Oxidative Degradation of Pharmaceuticals: The Role of Tetrapyrrole-Based Catalysts

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Abstract: Nowadays, society’s widespread consumption of pharmaceutical drugs and the consequent accumulation of such compounds or their metabolites in effluents requires the development of efficient strategies and systems that lead to their effective degradation. This can be done through oxidative processes, in which tetrapyrrolic macrocycles (porphyrins, phthalocyanines) deserve special attention since they are among the most promising degradation catalysts. This paper presents a review of the literature over the past ten years on the major advances made in the development of oxidation processes of pharmaceuticals in aqueous solutions using tetrapyrrole-based catalysts. The review presents a brief discussion of the mechanisms involved in these oxidative processes and is organized by the degradation of families of pharmaceutical compounds, namely antibiotics, analgesics and neurological drugs, among others. For each family, a critical analysis and discussion of the fundamental roles of tetrapyrrolic macrocycles are presented, regarding both photochemical degradative processes and direct oxidative chemical degradation.

Keywords: tetrapyrrolic macrocycle; porphyrin; phthalocyanine; antibiotics; pharmaceuticals; degradation; photodegradation; heterogeneous; oxidation

1. Introduction

The increasing presence of pharmaceuticals in wastewaters has become a huge environmental problem due to direct toxicity to living organisms and particularly the development of antibiotic-resistant bacteria. Therefore, it is urgent to develop processes capable of destroying these drug-based pollutants in the environment. Among the multiple oxidative processes described in the literature so far [1–7], this review intends to cover exclusively the ones based on the use of tetrapyrrolic macrocycle (TPM) catalysts over the last decade. First, for systematic-mechanistic clarification, we present the accepted photo- and non-photo oxidation mechanisms, and the following sections are focused on the photochemical and non-photochemical degradation of several families of pharmaceutical drugs using TPM-based catalysts.

Oxidation Mechanisms Using Tetrapyrrolic Macrocycle-Based Catalysts

The general photochemical mechanism involved in the degradation of pharmaceutical drugs using photosensitizers, such as tetrapyrrolic macrocycles, is depicted in Scheme 1.
Scheme 1. Adapted Jablonski diagram depicting the relevant electronic transitions that promote ROS formation in photocatalysis (in green), corresponding deactivating mechanisms (in gray) and other radiationless processes (in red): VR = vibrational relaxation; IC = internal conversion; ISC = intersystem crossing.

The absorption of visible light with an appropriate wavelength promotes the catalyst/photosensitizer excitation from the singlet ground state, \( S_0 \), to a singlet excited state (\( S_1, S_2, \ldots, S_n \)). Generally, if a transition occurs to singlet excited states of a higher order (\( S_2 \) to \( S_n \)), a quick transition to \( S_1 \) occurs through vibrational relaxation (VR) and internal conversion (IC). Singlet excited states are short-lived and can directly return to the ground state through fluorescence emission or IC. Alternatively, an intersystem crossing (ISC) can occur to a triplet excited state (usually \( T_1 \)), which is a longer-lived state capable of interacting with oxygen under two mechanisms. On the one hand, a direct or indirect electron transfer to molecular oxygen can occur (Type I mechanism), ultimately resulting in the formation of \( \text{HO}^\bullet \) and/or \( \text{O}_2^{-} \). On the other hand, an energy transfer (Type II mechanism) can occur between the catalyst in \( T_1 \) and \( \text{O}_2 \), resulting in the concomitant return of the catalyst to the ground state (\( S_0 \)) and the formation of singlet oxygen (\( \text{O}_2^\bullet \)) \([8,9]\).

For Type I reactions \([10]\), the photosensitizer (PS) in the triplet excited state (\( 3\text{PS}^* \)) can directly interact with substrates present in the medium to original either anionic or cationic radical species (\( \text{PS}^- \) and/or \( \text{PS}^+ \); Equations (1) and (2)). In particular, the anionic species \( \text{PS}^- \) can interact with molecular oxygen, forming superoxide anion (\( \text{O}_2^- \)), while returning to its ground state (Equation (3)). Then, the reversible protonation of \( \text{O}_2^- \) can lead to the formation of peroxo radicals (\( \text{HOO}^- \)); Equation (4)), which can then combine and form \( \text{H}_2\text{O}_2 \) (Equation (5)). Finally, the reaction of \( \text{H}_2\text{O}_2 \) with \( \text{O}_2^- \) can lead to the formation of \( \text{HO}^* \) (Equation (6)), which is considered the most reactive ROS as it possesses a higher one-electron redox potential and thus can oxidize a wider number of substrates \([9]\).

\[
\begin{align*}
3\text{PS}^* + \text{Substrate} & \rightarrow \text{PS}^- + \text{Substrate}^+ & (1) \\
3\text{PS}^* + \text{Substrate} & \rightarrow \text{PS}^+ + \text{Substrate}^- & (2) \\
\text{PS}^- + \text{O}_2 & \rightarrow \text{PS} + \text{O}_2^- & (3) \\
\text{O}_2^- + \text{H}_2\text{O} & \leftrightarrow \text{HOO}^- + \text{HO}^- & (4) \\
2 \text{HOO}^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & (5) \\
\text{O}_2^- + \text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + \text{HO}^* + \text{HO}^- & (6)
\end{align*}
\]
In the cases where there is a presence of either free Fe$^{3+}$/Fe$^{2+}$ or the corresponding metal tetrapyrrolic macrocycles complexes [11], a Fenton-type redox reaction of H$_2$O$_2$ with Fe$^{2+}$ can occur, leading to the formation of more OH$^•$ (Equation (7)). The reaction of the formed Fe$^{3+}$ with O$_2$$^•−$ can regenerate the active Fe$^{2+}$ species (Equation (8)).

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \rightarrow \text{HO}^• + \text{HO}^− + \text{Fe}^{3+} \\
\text{O}_2^•− + \text{Fe}^{3+} & \rightarrow \text{O}_2 + \text{Fe}^{2+}
\end{align*}
\]

Additionally, Fenton-type redox reactions can also occur with peroxymonosulfate (PMS) to generate sulfate radicals, also commonly used in several advanced oxidation processes (AOPs). Radiation, such as UV, can efficiently activate PMS. Two activation pathways might occur when using radiation. The first one is the O-O bond fission provoked by the input of energy (Equations (9) and (10)). Furthermore, the radiation might dissociate water molecules (Equation (11)), producing the electron, which activates PMS by electron conduction (Equations (12) and (13)) [12].

\[
\begin{align*}
\text{S}_2\text{O}_8^{2−} & \xrightarrow{\text{hv}} 2 \text{SO}_4^{•−} \\
\text{HSO}_5^{−} & \xrightarrow{\text{hv}} \text{SO}_4^{•−} + \text{HO}^• \\
\text{H}_2\text{O} & \xrightarrow{\text{hv}} \text{H}^• + \text{HO}^• \\
\text{S}_2\text{O}_8^{2−} + \text{H}^• & \rightarrow \text{SO}_4^{•−} + \text{SO}_4^{2−} + \text{H}^+ \\
\text{HSO}_5^{−} + \text{H}^+ & \rightarrow \text{SO}_4^{•−} + \text{H}_2\text{O}
\end{align*}
\]

For pharmaceutical degradation, the ideal outcome of ROS-promoted degradation would be the total mineralization of the products, as depicted in Equation (14).

\[
\text{ROS} + \text{Drug} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

It is worth noting that tetrapyrrrole-based catalysts for photodegradation are often used in hybrid materials containing semiconductors in order to take advantage of their absorption in the UV region and complementary mechanisms of ROS formation. These are summarized in Scheme 2.

![Scheme 2. General mechanism for ROS formation using semiconductors.](image-url)
Light absorption by semiconductors promotes charge dissociation, resulting in the formation of positively charged holes (h⁺) in the valence band (VB) and electrons (e⁻) in the conduction band (CB). Positively charged holes can promote oxidation reactions of organic molecules (drugs) adsorbed on the surface of the catalyst or generate ROS via water conversion into HO•. On the other hand, electrons in the CB can be transferred to molecular oxygen, generating O₂•−, or promote reduction in H₂O₂ to HO•. These semiconductor-promoted oxidation mechanisms are complementary to the ROS formation pathways mentioned above for the TPM-based catalysts and thus potentiate drug degradation. [1,13] Thus, a significant portion of the work developed in this field has been focused on the development of hybrid catalysts comprising TPM immobilized in semiconductors [2,14–22].

In the absence of light, metal complexes of tetrapyrrolic macrocycles can also promote substrate oxidation in the presence of oxidants such as O₂ or H₂O₂. In fact, this process plays a crucial role in human drug metabolism, where the heme group containing a Fe(II)/Fe(III) metalloporphyrin is the prosthetic group of the cytochrome P450, one of the most important oxidative enzyme families [23–26]. Typically, biomimetic drug degradation studies for environmental remediation use water as a matrix, H₂O₂ as the oxidant and a simplified mechanism, as depicted in Scheme 3. The first step involves the coordination of the central metal with H₂O₂ and the formation of a peroxo species. It is worth mentioning that in cases where O₂ is used as an oxidant, there are two additional reductive steps to activate it in order to form the peroxo species. Then, the formation of oxo species occurs after H₂O elimination and oxidation of the central metal [27,28]. In protic solvents, these intermediates can then react with drugs and promote a series of oxidative reactions, namely epoxidations, hydroxylation, dealkylation, deamination, decarbonylation, N- or S-oxidation, among others [29].

Scheme 3. Simplified mechanism for drug oxidation using H₂O₂ and a tetapyrrolic-based metal complex.

2. Degradation of Antibiotics

The term antibiotic derives from the ancient greek ἀντι (anti) + βιοτικός (biotikos), which means “against a living being”. Therefore, these drugs are exclusively used to treat bacterial infections and have no effect on viral infections. Typically, antibiotics are grouped according to their mechanism of action against specific types of bacteria. The main types of antibiotics are penicillins, tetracyclines, sulfonamides, quinolones, cephalosporins, aminoglycosides and macrolides [30].

The clinical overuse of antibiotics for humans and animals has led to the existence of active pharmaceutical ingredients of antibiotics in the environment, particularly in domestic wastewater (concentrations range from ng L⁻¹ to µg L⁻¹) and in hospital and pharmaceutical manufacturing wastewater (concentrations 100–500 mg L⁻¹) [31]. This occurrence has caused a huge human health problem due to the consequential development of multiresistant bacteria. Therefore, the development of AOPs for antibiotic degradation
in wastewaters is currently a topic of utmost relevance. The structures of the antibiotics degraded by TMP so far are shown in Figure 1.

![Antibiotic Structures](image1.png)

**Figure 1.** Structures of antibiotics tested in TPM-catalyzed degradation in the last decade.

### 2.1. Photochemical Degradation

Several TPM-based photocatalysts have been used in the degradation of antibiotics, and their main structures are presented in Figure 2. Antibiotics of the tetracycline family (tetracycline—TC, oxytetracycline—OTC and their corresponding hydrochloride salts—TC·HCl and OTC·HCl, Figure 1) are among the most prescribed and, fortunately, among the most studied regarding their photodegradation (Table 1, entries 1–12).

