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Review

An overview of homogeneous and heterogeneous photocatalysis applications for the removal of pharmaceutical compounds from real or synthetic hospital wastewaters under lab or pilot scale

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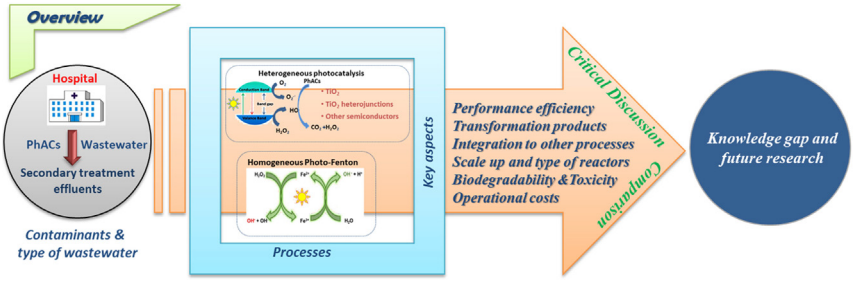
HIGHLIGHTS

- Photocatalytic applications for the treatment of hospital wastewaters are reviewed.
- Focus is placed on the removal of pharmaceutical compounds and their metabolites.
- Processes, catalytic systems, and operational parameters effects are presented.
- Overall efficiency and operational costs of the processes are assessed.
- Potential integration with other processes and perspectives for future work are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The last few decades, Pharmaceutical Active Compounds (PhACs) have been considered as emerging contaminants due to their continuous release and persistence to aquatic environment even at low concentrations. A growing number of research articles have shown the occurrence of numerous PhACs in various wastewater treatment plant influents, hospital effluents, and surface waters all over the world. The rising concern regarding PhACs, which present high recalcitrance towards conventional treatment methods, has provoked extensive research in the field of their effective remediation. This review provides a comprehensive assessment of homogeneous and heterogeneous photocatalytic applications for the removal of PhACs, from real or artificial hospital wastewater effluents. These two representative advanced oxidation processes (AOPs) are assessed in terms of their efficiency to remove PhACs, reduce the COD and toxicity as well as increase the biodegradability of the effluent. Simultaneously with their efficiency the operational costs of the processes are considered. Their potential combination with other processes is critically discussed, as this option seems to enhance the treatment efficiency and simultaneously overcome the limitations of each individual process. Moreover, the type of reactors as well as the main parameters that should be considered for the design and the development of photoreactors for wastewater treatment are reviewed. Finally, based on the literature survey, indications for future work are provided.

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Contents

1. Introduction

The past two decades have witnessed extensive scientific and public attention towards the presence of Pharmaceutical Active Compounds (PhACs) in the environment, as one of the most important groups of aquatic emerging contaminants (ECs) (Zhou et al., 2019). Global population growth and urbanization leads to the rise of resource consumption and chemical use, including pharmaceuticals (Mole and Brooks, 2019). PhACs are continuously entering the environment and show negative impact due to their persistence and adverse effects into the aquatic organisms (Carraro et al., 2016; Kosma et al., 2019).

Multiple studies have shown that the main sources emitting PhACs into the environment are urban and hospital wastewaters (HWW) (Frédéric and Yves, 2014; Kosma et al., 2019; Kosma et al., 2015; Kosma et al., 2014). HWW have complex composition with high concentrations of PhACs, deriving from innumerable activities (such as anesthesia, cancer treatment, diagnosis, analgesia etc.), disinfectants, heavy metals, reagents etc. (Konstas et al., 2019; Wielens Becker et al., 2020). The main PhACs that can be found in HWW are antibiotics, analgesics and anti-inflammatories, psychiatrics, β-blockers, anaesthetics, disinfectants and X-ray contrast media. These compounds are excreted mainly in urine (55–80%), less in faeces (4–30%), as unmetabolized substances, metabolites or conjugated with inactivating bio-substances (Carraro et al., 2016). In addition, biodegradation, photolysis by sunlight and other abiotic transformations such as hydrolysis regulate the persistence of PhACs in wastewaters. Thus, through these processes, metabolites and/or transformation products (TPs) could be formed that might be more toxic than the parent compound (Gómez-Oliván, 2017). It was reported that the average concentration of various PhACs in hospital effluents can be 2–150 times higher than those found in urban wastewaters. Furthermore, hospitals represent important sources of pathogens to urban wastewaters (Perini et al., 2018). In some countries hospital wastewaters are considered as domestic-type wastewaters and thus are discharged directly into the municipal sewage network, without any pretreatment (Carraro et al., 2016), while only in few countries hospital effluents are considered as industrial wastewaters and undergo pre-treatment before their discharge into the urban sewage system (Konstas et al., 2019).

The removal efficiency of common pollutants present in hospital effluents depends on various parameters such as biodegradability and physicochemical properties, wastewater treatment plant (WWTP) characteristics, operational conditions, environmental characteristics etc. (Verlicchi, 2018). However, conventional wastewater treatment plants (WWTPs) have been designed to remove easily or moderately biodegradable carbon, nitrogen and phosphorous compounds, and microorganisms but not the bioactive organic micropollutants such as pharmaceuticals at trace levels. Consequently, the applied treatments have been found to be ineffective to remove them (Konstas et al., 2019). When these uncompleted treated effluents are released into the aquatic environment and additionally are applied by end users for soil irrigation, the receiving water may impose risks to aquatic systems, humans, soil, crops and biota (Kanakaraju et al., 2018). Chronic exposure to trace levels of PhACs mixtures can induce antibiotic resistance, sexual disturbance, and endocrine disruption effects (Palma et al., 2020). The study of potential toxicity for different PhACs, as well as of their metabolites and TPs, in different trophic levels has gained more and more attention and reveals further adverse effects (Wielens Becker et al., 2020). A recent study reported teratogenic effects and alternations to embryonic development of oocytes *Cyprinus carpio* after exposure to hospital effluents, where the presence of antibiotics, antidiabetics, non-steroidal anti-inflammatory drugs, hormones and beta-blockers, was determined (Luja-Mondragón et al., 2019).

The failure of conventional WWTPs to remove PhACs, demonstrates the urgent need to develop suitable innovative technologies for the treatment of hospital effluents in order to effectively deal with these compounds and minimize undesirable effects in the environment (Kanakaraju et al., 2014; Perini et al., 2018). Therefore, advanced oxidation processes (AOPs) have been suggested as tertiary treatment in effluent wastewaters due to their versatility and ability to remove pollutants that are known to be non-biodegradable or have low biodegradability, persistence and possess high chemical stability (Kanakaraju et al., 2014; Konstas et al., 2019). AOPs are considered as environmental-friendly methods and are based on physicochemical processes that induce decomposition, simplification of chemical structure of the organic molecules and finally mineralization. These processes involve the generation of reactive transient species such as the hydroxyl ($HO^{\bullet}$), superoxide ($O_2^{\bullet-}$), hydroperoxyl ($HO_2^{\bullet}$) alkoxyl ($RO^{\bullet}$), sulfate ($SO_4^{\bullet-}$) and chlorine ($Cl^{\bullet}$) radicals (depending on the catalyst or the oxidant used), with the $HO^{\bullet}$ having attracted the most attention (Antonopoulou and Konstantinou, 2017; Gómez-Oliván, 2017; Kanakaraju et al., 2014). Hydroxy radicals ($HO^{\bullet}$) are usually generated from reactions involving oxidants such as hydrogen peroxide, ozone or catalysts including metal ions and semiconductors under UV–vis irradiation or other sources of energy (Perini et al., 2018). These species present high oxidation potential with a non-selective nature and high reaction rate, achieving the complete mineralization of the pollutants to CO_2, water, and mineral acids or under selected conditions, transforming them in more biodegradable molecules. Different AOP methods include heterogeneous and homogenous photocatalysis, depending on the catalysts phase. Photocatalysis can utilize solar energy to oxidize or reduce contaminants by stimulating electron excitation-transfer in a semiconductor photocatalyst. The most important factor

in this process is the photocatalyst that converts solar energy into chemical energy, and thus destroys the pollutants (Long et al., 2020).

2. Photocatalysts application in wastewater treatment

There is a wide variety of photocatalysts developed and studied during the last decade, but the most used catalyst is still TiO_2, and the so-called Degussa P25 (a mixture of anatase/rutile (≈70/30) crystal phases) as one of the most efficient commercially available photocatalytic materials. Several other modifications and proportions of the anatase/rutile phases have been studied presenting also good results (Gómez-Oliván, 2017; Long et al., 2020). TiO_2 has very strong oxidation power, i.e., 3.2 eV for anatase TiO_2 and 3.0 eV for rutile TiO_2, fullfiling the oxidation potential of water (≈1.2 eV) (Lee and Park, 2013). In addition, TiO_2 is an industrially mass-produced material that is easy to obtain, inexpensive, and can be synthesized easily in a laboratory, either as a white TiO_2 powder, or as a colloidal dispersion in a liquid phase, or as a thin film deposited on a suitable support substrate. Furthermore, it is very stable, both chemically and photochemically safe. TiO_2 has also a strong resistance against acids and alkalis (Horikoshi and Serpone, 2020; Lee and Park, 2013).

Irradiation of TiO_2 with a photon of energy equal to or greater than its band gap width, leads to the formation of electron/hole (e^-/h^+) pairs. In the empty conduction band (e^-_{CB}), free electrons are produced, leaving behind electron vacancies i.e. holes in the valence band (h^+_{VB}). On the other hand, in aqueous suspensions holes (h^+_{VB}) can react with surface HO^- groups and produce $HO^\bullet$ radicals. Reaction of $HO^\bullet$ radicals with wastewater pollutants concludes to the degradation of the compounds (Antonopoulou et al., 2013; Konstantinou and Albanis, 2004; Martins et al., 2009). In addition, TiO_2 as a photocatalyst for water and wastewater treatment displays fast response to irradiation and a non-negligible photonic efficiency, even under weak light conditions (Horikoshi and Serpone, 2020). The overall process can be described by the following reactions (Konstantinou and Albanis, 2004; Antonopoulou and Konstantinou, 2017; Wang and Zhuan, 2020):

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-_{CB} + h^+_{VB}) \quad (1)$$

$$TiO_2(h^+_{VB}) + H_2O \rightarrow TiO_2 + H^+ + HO^\bullet \quad (2)$$

$$TiO_2(h^+_{VB}) + OH^- \rightarrow TiO_2 + HO^\bullet \quad (3)$$

$$TiO_2\ (e^-_{CB}) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (4)$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \quad (5)$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \quad (6)$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow HO^\bullet + OH^- + O_2 \quad (7)$$

The degradation efficiency of a photocatalytic reaction depends on various factors, such as initial concentration of pollutant, type and intensity of irradiation, type and mass of catalyst, pH, temperature, radiant flux and concentration of oxygen (Malato et al., 2009; Gopinath et al., 2020). Furthermore, concerning TiO_2 heterogeneous photocatalysis at full-scale, there are some factors that can limit this application, such as the separation of the colloidal catalyst from the water suspension after the treatment, mass transfer limitations for immobilized catalytic systems and the low quantum yield for $HO^\bullet$ radical production (Miklos et al., 2018). Some recent review articles can be consulted for details on the TiO_2 photocatalysis basics (Malato et al., 2016; Bora and Mewada, 2017; Long et al., 2020).

Another way to generate $HO^\bullet$ radicals is by Fenton process. The Fenton process is an AOP in which $HO^\bullet$ are generated from a mixture of H_2O_2 and Fe^{2+} in an acid medium (Eq. (8)) (Perini et al., 2018). In the beginning of the reaction, fast degradation of contaminants occurs. This is attributed to the rapid production of $HO^\bullet$ radicals, due to the presence of Fe^{2+} species in the solution. At the second stage, due to the consumption of Fe^{2+} ions and generation of Fe^{3+}, the rate of reaction decreases, since the reaction of Fe^{3+} and H_2O_2 leads to the production of $HO_2^\bullet$ radicals ($E^\circ = 1.65$ V) which are weaker oxidants than $HO^\bullet$ radicals ($E^\circ = 2.80$ V) and have a lower rate of production (Eq. (9)) (Mirzaei et al., 2017).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \quad (8)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \quad (9)$$

When this process is enhanced by UV–vis radiation it is called photo-Fenton process, accelerating the photoreduction of Fe^{3+} to Fe^{2+} and establishing an Fe(II)/Fe(III) cycle on the Fenton reaction, generating also extra $HO^\bullet$ radicals (Eqs. 10–11) (Koltsakidou et al., 2019; Perini et al., 2018).

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+ \quad (10)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \quad (11)$$

The homogeneous photo-Fenton process is one of the most ubiquitous photo-assisted AOPs, for the removal of organic pollutants from wastewater (Koltsakidou et al., 2019; Mirzaei et al., 2017). In addition, this process seems to be the most appropriate sunlight driven AOP, since soluble iron-hydroxy and mainly iron-organic acid complexes absorb not only ultraviolet irradiation but a significant part of visible light spectrum (Malato et al., 2009). To avoid iron precipitation this process is conducted at pH around the value of 3. Nevertheless, the near-neutral pH conditions that needed in wastewater treatment consist a major challenge in application of homogeneous photo-Fenton process due to the increment of operating costs associated with acidification/basification. Furthermore, the iron sludge which is formed after the reaction should be removed (Mirzaei et al., 2017; Perini et al., 2018). Finally, another drawback concerning homogeneous Fenton process is the high concentrations of Fe^{n+} ions needed (50–80 mg L^{-1}) and consequently relatively high concentrations of them reaching the environment despite the removal though sludge precipitation. However, in photo-Fenton process, the appropriate amount of ferrous catalyst and the iron sludge produced are considerably lower than those in Fenton process (Mirzaei et al., 2017).

In addition, ions usually present in wastewaters can affect significantly photo-Fenton process. While the influence of the phosphate is known through the co-precipitation with ferric iron, other ions such as halogens and sulphate form complexes with the catalyst influencing its activity and/or promoting the formation of radicals less reactive than the hydroxyl radicals, depending on the concentrations of these ions and the solution's pH value. The knowledge of their influence on the process is crucial since wastewaters might contain various ions, with concentrations ranging from close to zero to dozens of grams of dissolved salts (Malato et al., 2009).

On the other hand, heterogeneous photo-Fenton catalysts seem to overcome the above described limitations. In heterogeneous photo-Fenton, iron-based solid catalysts are used (e.g. Fe_2O_3) allowing the easy removal of the catalysts from the treated wastewaters. Nevertheless, the use of catalyst suspensions presents limitations due to particle aggregation, formation of slurries and the costs of catalyst separation. Therefore, to overcome these limitations, magnetically recoverable catalysts as well as catalyst immobilization in the form of films, or coatings on fixed supports, have been used (Lima et al., 2017).

Another approach to avoid acidification of the wastewater and maintain iron stability, is to perform the photo-Fenton reaction in the presence of complexing agents. These complexes might be also photoactive in the visible region, thus a beneficial effect on the reaction

rate may occur. Therefore, several authors propose the addition of oxalic acid or the direct application of ferric oxalate as iron source (Malato et al., 2009). Detailed reports for photo-Fenton photocatalysis basics can be found elsewhere (Clarizia et al., 2017; Liu et al., 2018; Vorontsov, 2019).

After decades of research, semiconductor photocatalytic technology has made significant achievements. To circumvent some drawbacks concerning application of TiO_2 (e.g. low visible light utilization, quantum efficiency and weak photoreduction ability) and photo-Fenton (e.g. high concentrations of Fe^{n+} ions, iron sludge produce) the development and application of new semiconductors has received increasing attention (Long et al., 2020). Various new photocatalysts have been used in order to remove pollutants in water, such as various oxides and perovkites (e.g. ZnO, WO_3, V_2O_5, $BiVO_4$, Ag_3VO_4, $SrTiO_3$), sulfides (e.g. CdS, ZnS, MoS_2), and bismuth oxyhalides (e.g., BiOCl, BiOBr, BiOI), conducting polymers such as graphitic carbon nitride and various composite materials representing different heterojunctions among the single photocatalysts (Konstas et al., 2019; Long et al., 2020). Nevertheless, concerning wastewater treatment, except for TiO_2 and photo-Fenton, rather few photocatalysts were tested in the last ten years, such as TiO_2 modified with hydrotalcite and iron oxide, polypyrrole, Nb_2O_5, Fe_2O_3 and graphitic carbon nitride (Rueda-Marquez et al., 2020a). Furthermore, as for hospital wastewaters concern, very few researches have been published referring to the application of new catalysts (Dou et al., 2020; Gao et al., 2020; Gharaghani and Malakootian, 2017; Ghenaatgar et al., 2019; Konstas et al., 2019; Minh Tri et al., 2019; Sponza and Alicanoglu, 2018; Sponza and Güney, 2017).

Being aware of the above, in recent years, review articles concerning the types of photocatalysts and the removal of contaminants from wastewaters are increasing. Although in many cases, quality of urban wastewaters may be alike hospital wastewaters since similar characteristics such as BOD_5, COD or TSS might occur (Verlicchi, 2018), a considerable number of researches have focused mainly on the detoxification and purification of industrial or urban wastewaters, specific series of catalysts and certain types of pollutants. For instance, in previous years, review articles such as Kanakaraju et al. (2014, 2018) have highlighted the application of AOPs for the removal of PhACs mainly in distilled and urban wastewater. In addition, Mirzaei et al. (2017) and Jain et al. (2018) reviewed the removal of PhACs from water by homo/heterogeneous Fenton and Fenton type processes by focusing on distilled water, municipal and industrial wastewater. Furthermore, in a more recent study, Phoon et al. (2020) presented a review on application of conventional and emerging technologies for the removal of antibiotics from wastewaters, focusing mainly on spiked solutions and pharmaceutical wastewater. Moreover, most of the reported studies do not represent the real scenario of wastewaters as they use higher pollutants' concentrations than those found in real cases (Bansal et al., 2018; Rueda-Marquez et al., 2020a). To the authors' knowledge, until nowadays an extensive study concerning a review on the photocatalytic treatment and purification of hospital wastewaters is lacking. Therefore, this study provides an overview on the photocatalytic treatment used throughout the past decade to remove PhACs from artificial or real hospital wastewater effluents. The aim of this work is to systemize and analyze research results based on the use of TiO_2 and photo-Fenton as well as new catalysts applied. Based on the overview, the perspectives for future work are proposed.

