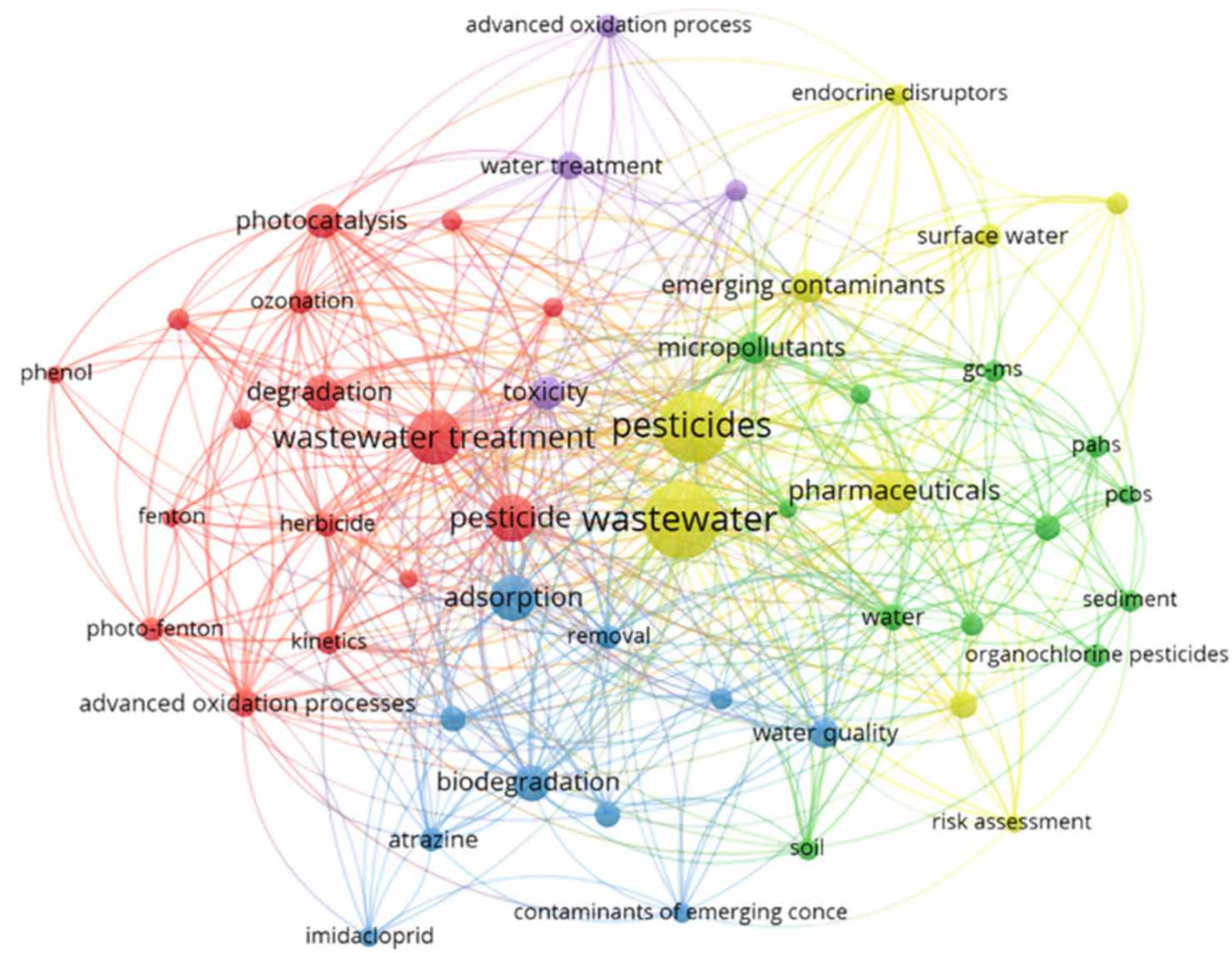


Figure 3 | VOSViewer bibliometric analysis.

The information analyzed from the co-occurrence map is coherent and is supported by the fact that the research topic addressed is a current and important trend. Therefore, based on the identified, related, and supported keywords, a search equation is developed, which must be specific to each database (WoS or Scopus) and which allows the consolidation of research related to the coupling between advanced oxidation processes and biological processes for the treatment and decontamination of wastewater containing pesticides; subsequently, the search is refined in detail for each particular coupling found.

AOP-Biological couplings in the decontamination of WWPC

Water contaminated by pesticides is a challenge, as it is not compatible with classical biological treatments due to the high toxicity for the microorganisms involved in those processes; that is where AOPs can be used as a pre-treatment step, to convert inhibitory compounds into more easily biodegradable intermediates or to reduce their concentrations to the point where inhibition is not so significant (Liberatore *et al.* 2012; Vela *et al.* 2019), so current treatment techniques involve a combination of physical, chemical and biological methods for the removal of pesticides from water (Saleh *et al.* 2020).

Intermediates generated during advanced treatment require special attention (Ballesteros Martín *et al.* 2010), through the application of toxicological methods that assess the effluent's harmful level and biodegradability before it can be transferred to biological treatment for complete oxidation (Oller *et al.* 2011), which enhances the benefits of the separate processes, so that the combination ultimately leads to significant removals of recalcitrant contaminants in wastewater that is complex to treat due to its toxic components.

Fenton/Photo-Fenton coupling and biological processes

The most widely used couplings in this area have been the Fenton/Photo-Fenton – Biological processes, whose AOP consists of a mixture of hydrogen peroxide (H_2O_2) and divalent iron (Fe^{2+}) catalyst species in low quantities, operating at room temperature and under acidic pH values (Vagi & Petsas 2020), highlighting that these chemical oxidation processes can successfully remove up to 100% of pesticides (Ahmed *et al.* 2017).

Table 1 details the design criteria and efficiencies obtained in each process studied, as well as the type of coupling evaluated. Starting with Benzaquén *et al.* (2016), the results show that the chemical oxidation process is favored by the presence of UV, since in comparison with the Fenton process alone, the removals in terms of total organic carbon (TOC) and Atrazine (ATZ) are higher when Photo-Fenton is applied; likewise, the consumption of iron and peroxide decreases notably when achieving these results in the intermediate doses evaluated, in comparison with the Fenton that required the highest doses, under the same treatment time.

Photooxidation of ATZ allows the transformation of the pesticide into cyanuric acid, establishing that this compound is not inhibitory to microorganisms, which proves the ability of AOPs to convert recalcitrant compounds into more biodegradable substances (Liberatore *et al.* 2012; Vela *et al.* 2019). However, Benzaquén *et al.* (2016) established that in the aerobic biological treatment the microbial population could not incorporate significant amounts of C or N from cyanuric acid, so the anaerobic process was where the removal of this by-product was achieved in 7 days.

In the case of Zapata *et al.* (2010) different percentages of mineralization were studied in the AOP in order to enhance the removal of dissolved organic carbon (DOC) in the immobilized mass biological reactor (IBR), having to increase the time of chemical oxidation to 2 hours, which results in the generation of ammonium and nitrate intermediates that cannot be removed in the biological process because there is not adequate colonization of nitrifying bacteria, which goes hand in hand with progressive and careful acclimatization in the IBR before disposing the effluent from the Photo-Fenton process. The intermediates generated are a product of the nature of the nitrogenous pesticides treated in this research.

The potential of the Fenton process without the presence of UV light has also been evaluated for the removal of specific pesticides in aqueous solutions, such as Sanchis *et al.* (2014) who treated Alachlor, ATZ and Diuron nitrochlorinated herbicides, determining that the degree of pollutant removal in terms of TOC and COD reported in Table 1 did not increase further, due to the refractory character of the by-products generated in the chemical oxidation, highlighting that the combination with a UV light source would have contributed to lower degradations in the treatment process. This is consistent with Fareed *et al.* (2021), who evaluated ATZ removal under Fenton and Photo-Fenton processes, determining that the latter was the more efficient process.

Analyzing the by-products in the process of Sanchis *et al.* (2014), DEIHA (desethyldesisopropyl-2-hydroxyatrazine), oxalic acid, and aniline are generated, which increase the ecotoxicity of the effluent and their appearance is related to the increase in peroxide doses. Furthermore, under low doses of H_2O_2 the biodegradability properties of the effluent decrease because inhibition occurs in the biomass due to the formation of 2,4-diethylaniline in the decomposition of Alachlor. Although the ecotoxicity was higher in the Fenton effluent compared to the original one, the generated compounds turned out to be more biodegradable, which allowed the anoxic stage of the sequencing batch reactor (SBR) to contribute to higher TOC and COD removals and the elimination of toxic by-products thanks to an important activity in the biomass in the aerobic conditions of the biological process.

Another case of the Fenton process without UV light is given for the herbicides Chlorophenoxy of 2.4D and MCPA (Sanchis *et al.* 2013), where it is established that high doses of peroxide make TOC and COD removals very slow due to the refractory characteristics of the by-products; likewise, acetic and oxalic acid are generated, the latter being related to the peroxide dose (the higher the dose, the higher the generation of this acid) and when the stoichiometric ratio of H_2O_2 decreases; hence the importance of evaluating different stoichiometric doses, the optimum dose reported in Table 1 being the one that allows a significant reduction of COD and TOC in the SBR, as well as the total elimination of the by-products generated in the AOP.

SBR type biological systems have been the most widely implemented in conjunction with Fenton oxidation, such as Gomez-Herrero *et al.* (2020), who treated a pure and commercial presentation of the insecticide Thiamethoxam (TXM), determining that the coupling system in the AOP-Biological configuration allows reducing H_2O_2 consumption and generating more biodegradable effluents; as well, the stoichiometric ratio based on peroxide consumption is very important, since a 25% stoichiometric ratio was sufficient to eliminate the active compounds of the pesticide, but doses around 50% generated ferric by-products that decrease the amount of iron available and inhibit the production of hydroxyl radicals; hence, the optimal dose reported in Table 1 is 75%.

