A General Overview of Heterogeneous Photocatalysis as a Remediation Technology for Wastewaters Containing Pharmaceutical Compounds

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Abstract: The presence of persistent, difficult to degrade pharmaceutical compounds in wastewaters is a significant environmental concern. While heterogeneous photocatalysis can degrade a range of pharmaceutical compounds, as a technology, it is yet to be applied. Current research on heterogeneous photocatalysis for pharmaceutical removal is focused on the development of photocatalytic materials that are both efficient photocatalysts and solar driven as well as materials that combine both adsorption and photocatalysis. The formation of toxic by-products during photocatalytic degradation can be an issue; hence, mechanistic studies to identify reaction pathways and intermediates are important and are discussed in this review. The potential application of photocatalytic systems coupled with other technologies, to achieve complete pollutant removal and avoid toxin formation are also discussed. Given the broad range of properties of these pharmaceutical compounds and their corresponding wastewater matrices, each system needs to be optimised accordingly, with the need for pilot scale studies. Other than end of pipe solutions to reduce the occurrence of pharmaceutical pollutants in the environment, a comprehensive environmental management approach involving strategies such as the reduction of pharmaceutical prescriptions and the introduction of take back schemes are also needed to achieve a reduction of pharmaceutical compounds in the environment.

Keywords: photocatalysis; AOPs; pharmaceutical; pollutants; toxicity; wastewater

1. Introduction

1.1. Pharmaceuticals in the Environment

Trace pharmaceutical pollutants began to be considered as part of an environmental problem in the early 1990s. These are biologically active compounds, and typically persistent with a potential to adversely affect human health and the health of other living organisms [1]. Schematic 1 illustrates how these compounds may enter the environment. Since their emergence as (micro)pollutants, pharmaceutical compounds are continuously being detected in waterways around the globe. These compounds enter sewage treatment plants mostly from patient excretion or through the disposal of unwanted pharmaceuticals into the sewer system. Sewage treatment plants (STPs) cannot completely remove them [2–4]. Pharmaceutical and personal care products (PPCPs), pharmaceutically active compounds (PhAcs) and endocrine disrupting chemicals (EDCs) often find their way into the environment most commonly through the solid waste component (sludge phase) [5,6], and as such, they give rise to background concentrations that are widespread at extremely low levels (less than one part-per-billion) [7]. While little information is available about measurable health effects due to exposure and/or ingestion of such chemicals, through drinking water for example, they are still of concern given their bioactivity and their persistence [5]. The direct contribution from pharmaceutical manufacturing processes to emissions and environmental contamination (in developed countries) is negligible.
From STPs, the residual pharmaceuticals in the liquid phase can end up in waterways, and potentially can be consumed by humans and animals. From the sludge phase, pharmaceuticals can enter the soil, hence groundwater and surface drinking water supplies. Such contaminants have been observed in the ng to µg per litre range in surface waters throughout the UK and across the rest of Europe with 200 different pharmaceuticals reported in river waters globally [8].

1.2. Technologies Applied to Remove Pharmaceutical Contaminants

Given that conventional STPs are not designed to remove pharmaceutical pollutants, it is now recognised that innovative wastewater treatment technologies or novel integrated processes are needed to address the problem. As such, the removal efficiencies of PPCPs, PhACs and EDCs by different technologies have been thoroughly studied as will be described below. A summary of typically assessed technologies and their effectiveness is listed in Table 1.

Table 1. A summary of typically assessed technologies and their effectiveness.

| Technology                        | Effectiveness                      | Notes                      |
|-----------------------------------|------------------------------------|----------------------------|
| Primary Treatment                 | Limited effectiveness              |                            |
| Secondary Treatment (floculation) | Not effective                      |                            |
| Biological Treatment              | Effectiveness is pharmaceutical    | compound dependent         |
| Advanced Oxidation Processes (AOPs)| Not sufficient on its own.          |                            |
| UV Irradiation (photolysis)       | Effective                          | With or without UV         |
| H₂O₂                              | Effective                          | With or without UV         |
| Ozonation                         | Effective                          | H₂O₂ can be added          |
| Photo-Fenton (UV/Fe²⁺/³⁺)         | Effective                          | High energy costs          |
| TiO₂ photocatalysis                | Effective                          | High energy costs          |
| Membrane Technologies (RO, ultrafiltration) | Effective                        | Further disposal required  |
| Activated carbon                  | Effective                          |                            |

Pharmaceutical compounds vary in their properties and chemical structures, as such their removal efficiencies depend on the technology implemented. Removal efficiencies also depend on initial pollutant concentrations and by the type of mixture of pharmaceutical compounds to be treated [7]. Removal efficiencies compare the amount of pharmaceutical compounds remaining relative to their initial concentration in the inlet flow. They do not give information on the formation of intermediate products or the degree of mineralisation (conversion to CO₂ and simple mineral acids). Some studies use the terms degradation and removal efficiencies interchangeably. Strictly speaking, removal efficiency may include removal due to adsorption, while degradation focusses on the breaking down of the pharmaceutical parent compound due to photocatalytic processes, and is as such, a more useful term.

Depending on the chemical and physical properties of the pharmaceuticals to be removed, such as aqueous solubility, volatility and lipophilicity, pharmaceuticals may be physically removed by varying degrees during primary treatment at a sewage treatment plant. Secondary treatment methods such as coagulation and flocculation processes do not remove them [9]. Biological treatment methods can be effective; however, certain pharmaceutical pollutants are not broken down by biological treatment [10,11].

High pharmaceutical compound removal rates can be achieved by adsorption on activated carbon [11]. Membrane filtration technologies (including reverse osmosis (RO) and ultrafiltration) can also achieve high removal rates, as can oxidation technologies [12]. Oxidation technologies include ozonation and hydrogen peroxide (H₂O₂) addition with UV irradiation [7,13]. UV irradiation on its own is not sufficient to remove (mineralise) pharmaceutical compounds, however it can be useful for reducing their biological activity [14]. The addition of H₂O₂, TiO₂, or TiO₂/activated carbon can increase removal rates.
up to 100%. UV/H$_2$O$_2$ and TiO$_2$ photocatalysis are the light driven oxidation processes most used to destroy pharmaceutical compounds and other EDCs and PPCPs [9].

It is important to note that process conditions such as hydraulic retention time as well as the season of the year may also influence the extent of pharmaceutical pollutant removal [7,11]. The season affects bacterial activity in biological treatment units, as well as inlet flows and Dissolved Organic Carbon (DOC) and Natural Organic Matter (NOM) concentrations. Certain combinations of treatment methods have also been used to achieve enhanced removal efficiencies, such as ozonation followed by a biological activated-carbon process [7]. Constructed wetlands may also play a role. Membrane bioreactors (MBRs) that integrate biological degradation with membrane filtration can achieve complete removal, with increased costs [4].

1.3. State of the Art of Pharmaceutical Contaminant Removal: Knowledge Gaps and Continuing Research

The varying properties of pharmaceutical compounds, coupled with their occurrence at trace levels (<1 µg/L), create unique challenges for both removal processes and analytical detection [2,15]. At present, there is no single treatment technology that addresses their complete removal and while a large volume of research has been carried out in this area, knowledge gaps persist. Such research may be critical to improve our current understanding and provide guidance as to which technology (or combination of technologies) is best suited and under which conditions.

This remains an important topic and a number of reviews and book chapters have been published on the removal of EDCs (including pharmaceuticals and personal products) in drinking water and STPs [16–20]. Given the vast number of publications in this area, recently reviews on the removal of these compounds using photocatalysis have become more specific, for example there are those which have focused on the photocatalytic materials, such as TiO$_2$ [21], TiO$_2$ based photocatalytic membranes [22], nano-based adsorbents and photocatalysts [23], TiO$_2$/SiO$_2$/carbon materials [24], metal oxides as photocatalysts [25], bismuth oxyhalide as photocatalysts [26], carbon nanotubes [27], Bi$_2$WO$_6$ [28], hematite based photocatalysts [29], Bismuth titanate [30], carbon based materials [31] carbon nitride based photocatalysts [32] MoS$_2$ based nano-photocatalysts [33], nano-photocatalysis [34], doped photocatalysts [35]. There are also reviews that have focused on the pharmaceutical compound to be degraded. Kaur et al.’s review [36] focused on the degradation of analgesic and non-steroidal anti-inflammatory drugs (NSAIDs). The removal of carbamazepine, diclofenac and sulfamethoxazole was reviewed by Mestre et al. [37], ibuprofen by Sruthi et al. [38], antibiotics [39] and oxytetracycline by Pelosato et al. [40]. The recent review by Marinho et al. [41] was on photocatalytic, electrocatalytic and photoelectrocatalytic degradation of pharmaceuticals in aqueous media.

Additionally, recently, Ahmed et al. [42] compared the removal of emerging contaminants by biological, chemical and hybrid technologies. Rivera-Utrilla et al. [5] summarised findings on water treatment systems for pharmaceutical removal based on conventional systems as well as tertiary (advanced) treatment methods. Kanakaraju et al. [43] reviewed AOP mediated removal of pharmaceuticals from water while Homem and Santos [44] focused on the degradation and removal processes for antibiotics by various AOPs.

In this review, a general overview is provided on heterogeneous photocatalytic degradation of pharmaceutical compounds which aims to update and collate findings in this significant research field. This review covers the following: (i) the significance of individual operational parameters; (ii) the issue of the formation of toxic by-products; (iii) mechanistic studies; (iv) most recent developments in the area such as studies on visible light driven photocatalysis coupled integrated systems; and (v) finally, insights are given into foreseen future developments, for end-of pipe solutions for the removal of pharmaceuticals from the environment while strategies to reduce or limit their entry into wastewaters are also briefly mentioned.
2. Heterogeneous Photocatalysis as an AOP

TiO₂ photocatalysis (UV/TiO₂) and other advanced oxidation processes have been said to offer the potential for good engineering solutions to eliminate the residual microconstituents derived from biological systems [19]. Photocatalysis can completely mineralise organic pollutants and therefore gives a complete solution to pollutant removal compared to technologies that rely on transferring the pollutants from the wastewater to another phase such as adsorption on activated carbon.

