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Wastewater Treatment by Heterogeneous Photocatalysis: A Systematic Review*

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Abstract: pharmaceutical wastewater contains compounds that, in low concentrations, affect ecosystems for being endocrine disruptors. Therefore, advanced oxidation processes have been proposed as an ideal treatment strategy. Within these technologies, heterogeneous photocatalysis stands out as a high-efficiency and low-cost technology. This research provides a systematic review on the degradation of wastewater from the pharmaceutical industry and the significant advances concerning its degradation by heterogeneous photocatalysis. We used Thesaurus, keywords, and Boolean search in the selected databases: Dialnet, Science Direct, Scopus, Redalyc, SciELO, ProQuest, and American Chemical Society. We also set inclusion/exclusion criteria based on the PRISMA statement, developed a bibliometric parameter, performed a statistical analysis, and established the best-operating conditions for technology implementation. In conclusion, heterogeneous photocatalysis is a promising proposal for treating the study matrix.

Keywords: decomposition; pharmaceutical industry; photochemistry; review; photocatalysis

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Tratamiento de aguas residuales por fotocatálisis heterogénea: una revisión sistemática

Resumen: las aguas residuales farmacéuticas contienen compuestos que, en bajas concentraciones, afectan los ecosistemas por ser disruptores endocrinos. Por tanto, se han propuesto procesos de oxidación avanzados como una estrategia de tratamiento ideal. Dentro de estas tecnologías, la fotocatálisis heterogénea se destaca como una tecnología de alta eficiencia y bajo costo. Esta investigación proporciona una revisión sistemática sobre la degradación de las aguas residuales de la industria farmacéutica y los importantes avances en su degradación por fotocatálisis heterogénea. Usamos Tesauro, palabras clave y búsqueda booleana en las bases de datos seleccionadas: Dialnet, Science Direct, Scopus, Redalyc, SciELO, ProQuest y American Chemical Society. También establecimos criterios de inclusión/exclusión basados en la declaración PRISMA, desarrollamos un parámetro bibliométrico, realizamos un análisis estadístico y establecimos las mejores condiciones operacionales para la implementación de la tecnología. En conclusión, la fotocatálisis heterogénea es una propuesta prometedora para el tratamiento de la matriz de estudio.

Palabras clave: descomposición; industria farmacéutica; fotoquímica; revisión; fotocatálisis

Tratamento de águas residuais por fotocatálise heterogênea: revisão sistemática

Resumo: as águas residuais farmacêuticas contêm compostos que, em baixas concentrações, afetam os ecossistemas por ser disruptoras endócrinas. Portanto, os processos avançados de oxidação vêm sendo propostos como estratégia de tratamento ideal. No âmbito dessas tecnologias, a fotocatálise heterogênea se destaca como uma tecnologia de alta eficiência e baixo custo. Nesta pesquisa, são apresentados uma revisão sistemática sobre a degradação de águas residuais da indústria farmacêutica e os avanços significativos relativos à sua degradação por fotocatálise heterogênea. Foi utilizado um dicionário de sinônimos, palavras-chave e busca booleana nas bases de dados selecionadas (Dialnet, Science Direct, Scopus, Redalyc, SciELO, ProQuest e American Chemical Society). Também foram determinados critérios de inclusão e exclusão com base na declaração Prisma, desenvolvido um parâmetro bibliométrico, realizada análise estatística e estabelecidas as melhores condições de operação para implementar a tecnologia. Em conclusão, a fotocatálise heterogênea é uma proposta promissora para tratar a matriz de estudo.

Palavras-chave: decomposição; indústria farmacêutica; fotoquímica; revisão; fotocatálise

Introduction

Due to their high organic load, wastewaters are considered highly complex matrices. Depending on their physicochemical nature and composition, their elimination capacity may be affected. This condition is reflected in waters from the pharmaceutical industry that, after traditional purification processes, retain traces of some medications, distinctive of this wastewater type [1]-[4]. Generally, due to their chemical nature, some of the active ingredients in pharmaceutical wastewater are analgesics, antihypertensives, and antimicrobials called emerging pollutants, which behave as hormone mimicking chemical, producing significant effects on ecosystems and consequently on human beings [5]-[6].

Accordingly, various removal processes have been applied, such as coagulation [7], flocculation [8]-[9], absorption [10], oxidation chemistry [11], and biological methods [12]. However, their main limitation is that they are unable to eradicate compounds (especially if they are highly persistent), increasing operating costs and reducing viability in industrial scaling [5].

