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Systematic Review

A Systematic Review of Heterogeneous Catalysis Applied to the Treatment of Pharmaceutical Wastewater: Operational Conditions and Statistical Analysis

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Abstract: The use of heterogeneous photocatalysis has garnered significant attention, mainly due to its remarkable efficacy in degrading recalcitrant compounds. The main objective of this research was to investigate this process applied to pharmaceutical treatment. For that, an analysis of a Final Bibliographic Portfolio (FBP), using the systematic review of the PRISMA and the ProKnow-C method, and a meta-analysis study in a historical series from 2010 to 2020, were performed for scientific works published in indexed journals from the Scopus and Web of Science databases and fully available in English. The works were filtered after a careful reading of the titles, followed by the exclusion of repeated documents and those that were not aligned with the research from 3498 articles, 40 of which were chosen to compose the FBP that addressed the classes of antibiotics, antihypertensives, analgesics, and anti-inflammatory drugs after scientific recognition and exclusion due to not fitting into one of the four FBP structured stages: (1) identification, (2) triage, (3) eligibility, and (4) inclusion. The following gaps were highlighted: (i) a limited number of studies working with interactions of the interfering variables; (ii) a large number of experiments not considering the natural constituents of wastewater; (iii) the use of drug concentrations high above the values found in aquatic matrices; (iv) little applicability of the process at the real scale. In this meta-analysis study, operational parameter optimization was fundamental to guarantee degradation efficiencies above 80% with a variety of pharmaceutical pollutants, the main representatives studied of which were tetracycline, nimesulide, diclofenac, ibuprofen, and atenolol. However, there is still a need to determine the best conditions for this technique when using real effluents, which have the utmost importance for the process on a large scale.

Keywords: emerging contaminants; photocatalytic removal; meta-analysis; ProKnow-C

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1. Introduction

Increasing human activities and the development of medical technologies have brought along a massive generation of pharmaceuticals with the high potential to pollute aquatic ecosystems, which are now a global concern. These emerging contaminants (ECs) are chemicals or microorganisms that are detected but not officially monitored in the environment, and that can produce undesirable effects on ecosystems and human beings. Among this wide range of pollutants are pharmaceuticals and personal care products, endocrine disruptors, persistent organic contaminants, pesticides, herbicides, and others. ECs are commonly found at trace levels such as nanograms per liter and micrograms per liter in the most diverse aquatic matrices, such as in sewage systems, surface or underground water,

or even in treated water, as the current conventional treatment system is not already able to treat these pollutants [1,2].

The release of these compounds occurs continuously in the environment through distinct routes, and they are frequently detected in wastewater treatment plants (WTPs) in the most diverse concentrations [3]. The WTPs usually show a variable removal rate of these organics, mainly pharmaceuticals, due to their wide range of physicochemical properties (chemical structure, solubility), such as the operational conditions of biological processes [4–6].

In this context, new methods have arisen for contaminant removal by chemical oxidation, such as heterogeneous photocatalysis, which is a process that uses natural or artificial light to activate a semiconductor material, characterized by the presence of valence and conduction bands (VBs and CBs, respectively). This activation accelerates the photoreactions, maximizing the absorption of the photons. Its main mechanism is based on the generation of the hydroxyl radical (•OH), a highly reactive and non-selective oxidant that, due to the capacity to react to a wide range of contaminants, promotes the degradation of the most recalcitrant molecules to biodegradable compounds, or even their complete removal by mineralization to innocuous substances [4,7–10].

The complexity of the photocatalysis process, the operational conditions, the dynamics of the chosen catalysts, and the characteristics of the water to be treated are nowadays interesting research fields, with an expressive number of publications in the last 15 years, mainly due to the environmental problems involved and the advances in oxidative process technologies [1,10–14]. Despite this high number of works dealing with this theme, only two review articles have been published regarding the treatment of pharmaceutical compounds in wastewater [15,16], but none provides a systematic methodology or statistical meta-analysis to corroborate their results, which makes this study important. From this perspective, a combined study of a systematic review followed by a meta-analysis, finally becoming a bibliographic portfolio of high scientific relevance, was performed. Previous work of the group has already been published in Portuguese, aiming to briefly investigate the main operational parameters in the treatment of pharmaceutical pollutants by heterogeneous photocatalysis, which affects the process efficiency, and also to show the difficulties and lack of information related to the research [17]. Here, despite a deeper investigation, this meta-analysis study brings a statistical refinement to the parameters of the process, between 2010 and 2020 [17].

2. Materials and Methods

2.1. Systematic Review

A systematic review of a selected group of publications was performed through the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines and also through the ProKnow-C (Knowledge Development Process—Constructivist) methodology adaptation (Ensslin, et al., 2014), developed by the Laboratory of Multicriteria Methodologies in Decision Support (Laboratório de Metodologias Multicritério em Apoio à Decisão—LabMCDA) from the Federal University of Santa Catarina (UFSC—Brazil).

This method aimed to identify works by a set of stages for the final-bibliographic-portfolio (FBP) generation, which was realized through a systematic analysis of the works' contents and the meta-analysis study, mapping and investigating the main results attained by the authors. For this purpose, some characteristics were imposed in the searching stage: (i) scientific works published in indexed journals from the Scopus and Web of Science databases; (ii) works from 2010 to 2020; and (iii) works made available in English and full format by the CAPES (Coordination for the Improvement of Higher Education Personnel, Brazil) website. The process was divided into four structured stages: (1) identification, (2) triage, (3) eligibility, and (4) inclusion.

The identification stage consisted of the choice of keywords, which were divided into two distinguished thematic axes and combined by the Boolean operators (OR, AND),

generating the search string ("emerging pollutants" OR "emerging contaminants" OR pharmaceuticals OR caffeine AND photocatalysis OR "photocatalytic degradation").

In the triage stage, the works were attached to the bibliographic manager StArt (State of the Art through Systematic Review), from the Software Engineering Researching Laboratory (Laboratório de Pesquisa em Engenharia de Software—LaPES, at the Federal University of São Carlos—UFSCAR), where they were filtered after a careful reading of the titles, following by the exclusion of repeated documents and those that were not aligned with the research. The implementation of the bibliographic manager has demonstrated exceptional utility, streamlining preliminary work to a degree unmatched by previous publications from the same research group. Its integration has not only enhanced the organization but also optimized the efficiency of the data management and literature review processes, marking advancements in research methodology [18].