Heterogeneous photocatalytic oxidation utilises semiconductor photocatalysts which consist of a conduction band and a valence band. These photocatalysts are activated upon illumination with light of sufficient energy which generates an oxidising hole and a reducing electron, as described in greater detail in Scheme 1. TiO₂ remains by far the most widely used photocatalyst due to its considerable activity, high stability and low cost although it is only UV-activated. Visible light activated photocatalysts are highly sought as they allow for the use of abundant solar energy without the costly use of UV irradiation. Lee et al. published a short review on photocatalytic systems for pharmaceutical removal [45] and concluded that to achieve cost effectiveness, photocatalytic technologies will need non-renewable energy resources for photocatalyst activation.

AOPs, into which heterogeneous photocatalysis falls, rely on the addition of oxidising agents or the creation of oxidising conditions through the generation of highly reactive, oxidative species, dominated by hydroxyl radicals (HO•). AOPs can use one or more oxidant, combine oxidant and irradiation, or combine oxidant and catalyst or oxidant and ultrasonic energy [4]. The characteristic features of HO• radicals are their non-selective nature, high reactivity and high oxidation potential (E° = +2.80 V). They are ranked second to fluorine (E° = +3.03 V) as oxidants. They can attack a wide range of organic contaminants with typical rate constants in the order of 10⁶−10⁸ M⁻¹ s⁻¹. Other oxidative species in AOPs include superoxide anion radicals (O₂•⁻), H₂O₂ and O₃ [46].

Compared to other AOPs, heterogeneous photocatalysis offers the advantages of mild (ambient) temperature and pressure operation, with the potential for the utilisation of sunlight for photocatalyst activation. The generation of oxidising species during a photocatalytic process can be described by a series of reactions, simplified as reactions 1 and 2, while the photoactivation process can be described schematically as shown in Figure 1. It involves the generation of an electron-hole pair upon the illumination of the semiconductor photocatalyst (typically TiO₂) with light that is energetic enough to excite

![Scheme 1](image-url)
an electron from the valence band to the conduction band leaving behind a highly oxidising hole \((h^+)\) in the valence band (reaction 1). The oxidising hole can either react directly with an adsorbed organic molecule or can oxidise adsorbed water to produce highly oxidising \(\text{OH}\) \((\text{reaction 2})\). The energy required for TiO\(_2\) activation is 3.2 eV, typically supplied by a UVA light source (315–400 nm wavelength range). The electron can react with dissolved oxygen in the system to produce \(\text{O}_2\)^\(-\)\. This is shown in reaction (3). This \(\text{O}_2\)^\(-\) species is also important for subsequent oxidation reactions.

\[
\begin{align*}
\text{TiO}_2 + hv & \rightarrow \text{TiO}_2(e^- + h^+) \\
\text{TiO}_2(h^+) + \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + \text{OH}^\bullet + \text{H}^+ \\
e^- + \text{O}_2 & \rightarrow \text{O}_2^{•-} \quad (3)
\end{align*}
\]

**Figure 1.** Simple schematic of semiconductor photo-activation showing the generation of an electron \((e^-)\) and hole \((h^+)\) pair when a semiconductor is irradiated with light with energy \((hv)\) greater or equal to the semiconductor’s bandgap. Irradiation excites an electron from the conduction band (CB) to the valence band (VB).

As mentioned above, AOPs can be photochemical, non-photochemical or a hybrid of the two [46]. Photochemical processes include UV oxidation (UV/H\(_2\)O\(_2\), UV/O\(_3\), UV/H\(_2\)O\(_2\)/O\(_3\)), photoenton (H\(_2\)O\(_2\)/UV/Fe\(^{2+}/3+\)), and photocatalysis (e.g., UV/TiO\(_2\)). Non photochemical processes include Fenton, ozonation, ultrasound sonolysis, electrolysis, and wet air oxidation. Hybrid processes include sonophotocatalysis, photocatalytic ozonation, sonobiphotoanalysis and photoelectrocatalysis.

AOPs have been studied extensively for removing pharmaceutical compounds both by mineralisation to CO\(_2\) or by degradation to less harmful compounds. Typically, these processes are very effective at completely mineralising or deactivating pharmaceutical compounds and have been used to supplement conventional systems [3,18]. By using solar irradiation, the capital cost of AOPs may be substantially reduced [18,45]. However, by-product formation due to interactions between the parent compounds and degradation products may occur and these require additional treatment.
Fast et al. [3] presented a study which gave a numerical ranking to score the performance of various AOPs (including ozonation, UV irradiation, photocatalysis, Fenton reactions, and integrated processes). The ranking examined several categories including engineering, environmental, and socioeconomic. From their preliminary analysis, \( \text{H}_2\text{O}_2/\text{O}_3 \) (Perozonation) had the highest ranking (3.45). All other processes showed comparable performance while TiO\(_2\) photocatalysis received the lowest ranking (2.11). In 2012, Chong et al. [47] carried out a feasibility study comparing various AOPs in a pilot scale case study to produce Class A recycled water. They concluded that the \( \text{H}_2\text{O}_2/\text{UV} \) treatment process was the best AOP for a decentralised wastewater treatment process when considering the technical, economic and environmental constraints for advanced wastewater treatment for the water quality existing in the case study. Despite unfavourable commercialisation prospects based on current knowledge, photocatalytic water treatment technologies remain potentially highly sustainable [1,48].

3. Studies on Heterogeneous Photocatalysis for Pharmaceutical Wastewater Treatment

UV/TiO\(_2\) processes have been tested thoroughly and have been shown to be efficient for removing pharmaceutical pollutants. Both mechanistic and kinetic studies have been conducted. Studies on such systems have investigated the effects of the photocatalyst type, catalyst loading, initial substrate concentrations, solution pH and the presence of other species typically found in wastewaters. In such studies a UVA light source is typically used. TiO\(_2\) photocatalysts typically tested are either made in-house or commercially available. Due to vast differences in reactor geometries, light intensities, photon fluxes and photocatalyst properties utilised in the studies described below, a quantitative comparison of such studies is challenging as differences in methodologies are difficult to account for. Therefore, a description of some of the studies carried out in the literature merely serves to highlight the applicability, and typically the effectiveness of TiO\(_2\) photocatalysis for pharmaceutical pollutant removal, while describing general trends.

In their review on the removal of antibiotics from wastewaters, Homem and Santos [44] reported that ozonation, Fenton/photo-Fenton and semiconductor photocatalysis were the most tested removal technologies for such pollutants. Photocatalysis produced intermediate compounds which were less toxic and more biodegradable than the parent compounds. In terms of removal efficiency, photocatalysis seemed to be promising for the treatment of effluents with low loads of organic matter (from river, groundwater and drinking water). Most recently Romao et al. [48] presented a high-throughput study on the TiO\(_2\) photocatalytic degradation of over 800 pharmaceutical compounds in water. The majority of the studied compounds were found to be photocatalytically degraded. A high degree of conversion was achieved for (relatively small) molecules with functional groups such as aldehydes, alcohols, ketones and nitriles. A low degree of conversion was observed for compounds composed of conjugated aromatic systems. No trends were observed on the basis of pharmacological class. Table 2 lists examples of studies on the use of heterogeneous photocatalysis for the removal of pharmaceutical compounds, describing the heterogeneous photocatalytic systems used and their effectiveness.

| Pharmaceutical | Photocatalytic System | Effectiveness | Notes, References |
|-----------------|-----------------------|---------------|------------------|
| Acetaminophen   | Two TiO\(_2\) photocatalytic reactor configurations were used: Photocatalyst solid suspension in a stirred photoreactor and TiO\(_2\) supported on glass spheres in a packed bed photoreactor (the latter is shown in Figure 2). | For the suspension type system almost 100% of paracetamol removal was achieved after 4 h of irradiation. For the packed bed reactor system approximately 42% of paracetamol removal from wastewater after 8 h. | [13] |
Table 2. Cont.

| Pharmaceutical  | Photocatalytic System                                                                 | Effectiveness                                                                 | Notes, References |
|-----------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|-------------------|
| Atenolol        | System compared graphene oxide-TiO₂ (TiO₂-G) and TiO₂ photocatalysts under UV-vis light and “simulated sun” irradiation conditions. | TiO₂-G exhibited much higher photocatalytic activity than that of bare TiO₂. Under solar irradiation, 72% degradation of Atenolol (25 ppm) was achieved with 1.5 g/L TiO₂-G in 1 h. Complete TOC removal for ATL degradation was obtained in 7 h. | [49]              |
| Carbamazepine   | Visible-light-degradation in an aqueous solution using a ZnIn₂S₄ photocatalysts.      | Complete degradation of Carbamazepine was achieved in 20 min, 44 intermediates were detected by LCMS-IT-TOF technique. | [50]              |
| Sulfamethoxazole| Visible light activated reduced graphene oxide-WO₃ were used as photocatalysts. P25-TiO₂/tetraethyl orthosilicate (TEOS) film on glazed ceramic surface under a visible light incubator. | Depending on catalyst preparation, 98% removal of SMX was achieved within 3 h. | [51]              |
| Ibuprofen       |                                                                                     | Ibuprofen degradation of 76% within 10 h of irradiation under optimal conditions. | [52]              |
| Acetylsalicylic acid (Aspirin) | Degussa P25 TiO₂ photocatalyst, Xenon lamp irradiation (to simulate solar irradiation) in a slurry type photoreactor. | Under optimised conditions: initial pH value of 5, initial aspirin concentration of 10 mg/L and P25 concentration of 50 mg/L, degradation efficiency of 98.9% was obtained. 84% photocatalytic degradation of Amoxicillin after 34.95 kJUV/L accumulated UVEnergy per liter of solution (t_ir = 240 min). | [53] [54]        |
| Amoxicillin     | Solar TiO₂ Photocatalysis                                                            |                                                                               |                   |

Figure 2. Packed-bed photoreactor system (with Degussa P25 TiO₂ coated glass spheres. A solar radiation sodium vapour lamp was used in this system, with a parabolic collector [13].
3.1. Heterogeneous Photocatalysis Operating Parameters

In the following sections we will review some of the significant findings on specific photocatalytic process parameters. Operational parameters need to be optimised to achieve best performance for applications and comparative purposes. Optimum conditions typically need to be empirically determined. Operating parameters include parameters such as catalyst type and concentration, substrate concentration, initial pH, incident radiation flux, and additional oxidants in the system.