Studies have been carried out where advanced oxidation processes have been incorporated as an outstanding tool for removing this pollutant, including Fenton [13], ozonation [14], UV/H_2O_2 [15]-[16], UV/H_2O_2/Fe^{2+} [4], and heterogeneous photocatalysis [17]. They have shown effectiveness in photodegradation processes between 30 and 100 % on average, proving highly efficient in treating these pollutants.

Specifically, heterogeneous photocatalysis has attracted considerable interest, as it is an affordable, versatile, and easy-to-implement technique. However, to date, there is no literature review that collects all the advances in operating conditions and effectiveness compared to other technologies for pharmaceutical wastewater treatment. Thus, this research provides a literature review on the advances in the heterogeneous photocatalysis process for pharmaceutical wastewater treatment between 2015 and 2020. We searched different databases, used inclusion/exclusion criteria, and reviewed contents, among other actions. Analysis of the bibliometric parameter, descriptive analysis of databases and study variables were also performed to obtain representative results for each variable and ensure that the selected literature has statistical credibility.

Materials and Methods

Literature sources and search strategies

Initially, for the methodological path of this research, the specialized metasearch engine Google Scholar was used. In parallel, we explored databases such as ProQuest, Redalyc, Dialnet, ScienceDirect, Scopus, Scielo, and American Chemical Society for publications between 2015 and 2020.

For the activation of those searches, we used syntactic combinations of keywords in English to improve the search, taken as repetitive terms from previous Thesaurus and other queries: "degradation of pollutants or pharmaceutical industry," "degradation of pollutants and heterogeneous photocatalysis," "pharmaceutical industry and heterogeneous photocatalysis," "pharmaceutical industry," "heterogeneous photocatalysis and degradation," and "pharmaceutical and photocatalyst." With these results, we carried out the descriptive analysis of the searches and developed a bibliometric parameter. Of note is that this parameter allows identifying trends in knowledge by applying quantitative methods that enrich the literature review [18].

Inclusion/exclusion criteria

First, duplicate papers found within the search in the different selected databases were excluded. Subsequently, the scoring rubric developed by the research group was applied, taking some criteria from the PRISMA Statement. We took into account seven items (title, DOI, basis, method, selection of studies, data collection, and conclusions), scoring articles on a scale from 1 to 5, 1 being the lowest and 5 five the highest [19]-[21]. After obtaining the respective score and the best-rated articles, we established the operating conditions in the heterogeneous photocatalysis process for this wastewater type.

Statistical analyses

According to descriptive statistical analyses, we prepared simple bar diagrams and horizontal bar diagrams with respect to different databases and their relationship with Boolean search, thus determining the bibliometric parameter. Additionally, for operating condition analysis, box plot analysis and histograms were performed for all variables, taking the numerical results reported. All the graphical analyses shown in this research were carried out through R statistical software.

Results

Descriptive database results

The databases above were used for article search to construct metadata with a combination of keywords and selected Boolean operators. Fig. 1 employs letters to identify each term. Since the Boolean operator "OR" is a generalized search, the Boolean operator "AND" was given greater relevance to ensure that all terms were included in the query.

While the ProQuest database had 259,007 articles, the best results were found on the ScienceDirect platform (4,247) since the articles consulted were consistent with the research needs using the three combined keywords. Thanks to these results, the following bibliometric parameter was developed. It should be remembered that bibliometric parameters are the set of terms that enhance an effective query [22]:

$$\frac{\textit{Photocatalytic degradation in}}{\textit{pharmaceutical wastewater}} \quad = \quad X \text{ and } Y \text{ and } Z$$

Inclusion/exclusion criteria

For discriminating the selected articles on this research, we identified 93.2854 records through database search, as shown in Fig. 2. discrimination started by searching within the last five years using the Boolean operator "AND," cutting down to 6,170 papers. Then, a second exclusion was made based on the preliminary review of the title and abstract, obtaining 3,020 preselected documents. Afterward, a third exclusion was performed concerning keywords and optimal Boolean operators, resulting in 1,970 documents. Within the preselected articles, we reviewed again the titles and abstracts to determine whether the publications met the needs of the research; therefore, 254 articles were selected. We conducted a preliminary review of the documents, reducing them to 54, assessed through the rubric developed in this research. This discrimination of results is explained in Fig. 2.