Several authors incorporated phthalocyanines onto semiconducting photocatalysts, e.g., α-substituted zinc(II) tetra(4-carboxyphenyl)phthalocyanine (α-ZnTCPc, Figure 2) embedded onto g-C₃N₄ (α-ZnTCPc@g-C₃N₄) [31], copper(II) β-tetranitrophthalocyanine (CuTNPc, Figure 2) deposited on the surface of CeO₂/Bi₂MoO₆ nanoflowers (TNCuPc@CeO₂/Bi₂MoO₆) [21], copper(II) phthalocyanine (CuPc, Figure 2) adsorbed onto polyoxometalate nanorods of the type AgₓH₃ₓPMo₁₂O₄₀ (CuPc@AgHPMo₁₂) [32] and zinc β-tetraaminophthalocyanine (ZnTAPc, Figure 2) covalently linked through amide linkages to a Cu₂O-TiO₂ blend (ZnTAPc@Cu₂O-TiO₂) by modification of the TiO₂ surface at the semiconducting Cu₂O-TiO₂ layer with maleic anhydride, followed by reaction ZnTAP [33]. Visible-light xenon lamps were used as irradiation sources in these experiments, showing efficiencies above 90% in the degradation of TC or TC·HCl, except with CuPc@AgHPMo₁₂, which could only degrade TC·HCl in 61% (Table 1, entry 3) [32]. It should be emphasized that the best catalysts showed reusability up to four cycles without significant loss of activity, TNCuPc@CeO₂/Bi₂MoO₆ being the most efficient catalyst (Table 1, entry 2) [21]. The authors described that after 120 min of irradiation with an 800 W xenon visible light, the TOC removal efficiency was 83% for photocatalyst TNCuPc@CeO₂/Bi₂MoO₆ nanofibers, which shows the high mineralization ability of
these semiconducting nanofibers as a photocatalyst when compared to TNCuPc alone (25.5%) and CeO$_2$/Bi$_2$MoO$_6$ nanofibers (36.4%) [21].

![Figure 2. Structures of tetrapyrrolic macrocycles (TPM) used as catalysts for photodegradation of antibiotics.](image)

The authors proposed two pathways for the photodegradation of TC (Scheme 4), HPLC-MS. During the photodegradation process of TC ($m/z = 445$), some intermediates with the $m/z$ of 402, 360, 290, 274, 242 and 198 were identified, resulting from dechlorination, dihydroxylation, ring-opening reactions and addition-elimination reactions, mainly by O$_2$•− and HO• ROS species. Prolonged irradiation allowed the formation of small molecular intermediates that were converted to CO$_2$ and H$_2$O [21].

![Scheme 4. Proposed pathway for the photodegradation of tetracycline](image)

Similarly, other authors prepared several photocatalysts based on porphyrin derivatives (Table 1, entries 5–7), e.g., meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP, Figure 2) embedded onto a graphene oxide-Bi$_2$WO$_6$, forming the ternary catalyst TCPP@rGO-Bi$_2$WO$_6$ [18], nanostructured zinc(II) meso-tetrakis(4-cyanophenyl)porphyrin metal organic complex (ZnTCNP-MOC, Figure 2) [34] and copper(II) meso-tetra(carboxyphenyl)porphyrin (CuTCPP, Figure 2) metal organic framework (CuTCPP MOF) [35]. Under visible-light irradiation (visible-light 550 W halogen lamp), the photocatalyst ZnTCNP-MOC showed the highest performance, degrading 96% of TC in just 60 min (Table 1, entry 6) [34]. Interest-
ingly, experiments using CuTCPP MOF were performed under a low catalyst concentration (0.05 g/L), reaching a satisfactory 72% TC degradation after 6 h of irradiation (Table 1, entry 7) [35]. Only TCPP@rGO-Bi_2WO_6 was able to be reused in five irradiation cycles (Table 1, entry 5) [18].

Other reports were delivered using tetrapyrrolic macrocycles incorporated onto/into semiconducting blends and used to degrade TC antibiotics, e.g., iron(II) meso-tetrakis(4-carboxyphenyl) porphyrin (FeTCP, Figure 2) covalently attached to TiO_2, through a toluene diisocyanate (TDI) linker (FeTCP@TDI–TiO_2) [36], iron phthalocyanine (FePc, Figure 2) embedded onto semiconductor BiOBr (FePc@BiOBr) [37] and meso tetra(carboxyphenyl)porphyrin (TCPP, Figure 2) embedded onto BiOCl (TCPP@BiOCl) [19] (Table 1, entries 8–10). Under visible-light irradiation with a 150 W xenon lamp, Yao and Zhang performed the full degradation of a 25 mg/L solution of TC·HCl in 120 min using the hybrid catalyst FeTCP@TDI–TiO_2 with a 1 g/L concentration [36], displaying a pseudo-first-order reaction kinetics with k_{obs} = 2.9 \times 10^{-2} \text{ min}^{-1} (Table 1, entry 8). On the other hand, Xia’s group used bismuth oxyhalide as semiconductors instead of titanium dioxide, adsorbing FePc and TCPP onto BiOBr and BiOCl, respectively [19,37]. These results showed lower degradation rates (65% and 74% TC degradation for FePc@BiOBr and TCPP@BiOCl, respectively; Table 1, entries 9 and 10), using just 0.4 g/L catalyst loading. Additionally, these catalysts showed high reusability along several cycles. It should be emphasized that some of the above reports also included degradation pathways for TC, proposing the structural assignment of most oxidation products, based on HPLC analysis [21,34,36].

| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|-------------------------|----------|
| 1 [31] | α-ZnTCPc@g-C_3N_4 | [TC] = 30 mg/L | - Matrix: Distilled water - Visible-light xenon lamp λ > 400 nm (power: N/A) - pH = N/A; T = N/A - Pre-dark for 30 min | - 91% TC in 120 min - TOC: N/A - k_{obs}: N/A - Mechanism by HO• - Reutilization: 5 cycles |
| 2 [21] | TNCuPc@CeO_2/Bi_2MoO_6 | [TC] = 50 mg/L | - Matrix: Distilled water - Visible-light 800 W xenon lamp λ > 400 nm - pH = N/A; T = N/A - Pre-dark for 30 min | - 95% TC in 120 min - 84% TOC decrease in 120 min - k_{obs}: N/A - Mechanism by h^+ , O_2•− - Degradation pathway proposed - Reutilization: 4 cycles |
| 3 [32] | CuPc@AgHPMo_{12} | [TC·HCl] = 20 mg/L | - Matrix: Distilled water - Visible-light 500 W xenon lamp λ > 400 nm - [CuPc@AgHPMo_{12}] = 1 g/L - pH = N/A; T = N/A | - 61% TC·HCl in 180 min - TOC: N/A - k_{obs}: N/A - Mechanism by h^+ - Reutilization: N/A |
| 4 [33] | ZnTAPc@Cu_2O-TiO_2 | [TC·HCl] = 20 mg/L | - Matrix: Distilled water - Visible-light 300 W xenon lamp λ > 420 nm - [ZnTAPc@Cu_2O-TiO_2] = 0.5 g/L - pH = 6; T = 25°C | - 95% TC·HCl in 200 min - TOC: N/A - k_{obs}: N/A - Mechanism by h^+ , O_2•− - Reutilization: 4 cycles |
| 5 [18] | TCPP@rGO-Bi_2WO_6 | [TC] = 15 mg/L | - Matrix: Distilled water - Visible-light 300 W xenon lamp λ > 420 nm - [TCPP@rGO-Bi_2WO_6] = 0.3 g/L - pH = 7.3; T = N/A - Pre-dark for 30 min | - 84% TC in 60 min - TOC: N/A - k_{obs}: N/A - Mechanism by O_2•− , h^+ - Reutilization: 5 cycles |
| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|-------------------------|----------|
| 6 [34] | ZnTCNP MOC | [TC] = 5 mg/L | - Matrix: Distilled water  
- Visible-light 550 W halogen lamp λ > 420 nm  
- [ZnTCNP MOC] = 1 g/L  
- pH = 7.3; T = N/A  
- Pre-dark for 20 min | - 96% TC in 60 min  
- TOC: N/A  
- kobs: N/A  
- Mechanism by HO•, O2•-  
- Degradation pathway proposed  
- Reutilization: N/A |
| 7 [35] | CuTCP@MOF | [TC] = 40 mg/L  
[NOR] = 20 mg/L | - Matrix: Distilled water  
- Visible-light 150 W xenon lamp λ > 420 nm  
- [CuTCP@MOF] = 0.05 g/L  
- pH = 5–9; T = 25 °C  
- Pre-dark: N/A | - 72% TC (pH = 5), 44% NOR (pH = 9) degradation in 360 min  
- TOC: N/A  
- kobs: N/A  
- 2nd order kobs: dominated by adsorption  
- Mechanism by h+ and O2•-  
- Reutilization: N/A |
| 8 [36] | FeTCP@TDI–TiO2 | [TC-HCl] = 25 mg/L  
[NOR] = 25 mg/L | - Matrix: Distilled water  
- Visible-light 150 W xenon lamp λ > 400 nm  
- [FeTCP@TDI–TiO2] = 1 g/L  
- pH = N/A; T = N/A  
- Pre-dark for 30 min | - >99% TC-HCl and NOR degradation in 120 min  
- TOC: N/A  
- kobs (TC) = 2.9 × 10−2 min−1  
- kobs (NOR) = 3.4 × 10−2 min−1  
- Mechanism: N/A  
- Degradation pathway proposed  
- Reutilization: 5 cycles (TC) |
| 9 [37] | FePc@BiOBr | [TC] = 20 mg/L  
[CIP] = 10 mg/L | - Matrix: Distilled water  
- Visible-light 350 W xenon lamp λ > 400 nm  
- [FePc@BiOBr] = 0.4 mg/L  
- pH = N/A; T = N/A  
- Pre-dark for 1 h | - >65% TC and ~55% CIP degradation in 240 min  
- TOC: N/A  
- kobs: N/A  
- Mechanism by h+, HO•, O2•-  
- Reutilization: 3 cycles |
| 10 [19] | TCP@BiOCl | [TC] = 20 mg/L  
[CIP] = 10 mg/L  
[ENR] = 10 mg/L | - Matrix: Distilled water  
- Visible-light 250 W xenon lamp λ > 400 nm  
- [TCP@BiOCl] = 0.4 mg/L  
- pH = N/A; T = 30 °C  
- Pre-dark for 30 min | - 74% TC, 42% CIP and 60% ENR degradation in 120 min  
- TOC: N/A  
- kobs: 11 × 10−2 min−1 (TC)  
- Mechanism by HO•, h+, O2•-  
- Reutilization: 4 cycles (TC) |
| 11 [38] | FePc@N-PR | [OTC-HCl] = 100 mg/L | - Matrix: Distilled water  
- Visible-light 50 W halogen lamp λ > 420 nm  
- [FePc@N-PR] = 0.75 g/L  
- [H2O2] = 60 mM  
- pH = 5.3; T = 35 °C | - 94% OTC-HCl degradation in 500 min  
- TOC: N/A  
- kobs: N/A  
- Mechanism by HO•  
- Reutilization: 5 cycles |
| 12 [17] | MTCPP@TiO2M = H2, Zn  
and Cu | [OTC] = –8 mg/L  
[OXA] = –8 mg/L | - Matrix: Distilled water  
- Sunlight simulator 300 W  
- [MTCPP@TiO2] = 0.02 g/L  
- Irradiation time: 40 min  
- pH = 7; T = N/A  
- Pre-dark for 15 min | - 63% OTC, 68% OXA degradation in 40 min (with CuTCP@TiO2)  
- TOC: N/A  
- kobs: N/A  
- Mechanism: N/A  
- Reutilization: N/A |
| 13 [39] | FeTPP@Cr-TiO2 | [NOR] = 25 mg/L  
[OFO] = 25 mg/L  
[LOM] = 25 mg/L | - Matrix: Distilled water  
- Visible-light 150 W xenon lamp λ > 400 nm  
- [FeTPP@Cr-TiO2] = 1 g/L  
- pH = N/A; T = N/A  
- Pre-dark for 30 min | - 98% NOR, 99% OFO, ~100%  
LOM degradation in 120 min  
- TOC: N/A  
- kobs (NOR) = 2.8 × 10−2 min−1  
- kobs (OFO) = 3.9 × 10−2 min−1  
- kobs (LOM) = 3.0 × 10−2 min−1  
- Mechanism: N/A  
- Reutilization: N/A |
### Table 1. Cont.

| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|--------------------------|----------|
| 14 [40] | PCN-222@g-C3N4(PCN-222 = FeTCPP Zr-MOF) | OFO | [OFO] = 20 mg/L | - Matrix: Distilled water  
- Visible-light 300 W xenon lamp > 400 nm  
- [PCN-222@g-C3N4] = 1 g/L  
- pH = N/A; T = N/A  
- Pre-dark for 120 min | - 96% OFO in 200 min  
- 89% TOC decrease in 12 h  
- $k_{obs}$: $1.4 \times 10^{-2}$ min$^{-1}$  
- Mechanism by $h^+$, $HO^+$, $O_2^{-}$  
- Reutilization: 4 cycles |
| 15 [41] | PCN-222@PW12/TiO2(PCN-222 = FeTCPP Zr-MOF) | OFO | [OFO] = 20 mg/L | - Matrix: Distilled water  
- Visible-light 300 W xenon lamp > 400 nm  
- [PCN-222@PW12/TiO2] = 0.4 g/L  
- pH = N/A; T = N/A  
- Pre-dark for 2 h | - 95% OFO in 120 min  
- 91% TOC decrease in 10 h  
- $k_{obs}$: $2.2 \times 10^{-2}$ min$^{-1}$  
- Mechanism by $h^+$, HO*, $O_2$•−  
- Reutilization: 4 cycles |
| 16 [42] | SnTCPP@g-C3N4/Bi2WO6 | LEV | [LEV] = 10 mg/L | - Matrix: Distilled water  
- Visible-light 250 W xenon lamp $\lambda$ > 400 nm  
- [SnTCPP@g-C3N4/Bi2WO6] = 1 g/L  
- pH = 7.3; T = N/A  
- Pre-dark for 30 min | - 86% LEV in 150 min  
- 59% TOC decrease in 4 h  
- $k_{obs}$: N/A  
- Degradation pathway proposed  
- Reutilization: N/A |
| 17 [43] | ZnPc@TiO2 | ERY | [ERY] = 7.5 mg/L | - Matrix: Distilled water  
- Visible-light 300 W xenon lamp $\lambda$ > 400 nm  
- [ZnPc@TiO2] = 0.4 g/L  
- pH = 5; T = 20 °C  
- Pre-dark for 30 min | - 74% ERY degradation in 180 min  
- TOC: N/A  
- Mechanism: N/A  
- Reutilization: 5 cycles |
| 18 [44] | FePc@P4VP/PET | SQX | [SQX] = 6 mg/L | - Matrix: Distilled water  
- UV-light 150 W mercury lamp  
- $[FePc@P4VP/PET] = 2$ g/L  
- $[H_2O_2] = 10$ mM  
- pH = 7; T = 50 °C | - 95% SQX in 240 min  
- TOC: N/A  
- $k_{obs}$: N/A  
- Mechanism by HO*, HOO*, and Fe(IV) = O  
- Reutilization: 5 cycles |
| 19 [16] | CoPc@K-TiO2 | TMP | [TMP] = 25 mg/L | - Matrix: Distilled water  
- UV-light 150 W mercury lamp  
- [CoPc@K-TiO2] = 0.75 g/L  
- pH = N/A; T = 25–45 °C | - 54% TMP in 240 min  
- TOC: N/A  
- $k_{obs}$: N/A  
- Mechanism by HO*  
- Degradation pathway proposed  
- Reutilization: 5 cycles |
| 20 [45] | Co(quin)4Pc@TiO2 | AMX | [AMX] = 20 mg/L | - Matrix: Distilled water  
- UV-light 12 W lamp  
- [Co(quin)4Pc@TiO2] = 1 g/L  
- pH = N/A; T = 25 °C | - 41% AMX in 150 min  
- TOC: N/A  
- $k_{obs}$: N/A  
- Mechanism by HO*  
- Reutilization: N/A |

Sun-prepared FePc@N-PR, by covalent grafting of iron phthalocyanine (FePc, Figure 2) onto a macroporous chloromethylated polystyrene-divinylbenzene resin (PR), partially pre-functionalized with 4-aminopyridine [38]. This ligand (denoted as N) was then used as an axial ligand to further coordinate the iron complex inside the resin. This catalyst (concentration = 0.75 g/L) was used to promote the photodegradation of oxytetracycline hydrochloride (OTC·HCl, Figure 2), using hydrogen peroxide (60 mM) as oxidant. A 94% degradation was observed in 500 min, and the catalyst was capable of being reused along 5 cycles without significant degradation [38] (Table 1, entry 11).
D’Urso prepared \textbf{MTCPP@TiO}_2 catalysts by adsorption of MTCPP (where M = H₂, Zn or Cu) (Figure 2) onto TiO₂ [17]. These catalysts (concentration = 0.02 g/L) were evaluated in the degradation of oxytetracycline (OTC, Figure 2), and similar results were obtained. The best catalyst, CuTCPP@TiO₂, gave 63% OTC photodegradation in 40 min of irradiation with a 300 W sunlight simulator (Table 1, entry 12).

Besides tetracyclines, other antibiotics have also been photodegraded, e.g., the quinolone family (Figure 1). Under visible-light irradiation (300 W Xe lamp), Li used CuTCPP MOF as a photocatalyst (concentration = 0.05 g/L) to promote the degradation of norfloxacin (NOR, Figure 1), reaching 44% degradation after 6 h of irradiation (Table 1, entry 7) [35]. Additionally, Yao used FeTCPP@TDI–TiO₂ as a catalyst (concentration = 1 g/L) to degrade the same antibiotic, reaching full degradation in just 2 h irradiation (Table 1, entry 8). This result emphasizes the influence of the toluene diisocyanate (TDI) linker, which allowed a higher efficiency, when compared with FeTCPP directly adsorbed onto TiO₂ or TDI-TiO₂ [36].

Xia used FePc@BiOBr and TCPP@BiOCl (concentration = 0.4 g/L) as photocatalysts in the degradation of ciprofloxacin (CIP, Figure 1). These catalysts were able to degrade CIP in 55% and 42%, respectively, after 4 h and 2 h of visible-light Xe-lamp irradiation, respectively (Table 1, entries 9 and 10) [19,37]. TCPP@BiOCl was further used as a photocatalyst to degrade enrofloxacin (ENR, Figure 1), reaching 60% degradation after 120 min of irradiation (Table 1, entry 10) [19]. Additionally, the same group prepared the catalyst FeTTP@Cr-TiO₂ by adsorbing FeTTP (Figure 2) onto chromium-doped TiO₂ [39]. With a catalyst concentration of 1 g/L, NOR was 98% degraded after 2 h of irradiation with 150 W Xe-lamp visible light, (Table 1, entry 13). This catalyst induced a first-order reaction-rate kinetics, with \( k_{\text{obs}} = 2.8 \times 10^{-2} \text{min}^{-1} \), while FeTCPP@TDI–TiO₂, reported by the same group, displayed \( k_{\text{obs}} = 3.4 \times 10^{-2} \text{min}^{-1} \) (Table 1, entry 8) [36].

Another recurrently tested antibiotic is ofloxacin (OFO, Figure 1). In that respect, Xu’s group reported the synthesis of PCN-222@g-C₃N₄ [40] and PCN-222@PW₁₂/TiO₂ [41] catalysts, where PCN-222 is a zirconium-based MOF capable of incorporating FeTCPP (Figure 2) units (Figure 3) [46].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Crystal structure and underlying network topology of PCN-222(Fe). The Fe-TCPP ((a); blue square) is connected to four 8-connected Zr₆ clusters ((b); light orange cuboid) with a twisted angle to generate a 3D network in Kagome-like topology ((d,e); with 1D large channels ((c); green pillar). Zr black spheres, C gray, O red, N blue, Fe orange. H atoms were omitted for clarity. Adapted with permission from ref. [46]. Copyright 2012 John Wiley & Sons.}
\end{figure}
First, the MOF was adsorbed onto g-C$_3$N$_4$ and PW$_{12}$/TiO$_2$ blends, respectively. The catalysts, along with FeTPP@Cr-TiO$_2$ [39], were tested in the degradation of OFO under 150 W Xe-lamp visible-light irradiation, and the latter was slightly more efficient, with 99% degradation in 120 min (Table 1, entry 13), when compared to 96% (200 min) and 95% (120 min) for PCN-222@g-C$_3$N$_4$ and PCN-222@PW$_{12}$/TiO$_2$, respectively (Table 1, entries 14 and 15). The first-order reaction kinetics were measured, and $k_{obs}$ followed the order FeTPP@Cr-TiO$_2$ > PCN-222@PW$_{12}$/TiO$_2$ > PCN-222@g-C$_3$N$_4$ ($k_{obs} = 3.9 \times 10^{-2}$ min$^{-1}$, $2.2 \times 10^{-2}$ min$^{-1}$ and $1.4 \times 10^{-2}$ min$^{-1}$, respectively). Interestingly, PCN-222@g-C$_3$N$_4$ and PCN-222@PW$_{12}$/TiO$_2$-based MOF catalysts were able to reach a TOC decrease of 89% (12 h) and 91% (10 h), respectively, and could be reused up to four cycles successfully [40,41].

D’Urso used the MTCPP@TiO$_2$ catalysts (M = H$_2$, Zn and Cu) to degrade oxolinic acid (OXA, Figure 1) under sunlight-simulator irradiation (300 W) and observed that CuTCPP@TiO$_2$ was the most active catalyst, with 68% OXA degradation in 40 min (Table 1, entry 12) [17]. Yao further studied the degradation of lomefloxacin (LOM, Figure 1) using FeTPP@Cr-TiO$_2$ as catalyst, reaching complete degradation after 120 min of visible-light irradiation (Table 1, entry 13).

He and Ma prepared an SnTCPP@g-C$_3$N$_4$/Bi$_2$WO$_6$ catalyst by adsorbing tin(IV) mesotetakis(4-carboxyphenyl)porphyrin (SnTCPP, Figure 2) onto a semiconducting g-C$_3$N$_4$/Bi$_2$WO$_6$ blend [42]. Under visible-light irradiation (250 W Xe lamp), the authors promoted the photodegradation of levofloxacin (LEV, Figure 1) at a catalyst concentration of 1 g/L, reaching 86% degradation in 150 min. Furthermore, total organic carbon was measured, and a value of 59% TOC, upon 4 h of irradiation, was described (Table 1, entry 16).