3. AOPs in hospital wastewaters for the removal of PhACs

3.1. Photo-Fenton process

Various studies have been conducted to examine the degradation efficiency of PhACs from aqueous solutions by homogeneous photo-Fenton, but most of them deal with distilled and urban wastewater (Mirzaei et al., 2017). Few researches until now have been conducted on the removal of PhACs from artificial or real hospital wastewater. Table 1 provides an overview of the PhACs' degradation by homogeneous photo-Fenton process and summarizes the removal efficiency of these contaminants, in synthetic and real hospital wastewaters.

Studies that were conducted in real hospital wastewaters included in many cases antibiotic pharmaceuticals. For instance, Martins et al. (2009) studied the degradation efficiency of the antibiotic amoxicillin (AMX), a β-lactam compound that can be classified as broad spectrum penicillin, in hospital effluents from the University hospital of Santa Maria in Brazil, by means of heterogeneous photocatalytic process and photo-Fenton process. The samples were collected from outlet pipes of the domestic-like treatment system of the hospital, which includes a simple cesspit and an anaerobic filter. The photocatalytic treatment was conducted on a bench scale using a batch recirculation 2 L Dewar-like photoreactor provided with a light intensity of 401 W m^{-2}, which was irradiated by a 125 W medium pressure mercury vapor lamp. Concerning the photo-Fenton process the operational conditions were pH = 4, $[H_2O_2]$ = 528 mg L^{-1}, $[Fe^{2+}]$ = 255 mg L^{-1} and the temperature was 30 °C. Selection of pH = 4 was based on the fact that photo-Fenton process runs better in acidic conditions, taking into account also the fact that AMX starts to decompose below pH 4 (Martins et al., 2009). It is worth noticing that a previous hydrolysis study of AMX in distilled water, conducted by Trovó et al. (2011) in pH = 2.5 (initial concentration of 10 mg L^{-1}), revealed 64% hydrolysis after 1.5 h, reaching 74% after 5.5 h, while in pH = 6.2 no hydrolysis was observed (Trovó et al., 2011). So, under the above-mentioned conditions 85% degradation of AMX was achieved after 60 min, by photo-Fenton process. In this case, the lower degradation of AMX can be attributed to the pH conditions (pH 4), which was less suitable because precipitated Fe species started to appear and this reduced the production of hydroxyl radicals (Martins et al., 2009). Furthermore, in the present study toxicity inhibition was examined during the photo-Fenton treatment of only hospital wastewaters by the bioassay *Artemia Salina*, in pH = 3 (pH 3, 528 mg L^{-1} H_2O_2 and 255 mg L^{-1} Fe^{2+}, 30 °C, 60 min) since preliminary studies revealed higher COD degradation in this pH value. The toxicity inhibition of the hospital effluent was 43.5%, which leads to the conclusion that the treatment presents moderate efficiency in removing toxicity. Based on the above, an interesting aspect for further study of this work would be the toxicity evaluation of AMX during the photo-Fenton treatment in the respective conditions (pH 4, 528 mg L^{-1} H_2O_2 and 255 mg L^{-1} Fe^{2+}, 30 °C, 60 min). In addition, in these conditions COD and TOC removal as well as the study of degradation pathway of AMX would constitute a more completed overview of the above study. Last but not least, studies concerning antibiotic compounds should include monitoring of the residual antibacterial activity, especially when dealing with hospital wastewaters.

In recent years, much progress has been made to operate photo-Fenton process at neutral pH or near-neutral pH concerning real wastewater samples (Kanakaraju et al., 2018). A recent literature survey indicated an increased activity in the field of photo-Fenton processes at near neutral pH, with more than 30 papers published in the last 15 years (Clarizia et al., 2017). In wastewaters from a pharmaceutical industry, the removal of the β-lactam antibiotic oxacillin was performed at pH ~ 6 (Giraldo-Aguirre et al., 2018), while in wastewaters from a municipal WWTP the removal of 22 micropollutants, including 15 pharmaceuticals, at pilot scale was performed at pH 6–7 (De la Cruz et al., 2013). Concerning hospital wastewaters Perini et al. (2018), studied the simultaneous degradation of four antibiotics (ciprofloxacin (CIP), amoxicillin (AMX), sulfathiazole (STZ) and sulfamethazine (SMZ)) in anaerobic hospital effluent (AHE) by applying low concentration of iron and hydrogen peroxide at the natural pH of the effluent (pH ≈ 7.4) and by the addition of citric acid. Citrate acts as a polydentate ligand that complexes iron, keeping it soluble, therefore there is no need to acidify/neutralize the wastewater. In addition, organic Fe^{3+} complexes, present higher molar absorption coefficients in the region of UV–vis, and higher quantum yields for generation of Fe^{2+} compared to iron aqua complexes. In this case, the use of UVC/H_2O_2/FeCit system resulted in total

Table 1
Photo-Fenton process for the removal of PhACs in real and synthetic hospital wastewaters.

Target compound/initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
[Amoxicillin] $_0 = 0.1$ mg L^{-1}	Photo-Fenton	Real hospital effluent (University Hospital of Santa Maria (HUSM), Brazil)	Homemade bench scale photoreactor (Dewar-like)/125 W Philips medium pressure mercury lamp	pH = 4; $[Fe^{2+}]_0 = 255$ mg L^{-1}; $[H_2O_2]_0 = 528$ mg L^{-1}; Temperature = 30 °C; Reaction time = 60 min	(ii) After 60 min 85% degradation was achieved	Martins et al. (2009)
[Ciprofloxacin] $_0 = 200$ μg L^{-1} [Amoxicillin] $_0 = 200$ μg L^{-1} [Sulfathiazole] $_0 = 200$ μg L^{-1} [Sulfamethazine] $_0 = 200$ μg L^{-1}	$Fe(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt)/Citric acid (Synth)	a.Real hospital effluents from the anaerobic treatment (AHE); b. Raw hospital wastewater (RHW) (University of Campinas hospital, Brazil)	Photoreactor: (i) Germicidal lamp (UVC) 15 W ($\lambda_{max} = 254$ nm) (ii) Direct exposure to sunlight (iii) Black light lamp (UVA) 15 W (λmax = 365 nm)	Natural pH (pH = 7.4); pH = 4.7; pH = 2.5/$[H_2O_2]_0 = 500$ μmol L^{-1}; [FeCit] $_0 = 10$ μmol L^{-1}; Max reaction time = 90 min	a. AHE: (i) UVC: At pH = 7.4 total degradation of the antibiotics after 90 min; At pH = 2.5 total degradation of the antibiotics after 30 min; At pH = 4.7 85% degradation of the antibiotics after 30 min. (ii) Under solar irradiation, 66% degradation of the antibiotics after 90 min. (ii) UVA-Under black light 47% global degradation after 90 min. b. RHW: (i) UVC: At pH = 7.4 global degradation after 30 min was 74%.	Perini et al. (2018)
[Flutamide] $_0 = 500$ μg L^{-1}	$FeSO_4.7H_2O$ (Neon, São Paulo, Brazil)	Raw hospital (Brazil)	Cylindrical batch reactor/Solar irradiation	(i) pH = 5; Single addition: $[Fe^{2+}]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}; Reaction time = 120 min (ii) pH = 5;Three successive Fe^{2+} additions: $[Fe^{2+}] = 5$ mg L^{-1} in $t_{w30} = 0$ min; $[Fe^{2+}] = 5$ mg L^{-1} in $t_{w30} = 11.5$ min; $[Fe^{2+}] = 5$ mg L^{-1} in $t_{w30} = 23.2$ min; $[H_2O_2]_0 = 150$ mg L^{-1}; Reaction time = 120 min	(i) After 120 min 20% degradation was achieved (ii) After 120 min 58% degradation was achieved	Della-Flora et al. (2020)
[Sulfacetamide] $_0 = 40$ μmol L^{-1}		Simulated hospital wastewater	Home-made aluminum reflective reactor/5 UV lamps (LuxTech T8 15W)	pH = 6.5; $[Fe^{2+}]_0 = 45$ μmol L^{-1}; $[H_2O_2]_0 = 500$ μmol L^{-1}; Reaction time = 60 min	After 60 min almost 20% degradation was achieved	Hincapié-Mejía et al. (2020)
[Acetaminophen] $_0 = 10^{-5}$ mol L^{-1} [Antipyrine] $_0 = 10^{-5}$ mol L^{-1} [Caffeine] $_0 = 10^{-5}$ mol L^{-1} [Metoprolol] $_0 = 10^{-5}$ mol L^{-1} [Testosterone] $_0 = 10^{-5}$ mol L^{-1}	Iron (III) perchlorate hydrate (Sigma–Aldrich) ($Fe(ClO_4)_3 \cdot xH_2O$)	Addition of inorganic compounds into aqueous solution at concentrations found in WW	Compound parabolic collector (CPC)/Sunlight	pH = 3; $[Fe^{3+}]_0 = 2.79$ mg L^{-1}; $[H_2O_2]/[Fe^{3+}] = 6.09$; Max reaction time = 20 min	Acetaminophen, antipyrine, metoprolol and testosterone were fully degraded after almost 10 min; Caffeine was fully degraded after almost 20 min	Quiñones et al. (2015a)
[Acetaminophen] $_0 \approx 10$ μg L^{-1} [Diclofenac] $_0 \approx 0.04$ μg L^{-1} [Carbamazepine] $_0 \approx 1.9$ μg L^{-1} [Venlafaxine] $_0 \approx 0.0015$ μg L^{-1} [Loratadine] $_0 \approx 8.1$ μg L^{-1} [Ciprofloxacin] $_0 \approx 15$ μg L^{-1} [Norfloxacin] $_0 \approx 5$ μg L^{-1} [Valsartan] $_0 \approx 2.5$ μg L^{-1} [Irbesartan] $_0 \approx 0.05$ μg L^{-1} [Sulfamethoxazole] $_0 \approx 0.001$ μgL^{-1}	Iron sulfate heptahydrate (Panreac)	Real hospital effluent (Tumaco, Colombia)	Meinhardt ultrasound reactor/OSRAM® UVC-lamp (G4T5/OF RG3) of 4 W	pH = 7.9; $[Fe^{2+}]_0 = 5$ mg L^{-1}; Reaction time = 90 min	After 90 min degradation of PhACs were: Acetaminophen: 46.30%; Diclofenac: 100%; Carbamazepine: 100%; Venlafaxine: 100%; Loratadine: 99.34%; Sulfamethoxazole: 100%; Trimethoprim: 100%; Norfloxacin: 88.96%; Ciprofloxacin: 69.91%; Irbesartan: 100%; Valsartan: 80.8%; Erythromycin: 33.77%; Azithromycin: 87.36%; Clarithromycin: 82.17%; Clindamycin: 98.74%.	Serna-Galvis et al. (2019)

(continued on next page)

Table 1 (*continued*)

Target compound/initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
[Trimethoprim]$_0 \approx 0.03$ μg L^{-1} [Clarithromycin]$_0 \approx 25$ μg L^{-1} [Azithromycin]$_0 \approx 27.9$ μg L^{-1} [Erythromycin]$_0 \approx 0.36$ μg L^{-1} [Clindamycin]$_0 \approx 25$ μg L^{-1} [Nimesulide]$_0 < 500$ μg L^{-1} [Furosemide]$_0 < 500$ μg L^{-1} [Paracetamol]$_0 < 500$ μg L^{-1} [Propranolol]$_0 < 500$ μg L^{-1} [Dipyrone]$_0 < 500$ μg L^{-1} [Fluoxetine]$_0 < 500$ μg L^{-1} [Progesterone]$_0 < 500$ μg L^{-1} [Diazepam]$_0 < 500$ μg L^{-1}	Alginate spheres containing Fe(II) and Fe(III) ions/hydrogen peroxide (H_2O_2, 35% *w/v*; Synth)	(i) Simulated hospital wastewater (SW) (ii) Raw hospital wastewater (RHW) (Brazil)	Solar batch photoreactor	pH 5.0; [Fe(III)-alginate spheres]$_0 = 3$ g; [H_2O_2] $= 25$ mg L^{-1} with additions at 0, 61, 88, and 117 min; Reaction time = 177 min	After 177 min concentrations were for (i) SW: DIP: <LOD; PCT: <LOD; PPN: 17.75 μg L-1; FRS: <LOD; NMD: <LOD; FXT: 47.75 μg L-1; DZP: <LOD and PRG: 10.71 μg L-1 (ii) RWE: DIP: <LOD; PCT: <LOD; PPN: 5.765 μg L-1; FRS: <LOD; NMD: 189.26 μg L-1; FXT: 276.01 μg L-1; DZP: 138.76 μg L-1 and PRG: 104.93 μg L-1	Cuervo Lumbaque et al. (2019)
TSS = 115 (mg L^{-1}) COD = 1350 (mg L^{-1}) BOD_5 = 410 (mg L^{-1}) TOC = 1050 (mg L^{-1})	$FeSO_4 \cdot 7H_2O$ (Merck)	Real hospital effluent (Bangkok, Thailand)	Cylindrical quartz reactor/UV lamps 10 W ($\lambda_{max} = 254$ nm)	pH = 3; [Fe^{2+}]$_0 = 135$ mg L^{-1}; [COD]:[H_2O_2]:[Fe^{2+}] = 1:4:0.1; Temperature = 25–31 °C; Reaction time = 120 min	Removal efficiencies of BOD_5, TOC and COD were 61%, 52% and 77%, respectively	Kajitvichyanukul and Suntronvipart (2006)
pH = 6.4 ± 0.5 TSS = 570 ± 30 (mg L^{-1}) COD = 1400 ± 500 (mg L^{-1}) BOD_5 = 300 ± 50 (mg L^{-1}) BOD/COD = 0.18 ± 0.03	$FeSO_4$ (Merck)/TiO_2 (P25) (Degussa)/H_2O_2 (30% *w/w*) (Merck)	Real hospital WW after primary treatment (Anna, University Campus, Tirunelveli, India)	Reactor (0.3 × 0.2 × 0.4 m)/Solar irradiation	(i) Solar/TiO_2/H_2O_2: pH = 7; [TiO_2]$_0 = 1.5$ g L^{-1}; [H_2O_2]$_0$=1.35 g L^{-1}; Reaction time = 4 h (ii) Solar/Fe^{2+}/H_2O_2: pH = 3; [Fe^{2+}]$_0 = 1.4$ g L^{-1}; [H_2O_2]$_0 = 1.35$ g L^{-1}; Reaction time = 4 h (iii) Solar/TiO_2/Fe^{2+}/H_2O_2: pH = 7; [TiO_2]$_0 = 0.2$ g L^{-1}; [Fe^{2+}]$_0 = 0.5$ g L^{-1}; [H_2O_2]$_0 = 1.35$ g L^{-1}, Reaction time = 4 h	(i) Solar/TiO_2/H_2O_2: COD removal efficiency was 85%, after 4 h of treatment (ii) Solar/Fe^{2+}/H_2O_2: COD removal efficiency was 94%, after 4 h of treatment (iii) Solar/TiO_2/Fe^{2+}/H_2O_2: COD removal efficiency was 99%, after 4 h of treatment	Adish Kumar et al. (2014)

degradation of the antibiotics and 8.5% mineralization after 90 min, with 82% consumption of the hydrogen peroxide. Degradation rate constants were 0.081 min^{-1}, 0.038 min^{-1}, 0.14 min^{-1} and 0.043 min^{-1} for AMX, CIP, STZ and SMZ, respectively. In addition, under the reported operational parameters, disinfection of total coliforms and *E.coli* was achieved after 90 min, resulting that the UVC/H_2O_2/FeCit system is very effective for the treatment of HWW, where high organic loads as well as PhACs and pathogens coexists (Perini et al., 2018).

It is worth noticing though, that the study on the effect of pH from 7.4 to 4.7 and to 2.5 resulted in higher rates of antibiotics' degradation, as well as mineralization, with total degradation (100%) at pH = 4.7 and 85% degradation at pH = 2.5, after 30 min. Degradation rate constants at pH = 4.7 have been determined 0.22 min^{-1}, 0.091 min^{-1}, 0.17 min^{-1} and 0.087 min^{-1} for AMX, CIP, STZ and SMZ, respectively, while at pH = 2.5 the degradation kinetics were 0.29 min^{-1}, 0.12 min^{-1}, 0.27 min^{-1} and 0.11 min^{-1} for MX, CIP, STZ and SMZ, respectively (Perini et al., 2018).

Furthermore, under solar irradiation at pH = 7.4, 66% of the total antibiotics were degraded after 90 min, with 43% consumption of H_2O_2 and 11% mineralization, resulting in better outcomes than the use of black light lamp (UVA) ($\lambda_{max} = 365$ nm) (47% global degradation after 90 min) at pH = 4.7. This result enhances the potential of applying solar process, in order to save energy costs, providing thus an important advantage (Fig. 1). Under solar irradiation degradation rate constants ranged between 0.011 min^{-1} (STZ) and 0.065 min^{-1} (SMZ) while, when the black light lamp was used the degradation of the sulfonamide antibiotics (STZ and SMZ) was severely reduced, with rate constants of 0.0033 and 0.0024 min^{-1}, respectively (40 and 20 times lower than the values obtained using the germicidal lamp) (Perini et al., 2018).

Finally, a raw hospital wastewater RHW was also studied (pH = 7.6) and despite its complexity compared to the AHE, the rate constants for antibiotics' degradation were very similar for CIP and SMZ, while the value decreased by 50% in the case of STZ. The global degradation percentage after 30 min was 74%, with 66% consumption of H_2O_2 and 16% of mineralization at the end of the experiment, while the rate constants ranged between 0.033 min^{-1} (SMZ) and 0.075 min^{-1} (STZ) (Perini et al., 2018).