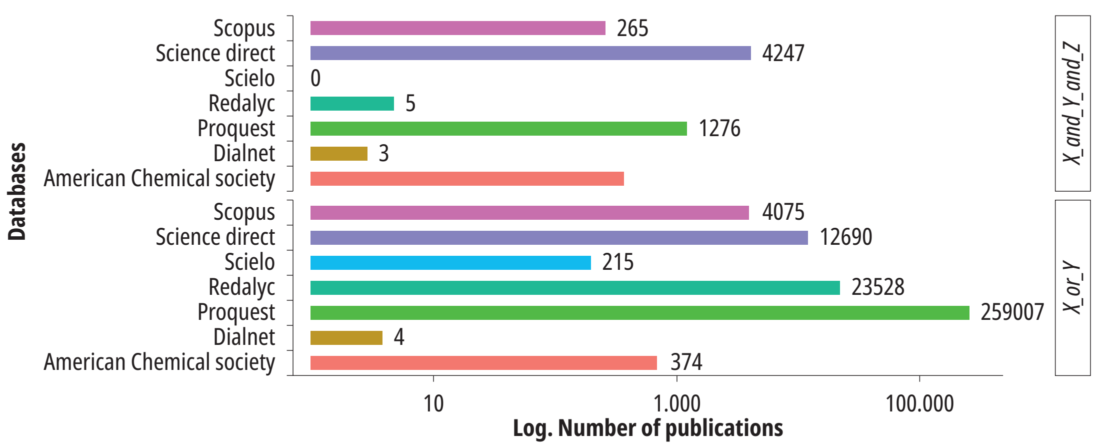

Fig. 1. Results of the keywords with the Boolean operators "OR" and "AND." **X =** degradation of pollutants; **Y** = pharmaceutical industry; **Z** = heterogeneous photocatalysis.

Source: own elaboration.