For confirming their eligibility, the works were organized on a worksheet and classified according to their numbers of citations in the Google Scholar database to verify their scientific relevance. Subsequently, the abstracts of the relevant ones were read, once more excluding the ones that were not aligned with the research.

Finally, in the inclusion stage, after verifying the availability of the full works' contents on the web, the complete reading of the repository was carried out, in which those that were not aligned with the scope of the research were also excluded. The works considered aligned remained on the list and composed the FBP.

2.2. Systematic Analysis of the FBP

The selected works from the FBP were analyzed individually regarding the main operational parameters discussed and analyzed by the authors: the type of radiation, the concentration of the catalyst and contaminating drug, the type of water matrix, and the pH. In addition, the main research gaps related to the optimization of these variables were identified through the evaluation of the knowledge currently published under the model of the treatment of pharmaceutical contaminants by heterogeneous photocatalysis, and from the information and data necessary to fill these gaps.

2.3. Meta-Analysis Study Design

To carry out the meta-analysis, stages were included in the data at which the experiments were carried out, the responses and input variables of which were fully available in their texts. The analysis was conducted using the statistical software MINITAB (Statistical Software Data Analysis, version 17), using the data that showed the best correlation after statistical refinement.

From the set of documents presented in the FBP, four works were chosen to compose the meta-analysis, which had the following contaminants and respective concentrations: nimesulide (5 mg/L), diclofenac (8 mg/L), amoxilin (10 mg/L), and metoprolol (50 mg/L), each of them representing a different drug class. The photocatalysts employed for the degradation of these contaminants were as follows: TiO_2, MWCNTox/TiO_2, TiO_2 P25, and 5%B-TiO_2. All experiments in this set of articles were performed in synthetic solution using ultrapure water with artificial UV radiation and wavelengths in the range of 350–400 nm. To compose the meta-analysis, the factors chosen were the (i) catalyst concentration; (ii) pH; and (iii) time. The response variable was the degradation efficiency.

3. Results and Discussion

3.1. Systematic Review

Figure 1 shows the flowchart of the systematic review in the search of the articles of the Final Bibliographic Portfolio from 2010 to 2020. The complete flowchart can be visualized in a previous work [17].

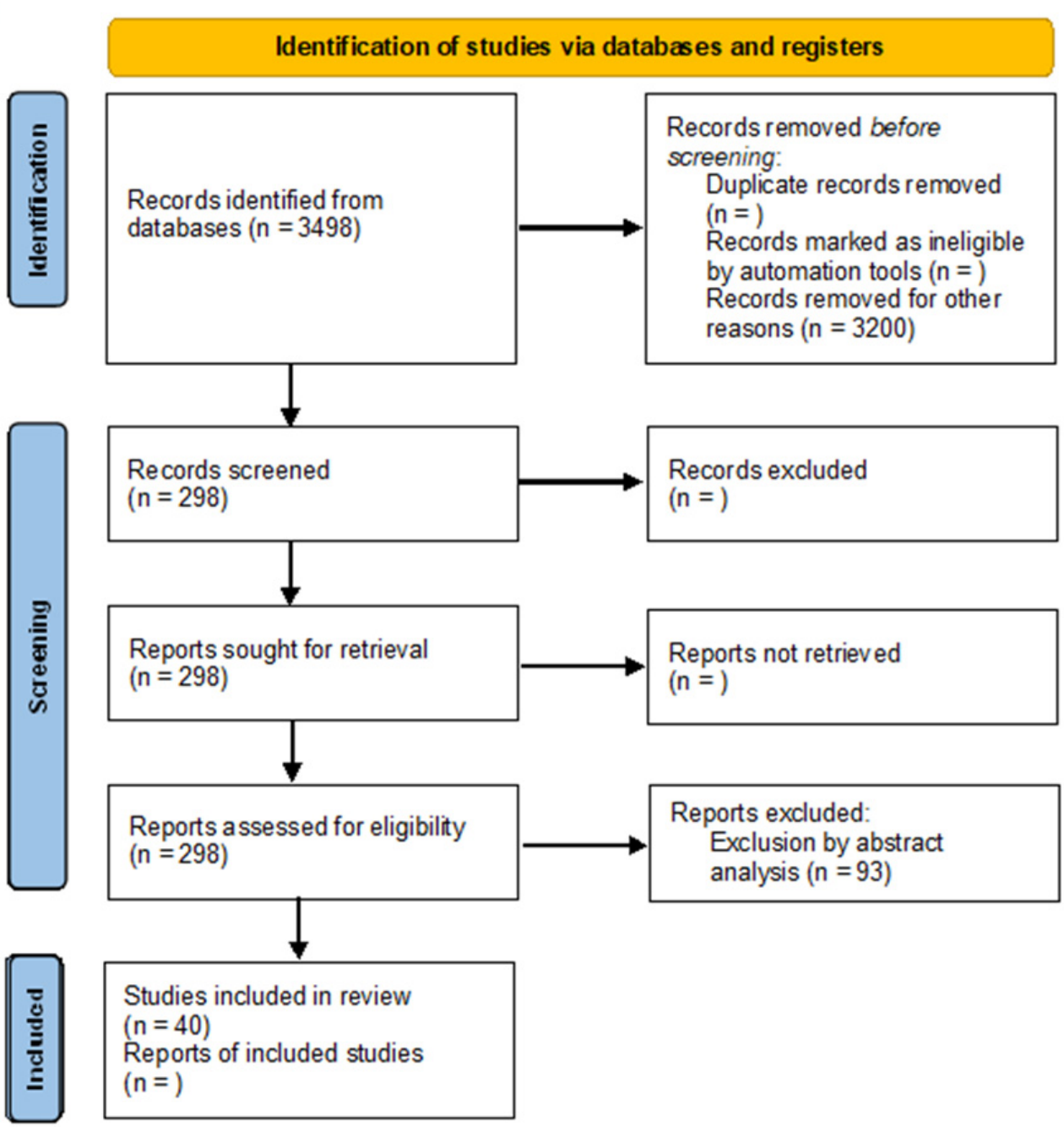


Figure 1. Flowchart of the FBP's search and selection from 2010 to 2020, following the PRISMA methodology.