Photocatalytic degradation rates are strongly affected by the catalyst loading and increase as the catalyst loading is increased until an optimum is reached. Beyond the optimum, a high catalyst loading leads to increased turbidity and as such can impede light penetration into the reactor. The optimum catalyst concentration depends on the incident radiation flux and reactor geometry [55]. Different photoreactor configurations are available to choose from, these can be broadly classified either as slurry type reactors or fixed bed reactors (such as that shown in Figure 2). Each offers advantages and disadvantages, for example, slurry type systems offer a higher available surface area and better mass transfer properties while fixed bed reactors offer the advantage of not having to collect the catalyst particles from the treated water post treatment.

The addition of chemical oxidants can improve the photocatalytic chemical process. Hapeshi et al. [56] investigated the effect of catalyst type and loading, initial substrate concentration, and H$_2$O$_2$ as an additional oxidant on substrate conversion and mineralisation in the photocatalytic degradation of the antibiotic ofloxacin (OFLOX) and atenolol (ATL) (a β1 receptor antagonist) in pure water, groundwater and treated municipal effluent. Degussa P25 (a well-known commercial TiO$_2$ photocatalyst) was found to be the most effective catalyst, with OFLOX being more easily degraded than ATL. Conversion generally increased with a higher catalyst loading, a lower initial substrate concentration and the addition of H$_2$O$_2$. The results for H$_2$O$_2$ were reaffirmed by Tsydenova et al. [55] who stated that a too low H$_2$O$_2$ concentration may result in a lower reaction rate, while a too high concentration would lead to radical scavenging/recombination and again lower reaction rates. Tsydenova et al. also reported that peroxodisulfate may be a more efficient oxidant than H$_2$O$_2$ when combined with TiO$_2$ photocatalysis. Zhang et al. [57] investigated the effect of pH on the photocatalytic degradation of paracetamol (also known as acetaminophen, APAP). pH was found to affect adsorption, with a pH of 3.5 being optimum. pH typically defines the surface charge of the TiO$_2$ particles and thereby affects the degree of attraction and repulsion between the catalyst particles and substrates. Doll and Frimmel [58] showed that Degussa P25 TiO$_2$ had a better photocatalytic activity for carbamazepine (CBZ) and clofibric acid (CFA) degradation than Hombikat UV 100 TiO$_2$ (another commercially available photocatalyst) whereas for iomeprol, Hombikat UV 100 was the better photocatalyst. This was explained in terms of the different adsorption behaviour of the two catalysts.

Hu et al. [59] studied the degradation of sulfamethoxazole (SMX) and its related sulfonamide antimicrobial agents by TiO$_2$ photocatalysis. Degradation rates were found to be dependent on the initial SMX concentration, catalyst crystalline phase and loading, type of electron acceptor and concentration and the presence of foreign water constituents. Reaction rates were not found to be sensitive to changes in the sulfonamide structure or reaction pH. Chuang et al. [60] studied the effects of pH on the photocatalytic degradation efficiencies of sulfamethoxypyridazine. Sulfamethoxypyridazine is a sulfonamide antibacterial. They found that photocatalytic reaction rates for the decomposition of sulfamethoxypyridazine in water were higher at pH 6 than pH 3 and pH 11 due to the highest adsorption at pH 6. At a higher pH of 11, sulfamethoxypyridazine loses a proton and the negative anion cannot be easily adsorbed onto the surface of TiO$_2$ which is also negative at pH > greater 6.3, the isoelectric point of TiO$_2$. 


Calza et al. [61] showed that an optimum catalyst loading existed for TiO$_2$ catalysts for the photocatalytic transformation of diclofenac (DCF) under simulated solar irradiation. Kanakaraju [48] also examined TiO$_2$ photocatalysis for the degradation of DCF, as well as Naproxen (NPX) and their mixtures in different water matrices. Initial concentrations of DCF and NPX, TiO$_2$ loading, solution pH and water matrices all influenced the reaction rates by different extents. The influence of the water matrix was significant. The degradation rates of both DCF and NPX in drinking water were suppressed in the presence of anions. Kanakaraju also carried out solar photocatalytic degradation studies on DCF and NPX which showed comparable performances with those undertaken under artificial irradiation although longer exposure times were generally required.

From the above discussion it is clear that the main operational parameters of photocatalysis for pharmaceutical removal have been identified and studied in detail. Table 3 summarises typical experimental ranges of the main operating parameters. While general trends have emerged, for example with regard to the existence of an optimum catalyst loading and reaction pH, pilot studies are essential for studying real wastewaters given the known effects of water constituents on photocatalytic reactions. It is also evident that most laboratory studies are typically carried out using initial pharmaceutical pollutant concentrations at mg/L levels which are much higher than those encountered in real wastewaters. This is due to the analytical challenges when working with ng/L concentrations which are more representative of pharmaceutical pollutant concentrations in real wastewaters. Therefore, more studies of reactions using µg/L-ng/L initial reactant concentrations are needed.

| Operating Parameter                      | Typical Range                      | Comments                                                                 |
|-----------------------------------------|------------------------------------|--------------------------------------------------------------------------|
| Initial pharmaceutical compound concentration | 1–10 mg/L.                        | Some studies utilised up to 50 mg/L initial concentrations, and as low as 0.1 mg/L. Real wastewaters contain mg/L levels of pharmaceutical pollutants. Current tests utilise initial concentration that are too high. |
| pH                                      | 3 (mildly acidic), 5 (close to neutral), 11 (alkaline). | pH has a strong effect on pollutant adsorption. It affects pollutant molecule dissociation and catalyst surface charge. pH is typically controlled by addition of HCl or NaOH to the system. |
| Light intensity                         | typically in the order of magnitude of 10 W/m$^2$. | An optimum catalyst loading exists. An increase in catalyst loading increase available active sites, however, a loading that is too high leads to photon scattering and light attenuation. |
| Catalyst loading                        | 0.1 g/L–1 g/L.                     |                                                                           |
| Irradiation wavelength                  | UVA—peak at 320 nm                 | To achieve complete degradation with no residual intermediate products, long, impractical reaction times may be needed, with added energy costs. |
| Chemical additives                      | Visible light studies > 400 nm     |                                                                           |
|                                         | H$_2$O$_2$, O$_3$                  |                                                                           |
| Total reaction time                     | 1 hr–several hours                 |                                                                           |
| Reactor types                           | Typical reactor configurations include slurry type, fixed bed packed bed and falling film reactors | slurry type is the most commonly used configurations, followed by packed bed reactors, and falling film reactors. |
3.2. Effect of Water Constituents

Wastewaters usually contain complex pollutant mixtures as well as numerous other organic and inorganic species. These can affect the pharmaceutical degradation process [55,62]. There have only been a few studies that have focused on the degradation of pharmaceutical pollutants in real effluents, hence the effects of water constituents remain poorly understood [63]. Tokumura et al. [64] found that generally, water constituents inhibited the oxidation process, however, some studies have reported enhancement effects, as will be discussed below.

For the TiO2 photocatalysis process, the competition between the pharmaceuticals and water constituents for adsorption sites on the catalyst surface was a less significant inhibitory factor than the scavenger effects of the constituents [64]. Water constituents such as Fe²⁺, Zn²⁺, Ag⁺, Na⁺, CO₃²⁻, HCO₃⁻, PO₄³⁻, SO₄²⁻, Cl⁻, and NO₂⁻ are known to affect photocatalytic processes by typically reacting with hydroxyl radicals [65]. Sirtori et al. [66] reported decreased trimethoprim (TMP) degradation in simulated seawater, while Pereira et al. [67] reported that phosphates considerably hindered oxolinic acid (OXA) and oxytetracycline (OTC) removal while chlorides, sulfates, nitrates, ammonium and bicarbonates did not significantly affect rates. Enhancement effects due to carbonates have been reported by Hu et al. [59] during SMX photocatalysis at pH 9.

Park and Choi [68] found that the effects of fluoride ions (F⁻) depended on the substrates to be degraded. F⁻ adsorbs strongly on the catalyst surface [65,68]. Park and Choi proposed that hydroxyl radical-mediated oxidation pathways were in fact enhanced on F⁻-TiO₂, while hole transfer mediated oxidations were largely inhibited due to hindered adsorption (or complexation) of substrates on F⁻-TiO₂. Suspended solids and colour can also affect photocatalytic reaction rates due to light scattering and adsorption [63].

Doll and Frimmel [58] studied the effect of natural organic matter on the photocatalytic degradation of a number of compounds and found that in general NOM led to a decrease in rates, due to a combination of radiation attenuation, competition for active sites and catalyst surface deactivation by adsorption. Additionally, dissolved organic matter can result in the formation of harmful oxidation by-products. Hu et al. [59] reported that for the photocatalytic degradation of SMX and related sulfonamide antimicrobial agents, the presence of NOM inhibited photocatalytic degradation of SMX to a much greater extent at pH 5 than pH 9.