Two decomposition pathways were proposed by the authors (Scheme 5). In pathway I, LEV (m/z 361) was decarboxylated, providing an intermediate with m/z 317. Then, via defluorination, demethylation and dehydrogenation on the piperazine ring, the intermediate with m/z 283 was formed and further demethylated and oxidized to give an intermediate with m/z 274. Due to the high oxidizing capability of HO*, the piperazine and morpholine ring-opening reactions occurred and the intermediate with m/z 184 was observed as well. In pathway II, a defluorination LEV anion was found at m/z 342, which suffered dehydrogenation to produce an intermediate with m/z 340. Then, the piperazine ring-opening reaction occurred, yielding an intermediate with m/z 317. Further HO* attack caused the demethylation, deamination, deethylation and decarboxylation reactions to form intermediates with m/z 246 or m/z 218, respectively. Finally, those ring-opening intermediates could be further degraded into the other compounds with lower molecular weight, such as CO$_2$ and H$_2$O [42].

Scheme 5. Proposed pathway for the photodegradation of levofloxacin [42].

Vignesh and Suganthi [43] used zinc phthalocyanine- (ZnPc, Figure 2) modified titania nanoparticles (ZnPc@TiO$_2$), prepared by adsorption, to catalyze the photodegradation of erythromycin (ERY, Figure 1), obtaining 74% degradation in 180 min under visible-light
irradiation (300 W Xe lamp). The catalyst was used in a 0.4 g/L concentration and could be reused up to five times without significant loss of activity (Table 1, entry 17).

Sulfaquinoxaline degradation (SQX, Figure 1) was also tested. Lu and Chen [44] prepared the hybrid catalyst FePc@P4VP/PAET by adsorbing iron phthalocyanine (FePc, Figure 2) onto poly(4-vinylpyridine)/polyester (P4VP/PET) nanofibers. With a catalyst concentration of 2 g/L, SQX was degraded 95% under ultraviolet light (150 W mercury lamp) after 240 min (Table 1, entry 18). Ciuffi [16] developed a composite photocatalyst, by mixing, under sol-gel conditions, kaolinite, TiO2 and cobalt(II) tetracarboxyphthalocyanine (CoPc, Figure 2), obtaining a CoPc@K-TiO2 hybrid catalyst. The authors promoted the degradation of trimethoprim (TMP, Figure 1) under ultraviolet irradiation (150 W mercury lamp) using a catalyst concentration of 0.75 g/L. Under those conditions, the authors described a 54% degradation of TMP in 240 min, and the catalyst was reused without significant loss of activity for up to five cycles (Table 1, entry 19).

Sökmen [45] reported the synthesis of Co(quin)4Pc@TiO2 by impregnation of Co(quin)4Pc (Figure 2) onto semiconducting TiO2. The catalyst, in a concentration of 1 g/L, was used in the photodegradation of amoxicillin (AMX, Figure 1), and 40% degradation was obtained after 150 min using a UV light lamp (12 W) at 254 nm. Nevertheless, neat TiO2 induced 38% degradation under the same conditions, which can be ascribed to the use of the UV light source, which enables TiO2 photocatalytic properties (Table 1, entry 20).

2.2. Oxidative Chemical Degradation

Martins [47–49] used a set of meso-tetrasubstituted porphyrins as catalysts for the degradation of antibiotics CIP, LEV and NOR (Figure 1). Chloro meso-tetraphenylporphyrinato manganese(III) (MnIII(TPP)Cl, Figure 4), chloro meso-tetrakis(4-carboxyphenyl)porphyrinato manganese(III) (MnIII(TCPP)Cl, Figure 4), chloro meso-β-octabromo-tetrakis(4-carboxyphenyl) porphyrinato manganese(III) (MnIII(Br8TCPP)Cl, Figure 4), chloro meso-tetrakis(2,3-dichlorophenyl) porphyrinato manganese(III) (MnIII(T2,3DCPP)Cl, Figure 4) and chloro meso-tetrakis(2-fluoro-6-chlorophenyl)porphyrinato manganese(III), (MnIII(T2,6CFPP)Cl, Figure 4) were chosen as catalysts and water/acetonitrile mixture was chosen as a solvent under homogeneous conditions (Table 2, entries 1–3). In the first study, the authors used MnIII(TCPP)Cl, and several oxidants were evaluated, such as iodosobenzene, hydrogen peroxide and meta-chloroperoxybenzoic acid (mCPBA). Among them the best oxidant to promote full CIP degradation (100%) was the toxic iodosobenzene (PhIO) (Table 2, entry 1) [47]. Further studies were performed using diacetoxyiodobenzene (PhI(OAc)2), but no improvements were observed (Table 2, entry 2) [48]. Further studies on NOR degradation, using MnIII(T2,3DCPP)Cl and MnIII(T2,6CFPP)Cl as catalysts, revealed that these catalysts were similarly active, reaching 58% and 57% NOR degradation, respectively, using PMS as the oxidant (Table 2, entry 3) [49].

![Figure 4. Structures of tetrapyrrolic macrocycles (TPM) used as catalysts for oxidative chemical degradation of antibiotics.](image-url)
| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|--------------------------|----------|
| 1 [47] | Mn^{III}(TPP)Cl, Mn^{III}(TCP)Cl, Mn^{III}(Br_{3}TCP)Cl | \(\text{CIP} = 10 \text{ mg/L}\) | Homogeneous - Matrix: Distilled water/acetoneitrile - \([\text{Mn}^{III}\text{(TPP)Cl}] = 0.02 \text{ g/L}; [\text{Mn}^{III}\text{(TCP)Cl}] = 0.03 \text{ g/L}; [\text{Mn}^{III}(\text{Br}_{3}\text{TCP})\text{Cl}] = 0.04 \text{ g/L}\) - [oxidant] = \(3 \times 10^{-4} \text{ M (PhIO, H}_{2}\text{O}_{2}, \text{MCPBA)}\) - pH = N/A; T = 25 °C | 100% CIP degradation in 24 h (with \(\text{Mn}^{III}\text{(TCP)Cl}\) and \(\text{PhIO}\)) - TOC decrease: N/A - \(k_{\text{obs}}\): N/A - Mechanism by HO• - Degradation pathway proposed - Reutilization: N/A - Cytotoxicity studies on human embryonic kidney cells HEK-293 (no toxicity found, both for CIP and oxidation products) |
| 2 [48,50] | Mn^{III}(TCP)Cl, Mn^{III}(Br_{3}TCP)Cl | \([\text{CIP} = 10 \text{ mg/L}\); \[\text{LEV} = 10 \text{ mg/L}\); \[\text{NOR} = 10 \text{ mg/L}\) | Homogeneous - Matrix: Distilled water/acetoneitrile - \([\text{Mn}^{III}\text{(TCP)Cl}] = 0.03 \text{ g/L}; [\text{Mn}^{III}(\text{Br}_{3}\text{TCP})\text{Cl}] = 0.04 \text{ g/L}\) - [oxidant] = \(3 \times 10^{-4} \text{ M (PhIO, \text{PhI(OAc)}_{2}, \text{H}_{2}\text{O}_{2}, \text{MCPBA)}\) - pH = N/A; T = 25 °C | 100% CIP degradation in 24 h (with \(\text{Mn}^{III}\text{(TCP)Cl}\) and \(\text{PhIO}\)) - 98% LEV degradation in 24 h (with \(\text{Mn}^{III}\text{(TCP)Cl}\) and \(\text{PhI(OAc)}_{2}\)) - TOC decrease: N/A - \(k_{\text{obs}}\): N/A - Mechanism by HO• - Degradation pathway proposed for LEV - Reutilization: N/A |
| 3 [49] | Mn^{III}(TPP)Cl, Mn^{III}(Tt_{3}DCPP)Cl, Mn^{III}(Tt_{2}6CFPP)Cl | \[\text{NOR} = 14 \text{ mg/L}\) (stock) | Homogeneous - Matrix: Distilled water/acetoneitrile - \([\text{Mn}^{III}(\text{Tt}_{3}\text{DCPP})\text{Cl}] = 0.04 \text{ g/L}; [\text{Mn}^{III}(\text{Tt}_{2}\text{6CFPP})\text{Cl}] = 0.04 \text{ g/L}\) - [oxidant] = \(2 \times 10^{-6} \text{ M (H}_{2}\text{O}_{2}, \text{BuOOH, PMS)}\) - pH = 6; T = 25 °C | 58% NOR degradation by \(\text{Mn}^{III}(\text{Tt}_{3}\text{DCPP})\text{Cl}\); 57% NOR degradation by \(\text{Mn}^{III}(\text{Tt}_{2}\text{6CFPP})\text{Cl}\) in 24 h (with \(\text{PMS}\)) - TOC decrease: N/A - \(k_{\text{obs}}\): N/A - Mechanism by HO•, SO•• - Degradation pathway proposed - Reutilization: N/A - Cytotoxicity studies human peripheral blood mononuclear cells (no toxicity found, both for NOR and oxidation products) |
| 4 [51] | CoPc@GO | \([\text{NOR} = 10 \text{ mg/L}\) | - Matrix: Distilled water/acetoneitrile - \([\text{CoPc@GO}] = 0.1 \text{ g/L}; [\text{PMS}] = 6.5 \times 10^{-3} \text{ M}\) - pH = 7; T = N/A | 100% NOR degradation in 60 min - TOC: N/A - \(k_{\text{obs}}\): N/A - Mechanism by HO•, SO•• - Reutilization for 3 cycles |
| 5 [52] | FePc@N-PR | \([\text{TC-HCl} = 100 \text{ mg/L}\) | - Matrix: distilled water, tap water, wastewater - \([\text{R-N-Fe}] = 1.0 \text{ g/L}; [\text{PMS}] = 2.0 \text{ mM}\) - pH = 6; T = 45 °C | 83% TC-HCl degradation in 280 min - 30% TOC decrease in 280 min - \(k_{\text{obs}}\): N/A - Mechanism by HO•, SO•• - Degradation pathway proposed - Reutilization: 5 cycles |
| 6 [53] | FePc@P4VP/PAN | \([\text{SQX} = 6 \text{ mg/L}\) | - Matrix: Distilled water, wastewater - \([\text{FePc@P4VP/PAN}] = 1.0 \text{ g/L}; [\text{H}_{2}\text{O}_{2}] = 10 \text{ mM}\) - pH = 3; T = 50 °C | 95% SQX degradation in 120 min - TOC decrease: N/A - \(k_{\text{obs}}\): N/A - Mechanism by HO• - Degradation pathway proposed - Reutilization: N/A |
| 7 [54] | MnTDCPPS@N-SiO_{2} | \([\text{TMP} = 130 \text{ mg/L}\) | - Matrix: Distilled water - \([\text{MnTDCPPS@N-SiO}_{2}] = 0.002 \text{ g/L}; [\text{H}_{2}\text{O}_{2}] = 0.26 \text{ mM}\) - pH = 7; T = 25 °C | 95% TMP degradation in 150 min - 24% TOC decrease in 150 min - \(k_{\text{obs}}\): \(2.0 \times 10^{-2} \text{ min}^{-1}\) - Mechanism by HO• - Degradation pathway proposed - Reutilization: 5 cycles -ecotoxicity studies on \(V.\ fischeri\), \(R.\ subcapitata\) and \(B.\ calyciflorus\) (oxidation products slightly increase toxicity)
Zhang [51] prepared the hybrid catalyst CoPc@GO by adsorption of cobalt phthalo-
cyanine (CoPc, Figure 4) onto graphene oxide (GO). NOR was 100% degraded in 60 min
using a catalyst concentration of 0.1 g/L and $6.5 \times 10^{-3}$ M PMS (as oxidant) (Table 2,
entry 4). Sun [52] used the hybrid catalyst FePc@N-PR, having iron phthalocyanine (FePc,
Figure 2) units covalently attached to macroporous chloromethylated polystyrenevinyl-
benzene resin (PR) [38] and used it to promote the degradation of TC-HCl, with PMS as
oxidant, at pH = 6 and a temperature of 45 °C. With a catalyst concentration of 1 g/L,
in the presence of a PMS solution (2.0 mM), 83% TC-HCl degradation was achieved in 280
min, with a TOC decrease of 30% (Table 2, entry 5). The authors further tested different
matrices, in addition to distilled water, and found that in tap water, the degradation was
accelerated, probably due to the presence of Cl$^-$ or HCO$_3^-$, which may react with PMS
and generate further reactive chlorine species. On the other hand, the same experiment
in wastewater was inhibited, probably due to the presence of organic impurities that can
block the catalyst’s activity [52].