Heterogeneous photocatalysis applied to the treatment of pharmaceuticals has been studied by several researchers. Table 1 presents a thematic synthesis of the publications of the FBP, categorized according to the types of catalyst and contaminant, the operational conditions of the process, time, and the efficiency of the degradation used and obtained in each work.

Table 1. Thematic synthesis of the Final Bibliographic Portfolio from 2010 to 2020.

	Compounds	Operational Conditions	Removal Rate (%)—Time (min)	References
ANTIHYPERTENSIVES	Atenolol	λ = 365 nm; LA [(1)]; SINT [(2)] and AR [(3)]; TiO_2 (2.0 g/L); pH 6.8; [C] [(4)] 37.6 μM	SINT 100%—60 min AR 100%—180 min	[19]
	Atenolol	λ = 290–400 nm; LA; SINT; bismuth oxychloride (0.4 g/L); pH 5; [C] 10 mM	100% < 50 min	[20]
	Metoprolol	λ = 280 nm; LA; SINT and ES; 5%B-TiO_2 (0.4 g/L AU; 2.0 g/L ES); pH 6.3; [C] 50 mg/L	SINT 70%—180 min ES 44%—180 min	[21]
	Metoprolol and propranolol	λ = 290–400 nm; LA; SINT; TiO_2 (0.4 g/L); pH 4.2 and 5.7; [C] 50 mg/L	100%—300 min 100%—360 min	[22]
	Propranolol	λ = 290–400 nm; LA; SINT and ES [(5)]; 5%Ce-TiO_2 (0.14 g/L); pH 7.5; [C] 25 mg/L	SINT 100%—90 min ES 100%—360 min	[23]
	Propranolol	λ = 280 nm; LA and natural light; SINT; TiO_2 (0.4 g/L); [C] 50 mg/L	Artificial 94%—240 min Solar 81%—240 min	[24]
	Antipyrine	λ = 300–400 nm; LA; SINT; Zr-TiO_2 (0.25 g/L); [C] 10 mg/L	90%—360 min	[25]
	Acetaminophen	λ = 254 nm; LA; SINT; 40% TiO_2/zeolite (1.0 g/L); pH 6.4; [C] 15 mg/L	96%—180 min	[26]
	Acetaminophen	λ = 800–200 nm; LA; SINT; $BaTiO_3/TiO_2$ (1 g/L); pH 7; [C] 5 mg/L	95%—240 min	[27]
	Acetaminophen and antipyrine	λ = 320 nm; LA; SINT; TiO_2-0.5%ZnO/clay (0.25 g/L); [C] 10 mg/L	95%—360 min	[28]
	Diclofenac	λ = 366 nm; LA; SINT; TiO_2 anatase (0.5 g/L); pH 6.22; [C] 8 mg/L	100%—30 min	[29]
	Diclofenac and fluoxetine	λ = 365 nm; LA; ES; hydroxyapatite (4 g/L); pH 6.1; [C] 5 mg/L	92%—24 h 100%—24 h	[30]
	Ibuprofen; acetaminophen; antipyrine	λ = 320 nm; LA; SINT; ZnO/sepiolite (0.25 g/L); [C] 10 mg/L	100%—600 min 85%—600 min 70%—600 min	[31]
ANTI-INFLAMMATORY ANALGESICS	Ibuprofen	λ = 382 nm; LA; SINT and FARM [(6)]; TiO_2 (1.0 g/L); pH 5.3; [C] 213 mg/L	SINT—100%—30 min FARM—18%—30 min	[32]
	Ibuprofen Naproxen	λ = 380–900 nm; LA; SINT; nanoparticles and nanosheets; N, S-TiO_2; (2 g/L); pH 6.0; [C] 2.5–10 mg/L	NanoP 85%, NanoS 71%—90 min; NanoP 99%, NanoS 99%—90 min	[33]
	Ketorolac tromethamine	Natural light; SINT; TiO_2/quantum dots (0.5 g/L); pH 4.4; [C] 750 mg/L	99%—120 min	[34]
	Naproxen	λ = 200–600 nm; LA; SINT; TiO_2 (0.1 g/L); [C] 30 mg/L	100%—25 min	[35]
	Nimesulide	λ = 290 nm; LA; SINT; TiO_2 (0.1 g/L); pH 6.0; [C] 5 mg/L	100%—45 min	[36]
	Paracetamol	λ = 200–800 nm; LA; SINT; 3%$WO_3/TiO_2/SiO_2$ (1.5 g/L); pH 9; [C] 5 mg/L	95%—240 min	[37]
	Paracetamol	λ = 420 nm; LA; SINT; 0.1%Cu-TiO_2 (4 g/L); pH 6.0; [C] 50 mg/L	100%—180 min	[38]