Taking into consideration the high loads of pathogens present in WW, the removal of total coliforms and *E. coli* was examined in RHW and AHW under UVA, UVC and solar irradiation. The results showed that irradiation with UVC alone or in the presence of FeCit (10 μM) and hydrogen peroxide (500 μM) in AHW resulted in effective disinfection with total coliforms and *E. coli* being below the quantification limits after 90 min (Perini et al., 2018). As expected, the exposure of bacteria

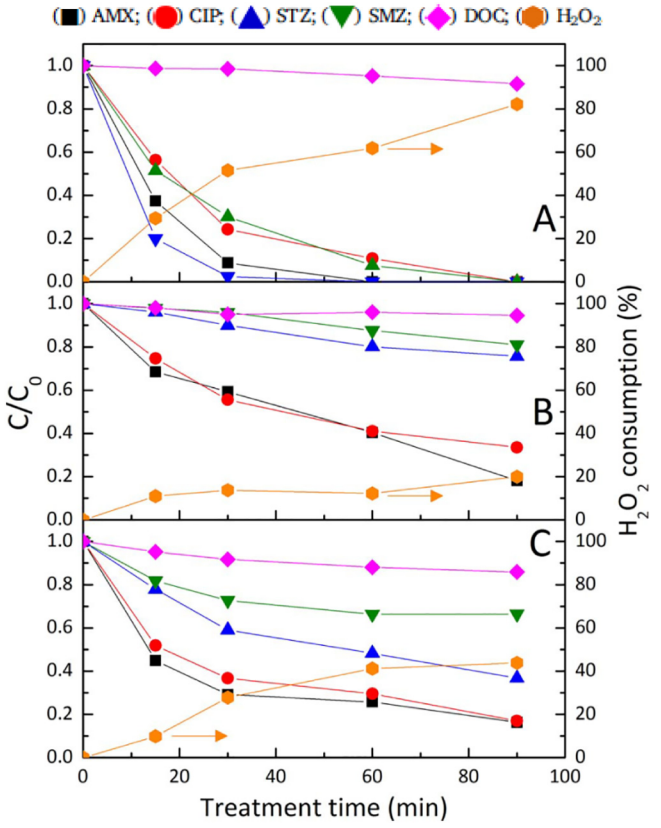

Fig. 1. Comparison of photo-Fenton processes using UVC lamp (A), UVA lamp (B), and sunlight irradiation (C) for degradation of the antibiotics' mixture in the AHE. Experimental conditions: [AMX] = [CIP] = [STZ] = [SMZ] = 200 μg L^{-1}; [H_2O_2] = 500 μmol L^{-1}; [FeCit] = 10 μmol L^{-1}; $pH_{initital}$ = 7.4 mg L^{-1}; $TOC_{initial}$ = 10.1 mg L^{-1}; $IC_{initial}$ = 74.5 mg L^{-1}.
Reproduced with permission from Perini et al. (2018).

to UVC irradiation results in damaging the nucleic acids, causing inactivation. Considering the above, the photo-Fenton UVC process seemed to be enough effective for the treatment of hospital wastewater where high organic loads and presence of antibiotics and pathogens can lead to harmful effects of the aquatic environment and human health. Thus, the effluent can be safely discharged, reused, or can be further treated with conventional technologies.

Another recently developed approach on the removal of PhACs from wastewaters, concerns the combination of solar photo-Fenton process (SPF) with adsorption. Michael et al. (2019) investigated the combined process consisting of SPF followed by granular activated carbon (GAC) for the removal of mixture of antibiotics from secondary effluent treatment urban wastewaters. The combined processes (30 min SPF and 15 min GAC) provided almost complete removal of toxicity and elimination of antibiotics, providing wastewater purification (Michael et al., 2019). In another recent study, Della-Flora et al. (2020) studied the elimination of the anti-cancer drug Flutamide (FLUT) and its Transformation Products (TPs) in real raw hospital wastewater in near-neutral pH (pH = 5) by combining solar photo-Fenton process (SPF) with adsorption, using avocado seed activated carbon (ASAC) derived from waste biomass (Della-Flora et al., 2020). Degradation of FLUT in SPF was based in (i) single addition approach (5 mg L^{-1} Fe^{2+} and 50 mg L^{-1} H_2O_2) which achieved only 20% FLUT primary degradation and only 3.05% mineralization after 120 min, with k_{obs} = 1.31×10^{-3} min^{-1}, and (ii) three consecutive additions of ferrous iron, with initial concentrations of Fe^{2+} and H_2O_2 of 5 and 150 mg L^{-1}, respectively. The three successive additions were made at t_{30W} = 0 min, t_{30W} = 11.5 min, and t_{30W} = 23.2 min, totaling 15 mg L^{-1} of ferrous iron, achieving 58% of primary compound degradation and 12.07% mineralization, after 120 min. The degradation of FLUT followed pseudo-first-order kinetics, with k_{obs} = 6.52×10^{-3} min^{-1}. It is worth noticing that the screening method applied for FLUT and the TPs in HWW enabled the identification of 10 TPs for the SPF process carried out using a single addition of Fe^{2+} (5 mg L^{-1}) and H_2O_2 (50 mg L^{-1}) (TP1, TP2, TP5, TP6, TP7, TP9, TP10, TP11, TP12, TP13), while 13 TPs (TP1-TP13) were identified in the SPF process performed using three consecutive additions (see Fig. 2). Afterwards, a Doehlert design was applied to optimize the variables for the adsorption process (contact time and ASAC). The optimal experimental conditions were applied (14 mg of ASAC and a contact time of 40 min) and finally, the study revealed that the combination of the SPF process with adsorption is an attractive option for the removal of FLUT as well as persistent and toxic TPs from aqueous media (Della-Flora et al., 2020).

Furthermore, various studies have been conducted by simulating hospital wastewater to examine whether photo-Fenton process can efficiently eliminate pharmaceuticals from hospital wastewaters. Hincapié-Mejía et al. (2020) used simulated hospital wastewater at near-neutral pH (6.5) to test the ability of process to degrade the antibiotic sulfacetamide (SAM) in such complex matrices. After 60 min of irradiation almost 20% of the initial concentration was degraded (Hincapié-Mejía et al., 2020). In this work, limited data are presented concerning the photo-Fenton treatment of SAM, therefore further study is needed, to export a more integrated aspect of the treatment.

In order to overcome the drawback of low pH, except of citric acid addition, as reported previously by Perini et al. (2018), a homo/heterogeneous photo-Fenton process using modified Fe(III)-alginate spheres, as a strategy to dose iron concentration, for the degradation of eight pharmaceuticals with different therapeutic use (nimesulide (NMD), furosemide (FRS), paracetamol (PCT), propranolol (PPN), dipyrone (DIP), fluoxetine (FXT), progesterone (PRG), and diazepam (DZP)) in simulated wastewater (SW) and raw hospital wastewater (RHW) at pH = 5, in Brazil, was studied (Cuervo Lumbaque et al., 2019). It is worth noticing that previous studies of Perini et al. (2018) and Della-Flora et al. (2020) also studied raw hospital wastewater. The SW composition was prepared in order to simulate the organic content of the real hospital wastewater (composition for 1 L of SW: 160 mg L^{-1} peptone, 110 mg L^{-1} beef extract, 30 mg L^{-1} urea, 2 mg L^{-1} $MgSO_4 \cdot 7H_2O$, and 4 mg L^{-1} $CaCl_2 \cdot 2H_2O$). The RHW was used without filtration. According to the results, the release of iron in SW is easier than that in RHW, being in agreement with the principle of counterion effect: the higher the conductivity, the higher the difficulty of transfer of ions into that solution. At the end of the processes, the total iron concentration in the SW and RHW matrices was 14.6 and 12.7 mg L^{-1}, respectively (below the maximum concentration limit (15 mg L^{-1}) for iron permitted by Brazilian legislation). These values provide the assurance that the effluent can be safely discharged and applied in further treatments. The final concentrations of the PhACs after 177 min for SW were: <LOD, <LOD, 17.75 μg L^{-1}, <LOD, <LOD, 47.75 μg L^{-1}, <LOD and 10.71 μg L^{-1} for DIP, PCT, PPN, FRS, NMD, FXT, DZP and PRG respectively, while for RHW were: <LOD, <LOD, 5.765 μg L^{-1}, <LOD, 189.26 μg L^{-1}, 276.01 μg L^{-1}, 138.76 μg L^{-1}, and 104.93 μg L^{-1}, for DIP, PCT, PPN, FRS, NMD, FXT, DZP and PRG, respectively. The compounds PPN and PRG showed persistence in all the experiments, while NMD, FXT, and DZP were persistent in the RHW matrix (Cuervo Lumbaque et al., 2019). This can be attributed to the fact that highly complex matrices affect the treatment processes. For instance, different ions present in the wastewater can act as scavengers of the hydroxyl radicals and lead to the formation of less reactive species, reducing PhACs degradation (Lanzafame et al., 2017).

In addition, based on an adapted purpose-built database, possible TPs formed during the process were identified in each case (for SW: TP1 DIP, TP2 DIP, TP1 DZP, TP1 FXT and TP1 PPN; for RHW: TP3 DIP, TP4 DIP and TP2 PPN) by means of a UHPLC-QTOF MS system, in positive ionization mode (Fig. 3). Moreover, the identified TPs were

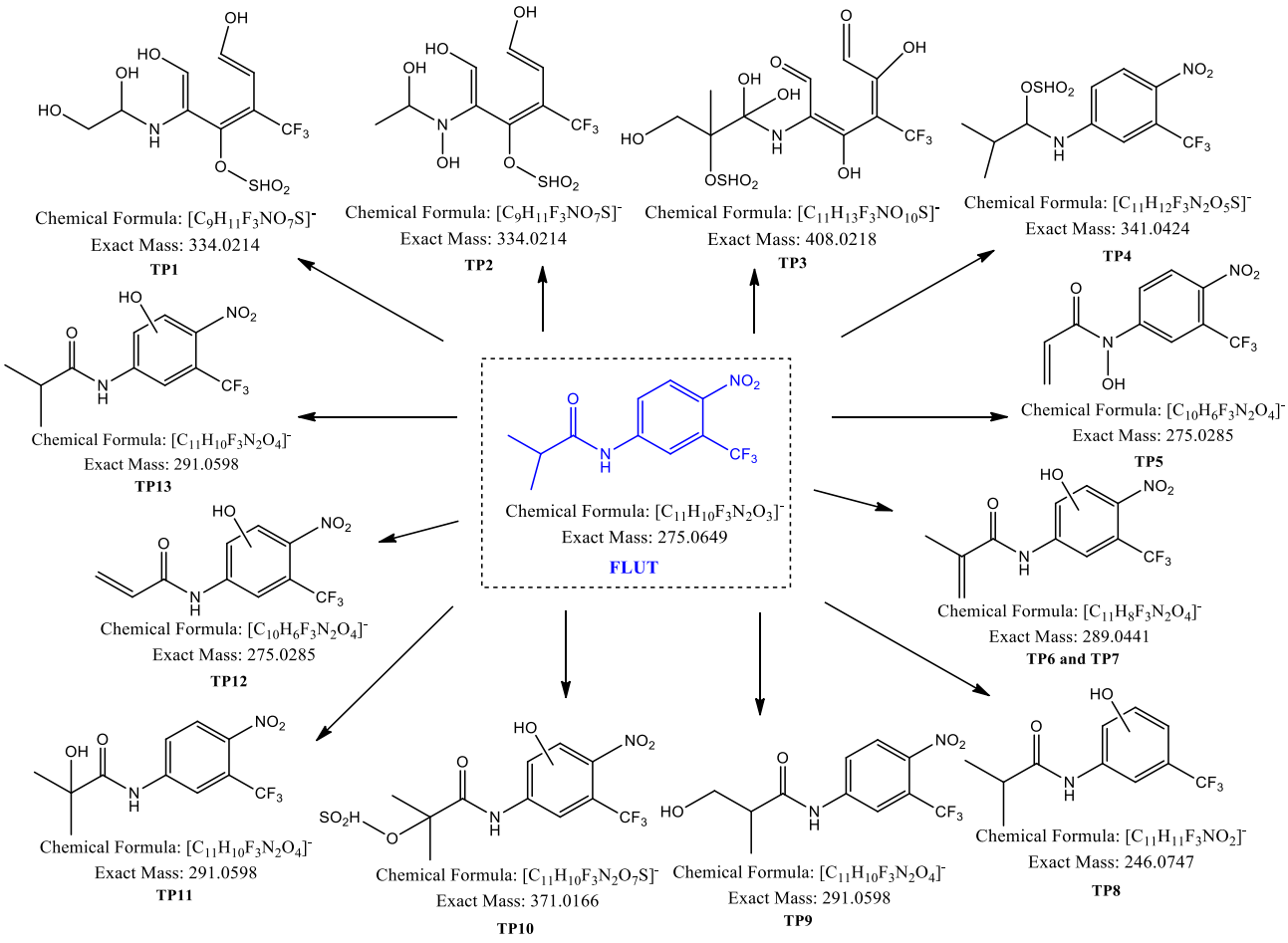

Fig. 2. Main TPs of Flutamide formed in HWW during solar photo-Fenton process, identified by means of LC-QTOF MS in negative ionization mode ($[M-H]^-$). Data are obtained from Della-Flora et al. (2020).

evaluated using Toxtree software, which employs the chemical structure of a molecule for estimation of its biodegradability (START biodegradability) and toxicological hazard (Cramer rules) (Cramer et al., 1976). Some TPs showed significant toxicity or the presence of reactive functional groups, and were therefore classified as highly toxic, according to the Cramer rules. More specifically, TP1 DIP, TP2 DIP, TP3 DIP and TP4 DIP did not present significant acute toxicity towards *D. magna*, while TP1 DZP presented toxicity to *Daphnia magna*, for TP1 FXT the toxicity towards the marine luminescent *Vibrio Fischeri* decreased after the treatment but not fully removed, while TP1 PPN and TP2 PPN presented toxicity, which accumulated with the cycles of treatment, in Green algae *P. subcapitata* and the bioluminescent marine *Vibrio fischeri*. Finally, biodegradability evaluation indicated that these compounds could be classified as persistent substances (Cuervo Lumbaque et al., 2019).

Except for the removal of PhACs only, several other studies have been conducted to examine the oxidation of organic pollutants load contained in HWW by photo-Fenton process. Kajitvichyanukul and Suntronvipart (2006) employed a lab-scale photo-Fenton process as a pretreatment step to improve the oxidation degree of pollutants in hospital effluents. It was found that in hospital effluents of average pollution degree (COD 1350–2250 mg L^{-1}, BOD_5/COD 0.30), a dosage ratio of COD:H_2O_2:Fe^{+2} = 1:4:0.1, at pH = 3 and reaction time of 120 min, the removal efficiencies of BOD_5, COD and TOC were 61%, 77% and 52%, while the BOD_5/COD ratio increased from 0.3 to 0.52. In addition, for higher COD concentrations, a decrease of biodegradability (BOD_5/COD) was found (Kajitvichyanukul and Suntronvipart, 2006). Similar to Martins et al. (2009), toxicity assessment indicated that the photo-Fenton process could be a suitable pretreatment method in reducing toxicity of pollutants up to a certain level.

Similarly, Anjana Anand et al. (2016) investigated a fluidized bed solar photo Fenton process (with silica granules used as carriers) and solar photo Fenton process for the treatment of a primary hospital wastewater (Karakonam, Kerala, India). Fluidized bed solar photo Fenton process showed higher efficiency. Under the optimum conditions (pH = 3, Fe^{2+} dosage = 5 mM, H_2O_2 = 50 mM and silica carrier amount of 40 g L^{-1}) in fluidized bed solar photo Fenton process, the COD removal efficiency was 92% whereas in solar photo Fenton process the corresponding efficiency was 67% for 60 min of reaction time. The application of fluidized bed solar photo Fenton process enhanced the biodegradability, (evaluated in terms of BOD_5/COD ratio) of the wastewater, indicating the possibility of coupling the process with biological treatment. Moreover, the COD and total suspended solid concentrations were found to be 30 mg L^{-1}, which met the requirements of the discharge quality standards (Anjana Anand et al., 2016).

One more advantage of the fluidized bed solar Fenton process is the reduction of iron sludge, as the ferric ions, produced in the Fenton reaction, can be transformed into iron oxide on the surface of carriers by crystallization or sedimentation. Consequently, the iron oxide immobilized onto silica carrier could be used as a catalyst for the degradation of COD load of hospital wastewater (Anjana Anand et al., 2016).

Based on the above available results it can be concluded that conventional photo-Fenton process for hospital effluent treatment usually occurs at a pH of approx. 3.0–4.0, iron and H_2O_2 concentration range of 2.5 to 279 mgL^{-1} and 5 to 1700 mgL^{-1} respectively, i.e. weight ratio

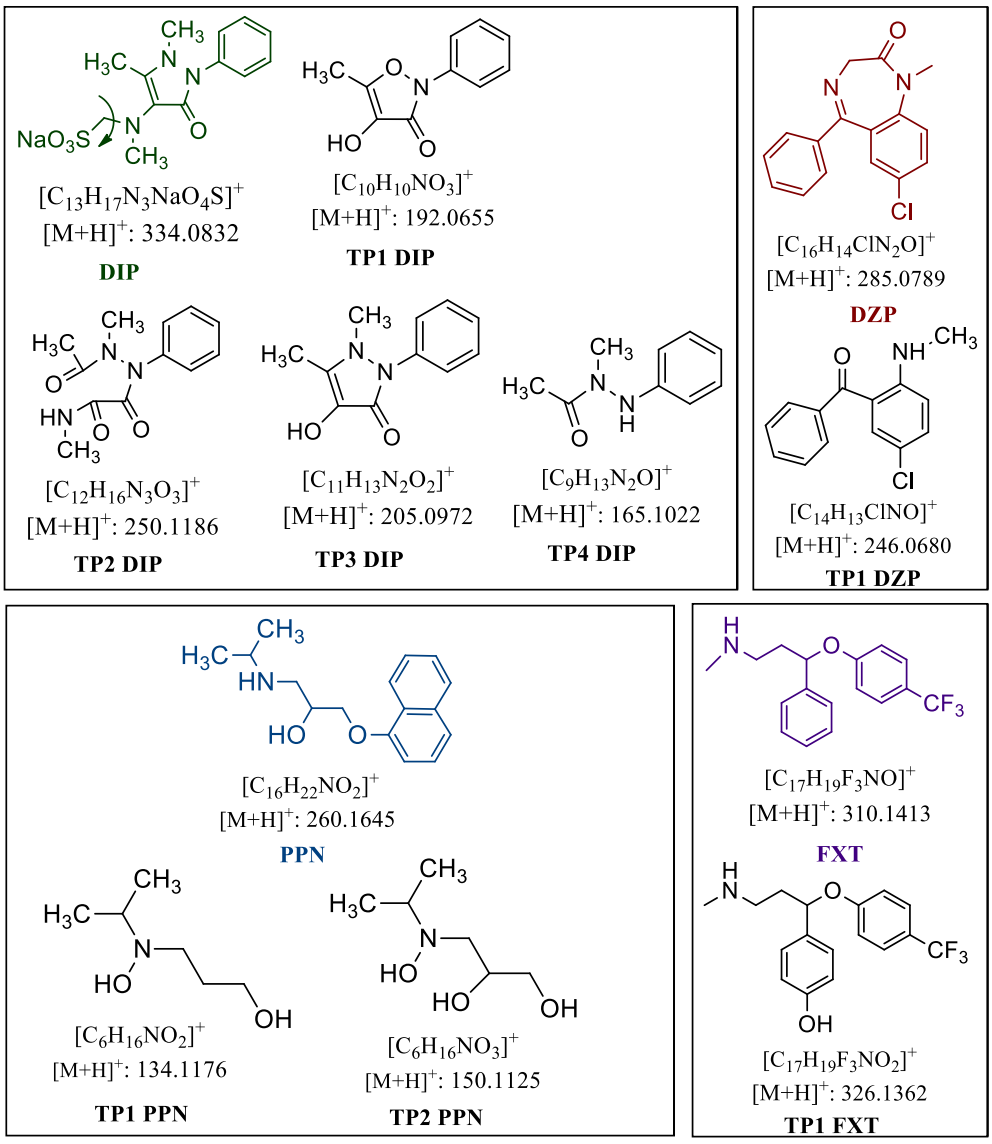

Fig. 3. TPs of the studied PhACs identified during homo/heterogeneous photo-Fenton treatment, in SW and RHW by means of UHPLC-QTOF MS in positive ionization mode. Data are obtained from Cuervo Lumbaque et al. (2019).

of H_2O_2/iron between 1 and 40 and weight ratio of H_2O_2/COD between 0.10 and 4.05. Removals of pharmaceuticals and COD or BOD values ranged between 20 and 100% and between 61 and 99%, respectively. Compound parabolic collectors (CPC) are most used reactor set-up for the large-scale solar photocatalytic applications. However, for full scale applications more data on the residual concentrations of iron and hydrogen peroxide should be reported for ensuring the effluent appropriateness for discharge.