Lu and Chen [53] prepared hybrid catalysts FePc@P4VP/PAN by adsorbing iron
phthalocyanine (FePc, Figure 4) onto poly(4-vinylpyridine)/polyacrylonitrile (P4VP/PAN)
nanofibers. Using a catalyst concentration of 1 g/L, in the presence of a 10 mM H$_2$O$_2$
solution (as oxidant), 95% of SQX was degraded in 120 min at pH = 3 and a temperature
of 50 °C.

Pereira and Calvete [54] reported the synthesis of an MnTDCPPS@N-SiO$_2$ hybrid catalyst by
covalent attachment of acetate meso-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinato manganese(III)
(MnTDCPPS, Figure 4) to aminopropylsilyle-functionalized silica (N-SiO$_2$). Remarkably,
the immobilized catalyst, despite being used in quite a low concentration (0.002 g/L) and
in the presence of 0.26 mM H$_2$O$_2$ as oxidant, was able to promote the oxidative degradation
of trimethoprim (TMP, Figure 1) in 95% (24% TOC decrease) after 150 min at pH = 7 and
25 °C. The catalyst could be reused up to five cycles without losing its activity (Table 2,
entry 7).

The authors proposed a degradation pathway for TMP (Scheme 6) and observed that
the major processes involved in the degradation of TMP were hydroxylation, oxidation and
demethylation, mostly by HO$. TMP could fully ($m/z$ 248) or partially ($m/z$ 291) demethyl-
ate, besides undergoing hydroxylation ($m/z$ 307). This intermediate could further undergo
hydroxylation, giving $m/z$ 323, or oxidize into $m/z$ 305. This last intermediate could either
demethylate to give $m/z$ 291 or hydroxylate to provide $m/z$ 321. This intermediate could
also be produced by oxidation of $m/z$ 323 by direct oxidation. Ultimately, the $m/z$ 291
intermediate could further suffer cleavage to yield $m/z$ 187 [54].
3. Degradation of Analgesic Drugs

Analgesics are drugs that relieve different types of pain. Most prescribed analgesics include anti-inflammatory drugs, which reduce inflammation (e.g., ibuprofen, diclofenac, acetaminophen derivatives and salicylic acid, known as nonsteroidal anti-inflammatory drugs), and opioid analgesics, which change the way the brain perceives pain (e.g., tramadol). These types of drugs are commonly encountered in municipal wastewaters since they are consumed in quite high quantities by the general population [55,56].

Dabrowski’s group investigated the photocatalytic degradation of tramadol (TRML, Figure 5) (Table 3, entry 1) [57] using LED-light irradiation (λ = 530 nm with light doses from 1 to 20 J cm$^{-2}$). The authors were able to degrade 80% of TRML in 60 min, using ZnTDFPPS@TiO$_2$ as hybrid catalyst (Figure 6). The zinc(II) meso-tetra-(2,6-difluoro-3(5)-sulfonatophenyl)porphyrin (ZnTDFPPS) was incorporated by impregnation (concentration = 0.67 g/L). Additionally, the authors did not observe any photocatalytic activity when TiO$_2$ was used under the same reaction conditions. The best results obtained with the hybrid catalyst were attributed to its higher visible-light absorption, with subsequent higher formation of ROS, namely HO$^\cdot$ radicals.
3.1. Photochemical Degradation

The Huang group used the iron complex of perchlorinated phthalocyanine, FePcCl\textsubscript{16} (Figure 6) (Table 3, entry 2) \cite{58}, as a heterogeneous photocatalyst to promote the degradation of salicylic acid (SA, Figure 5) upon irradiation with visible light from a 500 W halogen lamp. A 70\% SA degradation was achieved after 10 h irradiation, with a catalyst concentration of 0.4 g/L, using H\textsubscript{2}O\textsubscript{2} as oxidant (3 × 10\textsuperscript{−3} M), with a kinetics of k\textsubscript{obs} = 1.2 × 10\textsuperscript{−1} min\textsuperscript{−1}. Once again, the mechanism was attributed to the formation of HO• radicals.

Anucha and Altin \cite{15} developed the material CuPc(th)\textsubscript{4}@TiO\textsubscript{2}/ZnO by modifying TiO\textsubscript{2} and ZnO semiconductor blends with thiazol tetrasubstituted copper phthalocyanine (CuPc(th)\textsubscript{4}, Figure 6). This hybrid material was evaluated on the photodegradation of ibuprofen (IBU, Figure 5) in an aqueous matrix using five mercury lamps of 40 W at 365 nm (Table 3, entry 3). Under these conditions, 80\% of IBU photodegradation was achieved in 4 h at pH 6.5 and a degradation rate constant of k\textsubscript{obs} = 7.0 × 10\textsuperscript{−3} min\textsuperscript{−1}, against 42\% by TiO\textsubscript{2}/ZnO semiconducting catalyst. The authors also investigated the catalyst’s stability, and a small decline (77\%) of IBU degradation started only after the fifth cycle run. The authors put in evidence that a hydroxyl radical (HO•) and superoxide anion (O\textsubscript{2}•−) are the main ROS species involved in IBU degradation.
Table 3. Photochemical degradation of analgesic drugs using TPM-based catalysts.

| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|-------------------------|----------|
| 1 [57] | ZnTDFPPS@TiO₂ | TRML | - Matrix: Distilled water  
- LED light 530 ± 20 nm  
- [ZnTDFPPS@TiO₂] = 0.67 g/L  
- pH = N/A; T = N/A  
- Pre-dark: N/A  | 80% TRML degradation in 60 min  
TOC: N/A  
Mechanism: HO⁻  
Reutilization tests: N/A |
| 2 [58] | FePcCl₁₆ | SA | - Matrix: Distilled water  
- 500 W halogen lamp (λ ≥ 420 nm)  
- [FePcCl₁₆] = 0.4 g/L  
- [H₂O₂] = 3 × 10⁻³ M  
- Pre-dark for 30 min  
- pH = 7; T = 25 °C  | 70% SA removed in 600 min  
TOC: N/A  
[kobs] = 1.2 × 10⁻¹ min⁻¹  
Mechanism: HO⁻  
Reutilization tests: N/A |
| 3 [15] | CuPc(th)₄@TiO₂/ZnO | IBU | - Matrix: Distilled water  
- Mercury lamps 5 × 40 W (λ = 365 nm)  
- [CuPc(th)₄@TiO₂/ZnO] = N/A (thin films of unknown Pc content)  
- pH = 6.5; T = 25 °C  
- Pre-dark for 30 min  | 80% IBU degradation in 240 min  
TOC: N/A  
[kobs] = 7.0 × 10⁻³ min⁻¹  
Mechanism: HO⁻ and O₂⁻  
Reutilization: 5 cycles |
| 4 [20] | CuPc@TiO₂  
ZnPc@TiO₂ | IBU | - Matrix: Distilled water  
- 3 laser diodes 20 mW/cm² at λ = 365 nm (UV); at λ = 665 nm (Vis)  
- [MPc@TiO₂] = 1 g/L  
- pH = N/A; T ≤ 35 °C  | 0% IBU degradation in 240 min  
[Vis]  
95% IBU degradation in 240 min  
(UV) with CuPc@TiO₂  
55% IBU degradation in 240 min  
(UV) with ZnPc@TiO₂  
[kobs] = 3.8 × 10⁻¹ min⁻¹ with CuPc@TiO₂  
Mechanism: N/A  
Toxicity assessment: increase in toxicity (10%) in oxidation products |
| 5 [59] | FePc@ZnO | IBU | - Matrix: Distilled water  
- 300 W xenon lamp  
- [FePc@ZnO] = 0.5 g/L  
- [H₂O₂] = 10 mmol/L  
- pH = 6.5; T = 25 °C  | 90% IBU degradation in 10 min  
TOC: N/A  
[kobs] = N/A  
Mechanism: HO⁻  
Degradation pathway proposed  
Reutilization: 5 cycles |
| 6 [60] | PCN-134  
(TCPP@Zr-BTB MOF) | DF | - Matrix: Distilled water  
- 500 W Xe lamp λ ≥ 420 nm  
- [PCP@Zr-BTB MOF] = 0.1 g/L  
- pH = 7; T = 25 °C  
- Pre-dark for 30 min  | 99% DF degradation in 300 min  
Mechanism: h⁺ and O₂⁻ (Type II)  
Reutilization: 3 cycles |
| 7 [61] | TCPP@UiO-66 MOF | DF | - Matrix: Distilled water  
- Simulated-sunlight 350 W Xe lamp (290 nm ≤ λ ≤ 1200 nm)  
- [TCPN@UiO-66] = 0.1 g/L pH = 7; T = 25 °C  | 99% DF degradation in 240 min  
[kobs] = 8.4 × 10⁻³ min⁻¹  
Mechanism: h⁺ and O₂⁻ (Type II)  
Reutilization: 4 cycles |

Mlynarczyk also investigated the IBU aqueous photodegradation in the presence of zinc(II) and copper(II) phthalocyanines (ZnPc and CuPc, respectively, Figure 6) embedded onto pure anatase-phase TiO₂ nanoparticles (ZnPc@TiO₂ and CuPc@TiO₂) [20]. Catalyst photoactivity was evaluated on a 10 mg/L solution of IBU in water by irradiating with three lasers (20 mW/cm²) under either UV (365 nm) or visible light (665 nm) (Table 3, entry 4). They obtained 95% IBU degradation with CuPc@TiO₂ under UV light irradiation after 6 h and a rate constant kobs = 3.8 × 10⁻¹ min⁻¹, while using ZnPc@TiO₂, only 55%
degradation was observed (Figure 7a). Interestingly, this value is even lower than the one observed when TiO$_2$ was used as catalyst, which reached nearly 93% photodegradation. On the other hand, negligible degradation was observed for both catalysts under visible-light irradiation, as can be seen in Figure 7b, which may be attributed to low light absorption by the catalyst.