Table 1. *Cont.*

	Compounds	Operational Conditions	Removal Rate (%)—Time (min)	References
ANTIBIOTICS	Paracetamol	LA, ES; TiO_2/glass (0.50 g/L); [C] 51 mg/L	100%—240 min	[39]
	Phenazopyridine	λ = 400 nm; LA; SINT; graphene oxide hydroxide/sulfate (0.015 mg/L); pH 8.0; [C] 15 mg/L	60%—150 min	[40]
	Salicylic acid; ibuprofen; naproxen; diclofenac	SINT; natural light, P25-TiO_2 tetraethyl orthosilicate; (3 mg); pH 6.0; [C] 5 mg/L	76%—600 min 85%—600 min 94%—600 min 65%—600 min	[41]
	Tetracycline	λ = 253–2500 nm; LA and natural; SINT; metal–organic structure Fe/TiO_2 (1 g/L); pH 7; [C] 20 mg/L	Natural (solar) 92.76%—10 min Visible 91.24%—360 min	[42]
	Levofloxacin	λ = 400–520 nm; LA; SINT; bismuth tungstate (0.1 g/L); pH 7; [C] 750 mg/L	80%—180 min	[43]
	Amoxicillin	λ = 200 and 600 nm; LA; SINT; integrated photocatalytic adsorbents/TiO_2/zeolite (2 g/L); [C] 30 mg/L	88%—240 min	[44]
	Amoxicillin	λ = 350–400 nm; LA; SINT e ES; TiO_2 Degussa P25 (0.25 g/L); pH 5 (AUP); 7.5 (ES); [C] 10 mg/L (0.2 g/L); pH 5; [C] 10 mg/L	SINT 100%—25 min ES 100%—60 min	[45]
	Amoxicillin Cloxacillin Ampicillin	λ = 365 nm; LA; SINT; TiO_2 (1 g/L); pH 5.0; [C] 104 AMOX, 105 CLOX, 103 AMP mg/L	100%—30 min	[46]
	Azithromycin	λ = 254–185 nm; LA UV-C; SINT and ES; TiO_2/glass; pH 7; [C] 10 mg/L	SINT 100%—30 min ES 95%—120 min	[47]
	Cefixime	λ = 320–780 nm; LA; SINT; mixed-binder MIL-125 (Ti)/nanocomposite g-C_3N_4 (0.3 g/L); pH 4.0; [C] 20 mg/L	985—120 min	[48]
	Isoniazid; metronidazole; sulfadiazine; sulfamethoxazole; trimethoprim; norfloxacin; moxifloxacin; lincomycin	Natural light, LA; SINT and ES; ethylene terephthalate–TiO_2 (0.5 g/L); [C] 1 mg/L	SINT 100%; ES 90%—10 h SINT 100%; ES 90%—10 h SINT 100%; ES 80%—14 h SINT 100%; ES 80%—14 h SINT 100%; ES 70%—14 h SINT 100%; ES 90%—10 h SINT 100%; ES 90%—10 h SINT 100%; ES 90%—10 h	[49]
	Oxytetracycline	λ = 420 nm; LA; SINT; TiO_2-Ag (0.5 g/L); pH 5.8; [C] 0.5 mg/L	100% UV-Vis—60 min 100% Visible—360 min	[50]
	Oxytetracycline	λ = 290–400 nm; LA and natural light; SINT; TiO_2 (0.5 g/L); [C] 20 mg/L	Artificial 95%—35 min Solar 95%—35 min	[51]
	Tetracycline	λ = 240 nm; LA; FARM; multi-walled carbon nanotubes/TiO_2	100%—100 min	[52]
	Tetracycline hydrochloride	λ = 254 nm; LA; SINT; TiO_2/biochar (0.5 g); pH 4; [C] 5 mg/L	91%—360 min	[53]
	Tetracycline hydrochloride	λ = 400 nm; LA; FARM; Ag/$AgIn_5S_8$ (0.3 g/L); [C] 10 mg/L	95%—120 min	[54]
	Tetracycline	λ = 254 nm; LA; SINT; $FeNi_3/SiO_2/TiO_2$ (0.005 g/L); pH 9.0; [C] 10 mg/L	100%—200 min	[55]

Table 1. *Cont.*

Compounds	Operational Conditions	Removal Rate (%)—Time (min)	References
Tetracycline	λ = 400 nm; LA; ES; $BiOCl/TiO_2$/sepiolite (60 mg/100 mL); [C] 10μM	92%—180 min	[56]
Trimethoprim	λ = 254 nm; LA; SINT; TiO_2-P25-doped Au/Ag/Cu/Ni (0.25 g/250 mL); [C] 40 mg/L	100%—40 min	[57]

(1) Artificial light; (2) synthetic; (3) water from the river; (4) compound concentration; (5) secondary effluent; (6) pharmaceutical.

3.2. FBP Analysis

3.2.1. Operating Parameters

The FBP-listed studies used heterogeneous photocatalysis in the degradation of pharmaceutical contaminants, and the operational parameters that affect the overall efficiency of the process and the gaps associated with the optimization of these variables were identified.

3.2.2. Radiation Types

The incident light intensity determines the quantity that can be absorbed by the catalyst at a given wavelength, with its distribution in the solution determining the pollutant conversion and degradation efficiency. Kurniawan et al. [27] used UV-Vis irradiation on the $BaTiO_3/TiO_2$ composite, which achieved a satisfactory removal of 73% of acetaminophen after 4 h of photodegradation. Jallouli et al. [32] observed that the removal rate of ibuprofen using TiO_2 increased with the number of UV LED lamps used, once the light irradiation produces the necessary photons to transfer electrons from the valence band to the conduction band of the photocatalyst.

De la Cruz et al. [24] used two irradiation systems (solar and artificial). The degradation rates for propranolol in the solar plant achieved 64.8, 65.4, and 80.5% after 240 min, for 0.1, 0.2, and 0.4 g/L TiO_2, respectively. In contrast, the removal in the laboratory device with a Xe lamp after 240 min was 81.6, 88.0, and 94.1% for the three different catalyst concentrations. For Tobajas et al. [28] the degradation of acetaminophen and antipyrine with the TiO_2-ZnO/clay composite showed greater efficiency with the increase in the intensity of the incident sunlight since there was a greater availability of photons to activate the photocatalyst and generate more radicals.

3.2.3. Concentrations of the Catalyst and Drug Pollutant

It was observed that the overall efficiency of the process achieved more significant results at higher concentrations of the catalyst with lower concentrations of the drug. This fact is due to the higher probability of mass transfer between the photocatalytic active sites and the presence of the compound at higher levels. However, the photocatalytic degradation rate increases towards a limit value, depending on the used concentrations, due to the limited availability of the semiconductor active sites.

In the study carried out by Salimi et al. [48], the maximum degradation of cefixime was obtained with an increase in the catalyst concentration from 10 to 30 mg/L. A further increase in the catalyst amounts beyond 30 mg/L resulted in a decline in the removal efficiency due to the so-called screening effect: higher photocatalyst dosages can mask the photosensitive surfaces of the catalyst particles, hindering the light dissemination and decreasing the removal efficiency. In addition, for Ahmadi et al. [52], the photocatalytic degradation efficiency of tetracycline improved with an increasing photocatalyst dosage, and its complete removal was observed at a dosage of 0.2 g/L after 100 min. This result can be attributed to the higher number of adsorption and photocatalytic sites available on the catalyst surface.

The effect of the TiO_2 concentration was studied in the range from 50 to 400 mg/L, and it was observed that the initial degradation reaction rate increased with the addition of the catalyst (50–200 mg/L). This happens due to an increase in the photogeneration of active sites on the catalyst's surface, which forms greater amounts of reactive oxygen species. However, above an optimum concentration (200 mg/L), the initial reaction rate decreased. This phenomenon was also attributed to the increased scattering of light by suspended particles of the catalyst by the formation of aggregates obstructing the transmission of light passing through the sample [36,58,59].