Table 1 | Design criteria and efficiencies of Fenton/Photo-Fenton-Biological couplings

AOP – Biological Process Coupled	Design Criteria		Treatment Efficiency			Reference
	AOP	Biological Process	AOP	Biological Process	Coupling	
Fenton/Photo-Fenton in a laboratory scale reactor with borosilicate glasses and UV light + Batch aerobic reactor.	• pH 2.8 – 3.0. • UV black light lamp (315 – 400 nm). • Treatment time: 480 min. • Dose Fe^{3+}: 5, 15 and 25 mg·L^{-1}.	• Solution of nutrients and lyophilized bacteria as inoculums. • pH 6.5–7.0; Air flow 7–8 ppm; 120 h of treatment; Inoculum of consortium of acclimatized microorganisms.	• Photo-Fenton: TOC 60%; ATZ 100%. 175 H_2O_2/ATZ and 15 mg·L^{-1} Fe^{3+}. • Fenton: TOC 48%; ATZ 85%. 350 H_2O_2/ATZ and 25 mg·L^{-1} Fe^{3+}.	• There was no significant removal of cyanuric acid.	Conversion of ATZ to cyanuric acid in the AOP, which is a less toxic compound that can be eliminated under anaerobic treatment conditions.	Benzaquén *et al.* (2016)
Fenton/Photo-Fenton in a laboratory scale reactor with borosilicate glasses and UV light + Batch stirred anaerobic reactor.	• Dose H_2O_2: molar ratio H_2O_2/ATZ of 35, 175 and 350	• Inoculum sludge from a UASB reactor; 120 h of treatment	• Both in 120 min of treatment.	• Total elimination of cyanuric acid in 7 days		Benzaquén *et al.* (2016)
Solar Photo-Fenton in CPC + Immobilized Biomass Reactor (IBR)	• pH 2.8. • Fixed concentration Fe^{2+} 20 mg·L^{-1}. • H_2O_2 continuously measured until the required mineralization is obtained	• Composed of 1 neutralization tank +2 biomass reactors +1 conditioning tank. • Operating in continuous and discontinuous mode. • pH and DO control. • Inoculum of a WWTP. • HRT 20 h. • Direct acclimatization of biomass to AOP effluent.	• DOC: 54%. • Time 2 h. • Total elimination of the active ingredients of treated pesticides	• DOC: 35%. • Time less than 1 day. • The byproducts generated in the ammonium and nitrate AOP are not removed.	• DOC: 89%	Zapata *et al.* (2010)
Lightless Fenton Reaction + Sequencing Batch Reactor (SBR)	• Glass reactor with controlled temperature and constant agitation. • pH 3. • Molar rate Fe^{2+}/H_2O_2 of 20, 40, 60, 80 and 100.	• Inoculum sludge from a WWTP. • pH and DO control. • Constant agitation and aeration. • HRT: 12 h. • Organic load: 0.2 and 0.3 kg COD/kg VSS*day. • Cell retention: 30 d. • Ecotoxicity Microtox test with *Vibrio fischeri* bacteria.	• Complete elimination of pesticides in 3 hours. • COD: 60–65%. • TOC: 50–55%. • Optimal dosage of 60% of stoichiometric value.	-	• TOC and COD: >80%.	Sanchis *et al.* (2014)

Lightless Fenton Reaction + Sequencing Batch Reactor (SBR)	• Glass reactor with controlled temperature and constant agitation • pH 3. • Molar rate Fe^{2+}(1)/ H_2O_2(10)	• Inoculum sludge from a WWTP. • HRT: 12 h. • Biomass concentration was maintained at around 1 g VSS.L^{-1}. • Cell retention: 30d. • Ecotoxicity Microtox test with *Vibrio fischeri* bacteria.	• About 63% of COD and TOC. • Optimum dosage between 60–80% of stoichiometric value.	-	• About 90% of COD and TOC	Sanchis *et al.* (2013)
Lightless Fenton Reaction + Sequencing Batch Reactor (SBR)	• pH 3. • Between 25 and 100% of the stoichiometric value of Fe^{2+}(1)/H_2O_2(10)	• 6 h treatment: filling and anoxic conditions, aeration, sedimentation and removal. • Organic load 0.15 kg COD.VSS d^{-1} • Ecotoxicity Microtox test with *Vibrio fischeri* bacteria.	• Complete elimination of the pesticide. • TOC: 40–55%. • COD: 60–80%. • Optimum dose of 75% of stoichiometric value. • BOD_5/COD ratio from 0.09 to 0.43.	-	• TOC and COD removal >80%	Gomez-Herrero *et al.* (2020)
Lightless Fenton Reaction + Moving Bed Biofilm Reactor (MBBR)	• 1 L reactor with constant agitation and addition of iron and peroxide. • Fixed dose Fe^{2+} 40 mmol/L. • Varied H_2O_2 dosage. • Working pH 2.0. • Time 2 h. • Subsequent pH adjustment to 7.5 to precipitate iron ions.	• Microbial inoculums with a concentration of 5,000 mg·L^{-1}. • 12 h aeration. • HRT 1.5d. • Working volume: 5 L. • DO >4 mg·L^{-1}.	• COD removal: 56%. • Biodegrability from 0.18 to 0.47. • Optimal conditions of Fe^{2+} 40 mmol/L and H_2O_2 97 mmol/ L.	-	• COD removal >80%.	Chen *et al.* (2007)
Solar Photo-Fenton in CPC + Microorganism *Pseudomonas putida* CECT 324.	• Constant solar UV dose of 30 W. • pH 2.7–2.9. • Fixed dose of Fe^{2+} at 20 mg·L^{-1}. • Constant H_2O_2 dose of 100 mg·L^{-1} measured and added all the time.	• *Pseudomonas putida:* bacteria found in activated sludge. • Culture seeded in a bubble column bioreactor. • Culture times of 0, 48, 72 and 120 h.	• Elimination of active ingredients of pesticides in 78 min. • COD degradation of 40%.	• Biodegradation efficiency of 97% after 199 min in the AOP.	-	Ballesteros Martín *et al.* (2008a, 2008b)

(*Continued.*)

Table 1 | Continued

AOP – Biological Process Coupled	Design Criteria		Treatment Efficiency			Reference
	AOP	Biological Process	AOP	Biological Process	Coupling	
Solar Photo-Fenton in CPC + Microorganism *Pseudomonas putida* CECT 324.	• Constant solar UV dose of 30 W. • pH 2.7–2.9. • Fixed dose of Fe^{2+} at 20 mg·L^{-1}. • Constant H_2O_2 dose of 100 mg·L^{-1} measured and added all the time.	• *Pseudomonas putida:* bacteria found in activated sludge. • Turntable shaker in 100 mL Erlenmeyer flasks. • Analysis for different concentrations of the treated pesticides. • Culture times of 0, 48, 72 and 120 h.	• Treatment time of 224 min. • Mineralization >40%.	• 96 h of culture. • Biodegradation efficiency of 91%.	-	Ballesteros Martín *et al.* (2008a, 2008b)
Solar Photo-Fenton in CPC + Batch activated sludge reactor	• Constant solar UV dose of 30 W. • pH 2.7–2.9. • Fixed dose of Fe^{2+} at 20 mg·L^{-1}. • Constant H_2O_2 dose of 100 mg·L^{-1} measured and added all the time.	• Biodegradability with *Pseudomonas putida* bioassays. • PVC stirred tank batch reactor for the biological process. • Air flow 4 L·min^{-1}. • Agitation at 150 rpm. • Inoculum sludge from a WWTP.	• Active ingredients of pesticides completely eliminated. • COD removal 31% in 140 min.	-	• COD removal 90% in 300 min.	Ballesteros Martín *et al.* (2009a, 2009b)
Immobilized Biomass Reactor (IBR) + Solar Photo-Fenton in CPC + Biological Oxidation.	• Constant solar UV dose of 30 W. • Fixed dose of Fe^{2+} at 140 mg·L^{-1}. • H_2O_2 dosage was maintained between 200 and 500 mg·L^{-1} controlling its concentration to compensate for consumption.	• Zahn Wellens biodegradability test. • IBR Flat-bottom conditioning tank with 62 propylene ring units and inoculated with activated sludge. • DO and aeration control in the IBR.	• Total elimination of the active ingredients of the pesticides. • After Photo-Fenton treatment the effluent was biodegradable under the Zahn Wellens test. • Optimal conditions: 2.3 kJUV·L^{-1}; 45 min; 16 mM H_2O_2. • Degradation of pre-oxidized effluent in IBR: COD 68% and DOC 60%	• Preliminary biological: BOD_5 88–99%; COD 46–45%; DOC 41–56% • BOD_5/COD ratio of 0.18. • Did not remove pesticide active ingredients.	• COD removal of 82% and DOC of 79%	Vilar *et al.* (2012)

Solar Photo-Fenton in CPC + Membrane Bioreactor (MBR)	• Constant solar UV dose of 30 W • Fixed dose of Fe^{2+} at 20 mg·L^{-1}. • Constant H_2O_2 dose of 100 mg·L^{-1} measured and added all the time.	• Working volume of 20 L • Activated sludge inoculum. • 3 flat leaf membranes, filtration area of 0.32 m^2. • HRT 5.5 and 8.3 h. • Operated in 100 days during 4 stages: 3 acclimatization, 1 of coupled treatment.	• Mineralization of 34% and total elimination of pesticide active ingredients.	• High toxicity and low biodegradability mediated by inhibition of *Vibrio fischeri* and Zahn Wellens, respectively	• DOC removal of 94.1%. • Effluent with reuse conditions.	López *et al.* (2010)
Effluent from a solar Photo-Fenton process + Membrane Bioreactor (MBR)	• The AOP was not developed since the objective was to determine a HRT at the optimum MBR under an assay in the BOD_5 measurement.	• Anoxic reactor coupled to the MBR. • 1 flat sheet membrane with a filtration area of 0.1 m^2. • Inoculum sludge from a municipal wastewater plant. • BOD_5 analysis in WTT Oxitop© bottles incubated for 5 days.	• Mineralization of 57% in 383 min. • Mineralization of 40% in 260 min. • 1.306 mg·L^{-1} of H_2O_2 consumed.	-	• 99% mineralization for 57% pretreatment. • 98% mineralization for 40% pretreatment.	Cabrera Reina *et al.* (2015)

By-products generated in the treatment process in the research of Gomez-Herrero *et al.* (2020) were formic and acetic acid, whose concentration is directly proportional to the applied peroxide dose; however, it is concluded that stoichiometric ratio doses lower than 75% generate more ecotoxic by-products and on the contrary, higher doses do not significantly improve the biodegradability of the effluent. Thus, these optimal experimental conditions allow the biological coupling process with the SBR to further enhance TOC and COD removal and reduce the formation of unknown by-products and short-chain organic acids.