Figure 7. The changes in IBU concentration after irradiation of the solution containing photocatalyst at (a) 365 nm light and (b) 665 nm light. Adapted with permission from ref. [20]. Copyright 2020 MDPI.

Furthermore, Ju and Hou [59] prepared the photocatalyst FePc@ZnO by impregnation of FePc (Figure 6) onto semiconducting ZnO. The authors studied the photo-Fenton-type degradation of IBU (Figure 5) in the presence of the catalyst, using H$_2$O$_2$ as the oxidant and a visible-light Xe lamp (330 W) as the irradiation source. A 90% degradation of IBU was achieved in just 10 min, for which HO$^\cdot$ was found to be the main oxidation species. The catalysts showed reusability for up to five cycles without significant loss of activity (Table 3, entry 5).

Several groups studied the ability of TPM-based catalysts to degrade diclofenac (DF, Figure 5). Yu’s group studied its photodegradation using two different porphyrin-based MOFs. In a first study, they prepared PCN-134, TCPP@Zr-BTB MOF [60] based on a meso-tetra(carboxyphenyl)porphyrin (TCPP, Figure 6) metal organic framework. After stirring a DF aqueous solution (30 mg/L) for 30 min in the dark to favor the adsorption-desorption equilibrium, the solution was irradiated with a visible-light Xe lamp (500 W) for 5 h, 99% of DF photodegradation was achieved using PCN-134 as photocatalyst (0.1 g/L; Table 3, entry 6). Moreover, the authors established that the mechanism of PCN-134 photodegradation is type II due to the generation of singlet oxygen ($^1$O$_2$). Additionally, the authors also performed catalyst-reutilization studies for three cycles, providing removal rates > 95%.

In a subsequent study, the same group developed another MOF-type catalyst, TCPP@UiO-66 [61]. Particularly, TCPP (Figure 6) was introduced onto UiO-66 crystals via an in situ solvothermal one-pot reaction, preserving the morphologic characteristics of UiO-66. Then, the authors irradiated a DF aqueous solution (30 mg/L) containing a catalyst concentration of 0.1 g/L, at pH 7, by simulated-sunlight 350 W Xe lamp (290 nm $\leq \lambda \leq$ 1200 nm) (Table 3, entry 7). Under these conditions, 99% of DF photodegradation was obtained after 4 h ($k_{\text{obs}} = 8.4 \times 10^{-3}$ min$^{-1}$). The catalyst showed good recyclability for four reaction cycles without loss activity. As in the previous study, the authors attributed the photodegradation of DF mainly to the generation of $^1$O$_2$, along with h$^+$ (holes), to a minor extent.

3.2. Oxidative Chemical Degradation

The degradation of DF (Figure 5) was also studied under nonphotochemical conditions. The Nackiewicz group studied the catalytic activity of iron(II) octacarboxyphthalal-
Cyanine (FeC8Pc, Figure 8) in the homogenous oxidation of an aqueous solution of DF at pH 8, using H2O2 or NaIO4 as oxidants (Table 4, entry 1) [55]. At a substrate/catalyst 50:1 molar ratio, the authors obtained full DF degradation in 35 min and 25 min when using H2O2 and NaIO4, respectively. FeC8Pc also self-degraded completely due to the production of hydroxyl radicals formed by H2O2. The authors further studied the degradation pathway for DF, observing the generation of an unstable dimeric DF oxidation compound as intermediate, further leading to the final oxidation products.

![Figure 8. Structures of tetapyrrolic macrocycles (TPM) used as catalysts for oxidative chemical degradation of analgesic pharmaceuticals.](image)

Table 4. Nonphotochemical degradation of analgesic drugs using TPM-based catalysts.

| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|-------------------------|----------|
| 1 [55] | FeC8Pc | DF | - Matrix: Distilled water | - Homogenous |
|       |          |     | - pH = 8; T = 25 °C | - 99% DF degradation in 35 min with H2O2 |
|       |          |     | - [FeC8Pc] = 0.003 g/L | - 99% DF degradation in 25 min with NaIO4 |
|       |          |     | - [H2O2] = 3.52 × 10−4 M | - Mechanism: HO• |
|       |          |     | - [NaIO4] = 3.52 × 10−4 M | - Degradation pathway proposed |
|       |          |     |                         | - Reutilization: N/A |
| 2 [62] | CoC4Pc@CNOMS | DF | - Matrix: Distilled water | - 99% DF degradation in 20 min |
|       |          |     | - [CoC4Pc@CNOMS] = 0.1 g/L | - kobs = 1.87 × 10−1 min−1 |
|       |          |     | - [PMS] = 3.2 × 10−4 M | - Mechanism: HO•, SO4•− and 1O2 |
|       |          |     | - pH = 7; T = 25 °C | - Degradation pathway proposed |
|       |          |     |                         | - Reutilization: 4 cycles |
| 3 [63] | FeII(TDPP)Cl, FeII(TDFPP)Cl, FeII(Br8TDPP)Cl | MET | - Matrix: 3.2 mixture ACN//PrOH | - Homogenous |
|       |          |     | - [porphyrin] = 5.4 g/L | - 85% MET degradation in 24 h, 45% ACE degradation in 24 (using FeII(Br8TDPP)Cl) |
|       |          |     | - [mCPBA] = 0.4 M | - Degradation pathway proposed |
|       |          |     | - pH = N/A; T = 25 °C | - Reutilization: N/A |

The authors further proposed a degradation pathway for DF (Scheme 7). DF (m/z = 295) was oxidized by HO• into m/z 311 and m/z 309. Their referred quinone’s ability to form charge-transfer complexes through electron transfer from donor to acceptor allowed DF and m/z 309 to be transformed into cation (m/z 295) and anion (m/z = 309) radicals, forming a charge-transfer complex [55].
Shi and Deng studied the catalytic performance of \( \text{CoC}_4\text{Pc@CNOMS} \), prepared by electrostatic linking of cobalt(II) tetracarboxyphthalocyanine (\( \text{CoC}_4\text{Pc} \), Figure 8) to an amino-functionalized manganese octahedral molecular sieve (CNOMS) on the degradation of a 10 mg/L DF aqueous solution, using PMS (\( 3.2 \times 10^{-4} \text{ M} \)) as oxidant (Table 4, Entry 2) \[62\]. After a 20 min reaction, 99% of DF degradation was achieved, following a pseudo-first-order kinetics (\( k_{\text{obs}} = 1.87 \times 10^{-1} \text{ min}^{-1} \)). The authors observed that at \( pH = 7 \) and light activation of PMS, the degradation was promoted by both type I and type II mechanisms (\( \text{HO}^\bullet, \text{SO}_4^{\cdot -} \) and \( {^1}\text{O}_2 \text{ROS species} \)). The catalyst was also reused in four cycles, and a continuous slight decrease in the activity was observed.

Jones’s group studied the effect of several iron(III) porphyrins, chloro \( \text{meso}\text{-tetra(2,6-dichlorophenyl)porphyrinate iron (Fe}^{\text{III}}(\text{TDCPP})\text{Cl} \), Figure 8), chloro \( \text{meso}\text{-tetra(2,6-difluorophenyl)porphyrinate iron (Fe}^{\text{III}}(\text{TDFPP})\text{Cl} \), Figure 8) and chloro \( \beta\)-octabromo-\( \text{meso}\text{-tetra(2,6-dichlorophenyl)porphyrinate iron (Fe}^{\text{III}}(\text{Br}_8\text{TDCPP})\text{Cl} \), Figure 8), in the catalytic degradation of acetaminophen-derived drugs methacetin (\( \text{MET} \), Figure 5) and acetanilide (\( \text{ACE} \), Figure 5) (Table 4, entry 3) \[63\]. Using \( \text{Fe}^{\text{III}}(\text{Br}_8\text{TDCPP})\text{Cl} \) as a catalyst (0.75 g/L) and mCPBA as oxidant (75 g/L), 85% \( \text{MET} \) and 45% \( \text{ACE} \) degradation, respectively, was achieved in 24 h. Moreover, they identified the oxidation metabolites by GC-MS, and the acetaminophen was the main product obtained in both experimental cases.

4. Degradation of Neurological Pharmaceuticals

Neurology drugs manage diseases, disorders and conditions that affect the brain and nervous system. Carbamazepine is the only known neurological-system pharmaceutical evaluated in TPM-based degradation studies (Figure 9). This psychotropic drug is commonly used to treat epilepsy. The mechanism of action involves the blocking of the sodium channels of the neuron’s membranes. This drug is commonly found in wastewaters due to its frequent use and incomplete removal by the traditional processing methods. \[64\]

\[ \text{carbamazepine - CBZ} \]
4.1. Photochemical Degradation

The Lu and Chen group has been very active in the preparation of phthalocyanine-based ternary catalysts for the degradation of pharmaceuticals, namely carbamazepine (CBZ, Figure 9) [64–69]. They used zinc(II) tetra(carboxy)phthalocyanine (ZnTCPc, Figure 10) and blended it with polyacrylonitrile (PAN) supported graphitic carbon nitride (g-C_3N_4), producing ZnTCPc@g-C_3N_4/PAN nanofibers (Table 5, entry 1) [65]. The same phthalocyanine was also coupled with g-C_3N_4 and enriched with graphene quantum dots (GQD), yielding the hybrid catalyst ZnTCPc@g-C_3N_4/GQD (Table 5, entry 2) [66]. When CBZ degradation tests were performed using ZnTCPc@g-C_3N_4/PAN and ZnTCPc@g-C_3N_4/GQD hybrid catalysts, CBZ was fully degraded in 5 h under visible-light Xe irradiation. However, in one case, [CBZ] = 2.5 mg/L and [ZnTCPc@g-C_3N_4/PAN] = 1 g/L (Table 5, entry 1) [65], while in the other experiment, the CBZ concentration was raised to 6 mg/L, with a catalyst concentration of just 0.1 g/L (25× higher substrate:catalyst ratio) (Table 5, entry 2) [66].