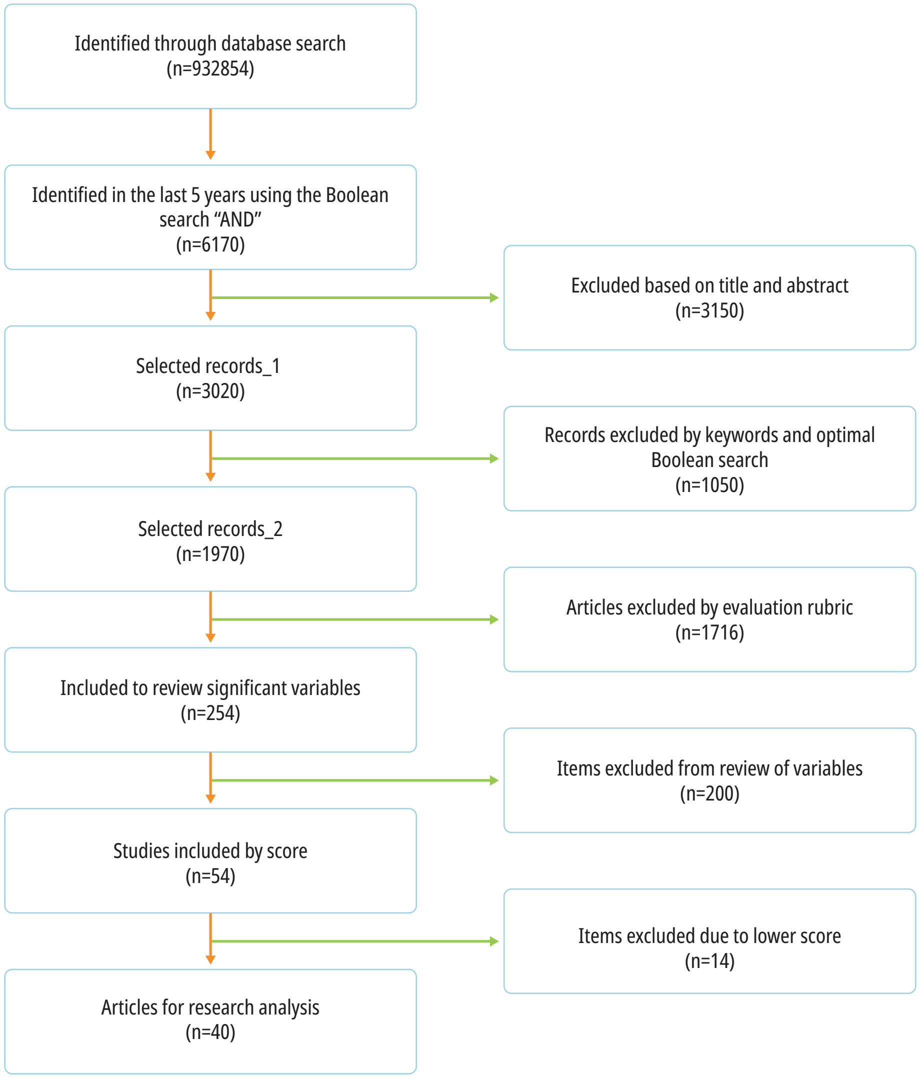

Fig. 2. Discrimination of the selected articles.

Source: own elaboration.

Then, we performed a graphic analysis of the 54 articles discriminated by score, as shown in Fig. 3; the yellow bar represents 14 articles with a score equal to 2, the green bar represents 24 articles with a score equal to 3, and finally, the red bar represents 16 articles scoring 4. Those scored between 3 and 4 were taken to ensure a significant number of articles.

After critically reading the 54 articles chosen, we could establish at a general level the influential variables within the photocatalytic process for this matrix type, particularly pH, pollutant concentration, photocatalyst concentration, irradiation time, and the life cycle of the photocatalyst

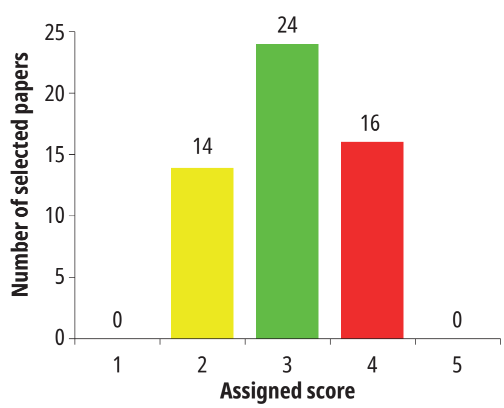

Fig. 3. Relationship between score and number of selected articles.

Source: own elaboration.

as highly significant variables within the process [23].

Descriptive analysis of the variables

Research carried out on the subject matter and its recurrence in reports were taken as a reference for the descriptive analysis of variables. Initially, in Fig. 4 shows the histogram and the boxplot of pH in the photodegradation process. The best results occurred round pH 6 and the greatest dispersion of results occurred when the pH tends to increase. Furthermore, the degradation processes are highly dependent on the characteristics of each pollutant, taking into account that there is a part of the process where adsorption is essential. The generation of pollutant microspecies due to changes in pH would also significantly affect the process.

A clear example of this is the variability of ibuprofen at different pH levels. It can be observed that at an acidic pH ranging from 1 to 4, the species is conserved, and from pH 5 onwards, a proton is lost, making the conditions in which it can be treated different. This variability would affect the efficiency in the photodegradation process [24]-[30]. Moreover, extreme acidity values can create an excess of hydrogen ions on the surface of the material, which impact its adsorption processes [29]. The pKa of drugs has a significant incidence within in the photocatalytic process; its equilibrium favors reactants, protonates the surface, and consequently helps in degradation processes. A clear example is ibuprofen, found that at pH 5.2, the ibuprofen is a weak acid, as reported in the research [31]-[36].

For the analysis of pollutant concentration shown in Fig. 5, the best results occurred at very low concentrations (speaking of ppm). This result is very consistent with the study matrix, given that emerging pollutants are in the order of ppb (parts per billion), proof of the potential application of the technique for this pollutant. In the case of the boxplot, the variability within the results was very low compared to the mean, clarifying that when initial concentrations are deficient, degradation is easier. When the initial concentration is high, it is used to show degradation paths since it is not possible at low concentrations.

When reviewing the graphic analysis, the pollutant concentration is not a significant variable in the photocatalytic process since it could be established that at low or high concentrations, the effective rates of photodegradation are high [37]. However, in agreement with the results reported in Fig. 5, the studies mentioned that the photodegradation can work at low concentrations, and although it was not a significant variable, its efficiency was an added value in this concentration [25]-[26], [38]-[43].