Biological processes such as MBBR have also been coupled with light-free Fenton processes such as Chen *et al.* (2007) to treat effluents from pesticide factories with a large variety of these toxic compounds and recalcitrant conditions. In this case, the experimental designs are based on fixing the iron dose and varying the peroxide doses, to analyze the behavior of this oxidant versus the treatment efficiencies. The results show that the removal of COD and TOC is related to the increase in the biodegradability of the effluent and that this in turn is enhanced by the increase in H_2O_2 doses; however, a saturation point is reached where no further removal occurs.

Also, an uncontrolled increase in peroxide doses can inhibit the generation of OH radicals (Chen *et al.* 2007), as also reported in Gomez-Herrero *et al.* (2020). One aspect to highlight that has not been discussed in previous research is that the Fe^{2+} dose influences the reaction rate of the Fenton process, as reported by Chen *et al.* (2007); however, a concentration that does not affect bacterial growth must be guaranteed (Ballesteros Martín *et al.* 2008a, 2008b), so optimizing this parameter in the experimental design contributes to significant improvements in the advanced oxidation process. (Chen *et al.* 2007) attacked this problem by neutralizing the oxidized effluent in the Fenton process to a value of 7.5 and thus precipitating the ferric ions for subsequent coagulation and removal.

An important and outstanding feature of advanced oxidation processes is that they improve the biodegradability conditions of recalcitrant effluents and provide suitable conditions for further degradation in biological reactors (Barba-Ho & Becerra 2011; Barba-Ho *et al.* 2011; Loveira *et al.* 2019). This is demonstrated by (Ballesteros Martín *et al.* 2008a, 2008b) who evaluated the biodegradation efficiency of an effluent previously treated in a solar Photo-Fenton process for the removal of four commercial pesticides, whose purpose was to determine the appropriate photo-treatment intensity and the effects of the intermediates generated in the AOP on the growth of the bacterium *Pseudomonas putida* CECT 324.

During their biodegradability analysis, Ballesteros Martín *et al.* (2008a, 2008b) determined that when the active ingredients of the pesticides are eliminated in the AOP there is a faster cell growth due to decreases in the concentration of DOC, which highlights the importance of these toxic compounds being eliminated as they damage the metabolism of the biomass. Likewise, a directly proportional relationship is established between biodegradation and irradiation time in chemical oxidation, however, the use of combined systems must consider the minimum intensity of photo-treatment at which pesticides are destroyed and begin to increase the efficiency of biodegradation, which goes hand in hand with the optimization of experimental designs in the advanced oxidation process (Becerra *et al.* 2020c).

Another biodegradability test under the same process above but this time on two particular pesticides: a fungicide (Pyrimethanil) and a herbicide (Alachlor) (Ballesteros Martín *et al.* 2008a, 2008b) determined that in the absence of light for the Fenton process some pesticides manage to be eliminated, as in the case of Alachlor, however, illumination is necessary to achieve significant mineralizations. They determine toxic by-products such as aniline which decreases the efficiency of biodegradation on the bacterial substrate, establishing that a longer photo-reaction time is required so that the toxic intermediates generated are degraded, the toxicity of the Photo-Fenton effluent decreases, and the biodegradation efficiencies are significant.

It is established that the behavior of each pesticide in the process is different due to their chemical compositions (Chu & Rao 2012; Díez *et al.* 2019) that for this case, the conversion time needed for Alachlor was always longer than for Pyrimethanil, but in all cases, the by-products managed to be more biodegradable than the original compounds (Ballesteros Martín *et al.* 2008a, 2008b) highlighting the importance as in (Ballesteros Martín *et al.* 2008a, 2008b) where total removal of the pure substance is required for the biodegradation of the intermediates formed.

This is how (Ballesteros Martín *et al.* 2009a, 2009b) achieved low AOP mineralization in a short treatment time, which was sufficient to completely eliminate the active ingredients of the mixture of the 4 treated pesticides, contributing to an additional mineralization efficiency in the biological process, which allows the coupling to contribute satisfactorily to the efficient removal of pollutants. Similarly, the authors propose to mix the effluent of the Photo-Fenton intermediates with a source of biodegradable carbon in order to achieve greater acclimatization of the activated sludge and thus obtain better results, as this allows overcoming the low biodegradability present.

This is in line with the research of (Ballesteros Martín *et al.* 2009a, 2009b) who evaluated the same processes described above for Photo-Fenton/Biological couplings but this time for two different DOC concentrations (200 and 500 $mg{\cdot}L^{-1}$) in the same pesticide mixture, concluding that the amount of chemical oxidation necessary before the biological oxidation step depends on the concentration of the pollutants and their nature, which precedes a particular study in each case. In addition, the original concentration of the pesticide is a relevant aspect since the higher the concentration, the longer the treatment time required with Photo-Fenton, as well as the recalcitrant condition of the intermediates formed, which goes hand in hand with mixing these effluents with a source of biodegradable carbon as initially proposed in Ballesteros Martín *et al.* (2009a, 2009b).

Chemical oxidation has always been specified as a pretreatment due to the recalcitrant conditions of the wastewater in order to decrease toxicity levels and improve conditions for subsequent biodegradation in biological reactors (Manenti *et al.* 2015; Paździor *et al.* 2019); however, some cases have been reported, such as Vilar *et al.* (2012), who treated wastewater from the washing of plastic pesticide containers whose characteristics of high biodegradability (BOD_5/COD ratio of approximately 0.8) and low toxicity allowed a preliminary biological process to be carried out, with this system having a treatment configuration of initial biological oxidation to remove the biodegradable organic carbon fraction; subsequent solar AOP Photo-Fenton for the conversion of pesticides into low molecular weight carboxylate anions; followed by a biological oxidation polishing stage to remove the residual biodegradable organic carbon.

The results obtained in Vilar *et al.* (2012) establish that in the preliminary biological process almost 90% of the biodegradable organic carbon represented as BOD_5 and around 50% in COD and DOC are removed, which led to the effluent biodegradability decreasing drastically due to the recalcitrant condition of the active compounds of the pesticides that were not removed in this stage. The application of the subsequent AOP allows the complete removal of the pesticides, and the effluent under the Zahn Wellens test showed biodegradation efficiencies higher than 80%, which favored the final biological polishing stage and the complete removal of organic nitrogen, as a consequence of the by-products generated in the chemical oxidation.

The hybrid treatment structures studied so far, being so innovative and thought of as the future of wastewater treatment with recalcitrant characteristics, should provide more than an effluent to be discharged into the environment and instead achieve an effluent with reuse characteristics, as the continuous reuse of treated water is a technique thought to enhance the benefits of the technologies, which is consistent according to Rosa *et al.* (2020), who after treatment determined that reuse provides a 92.86% reduction in water use and a 22.47% reduction in total cost, demonstrating that it is possible to reduce the consumption of water and chemicals, along with a reduction in environmental impacts and costs.

In the area of WWPC treatment, the reported couplings that have achieved water reuse have been in applications of biological processes such as MBR, which are a combination of conventional activated sludge with membrane separation technique, which allows meeting reuse standards (Santos *et al.* 2011; de Almeida Lopes *et al.* 2020); however, in the case of effluents containing emerging pollutants such as pesticides, complete biodegradation does not occur, giving rise to the need to combine MBR technology with other treatment technologies (Ruel *et al.* 2011; de Almeida Lopes *et al.* 2020).

At this point, AOPs become important because they are ideal as an alternative for pretreatment in membrane bioreactor processes as their integration is a great advantage due to higher purification efficiencies, lower chemical and energy costs, better membrane flux, and reduced fouling (Iglesias *et al.* 2016; Rostam & Taghizadeh 2020).

Thus, the coupling between Photo-Fenton processes and MBR for the decontamination of wastewater containing pesticides arises as López *et al.* (2010), who corroborate the toxic conditions and low biodegradability of these effluents, in this case, a mixture of five commercial pesticides, utilizing the tests described in Table 1. Likewise, chemical oxidation allows the pesticide molecules to be attacked with hydroxyl radicals, which give rise to organic intermediates, but without a strong decrease in DOC concentration. The MBR output provides a high-quality effluent, with low residual DOC concentration, absence of the original pesticides, absence of suspended solids, and turbidity values (NTU) below 0.5, which are particular characteristics of wastewater for reuse.

It should be noted that the acclimatization time of the biological process mediated in the MBR (López *et al.* 2010) results in good stability of the treatment system, since the operating conditions, transmembrane pressure, aeration conditions, flow, and aerator design were adequate for the biological conditions, which is evident in the quality of the treated water at the end of the coupling process.

Cabrera Reina *et al.* (2015) treated five pesticides of different commercial names, but with the same active ingredients of the previous treatment and under the same Photo-Fenton/MBR configuration, but coupling this time an anoxic reactor to the MBR. For this case, the research aimed to find an optimal HRT in the biological process for the effluent pretreated by Photo-Fenton and to ensure the shortest possible total time. For this reason, they evaluated two different mineralization percentages in the AOP as shown in Table 1, which determines that the lowest mineralization level (40%) results in a 30%

reduction in treatment time and 25% reduction in hydrogen peroxide consumption, which affects the process costs, comparing that in the coupling efficiency the difference between both mineralization percentages (40 and 57%) is not significant, being conclusive that the effluent quality is not affected.

The decomposition of pesticides in the AOP in this research (Cabrera Reina *et al.* 2015) generates nitrogen by-products that greatly increase the concentration of this compound; therefore the addition of simulated wastewater was required, allowing the C:N ratio to approach its optimum value; likewise, the anoxic reactor helped to counteract this limitation to provide more suitable conditions for subsequent biological oxidation in the MBR. This demonstrates what was previously discussed related to the fact that the behavior of each pesticide in the process is different due to their chemical compositions (Chu & Rao 2012; Díez *et al.* 2019), with which each problem related to WWPC becomes a particular study that depends on the type of pesticide targeted in the treatment.