Other examples of studies on the degradation of pharmaceuticals in real effluents are those by Van Doorslaer et al. [69] who examined the degradation of the antibiotic moxifloxacin (MOX) in hospital effluents containing organic (humic and fulvic acids and bovine serum albumin) and inorganic ions (chloride ions and inorganic carbon). They found that degradation was 70% inhibited in real waters compared to degradation in demineralised water. Rioja et al. [70] demonstrated the inhibiting effect of Cl⁻ and HCO₃⁻ on the degradation of CFA while Rimoldi et al. [62] reported on the inhibiting effects of the HCO₃⁻ species on the tetracycline (TC) degradation process.

As can be seen from the above discussions, effects due to interference of matrix components can be significant. Thus, studies in real wastewaters are crucial to achieve optimal pharmaceutical pollutant removal. The different results reported by different studies on the effects of water constituents such as carbonates for example, point to the fact that the observed degradation may be compound and methodology dependent.

3.3. Toxicity Assessment of the Degradation Intermediates and Products

During the heterogeneous photocatalytic removal of pharmaceutical compounds, it is known that the formation of toxic by-products can be an issue [62]. Toxic by-product formation needs to be seriously considered when assessing the application of photocatalysis for the removal of certain pharmaceutical pollutants. In most studies, to achieve complete degradation of the pharmaceuticals, long reaction times are required, with subsequent low mineralisation rates affecting energy costs [13,71]. Most of the by-products and intermediate
products from oxidised PhACs and EDCs have been said to be typically less harmful to the environment compared to their parent compounds while hydroxyl radicals attack EDCs at their phenolic functional groups which are responsible for estrogenic activity ([14] and references within, 2016).

Successful application of photocatalysis to remove toxicity of parent compounds by degrading them to less harmful by-products has been reported for OXA, OTC, APAP, DCF, metoprolol (MET) and tylosin (TYL). It is important to note that toxicity has been reported to be concentration and toxicity test dependent [72,73] hence the need to compare these two test parameters to ascertain non-toxicity of by-products. Pereira et al. [67] found that for photocatalytically treated antibiotics OXA and OTC, after their complete removal, the remaining degradation by-products no longer showed antibacterial activity.

Zhang et al. [57] showed that TiO$_2$ photocatalytic degradation was able to completely remove APAP from wastewater and drinking water without any generation of toxic products. Calza et al. [61] reported that photocatalysis led to complete detoxification of DCF-containing solutions. Romero et al. [74] reported that the toxicity of MET decreased when MET was degraded by either photocatalysis/TiO$_2$ or UV-Vis/H$_2$O$_2$/TiO$_2$ processes. Yahiat et al. [75] reported that TYL by-products showed significant biodegradability.

In the following, studies that have reported increased toxicity during photocatalytic removal of certain pharmaceuticals are described. A list of these is given in Table 4. Gong et al. [76] studied the toxicity of antipyrine (AP) after photodegradation using UV/CoFe$_2$O$_4$/TiO$_2$ systems. The parent compound AP and its degradation products showed positive effects on the growth of the green algae _Chlorella vulgaris_. However, acute toxicity of AP was detected on brine shrimps _Artemia salina_. The toxicity was eliminated gradually with the decomposition of AP and the generation of non-toxic by-products. However, this is not always the case as will be discussed below.

**Table 4. Pharmaceutical Compounds with Reported Toxic Photocatalytic Degradation By-Products.**

| Pharmaceutical Compound | Comments, References |
|-------------------------|----------------------|
| AP                      | No toxicity for _Chlorella vulgaris_. Acute toxicity on brine shrimps _Artemia salina_ [76]. |
| NPX                     | Photocatalysis did not result in improvements in biodegradability [77]. |
| IBP                     | The degradation product 4-IBAP was more toxic than IBP [78]. |
| CP                      | Degradation products had comparable toxicity to CP [78,79]. |
| OFLOX                   | Toxicity was initial concentration dependent [56]. |
| ATL                     | Toxicity was initial concentration dependent [56]. |
| TC                      | Absence of TC by-products biodegradability [75]. |
| AMX                     | Toxicity was concentration and toxicity test dependent [72]. |
| MET                     | Toxicity was toxicity test dependent [73]. |
| Warfarin                | Toxicity was toxicity test dependent [73]. |
| TMP                     | Toxicity was toxicity test dependent [73]. |
| CBZ                     | Toxicity was toxicity test dependent [73]. |
| Gemfibrozil             | Toxicity was toxicity test dependent [73]. |

Méndez-Arriaga et al. [77] reported that using the Microtox test based on the bioluminescent bacteria _Vibrio fischeri_ for NPX photocatalysis did not result in improvements in biodegradability. Sora et al. [78] reported on the photocatalytic degradation of aqueous solutions of ciprofloxacin (CP) and ibuprofen (IBP) using LaFeO$_3$ as a photocatalyst, using H$_2$O$_2$ oxidation systems, or a combination of LaFeO$_3$ and H$_2$O$_2$ under visible light irradiation. The main degradation product of IBP was 4-isobutylacetophenone (4-IBAP), which was more toxic than IBP and showed a slower photocatalytic degradation than the parent compound.

In the case of CP, Sora et al. [78] reported that the toxicity of CP degradation products was comparable to that of CP itself. Silva et al. [79] also studied the toxicity of CP-containing wastewaters treated by UVA-irradiated TiO$_2$ and ZnO photocatalysts. For the lowest
concentration of CP tested, 10 µg L\(^{-1}\) remaining toxicity was still observed. Interestingly, the ZnO photocatalyst particles themselves also showed high toxicity but not TiO\(_2\). When using TiO\(_2\) as photocatalyst, the toxicity of the treated water initially decreased (due to CP adsorption on the photocatalyst) but after 15 min increased significantly due to toxic by-product formation.

Hapeshi et al. reported on the ecotoxicity of OFLOX and ATL to freshwater species, *Daphnia magna*. This was found to increase with increasing substrate concentration (1–10 mg/L) and exposure time (24–48 h), with ATL being more toxic than OFLOX [56]. Yahiat et al. [75] highlighted the importance of toxicity studies when considering coupling photocatalysis with biological treatment. A major problem to avoid was said to be the generation of antibiotic resistant strains in biological systems due to recalcitrant antibiotics not being degraded but being adsorbed on sludge and released to the environment. Yahiat et al. [75] studied the heterogeneous photocatalytic degradation of the antibiotic TC known to be toxic to microorganisms in biological treatment systems. The absence of biodegradability of TC by-products was noted.

Dimitrakopoulou et al. [72] studied amoxicillin (AMX) degradation and mineralisation by UVA/TiO\(_2\). Antimicrobial activity was found to be dependent on AMX concentration and the test microbe. In the case of *E. coli* and *K. pneumoniae* inactivation was due to the presence of AMX at relatively high concentrations. Conversely, *E. faecalis* was less resistant to AMX and its reaction by-products. Murgolo et al. [73] carried out toxicity testing during the degradation of warfarin, TMP, MET, CBZ and Gemfibrozil using a nanostructured TiO\(_2\) film deposited on a stainless-steel mesh (nanoTiO\(_2\)-SS). In agreement with Dimitrakopoulou et al. (2012), Murgolo et al. [73] also pointed to the need to identify the correct toxicity test. They found the AMES fluctuation test (which tests whether a chemical is a mutagen), the Fish Embryo acute toxicity test and the *Green alga Selenastrum capricornutum* test to be suitable for bioactivity testing. Overall, for all the tested pharmaceuticals, the AMES fluctuation test and the Fish Embryo acute toxicity test showed a slight increase in toxicity in the early stages of the reactions followed by a decrease at 60 min.

As discussed in the above section, it is crucial that toxicity studies are conducted as part of assessing the effectiveness of photocatalysis for the treatment of wastewaters containing pharmaceutical pollutants. From the studies carried out thus far, it is clear that at least one appropriate, practical toxicity test needs to be identified. Additionally, long reaction times may be required for complete mineralisation of certain pharmaceutical compounds however this would hinder practical applications. In some cases, degradation to harmless compounds, without complete mineralisation of the parent compound may be sufficient. For example, in coupled photocatalysis-biological treatment systems, where photocatalysis is a pre-treatment step, toxicity of by-products is a very important parameter to monitor, however complete mineralisation is not sought.

### 3.4. Mechanistic Studies

During the photocatalytic degradation of pharmaceutical compounds, the formation of harmful by-products is of concern and warrants thorough mechanistic investigations to identify reaction pathways with an aim to avoid their formation. Mechanistic studies have been carried out on the degradation of a number of pharmaceutical compounds, but information is still lacking in this field. The identification of intermediate and final products of pharmaceuticals requires powerful analytical tools. For example, Radjenovic et al. [80,81] successfully used tandem mass spectrometry (MS2) experiments with a quadrupole-time of flight (QqToF) mass analyser coupled to ultra-performance liquid chromatograph (UPLC) for the identification of ATL’s main intermediate products.

The nature of pharmaceutical compounds and the size of these molecules, together with the unselective nature of OH radical attacks, result in photocatalytic degradation pathways that are highly complex with numerous intermediate products being formed. Bo
et al. [50] carried out a thorough mechanistic study on the visible-light-degradation of CBZ in an aqueous solution using a ZnIn$_2$S$_4$ photocatalyst. While complete degradation of CBZ was achieved in 20 min, 44 intermediates were detected by LCMS-IT-TOF technique. The degradation mechanism was dominated by OH radical attacks, beginning with attacks on carbon atoms of the aromatic ring to produce 2-hydroxy CBZ and 3-hydroxy CBZ, followed by hydration steps and further hydroxyl radical attacks. Compounds detected included hydroxy- and keto- derivatives, carboxylic products derived from ring cleavage, benzenic compounds and short chain aliphatic acids. The complete proposed degradation pathway is shown in Figure 3.