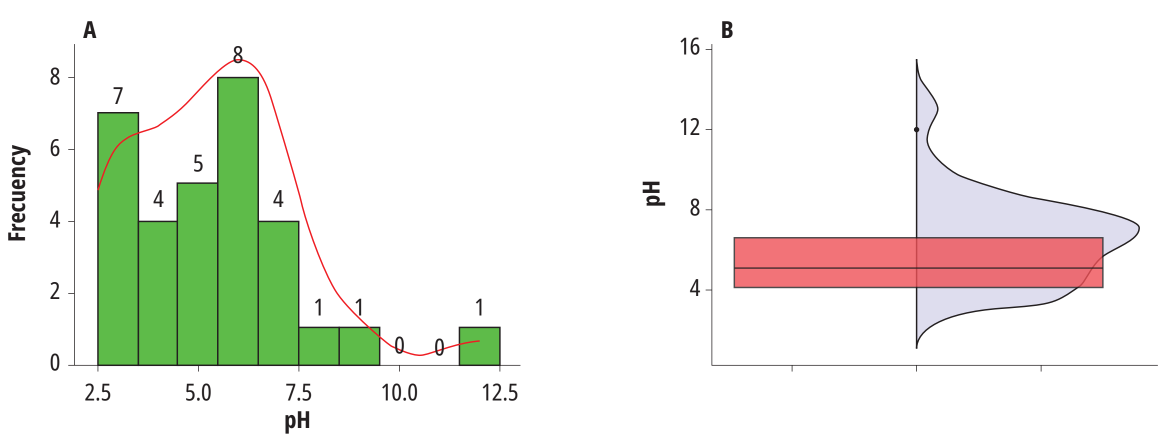

Fig. 4. Histogram and boxplot of the pH variable.

Source: own elaboration.

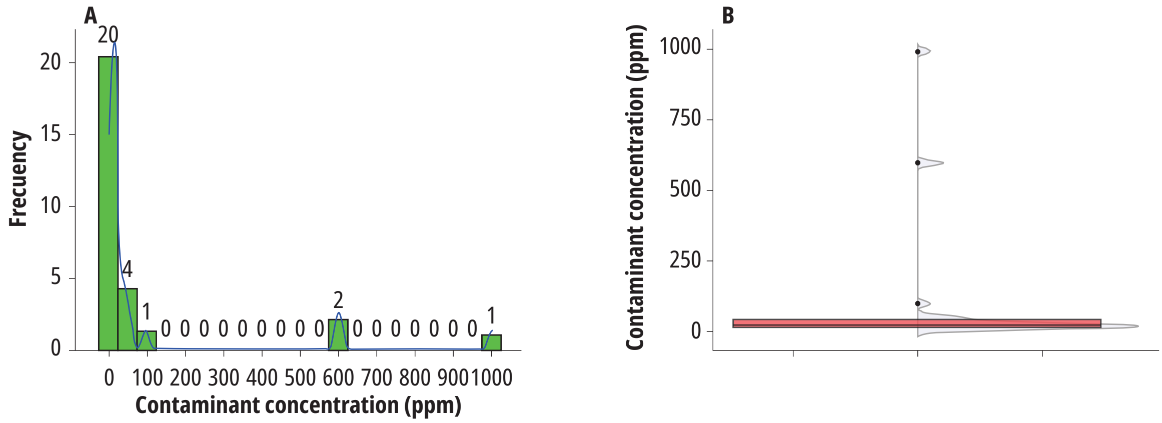

Figure 5. Histogram and boxplot of the pollutant concentration.
Source: own elaboration.

Then, for the concentration analysis of the photocatalyst based on the studies reported (Fig. 6), the boxplot reveals that there is dispersion in the data from 40 to 200 ppm, as demonstrated in the histogram too, followed by data with values ranging from 500 to 2,000. Therefore, we established that the lower the concentration of the photosensitizer, the better the photodegradation, without underestimating that the operating conditions produce a transcendent effect on the results of the process. Several studies determined that at lower concentrations such as 1.52 and 2 mg/L, the removal percentage has been 86.75 in synthetic wastewater treatments, while it has been 36.31 in real effluent, considering the time spent as it significantly influences the photocatalytic process [44]. It was also found that at a lower concentration of TiO_2 and H_2O_2, the percentage of degradation increases, and it occurs more quickly and efficiently [45]. Moreover, the effect of the typology of the light source (translated into energy) that participated in the process was established since sunlight increased its photocatalytic activity. In the case of ultraviolet light irradiation, a selective behavior was observed in the degradation of some drugs [25]-[26], [38]-[40], [42], [46]-[47].