At this point of the research, it can be inferred that the main limitations in the application of the Fenton or Photo-Fenton process have been the generation of intermediate oxidation by-products due to two aspects: 1. the reaction of the oxidant with the typical characteristics of the group of pesticides treated; 2. The reaction of the catalyst (Fe^{2+}) with the oxidant, which leads to the generation of iron by-products when the stoichiometric ratio is not adequate since the concentration of the catalyst decreases completely and there is no adequate consumption of the oxidant. These limitations establish two aspects of importance: 1. The ecotoxicity of the effluent from advanced oxidation increases, limiting the conditions for biological oxidation; 2. The maximum oxidizing conditions applied cannot contribute more to the reduction of the recalcitrant characteristics of the target wastewater, so the most applied combination has been to advanced biological processes, allowing the removal of compounds that are not eliminated in the AOP and improving the conditions for subsequent biological oxidation.

TiO_2/UV photocatalyst coupling and biological processes

Table 2 details the design criteria and efficiencies obtained in each process studied, as well as the type of coupling evaluated.

Photocatalytic processes involve the use of a series of semiconductors that allow the conversion of photon energies into chemical energy. Among the most commonly used semiconductors, TiO_2 has photochemical stability and photocatalytic activity favorable to the treatment of several pollutants (Hoffmann *et al.* 1995; Yuan *et al.* 2019). It has also been shown that better results are obtained in these treatments when they are developed in the presence of UV radiation (Del Moro *et al.* 2013; Liu *et al.* 2016).

These AOPs have been effective in the treatment of pesticides in aqueous solutions, improving the biodegradability conditions of the effluent and highlighting their use as a pretreatment for subsequent biological oxidation (Affam & Chaudhuri 2013). Likewise, the efficiency of the process benefits from the addition of H_2O_2, but there is a limitation related to the increased catalyst loading, as this increases the turbidity conditions of the treated wastewater, which limits the amount of light reaching the active surfaces (Gar Alalm *et al.* 2015).

Hybrid treatment techniques are important because implementing an AOP as a single treatment step is costly, so advanced oxidation is intended to be as short as possible until a more biodegradable and less toxic effluent is available for further degradation in biological treatments (Da Costa *et al.* 2018), or used as a final polishing step to remove specific pollutants that cannot be removed in conventional treatments (Zhao *et al.* 2020).

Constructed wetlands are systems involving natural processes associated with the type of vegetation and soil used, which determine specific microbial assemblages to treat wastewater (Vymazal & Březinová 2015), and their efficiency has been extended to the field of pesticide and/or pesticide-contaminated water removal, becoming a sustainable, economical, robust and ecological technique for the removal of these toxic compounds (Lv *et al.* 2016; Lyu *et al.* 2018).

However, the future trend in this engineered wetland technology faces new challenges resulting from the need to treat wastewater with new technologies, the presence of newly found organic compounds in wastewater, and also stricter discharge limits worldwide (Vymazal *et al.* 2021), which is where the importance of the hybrid techniques discussed above lies as an emerging and viable alternative for the removal of toxic and recalcitrant compounds such as pesticides.

Thus, Araña *et al.* (2008) developed a coupling with these surface wetland technologies, as shown in Table 2, for the elimination of a mixture composed of two herbicides and two fungicides. They determined the toxicity of the initial mixture to be 90% for most of the compounds studied, and after 6 h of irradiation in the AOP, reductions of between 22 and 13% were achieved. In contrast, the coupling configuration allowed a reduction of the photocatalytic treatment time to 2 and 12 h in the wetlands, for final effluent toxicity of less than 1%. It is important to note that the artificial wetlands alone could not

Table 2 | Design criteria and efficiencies of TiO_2/UV-biological photocatalysis couplings

AOP – Biological Process Coupled	Design Criteria		Treatment Efficiency			Reference
	AOP	Biological Process	AOP	Biological Process	Coupling	
TiO_2/UV photocatalysis + Surface wetlands	• Aqueous suspension in glass containers with constant agitation. • Catalyst dosage 1 $g{\cdot}L^{-1}$ (Degussa P25). • pH = 5. • UV dosage 60 W.	• Reactors in plastic containers. • Three different reactors: one with only gravel and no plants, one with gravel and four common reed mats, and one with gravel and four papyrus mats. • Acclimation of 15 d to treated pesticides. • Toxicity test *Lemna minor* in Petri dishes.	• Pesticide degradation at 120 min of treatment. • After 6 h, the inhibition percentages ranged from 22 to 33%	• Toxicity. Inhibitions higher than 90% • There was no degradation of the active ingredients of the pesticides and no decrease in the toxicity of the effluent.	• After 12 h the inhibitions were less than 1%	Araña *et al.* (2008)
Immobilized Biomass Reactor (IBR) + Solar Photocatalysis in CPC with TiO_2 and H_2O_2	• TiO_2 supported on glass beads with sol-gel technique and in suspension (two different experiments) • Volume 8 L, irradiated area 0.250 m^2. • Dosage of H_2O_2 100, 200 and 500 $mg{\cdot}L^{-1}$.	• Organic load: 1.2–2.4 $g{\cdot}L^{-1}$. • DO >2 $mg{\cdot}L^{-1}$.	• TiO_2 supported: at 20 $kJ{\cdot}L^{-1}$ eliminations of pesticides around 20–40% • Suspended TiO_2: at 20 $kJ{\cdot}L^{-1}$ pesticide eliminations between 60 and 80%. • TiO_{2+}500 $mg{\cdot}L^{-1}$ H_2O_2: at 15 $kJ{\cdot}L^{-1}$ two of the three pesticides were completely eliminated, and the remainder in a percentage of 92%.	• 95% DOC and COD removal.	• Complete elimination of the pesticides studied	Jiménez-Tototzintle *et al.* (2015)
Solar Photo-Fenton + Subsurface flow artificial wetlands	• pH 3.0. • Pilot scale photoreactor. • UV-A intensity of sunlight between 2.5 and 4.5 $mW{\cdot}cm^{-2}$. • Dose: 7 $mg{\cdot}L^{-1}$ Fe^{3+} , 100 $mg{\cdot}L^{-1}$ H_2O_2.	• Three wetlands. • HRT 6 d. • Hydraulic load 1.5 $L{\cdot}d^{-1}$. • Substrate: sandy loam soil and zeolite (5:1) • Seeded with *Typha spp* macrophytes.	• 49% DOC reduction • 60 min of treatment. • Complete elimination of the pesticide.	• Reduction of nitrate ions by 89%, generated as by-products of advanced oxidation	• 93% reduction in DOC.	Berberidou *et al.* (2017)
Solar ferrioxalate + Subsurface flow artificial wetlands	• pH 3.0. • Pilot scale photoreactor. • UV-A intensity of sunlight between 2.5 and 4.5 $mW{\cdot}cm^{-2}$. • Dose: 7 $mg{\cdot}L^{-1}$ Fe^{3+} , 100 $mg{\cdot}L^{-1}$ H_2O_2; 33 $mg{\cdot}L^{-1}$ $C_2O_4(^{2-})$.	• Acclimatization of 10 d with AOP effluent.	• 47% reduction in DOC. • 60 min of treatment. • Complete elimination of the pesticide.	• Reduction of nitrate ions by 87%, generated as by-products of advanced oxidation	• 92% reduction in DOC.	

(*Continued.*)

Table 2 | Continued

AOP – Biological Process Coupled	Design Criteria		Treatment Efficiency			Reference
	AOP	Biological Process	AOP	Biological Process	Coupling	
Solar Photo-Fenton + TiO_2 Degussa P25 + Ferrioxalate + Subsurface flow artificial wetlands	• pH 3.0. • Pilot scale photoreactor. • UV-A intensity of sunlight between 2.5 and 4.5 $mW{\cdot}cm^{-2}$. • Dose: 3.5 $mg{\cdot}L^{-1}$ Fe^{3+}, 100 $mg{\cdot}L^{-1}$ H_2O_2; 33 $mg{\cdot}L^{-1}$ $C_2O_4(^{2-})$; 0.5 $g{\cdot}L^{-1}$ TiO_2.		• 53% reduction in DOC. • 60 min of treatment. • Complete elimination of the pesticide.	• Reduction of nitrate ions by 66%, generated as by-products of advanced oxidation	• 87% reduction in DOC.	
Solar photocatalysis in CPC with TiO_2/H_2O_2 + Batch activated sludge at laboratory scale	• Collector area of 0.83 m^2. • pH: 3, 6 and 9. • TiO_2 dose: 100, 350 and 600 $mg{\cdot}L^{-1}$. • Fixed H_2O_2 dose at 100 $mg{\cdot}L^{-1}$. • Accumulated energy of 20, 40 and 60 $kJ{\cdot}L^{-1}$.	• Zahn Wellens test. • 2 reactors with pesticide, 2 blank reactors, 2 reactors with ethylene glycol as reference compound, 2 reactors for volatilization control. • Respiration inhibition test and oxygen consumption rate. • Sludge volumetric index for inoculum.	• 47% reduction in DOC. • Conditions 60 $kJ{\cdot}L^{-1}$; 159.9 $mg{\cdot}L^{-1}$ TiO_2; pH 3.47.	• Degradations below 30% indicate the recalcitrant condition of the pesticide-containing wastewater.	• Removal DOC 67%.	Becerra *et al.* (2020a)
Solar photocatalysis in CPC with TiO_2/H_2O_2 + Specific Methanogenic Activity Test (SMA).		• Volumetric method with quantification of methane production by use of a displacer substance. • pH >12 • Flocculant sludge at a concentration of 2.0 g $VSS{\cdot}L^{-1}$.	• COD removal 59.6%. • Conditions 60 $kJ{\cdot}L^{-1}$; 100 $mg{\cdot}L^{-1}$ TiO_2; pH 3.	• COD removal 46%.	• COD removal 72%.	Becerra *et al.* (2020b)

eliminate the active ingredients of the pesticides or lower the toxic load of the effluent; it is not until after pretreatment with the AOP that an effluent with suitable conditions for the subsequent biological process is provided. It was also determined that the different plant species used in the reactors did not affect the degradation of the process.