The applications of Fenton and photo-Fenton processes for the treatment of hospital effluents are rather limited in comparison with available applications of these technologies for the treatment of municipal or various industrial (refinery, textile, pesticide, etc. industry) wastewaters. Photo-Fenton process can be successfully applied both as pre-treatment (before the biological process) providing an increase of raw effluent biodegradability as well as post-treatment (after biological process) of hospital effluents leading to the degradation of pharmaceuticals and other organic emerging contaminants and the decrease of toxicity. In addition, only few studies concerned the abatement of the overall toxicity of real hospital wastewaters.

3.2. Heterogeneous photocatalysis

Heterogeneous photocatalysis is a representative advanced oxidation process (AOP) which was widely investigated the last decades for the removal of pharmaceutical compounds in aqueous media. In this environmental application, the process involves the acceleration of the contaminant degradation (in aqueous phase) in the presence of a semiconductor solid catalyst which is activated by light with a certain energy. In general, heterogeneous photocatalysis can produce highly reactive species and mainly hydroxyl radicals ($HO^{\bullet}$), holes (h^+), superoxide ions ($O_2^{\bullet-}$) and peroxide radicals ($HO_2^{\bullet}$) that can oxidize a large variety of pharmaceuticals. In many cases, total mineralization of the organic pollutant is succeeded (Antonopoulou and Konstantinou, 2017; Antonopoulou and Konstantinou, 2016; Konstas et al., 2019; Vasconcelos et al., 2009).

Although, intensive research has been conducted for the removal of pharmaceutical compounds in water and municipal wastewater, limited data exists for the removal in real hospital wastewater. Up to now, solid semiconductors such as titanium dioxide (TiO_2), cerium oxide (CeO_2), zinc oxide (ZnO), zirconium oxide (ZrO_2), tungsten

Table 2
Heterogeneous photocatalysis for the removal of PhACs in real and synthetic hospital wastewaters.

Target compound initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
[Ciprofloxacin] $_0$ = 200 μg L^{-1}	TiO_2 P-25 Degussa (São Paulo)	Real hospital effluent (Federal University of Santa Maria (HUSM) State of Rio Grande do Sul)	Batch recirculation reactor/125 W Philips medium pressure mercury lamp & and quartz irradiation tube	[TiO_2] $_0$ = 571.5 mg L^{-1}; pH = 3	After 60 min 100% was achieved	Vasconcelos et al. (2009)
[Venlafaxine] $_0$ = 391.2 ng L^{-1} [*O*-desmethyl venlafaxine] $_0$ = 748.5 ng L^{-1} [Amisulpride]$_0$= 505.5 ng L^{-1} [Sulfamethoxazole] $_0$ = 349.8 ng L^{-1} [Carbamazepine] $_0$ = 242.0 ng L^{-1}	TiO_2-P25 (Evonik-Degussa Corporation)	Secondary hospital wastewater effluent (University hospital WWTP, Ioannina city, Epirus region, Greece).	Suntest XLS+ instrument (Atlas, Linsengericht, Germany) (simulated solar light >290 nm).	[TiO_2]$_0$ = 100 mg L^{-1}; Irradiation intensity = 500 Wm^{-2}; Temperature = 23 °C; Reaction time = 180 min	After 90 min 78% of venlafaxine removal was achieved After 90 min 76% of *O*-desmethyl venlafaxine removal was achieved After 90 min 74% of amisulpride removal was achieved After 90 min 78% of carbamazepine removal was achieved After 90 min 71% of sulfamethoxazole removal was achieved	Konstas et al. (2019)
[Amoxicillin] $_0$ = 0.1 mg L^{-1}	TiO_2 P-25 Degussa	Real hospital effluent (Federal University of Santa Maria (HUSM) State of Rio Grande do Sul)	Homemade bench scale photoreactor (Dewar-like photoreactor)/125 W Philips medium pressure mercury lamp (incident light intensity of 401 W m^{-2})	[TiO_2]$_0$ = 800 mgL^{-1}; pH = 4; Temperature = 30 °C; Reaction time = 30 min	After 30 min 100% degradation was achieved	Martins et al. (2009)
[Ciprofloxacin] $_0$ = 500 μg L^{-1}	TiO_2	Raw hospital Wastewater (Dokuz Eylul University Hospital, Izmir, Turkey)	Laboratory-scale photocatalytic reactor/UV light	[TiO_2]$_0$ = 500 mg L^{-1}; Temperature = 25 °C pH = 7; UV light power = 210 W	After 45 min removal of 88% and 98% of ciprofloxacin and COD, respectively, was achieved	Guney and Sponza (2016)
[Metformin]$_0$; [Amoxicillin] $_0$ = 10 mg L^{-1}	TiO_2 (99% anatase Sigma-Aldrich)	Synthetic hospital wastewater	Photoreactor procured from M/s Heber Scientific, Chennai/125 W low-pressure mercury vapor lamp (emitting predominantly at 365 nm)	[TiO_2]$_0$ = 563 mg L^{-1}; pH = 7.6; Reaction time = 150 min	After 150 min 86.4% removal of amoxicillin and 92.3% of metformin was achieved	Chinnaiyan et al. (2019)
[Sulfamethoxazole] $_0$ = 50 mg L^{-1}	TiO_2 (Sigma-Aldrich)	Raw hospital Wastewater (Tehran, Iran)	Cylindrical batch photoreactor/ UV (UVC, 254); BLB (UVA, 365); Halogen lamps above 380 nm	[TiO_2]$_0$ = 500 mg L^{-1}; pH = 4; Ambient temperature	After 120 min 100% removal was achieved by UV/TiO_2 After 160 min ~ 20% removal was achieved by BLB/TiO_2 After 160 min < 20% removal was achieved by Halogen/TiO_2	Beheshti et al. (2019)
[Sulfamethoxazole] $_0$ = 50 mg L^{-1}	WO_3 (Sigma-Aldrich)	Raw hospital Wastewater (Tehran, Iran)	Cylindrical batch photoreactor/UV (UVC, 254); BLB (UVA, 365); Halogen lamps above 380 nm	[WO_3] $_0$ = 750 mg L^{-1}; pH = 3; Ambient temperature	After 160 min ~ 50% removal was achieved by UV/WO_3 After 160 min ~ 70% removal was achieved by BLB/WO_3 After 160 min 93.96% removal was achieved by halogen/WO_3	Beheshti et al. (2019)
[Dexamethasone] $_0$ = 25 mg L^{-1}	WO_3 (US Research Nanomaterial company)	Raw hospital Wastewater (Tehran, Iran)	Cylindrical batch photoreactor/ UV (UVC, 254); BLB (UVA, 365); Halogen lamps above 380 nm	[WO_3] $_0$ = 500 mg L^{-1}; pH = 3; Reaction time = 180 min	After 180 min 38.2% removal was achieved by UV/WO_3 After 180 min ~ 80% removal was achieved by BLB/WO_3 After 180 min 100% removal was achieved by halogen/WO_3	Ghenaatgar et al. (2019)
[Dexamethasone] $_0$ = 25 mg L^{-1}	ZrO_2 (US Research Nanomaterial company)	Raw hospital Wastewater (Tehran, Iran)	Cylindrical batch photoreactor/ UV (UVC, 254); BLB (UVA, 365); Halogen lamps above 380 nm	[ZrO_2] $_0$ = 1500 mg L^{-1}; pH = 3; Reaction time = 180 min	After 180 min ~70% at removal was achieved by UV/ZrO_2 After 180 min ~60% at removal was achieved by BLB/ZrO_2 After 180 min less than 60% removal was achieved by halogen/ZrO_2	Ghenaatgar et al. (2019)
[Chloramphenicol] $_0$ = 10 mg L^{-1} [Paracetamol] $_0$ = 10 mg L^{-1} [Salicylic acid] $_0$ = 10 mg L^{-1} [Sulfamethoxazole] $_0$ = 10 mg L^{-1} [Diclofenac] $_0$ = 10 mg L^{-1}	TiO_2 (Sigma-Aldrich Chemicals)	Simulated hospital wastewater	Commercial metal halide lamp (HQI-T 400 W/Daylight, OSRAM GmbH, Germany)	[TiO_2] $_0$ = 1000 mg L^{-1}; pH = 5.3; Reaction time = 180 min	After 180 min ~50% total pharmaceutical degradation was achieved	Badawy et al. (2014)
[Chloramphenicol] $_0$ = 10 mg L^{-1}	TiO_2 (Anatase/rutile, Prepared in this	Simulated hospital wastewater	Commercial metal halide lamp (HQI-T	[TiO_2] $_0$ = 1000 mg L^{-1};	After 180 min ~60% total pharmaceutical degradation was	Badawy et al. (2014)

Table 2 (*continued*)

Target compound initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
[Paracetamol] $_0$ = 10 mg L^{-1} [Salicylic acid] $_0$ = 10 mg L^{-1} [Sulfamethoxazole] $_0$ = 10 mg L^{-1} [Diclofenac] $_0$ = 10 mg L^{-1}	study)		400 W/Daylight, OSRAM GmbH, Germany)	pH = 5.3; Reaction time = 180 min	achieved	
[Chloramphenicol] $_0$ = 10 mg L^{-1} [Paracetamol] $_0$ = 10 mg L^{-1} [Salicylic acid] $_0$ = 10 mg L^{-1} [Sulfamethoxazole] $_0$ = 10 mg L^{-1} [Diclofenac] $_0$ = 10 mg L^{-1}	0.1% Ag/TiO_2 nanoparticles	Simulated hospital wastewater	Commercial metal halide lamp (HQI-T 400 W/Daylight, OSRAM GmbH, Germany)	[0.1% Ag/TiO_2] $_0$ = 1000 mg L^{-1}; pH = 5.3; Reaction time = 180 min	After 180 min ~85% total pharmaceutical degradation was achieved	Badawy et al. (2014)
[Triclosan] $_0$ = 860.00 ± 0.05 μg L^{-1}	TiO_2 (Anatase, Prepared in this study)	Raw hospital wastewater (Dokuz Eylul University Hospital, Izmir, Turkey)	Quartz glass reactors/ UVC light lamps (254 nm)	$[TiO_2]_0$ = 500 mg L^{-1}; pH = 8.50; Temperature = 25 °C; UV light power = 210 W; Reaction time = 45 min	After 45 min 94% triclosan removal was achieved	Sponza and Güney (2017)
[Triclosan] $_0$ = 860.00 ± 0.05 μg L^{-1}	CeO_2	Raw hospital wastewater (Dokuz Eylul University Hospital, Izmir, Turkey)	Quartz glass reactors/ UVC light lamps (254 nm)	[CeO_2] $_0$ = 500 mg L^{-1}; pH = 8.50; Temperature = 25 °C; UV light power = 210 W; Reaction time = 45 min	After 45 min 97% triclosan removal was achieved	Sponza and Güney (2017)
[Gemfibrozil] $_0$ = 53.30 ± 0.05 μg L^{-1}	TiO_2 (Anatase, Prepared in this study)	Raw hospital wastewater (Dokuz Eylul University Hospital, Izmir, Turkey)	Quartz glass reactors/ UVC light lamps (254 nm)	$[TiO_2]_0$ = 500 mg L^{-1}; pH = 8.50; Temperature = 25 °C; UV light power = 210 W; Reaction time = 45 min	After 45 min 93% gemfibrozil removal was achieved	Sponza and Güney (2017)
[Gemfibrozil] $_0$ = 53.30 ± 0.05 μg L^{-1}	CeO_2	Raw hospital wastewater (Dokuz Eylul University Hospital, Izmir, Turkey)	Quartz glass reactors/ UVC light lamps (254 nm)	[CeO_2] $_0$ = 500 mg L^{-1}; pH = 8.50; Temperature = 25 °C; UV light power = 10 W Reaction time = 45 min	After 45 min 95% gemfibrozil removal was achieved	Sponza and Güney (2017)
[Ofloxacin] $_0$ = 5 mg L^{-1} [Ketorolac] $_0$ = 5 mg L^{-1} [Paracetamol] $_0$ = 5 mg L^{-1}	CdS/TiO_2	Simulated hospital wastewater	85 W Oreva bulb with 4150 lm intensity (λ = 450–650 nm)	[CdS/TiO_2] $_0$ = 450 mg L^{-1}; pH = 8.05; Temperature = 25 °C; Reaction time = 270 min	After 270 min about 48.5% TOC reduction was achieved	Kaur et al. (2018)
[Terbutaline] $_0$ = 100 μg L^{-1} [Lincomycin] $_0$ = 100 μg L^{-1} [Sulfamethoxazole] $_0$ = 100 μg L^{-1} [Paracetamol] $_0$ = 100 μg L^{-1} [Diclofenac] $_0$ = 100 μg L^{-1} [Metoprolol] $_0$ = 100 μg L^{-1} [Phenazone] $_0$ = 100 μg L^{-1} [Carbamazepine] $_0$ = 100 μg L^{-1} [Clofibric acid] $_0$ = 100 μg L^{-1} [Diatrizoic acid] $_0$ = 100 μg L^{-1}	Carbon-doped TiO_2 (Anatase,'Kronoclean 7000' Kronos, Germany) TiO_2 (50% w/w)	Hospital effluent (Maria Middelares Hospital, Ghent, Belgium)	Solar reactor/Xenon arc lamp (Irradiation intensity= 65 W m^{-2}(300–400 nm) Irradiation intensity = 1844 W m^{-2} (400–570 nm))	[Catalyst] $_0$ = 700 mg L^{-1}; Temperature = 25 °C; Reaction time = 120 min	After 120 min 100%, ~99%, ~98%, 100%, 100%, ~60%, ~35%, ~45%, ~40%, ~25% removal of terbutaline, lincomycin, sulfamethoxazole, paracetamol, diclofenac, metoprolol, phenazone, carbamazepine, clofibric acid and diatrizoic acid was achieved, respectively	An et al. (2016)

(*continued on next page*)

Table 2 (*continued*)