Another highlight is the internal porosity and the uniform distribution of the particle size of the photocatalyst since it facilitated the adsorption process. For this reason, micrometer powders were regularly used for this treatment [37]. A clear example was anatase, considering its photocatalytic properties when in crystalline form, which is due to its remarkable photo-adsorption capacity and

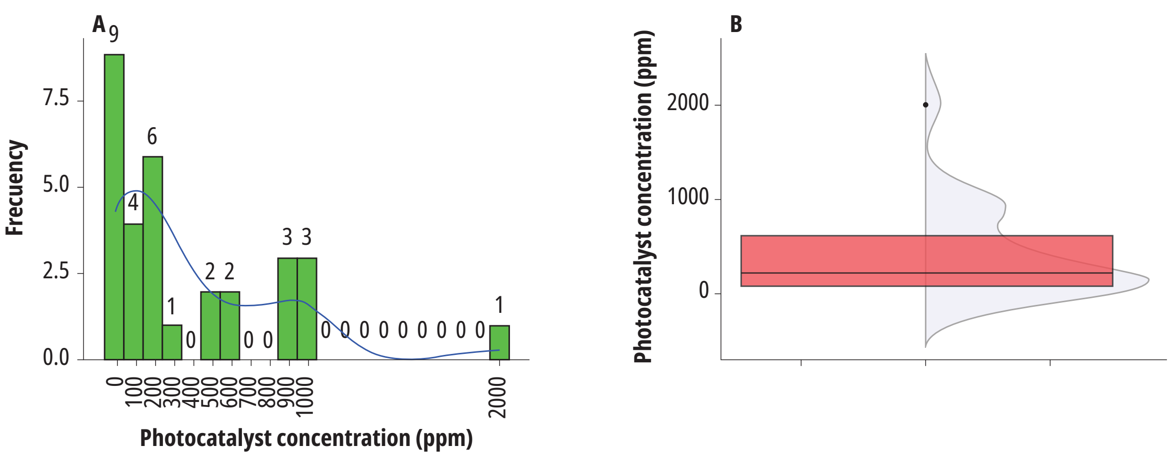

Fig. 6. Histogram and boxplot of photocatalyst concentration.
Source: own elaboration.

the relatively low speed of hole-electron pairs. Chemical reactivity depends on how the particles are formed in general [48]-[49].

The histogram and boxplot in Fig. 7 show the irradiation time variable. The histogram demonstrates that significant results were found in times ranging from 100 to 400 minutes and that around 100 minutes is the optimal working time with good dispersion of data, as established by the boxplot (for drugs such as tetracycline, theophylline, ibuprofen, levofloxacin, paracetamol, thiacloprid, and amoxicillin). Moreover, there was a variation from 20, 30, 90 minutes, obtaining high percentages of degradation of pollutants, compared to time ranges from 180 and 360 min, with a somewhat lower result. This was possible because within photochemical processes, the photocatalyst material could undergo photobleaching and thus decreased its photocatalytic capacity [17], [26]-[27], [38]-[41], [42], [50], [51].

In the analysis of the life cycle of the photocatalyst shown in Fig. 8, the results had greater dispersion above the mean (boxplot), revealing a more significant number of documents reporting the use of eight cycles or less. In the histogram, the best results are around four cycles. One highlight is that some authors carried out suspension and shaking processes at least twice prior to practical application to guarantee reproducibility [27]. Besides, to calculate efficiency, complete analyses were carried out on the interaction of the photocatalyst in the reaction system (a chemical reaction between the material and the pollutant) and the chemical response of the photocatalysts that measure the reaction activity and the selectivity of the pollutant [27], [38], [42], [52]-[57].