The results obtained above are in agreement with Arshad *et al.* (2020) and Chen *et al.* (2020), who established that determining the optimal conditions in an AOP goes hand in hand with the efficient use of resources and that the treatment objectives are enhanced towards the maximum possible degradation of pollutants. It is also important to study the intermediates generated in the oxidation and to exercise control to avoid inhibition in the subsequent biological process.

Berberidou *et al.* (2017) evaluated the coupling between three advanced oxidation processes to biological treatment of artificial wetlands, determining that the photocatalytic process mediated by TiO_2 alone and in the presence of H_2O_2 does not lead to significant mineralization. Among the couplings evaluated, the highest photocatalytic oxidation in terms of DOC is given for the coupling involving the three AOPs, although the difference between them is not so significant; however, the coupling efficiencies differ in this result as the highest DOC removal is given for the solar Photo-Fenton case, which may be related to this AOP being one of the most effective for pesticide removal (Ahmed *et al.* 2017), as discussed in the previous section.

By-products generated in this treatment (Berberidou *et al.* 2017) are related to nitrate ions, which increased in all photocatalytic oxidation processes due to the mineralization of organic nitrogen; on the other hand, the artificial wetlands were able to reduce these levels but they were not completely removed. Importantly, the pesticide was already absent at the outlet of the AOP, as well as at the outlet of the wetlands, so the final effluent was free of the original herbicide molecule.

Cases have been reported in which the efficiency of photocatalytic oxidation treatment is evaluated in different biological processes for the same pesticide, such as the case of Becerra *et al.* (2020a, 2020b), who treated wastewater containing the pesticide Chlorpyrifos, coming from the washing of manual crop spraying equipment, under the coupling processes described in Table 2. Both investigations carried out the same design of experiments for the AOP, with a 3^2 factorial design for TiO_2 dose and pH level, at fixed cumulative energy levels where samples were taken at each of them and analyzed in terms of COD and DOC. The optimization of the response was to obtain the maximum possible degradation in the AOP, and then this effluent was the input for the biological processes evaluated.

Optimal conditions in photocatalytic oxidation (Becerra *et al.* 2020a) were determined at acidic pH, low TiO_2 concentration, and at the maximum cumulative energy evaluated. The evaluation of the batch-activated sludge biological system mediated by the Zahn Wellens test determined that the treated wastewater was not biodegradable under aerobic reactors as the percentage of biodegradation was below 70%. The AOP under optimal conditions achieved low but sufficient mineralization to promote biodegradability and enhance pollutant degradation, as the photocatalytic effluent input to the biological coupling process allowed the removal of 67% DOC, compared to 47% in the AOP alone and <30% in the biological process alone.

For the case of Becerra *et al.* (2020b), the optimal conditions of the photocatalytic process also occurred at the lowest TiO_2 dosage, the most acidic pH, and under the highest accumulated energy. The biological process mediated by the Specific Methanogenic Activity (SMA), which simulates an anaerobic system, was able to support the toxic load of the evaluated wastewater but with a low COD removal; however, the effluent coming from the AOP manages to improve the wastewater conditions since the COD removal in the SMA is enhanced by almost 50%, which is consistent with the results obtained in Becerra *et al.* (2020a), since the photocatalytic process improves the effluent conditions for its subsequent oxidation in aerobic and anaerobic biological reactors.

The two previous types of research allow concluding that the optimization of the design parameters in the AOP is an important aspect, as this helps to obtain the highest process efficiencies hand in hand with the efficient use of treatment resources (Arshad *et al.* 2020; Chen *et al.* 2020). About Degussa P25 TiO_2 doses, high catalyst loadings increase the turbidity conditions and this limits the amount of light reaching the active surfaces (Gar Alalm *et al.* 2015); therefore the maximum degradation conditions were related to the lowest doses. The pH is a parameter that enhances the benefits of these processes, as at acidic values significant photocatalytic activity develops due to a positive charge on the catalyst that attracts negatively charged pollutants (Lu *et al.* 2017; Chen *et al.* 2020).

UV energy doses contribute significantly to the efficiency of the process because longer irradiation times allow higher contaminant removals, which determines that photocatalytic degradation rates are related to the amount of illumination reaching the catalyst (Hassan *et al.* 2017). Likewise, the solar radiation source makes the system a viable and low-cost choice (Maniakova *et al.* 2020) contributing to the application of sustainable alternatives that promote in AOPs the reduction of energy consumption compared to systems using artificial UV (Borges *et al.* 2016; Rueda-Marquez *et al.* 2020).

Moreover, the combination of TiO_2 with UV makes it an efficient photocatalyst due to its high stability and ultraviolet absorption resulting in the removal of toxic and recalcitrant pollutants in the photocatalytic process (Li *et al.* 2006; Al-Mamun *et al.* 2019), which has been evidenced in the application of these AOPs for the decontamination of pesticide-containing wastewaters into a less toxic effluent and more suitable conditions for subsequent biological oxidations.

Couplings in the Biological-AOP configuration are less common; however, Jiménez-Tototzintle *et al.* (2015) studied the removal of an effluent containing Imazalil (IMZ), Acetamiprid (ACP) and Thiabendazole (TBZ) from an agri-food processing plant. The research was able to determine that the IBR biological process alone does not achieve significant pesticide removals, but high removal in terms of DOC and COD, as shown in Table 2. However, the input of the effluent from the IBR to the photocatalyst with TiO_2 supported on glass beads allows under the cumulative energies of 4 $kJ{\cdot}L^{-1}$ the complete removal of IMZ and for more, 20 $kJ{\cdot}L^{-1}$, only 22 and 46% for ACP and TBZ, respectively.

A second experiment in Jiménez-Tototzintle *et al.* (2015), treated the same effluent coming from the IBR but this time with suspended TiO_2, achieving total removal of IMZ after 2.5 $kJ{\cdot}L^{-1}$, and after 20 $kJ{\cdot}L^{-1}$ 68 and 85% of ACP and TBZ, respectively. This positive effect was due to the larger surface area of TiO_2 in the suspension, as many more particles of this catalyst can absorb radiation photons, increasing the active sites and favoring the generation of hydroxyl radicals. A third experiment is developed where the TiO_2 process supported on glass beads is combined with an electron acceptor, H_2O_2, at an optimal dose of 500 $mg{\cdot}L^{-1}$, where the efficiency of the process is notably enhanced since TBZ and IMZ are completely removed at 3.2 and 1.8 $kJ{\cdot}L^{-1}$, respectively, and in the case of ACP, 15 $kJ{\cdot}L^{-1}$ were required for removal of 92%.

Something important to highlight from the results described above is that in the case of the Biological-AOP treatment configurations, what is sought is a pretreatment capable of degrading the greatest amount of organic matter and in the photocatalytic oxidation process to seek the elimination of specific compounds, which in this case are the active ingredients of the pesticides studied; this is consistent with that discussed previously by Zhao *et al.* (2020) and studied in Vilar *et al.* (2012), establishing that the purpose of preliminary biological oxidation is to eliminate the biodegradable organic carbon fraction.

Coupling of electrochemical oxidation and biological processes

Table 3 details the design criteria and efficiencies obtained in each process studied, as well as the type of coupling evaluated.

Advanced electrochemical oxidation has been widely used in the degradation of various wastewaters due to its low cost, high efficiency, and environmental friendliness (Oturan *et al.* 2013; Solano *et al.* 2016); however, high energy consumption limits its applications, which is why recent research has seen a promising application with biological processes and thus enhancing its benefits (Yazdanbakhsh *et al.* 2015).

Accordingly, electrochemical oxidation has been coupled to biological processes in the decontamination of WWPC as by Zhang *et al.* (2020), who decontaminated wastewater from the herbicide industry containing mostly 2,4-dichlorophenoxyacetic acid (2,4-D), organophosphates, and dinitroaniline and with the particularity that these WWPC had already been previously treated by evaporation and Fenton oxidation. The experiments in the AOP had a one-factor design about COD degradation where initially the current density is optimized, then with the optimum of this factor followed by pH; then, with the current density and pH optimum, proceed to the electrode spacing. The biological process was optimized for the HRT and airflow factors. The levels of each factor are detailed in Table 3.

The electrochemical oxidation in Zhang *et al.* (2020) achieves in 120 min of treatment an improvement of the effluent biodegradability conditions represented as the BOD_5/COD ratio, as it rises from 0.18 to 0.43. However, values higher than 5 $A{\cdot}dm^{-2}$ increase the temperature of the electrolyte, which in turn influences the efficiency of the electrodes and increases energy consumption. Furthermore, the differences in removal between 4 $A{\cdot}dm^{-2}$ and 5 $A{\cdot}dm^{-2}$ are not very different, which is the reason why 4 $A{\cdot}dm^{-2}$ is the optimum value for current density. The phenomenon described above is explained by the fact that the high current density favors a secondary reaction of oxygen release at the anode, and this leads to a higher charge consumption.

As for the effect of pH in Zhang *et al.* (2020), acidic environments provide higher hydroxyl radical activity (Horáková *et al.* 2014; Sun *et al.* 2019), while in alkaline environments oxygen release reactions occur and this reduces electrochemical oxidation; thus, the two acidic pHs specified in Table 3 correspond to levels of 2 and 4. The difference between COD removals between these levels is not significant, so it works at the natural pH coming from the wastewater of 4.28; this acidic character may be related to the Fenton pre-treatment that the effluent had already had.