The target pollutant concentration must be compatible with the absorption capacity of the catalyst, since the active sites must be sufficient to interact comparatively with the contaminant molecules, with no need to increase reactive species in the process. The results discussed by Kurniawan et al. [27] showed that the removal rate of acetaminophen decreased from 81% to 19% as the initial contaminant concentration increased from 5 to 25 mg/L. A similar effect was verified by Yanyan et al. [37] when the concentration of acetaminophen increased from 5 to 25 mg/L and its photodegradation rate decreased from 85% to 26%. Tobajas et al. [28] found that the highest acetaminophen conversion values were obtained when working with an initial concentration of 10 mg/L, decreasing significantly beyond that. As the initial concentration of the compound increased, the adsorption layer became thicker, thereby preventing the photon from the UV-Vis light source from reaching the surface of the photocatalyst.

Tables 2 and 3 summarize the influence of each catalyst and contaminant concentration on the photocatalytic degradation of a variety of pharmaceutical pollutants studied under different irradiation sources.

Table 2. Influence of catalyst concentration on the photocatalytic degradation of different drugs.

Pollutants	Radiation Source	Photocatalyst	Catalyst Dose Range (g/L)	Optimal Dosage (g/L)	Efficiency (%)	References
Amoxicillin and ampicillin	UV	TiO_2	0.5–2	1.0	100	[46]
Atenolol	UV	BiOCl	0.05–0.4	0.3	100	[56]
Cefixime	UV	MIL-125 (Ti)/ g-C_3N_4	0.01–0.04	0.03	98	[48]
Diclofenac	UV-Vis	TiO_2 anatase P25	0.1–2	0.5	100	[29]
Diclofenac Fluoxetine	UV	Hydroxyapatite	1–4	4.0	92 100	[30]
Ibuprofen	LED	TiO_2	0.5–1.5	1.5	SYNT [1]—100 SE [2]—18	[32]
Ibuprofen Naproxen	UV	N, S-TiO2	0.5–5	2.0	78 99	[33]
Naproxen	UV	TiO_2	0.01–2	0.1	100	[35]
Nimesulide	UV	TiO_2	0.05–0.4	0.1	100	[36]
Propranolol	Solar UV	TiO_2 Degussa P25	0.1–0.4	0.4	81 94	[24]
Tetracycline	UV	MWCNTs/TiO_2	0.1–0.4	0.2	100	[52]

[1] Synthetic; [2] secondary effluent.

Table 3. Influence of the initial drug concentration on the photocatalytic degradation of different contaminants.

Pollutant	Radiation Source	Photocatalyst	Catalyst Dose Range (g/L)	Optimal Dosage (g/L)	Efficiency (%)	References
Acetaminophen	UV	TiO_2/zeolite	0.0075–0.06	0.015	96	[26]
Amoxicillin	UV	TiO_2 Degussa P25	0.0025–0.03	0.01	SYNT [1] 100 SE [2] 100	[45]
Cefixime	UV	MIL-125 (Ti)/g-C_3N_4	0.015–0.025	0.02	98	[48]
Diclofenac and fluoxetine	UV	Hydroxyapatite	0.002–0.008	0.005	92 100	[30]
Ketorolac tromethamine	Solar	TiO_2/quantum dots	0.01–0.04	0.01	80	[34]
Phenazopyridine	LED	Graphene oxide/ sulfate/hydroxide	0.005–0.025	0.015	60	[40]
Tetracycline	UV	MWCNTs/TiO_2	0.0005–0.03	0.01	100	[52]

[1] synthetic; [2] secondary effluent.

3.2.4. Type of Water Matrix

The different types of constituents present in the water matrix can determine the degradation kinetics, altering the final catalytic mechanism of the process and the reaction speed, since the natural constituents of the solution can compete for the active sites of the catalyst, reducing the chance of the contaminant's degradation.

According to Jallouli et al. [32], heterogeneous TiO_2 photocatalysis was efficient in removing ibuprofen from ultrapure water and wastewater from the pharmaceutical industry, both enriched with the pollutant and less efficient at treating wastewater from the municipal treatment plant, due to the matrix complexity. The UV/TiO_2 degradation rate of naproxen in river water in the absence of anions was 0.21 min^{-1}. After adding anions to the aquatic matrix, the degradation rate decreased sharply to 0.10 min^{-1}. This fact can be explained by the presence of natural organic matter that possibly filtered the necessary radiation for the activation of TiO_2 and competed for reactive sites of the photocatalyst (Kanakaraju; Glass; Oelgemöller, 2014). Compared to ultrapure water, a secondary effluent containing around 8 mg/L of organic matter reduced the photocatalytic conversion of amoxicillin. This can also be explained by the fact that the compounds present in natural waters are known as radical scavengers, as they compete for the oxidative radicals and other oxidizing species formed during the photocatalytic process [45].

Malesic-Eleftheriadou et al. [49] observed that slower kinetics are obtained as the complexity of the matrix increases. Lower velocity values and longer half-lives were recorded for all drugs studied when photocatalysis was performed in sewage effluent compared to distilled water. The large amount of organic matter in the effluent constitutes one of the main retardants, as it consumes a large part of the hydroxyl radicals formed and oxidative species in general, competing with the degradation of antibiotics. Furthermore, organic or inorganic constituents can be adsorbed on the catalyst surface, leaving fewer active sites available for the target compound.

3.2.5. pH and Catalyst Concentration

The wastewater pH varies significantly and can play an important role in the photocatalytic degradation of organic contaminants, as it influences the species distribution in the aquatic matrix and determines the surface charge of the photocatalyst and the size of the aggregates it forms, as well as the repulsion or electrostatic attraction between them. In the study conducted by Koltsakidou et al. (Koltsakidou et al., 2019), it was observed that the highest initial reaction rate occurred at a pH of 6, (close to the pH at the point-

of-zero charge of TiO_2 and the pKa value of nimesulide, 6.5). For pH values above 6.5, nimesulide is negatively charged, and for values below 6.5, the surface charge of nimesulide is positive. Consequently, for pH values lower or higher than 6.5–6.7, both the drug molecule and the catalyst surface are charged with the same type of charge, which results in electrostatic repulsion.