Figure 10. Structures of tetrapyrrolic macrocycles (TPM) mostly used as catalysts for degradation of carbamazepine.

| #/#Ref | Catalyst | Drug | Experimental Conditions | Comments |
|--------|----------|------|-------------------------|----------|
| 1 [65] | ZnTCPc@g-C_3N_4/PAN nanofibers | [CBZ] = 2.5 mg/L | Matrix: Distilled water, Visible Light 100 W lamp λ > 400 nm, [ZnTCPc@g-C_3N_4/PAN] = 1 g/L, pH = N/A, T = 25 °C, Pre-dark: 10 min | 98% CBZ degradation in 5 h, TOC: N/A, k_{obs}: N/A, Mechanism by h^+, 1O_2, O_2^−, Reutilization: N/A, Degradation pathway proposed |
| 2 [66] | ZnTCPc@g-C_3N_4/GQD | [CBZ] = 6 mg/L | Matrix: Distilled water, Visible-light Xe solar simulator λ > 420 nm, [ZnTCPc@g-C_3N_4/GQD] = 0.1 g/L, pH = 5.3, T = 25 °C, Pre-dark: 10 min | 99% CBZ degradation in 5 h, TOC: N/A, k_{obs}: N/A, Mechanism: by h^+, 1O_2, O_2^−, Reutilization: N/A |
| 3 [64] | FePcCl_16 | [CBZ] = 6 mg/L | Matrix: Distilled water, Visible-light Xe solar simulator λ > 420 nm, [FePcCl_16] = 0.1 g/L, [PMS] = 3 × 10^{-3} M or [H_2O_2] = 5 × 10^{-3} M, pH = 7, T = 25 °C | 98% CBZ degradation in 90 min (using PMS), < 10% CBZ degradation in 90 min (using H_2O_2), TOC: 82% after 120 min, k_{obs}: 8.2 × 10^{-3} min^{-1}, Mechanism by 1O_2, HO^*, SO_4^−, Reutilization: 20 cycles, Degradation pathway proposed |
Table 5. Cont.

| #/Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|-------------------------|----------|
| 4     | FePcCl$_{16}$$@g$-C$_3$N$_4$-IMA | [CBZ] = 6 mg/L | - Matrix: Distilled water  
  - Visible-light Xe solar simulator  
  - [catalyst] = 0.1–0.3 g/L  
  - [PMS] = 3 $\times$ $10^{-4}$ M  
  - pH = 7; T = 25 $^\circ$C | 98% CBZ degradation in 25 min  
  TOC: N/A  
  $k_{obs}$: N/A  
  Mechanism by O$_2^•$ and 1O$_2$  
  Reutilization tests: N/A  
  Degradation pathway proposed |

| 5 [14] | SiPc@B/NaF-TiO$_2$ | [CBZ] = 10 mg/L | - Matrix: Distilled water  
  - Visible-light 1500 W xenon lamp  
  - [SiPc@B/NaF-TiO$_2$] = 1 g/L  
  - pH = 6.5–6.9; T = 25 $^\circ$C | 70% CBZ degradation in 240 min  
  TOC: N/A  
  $k_{obs}$: 6.7 $\times$ $10^{-3}$ min$^{-1}$  
  Mechanism: N/A  
  Reutilization: N/A  
  Degradation pathway proposed |

The same group further extended their studies of CBZ degradation, always using iron(II) hexadecachlorophthalocyanine (FePcCl$_{16}$, Figure 10) as TPM and oxone peroxy-monosulfate (PMS) as oxidant. The authors performed studies with FePcCl$_{16}$ [64] and by combining the phthalocyanine with g-C$_3$N$_4$ through axial coordination, using isonicotinic acid (INA) [67] 1-methyl-1H-imidazole-5-carboxylic acid (IMA) [68] and poly (4-vinylpyridine)/polyacrylonitrile) (P$_4$VP/PAN) [69]. The corresponding catalysts, FePcCl$_{16}$, FePcCl$_{16}$$@g$-C$_3$N$_4$-INA, FePcCl$_{16}$$@g$-C$_3$N$_4$-IMA and FePcCl$_{16}$$@P_4$VP/PAN, were then used in the degradation of concentrated solutions of CBZ (6 mg/L) using a visible-light Xe-solar simulator in all experiments (Table 5, entries 3–4). The authors observed that heterogeneous but non-immobilized FePcCl$_{16}$ provided a TOC of 82% after 120 min of reaction time, with a $k_{obs}$ = 8.2 $\times$ $10^{-2}$ min$^{-1}$. This catalyst was reused along 20 cycles with no significant loss of activity (Table 5, entry 3) [64]. Then, they evaluated the effect of catalyst concentration onto g-C$_3$N$_4$ (0.1 g/L–0.3 g/L), and the best result was achieved using FePcCl$_{16}$$@P_4$VP/PAN nanofibers (load = 0.3 g/L), with 98% in CBZ degradation (Table 5, entry 4) [68].

Furthermore, based on the intermediates of CBZ identified by authors using UPLC–HDMS, a possible degradation pathway was proposed, with h+, O$_2^•$– and HO$^•$ being the main oxidizing species (Scheme 8). Firstly, the intermediates with $m/z$ 253 were the initial photodegradation products of CBZ ($m/z$ 237), subsequently undergoing a second HO$^•$ addition to produce a dihydroxy-CBZ species with $m/z$ 269 or the intermediate $m/z$ 287. An alternative pathway would be the attack of the O$_2^•$– and HO$^•$ on the olefinic double bond of the central seven-member ring, which resulted in the formation of 10,11-epoxy-CBZ ($m/z$ 253). Additionally, a hydrogen-rearrangement reaction followed by the loss of the amide group could yield a compound with $m/z$ 208, which could be further oxidized into acridine ($m/z$ 180) or suffer the addition of HO$^•$ to form an intermediate with $m/z$ 224. Subsequently, the intermediate acridine could possibly further oxidize into the intermediate with $m/z$ 196. All intermediates transformed to several biodegradable small molecules (below) [64–69].
Scheme 8. Proposed degradation pathway for carbamazepine.

As peroxymonosulfate (PMS) was the oxidant used in all cases, sulfate (SO$_4^{2-}$) and hydroxyl (HO$^\bullet$) radicals were the dominant active species in the oxidation catalytic process. As shown in Figure 11, the authors proposed that FePcCl$_{16}$ could be induced to the excited state (*FePcCl$_{16}$) under visible-light irradiation, then coordinating with the oxygen atoms of PMS to form a Fe(II)-O-O-SO$_3^{2-}$ species. The electron-donating effect of axial pyridine in P4VP can activate the heterolytic cleavage of the O–O bond and generate the high-valent iron-oxo (Fe$^{IV}$=O) species, which is proposed as the major active species in this reaction system [69].
Figure 11. Proposed main pathway for the formation of active species when using FePcCl\textsubscript{16}-P\textsubscript{4}VP/PAN catalyst under visible-light irradiation (λ > 420 nm) in CBZ photodegradation. Adapted with permission from ref. [69]. Copyright 2019 Springer Nature.

Anucha [14] reported the synthesis of a hybrid catalyst consisting of a silicon phthalocyanine (SiPc, Figure 10) axially linked to a boron-sodium fluoride-doped TiO\textsubscript{2} semiconductor, producing the catalyst SiPc@B/NaF-TiO\textsubscript{2} (Table 5, entry 5). The authors compared the effect of the support B/NaF-TiO\textsubscript{2} with the hybrid catalyst, SiPc@B/NaF-TiO\textsubscript{2} on the photodegradation of CBZ (10 mg/L) with visible light (1500 W xenon lamp λ > 340 nm). They observed that the support B/NaF-TiO\textsubscript{2} provided the best result, with 70% degradation in 4 h (k\textsubscript{obs} = 1.8 \times 10^{-2} \text{ min}^{-1}) [14,64–69].

4.2. Oxidative Chemical Degradation

Lu’s group extended their exhaustive studies of CBZ degradation, using other phthalocyanine-based catalysts (Table 6, entries 1–3) [70–72] under Fenton-like oxidation conditions, using H\textsubscript{2}O\textsubscript{2} as the oxidant. In a first study, the authors blended iron phthalocyanine (FePc, Figure 12) onto polyacrylonitrile (PAN), obtaining FePc@PAN nanofibers [70]. This catalyst, in a 1 g/L load, was then used in the degradation of CBZ (6 mg/L) in the presence of H\textsubscript{2}O\textsubscript{2} (20 mM) at pH = 3 and temperature = 70 °C (Table 6, entry 1). The authors proposed that the hydroxyl (HO\textsuperscript{•}) radicals were the dominant active species in the oxidation catalytic process. The catalyst could be reused eight times without significant loss of activity. Later, the same group tested the iron(II) hexadecafluorinated phthalocyanine μ-oxo dimer (FePcF\textsubscript{16})\textsubscript{2}O (Figure 12) as catalyst for CBZ degradation, again using H\textsubscript{2}O\textsubscript{2} as oxidant [71]. In a 0.1 g/L catalyst concentration and 20 mM H\textsubscript{2}O\textsubscript{2}, a 6 mg/L solution of CBZ was fully degraded in 40 min, regardless of the pH tested (Table 6, entry 2). By electron paramagnetic resonance and electrospray ionization–mass spectrometry, the authors proposed that the Fe\textsuperscript{IV}=O is the main active species arising from heterolytic cleavage of Fe\textsuperscript{III}–OOH species. Similar results were obtained later [72] using the same phthalocyanine μ-oxo dimer (FePcF\textsubscript{16})\textsubscript{2}O (Figure 12) impregnated onto MWCNTs, providing the hybrid catalyst (FePcF\textsubscript{16})\textsubscript{2}O@MWCNT (Table 6, entry 3). The system (FePcF\textsubscript{16})\textsubscript{2}O@MWCNT/H\textsubscript{2}O\textsubscript{2} (0.2 g/L and 5 mM, respectively) was also used to degrade CBZ, reaching full degradation in 60 min. Reutilization studies showed that the catalyst is active along 10 reutilization cycles. [70–72].
5. Degradation of Miscellaneous Pharmaceuticals

Other miscellaneous drugs have been also evaluated in environmental degradation studies. Limson studied the degradation of regulatory hormones estrone (E1, Figure 13) and estradiol (E2, Figure 13), using unsubstituted manganese(II) and iron(II) phthalocyanines (MnPc and FePc, respectively, Figure 14) [73]. When MnPc was used (6.8 mg/L), both E1 and E2 (8 mg/L) were almost fully degraded, using H2O2 as oxidant (0.56 mM) at pH = 3, in 30 min (Table 7, entry 1).
Tomé [74] reported the preparation of hybrid catalysts $\text{TPPF}_{20}@\text{MNP}$, $\text{TPPF}_{16}(\text{SGlc})_4@\text{MNP}$, $\text{TPPF}_{17}(\text{SGlc})_3@\text{MNP}$, $\text{ZnPcF}_{16}@\text{MNP}$ and $\text{ZnPcF}_8(\text{SGlc})_8@\text{MNP}$ via covalent linkage of meso-substituted porphyrins ($\text{TPPF}_{20}$, $\text{TPPF}_{16}(\text{SGlc})_4$ and $\text{TPPF}_{17}(\text{SGlc})_3$, Figure 14) and phthalocyanines ($\text{ZnPcF}_{16}$ and $\text{ZnPcF}_8(\text{SGlc})_8$, Figure 14) to aminopropyl-functionalized silica-coated magnetic nanoparticles (MNP)(Table 7, entry 2). These catalysts were evaluated in the photodegradation of estradiol (E2, Figure 13), and the best results were obtained with $\text{TPPF}_{17}(\text{SGlc})_3@\text{MNP}$ and $\text{ZnPcF}_8(\text{SGlc})_8@\text{MNP}$, reaching
82% degradation of E2 after 8 h irradiation with a visible-light white lamp (4 mW/cm²). The authors obtained better results (100% E2 degradation) under flow conditions with a residence time of 60 min. The authors attributed this higher efficiency in flow mode to the better penetration of light into the suspension since the narrowness of the tube allowed a much more efficient irradiation.