The electrode spacing discussed in Zhang *et al.* (2020) establishes an inversely proportional relationship with COD removal whereby smaller plate spacing is more favorable for degradation and yet spacings smaller than 1.0 cm gave negligible

Table 3 | Design criteria and efficiencies of electrochemical-biological couplings

AOP – Biological Process Coupled	Design Criteria		Treatment Efficiency			Reference
	AOP	Biological Process	AOP	Biological Process	Coupling	
Electrochemical + Activated sludge at laboratory scale	• Homemade flow cell using a graphite felt as a working electrode • pH 3.0 units. • Oxidant at 1.6 V/SCE. • Flow rate 1 mL·min^{-1}.	• Experiments in Erlenmeyer flasks inoculated with 0.5 g·L^{-1} of activated sludge.	• BOD_5/COD ratio of 0.04 to 0.25. • Mineralization of 34%.	• COD and COD degradations >70% at day 12. • Pesticides removed by day 14.	• In 2 days 79% was mineralized, on the 21st day 85%	Fontmorin *et al.* (2013)
Electrochemical + Activated sludge at laboratory scale	• Graphite felt. • Two interconnected stainless steel plates as counter electrodes. • 200 mA and flow rates of 1 and 3 mL·min^{-1}.	• Blank test without pesticide. • HRT 21 d.	• Biodegradability is not improved, the compound solution originally has it at 0.21.	• Mineralization of 33.7%.	• Final mineralization of 82.1% • 14 days of cultivation.	Fontmorin *et al.* (2014)
Electrochemical + Biological contact oxidation reactor	• Discontinuous electrochemical reactor with a capacity of 1.056 L • Equipped with 7 plate electrodes: 3 PbO_2 and 4 Ti anodes. • Effective area of 540 cm^2. • Experiment design: current density (2, 3, 4, 5 A·dm^{-2}), initial pH (2, 4, 6 and 8) and electrode spacing (0.5, 1.0, 1.5, 2.0 cm)	• 20 L capacity • Inoculated with activated sludge from a WWTP. • Constant aeration. • Experiment design: TRH 8, 10, 12 and 14 h and the amount of aeration 0.2, 0.4, 0.6, 0.8 m^3.h $^{-1}$.	• COD removal of 87% in 120 min at 4 A·dm^{-2} , pH of 4 and plate spacing of 1.0 cm. • BOD_5/COD ratio of 0.18 to 0.43.	• COD removal of 67% for a HRT of 12 h and 0.6 m3.h^{-1} of aeration.	• COD removal of 95.8%.	Zhang *et al.* (2020)
Electrochemical + Biofilter	• Discontinuous reactor • Boron doped electrode (BDD) • Current density of 5–40 mA·cm^{-2}. • Electrode spacing of 1 cm. • Flow rates of 5, 10, 20 and 40 mL·min^{-1}	• Glass tube with low porosity polypropylene packing • Activated sludge inoculum from a WWTP. • 10 days of culture for biofilm attachment.	• TOC elimination of 70.4% in 10 hours.		• TOC elimination of 85.4% in 4 h.	Liu *et al.* (2010)
Electrochemical + Activated sludge	• Graphite felt as working electrode • Conventional three-electrode cell • Cation exchange membranes • Flow rate of 1 mL·min^{-1}. • Signal of −1.3 V/SCE at neutral pH.	• Cultures in 250 mL Erlenmeyer flasks containing 100 mL of medium with 0.5 g·L^{-1} of activated sludge. • Toxicity with Microtox and *Vibrio fischeri* test.	• A single pass allowed the elimination of Fosmet • Reduction of toxicity in 15 min. • BOD_5/COD of 0.14 to 0.42.	• High toxicity of the pesticide studied.	• Mineralization of 97%.	Salles *et al.* (2010)

results; hence, the optimum plate spacing was 1.0 cm. Resistance increases with increasing electrode spacing (Prajapati & Chaudhari 2014; Fang *et al.* 2017), which increases energy consumption; hence, a spacing not so far apart is appropriate as, it allows boosting the AOP towards higher removal of target pollutants and thus ensuring optimal energy consumption, this aspect being one of the main disadvantages of the electrocatalysis process.

The biological process conditions in Zhang *et al.* (2020) were able to determine that biofilm cultivation and microbial acclimatization are important steps to enhance efficiencies, and also the electrochemical pretreatment technique solves the inhibition and toxicity conditions for microorganisms in herbicide-containing wastewater, determining the importance of biological treatment to degrade the intermediates formed in the electrochemical process that are difficult to continue with mineralization and how degradation is enhanced in terms of COD after biological oxidation, which positions electrocatalysis as a very promising pesticide-containing wastewater pretreatment with a high degradation rate of organic pollutants (Sun *et al.* 2019).

Fontmorin *et al.* (2013) treated the chlorinated pesticide (2,4-D), highlighting an increase in the biodegradability of the effluent after electrolysis as detailed in Table 3. Chlorohydroquinone is identified as the main by-product generated in the AOP, representing 35% of the residual organic carbon. Furthermore, it is established that the passage of the effluent from the electrolysis to the biological process allows the microorganisms to adapt quickly and begin to degrade the pollutants due to the mineralization that occurs in the AOP.

The above allows concluding that the electrochemical pretreatment significantly improves the mineralization rate and therefore shortens the duration of the biological treatment; the reason for this is highlighted in Table 3 (Fontmorin *et al.* 2013) when the direct biological process achieves DOC degradations $>70\%$ in 12 days, and on the contrary, the electrolyzed sample in 2 days achieves mineralization by almost 80%. However, at the end of the biological process there are no further contaminant removals, showing that a small part of the degradation products cannot be easily assimilated by the sludge. This can be improved by better optimization of the conditions at the pre-treatment stage.

Fontmorin *et al.* (2014) treated a commercial submission containing the same active ingredient 2,4-D, under the same biological process as above, but with modifications to the AOP such as the placement of two interconnected stainless steel plates as counter electrodes and where two flow rates were evaluated, a variable that had not been analyzed in previous processes. The dimethylamine salt by-product is identified, which is responsible for this effluent being more biodegradable than the pure presentation in Fontmorin *et al.* (2013), and which means that the passage through the electrolysis step does not improve this parameter but is still an adequate value for the subsequent biological process.

It highlights the low mineralization in the direct biological process and how after AOP this result is enhanced, achieving around 50% more DOC removal, as illustrated in Table 3 (Fontmorin *et al.* 2014) related to the treatment efficiencies. However, during the coupled biological process, low biodegradation rates are identified, demonstrating the presence of refractory compounds generated during the electrochemical pre-treatment at a small concentration. In all conditions analyzed, the higher flow rate in the AOP allowed more favorable results in the coupling process, but as in Fontmorin *et al.* (2013), the need for better optimization of the conditions in the pre-treatment stage is highlighted.

The graphite felt used as a working electrode has also been implemented by Salles *et al.* (2010) in an electrochemical pretreatment for the decontamination of the organophosphorus pesticide Fosmet with the use of a reference electrode, the SCE (Saturated Calomelane Electrode), for the measurement of the potential of the other electrodes. During the applied AOP, they determined that acidic and basic pHs showed no signs of significant electrochemical reductions of the pesticide, while at neutral pH total removal was achieved in a single pass through the cell at the value of -1.3 V/SCE, reported in Table 3. The optimal electrolysis conditions ensured that a highly toxic by-product, phosmet-oxon, was not formed in the pre-treated solution and that the working flow rate prevented recirculation of the solution through the electrode.

The toxicity test on Fosmet in Salles *et al.* (2010) determined the toxic nature of the pesticide in only 15 minutes, which reaffirms the recalcitrant condition of the compound analyzed and its low biodegradability, establishing that activated sludge as a direct treatment does not manage to assimilate the target compound. With the electrochemically pre-treated effluent, a TOC elimination of 97% is achieved in the biological oxidation, since in the AOP the active ingredient of the pesticide is completely degraded, which reduces the toxicity and improves the biodegradability conditions, allowing the appropriate conditions in the biological oxidation, determining the viability of the coupled process. It is also important to note that to avoid Fosmet precipitation, ethanol was used, which must be evaporated before entering the biological oxidation because it can inhibit the process.

Liu *et al.* (2010) worked the electrochemical process with a boron-doped diamond electrode in an Acetamiprid solution of 1,000 $mg \cdot L^{-1}$ and a BOD_5/TOC ratio of 0.0057, which indicates the high refractory property of the wastewater to be treated and which is reflected in the direct biological oxidation not contributing to significant TOC removals, reaffirming its low biodegradation capacity. Electrochemical oxidation manages to improve the BOD_5/TOC ratio to 1.17 and reduce toxicity by 40% in 3 hours of treatment, which provides a suitable effluent for the activity of microorganisms in the subsequent biological process. The current density is directly proportional to the biodegradability, but at the highest level evaluated no significant degradation is obtained, and on the contrary, for low values the efficiency is not improved; this is consistent with what is reported and discussed in Zhang *et al.* (2020).

The behavior concerning flow rates in Liu *et al.* (2010), states that an increase in their values increases TOC removal, but it is important to determine an optimal condition because after higher rates the process efficiencies do not improve significantly, highlighting the flow rate as an important variable in the process, as in Fontmorin *et al.* (2014). Coupling improves TOC removal and energy consumption, boosting process efficiency, as direct electrochemical oxidation requires 96 $kW \cdot h \cdot m^{-3}$ and 9 hours, but only 53.3 $kW \cdot h \cdot m^{-3}$ and 5 hours to achieve the same TOC removal in the coupled treatment, representing a reduction in energy consumption of 44.5%.

The above discussed is one of the most important aspects of electrochemical oxidation due to its high energy consumption limiting its applications in various processes (Zhang *et al.* 2013; Meng *et al.* 2021); however, it is considered an effective alternative for pollutant mineralization (Yang 2020) and as a technology that can treat various high-concentration organic wastewaters, especially pesticide wastewaters with high organic content (Tijani *et al.* 2014; Sun *et al.* 2019), as in the case of Liu *et al.* (2010), where the concentration of Acetamiprid-containing wastewater was 1,000 $mg \cdot L^{-1}$.

Ozonation and biological processes coupling

Table 4 details the design criteria and efficiencies obtained in each process studied, as well as the type of coupling evaluated.

Ozonation belongs to the group of homogeneous AOPs without energy requirements, with a high efficiency to degrade a large number of pollutants, ozone being a highly selective oxidizing agent and often used for the oxidation of organic compounds at high pH values (Vagi & Petsas 2020), and recent scientific research proves its potential in an individual way, such as de Souza *et al.* (2018), who evaluated ozone treatment for two types of pesticides, finding a removal of more than 80%; or the case of Poznyak *et al.* (2019), who established as viable and efficient the alternative of combining ozonation with biodegradation processes, concluding that after the appropriate ozonation time the amount of toxic pollutants decreases and allows subsequent degradation.