![Figure 3. Proposed degradation pathways for CBZ. Reproduced with permission [50]. Copyright (2017), Elsevier.](image-url)
For the photocatalytic degradation of SMX and related sulfonamide antimicrobial agents, kinetic trends were consistent with a mechanism involving sulfonamide oxidation by hydroxyl radicals [59]. Identified transformation intermediates and products were consistent with SMX mineralisation initiated by hydroxyl radical attack on either the aromatic or heterocyclic rings or the sulfonamide bond. For the degradation of NPX, Méndez-Arriaga et al. [77] showed that demethylation and decarboxylation were the principal initial processes in the degradation of this pharmaceutical compound.

Calza et al. [61] proposed a tentative degradation pathway for the photocatalytic degradation of DCF which was said to be based on the formation of hydroxy-derivatives before the complete mineralisation of the starting molecule. Calza et al. observed several hydroxyl- and bihydroxy DCF derivatives, which were further transformed into chloro or hydroxyl-phenol derivatives. The formation of carboxylic acids was achieved through the ring opening followed by complete mineralisation. Gou et al. [82] used visible light-activated Ag₃PO₄ sub-microcrystals as photocatalysts and proposed three removal degradation pathways of DCF, including OH-adduct to aromatic ring, direct oxidation by photoinduced holes and decarboxylation of side chain from the parent compound. Kanakarju [46] identified eight degradation products of DCF and NPX mainly as a result of decarboxylation and hydroxylation. Degradation of DCF and NPX mixtures produced fifteen degradation products corresponding to the degradation of the individual compounds while two degradation products with much higher molecular weights than DCF and NPX were identified. The latter observation indicates reactions between reaction intermediates.

Sirtori et al. [66] studied the photocatalytic degradation of TMP in which hydroxylation, demethylation and cleavage of the original drug molecule were observed. Lambropoulou et al. [83] identified 21 degradation products during the photocatalytic degradation of bezafibrate (BZF). They proposed a possible multi-step degradation scheme, with multiple hydroxylation of BZF with subsequent phenoxy ring opening and the cleavage of the amide and ether bonds.

For APAP, Zhang et al. [57] reported that the degradation involved direct hole oxidation and ipso-substitution as the main initial steps. Radjenovic et al. [80,81] discussed the release of heteroatoms and formation of carboxylic acids for APAP, as well as ATL and ranitidine (RNTD). For ATL, six transformation products were identified, said to have been formed by consecutive attacks of hydroxyl radicals. For both APAP and ATL organic short-chain acids were formed before being mineralised. The initial steps for the TiO₂ photocatalytic degradation of RNTD went through hydroxylation (hydroxyl radical attack), dealkylation, deamination, and oxidation by hydroxyl radicals and O₂. Additionally, a product formed by the reduction of RNTD by conductive band electrons was detected. Carboxylic acids were also detected at the end of the reaction.

Sousa et al. [84] reported on the TiO₂ photocatalytic transformation pathways of Lorazepam (LZP) under artificial UV and natural solar irradiation. They proposed a LZP photodegradation mechanism based on the initial opening of the diazepinone seven-membered ring, followed by a rearrangement into a highly stabilised six-membered aromatic ring and subsequent cleavage and/or hydroxylation reactions. For AP, Gong et al. [76] reported on its photocatalytic degradation using UV/CoFe₂O₄/TiO₂. Ten organic intermediates were identified. Hydroxylation, demethylation and the cleavage of the pentacyclic ring were included in the decomposition pathways.

The above-described mechanistic studies are highly valuable to better understand the effectiveness of photocatalytic technologies for pharmaceutical removal. They are also important to assess the potential for toxic by-product formation and avoidance. Such studies however do require specialised equipment and methodologies given the low range of concentrations (µg/L and ng/L levels) and the complexity of the product matrix. This is an ongoing challenge which continues to be addressed by regulatory bodies and academic research laboratories.
3.5. Pilot Scale Reactors

The effectiveness of the photocatalytic process for removing and degrading many organic compounds has been well demonstrated in laboratory and pilot scale studies. From such studies it has been shown that operational costs of AOPs are high due to the high electricity demand of UV lamps. Compound parabolic collectors (CPCs) are highly efficient in collecting solar radiation and are typically used in pilot plant studies [54]. In this section, such studies on larger scale pilot plant systems are reviewed.

Radjenovic et al. [80] studied the technical feasibility and performance of photocatalytic degradation of the anti-inflammatory drug APAP and β-blocker ATL in a pilot-plant scale CPCs, in distilled water and in synthetic municipal wastewater treatment plant effluent. In distilled water, the concentration of APAP decreased rapidly, and APAP completely disappeared after 24 min. Dissolved Organic Carbon (DOC) exhibited a slower mineralisation indicating the formation of harder to mineralise intermediates. In synthetic municipal wastewater, APAP degraded much more slowly than in distilled water implicating the hindering effect of wastewater constituents. Similarly, to APAP, the degradation of ATL was faster in distilled water than in synthetic municipal water. The main intermediates were finally degraded to organic short-chain acids prior to being mineralised. Radjenovic et al. [81] also examined the photodegradation of RNTD in the same system described above, again using distilled water and synthetic wastewater effluent matrices. Mineralisation was slow in both matrices at 37% (after 73 min of illumination) and 8% (after 55 min of illumination). What can be learned from this study is that longer photocatalytic reaction times can be avoided by stopping the reaction when biodegradable organic short-chain acids are formed. These effluents may then be discharged (if they meet the requirements) or can be fed to a biological treatment unit, without the need for complete photocatalytic mineralisation.

The photocatalytic degradation of AMX has also been demonstrated in CPC pilot plants in studies by Elmolla and Chaudhuri [85] and Moosavi and Tavakoli [54]. Moosavi and Tavakoli used the response surface methodology (RSM) based on Box–Behnken statistical experimental design to optimise the independent variables TiO$_2$ catalyst loading, initial AMX initial concentration and initial pH. The optimum conditions were found to be 1.5 g/L catalyst loading, 17 mg/L initial AMX concentration and initial pH of 9.5. At the solar plant, under these optimised conditions, the degradation of AMX achieved in 240 min (after 34.95 kJ/UV/L accumulated UV energy per liter of solution) was 84.12 % (as can be seen in Figure 4). While high degradation efficiencies of AMX were achieved in this system, no information was given with regard to formation, persistence or toxicity of intermediate products.

![Figure 4](image-url)

**Figure 4.** AMX degradation under solar irradiation, and optimised conditions in systems used by Moosavi and Tavakoli, reproduced with permission [54]. Copyright (2016), Springer Nature. Springer-Verlag Berlin Heidelberg.
Pereira et al. [67] studied the TiO$_2$ photocatalytic degradation of two veterinary antibiotics, OXA and OTC, using pure solutions of individual or mixed antibiotics in a pilot-plant with CPCs. The removal profiles of each antibiotic, both as a single component or in a mixture were found to be similar. Pereira et al. also showed that the remaining degradation by-products of OXA and OTC no longer had antibacterial activity.

Quiñones et al. [86] reported on CPC pilot scale treatment of aqueous mixtures of APAP, AP, bisphenol A, caffeine, MET and testosterone. The combination of photocatalytic oxidation and ozonation was found to considerably enhance system efficiency by reducing the ozone demand and energy requirements to completely remove the contaminants. Romero et al. [74] compared the removal of MET by TiO$_2$ photocatalysis and UV-Vis/H$_2$O$_2$/TiO$_2$ processes using two different experimental devices: (i) solar box (SB) with a Xe lamp and (ii) a solar pilot plant reactor with CPCs. The UV-Vis/H$_2$O$_2$/TiO$_2$ process performed better compared to the photocatalytic process without H$_2$O$_2$.

Sousa et al. [87] also examined TiO$_2$ photocatalytic removal of LZP under artificial UV and natural solar irradiation. They used three experimental set-ups; two laboratory-scale photoreactors, each provided with a UV lamp (one medium pressure mercury lamp and one blacklight blue lamp), and a pilot-scale Solar Plant with CPCs. The CPC Solar Pilot Plant proved to be the most efficient set up for photocatalysis [84,87]. LZP photocatalytic degradation was also further assessed in a municipal effluent, however in this matrix the photoproducts generated were more persistent than LZP itself.

Finally, De la Cruz et al. [88] focused on the removal of propranolol (PRO) by TiO$_2$ photocatalysis using a laboratory scale system with artificial light (Xe-lamp) and a pilot scale system using solar irradiation based on CPC photoreactors. The laboratory device gave rates 1.1–1.5 times higher than the solar installation. Toxicity was shown to decrease with treatment time.

As can be seen from the above examples, the pilot scale plant studies have thus far demonstrated the effectiveness of photocatalytic technologies for the removal and partial mineralisation of pharmaceutical contaminants from wastewaters. The use of additives such as H$_2$O$_2$ and or combination with ozonation have been demonstrated to show process improvements. A few studies utilised real wastewater matrices or mixture of pharmaceutical pollutants to better replicate conditions encountered in wastewater treatment plants. In such studies the formation of harmful by-products has been raised as an issue. This points to the significance of carrying out pilot plant studies in either real wastewaters or at least with added water constituents.