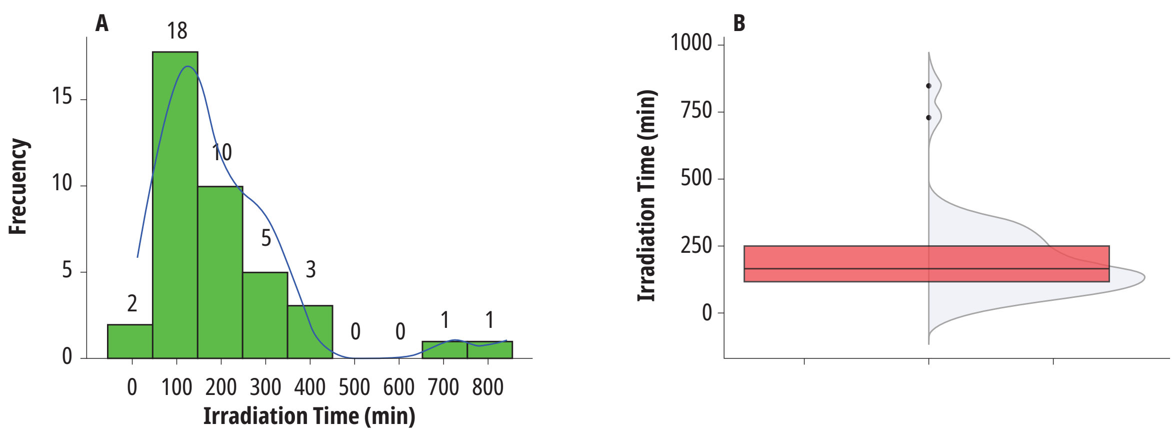

Fig. 7. Histogram and boxplot of irradiation time.

Source: own elaboration.

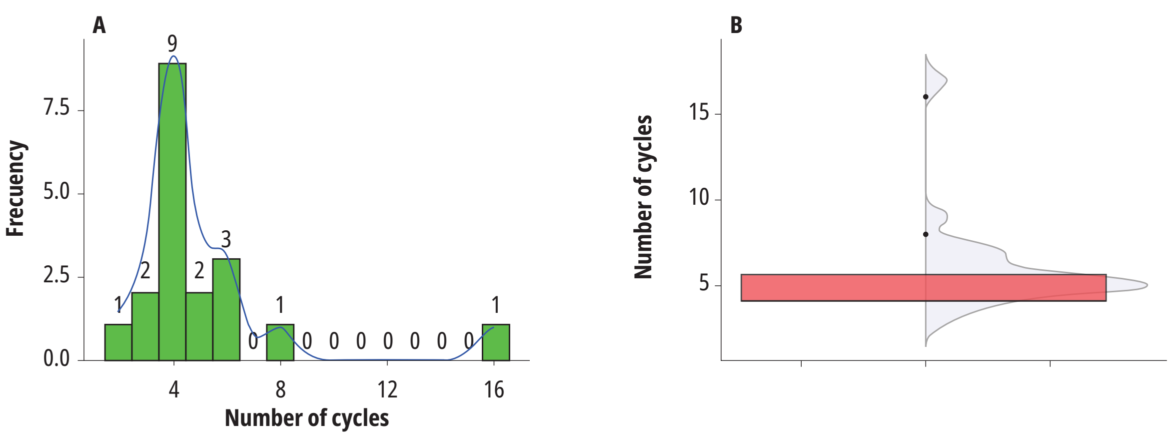

Fig. 8. Histogram and boxplot of the photocatalyst life cycle.

Source: own elaboration.

Finally, the photocatalyst type was analyzed to understand the interaction between the photocatalyst and the reaction with the pollutant. Currently, photocatalysts such as TiO_2-based photocatalysts, TiO_2 nanoparticle-based photocatalysts based, perovskite-type photocatalysts, hierarchical microspheres catalysts, plasmonic photocatalysts, and bismuth oxyhalide photocatalysts stood out for having high percentages of photodegradation between 73 and 100 %. However, in terms of costs, the TiO_2-based catalysts are less expensive since they only need the light source and the photocatalyst for degradation. and do not produce intermediate toxic products in photocatalytic decomposition. The drawback is their dependence on ultraviolet (UV) light for activation ($\lambda < 385$ nm) [17], [38]-[40], [42], [50], [60]-[67].

Although titanium dioxide is the most widely used, WO_3, SnO_2, Bi_2O_3, ZnO, CdO semiconductor photocatalysts are also reported. Their downside is their stability under irradiation because they present with narrow band spaces that can be breached by photoelectric corrosion [58]. The $Bi_2O_3/g\text{-}C_3N_4$ compounds have changed in absorbance by additional absorption at lower energetic wavelengths, which provides good photocatalytic activity in the visible light spectrum [59].