Target compound initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
[Terbutaline] $_0$ = 100 μg L^{-1} [Lincomycin] $_0$ = 100 μg L^{-1} [Sulfamethoxazole] $_0$ = 100 μg L^{-1} [Paracetamol] $_0$ = 100 μg L^{-1} [Diclofenac] $_0$ = 100 μg L^{-1} [Metoprolol] $_0$ = 100 μg L^{-1} [Phenazone] $_0$ = 100 μg L^{-1} [Carbamazepine] $_0$ = 100 μg L^{-1} [Clofibric acid] $_0$ = 100 μg L^{-1} [Diatrizoic acid] $_0$ = 100 μg L^{-1}	Carbon-doped TiO_2 (Anatase,'Kronoclean 7000' Kronos, Germany) TiO_2 (50% w/w)	Hospital effluent (Maria Middelares Hospital, Ghent, Belgium)	Natural solar light	[Catalyst] $_0$ = 700 mg L^{-1}; Temperature = 25 °C; Reaction time = 120 min	After 120 min 100%, ~99%, ~95%, ~99%, 100%, ~58%, ~42%, ~53%, ~40%, ~48% removal of terbutaline, lincomycin, sulfamethoxazole, paracetamol, diclofenac, metoprolol, phenazone, carbamazepine, clofibric acid and diatrizoic acid was achieved, respectively	An et al. (2016)
[Terbutaline] $_0$ = 100 μg L^{-1} [Lincomycin] $_0$ = 100 μg L^{-1} [Sulfamethoxazole] $_0$ = 100 μg L^{-1} [Paracetamol] $_0$ = 100 μg L^{-1} [Diclofenac] $_0$ = 100 μg L^{-1} [Metoprolol] $_0$ = 100 μg L^{-1} [Phenazone] $_0$ = 100 μg L^{-1} [Carbamazepine] $_0$ = 100 μg L^{-1} [Clofibric acid] $_0$ = 100 μg L^{-1} [Diatrizoic acid] $_0$ = 100 μg L^{-1}	50% w/w Carbon doped-TiO_2 coated on zeolites SiO_2/Al_2O_3: 18	Hospital effluent (Maria Middelares Hospital, Ghent, Belgium)	Solar reactor/Xenon arc lamp (Irradiation intensity= 65 W m^{-2} (300–400 nm) Irradiation intensity = 1844 W m^{-2} (400–570 nm)	[Catalyst] $_0$ = 700 mg L^{-1}; Temperature = 25 °C; Reaction time = 120 min	After 120 min 100%, ~99%, ~97%, ~99%, 100%, ~99%, ~55%, ~65%, ~60%, ~25% removal of terbutaline, lincomycin, sulfamethoxazole, paracetamol, diclofenac, metoprolol, phenazone, carbamazepine, clofibric acid and diatrizoic acid was achieved, respectively	An et al. (2016)
[Terbutaline] $_0$ = 100 μg L^{-1} [Lincomycin] $_0$ = 100 μg L^{-1} [Sulfamethoxazole] $_0$ = 100 μg L^{-1} [Paracetamol] $_0$ = 100 μg L^{-1} [Diclofenac] $_0$ = 100 μg L^{-1} [Metoprolol] $_0$ = 100 μg L^{-1} [Phenazone] $_0$ = 100 μg L^{-1} [Carbamazepine] $_0$ = 100 μg L^{-1} [Clofibric acid] $_0$ = 100 μg L^{-1} [Diatrizoic acid] $_0$ = 100 μg L^{-1}	50% w/w Carbon doped-TiO_2 coated on zeolites SiO_2/Al_2O_3: 18	Hospital effluent (Maria Middelares Hospital, Ghent, Belgium)	Natural solar light	[Catalyst] $_0$ = 700 mg L^{-1}; Temperature = 25 °C; Reaction time = 120 min	After 120 min 100%, 100, ~95%, ~98%, 100%, 100%, ~46%, ~78%, ~48%, ~17% removal of terbutaline, lincomycin, sulfamethoxazole, paracetamol, diclofenac, metoprolol, phenazone, carbamazepine, clofibric acid and diatrizoic acid was respectively achieved	An et al. (2016)
[Terbutaline] $_0$ = 100 μg L^{-1} [Lincomycin] $_0$ = 100 μg L^{-1} [Sulfamethoxazole] $_0$ = 100 μg L^{-1} [Paracetamol] $_0$ = 100 μg L^{-1} [Diclofenac] $_0$ = 100 μg L^{-1} [Metoprolol] $_0$ = 100 μg L^{-1} [Phenazone] $_0$ = 100 μg L^{-1} [Carbamazepine]	50% w/w Carbon doped-TiO_2 coated on zeolites SiO_2/Al_2O_3: 240	Hospital effluent (Maria Middelares Hospital, Ghent, Belgium)	Solar reactor/Xenon arc lamp (Irradiation intensity= 65 W m^{-2} (300–400 nm) Irradiation intensity = 1844 W m^{-2} (400–570 nm)	[Catalyst] $_0$ = 700 mg L^{-1}; Temperature = 25 °C; Reaction time = 120 min	After 120 min 100%, 100%, ~98%, ~99%, 100%, ~97%, ~95%, ~70%, ~65%, ~45% removal of terbutaline, lincomycin, sulfamethoxazole, paracetamol, diclofenac, metoprolol, phenazone, carbamazepine, clofibric acid and diatrizoic acid was achieved, respectively	An et al. (2016)

Table 2 (*continued*)

Target compound initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
$_0 = 100\ \mu g\ L^{-1}$ [Clofibric acid] $_0 = 100\ \mu g\ L^{-1}$ [Diatrizoic acid] $_0 = 100\ \mu g\ L^{-1}$ [Terbutaline] $_0 = 100\ \mu g\ L^{-1}$ [Lincomycin] $_0 = 100\ \mu g\ L^{-1}$ [Sulfamethoxazole] $_0 = 100\ \mu g\ L^{-1}$ [Paracetamol] $_0 = 100\ \mu g\ L^{-1}$ [Diclofenac] $_0 = 100\ \mu g\ L^{-1}$ [Metoprolol] $_0 = 100\ \mu g\ L^{-1}$ [Phenazone] $_0 = 100\ \mu g\ L^{-1}$ [Carbamazepine] $_0 = 100\ \mu g\ L^{-1}$ [Clofibric acid] $_0 = 100\ \mu g\ L^{-1}$ [Diatrizoic acid] $_0 = 100\ \mu g\ L^{-1}$	50% w/w Carbon doped-TiO_2 coated on zeolites SiO_2/Al_2O_3: 240	Hospital effluent (Maria Middelares Hospital, Ghent, Belgium)	Natural solar light	[Catalyst] $_0 = 700\ mg\ L^{-1}$; Temperature = 25 °C; Reaction time = 120 min	After 120 min 100% 100%, ~95%, ~95%, 100%, ~98%, ~97%, ~80%, ~45%, ~0% removal of terbutaline, lincomycin, sulfamethoxazole, paracetamol, diclofenac, metoprolol, phenazone, carbamazepine, clofibric acid and diatrizoic acid was achieved, respectively	An et al. (2016)
[Ciprofloxacin] $_0 = 3\ mg\ L^{-1}$	TiO_2 nanoparticles (Sigma Aldrich Co., United States) immobilized on a glass plate	Real hospital wastewater (Kerman city, sIran)	Laboratory scale reactor/ultraviolet, 6w lamps (UV-C)	[TiO_2] $_0 = 1000\ mg\ L^{-1}$; pH = 5; Reaction time = 105 min,	After 105 min 86.57% ciprofloxacin removal was achieved	Malakootian et al. (2020)
[Carbamazepine] $_0 = 5000\ \mu g\ L^{-1}$	TiO_2 nanofiber catalyst Anatase particles (~325 mesh from Sigma–Aldrich)	Synthetic hospital wastewater	Batch annular slurry photoreactor/UV-A black light of 8 W (NEC, Holland)	Reaction time = 240 min	After 240 min 78% of carbamazepine, 40% of COD and 23% of PO_4^{3-} were removed	Chong and Jin (2012)
[Ciprofloxacin] $_0 = 3\ mg\ L^{-1}$	ZnO immobilized on a glass plate	Hospital wastewater (Kerman city,Iran)	Laboratory scale reactor/ultraviolet, 6 W lamps (UV-C)	$[ZnO]_0 = 600\ mg\ L^{-1}$; pH = 11; Reaction time = 90 min	After 90 min 90.25% of ciprofloxacin removal was achieved	Gharaghani and Malakootian (2017)
[Ofloxacin] $_0 = 7–10\ \mu g\ L^{-1}$	Nano graphene oxide magnetite (Nano-GO/M) particles	Raw hospital wastewater from Dokuz Eylul University Hospital (Izmir, Turkey)	Quartz glass reactors/UV lamps with a power of 30 W	[Nano-GO/M] $_0 = 2000\ mg\ L^{-1}$; pH = 7.8; UV power = 300 W; Reaction time = 60 min	After 60 min COD, BOD5, TSS, TKN, TP and ofloxacin removal were 88%, 89%, 82%, 95%, 79%, and 97%, respectively	Sponza and Alicanoglu (2018)
[Venlafaxine] $_0 = 391.2\ ng\ L^{-1}$ [*O*-desmethyl venlafaxine] $_0 = 748.5\ ng\ L^{-1}$ [Amisulpride]$_0$= 505.5 ng L^{-1} [Sulfamethoxazole] $_0 = 349.8\ ng\ L^{-1}$ [Carbamazepine] $_0 = 242.0\ ng\ L^{-1}$	$g\text{-}C_3N_4$	Secondary hospital wastewater effluent (University hospital WWTP, Ioannina city, Epirus region, Greece).	Suntest XLS+ instrument (Atlas, Linsengericht, Germany) (simulated solar light >290 nm).	[$g\text{-}C_3N_4$] $_0 = 100\ mg\ L^{-1}$; Irradiation intensity = 500 Wm^{-2}; Temperature = 23 °C; Reaction time = 180 min	After 90 min 96% of venlafaxine removal was achieved After 90 min 75% of *O*-desmethyl venlafaxine removal was achieved After 90 min 98% of amisulpride removal was achieved After 90 min 86% of carbamazepine removal was achieved After 90 min 62% of sulfamethoxazole removal was achieved	Konstas et al. (2019)
[Venlafaxine] $_0 = 391.2\ ng\ L^{-1}$ [*O*-desmethyl venlafaxine] $_0 = 748.5\ ng\ L^{-1}$ [Amisulpride] $_0 = 505.5\ ng\ L^{-1}$ [Sulfamethoxazole] $_0 = 349.8\ ng\ L^{-1}$ [Carbamazepine] $_0 = 242.0\ ng\ L^{-1}$	$g\text{-}C_3N_4/SrTiO_3$ with $g\text{-}C_3N_4$ to $SrTiO_3$ ratio of 20%	Secondary hospital wastewater effluent (University hospital WWTP, Ioannina city, Epirus region, Greece).	Suntest XLS+ instrument (Atlas, Linsengericht, Germany) (simulated solar light >290 nm).	[$g\text{-}C_3N_4/SrTiO_3$] $_0 = 100\ mg\ L^{-1}$; Irradiation intensity = 500 Wm^{-2}; Temperature = 23 °C; Reaction time = 180 min	After 90 min 31% of venlafaxine removal was achieved After 90 min 31% of *O*-desmethyl venlafaxine removal was achieved After 90 min 77% of amisulpride removal was achieved After 90 min 28% of carbamazepine removal was achieved After 90 min 2% of sulfamethoxazole removal was achieved	Konstas et al. (2019)
[Amoxicillin] $_0 = 2\ mg\ L^{-1}$ [Cefotaxime]	Mesoporous $g\text{-}C_3N_4$	Effluent of secondary treatment unit of hospital wastewater	300-W xenon lamp ($\lambda > 420$ nm).	[Catalyst] $_0 = 1000\ mg\ L^{-1}$; pH = 7.5; Reaction	After 60 min ~60% of amoxicillin removal was achieved After 60 min ~90% of cefotaxime	Dou et al. (2020)

(*continued on next page*)

Table 2 (*continued*)

Target compound initial concentration	Catalyst	Matrix	Scale/irradiation source	Experimental conditions	Removal efficiency	Reference
$_0 = 2$ mg L^{-1}				time = 60 min	removal was achieved	
[Tetracycline] $_0 = 48.6$ mg L^{-1}	g-C_3N_4	Hospital wastewater (Hong Ngoc Hospital, Hanoi, Vietnam)	Solar light	[g-C_3N_4] $_0 = 2000$ mg L^{-1}; Reaction time = 120 min	After 120 min 52.8% removal was achieved	Minh Tri et al., 2019
[Tetracycline] $_0 = 48.6$ mg L^{-1}	Ag-doped g-C_3N_4 (with $AgNO_3$ 3 mmol)	Hospital wastewater (Hong Ngoc hospital located in Hanoi, Vietnam)	Solar light	[Ag-doped g-C_3N_4] $_0 = 2000$ mg L^{-1}; Reaction time = 120 min	After 120 min 89.6% removal was achieved	Minh Tri et al., 2019
[Amoxicillin] $_0 = 5$ mg L^{-1}	Ag/TiO_2/mesoporous g-C_3N_4 (1.94 wt%) (TiO_2 P25 from Aladdin Reagent Co. Ltd.)	Hospital wastewater	300-W xenon lamp ($\lambda > 420$ nm)	[Catalyst] $_0 = 1000$ mg L^{-1} Reaction time = 60 min	After 60 min 71% of amoxicillin removal was achieved	Gao et al. (2020)

oxide (WO_3), have been investigated for the removal of pharmaceuticals in real and synthetic hospital wastewater. Moreover, doped TiO_2, composite catalysts (cadmium sulfide (CdS)/TiO_2), immobilized TiO_2, immobilized ZnO, graphene based photocatalysts, g-C_3N_4 and g-C_3N_4/$SrTiO_3$ have also been used. The literature survey of photocatalytic degradation of pharmaceuticals in real and synthetic hospital wastewater is presented in Table 2.

TiO_2, an n-type semiconductor, which has been found one of the most effective and efficient photocatalysts for the removal of various pollutants in water, has also been investigated for the removal of pharmaceuticals in real and synthetic hospital effluents. TiO_2 nanoparticles, immobilized on a substrate, doped with non-metal and metal as well as composite with another semiconductor has been used up to now. The removal of different pharmaceuticals such as ciprofloxacin (CIP) (Vasconcelos et al., 2009), amoxicillin (AMX) (Martins et al., 2009), venlafaxine (VNX), *O*-desmethyl venlafaxine (ODV), amisulpride (AMS), sulfamethoxazole (SMX) and carbamazepine (CBZ) (Konstas et al., 2019), was investigated using commercially available TiO_2 P-25 in real hospital wastewaters. Vasconcelos et al. (2009) investigated the efficiency of heterogeneous photocatalysis to remove ciprofloxacin (200 μg L^{-1}) with a 125 W medium-pressure mercury lamp in real samples collected from the treatment system of the University Hospital of Santa Maria (HUSM) at pH 3. The process showed high efficiency and led to almost complete degradation of ciprofloxacin after 60 min treatment. However, a relatively low reduction (lower than 40%) of COD and integrated UV–vis absorbance was observed after this period (Vasconcelos et al., 2009).

In this study apart from heterogeneous photocatalysis, the performance of photo-induced oxidation, ozonation and peroxone in degrading CIP in the real hospital effluent was also examined and compared, demonstrating that all processes have a good prospect of degrading CIP. However, the need for elucidation of CIP by-products and their toxicity and biodegradability in the future was also highlighted (Vasconcelos et al., 2009).

Using the same catalyst, the removal of five other PhACs venlafaxine, *O*-desmethyl venlafaxine, amisulpride, sulfamethoxazole and carbamazepine in secondary effluent from the university hospital WWTP (Ioannina city, Epirus region, Greece) under simulated solar light was studied (Konstas et al., 2019). High removal percentages (71%-78%) were noticed for all the studied pharmaceuticals, under environmental relevant concentrations. Rate constants of 0.0176, 0.0177, 0.0155, 0.0128, 0.0161 min^{-1} were calculated for venlafaxine, *O*-desmethyl venlafaxine, amisulpride, sulfamethoxazole and carbamazepine, respectively. Similarly, to the previously reported study, COD decreased moderately (from 13 mg L^{-1} to <10 mg L^{-1}) indicating the formation of intermediates products derived mainly from hydroxylation, oxidation and demethylation pathways, as well as the presence of organic matter substances. The formation of intermediates was also confirmed by the authors using advanced accurate high-resolution spectrometric techniques. A more significant decrease of COD could probably be achieved with prolonged treatment times, however the main objective of the study was to evaluate and compare the photocatalytic degradation of PhACs using TiO_2-P25, graphitic carbon nitride (g-C_3N_4), and a heterojunction of perovskite strodium titanate and graphitic carbon nitride $SrTiO_3$/g-C_3N_4. Moreover, nitrate ions and conductivity increased after 180 min of irradiation whereas phosphate ions showed a significant decrease (Konstas et al., 2019). The enhancement of conductivity can be correlated with the increment of mineralization during the photocatalytic process, whereas the decrease in the concentration of phosphate ions indicates their probable absorption on the photocatalysts' surface.

TiO_2 (P-25 Degussa) heterogeneous photocatalysis was evaluated to remove chemical oxygen demand (COD) and amoxicillin (AMX) in real samples collected from the treatment system of the University Hospital of Santa Maria (HUSM). To increase the efficiency of the photocatalytic process, a factorial design was applied for the removal of COD from the hospital wastewater. Slightly acidic conditions were found to be favorable as the semiconductor surface becomes positively charged under pH 6.5, and this increases the adsorption and the degradation efficiency of the anionic species. The efficiency of the process was also enhanced with the increase of catalyst's concentration. In contrast, the influence of temperature in COD reduction efficiency was insignificant. 44% in COD reduction was observed with 800 mg L^{-1}, at pH 3 and 30 °C. Quite similar COD reduction percentages were observed by Vasconcelos et al. (2009), as reported previously. In contrast to the above-mentioned publications, the toxicity evolution during the treatment of HWW was also assessed by Martins et al. (2009). An appreciable reduction of the acute toxicity (by means of the bioassay *Artemia salina*) was achieved. Compared to the effluent LC_{50} without treatment, a toxicity inhibition of 46.3% was achieved by TiO_2 photocatalysis. Amoxicillin was degraded 100% in spiked samples of hospital effluent after treatment by heterogeneous photocatalysis for 30 min adopting the following conditions pH = 4, [TiO_2] = 800 mg L^{-1} and temperature 30 °C (Martins et al., 2009). Removal of Ciprofloxacin (CIP) by TiO_2 mediated photocatalysis has also been investigated by Guney and Sponza (2016) in raw hospital wastewater taken from Dokuz Eylul University Hospital (Izmir, Turkey) under UV light and pH 7. UV light intensity was found to be a significant parameter and an enhancement of removal was observed with increasing UV light intensity from 120 W up to 210 W. This trend was ascribed to an increase in the hydroxyl radical concentration as more photons were absorbed in higher UV light intensities (Guney and Sponza, 2016). Similar to Vasconcelos et al. (2009), high removal of CIP was observed. The main difference between these studies regards the reduction of COD, as 98% removal of COD after 45 min, was reported by Guney and Sponza (2016).

Using TiO_2 nanoparticles the removal of metformin (MTF) and amoxicillin (AMX) (10 mg L^{-1}) in synthetic hospital wastewater was examined under UV-A irradiation and removal over 90% was achieved for both compounds (Chinnaiyan et al., 2019). The removal of sulfamethoxazole (SMX) from actual hospital wastewater (Tehran, Iran)

was studied using TiO_2 (anatase, Sigma-Aldrich) and WO_3 under different irradiation sources UVC (254 nm), UVA (365 nm) and halogen lamps (above 380 nm) (Beheshti et al., 2019). As expected, due to the wide gap band (~3.2 eV) of TiO_2, the photocatalytic process using UVC light and TiO_2 was the most effective and complete removal of SMX was achieved aster 120 min. In contrast, halogen/WO_3 photocatalytic process showed the highest efficiency and 93.96% removal at 160 min was observed. Considering the properties of WO_3 that has small band gap and capability of visible light absorption, the performance of halogen/WO_3 photocatalytic process can be explained (Beheshti et al., 2019).