The removal of acetaminophen by the $BaTiO_3/TiO_2$ compound tended to improve with an increase in the pH from 3 to 7. The maximum removal rate of acetaminophen occurred at a pH of 7, and 95% degradation was achieved after 4 h with an initial concentration of 5 mg/L since •OH was formed, attacking the acetaminophen molecules. At the same initial concentration of 5 mg/L, the photocatalytic degradation rate improved from 56% to 95% with an increase in the dose of photocatalysts from 0.5 g/L to 1.0 g/L after 4 h of reaction [27].

Figure 2 presents the dot graph of the pH and catalyst concentration parameters used in the FBP articles, accumulating the values according to the frequency at which the data are repeated. The most used pH was around 6, while catalyst concentrations lower than 0.6 g/L were the most chosen, with an emphasis on the concentration of 1.0 g/L that was used in six articles.

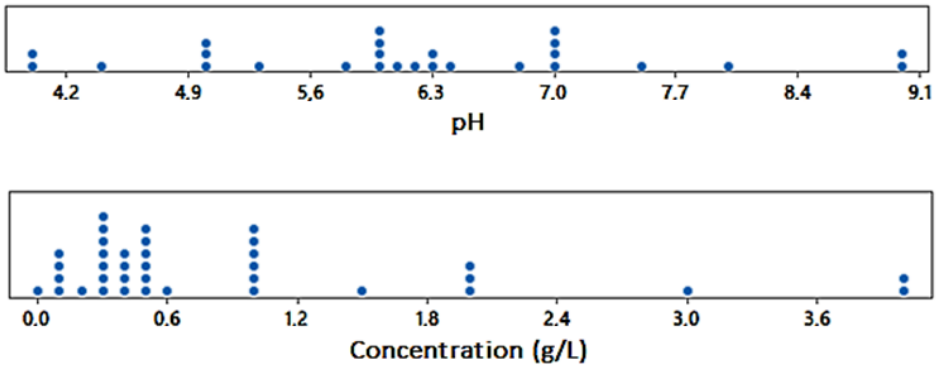


Figure 2. Graphical representation of points of the catalyst concentration and pH parameters used in the articles of the Final Bibliographic Portfolio in the period from 2010 to 2020.

Considering the gaps associated with the optimization of the operational parameters, it was observed that a large part of the FBP articles are characterized by a limited number of studies related to the interactions of all these control variables, in which it would be possible to establish acceptable optimal values of the efficiencies of degradation. The optimization of these complex variables would provide greater security related to their effects from studies with factorial designs, in which the parameters are continually modified until the optimal experimental conditions and treatment efficiency are reached.

Furthermore, it was found that most studies sought to determine the ideal conditions for photocatalysis by varying one parameter at a time, to isolate the effects of each factor. Although this conventional approach is widely accepted, it may neglect interactions between factors, as parameters may be interrelated, leading to results with lower predictive power [60].

Many researchers in the current literature optimized the reaction parameters by factorial design [24,60,61], through which the effects of all the experimental variables of interest and the interaction effects on the desired response were determined. Some examples are complete factorial planning, factorial planning with a central point, and rotational central composite planning associated with the response surface methodology, which have as their main objectives an analysis of the reaction condition that has the greatest influence on the photodegradation, facilitating the researcher's understanding. Therefore, this was an important gap identified in the FBP.

Another lack regarding what was presented concerns the scarce use of solar radiation in experiments as a source of light. The use of solar radiation favors the use of narrower

gap catalysts, which are, consequently, more suitable for excitation at wavelengths outside the UV spectrum. The solar spectrum brings a great advantage associated with the use of clean and free energy, which is easily accessible and inexhaustible, while the lifespans of conventional lamps are short and, therefore, have a relatively high economic cost [54]. Furthermore, if sunlight is applied, the treatment technology has great potential for practical application on a full scale, especially in areas with abundant solar energy resources. This scarcity, however, may be related to the fact that most of the freely available solar energy is made up of visible light, making it necessary to modify the nanomaterial in such a way that it can facilitate the absorption of the light, aiming to increase the efficiency of broadband semiconductors under solar irradiation, which would generate more costs for the process.

Another gap identified concerns the large number of experiments that used synthetic effluents (27) compared with the number that used natural water samples or real effluents (11). Furthermore, drug concentrations outside the reality of what is normally found in real effluents were used, as noted in the summary of some studies in Table 4.

Table 4. Emerging-contaminant concentrations in environmental water samples from 1997 to 2016.

Class/Pollutant	Raw Effluent	Treated Effluent	Surface Water	Tap Water	Groundwater
Pharmaceuticals	13.9–3800 ng/L	680–3800 ng/L	0.50–30.421 ng/L	18.5 ng/L	-
Analgesics and anti-inflammatories	-	60.00 µg/L	5.00 µg/L	0.12 µg/L	-
β blockers	-	9.00 µg/L	2.00 µg/L	0.27 µg/L	-
Antibiotics	-	6.00 µg/L	1.90 µg/L	-	0.20 µg/L
Paracetamol	-	0.13 µg/L	0.84 µg/L	-	-
Acetaminophen	-	-	0.01 µg/L	-	-
Diclofenac	-	0.27 µg/L	0.10 µg/L	-	-
Atenolol	-	-	0.98 µg/L	-	-
Ibuprofen	-	0.23 µg/L	0.50 µg/L	-	-
Naproxen	-	0.07 µg/L	0.39 µg/L	-	-
Propranolol	-	-	0.04 µg/L	-	-

Source: adapted from [62–64].

Tests on the pilot and real scales were quite scarce, without the use of continuous flow effluents or the presence of interfering constituents in the real environmental matrix, factors that can limit the catalyst's greater efficiency. The presence of a large amount of organic and inorganic matter in the aquatic matrix has a detrimental impact on the photocatalysis of emerging contaminants, due to the competition of active sites and the absorption of light by the natural constituents of the water. With this premise, it is noted that the highest speed rates occurred with the use of the ultrapure water matrix, which demonstrated a superior performance, where the process took place more quickly and the highest conversions were achieved in shorter periods.

Koltsakidou et al. [36] noticed that the reaction rate constants decreased and the nimesulide half-lives increased in aqueous WWTP samples, compared to ultrapure water, in both processes studied. This decrease was attributed both to a large amount of organic matter dissolved in the WWTP samples, which consumes the oxidizing species generated, and to the inorganic components present, such as Cl^-, $NO_3{}^-$, $NO_2{}^-$, and $CO_3{}^{2-}$ e $HCO_3{}^-$. These inorganic ions can scavenge the generated hydroxyl radical, affecting the efficiency of the applied photocatalytic treatment.