This proves that these AOPs increase biodegradability and decrease toxicity, making them suitable to be implemented as pretreatments for further degradation in biological reactors (Bilińska *et al.* 2016). Furthermore, the combination of catalysts, oxidants, UV radiation, and even with other AOPs accelerates the removal of pollutants compared to using the ozonation process alone (Malakootian *et al.* 2020).

Highlighting the potential for coupling ozonation processes with biological processes is the study of Mezzanotte *et al.* (2005), who treated wastewater from a chemical industry producing herbicides, containing mostly Triazines and Thiocarbamates, with a very high and variable COD concentration (5,000–10,000 $mg \cdot L^{-1}$), high salinity (50 $g \cdot L^{-1}$) and pesticide concentration of 13–150 $mg \cdot L^{-1}$. The high concentration of pollutants in the conditions of the effluent to be treated establishes the need to experiment with six different types of couplings, under variable doses of ozone, in particular configurations and with the addition of oxidants to the process, with pre-ozonization-biological process-recirculation to pre-ozonization and pre-ozonization-biological process-postozonization + H_2O_2 being the alternatives with the best results, but the second being the most efficient in terms of eliminating pesticides.

Based on the optimal coupling configuration, pre-ozonization-biological process-biological process-postozonisation + H_2O_2, in Mezzanotte *et al.* (2005), it is important to highlight that although ozone pretreatment improves biodegradability and eliminates a large percentage of the pesticides present, the removal of COD is not relevant. At this point, the contribution of the biological process is to improve the elimination of COD, TOC, and an additional part of the pesticides, and it also has an important efficiency in the total elimination of aldehydes generated as by-products of chemical oxidation, since their concentrations after pre-ozonization were high. However, the concentration of pollutants remaining up to this point was still high, hence the need for subsequent ozonation, allowing the high efficiencies reported in Table 4 and highlighting the total removal of pesticides from an initial process input concentration of 124,957 $mg \cdot L^{-1}$.

Based on the ozone concentrations used in this research (Mezzanotte *et al.* 2005), it is true that they were very high; however, the recalcitrant, toxic, and high pollutant concentration character justifies its use, since it provides an effluent with very

Table 4 | Design criteria and efficiencies of Ozonation-Biological couplings

AOP – Biological Process Coupled	Design Criteria		Treatment Efficiency			Reference
	AOP	Biological Process	AOP	Biological Process	Coupling	
O_3 + Adhered Biomass	• Two stainless steel contact columns. • HRT 1.5 h each column • Ozone doses: 650 and 2,000 mg·L^{-1}. • Post-ozonation with H_2O_2: molar ratio $H_2O_2/O_3 = 0.3$.	• BIOFOR submerged Filter. • Active volume of 200 L. • Expanded clay support medium. • HRT between 20 and 30 min.	• COD removal not significant in pre-ozonization • Pre-ozonization dose: 1,000 mg·L^{-1}. • Post-ozonization dose: 200 mg·L^{-1} H_2O_2/500 mg·L^{-1} O_3. • Pesticide degradation of 95%.	• Removal of aldehydes generated • 86% pesticide degradation	• Optimal coupling: Pre-ozonization + Biological + Post-ozonization • COD removal of 97%. • TOC removal of 95%. • Total pesticide concentration 0 mg·L^{-1}.	Mezzanotte *et al.* (2005)
O_3/O_3-UV + Stirred tank bioreactor with aeration	• Tank volume of 5 L. • Ozone generator: generation rate of 1.2 g O_3/h. • Mercury vapor UV lamp (253 nm). • pH control at 7.	• Volume of 6 L. • Air flow rate of 200 L·h^{-1} with a gas sprayer. • Inoculum sludge from a WWTP. • Biomass acclimatization in 50 days.	• Ozone dose 4,200 mg • Pesticide elimination greater than 80%. • Treatment time 210 min. • pH greater than 4 units.	• There was no COD removal	• O_3-UV effluent. 95% COD removal. • Biological treatment of 64 h and pH 7.	Lafi & Al-Qodah (2006)
HC/HC-O_3 + Biodegradability analysis	• Based on a slit Venturi with storage tank, pump for rated power, pressure gauges and control valves (Thanekar *et al.* 2018b). • Pressure: 4 to 7 bar. • pH: 4 to 9 units. • DDVP concentrations: 10 to 50 ppm. • Ozone generator with a flow rate of 200 mg·h^{-1}.	• OECD Protocol, 301B. • 250 mL conical flask with 150 mL of mineral medium. • Period of 28 days. • Inoculum from a WWTP and without acclimatization.	• Optimal HC conditions: 5 bar and pH 4. • Pesticide degradation: HC 14%; O_3 39%; HC + O_3 84.8%. • TOC elimination: O_3 25.7%; HC + O_3 39%.	• TOC removal of 14.4%.	• TOC removal with HC pretreatment: 50.6%. • TOC removal with HC-O_3 pretreatment: 86.1%.	Thanekar *et al.* (2018a)

suitable characteristics for disposal. A key point is that the use of UV radiation could have allowed better efficiency of the process in the aspect of reagent consumption, since it has been proven that the reaction rates in AOPs are highly enhanced by the use of photocatalysts (presence of UV) and oxidants (Vela *et al.* 2019), which results in increased oxidation rates of pollutants and reduced ozone consumption (Malakootian *et al.* 2020).

In this sense, the ozonation process without the presence of UV has highlighted a limitation as a pretreatment to improve the effluent conditions towards subsequent biological oxidation, as in the case of Maldonado *et al.* (2006), who treated five pesticides in aqueous solution: Alachlor, Atrazine, Chlorfenvinphos, Diuron and Isoproturon, highlighting that although the pesticides were eliminated, longer times were required for some of them, such as Alachlor, which required 270 min to degrade, compared with Isoproturon, which only required 30 min. However, after 1,000 min of treatment and high ozone consumption, only 26% of the initial TOC was mineralized, which implies high electricity consumption and environmental impacts to achieve the desired biodegradability, which determines that the partial mineralization obtained in this mixture of pesticides is not viable for subsequent biological treatment.

Lafi & Al-Qodah (2006) studied the application of ozonation alone and with UV for wastewater from a pesticide factory, containing Triadimenol, Lambda-Cyhalothrin, and Deltamethrin at concentrations of 100 $mg \cdot L^{-1}$ and an average COD value of 6,500 $mg \cdot L^{-1}$. In the two AOP cases analyzed, the O_3/UV combination was always better because ultraviolet radiation accelerates the oxidation process by enhancing the generation of hydroxyl radicals, thus removing most of the pesticide molecules from the solution, with a degradation efficiency of more than 80% in 210 min, which is consistent with the previous discussion that these combinations contribute to increased degradation rates (Malakootian *et al.* 2020).

However, total degradation of the three pesticides present is not achieved, as in the case of Lambda-Cyhalothrin and Deltamethrin, only 96 and 92% are removed, respectively, thus establishing that higher degradations are possible if ozonation is combined with other AOPs or the oxidation time is increased, as discussed in Mezzanotte *et al.* (2005). Optimal conditions in the O_3/UV system required a high ozone dose and neutral pH values, since as pH increases, the oxidation rate of the pesticide increases, which determines that this ozone-mediated AOP works very well at high pH levels (Vagi & Petsas 2020).

The biological coupling treatment in Lafi & Al-Qodah (2006) had better conditions with the effluent pretreated by O_3/UV as expected, and it was necessary because in the direct biological oxidation there was no COD removal, which shows that the property of the studied pesticides, being halogenated and non-halogenated compounds, makes it difficult to treat them by a single method, making necessary the combination of the processes. The AOP allows converting the toxic and recalcitrant effluent into another with suitable characteristics for the biological process, which is reflected in the COD removal of the coupled process by 95%, as reported in Table 4. Finally, it can be concluded that the coupling of ozonation to biological treatment with the principle of activated sludge leads to high rates of pollutant removal, enhancing the subsequent biological oxidation and degradation levels (Espejo *et al.* 2014; Khan *et al.* 2019).

During the development of this section, the combination of ozonation with other advanced oxidative processes has always been discussed, and this is reflected in the fact that the degradation efficiency of refractory organic compounds can be improved (Wang *et al.* 2021). At this point, hydrodynamic cavitation (HC) emerges as a promising alternative in current wastewater treatment technologies (Gągol *et al.* 2018) due to the advantages of cost-effectiveness in operation, higher energy efficiency, and large-scale operation (Wang *et al.* 2021), achieving that its combination with other AOPs contributes to reducing chemical consumption and thus having a low-cost operation system (Thanekar & Gogate 2018).

Thanekar *et al.* (2018a) studied the efficiency of an HC process alone and in combination with ozone as an intensified pretreatment for the decontamination of an aqueous solution of Dichlorvos pesticide (DDVP) and the biodegradability conditions of the effluent after chemical oxidation using the test detailed in Table 4. The experimental design in HC consisted of initially knowing the pressure behavior in degradation at a fixed pH; then at a fixed pressure knowing the pH behavior; and with these optimized parameters developing the HC/O_3 combination. The relationship between degradation and HC inlet pressure is particular to the type of pollutant, hence the importance of finding the optimal operating value; typically, an increase in inlet pressure allows higher OH radical production; however, higher values reduce cavity intensity, and with it degradation rates (Joshi & Gogate 2012).

The pH level influences the process, as acidic levels favor much higher degradation rates because OH radicals are more easily generated, have a high oxidation potential and their regrouping is lower (Raut-Jadhav *et al.* 2013; Barik & Gogate 2016), which enhances the process because the combination of ozone with HC additionally results in a large amount of highly reactive OH radicals, which enhances the efficiency of the treatment (Gogate *et al.* 2014). This is reflected in that in Thanekar *et al.* (2018a), both pesticide degradation and TOC removal are higher in the HC-O_3 process, as highlighted in Table 4.

Likewise, in Thanekar *et al.* (2018a), the passage of the effluent through the biodegradability test allows concluding that the best levels of mineralization in terms of TOC are obtained when the aqueous solution of the pesticide is pre-treated by the HC-O_3 combination. It is important to note that the direct oxidation of DDVP in the biodegradability test did not contribute to significant mineralization rates; on the other hand, the optimal pre-treated effluent allowed to improve the recalcitrant conditions and did not require prior acclimatization in the biological process.