Photocatalytic process using zirconium dioxide (ZrO_2) and tungsten trioxide (WO_3) nanoparticles have also been investigated for the removal of dexamethasone (DXM) from hospital wastewater (Tehran, Iran) under the above-mentioned irradiation sources Ghenaatgar et al., 2019. Halogen lamp/WO_3 system showed the highest removal efficiency for the removal of dexamethasone (100% after 180 min). In general, the efficiency of the systems followed the order Halogen/WO_3 > UVA/WO_3 > UVC/ZrO_2 > UVA/ZrO_2 > Halogen/ZrO_2 > UVC/WO_3 (Fig. 4).

A synthetic hospital wastewater containing much higher concentrations of pharmaceuticals than those detected in real effluents, (chloramphenicol (CRM) (10 mg L^{-1}), paracetamol (PCT) (10 mg L^{-1}), salicylic acid (SA) (10 mg L^{-1}), sulfamethoxazole (SMX) (10 mg L^{-1}) and diclofenac (DCF) (10 mg L^{-1})) was subjected to photocatalytic treatment using TiO_2 (Sigma Aldrich), TiO_2 and Ag/TiO_2 nanoparticles prepared by sol–gel technique, under simulated solar light irradiation, by Badawy et al. (2014). Ag/TiO_2 with 0.1% Ag (heated at 300 °C for 2 h) was the most efficient photocatalyst and ~ 85% total pharmaceutical degradation was accomplished. Maximum photodegradation rate of the simulated hospital wastewater was obtained using 1000 mg L^{-1} of the photocatalyst with 0.1% Ag/TiO_2 and pH 5. However, it should be noticed that the optimum pH value for the removal of each of the studied pharmaceuticals differentiates and depends on the pKa of the compounds (Badawy et al., 2014).

Triclosan (TCS) and gemfibrozil (GFZ) in raw hospital wastewater from Dokuz Eylul University Hospital (Izmir, Turkey) were investigated with cerium (IV) oxide and titanium (IV) oxide nanoparticles with UV-C irradiation. The effect of photocatalysts concentration, irradiation times, UV light power and hospital wastewater pH on the degradation yield of pharmaceuticals were studied (Sponza and Güney, 2017). All the parameters were found to influence the process significantly. Under the applied experimental conditions (0.25 g L^{-1} catalysts concentration, 120 W UV power and pH 7), 45 min was the optimum irradiation time for the maximum photocatalytic removals of both compounds. Any further increase in irradiation time decreased all the micropollutants' photodegradation rates because of the deactivation of active sites by the deposition of by-products. Increasing the amount of photocatalysts up to a certain level resulted in an increase in the degradation efficiency. In contrast, a slight decrease of the photodegradation yields for both pharmaceuticals were observed with photocatalyst's concentration higher than 0.50 g L^{-1}. A similar trend was noticed for the effect of UV light power. The degradation yields increased significantly when the UV light power was increased from 120 to 210 W, whereas the photodegradation yields for both compounds decreased slightly when UV light power was increased to 300 W. The formation of intermediate by-products which accumulate in the solution and decrease in $HO^{\bullet}$ radical production can explain the lower degradation yields with application of high UV power (300 W). Regarding the pH, the maximum Triclosan (TCS) and gemfibrozil (GFZ) degradation yield was achieved at alkaline pH values and can be explained by the enhanced production of $HO^{\bullet}$ radicals at alkaline conditions.

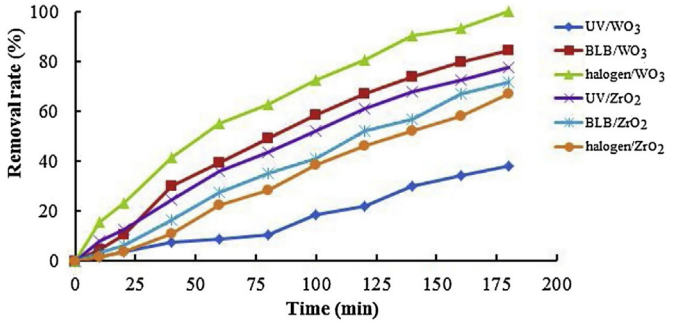

Fig. 4. Removal efficiency of DXM from real hospital wastewater by ZrO_2 and WO_3 through various irradiation sources.
Reproduced with permission from Ghenaatgar et al. (2019).

Under optimum operational conditions (45 min irradiation time, 0.50 g L^{-1} catalyst concentration, 210 W UV light power, pH 8.50 and 25 °C) CeO_2 (97% TCS, 95% GFZ) had a slightly higher photocatalytic activity than TiO_2 (94% TCS, 93% GFZ) to remove these pharmaceuticals. The higher activity of CeO_2 was due to the properties of the oxide i.e. pore volume, average size and pore diameter (Sponza and Güney, 2017).

CdS/TiO_2 heterojunction, hydrothermally prepared, was used as a photocatalyst for the treatment of a simulated hospital wastewater containing ofloxacin (OFC), ketorolac (KTR) and paracetamol (PCT). 48.5% TOC reduction of the solution was observed with CdS/TiO_2 (0.45 g L^{-1}) in 270 min under visible light. Comparing the photocatalytic degradation of mixture at pH 8.05 led to the following order: ofloxacin > ketorolac > paracetamol (Kaur et al., 2018).

An et al. (2016), investigated the performance of carbon-doped TiO_2 as well as zeolite-supported carbon-doped TiO_2 composite catalysts (SiO_2/Al_2O_3 ratio of 18 and 240) towards nine pharmaceutical compounds under solar light irradiation (Terbutaline, Lincomycin, Sulfamethoxazole, Paracetamol, Diclofenac, Metoprolol, Phenazone, Carbamazepine, Clofibric acid). As matrix, hospital wastewater effluent obtained from Maria Middelares Hospital (Ghent, Belgium) was used. Unsupported carbon-doped TiO_2 showed a higher removal for terbutaline, lincomycin, sulfamethoxazole, paracetamol and diclofenac in hospital effluent. Zeolite-supported carbon-doped TiO_2 catalysts (SiO_2/Al_2O_3 ratios of 240) effectively degrade most of the studied pharmaceuticals in the hospital wastewater and combined effects of adsorption and photochemical degradation can be considered (An et al., 2016).

To overcome the difficulties related to separation of catalysts from the treated solution as well as to promote reusability, Malakootian et al. (2020) studied the photocatalytic degradation of ciprofloxacin (CIP) (3 mg L^{-1}) by titanium dioxide nanoparticles immobilized on a glass plate in a hospital wastewater sample from Kerman city in Iran. Under the optimal conditions (pH of 5, contact time of 105 min, 1 g L^{-1} of TiO_2), ciprofloxacin removal efficiency of 86.57% was obtained (Malakootian et al., 2020).

Interestingly, the immobilized TiO_2 showed quite similar performance to TiO_2 nanoparticles in suspension used for the removal of CIP by Vasconcelos et al. (2009) and Guney and Sponza (2016).

Photocatalytic process using TiO_2 nanofiber was assessed by Chong and Jin (2012) as a pre-treatment process to enhance the biodegradability of 5000 μg L^{-1} of carbamazepine (CBZ), in synthetic hospital wastewater. The studied system was capable of removing 78% of CBZ, 40% of COD and 23% of PO_4^{3-} from the influent wastewater within a 4 h reaction time, In contrast, an increase in NO_3^- ions concentration (24%) was observed. Organic degradation by-products with lower molecular weight and easily degradable were also produced indicating that the TiO_2 based system has a high potential to be utilized as an effective pre-treatment system for hospital wastewater (Chong and Jin, 2012).

Another supported photocatalyst, zinc oxide (ZnO) nanoparticles immobilized on a glass plate was used for the photocatalytic degradation of the ciprofloxacin (CIP) in hospital wastewater sample from Kerman city in Iran (Gharaghani and Malakootian, 2017) and presented similar performance with the immobilized TiO_2 on the glass plate

prepared by Malakootian et al. (2020). The prepared immobilized photocatalyst showed relatively high efficiency in removing ciprofloxacin and 90.25% removal was achieved under optimum conditions (pH = 11, reaction time = 90 min, ZnO concentration on the plate = 0.6 g L^{-1} and initial concentration of CIP = 3 mg L^{-1}) (Gharaghani and Malakootian, 2017).

Nano graphene oxide magnetite (Nano-GO/M) particles, which can be easily separated by an external magnetic field and decrease the treatment cost of the process, were used to remove ofloxacin (OFX) (7–10 μg L^{-1}) in raw hospital wastewater from Dokuz Eylul University Hospital (Izmir, Turkey). The maximum pollutant photodegradation yields for COD, BOD_5, TSS, TKN, TP and OFL were 88%, 89%, 82%, 95%, 79%, and 97%, respectively which were obtained with 2 g L^{-1} Nano-GO/M concentration, at pH 7.8 after 60 min irradiation time under 300 W UV power (Sponza and Alicanoglu, 2018).

Similar to the trend reported previously in the study by Sponza and Güney (2017), a higher dosage of the catalyst (5 and 10 g L^{-1}) led to an increase in the suspension turbidity hindering the catalyst's activation. Increasing the UV power from 100 W to 300 W enhanced the removal efficiency as the catalyst absorbs more photons, producing more electron-hole pairs and consequently more hydroxyl radicals. The catalysts showed good reusability for two sequential treatments of pharmaceutical wastewater. According to Turkish Water Pollution Control Regulations after the second treatment of the hospital wastewater, the effluent values of the treated hospital wastewater could be classified as first-class quality and the treated wastewater can be further reused (Sponza and Alicanoglu, 2018).

The removal of different pharmaceuticals, i.e. venlafaxine (VNX), *O*-desmethyl venlafaxine (ODV), amisulpride (AMS), sulfamethoxazole (SMX) and carbamazepine (CBZ) was investigated using graphitic carbon nitride (g-C_3N_4, CN) and a heterojunction of perovskite strontium titanate and graphitic carbon nitride $SrTiO_3$/g-C_3N_4 (20% g-C_3N_4, 20CNSTO) in secondary effluent from the university hospital WWTP (Ioannina city, Epirus region, Greece) under simulated solar light was studied by Konstas et al. (2019). Rate constants of 0.0327, 0.048, 0.0308, 0.0103, 0.0232 min^{-1} were calculated using graphitic carbon nitride (g-C_3N_4) for VNX, ODV, AMS, SMX and CBZ, respectively. The heterojunction of perovskite strontium titanate and graphitic carbon nitride $SrTiO_3$/g-C_3N_4 showed lower photocatalytic performance and rate constants of 0.0038, 0.0040, 0.0153, 0.0035 min^{-1} were determined for venlafaxine, *O*-desmethyl venlafaxine, amisulpride, and carbamazepine, respectively. Similarly, to TiO_2 P25 photocatalytic process studied by the same group and reported previously, COD decreased moderately, phosphate ions showed a decrease and nitrate ions and conductivity increased after 180 min of irradiation. A comparison between the employed catalysts revealed that TiO_2 and CN presented higher photocatalytic performance than 20CNSTO in all cases with CN presenting similar or better degradation rates that TiO_2, depending on the pharmaceutical compound (Fig. 5) (Konstas et al., 2019).

The photocatalytic degradation of two typical β-lactam antibiotics, amoxicillin (AMX) and cefotaxime (CFX), was also studied using mesoporous carbon nitride synthesized by a template-free method. The studied system showed ~60% and ~ 90% removal at 60 min for amoxicillin and cefotaxime, respectively. A partial TOC and COD removal was also observed (Dou et al., 2020).

The degradation of tetracycline (TC) from hospital wastewater by g-C_3N_4 and Ag-doped g-C_3N_4 were carried out under solar light experiments. The TC (48.6 mg L^{-1}) removal efficiency of g-C_3N_4 and The Ag-doped g-C_3N_4 (fortification with 3 mmol $AgNO_3$) were 52.8% and 89.6%, respectively (Minh Tri et al., 2019).

An efficient ternary Ag/TiO_2/mesoporous g-C_3N_4 (1.94 wt%) photocatalyst was also successfully synthesized by Gao et al. (2020) and the removal of another antibiotic, amoxicillin (AMX) was studied under visible light. In hospital wastewater with a COD background of 55.2 mg L^{-1}, AMX was removed at about 71% (Gao et al., 2020). A higher removal of the same antibiotic (AMX) was observed by Martins et al. (2009) using TiO_2 P-25 Degussa as photocatalyst and initial concentration of AMX equal to 0.1 mg L^{-1}.

Taking into account all above results, bare TiO_2 (P25 or anatase) and doped or heterojuncted TiO_2 materials have received the great part of applications for HWW so far, while the application of alternative catalysts such as g-C_3N_4, g-C_3N_4/$SrTiO_3$, CeO_2, ZnO, ZrO_2, and WO_3, started to be studied very lately. Variations in photocatalytic efficiency can be explained by the differences in morphology, crystal phase, specific surface area-porosity, surface charge, and band gap. Catalyst loadings in the range 100–2000 mg L^{-1}, closely neutral or inherent pH conditions and environmental conditions are usually followed. Water matrix is significantly affected the process efficiency in most cases. Most studies target on specific compounds and limited information is available on the efficiency of this process for the removal of pharmaceuticals in mixtures with different concentration levels, as usually detected, particularly in real wastewater matrices. With the reservations of making comparisons between processes performed under different experimental conditions, heterogeneous systems presented similar efficiencies in degradation of pharmaceutical compounds but needed longer irradiation times for reduction of TOC/COD levels.

3.3. Homogeneous vs heterogeneous AOPs

In the previous sections, homogeneous and heterogeneous photochemical AOPs were discussed concerning the treatment of hospital wastewater for PhACs' removal. Depending on the process, several advantages as well as drawbacks exist not only in terms of efficiency but also environmental impact, cost, feasibility, as well as reliability. Nevertheless, the application of hybrid technologies is possible to minimize some disadvantages and improve the efficiency of PhACs removal (Maniakova et al., 2020; Phoon et al., 2020). Concerning photo-Fenton process, to overcome the low pH drawback, different processes have been applied such as homo/heterogeneous photo-Fenton, by using modified F(III)-alginate spheres (Cuervo Lumbaque et al., 2019) or the addition of complexing agents, such as citric acid (Perini et al., 2018), avoiding metal precipitation and making the process efficient even at neutral pH. Photo-Fenton process is an environmentally friendly application since applies Fe as a catalyst, which is low toxic and highly abundant. Additionally, the cost of H_2O_2 is lower than other oxidants (Phoon et al., 2020). Nevertheless, in some cases the use of excessive oxidant concentration can induce antagonistic reactions and thus the formation of radicals which are less reactive than the hydroxyl radicals (Rizzo et al., 2019). Furthermore, it was found that the presence of inorganic anions (such as carbonate, chlorides, sulfates) in wastewater, might influence the degradation rates of emerging contaminants in photo-Fenton process, by consuming hydroxyl radicals (Michael et al., 2012). Despite the above limitations, photo-Fenton has reported to efficiently operate under natural solar irradiation, therefore the development and application of concentrating parabolic collectors (CPCs), for the removal of emerging contaminants in wastewaters has reinforced, thus lowering the operational costs and providing a major step towards full-scale application (Rizzo et al., 2019; Mirzaei et al., 2017).

On the other hand, major drawbacks of heterogeneous photocatalysis is the rate of recombination and light absorption wavelength. Catalysts such as TiO_2 and ZnO are more photoactive in UV regions due to the wide bandgap (Phoon et al., 2020; Beheshti et al., 2019). Therefore, solar heterogeneous photocatalysis is known to be less effective than solar photo-Fenton, since photocatalysts such as TiO_2 have found to be less efficient under solar light sources (Maniakova et al., 2020). Nevertheless, different approaches have been developed to broaden the absorption of TiO_2 towards the visible region and improve the efficiency. These approaches also include TiO_2 doping by non-metallic species, such as nitrogen (Rizzo et al., 2019). In addition, although most of the photocatalysts applied are cheap, non-toxic and have good stability in the aqueous solution, those that are used in powder form, require an additional treatment after the

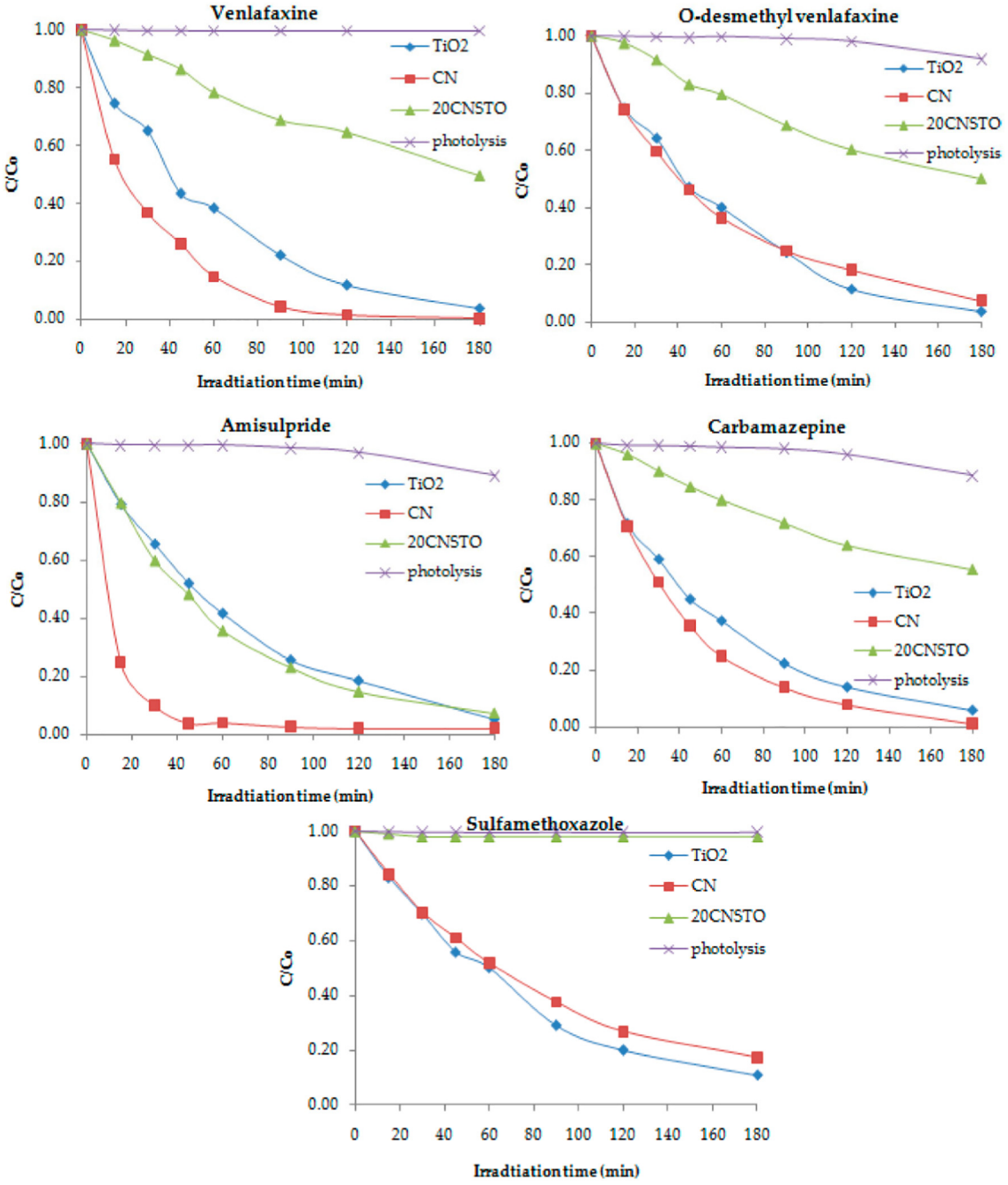

Fig. 5. Photolytic and photocatalytic degradation of PhACs versus irradiation time in hospital wastewater effluent using TiO_2, CN and 20CNSTO. Reproduced from Konstas et al. (2019).

process, increasing the cost of the treatment. To overcome this, efficient recovery and reasonable recyclability of photocatalysts has been achieved the last years (Maniakova et al., 2020; Rizzo et al., 2019), such as the application of photocatalytic membranes systems (i.e. TiO_2 modified ceramic membranes and graphene oxide-based ultrafiltration membranes) (Rizzo et al., 2019) or TiO_2 nanoparticles immobilized on a glass plate (Malakootian et al., 2020). In view of the above, in Table S1 a comparison regarding the degradation of PhACs in real and synthetic hospital wastewaters between the two processes, using solar and artificial irradiation, is shown. Concerning photo-Fenton process the pH applied ranged between 2.5 and 7.9, while in photocatalysis broader range of pH values were applied between 3 and 11. In both processes most studies used artificial irradiation, indicating the requirement for conducting more studies on hospital wastewaters applying solar irradiation. Taking into consideration the fact that different experimental conditions were applied in each case, a cautious comparison between the removals of PhACs indicates that under photo-Fenton process removals ranged between 20 and 100%, while in photocatalysis between 0 and 100%.