In this scenario, when a real-water matrix is used, there is the need to increase the concentration of the catalyst in use. This way, the substrate can have more contact and time to react, given the situation of the competition between the constituents of the environmental matrix for the active sites of the catalyst. This basic understanding of the effect of the

organic and inorganic constituents present in aquatic matrices is crucial in the performance of photocatalytic systems to ensure the operational stability of a full-scale project.

3.3. Meta-Analysis Study

From the systematic review data, it was possible to identify the existence of a correlation between the photocatalytic treatment variables and the contaminant degradation efficiency results obtained by each selected primary study. Initially, when analyzing the variables separately, it was not possible to establish a correlation between them and the degradation efficiency, with an R^2 lower than 0.1 found for all analyses. These low R^2 values corroborate the hypothesis that it is not possible to analyze the variables independently once the photocatalysis process is controlled by many parameters, which will have a significant influence on the removal of the contaminant. To compare all the tabulated variables, the catalyst concentration and pH parameters were divided into ranges, and the reaction time-versus-degradation efficiency graph was then generated.

The division into ranges demonstrated a correlation between the data from a group of four articles. The pH and catalyst concentration ranges that best correlated the reaction time with the contaminant degradation efficiency were 6–6.3 and 0.1–0.5 g/L, respectively. Time was chosen as a dependent parameter because it is of great practical and economic importance when applying the process on a real scale.

The selected data presented a normal distribution according to a p-value > 0.05 (p = 0.115). Therefore, the regression model was adjusted, and the Pearson correlation coefficient was found. From the analysis of these results, it was verified that there is a very conclusive correlation between the studied variables (R^2 = 98.7%), as observed in Figure 3.

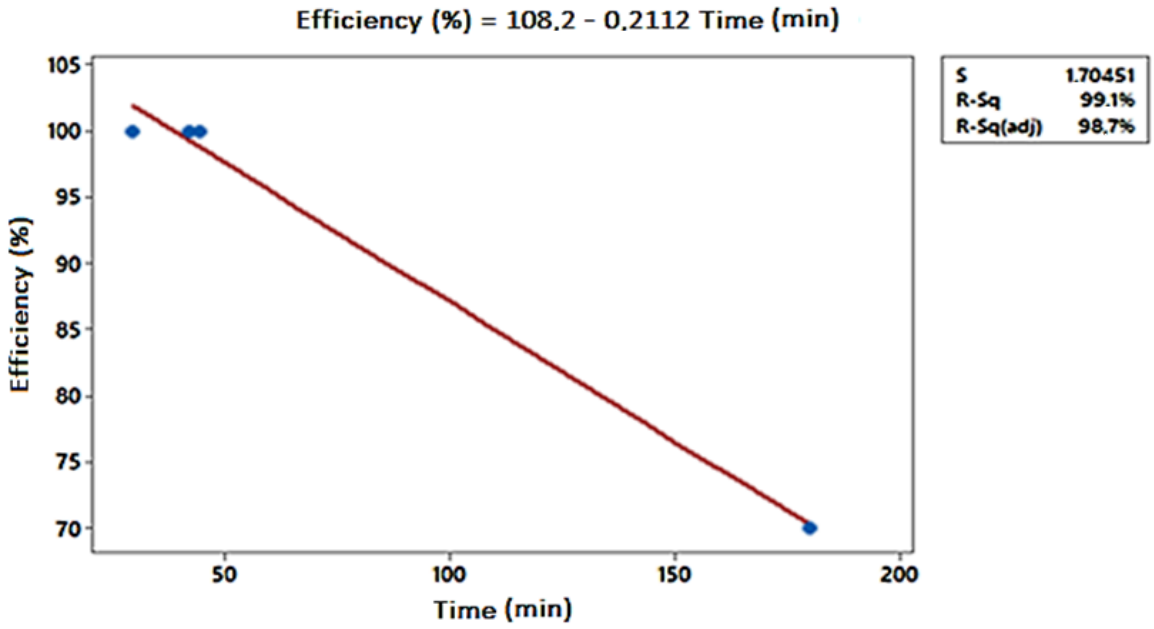


Figure 3. Fit of the regression model.

The given regression line has a negative slope, as does the Pearson's correlation coefficient (−0.996), demonstrating that time and efficiency for this specific data set are inversely proportional, with a tendency towards increased degradation over time, possibly due to the higher concentrations of the catalysts used in these experiments.

The meta-analysis results of the selected articles confirmed that TiO_2 nanoparticles and their composites formed from other semiconductors can remove pharmaceutical pollutants with an average efficiency of 92.5%. Figures 4 and 5 show the contour surface of the three-dimensional relationship in two dimensions with the factors represented on the x and y scales and the response value represented by the contours.