Performance of photocatalytic technologies is pollutant specific and hence pilot plant studies are essential to assess effectiveness. While questions may remain on the toxicity of intermediate and residual products of certain pharmaceuticals, form a regulatory perspective, regulations may require only removal of pharmaceutical compounds. One example is legislation that has been introduced in Switzerland for example where 80% pharmaceutical pollutant is required [89]. Hence, at those removal levels, photocatalytic technologies would be a viable option. The further development of solar driven processes would make the economics more favourable as is highlighted in a later section of the review.

### 3.6. Photocatalysis Coupled with Other Processes for Pharmaceutical Removal

While it is evident from the aforementioned studies that AOPs are effective in removing pharmaceutical compounds, all AOPs are labelled as expensive methods. Materials and equipment costs as well as energy requirements and removal efficiencies must be considered when assessing the overall performance of AOPs [90]. Additionally, the slow mineralisation rates of photocatalysis and the possibility of lingering toxic by-products unless complete mineralisation is achieved (which requires long processing times and higher energy usage), mean that in order to degrade recalcitrant compounds at reduced operational costs, integrated processes may be needed [65,75]. To overcome drawbacks of AOPs, they are often coupled with existing water treatment methods for cost effectiveness and efficiency improvements [65].
A combination of biological and chemical oxidation processes are typical integrated treatment options [91]. Augugliaro et al. [92] reviewed the various possibilities to couple heterogeneous photocatalysis with other technologies and identified two categories: (i) Coupling with ultrasonic irradiation, photo-Fenton reaction, ozonation, or electrochemical treatment. This combination was said to affect photocatalytic mechanisms; (ii) Coupling with biological treatment, membrane reactors, membrane photoreactors, or physical adsorption. This combination does not affect photocatalytic mechanisms but does improve the efficiency of the overall process.

The choice of the coupled process is dependent on the type of wastewater to be treated. For example, photocatalysis pre-treatment could be used to increase the biodegradability of persistent pollutants and/or to reduce their toxicity as presented in the study by Yahiat et al. [75] who examined the degradation of the two antibiotics TC and TYL. It is important to note that when applied as a pre-treatment to biological treatment, a sufficient residual organic carbon (i.e., limited photocatalytic mineralisation) is needed for the subsequent microbial culture. Toxicity of by-products is a significant parameter to monitor when considering photocatalysis as a pre-treatment for biological treatment.

Gimeno et al. [93] studied the treatment of primary wastewater effluents containing a mixture of nine pharmaceuticals model compounds (APAP, AP, ANT, caffeine CAF, ketorolac KET, MET, SMX, CBZ, hydrochlorothiazide (HCT) and DCF) using aerobic biodegradation coupled with solar TiO\textsubscript{2} photocatalysis. From these compounds only ACM and CAF were completely removed. SFX led to bacterial growth inhibition. Gimeno et al. also found that photocatalysis combined with ozonation (after the biological treatment) led to the highest degradation rates. For such systems, toxicity analyses by Daphnia magna showed no effluent toxicity after treatment.

Encinas et al. [94] studied the removal of a mixture of emerging pollutants (analgesics, antibiotics, anti-inflammatory) using a combination of ozonation and black-light TiO\textsubscript{2}/photocatalysis (supported on activated carbon or non-supported). Single ozonation and photocatalytic ozonation led to complete degradation in less than 5 min. Except for caffeine, a detrimental effect of other organic/inorganic compounds present in secondary effluents was observed [94]. Di et al. [95] combined adsorption and photocatalysis for the removal of IBP, APAP and DCF in the presence of arsenic on Zn-Fe mixed metal oxide photocatalysts. Aziz et al. [96] found that the degradation of DCF and IBP in an aqueous solution by photocatalytic oxidation was only moderate while a combination of ozonation with photocatalysis had a synergetic enhancing effect for the degradation of IBP and its mineralisation. The synergistic effect was said to be due to oxidation of IBP by hydroxyl radicals, generated either by ozone photolysis or by ozone molecules reacting with photo-generated electrons on the surface of the TiO\textsubscript{2} photocatalyst.

Ganiyu et al. [97] reviewed the coupling of photocatalysis with membrane technologies. Photocatalytic membrane reactors (PMRs) combine membrane separation and heterogeneous photocatalysis and can be either slurry type or immobilised type photoreactors. This coupling can be either as (i) two separate consecutive steps with photocatalysis either as pretreatment or post-treatment stage to membrane separation (shown in Figure 5) or (ii) a hybrid/one pot system. Many of the studies on combined membrane filtration and photocatalysis (as a post-treatment stage) have investigated the removal of organics in the concentrate stream to allow disposal to the environment [97]. In such systems, a slurry type TiO\textsubscript{2} photocatalytic system is typically used. Martinez et al. [98] combined photocatalysis and photo-Fenton processes to treat the concentrated stream of pharmaceutical pollutants following membrane separation, achieving removal values between 80 and 100%. For the immobilised photocatalytic membranes strong adherence with the catalyst, high abrasion and chemical resistance and high stability against photocatalysis are important. Suitable materials can be alumina, polymeric, glass fiber and stainless steel [97].
Molinari et al. [99] reviewed PMR applications for the degradation of pharmaceuticals. They concluded that PMRs could represent a useful solution to the problem of pharmaceutical pollutants, with the development of nanofiber-based PMRs such as the use of TiO$_2$ nanotubes being a promising approach. Ramasundaram et al. [100] used TiO$_2$ nanofibers integrated stainless steel filters, with a poly(vinylidene fluoride) nanofiber interlayer as a binder, for the photocatalytic degradation of cimetidine. Molinari et al. [101] tested a hybrid photocatalytic/ultrafiltration PMR system using NTR 7410 membrane (shown in Figure 6) for the removal of furosemide and RNDT with no rejection in the presence of light. Molinari et al. [102] also investigated the degradation of Gemfibrozil and Tamoxifen with both drugs being quickly and completely photodegraded in the PMRs. Ganiyu et al. [97] gave a summary of other relevant studies on the removal of PhACs by PMRs as presented in Table 5.
Table 5. Summary of relevant studies on removal of PhACs by PMRs (adapted with permission [97]. Copyright (2019), Elsevier.

| Pharmaceutical Degraded | Removal Efficiency (%) |
|--------------------------|------------------------|
| Lincomycin               | TOC Removal < 60       |
| Clofibric acid, CBZ and Imeprol | DOC Removal < 91 |
| 32 pharmaceutical pollutants | PhACs removal 50–70 |
| IBP                      | TOC removal > 84       |
| DCF                      | TOC removal 40–70      |
| DCF, IBP, NPX            | PhACs removal 73–100   |

As can be seen from the above discussion, photocatalysis has been combined with different technologies for treating pharmaceutical pollutant containing wastewaters. Photocatalysis can be a pre-treatment step (prior to biological treatment) or an advanced treatment step (by coupling with other AOPs for example). According to Homem and Santos [44], such coupled systems seem to show the most promise for applying photocatalysis for the treatment of pharmaceutical containing effluents, especially when using renewable energy.

3.7. Solar Driven Photocatalysis for Pharmaceutical Removal

One of the limitations for the application of photochemical AOPs at an industrial scale is their high operating costs. To address this, the use of sunlight as a natural source of radiation has been studied extensively for the heterogeneous photocatalytic degradation of a range of organic contaminants including pharmaceutical pollutants. The use of solar energy avoids the costs associated with acquisition, maintenance, replacement and power consumption of UV lamps [103]. Despite this, studies on the photocatalytic degradation of pharmaceutical compounds are typically carried out using TiO\(_2\) as photocatalyst, since this allows for a better comparison with existing literature [48]. However, there is intense research interest in photocatalysts which can be efficiently activated by solar light for the degradation of pharmaceutical contaminants. Perovskites photocatalysts are a current hot topic in this field. For example, the use of bismuth oxyhalide as photocatalysts for pharmaceutical removal was reviewed by Gao et al. [26] while the use of Bi\(_2\)WO\(_6\) was reviewed by Orimolade et al. [28]. Other reviews on novel photocatalytic materials were previously mentioned in the introduction (Section 1.3). A few examples on visible light photocatalysts are mentioned below.

Enhancement of the visible light response of photocatalysts can be achieved by methods such as metal ion doping, coupling with other semiconductor oxides, and nanostructuring of the catalyst [55]. Wang and Xu [65] relied on photosensitisation of dyes and pigments to enhance activity under visible light illumination. The photosensitisation process involves initial excitation of the dye molecules rather than TiO\(_2\) particles. Although visible light sensitive catalysts exist, such as BiVO\(_4\) or WO\(_3\), the efficacy is typically significantly smaller than of TiO\(_2\) upon UV excitation. Mirzaei et al. [104] reviewed the photocatalytic removal of emerging contaminants using nanostructured ZnO catalysts. Nanostructured ZnO has a larger absorption fraction of the solar spectrum and can be excited by about 43% of solar radiation (compared to 10% for TiO\(_2\)). However, at the nanoscale, ZnO particles present toxicity issues. Choina et al. [105] studied the photocatalytic degradation of TC and IBP using ZnO as the photocatalyst. They found that smaller ZnO particles were more active than larger ones due to their greater surface area and subsequent adsorption effects.

Kaur et al. [106] studied solar light driven photocatalytic degradation of ketorolac tromethamine, using TiO\(_2\) quantum dots (QDs), which due to their quantum size, have a larger bandgap compared to bulk TiO\(_2\) and therefore a broader wavelength response to the solar spectrum. Kaur et al. optimised the photocatalytic degradation conditions and achieved 99% photodegradation of the ketorolac tromethamine drug solution (10 mg L\(^{-1}\)) under solar-light irradiation. Zhang et al. [52] studied the photocatalytic degradation of
salicylic acid, IBP, NPX and DCF in water using a novel P25-TiO$_2$/tetraethyl orthosilicate (TEOS) film on glazed ceramic surface under a visible light incubator. They achieved good degradation of salicylic acid, IBP, NPX and DCF under optimum conditions of 76%, 85%, 94% and 65%, respectively, within 10 h of irradiation.