GENERAL DISCUSSION AND FUTURE TRENDS

Complete mineralization of contaminants in any AOP requires a large amount of energy along with chemicals such as catalysts and oxidants that increase the cost of treatment (Thanekar *et al.* 2018a), and having that the purpose of coupling is to compete with conventional treatments, the goal should be aimed at improving the purification performance at a lower cost than a one-step treatment (Minière *et al.* 2019).

It is at this point that technologies should not be considered only in terms of pollutant removal, but also in aspects related to operating and treatment costs, since a treatment alternative, if it goes out of the real scale in its application to a pure laboratory scale, would be complex to apply and we could only see the processes as a test of treatability.

In this way, it is clear that the investigations studied in terms of AOP-Biological couplings in the decontamination of WWPC have not studied these costs when scaled to an industrial environment, which is a shortcoming in this branch of research, since future investigations should specify, study and estimate the real costs of treatment in the configurations studied on an industrial scale, and in this way carry out strategies much more oriented towards the optimization of resources in line with the expectations of decontamination.

In the case of reagents, there is a present difficulty, and that is that these AOPs have been shown to work better under acid pH, and at the time of passing to the biological oxidation phase, reagents must be consumed for conditioning to the requirements of the biological system, since a pre-treated effluent without the stabilization of this parameter can contribute to inadequate functioning of the system, which leads to not meeting the expectations or the minimum requirements.

Research by López *et al.* (2010) and Cabrera Reina *et al.* (2015) determined that the main result of the coupled treatment is high-quality water with reuse conditions. This evidences a gap in the scientific field oriented towards the lack of research regarding this type of objectives, taking as a starting point that it is in the interest of industries to reduce excessive water and energy consumption, together with the operating costs of wastewater treatment and in synergy with the reduction of the environmental impacts associated with their different productive activities, as specified by Rosa *et al.* (2020).

The above goes hand in hand with the study of operating costs and excessive energy consumption of AOPs, since reusing treated wastewater positively favors the economic end, resulting in a consistent view that water pollution is becoming one of the main environmental problems and wastewater treatment is a research topic to develop effective treatments for the removal of recalcitrant pollutants (Bendjabeur *et al.* 2017).

It is pertinent to note that the couplings with the highest efficiencies are primarily related to advanced biological processes, as detailed in Figure 1, where the main findings are summarised and whose operating philosophy follows an activated sludge process, as they have proven to be powerful and effective in withstanding some of the unforeseen and specified disadvantages of AOPs, such as the case of oxidation by-products, which can end up inhibiting the biological process and thus the efficiency of the couplings. Subject to this, in the AOPs, an optimal design of experiments should be carried out according to each applied process and target contaminant, taking into account that each pesticide studied belongs to a different chemical group and reacts uniquely in each advanced oxidation process during the treatment and in the levels of the influential variables studied; hence, it is complex to assume values to start the experiments based on secondary information, being necessary to study the particularity of the process.

The characteristics of the WWPC depend directly on the type of pesticide studied, and it is known that there is a wide range of pesticides and each particular pesticide belongs to a specific chemical group with a different action characteristic. It is an important aspect to study and evaluate the chemical oxidation times and the doses of catalysts and oxidants, as well as to properly identify the by-products generated during the chemical oxidation pretreatment in the AOP and thus optimize the experimental design, allowing the subsequent biological oxidation to enhance the treatment conditions in the maximum reduction of pollutants and efficient use of resources.

In AOPs – Biological couplings, the importance of the pesticide removal mechanisms lies in the chemical conversion that takes place in the pretreatment with advanced oxidation, where the identification and reaction of reactive species are important, since they allow understanding the degradation mechanisms of these recalcitrant organic compounds (Wang & Wang 2020). Likewise, the analysis of the by-products generated provides insight into these degradation mechanisms by identifying the active species during chemical conversion (Titchou *et al.* 2021).

It has been previously discussed that any advanced oxidation process requires the optimization of its operating parameters to obtain the highest possible mineralization, generating non-selective hydroxyl radicals, which attack the organic pesticide and result in the production of CO_2, H_2O, and inorganic acids or inorganic ions (Poyatos *et al.* 2010; Vagi & Petsas 2020; Titchou *et al.* 2021).

Inorganic acids represent the chemical transformation of the pesticide into the different oxidation by-products, since this type of reaction reduces the reactivity of the contaminants through the production of new species that influence the degradation mechanism (Wang & Wang 2020), turning them into substances more suitable for further degradation in biological reactors, justifying the fact that chemical oxidation allows attacking pesticide molecules with hydroxyl radicals to give rise to inorganic intermediates (López *et al.* 2010).

Elimination mechanisms of these persistent organic compounds depend on the type of pesticide and the effectiveness of the treatment process (Saleh *et al.* 2020), where the transformation that occurs with inorganic acids is particular, as happens in general in the case of organochlorine pesticides, where Cl^- anions are generated, and in the case of organophosphates PO_4^{3-} anions (Miguel *et al.* 2012). Similarly, each treatment process in combination with the specific pesticide has a particular transformation.

In the case of Photo-Fenton processes, the transformation of Atrazine into cyanuric acid (Benzaquén *et al.* 2016) and the transformation of nitrogenous pesticides into ammonium and nitrate (Zapata *et al.* 2010; Cabrera Reina *et al.* 2015) have been identified, while solar Photo-Fenton processes have identified the conversion of pesticides into low molecular weight carboxylate anions (Vilar *et al.* 2012), into nitrate ions due to the mineralization of organic nitrogen (Berberidou *et al.* 2017) and the conversion of the organophosphorus pesticide Dimethoate into carboxylic acid and oxalate (Oller *et al.* 2007).

Fenton processes without the presence of light have identified the transformation mechanisms of nitrochlorinated pesticides into oxalic acid and aniline (Sanchis *et al.* 2014), and chlorophenoxy herbicides into acetic and oxalic acid (Sanchis *et al.* 2013). Likewise, Gomez-Herrero *et al.* (2020) identified the transformation of Thiamethoxam into acetic and formic acid in the Fenton process.

On the other hand, ozone processes without the presence of UV light have identified the transformation of the herbicides Triazines and Thiocarbamates into aldehydes as by-products of chemical oxidation (Mezzanotte *et al.* 2005), highlighting that in all cases the active ingredients of the pesticides are eliminated and this results in faster cell growth in subsequent biological processes (Ballesteros Martín *et al.* 2008a, 2008b).

Knowing the mechanisms of transformation that pesticides undergo in chemical oxidation, including products, by-products and intermediate phases, is very important because this aspect directly influences the subsequent biological process that takes place in the couplings analyzed; however, most of the research analyzed does not take it into account, which represents a shortcoming and disadvantage in the application of these processes, since, as discussed above, on many occasions the by-products generated can be more toxic than the original compounds; therefore, their identification plays an important role in the degradation mechanisms and, as a consequence, in the efficiency of the treatments.

Efficient implementation of the treatment configurations presented in this research can be favored by an uncommon alternative applied in the scientific field, taking into account that wastewater treatment involves the use of a series of inputs such as energy, chemicals, and water, and a focus on the efficient operation of energy and resources in these processes is emerging, identifying exergy as a useful tool for optimization. Exergy analysis is an analytical method that seeks to quantify and evaluate the thermodynamic potential of a process in terms of energy and resource efficiency as a tool for environmental degradation by providing appropriate sustainability indices (Khosravi *et al.* 2013; Fitzsimons *et al.* 2016).

Although the exergy study in wastewater is limited, there is research that supports its potential, as in the case of Różycki & Banaś (2018), who compared two wastewater treatment systems through an exergy analysis, determining energy efficiency in the development of treatments and the reduction of harmfulness; in a similar case, Vakalis *et al.* 2017) evaluated the chemical exergy in four different methods for the removal of heavy metals from industrial wastewater, determining the removal of more than 96% of two of the metals studied.

CONCLUSIONS

Due to the wide range of pesticides applied around the world, each pesticide has specific characteristics of action and belongs to a particular chemical group, which makes the aqueous solutions contaminated with these agents have their characteristics of reaction with the reagents, catalysts, and oxidants in the chemical oxidative processes, hence the importance of identifying the intermediate by-products generated, as there may be scenarios in which the treated wastewater turns out to be much more toxic than the original and this, in the case of configurations coupled to biological processes, inhibits the micro-organisms present and the objectives are not met.

Current trends in the decontamination of WWPC have focused their success on the coupling of advanced oxidative processes with advanced biological processes such as SBR (sequential biological batch reactor), MBR (membrane bioreactor), MBBR (moving bed biofilm reactor), and IBR (immobilized mass biological reactor), as these are much more stable in withstanding the pre-oxidized wastewater conditions in the AOP, which leads to the removal of some still recalcitrant compounds that cannot be removed in the advanced oxidation and can impair the subsequent biological oxidation. Therefore, it has always been mentioned that the main function of coupling these processes is to enhance the advantages of each process separately and to provide a viable alternative with promising results not only in the high removal of recalcitrant compounds but also in the efficient use of resources.

While it is true that the main objective of wastewater treatment is focused on the highest possible pollutant removal, the study and analysis of treatment costs related to reagent and energy consumption cannot be neglected, as these are equally important aspects for the application of the processes on an industrial scale, taking into account that the problem of pesticide-contaminated wastewater is a reality all over the world. Alternatives must therefore be provided that are capable of working, but equally possible to apply. One reason for this is that such couplings are capable of providing an effluent with reusable characteristics, which would reduce costs and make their application much more efficient.

In the scientific field, new alternatives for the applicability of processes should be proposed, as is the case of the exegetical analysis, discussed in a very general way in this research, where the aim is to quantify and evaluate the thermodynamic potential of a process in terms of energy and the efficient use of resources as a tool for environmental degradation, providing adequate sustainability indices.

AUTHORS' CONTRIBUTIONS

This work was planned, executed, and discussed by all authors in equal contribution.

DECLARATION OF COMPETING INTEREST

The authors declare that there are no conflicts of interest.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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