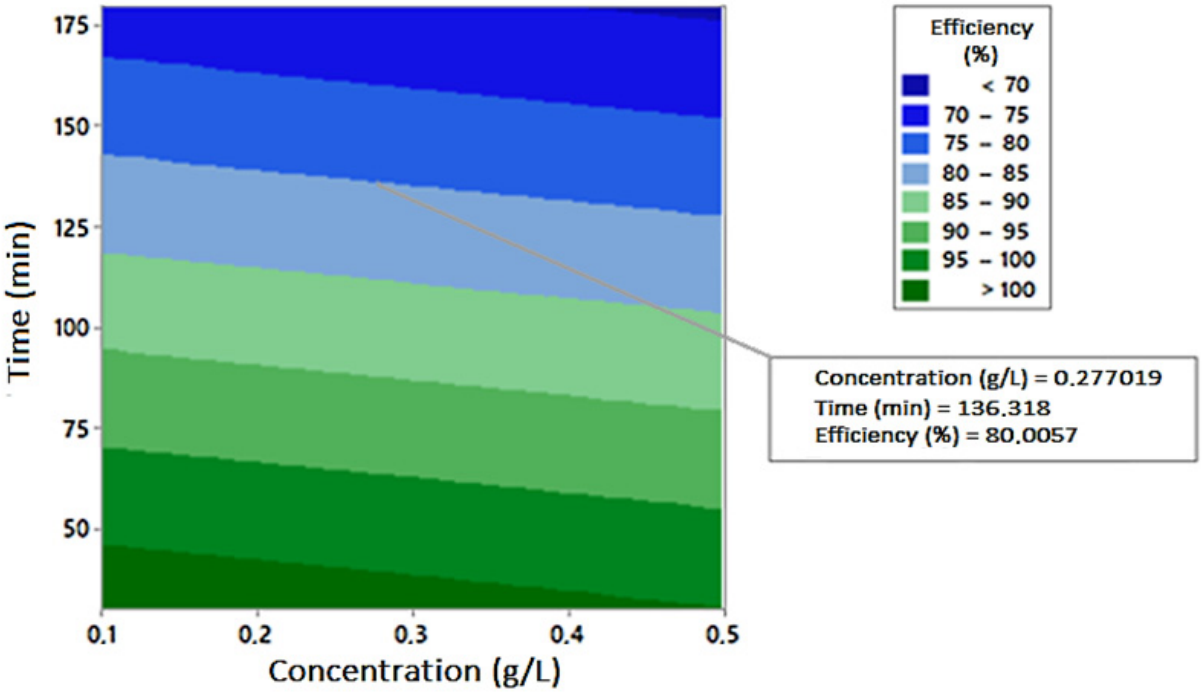


Figure 4. Contour surface of efficiency vs. time and concentration.

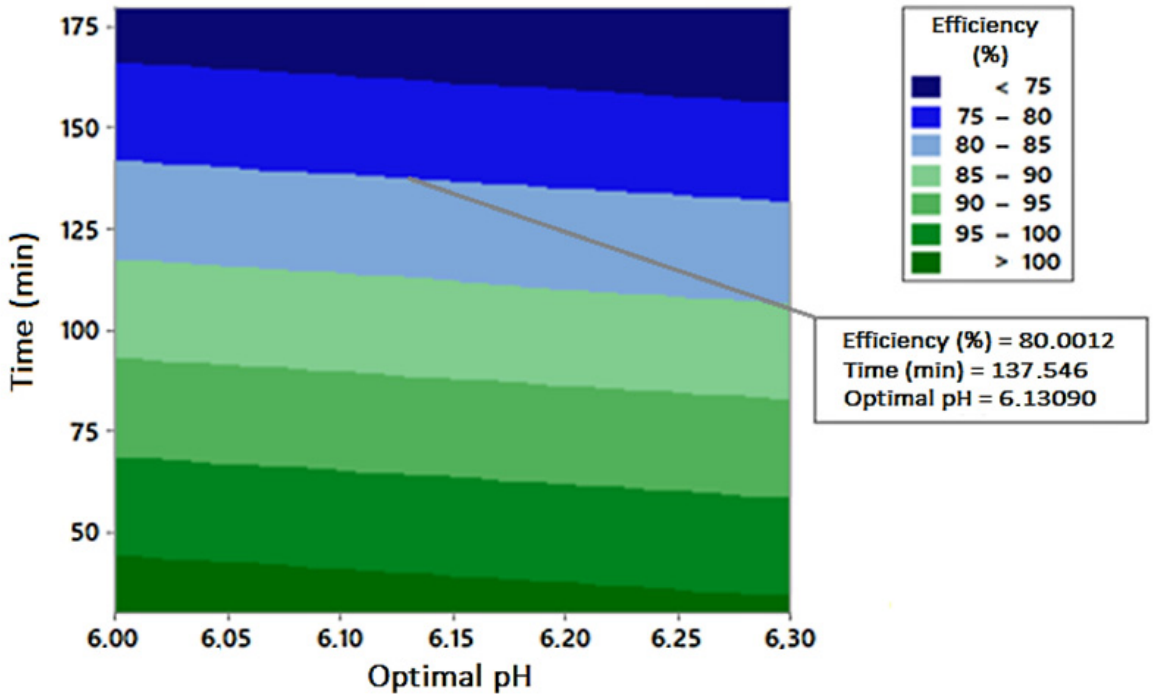


Figure 5. Contour surface of efficiency vs. time and pH.

The highlighted points underscore that achieving a degradation efficiency of at least 80% in the pollutant concentration requires specific conditions: a catalyst concentration of 0.27 g/L, a pH level of 6.13, and an average reaction time of approximately 136.9 min. These parameters are crucial for optimizing the degradation process. This finding aligns well with previous research, which has reported comparable outcomes under similar experimental conditions. The consistency between our model's predictions and the existing studies not only validates our approach but also reinforces the reliability and accuracy of our results [8,23,27,38,48,52,56].

4. Conclusions

The use of the PRISMA and the ProKnow-C methodology to carry out a systematic review followed by a meta-analysis of a Final Bibliographic Portfolio proved to be quite effective in terms of selecting articles published in relevant and scientifically recognized databases. The resulting bibliographic portfolio, consisting of 40 articles, revealed some gaps regarding the treatment of drugs by heterogeneous photocatalysis in the studied period.

Most studies were conducted under well-planned conditions, using simplified experimental systems, and with few results for real effluent treatment. The experiments were carried out using concentrations of pollutants higher than those found in natural aquatic matrices (nanograms/liter–micrograms/liter), and the samples investigated in the treatment were, for the most part, synthetic ultrapure water; the target contaminant was studied in the absence of constituents that are normally present in natural water matrices and that directly affect the process. Studies on the photocatalytic degradation of pharmaceutical contaminants using visible- and solar-light-active photocatalysts are still limited.

After evaluating the analysis of the FBP, it was observed that the role of the operational parameters (light source, catalyst and contaminant concentration, pH and type of water matrix) in photocatalytic degradation is fundamental to the final result of the process efficiency. However, there is still a need to determine the best experimental conditions for this technique, especially using tests on real effluents, which have greater potential for using the process on a large scale.

In this meta-analysis study, it was observed that for a degradation efficiency of at least 80% of the pollutant concentration, the catalyst concentration and pH must have values of 0.27 g/L and 6.13, respectively, and an average reaction time of 136.9 min.

Therefore, to advance this research topic, carrying out studies on the interaction of the operational variables must become an essential point for researchers, as they can allow further advances in the heterogeneous photocatalysis process applied to the treatment of pharmaceutical contaminants. Even though it is largely evaluated only in relatively simple matrices, an attempt must be made to guarantee the applicability of its activity in real matrices, virtually ensuring the stable use of different catalysts, which requires enhancing the use of the mentioned operational parameters.

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