There have been many studies on doped TiO$_2$ photocatalysts with a visible light response, some recent ones are mentioned here. Aba-Guevara et al. [107] reported on visible light-active iron-nitrogen co-doped titanium dioxide (Fe$^{3+}$-TiO$_2$–xN$_y$) nanostructured catalysts prepared by either a sol-gel method or a microwave assisted method. They evaluated these catalysts for the degradation of AMX, streptomycin (STR) and DCF in aqueous solution. The amount of Fe, N and C doping was affected by the synthesis method. Carbon ions were present in the structure due to incomplete decomposition of Ti precursors and polymer surfactant. The sol-gel method led to the incorporation of carbon ions in higher amounts, and this was said to be the reason for the observed higher degradation efficiencies of these samples compared to the microwave prepared samples. Solis-Casados et al., [108] studied Sn-modified TiO$_2$ powders with different amounts of Sn (0, 2.4, 5.1 and 7.2 at. %) and tested these for the degradation of DCF, IBP and Paracetamol, in real wastewaters under visible light. The drugs degraded at different rates depending on the photocatalyst employed. For example, catalysts containing Sn were not the best option to degrade paracetamol whereas ibuprofen degraded more efficiently as the Sn content increased up to 5.1 at.%. Bhatia et al. [49] studied graphene oxide-TiO$_2$ (TiO$_2$-G) for the photodegradation of ATL under UV–vis light and ‘simulated sun’ irradiation conditions. TiO$_2$-G exhibited much higher photocatalytic activity than that of bare TiO$_2$. Under solar irradiation, 72% degradation of ATL (25 ppm) was achieved with 1.5 g/L TiO$_2$-G in 1 h. Complete TOC removal for ATL degradation was obtained in 7 h.

Other than TiO$_2$ and doped TiO$_2$, there exists a broad range of material types used to capture visible light. Sora et al. [78] used visible light activated LaFeO$_3$ for the photocatalytic degradation of CP and IBP. The degradation rate in the presence of both LaFeO$_3$ and H$_2$O$_2$ after 5 h irradiation was more than 90% for CP and 40% for IBP, much higher than that with only H$_2$O$_2$ under visible light. Toxicity tests were however not favourable with more toxic by-products and comparably toxic by-products being detected for IBP and CP, respectively. Sturini et al. [109] reported on the photodegradation of OFLOX using g-C$_3$N$_4$ as photocatalyst activated by simulated solar light. Using this photocatalyst, photodegradation occurred at a rate 10 times faster than direct photolysis, in addition, the photodegradation kinetics of sonicated g-C$_3$N$_4$ were the same order of magnitude obtained using commercially available P25 TiO$_2$. Bo et al. [50] reported on the visible-light-driven ZnIn$_2$S$_4$ photocatalyst for the photocatalytic degradation of CBZ in an aqueous solution. This photocatalyst demonstrated a complete degradation of CBZ in 20 min under a 100 W iodine-gallium lamp irradiation source. The degradation efficiency of CBZ was slightly decreased from 91% to 84% after five consecutive cycles. Gou et al. [82] studied the visible light response of body-centered cubic Ag$_3$PO$_4$ sub-microcrystals for the photocatalytic removal of DCF. The removal efficiency of DCF was significantly affected by the Ag$_3$PO$_4$ content and solution pH. Under the optimised conditions, 99.9% of DCF was degraded within 16 min Xenon illumination.

Recently, the application of rational design and the development of visible light driven nanostructured photocatalytic materials for pharmaceutical removal have also been demonstrated. For example, Selvaraj et al. [110] studied flower-like indium (III) sulfide (In$_2$S$_3$) hierarchical nanostructures for the photocatalytic degradation of Lisinopril. The prepared In$_2$S$_3$ nanoflowers exhibited excellent photocatalytic performance, degrading Lisinopril rapidly, in the visible light range. Wang et al. [111] presented a rational design-prepared novel atomic scale g-C$_3$N$_4$/Bi$_2$WO$_6$ heterojunction photocatalyst. Their photocatalysts were highly efficient under visible light irradiation, and achieved a IBP removal efficiency of 96%. Zhang et al. [112] studied heterostructured AgI/g-C$_3$N$_4$ as visible light driven photocatalysts for the degradation of DCF. The heterostructures exhibited higher photocatalytic activities than the separate AgI or g-C$_3$N$_4$ nanoparticles. DCF was completely degraded
and partly mineralised during the photodegradation. However, for these systems, the formation and accumulation of toxic intermediate by-products, such as chloro-derivatives and carbazole group-containing products were encountered. The toxicity increased during the reaction but decreased after 240 min although to a similar value as at the beginning of the reaction. The photocatalysts showed excellent stability over multiple reaction cycles. Zhu et al. [51] studied the degradation of sulfonamides using reduced graphene oxide-WO$_3$ (RGO-WO$_3$) photocatalysts, activated by visible light. Depending on catalyst preparation, 98% removal of SMX was achieved within 3 h. These catalysts also showed excellent recyclability.

As can be seen from the reviewed literature there have been numerous studies on the development of visible light driven photocatalysis specifically for pharmaceutical contaminant removal. Most studies have shown positive results although for some, issues with toxicity need to be addressed; both the toxicity of the catalysts themselves and the formation of toxic by-products. Studies are lacking in the literature on scale up and costing of photocatalyst preparation methods. The recyclability of these catalysts and their costs (despite gains in reduced irradiation costs) are also important factors requiring further investigation. For example, Asahi et al.’s [113] and Abu Bakar et al.’s reviews [114] on nitrogen-doped titanium dioxide photocatalysts addresses some of these issues and considers practical applications and material design of these photocatalysts. Given that clean water remains a relatively low value product, the costs associated with photocatalytic technologies, whether the cost of photocatalytic materials or the cost of energy sources and utilisation, need to be minimised. Here, low cost photocatalysts other than TiO$_2$ are relevance, for example zinc oxide is both non-toxic and cheap, however its stability is restricted to a narrower pH range when compared to TiO$_2$.

### 3.8. Other Novel Developments in Photocatalytic Systems for Pharmaceutical Pollutant Removal

In this section, a selection of recent studies, which have aimed at improving photocatalytic processes for pharmaceutical removals using novel approaches not covered so far in this review, are discussed. Eskandarian et al. [115] studied the application of UV-LED for the TiO$_2$ photocatalytic decomposition of APAP, DCF, IBP, and SMX. Light emitting diodes (LEDs) have been recognised as a cost-effective, environmentally friendly, and sustainable source of UV to replace conventional mercury lamps. For the conditions tested, UV wavelength was found to be a more important parameter for decomposition than light intensity. Decomposition kinetics of the pharmaceuticals followed SMX > DCF > IBP > APAP, reflecting their molecular structures.

Sarkar et al. [116] addressed the issue of collecting the photocatalyst particles following the photocatalytic treatment process by impregnating TiO$_2$ on alginate beads (TIAB) for the removal of chlorhexidine digluconate (CHD), an antibiotic drug. The degradation efficiency was reduced considerably compared to suspended TiO$_2$ using TIAB. However, in a packed bed photo reactor (PBPR) system utilising TIAB, good pharmaceutical pollutant removal was achieved, and large amounts of wastewater could be treated. TIAB was recycled five times in continuous mode, and the minimal decrease in efficiency from 99% to 85% justified recycling and hence presented an overall improvement on slurry catalyst type systems.

Rimoldi et al. [62] studied a green and low-cost TC degradation process by nanometric and immobilised TiO$_2$ systems with two different substrate geometries laminas and pellets. Both immobilised systems proved effective, in particular, the TiO$_2$-coated pellets. Hu et al. [117,118] synthesised highly entangled TiO$_2$ nanowires (10–20 nm diameters, 100 µm lengths) and studied their photocatalytic degradation kinetics towards PPCPs under UV irradiation with promising results. Liang et al. [119] studied the use of TiO$_2$ anatase phase nanobelts (30–100 nm in width and 10 µm in length) for the oxidation of NPX, CBZ, and theophylline. They found that the TiO$_2$ nanobelts facilitated faster photodegradation of theophylline.
An et al. [120] studied the solar light performance of zeolite-supported carbon-doped TiO$_2$ composite catalysts. The composite catalysts were tested in demineralised, surface, and hospital wastewater. In surface and hospital wastewaters, the zeolite-supported carbon-doped TiO$_2$ systems presented excellent anti-interference capability against radical scavengers and competitive organics for pollutant removal. This was believed to be due to the higher pollutants adsorption on zeolites which enhanced the removal rate of target pollutants via “the adsorb and shuttle” approach.

The above examples of novel research approaches to achieve improvements in photocatalysis, as tested for the removal of pharmaceutical compounds, show that many opportunities exist for the optimisation of parameters affecting the photocatalytic reaction spanning choice of energy efficient light sources, photoreactor configuration to improvements in catalyst adsorption properties through better materials design. Optimisation opportunities and knowledge gaps exist which cannot be addressed by one single research group but require a concerted effort to bring photocatalysis for pharmaceutical removal closer to practical applications.