3.4. Hybrid systems - integration of photocatalysis to other processes

The hybrid systems are considered as an attractive potential alternative for development of technically and economically feasible wastewater treatment technologies. In this context, the combination of heterogeneous and homogeneous photocatalysis as well as their integration with other processes has been tested for the treatment of real

hospital wastewater. Representative hybrid systems that have been used up to now are reported in the following part.

The combination of heterogeneous and homogeneous photocatalytic degradation to remove pollutants, present in HWW, was investigated, by evaluating three different processes (Adish Kumar et al., 2014). The tests were performed with primary treated wastewater (collected at the outlet of the plain sedimentation tank) and the three processes included solar/TiO_2/H_2O_2, solar/Fe^{2+}/H_2O_2 and solar/TiO_2/Fe^{2+}/H_2O_2. Various parameters were tested in each case such as effect of pH, TiO_2 dosage, Fe^{2+} dosage, H_2O_2 concentrations, contact time and biodegradability. Under the optimum condition, a 4-h treatment enhanced the biodegradability value to 0.6 in both solar/TiO_2/H_2O_2 and solar/Fe^{2+}/H_2O_2 treatment, while a 1-h treatment of solar/TiO_2/Fe^{2+}/H_2O_2 enhanced biodegradability value to 0.7. The order of rate constants was solar/TiO_2/Fe^{2+}/H_2O_2 (0.771 h^{-1}) > solar/Fe^{2+}/H_2O_2 (0.274 h^{-1}) > solar/TiO_2/H_2O_2 (0.253 h^{-1}). The solar/TiO_2/Fe^{2+}/H_2O_2 process displayed increased efficiency due to the synergetic effect of homogeneous and heterogeneous photocatalytic reaction (1.5 times more efficient than the individual processes) by decreasing the reaction time of the separate operations and decreasing also the cost of treatment. In this case, the optimal conditions enabling over 99% reduction of COD were pH = 7; $[Fe^{2+}]$ = 0.5 g L^{-1}; $[TiO_2]$ = 0.2 g L^{-1} and $[H_2O_2]$ = 1.35 g L^{-1}. Furthermore, the effluent COD and total suspended solids concentrations were 20 and 30 mg L^{-1}, respectively, which met the discharge standard requirements (Adish Kumar et al., 2014).

The combination of photocatalytic oxidation and ozonation was found to enhance the system efficiency and achieve the complete removal of the contaminants with the parallel reduce of the ozone demand and energy requirements (Machado et al., 2007; Quiñones et al., 2015a; Zazouli et al., 2018).

Kinetic studies on the removal of six commonly detected ECs, including five PhACs, acetaminophen (ACE), antipyrine (ANT), caffeine (CAF), metoprolol (MTP), testosterone (TST) and bisphenol A (BIS), in aqueous solutions, using ultrapure water, were studied by Quiñones et al. (2015a). Experiments were carried out in a compound parabolic collector photoreactor (CPC) by applying different solar-driven photochemical processes i.e. photocatalytic oxidation with Fe(III) or TiO_2, photo-Fenton and photocatalytic ozonation. Quiñones et al. (2015a) studied also the effect of the presence of inorganic compounds in the aqueous matrix, such as nitrate, phosphate, chloride, carbonate and sulfate ions, by adding them into the aqueous solution at concentration levels commonly found in WWTP effluents. Thus, concentrations of Cl^- = 79 mg L^{-1}, SO_4^{2-} = 107 mg L^{-1}, CO_3^{2-} = 270 mg L^{-1}, NO_3^- = 55 mg L^{-1} and PO_4^{3-} = 6 mg L^{-1} were added in ultrapure water and the AOPs applied were Fe(III)/H_2O_2/O_3/hν/pH = 3 and TiO_2/O_3/hν/pH = 7. Furthermore, initial concentration of each emerging contaminant (EC) was 10^{-5} mol L^{-1} (i.e., in mg L^{-1}, 1.51 ACE, 1.88 ANT, 2.28 BIS, 1.94 CAF, 2.67 MTP and 2.88 TST). Initial Fe (III) and TiO_2 concentrations were 2.79 and 200 mg L^{-1}, respectively, initial H_2O_2/Fe(III) mass ratio was 6.09, while initial ozone concentration was 13 mg L^{-1}. The results revealed that ionic species seemed to induce negative effect. When TiO_2/O_3/hν/pH = 7 system was applied, removal of ECs at 99% was delayed for about 20 min compared to ultrapure water, also decreasing their mineralization rate. This decrease showed that in the TiO_2-based systems the presence of the selected anions reduces the active surface of the semiconductor exerting a scavenging effect on radical production. Similar results were obtained by the Fe(III)/H_2O_2/O_3/hv/pH = 3 system. Nevertheless, photo-Fenton photocatalytic ozonation was found to be more efficient than the corresponding TiO_2 system (Quiñones et al., 2015a).

UV/TiO_2 process with the commercial catalyst Degussa P25 was also combined with ozonation for the treatment of a secondary wastewater collected from a regional hospital located in the Vale do Rio Pardo (State of Rio Grande do Sul, Brazil). The sole photocatalytic process showed moderate efficiency, eliminating slightly the turbidity, decreasing COD from 767 mg L^{-1} to 730 mg L^{-1} and reducing MPN/100 mL of 1.1×10^6 to 40. However, the addition of ozone (UV/TiO_2/O_3) can result in total detoxification and disinfection of the effluent as well as in enhancement of its biodegradability (Machado et al., 2007).

Another interesting option concerning the treatment of HWW is the combination of biological treatment, which typically removes macrocomponents (e.g. sugars, peptides, or lipids), with sonochemistry which can degrade recalcitrant PhACs from water. Serna-Galvis et al. (2019), in order to improve the above AOP in real effluent HWW, added ferrous ions and UVC irradiation and promoted an in-situ photo-Fenton process (named sono-photo-Fenton) consuming the sonogenerated H_2O_2 (Serna-Galvis et al., 2019). Thus, the degradation of fifteen PhACs in inherent concentrations of HWW effluent was studied, under a biological process (BP)/sono-photo-Fenton system. Initial concentrations were: acetaminophen (293.8 μg L^{-1}), diclofenac (0.04 μg L^{-1}), carbamazepine (1.9 μg L^{-1}), venlafaxine (0.0015 μg L^{-1}), loratadine (8.1 μg L^{-1}), ciprofloxacin (10.7 μg L^{-1}), norfloxacin (3.9 μg L^{-1}), valsartan (17.7 μg L^{-1}), irbesartan (0.05 μg L^{-1}), sulfamethoxazole (0.001 μg L^{-1}), trimethoprim (0.03 μg L^{-1}), clarithromycin (23.4 μg L^{-1}), azithromycin (27.9 μg L^{-1}), erythromycin (0.36 μg L^{-1}) and clindamycin (25.4 μg L^{-1}). First, after the BP stage most of the PhACs presented very low removals. Specifically, an enhancement on the concentrations of norfloxacin, ciprofloxacin and clarithromycin was observed, probably due to the deconjugation of metabolites to liberate the parent compound or the release of PhACs from suspended solids, while only acetaminophen and valsartan were significantly removed after 36 h of bio-treatment, due to their bio-transformation and/or adsorption on sludge flocs generated in BP. Afterwards, the resultant water from the BP was submitted to the sono-photo-Fenton system (addition of ferrous ions and UVC light to the ultrasonic reactor) which required no addition of H_2O_2 since it is initially formed in the sonochemical process. The sono-photo-Fenton reaction time was 90 min and finally, the results showed that even at first 30 min of treatment a strong degradation of all PhACs was observed. Degradation percentage of the studied PhACs after 90 min ranged between 33.77% for erythromycin and 100% for diclofenac, carbamazepine, venlafaxine, sulfamethoxazole, trimethoprim and irbesartan, while their average degradation was 85.82%. Furthermore, the BP-sono-photo-Fenton system eliminated 91.13% of the initial PhACs load, suggesting that the BP/sono-photo-Fenton combination is a powerful alternative for the treatment of complex matrices such as HWW (Serna-Galvis et al., 2019).

In a recent work, the feasibility of the Catalytic Wet Peroxide Oxidation (CWPO)-Photoassisted process for the on-site treatment of real hospital wastewaters using the low-cost mineral ilmenite was proved by García-Muñoz et al. (2017). The combined process was able to remove sulfamethoxazole in hospital wastewater matrix [Ilmenite] = 1000 mg L^{-1}; $[H_2O_2]_0$ = 780 mg L^{-1}; T = 30 °C; pH = 3). High TOC and COD removals (above 80%) were also achieved operating at 50 °C with a catalyst load of 1 g L^{-1} and the stoichiometric amount of H_2O_2. The high efficiency of this process can be related to the combination of both systems (CWPO and photocatalysis). Fast transformation of the organic pollutants into hydroxylated species by CWPO, followed by their degradation to short-chain organic molecules and their subsequent mineralization applying photocatalysis can be considered (García-Muñoz et al., 2017).

3.5. Photocatalytic reactor systems and scale-up

The light source, design and configuration of a reactor are crucial factors for the performance of the photocatalytic reaction (Koe et al., 2020). Depending on the light source, reactors are classified based on artificial light sources, with different types (i.e. conventional high or low pressure lamps, light emitting diodes, optical fibers) or emitting light (i.e. ultraviolet, visible, simulated solar), and natural solar light irradiation. In addition, based on the catalyst, they can be classified as homogeneous (photo-Fenton) and heterogeneous systems (TiO_2 based and non-TiO_2

based systems; suspended or immobilized). Moreover, further classification of the reactors is based on batch, continuous or batch recirculation mode or by their hydrodynamic regime (Sundar and Kanmani, 2020). Reactors that are used for small sample volumes (less than 1 L) are classified as lab-scale reactors, while unit operation reactors applied in wastewater treatment plants are pilot or large scale demonstrations which use solar or artificial light simulated irradiation (Abdel-Maksoud et al., 2016). Most of the studies reviewed here-in (see Tables 1-2) dealing with lab-scale reactors operated at batch or batch recirculation mode while few studies referred to pilot or large scale photocatalytic reactors.

Concerning the photoreactors that apply artificial light as a source (see Tables 1-2), the most common artificial light sources can be further classified into low-pressure lamps (254 nm), fluorescent lamps (~365 nm), medium-pressure lamp (UV–visible range), high-pressure lamp (UV). Among them, the fluorescent lamp is mostly recommended since it is cost-effective without consuming much power and produce desired quantum yield of degradation (Koe et al., 2020). In addition, for simulated solar light irradiation Xe-arc lamps are mostly used. Finally, studies with LED lamps are lacking and should be performed in the future.

As for photoreactors that apply solar irradiation concern, Parabolic Trough Reactor (PTR) was the first solar reactor which was developed by Plataforma Solar de Almeria (PSA) in Spain and National Renewable Energy Laboratory (NREL), California (US) in the early nineties (Sundar and Kanmani, 2020). The PTR is a modification of conventional photoreactor which consists of transparent trough tube for the flow of wastewater while the surface of the collectors is reflective and parabolic. These features enable the solar radiation to be concentrated on the collectors along the parabolic focal line (Koe et al., 2020). Afterwards, several solar photocatalytic reactors were design and constructed based on PTR (Sundar and Kanmani, 2020). The Compound Parabolic Concentrator (CPC) photoreactor, the design of which is modified from the PTR, is very popular and it's a static reactor which consists of a number of pyrex tubes connected in series and irradiated by concentrated solar light transmitted by the parabolic reflective surface (Sacco et al., 2020). Further solar photocatalytic reactors include the Falling Film Reactor – often referred to as Thin-Film Fixed-Bed Reactor (TFFBR), Double Skin Dheet Reactor (DSSR), Concentrating Falling Film Reactor, Tubular Reactor, Shallow Pond Reactor, Flat Plate Reactor, Falling Film Photoreactor, Thin Film Cascade Photoreactor, Step Photoreactor, Fountain Photocatalytic Reactor, Slurry Bubble Column Reactor, Flat Plate Column Reactor, Pebble Bed Photoreactor and Flat Packed Bed Reactor (Abdel-Maksoud et al., 2016; Horikoshi and Serpone, 2020). In a recent review articles, Sundar and Kanmani (2020), presented the advancements of photocataytic reactors through three decades while Sacco et al. (2020) reviewed the parameters influencing the design of photocatalytic reactors for wastewater treatment.

CPC reactor, that is currently the most used for hospital (see Tables 1-2) and municipal wastewaters, possess excellent characteristics of both parabolic concentrator and static flat system. Unlike PTR, the CPC does not have solar tracking system and rotating motor. In addition, its collectors consist of two halved cylinders of parabolic profiles aligned with each other. The parabolic geometry of the collectors captures both direct and diffuse sunlight, reflecting and distributing them onto the receiver tube, thus CPC reactor can function during cloudy days. Moreover, the quantum efficiency is promoted due to the reduction of electron-hole recombination when the photon concentration is high. The only drawback concerning CPC is the concentration of the dissolved oxygen in the reaction tubes for redox reaction, since it consists a closed system (Koe et al., 2020). An example of a solar photocatalytic CPC reactor plant was developed for SOLARDETOX project in HIDROCEN, Madrid and it is a fully automated plant that can treat 1000 L of water (Horikoshi and Serpone, 2020). In addition, a homogeneous solar photocatalytic plant at pre-industrial scale for the pretreatment of saline industrial wastewater containing pharmaceuticals is used by a Spanish pharmaceutical company (Sacco et al., 2020). Furthermore, concerning PhACs removal from wastewaters Klamerth et al. (2010) studied in an extended research, the degradation of 15 ECs, including 12 PhACs of different chemical families, (Acetaminophen (ACE), Antipyrine (ANT), Caffeine (CAF), Carbamazepine (CBZ), Diclofenac (DCF), Flumequine (FLQ), Ibuprofen (IBU), Ketorolac (KET), Ofloxacin (OFX), Progesterone (PRGS), Sulfamethoxazole (SMX) and Triclosan (TCS)), by photo-Fenton without pH adjustment (pH = 7.8), using simulated municipal effluent (SE) and real effluent municipal wastewater (RE) in the Plataforma Solar de Almería in a pilot compound parabolic collector (CPC) solar plant. The experiments were conducted in a "normalized illumination time" t_{30W} which refers to a constant solar UV power of 30 W m^{-2}, the typical solar UV power on a perfectly sunny day around noon, and the results revealed higher degradation in SE (Klamerth et al., 2010).

One of the main problems in photocatalytic reaction engineering is providing a methodology for the photoreactor scale-up. Therefore, there are some significant parameters that must be considered for the development of a photoreactor pointed for wastewater treatment such as the irradiation source, the mode of operation, the geometry, the configuration, the photocatalyst, the phases present in the reactor, the hydrodynamic behavior and the operative conditions (Sacco et al., 2020). The parameter that is commonly used for scale-up is the $E_{E/O}$, which represents the electrical energy (given in kWh) required to remove a pollutant by one order of magnitude (90%) in 1 m^3 of polluted water (Sacco et al., 2020). Nevertheless, the lack of such comparison among different photocatalytic systems but also between photocatalysis and other AOPs still limit the scale-up of photocatalytic systems. Finally, a standard photocatalytic reactor type and configuration should be proposed in order to make the appropriate comparisons and permit applications in various scales while matrix-matched designing factors related to light attenuation, scavenging, pH etc. of the treated matrix should be considered.