Comparison with other advanced oxidation processes (AOPS)

The development of AOPs could be highlighted to show their merit, mainly for two reasons: (a) the diversity of technologies involved and (b) the areas of potential application, as shown in Table 1. Among the AOP methods, the following stood out: heterogeneous and homogeneous photocatalysis based on UV light or the use of solar panels, visible irradiation, electrolysis, ozonation, Fenton's reagent, ultrasound, and humid air oxidation. Ionizing radiation, microwaves, pulsed plasma, and ferrate were also included [68]-[69].

While drinking water and wastewater treatment is the most common area for research and development, AOPs have found applications as diverse as groundwater treatment, soil remediation, municipal wastewater sludge conditioning, pure water production, volatile organic compound treatment, and odor control. However, the main interest of this research was the implementation of AOPs in pharmaceutical wastewater. Table 1 compares the studies carried out for pharmaceutical wastewater using different AOPs.

The AOPs displayed high degradation, which ranges between 80 and 100 %. Depending on each, they have different reaction mechanisms but with a high predominance of hydroxyl radical formation. It should be noted that the main limitation for some of these technologies may be related to their high operating costs associated with energy consumption and the use of chemical products. A clear example of this was Sonolysis since the reactor type used represents a costly technology compared to other methods.

A method that was considered highly effective was the Fenton-based processes. Since the

Table 1. Comparison of the efficiency of different advanced oxidation processes in degrading pharmaceutical pollutants

Reference	Study matrix	Applied oxidation process	Percentage of degradation
[13], [70]	Wastewater (acetylsalicylic acid, diclofenac, dipyrone, and paracetamol)	Homogeneous Fenton-type processes ($FeSO_4$, $7H_2O$)	84 %
[14]	Wastewater (pharmaceutical compounds of anti-inflammatory antibiotics and estrogens)	Heterogeneous Fenton-type processes ($FeSO_4$, $7H_2O$)	100 %
[15]	Simulated water (drug mix)	Ozonation	> 99.9 %
		UV/H_2O_2	93.3 %
[71]	Wastewater (ibuprofen and benzophenone-3)	UVC/H_2O_2 activated sludge	81 %
[4]	Wastewater (antibiotic cefoxitin sodium)	$UV/H_2O_2/Fe^{2+}$	100 %

Source: own elaboration

reagents used for its preparation are non-toxic, cheap, and common and can potentially be implemented using solar panels, they will considerably reduce the cost of removal of recalcitrant pollutants. Nonetheless, a disadvantage of homogeneous Fenton processes [72] is the high amounts of iron-containing sludge generated and the limited operating range of pH [13].

Another outstanding method is ozonation, both individually and in combination with other technologies [37], [43], [73]; for example, in the application combined with biological processes [74], but it produces activated sludge [75] that, when operated, poses health risks. Besides, it reacts with water containing bromide and produces bromate, which is a potential genotoxic human carcinogen [15], [76]-[78].

Lastly, comparing these results with heterogeneous photocatalysis, TiO_2 was a low-cost photocatalyst [79]. It is unnecessary to think of it as a tertiary method, as it did not have limitations, making it a competitive method with other AOPs.

Conclusions

The use of bibliometric tools is the beginning of a new era of statistical strategies to validate the credibility of a publication. For this reason, recent research uses these descriptive and other comparative tools to verify and ensure truthfulness in the publication. Thanks to these resources, we could establish the best bibliometric parameter to generate the best search engine.

Heterogeneous photocatalysis as a technology for degrading pharmaceutical residues in wastewater shows excellent degradation percentages, which has been and continues to be a promising treatment strategy. Additionally, we could conduct a literature search that determined what advances have been made in applying photocatalytic processes to treating pharmaceutical wastewater.

Taking into account the information collected, it could to establish that a photocatalytic concentration of around 40 ppm at pH 6, for around 100 minutes shows good results for treating pharmaceutic wastewaters. However, it is possible the reuse the photocatalytic materials for four cycles, without compromising their photocatalytic capacity.

Also, the physicochemical properties of the photocatalyst and the chemical nature of the pollutant play a vital role in the technology effectiveness.

In terms of technology efficiency concerning the photocatalyst type in the last five years, various authors demonstrated greater degradation when they used plasmonic photocatalysts and TiO_2 nanoparticle-based photocatalysts, which are considered quite competitive technology innovations compared to other technologies.

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