Table 7. Summary of miscellaneous pharmaceuticals’ degradation processes using TPM-based catalysts.

| #:Ref | Catalyst | Drug | Experimental Conditions | Comments |
|-------|----------|------|-------------------------|----------|
| 1 [73] | FePc | [E1] = 8 mg/L | Matrix: phosphate buffer (50 mM) + 30% v/v MeCN | 100% E1 degradation in 30 min (both catalysts) |
| | MnPc | [E2] = 8 mg/L | - [MnPc] = 6.8 mg/L, [H₂O₂] = 5.6 × 10⁻⁴ M, pH = 3 | -100% E2 degradation with MnPc and 91% E2 degradation with FePc (in 30 min) |
| | | | - [FePc] = 1.3 mg/L, [H₂O₂] = 3 × 10⁻³ M, pH = 7, T = 35 °C | - kobs: N/A |
| | | | - 100% E1 degradation in 30 min (both catalysts) | - Reutilization: N/A |
| 2 [74] | TPPF₁₇(SGlC)₃ @MNP | [E2] = 5 mg/L | - Matrix: Distilled water | 82% E2 degradation with TPPF₁₇(SGlC)₃ @MNP (flow—1 h) |
| | | | - White visible-light lamp (4 mW/cm²) | - Mechanism: mainly by O₂ |
| | | | - [MNP-catalyst] = ~0.1 g/L to ~0.2 g/L | - TOC: N/A |
| | | | - pH = 4, 6 and 8; T = 25 °C | - kobs: for TPPF₁₇(SGlC)₃ @MNP (5.7 × 10⁻² min⁻¹ in flow) |
| | | | - Pre-dark for 1 h | - Reutilization: 3 cycles in batch |
| 3 [22] | TCPP@TiO₂ | [FAM] = 28 mg/L | Matrix: Distilled water | 100% FAM removed in 180 min. |
| | | [SOL] = 30 mg/L | - 500 W halogen lamp | < 10% for SOL and TAM in 180 min |
| | | [TAM] = 34 mg/L | - [TCPP@TiO₂] = 0.3 g/L | - TOC: N/A |
| | | | - pH = N/A; T = 25 °C | - reutilization on FAM decreased degradation to 65% |
| | | | - Pre-dark: 30 min | - Degradation pathway proposed for all drugs |
| 4 [75] | TCPP@ATINT | [FAM] = 100 mg/L | Matrix: Distilled water | using TCPP@Si-ATINT: 60% degradation upon UV irradiation in 240 min and 80% degradation upon Visible irradiation in 240 min. |
| | | | - UV-light 150 W mercury lamp | using TCPP@ATINT: 99% degradation upon Visible irradiation in 240 min. |
| | | | - Visible-light 500 W halogen lamp | - Mechanism by h⁺ |
| | | | - [catalysts] = 0.25 g/L | - kobs = 8.0 × 10⁻³ min⁻¹ by TCPP@Si-ATINT |
| | | | - pH = N/A; T = N/A | - kobs = 2.17 × 10⁻³ min⁻¹ by TCPP@ATINT |
| | | | - Pre-dark: 1 h | - Reutilization: N/A |
| 5 [76] | TPFPP@NH₂-SiO₂ | [MEP] = 50 mg/L | Matrix: Distilled water, wastewater | 63% MEP degradation in 12 h (solar simulator, distilled water) |
| | | | - Solar-simulator 1500 W arc xenon lamp 295 nm < λ < 400 nm | 58% MEP degradation in 6 h (sunlight, distilled water) |
| | | | - Direct sunlight | 62% MEP degradation in 12 h (solar simulator, wastewater) |
| | | | - [TPFPP@NH₂-SiO₂] = 2.5 g/L | TOC = N/A |
| | | | - pH = 7.5; T = 25 °C | k obs = 6.5 × 10⁻³ min⁻¹ (solar simulator, distilled water) |
| | | | | Mechanism by 'O₂ |
| | | | | Reutilization: N/A |
| | | | | Degradation pathway proposed |
Table 7. Cont.

| #/Ref | Catalyst          | Drug | Experimental Conditions | Comments                                      |
|-------|-------------------|------|-------------------------|-----------------------------------------------|
| 6 [77]| Co₂CPC@CNOMS      | [PRP] = 5 mg/L | - Matrix: Distilled water  
- [Co₂CPC@CNOMS] = 0.1 g/L  
- [PMS] = 3.2 × 10⁻⁴ M  
- pH = ~6; T = 25 °C | - 93% PRP degradation in 30 min  
- 47% TOC in 30 min  
- k_{obs} = 9.2 × 10⁻² min⁻¹  
- Mechanism by SO₄•⁻ and ¹O₂  
- Reutilization: 4 cycles  
- Degradation pathway proposed |

Nolan [22] prepared the hybrid catalyst TCPP@TiO₂ by adsorbing meso-tetra(4-carboxyphenyl)porphyrin (TCPP, Figure 14) onto TiO₂. Three pharmaceuticals were tested (famotidine (FAM), solifenacin succinate (SOL) and tamsulosin HCl (TAM); Figure 13) in 0.083 mM solutions (28 mg/L, 30 mg/L and 34 mg/L for FAM, SOL and TAM, respectively) under irradiation with a 500 W visible-light halogen lamp (Table 7, entry 3). Under these conditions, only FAM was fully degraded (100%) after 180 min, while the other pharmaceuticals gave less than 10% degradation products. Additionally, the authors mentioned that after the second cycle, a drop in FAM degradation to 65% was observed.

Chetty [75] used the same porphyrin (TCPP, Figure 14) to prepare the hybrid photocatalysts TCPP@ATiNT and TCPP@Si-ATiNT by immobilizing it onto anatase titanium nanotubes (ATiNT) and Si-ATiNT (Table 7, entry 4). The authors irradiated 100 mg/L of FAM aqueous solutions, using both a 150 W UV-light mercury lamp and a 500 W visible-light halogen lamp containing both catalysts in concentrations of 0.25 g/L. The authors concluded that TCPP@ATiNT was the best catalyst to promote full FAM degradation upon 240 min of irradiation, as demonstrated by its higher kinetic rate, k_{obs} = 21.7 × 10⁻³ min⁻¹ against k_{obs} = 8.0 × 10⁻³ min⁻¹, when TCPP@Si-ATiNT was used. This difference was ascribed to the higher recombination rate favored by the silane-linker group present in the TCPP@Si-ATiNT catalyst, with a consequent decrease in electron injection. The authors also suggested that h+ holes formed in the HOMO of TCPP upon photoexcitation may be the most relevant oxidizing agent, rather than ¹O₂, once photocatalytic experiments under oxygen-deficient conditions showed a similar rate of FAM degradation (Figure 15).

Figure 15. Schematic illustration of the proposed visible-light photocatalysis mechanism for FAM degradation using TCPP@ATiNT and TCPP@Si-ATiNT. Adapted with permission from ref [75]. Copyright 2020 Elsevier.
Other β-blocker pharmaceuticals like propranolol (PRP, Figure 13) and metoprolol (MEP, Figure 13) have also been studied by Neves and Simões [76], using mesotetrakis(pentafluorophenyl)porphyrin (TPFPP, Figure 14) covalently immobilized onto amino functionalized silica oxide (NH$_2$-SiO$_2$) as heterogeneous catalyst (TPFPP@NH$_2$-SiO$_2$). MEP photodegradation was carried out using both a solar simulator and direct-sunlight irradiation. After 12 h, 63% and 58% MEP degradation was obtained, respectively (Table 7, entry 5).

Regarding the degradation of PRP with PMS (0.2 g/L) as oxidant, Huiping [77] described the synthesis of a catalyst based on a binuclear cobalt carboxyl-substituted phthalocyanine (Co$_2$CPc, Figure 14) supported by electrostatic interactions onto amino-functionalized manganese octahedral molecular sieves (CNOMS) (Table 7, entry 6). A 93% PRP degradation ($k_{obs} = 9.2 \times 10^{-2}$ min$^{-1}$) was observed after 30 min, and 47% TOC. The authors proposed that both SO$_4^{•-}$ radicals and $^{1}$O$_2$ were the main oxidation species. Furthermore, reutilization was performed, and the catalyst remained active and stable for four cycles, as shown in Figure 16.

![Figure 16](image_url)

**Figure 16.** (a) Reutilization cycles for PRP degradation; (b) FT-IR spectra of Co$_2$CPc@NOMS-2 before and after the reutilization cycles. Adapted with permission from ref. [77]. Copyright 2019 Elsevier.

6. Conclusions and Perspectives

Considering the literature herein reviewed, one can generally conclude that the scientific community has been committed to finding more sustainable and alternative catalytic processes for the degradation of pharmaceuticals in the environment, particularly using tetapyrrole macrocycle- (TPM) based catalysts. The main parameters requiring attention when developing such a catalytic system aiming its transposition at real-world application must include:

(i) the TPM, considering its modulability and functionality, including substitution patterns for activity/stability;
(ii) the type of support, aiming preferential immobilization at efficient reutilization and/or the holding of suitable semiconducting characteristics;
(iii) the light source, when designing a photocatalytic system, preferentially using visible/solar energy;
(iv) the oxidants, when designing oxidative chemical systems, giving preference to environmentally benign ones.

The most relevant examples discussed above can be highlighted by, for instance, the TNCuPc@CeO$_2$/Bi$_2$MoO$_6$ (copper(II) β-tetranitrophthalocyanine deposited on the surface of semiconducting CeO$_2$/Bi$_2$MoO$_6$ nanoflowers), which, when used in 1.5 g/L concentration, showed high catalytic performance in the photodegradation of antibiotic tetracycline (0.05 g/L concentration), with reusability up to four cycles without significant
loss of activity, reaching, after 120 min irradiation with 800 W xenon visible light, a TOC removal efficiency of 83%, one of the highest reported so far [21].

In another relevant study, a porphyrin-MOF-type catalyst (TCPP@UiO-66), prepared by introducing meso-tetra(carboxyphenyl)porphyrin (TCPP) onto UiO-66 crystals, was used to degrade a diclofenac aqueous solution (0.03 mg/L) containing a catalyst concentration of 0.1 g/L, reaching complete photodegradation when irradiated by a simulated-sunlight 350 W Xe lamp (290 nm ≤ λ ≤ 1200 nm) and showing good recyclability [61].

For oxidative chemical degradation systems, the use of an MnTDCPPS@N-SiO₂ catalyst (meso-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinato manganese(III) covalently attached to aminopropyl functionalized silica gel) in the degradation of recalcitrant trimethoprim antibiotic must be highlighted. The immobilized catalyst, notwithstanding its use in quite a low concentration (0.002 g/L) and in the presence of 0.26 mM H₂O₂ as oxidant, was able to promote the oxidative degradation of trimethoprim (0.13 g/L) in 95% (24% TOC decrease) after 150 min, showing reusability for up to five cycles without losing its activity [54].

As a whole, efforts in the design and larger-scale preparation of efficient catalysts should point to the modulation/functionalization of TPMs holding appropriate substituent-imparting catalyst stability (e.g., bearing electron-withdrawing groups at the periphery) and suitable functionalities to promote covalent immobilization to supports, therefore avoiding catalyst leaching upon reutilization. When developing photocatalytic systems, these should aim for longer wavelength absorption and lower-charge carrier recombination (when using semiconductors as supports), where solar energy irradiation sources should be preferred. On the other hand, oxidants should be of primary concern when using catalysts for chemical oxidation, giving preference to benign sources, such as molecular oxygen, hydrogen peroxide or potassium peroxymonosulfate.

Another important challenge concerns the achievement of complete degradation of pharmaceuticals. When only partial/low mineralization occurs (the large majority of the studies herein reported), we consider that it is crucial to evaluate the byproducts generated to ensure their lower toxicity and environmental persistence since they can also contribute to increase the environmental toxicity and, particularly, the development of multi-resistant bacteria when dealing with antibiotics.

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