### 3.9. Patents on Photocatalytic Systems for Pharmaceutical Pollutant Removal

A scan of the patent literature did not reveal a substantial number of patents in this area, pointing to remaining opportunities in the field. The patent literature was found to contain several Chinese patents concerned with applying photocatalytic technologies for the treatment of waters containing pharmaceutical contaminants. For example, the patent by Li et al. [121] was associated with an antibiotic pharmaceutical wastewater advanced treatment process. The invention by Chen et al. [122] discloses a wastewater treatment system specifically targeting PPCPs and a method which amongst other units, includes a membrane distillation device with a graphene-Bi tungstate PVDF (polyvinylidene fluoride) photocatalysis membrane used for degrading the wastewater contaminants by catalytic reaction under visible light excitation. The invention by Lan et al. [123] discloses an integrated treatment decontamination process of difficult-to-degrade industrial effluents, including pharmaceutical effluents. It divulges a process containing a photocatalytic oxidation system, micro-electrolysis systems and a membrane bioreactor. The photocatalytic oxidation system combines a particular light source and catalyst which degrades organic wastewater. The invention by Liu et al. [124] relates to the treatment of sulfur containing pharmaceutical wastewaters and includes a photocatalytic oxidation unit. Liu et al.’s patent for a pharmaceutical wastewater treatment also includes a photocatalytic oxidation unit [125].

### 4. Economic and Social Considerations

There are two approaches which have emerged to address the problem of pharmaceuticals in the environment: (i) identifying opportunities for pollution prevention; and (ii) source reduction based on minimising the types and quantities of drugs dispensed to consumers [126]. Velagaleti and Burns [127] reviewed waste minimisation approaches. As was described in the introduction to this review paper, disposing of unused medications through household refuse and toilet/sink continues to be a common practice. Together with patient excretion these are the primary paths through which pharmaceuticals enter STPs and, from there, the environment. Clearly, the problem of pharmaceuticals in wastewaters cannot be solved merely by adopting only end of pipe measures [20].

Bound et al. [128] reported that it would be beneficial to include pharmaceuticals in a more integrated recycling policy, such as those that include other potentially hazardous items such as household chemicals and batteries. Kotchen et al. [6] investigated disposal practices, willingness to pay for a disposal program, and willingness to participate in an environmentally sustainable disposal program. As part of the study a survey was conducted in Southern California which illustrated that the public was willing to pay $1.53 per prescription, equivalent to $14/year. Kotchen’s study showed that substantial benefits would easily outweigh the costs of establishing pharmaceutical disposal programs with the
pharmaceuticals then being destroyed in a hazardous-waste high-temperature incinerator. From a study in Xiamen, China, Wang et al. [129] found that willingness to pay for measures aimed at preventing pharmaceutical pollution were income dependent. A similar study in Beirut, Lebanon found that willingness to participate in a collection program was a function of age and medical expenditure [130]. The reduction of unwarranted prescriptions is another strategy for minimising the entry of pharmaceuticals into the environment.

The number of studies on the economics of wastewater treatment processes for pharmaceutical removal is lacking. Woche et al. [131] reported a rough estimate of the cost of applying photocatalytic technologies for the treatment of zanamivir containing wastewaters at $US1.5/m$^3$. Their cost estimates relied on taking into consideration the cost of TiO$_2$, energy costs based on using a UVA light source for the time required to decrease the pollutant concentration to below the limits of detection (determined by HPLC–MS/MS). Larger, more accurate cost analysis typically require pilot plant scale studies which consider operational parameters such as power usage, consumables and maintenance costs. Michael et al. [132] carried out a study on a photo-Fenton process and found that economic evaluations are highly dependent on the type of wastewater to be treated. Compared to such systems, photocatalysis does not produce a sludge to be disposed of [131] despite the higher energy demands. The level of pollutant removal from wastewater exponentially increases the associated costs [4]. Jones et al. [133] discussed that retrofitting current STPs to achieve the required removal of pharmaceutical pollutants would mean utilising expensive technologies used to achieve drinking water standards. Stricter regulations are needed to initiate the initial investment in expensive technologies while tariffs on end uses are needed to cover the cost of improved water qualities.

What needs to be highlighted are the costs of not otherwise removing such pollutants on public health and the environment. Switzerland is one of the first countries to start implementing a national policy to reduce micropollutants in the effluents of municipal sewage treatment plants [89]. Given the public demand for the reduction of the environmental and health risks of micropollutants the average willingness to pay per household was CHF 100/year. Based on current knowledge and developments of processes that can be practically applied to remove pharmaceuticals from wastewaters, ozonation and activated carbon processes were identified by the Swiss initiative as being the most cost-effective technologies for this purpose. These can be retrofitted to existing STPs to achieve complete removal of pharmaceutical pollutants [3].

To compete effectively, photocatalytic based technologies need to achieve at least the same removal efficiencies of currently accepted technologies without an increase in costs. An approach to lowering the operating costs of UV driven photocatalysis is to use alternative cheaper energy sources. In Australia, most sewage treatment plants are now self-sufficient when it comes to their energy needs as they can generate electricity on site from methane obtained from biosolids digestion. This strategy paves the way for the application of UV light activated cheap, non-toxic photocatalysts such as TiO$_2$ without the burden of high energy costs. It is also worthwhile noting that many tertiary water treatment plants which rely on UV disinfection have these energy costs factored into their existing operating costs and are therefore more likely to accept UV activated TiO$_2$ photocatalytic technologies as a competing technology for pharmaceutical pollutant removal.

5. Conclusions

Heterogeneous photocatalysis is effective for degrading most pharmaceutical compounds, however, gaps in knowledge remain. While photocatalysis provides a clean approach, other advanced oxidation processes have been proven to be just as effective, in particular ozonation. Ozonation and adsorption using activated carbon are in fact accepted technologies for the remediation of waters containing pharmaceutical compounds. Membrane technologies are strong contenders with running costs being an issue.
From the review of the literature on the photocatalytic removal of pharmaceuticals, it is evident that few studies have focused on the identification of the by-products formed during the photocatalytic reaction (to address toxicity issues which exist) and propose possible mechanistic degradation pathways useful for process modelling and scale up. Most studies have focused on pure water rather than real wastewater matrices, degrading a single pharmaceutical compound rather than a mixture of compounds. Most laboratory studies have been carried out using a higher initial pharmaceutical pollutant concentration than those that would be encountered in real wastewaters due to challenges in analytical detection methods at the ng/L levels. This points to the need for improved analytical methodologies for detecting organic pollutants at ng/L levels and the need for more studies using lower initial pollutant concentrations. Additionally, most of the work is still on a laboratory scale using artificial light sources rather than on a pilot scale with sunlight. Given that removal and degradation rates of pharmaceuticals are dependent on several operational parameters such as catalyst type and loading, pH and water constituents and incident radiation flux, optimisation work is required with pilot plant studies to achieve optimal scalable pollutant removal and mineralisation (or at minimum degradation to less harmful, less toxic or less bioactive compounds). Pilot scale studies will also allow for a better understanding of the economics of the process.

\( \text{TiO}_2 \) remains by far the most studied photocatalyst as it is inert, non-toxic and not expensive, and hence the most relevant photocatalytic material when it comes to scaling up for commercial water treatment applications. Solar driven processes require photocatalytic materials that have a better and broader response to the solar spectrum than TiO\(_2\). Studies on the development of visible light driven photocatalysts require a better assessment of their recyclability, toxicity and preparation costs. Inertness and non-toxicity are crucial for safe water treatment applications. Many studies on novel photocatalytic materials do not adequately address these two key points. Given that clean water remains a relatively low value product, the development of a low-cost treatment process is important, therefore cheap photocatalysts and cheap energy are both important. For example, for STPs, operating costs associated with photocatalytic technologies reliant on UV irradiation may be minimised through on-site energy generation. It is also worthwhile noting many tertiary water treatment plants which rely on UV disinfection have these energy costs factored into their existing operating costs and are therefore more likely to accept UV based TiO\(_2\) photocatalytic technologies. Based on current knowledge and understanding of the photocatalytic removal of pharmaceutical pollutants from wastewaters, photocatalytic technologies lend themselves to be coupled with other treatment processes such as biological processes as pre- or post-treatment processes to achieve better overall removal and mineralisation rates.

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**Abbreviations**

| Acronym | Definition |
|---------|------------|
| 4-IBAP  | 4-isobutylacetophenone |
| AMX     | Amoxicillin |
| AOPs    | Advanced oxidation processes |
| AP      | Antipyrine |
| APAP    | Acetaminophen |
ATL Atenolol
BZF Bezafibrate
CB Conduction band
CBZ Carbamazepine
CFA Clofibrate acid
CHD Chlorhexidine digluconate
CHF Swiss Francs
CP Ciprofloxacin
CPCs Compound parabolic collectors
DCF Diclofenac
DOC Dissolved organic carbon
EDCs Endocrine disrupting chemicals
HCT Hydrochlorothiazide
HPLC-MS/MS High performance liquid chromatography-Mass spectrometry/Mass spectrometry
IBP Ibuprofen
LCMS-IT-TOF Liquid chromatography mass spectrometry-ion trap-time of flight
LEDs Light emitting diodes
LZP Lorazepam
MBRs Membrane bioreactors
MET Metoprolol
MOX Moxifloxacin
MS2 Mass spectrometry (tandem)
NOM Natural organic matter
NPX Naproxen
NSAIDs Non-steroidal anti-inflammatory drugs
OFLOX Antibiotic ofloxacin
OTC Oxytetracycline
OXA Oxolinic acid
PBPR Packed bed photoreactor
PhAcs Pharmaceutically active compounds
PMRs Photocatalytic membrane reactors
PPCPs Pharmaceutical and personal care products
PRO Propranolol
PVDF Polyvinylidene fluoride
QDs Quantum dots
QqToF Quadrupole-time of flight
RGO Reduced graphene oxide
RO Reverse osmosis
RSM Response surface methodology
SB Solar box
SMX Sulfamethoxazole
STPs Sewage treatment plants
STR Streptomycin
TC Tetracycline
TEOS Tetraethyl orthosilicate
TMP Trimethoprim
TOC Total organic carbon
TYL Tylosin
UPLC Ultra-performance liquid chromatograph
UV Ultraviolet
VB Valence band

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