4. Toxicity

Since the generation of toxic TPs can occur during the photocatalytic degradation of PhACs before mineralization, the evaluation of treated wastewater effluent toxicity is of high importance. However, the studies investigating simultaneously the photocatalytic degradation of PhACs and the toxicity of their TPs in real and synthetic hospital wastewater are limited. The existing research results on the toxicity evolution during the photocatalytic treatment of HWW and photocatalytic degradation of PhACs in real and synthetic HWW has been compiled in Table 3. Bioassays with bacteria such as *Vibrio fischeri* or crustaceans such as *Artemia salina* as well as computational approaches, i.e. Toxtree software, have been applied for the toxicity evaluation (Cuervo Lumbaque et al., 2019; Martins et al., 2009; Kajitvichyanukul and Suntronvipart, 2006). As reported in the majority of the studies, after the photocatalytic treatment, the toxicity generally decreases (Martins et al., 2009; Kajitvichyanukul and Suntronvipart, 2006). In most cases, reduction of the toxicity over 43.5% was achieved (Martins et al., 2009; Kajitvichyanukul and Suntronvipart, 2006). In contrast, the generation of more toxic by-products than the parental compounds has been reported by Cuervo Lumbaque et al. (2019). A comparison study between homogeneous and heterogeneous photocatalysis revealed similar toxicity reduction in both processes (Martins et al., 2009). The use of an integrated system ($UV/TiO_2/O_3$) also showed potential capacity for detoxification of hospital wastewater effluents, decreasing toxicity to nontoxic levels (Machado et al., 2007).

Based on the available literature data, it can be suggested that photocatalysis can be a promising treatment method for the treatment of HWW and the degradation of PhACs in this matrix. However, comprehensive studies focusing on the evaluation of toxicity during the application of the process, using a battery of bioassays should be

Table 3
Assays applied for the assessment of toxicity during the photocatalytic treatment of HWW and photocatalytic degradation of PhACs in real and synthetic hospital wastewaters.

Process	Experimental Conditions	Type of the water	Toxicity assessment	Main outcomes	Reference
Photo-Fenton	Homemade bench scale photoreactor (Dewar-like photoreactor)/125 W Philips medium pressure mercury lamp pH = 3; $[Fe^{2+}]_0$ = 255 mg L^{-1}; $[H_2O_2]_0$ = 528 mg L^{-1}; Temperature = 30 °C; Reaction time = 60 min	Real hospital effluent (University Hospital of Santa Maria (HUSM), Brazil: COD = 420 ± l 7 mg L^{-1}; Amoxicillin = 27 ± 11 μg L^{-1} (n = 3); Chloride = 132 ± l 4 mg L^{-1}; Potassium = 21.9 ± l 0.3 mg L^{-1}; Total phosphate = 7.73 ± l 0.03 mg L^{-1}; Sodium = 150.5 ± l 4.0 mg L^{-1}; TSS = 484 ± l 1 mg L^{-1}; pH = 7	*Artemia salina*	The initial value of inhibition was 100% for the untreated wastewater. After the treatment, a toxicity inhibition of 43.5% was achieved.	Martins et al. (2009)
Photo-Fenton	Cylindrical quartz reactor/UV lamps 10 W (λ_{max} = 254 nm) pH = 3; [COD]:$[H_2O_2]$:$[Fe^{2+}]$ = 1:1:0.1; Temperature = 25–31 °C; Reaction time = 120 min	Real hospital effluents (Bangkok, Thailand): COD = 450–4500 mg L^{-1}	*Vibrio fischeri*	The inhibition percentage rises from 10.51% at 450 mg L^{-1} initial COD concentration to 18.25%, 28.3% and 45.2% for the initial respective COD values of 900, 1350, and 2250 mg L^{-1}. An inhibition percentage of higher than 50% was found for the rest of the conditions.	Kajitvichyanukul and Suntronvipart (2006)
Photo-Fenton	Solar batch photoreactor pH 5.0; [Fe(III)-alginate spheres]$_0$ = 3 g; $[H_2O_2]_0$ = 25 mg L^{-1} with additions at 0, 61, 88, and 117 min; Reaction time = 177 min	(i) Simulated hospital wastewater (SW) Peptone = 160 mg L^{-1}; Beef extract = 110 mg L^{-1}; Urea = 30 mg L^{-1}; $MgSO_4 \cdot 7H_2O$ = 2 mg L^{-1}; $CaCl_2 \cdot 2H_2O$ = 4 mg L^{-1}). (ii)Raw hospital wastewater (RHW) (Brazil) pH=; 8.98, Chloride = 49.1 mg L^{-1}; Conductivity = 722 μS cm^{-1}, BOD = 69 mg $L^{-1}$of O_2; DOC = 67.56 mg L^{-1}, COD = 217 mg L^{-1} of O_2; Phosphate = 9.45 mg L^{-1}; TSS = 67 mg L^{-1}; TS = 261 mg L^{-1} (Both wastewaters: $[Nimesulide]_0$ < 500 μg L^{-1} $[Furosemide]_0$ < 500 μg L^{-1} $[Paracetamol]_0$ < 500 μg L^{-1} $[Propranolol]_0$ < 500 μg L^{-1} $[Dipyrone]_0$ < 500 μg L^{-1} $[Fluoxetine]_0$ < 500 μg L^{-1} $[Progesterone]_0$ < 500 μg L^{-1} $[Diazepam]_0$ < 500 μg L^{-1})	Toxtree software (v. 2.6.13) for the evaluation of the toxicological hazard (Cramer rules) of the TPs	Most of the Identified TPs showed significant toxicity or the presence of reactive functional groups, and were therefore classified as highly toxic, according to the Cramer rules.	Cuervo Lumbaque et al. (2019)
TiO_2 photocatalysis	Homemade bench scale photoreactor (Dewar-like photoreactor)/125 W Philips medium pressure mercury lamp pH = 3; $[TiO_2]_0$ = 800 mgL^{-1}; Temperature = 30 °C; Reaction time = 60 min	Real hospital effluent (University Hospital of Santa Maria (HUSM), Brazil: COD = 420 ± l 7 mg L^{-1}; Amoxicillin = 27 ± 11 μg L^{-1} (n = 3); Chloride = 132 ± l 4 mg L^{-1}; Potassium = 21.9 ± l 0.3 mg L^{-1}; Total phosphate = 7.73 ± l 0.03 mg L^{-1}; Sodium = 150.5 ± l 4.0 mg L^{-1}; TSS = 484 ± l 1 mg L^{-1}; pH = 7	*Artemia salina*	The initial value of inhibition was higher than 95% for the untreated wastewater. After the treatment, a toxicity inhibition of 46.3% was achieved.	Martins et al. (2009)

conducted in the future. Toxicity assessment can be a useful tool to optimize the photocatalytic treatment as can indicate the possible formation of toxic TPs or the detoxification of the treated wastewater, which is of high significance in practical applications.

5. Operational costs

Limited economic data about operation costs are available in the literature. Adish Kumar et al. (2014) estimated the cost of treatment including direct costs (reactor civil works, piping and tanks, auxiliary equipment) indirect costs (contingences and spare parts) and annual costs (consumables, operation, and maintenance) for three processes: solar/TiO_2/H_2O_2, solar/Fe^{2+}/H_2O_2 and solar/TiO_2/Fe^{2+}/H_2O_2. The primary treated wastewater (collected at the outlet of the plain sedimentation tank) used in this study showed COD and BOD_3 values equal to 1400 ± 500 and 300 ± 50 mg L^{-1}, respectively. Thus, the treatment costs were estimated to be 26.97 €/m^3, 14.39 €/m^3 and 10.22 €/m^3 for solar/TiO_2/H_2O_2, solar/Fe^{2+}/H_2O_2 and solar/TiO_2/Fe^{2+}/H_2O_2 processes, respectively (Adish Kumar et al., 2014). The combined process (solar/TiO_2/Fe^{2+}/H_2O_2) was found to be the most effective as enhanced the oxidation and biodegradability of the wastewater in less time, reducing simultaneously the cost of the treatment.

For photo-Fenton process, comparing different reactor types, removal efficiency of a pharmaceutical mixture increased from 0.26 mg kJ^{-1} in the CPC reactors to 1.07 mg kJ^{-1} with 15-cm-deep raceway pond reactors (PRP) (De la Obra et al., 2017). Although

pharmaceutical removal efficiency in terms only of degraded micropollutant mass per kJ of solar UV energy incident on the reactor surface was improved, economic analysis was not conducted.

Regarding the irradiation sources and as expected, the operating costs (€/m^3) are considerably lower for the solar process thus, in this case the expenses for the reagents can be considered as the main cost (Durán et al., 2013). The cost of hydrogen peroxide, iron (II) sulfate, oxalic acid and sulfuric acid was estimated to be 0.5 €/L, 0.75 €/kg, 2.6 €/kg and 0.183 €/L, respectively (Durán et al., 2013).

In contrast, in photo-Fenton process using UV lamps for wastewater detoxification, the electrical consumption of sources was found to contribute significantly to the operational and maintenance cost of the treatment (1.2–1.73 €/m^3 and 0.28–1.25€/m^3 when medium pressure (MP) and low pressure (LP) lamps were used, respectively) (Rueda-Marquez et al., 2020b).

In a recent study by Cabrera Reina et al. (2020) an economical assessment of solar photo-Fenton in three cities (Tabernas -Spain-, Arica -Chile- and Doha -Qatar-) with good solar conditions but different climate characteristics, for the treatment of paracetamol contaminated wastewater (DOC = 100 mg L^{-1}, Fe(II) = 20 mg L^{-1}, H_2O_2 = 1200 mg L^{-1}), was conducted with 75% of mineralization being the treatment target. Based on yearly averages, the lowest total costs were found for Doha (2.23 €/m^3), mainly due to the higher average temperatures of this location, Arica followed with 2.45 €/m^3 and Tabernas with 2.67 €/m^3. The total costs were slightly higher and values of 2.29 €/m^3, 2.55 €/m^3 and 3.11 €/m^3 were estimated for Doha, Arica and Tabernas respectively, for the most unfavorable monthly ambient conditions. According to their results (i) cost breakdowns were analogous independent of scaling-up method and location and (ii) amortization costs more influenced by location than operation costs (Cabrera Reina et al., 2020).

Regarding heterogeneous photocatalysis with TiO_2, high operation costs has been estimated up to now that are increased when the catalyst in suspension is used (Durán et al., 2018). In general, homogeneous photo-Fenton is a more economically feasible process, especially with the presence of ferrioxalate (up to 43.5 g TOC removed/€), than heterogeneous photocatalysis even with the use of photovoltaic panels and drum reactors (5 g TOC removed/€). Quiñones et al. (2015b) estimated operating costs of 0.80 €/m^3 and 1.68 €/m^3 for the treatment of a secondary effluent from a municipal wastewater treatment plant containing acetaminophen, antipyrine, bisphenol A, caffeine, metoprolol and testosterone for the complete removal of ECs and 20% reduction of TOC, respectively by a solar photo-Fenton process. The application of the solar photocatalytic systems using TiO_2 as catalyst increases significantly the cost (2.57€/m^3 and 1.92 €/m^3 for the complete removal of ECs and the 20% reduction of TOC, respectively). However, the neutral pH in heterogeneous process is a major advantage and the development of new reactors and modified efficient photocatalysts can render it in an applicable technology in the next years (Durán et al., 2018). A comparative study showed that heterogeneous photocatalysis using UV-A lamps needs 2.7 times more electrical energy per gram of demineralized sulfamethazine than the process used UV-C irradiation. Nevertheless, natural UV-A solar radiation could be used, which significantly decreases the overall cost of the treatment (Babic et al., 2015). It is worth mentioning that a significant reduction of the cost can be achieved by minimizing the reaction time to the time needed to succeed sufficient high biodegradability and toxicity decrease of the treated wastewater.

Finally, for other heterogeneous catalysts, i.e. nano-graphene oxide/magnetite composite, cost analysis was carried out for the photodegradation of 1 L hospital wastewater (COD = 630 mg L^{-1}; BOD_5 = 260 mg L^{-1}) using 2000 mg L^{-1} of catalyst under 300 W UV light and the total cost was estimated to be 80.65 €. More specifically, electricity, 10 UV lamps and catalyst cost were calculated to be 0.014 €, 76.20 € and 4.40 € for the treatment of 1 L = 0.001 m^3 HWW (Sponza and Alicanoglu, 2018).

Electrical energy is a major fraction of the operating costs of both heterogeneous photocatalysis and photo-Fenton due to their nature. In general, the electrical energy consumption is influenced by various experimental factors such as type of pollutant, water matrix, oxidant or catalyst dose, configuration of the reactor, type of light source etc. Process specific energy consumption is estimated with the Electrical Energy per Order, E_{EO} (kWh/m^3/order), which is defined as the electrical energy in kWh required to degrade a pollutant by one order of magnitude in 1 m^3 of contaminated water (Bolton et al., 2001; Lam et al., 2018). Photocatalysis for PhCs removal has EEO values ranging from ~25 kWh/m^3/order to ~13,000 kWh/m^3/order (Majumder et al., 2019). In general, UV-based photocatalysis presents median E_{EO} values >100 kWh/m^3/order for the removal of various organic contaminants and is not characterized as an energy efficient AOP up to now (Miklos et al., 2018). However, upon the proper optimization of process's parameters, the values of EEO can be significantly decreased and can be up scaled (Majumder et al., 2019). Upon removal of PhCs by photo-Fenton, EEO values from ~0.7 kWh/m^3/order to ~22,146 kWh/m^3/order have been calculated (Majumder et al., 2019). In case of photo-Fenton a median EEO value of 2.6 kWh/m^3 has been reported during the removal of various organic contaminants (Miklos et al., 2018), rendering this process a more attractive option for up-scaling.

6. Knowledge gap and future research

The present review has highlighted the potential application of both homogeneous and heterogeneous photocatalysis for the removal of pharmaceuticals in real and synthetic hospital wastewaters. Despite the efficiency and progress made in the photocatalytic degradation of pharmaceuticals, there are many issues and crucial challenges that should be addressed in future works in order to receive applications at lager scale deployment.

Regarding photo-Fenton process, one of the main drawbacks remain the low pH that is generally regarded as not economically feasible for application on full scale (taking into account also the subsequent neutralization of water and separation of generated sludge). As a result, further research efforts should be oriented to the application of photo-Fenton reaction under circumneutral pH (6.5–7.5) using naturally or chemically synthesized chelating agents, forming dissolved organic complexes of iron or alternatively solid-phase processes. In these cases, the assessment of chelate agents for secondary pollution (e.g. eutrophication) as well as toxicity should be also incorporate in the objectives of future studies. Toxicity should be carefully investigated using a battery of bioassays at various trophic levels after the removal of residual H_2O_2 concentrations as well as the effect of chelating agents. The formation of more toxic transformation products during the photo-Fenton process than parent compounds and their possible additive or synergetic effect should be further investigated. Applications of other promising and highly efficient Fenton-based technologies such as electro-Fenton (EF) and photo-electro-Fenton (PEF) as well as other homogeneous photocatalytic processes based on sulfate radicals for the treatment of hospital effluents are lacking and should be considered for future research.

The identification of transformation products, the evolution of toxicity during the process and the quality of the treated effluents are crucial aspects that should also be further investigated during the application of heterogeneous photocatalysis, giving a better understanding on its suitability for large scale treatment. Compare to homogeneous photocatalytic applications most studies were performed at lab-scale, so the overall assessment of the treatment should be further assessed in pilot or full scale. One of the major reasons for this gap, is the need for efficient recycling of the catalyst particles before effluent discharging, thus future studies should incorporate the catalyst separation step in the overall process assessment. In addition, the efficiency of the process in repetitive catalytic cycles is rarely reported and forthcoming studies should also consider this aspect. Future studies should consider

developing immobilized and novel photocatalysts with enhanced visible light absorbing capacity. Mostly TiO_2 catalysts have been studied in various set-up scales while there is a need for real-word applications with modified or alternative photocatalysts. Further research should also be undertaken to examine the usage of alternative irradiation sources (UV-LEDs, sunlight) that consume less energy and do not require warming up times.

The removal of pharmaceuticals in mixtures with concentration levels equal to those usually detected in real wastewater by photocatalysis (heterogeneous/homogeneous) should also be explored to simulate the real application. Furthermore, even though many types of photoreactors for wastewater treatment have been studied and developed, there is still need to consider several aspects for the scale-up and standardization of solar photocatalytic reactors. Considering the herein presented data, the assessment of both processes based on the technology readiness level (TRL) (ranged from proof-of-concept (TRL = 1) to full operational scale proof (TRL = 9)) can be ascribed to a value of 4–5 (i.e. lab-scale validation (TRL value = 4), on-going pilot scale applications (TRL value = 5). Finally, as the cost is the more restrictive factor for the large-scale application of photocatalysis, comprehensive techno-economic assessment should be concluded in future works. In view of this, the electrical energy per order (EEO) value should be consider as the most important assessment tool for the studied photocatalytic processes in order to achieve the higher TRL value of full operational scale, as it measures activity based on the multiple parameters affecting the process. Based on the EEO value, the previous mentioned chemical (catalyst, operational parameters) and engineering (photoreactors set-up) parameters of the photocatalytic process can be identified for further developments. Finally, hybrid or combined technologies to achieve better treatment efficiency and economic feasibility can be more extensively investigated for the degradation of pharmaceutical mixtures in hospital wastewaters.

7. Conclusions

Although the treatment of pharmaceutical residues by means of homogeneous and heterogeneous photocatalysis is progressively receiving a great attention, limited studies have been dedicated to the removal of these compounds in real hospital wastewaters. Among the existed studies, most of them are focused mainly on the removal of some pharmaceuticals and COD reduction. Only a few works have focused on the identification of the TPs formed as well as on the toxicity assessment during and after the treatment.

Overall, homogeneous, and heterogeneous photocatalysis are promising technologies for the treatment of hospital wastewaters under laboratory and pilot scale. In comparison studies, photo-Fenton process showed better performance for COD reduction but lower degradation of individual pharmaceuticals than heterogeneous photocatalysis. Based on the existed literature, homogeneous photo-Fenton process is much more efficient in terms of operation costs than heterogeneous photocatalysis. Future research should be conducted using a more real-case scenarios approach regarding wastewater pre-treatment avoiding when possible, the acidification of wastewater prior treatment for photo-Fenton process, addition of excessive amount of reagents or catalysts, removing residual H_2O_2, etc.

The biodegradability of complex effluent's was enhanced by both homogeneous and heterogeneous photocatalysis, permitting their application as a pre-treatment method and the disposal of treated wastewater in a WWTP. However, more intensive research is needed especially under pilot scale as well as from engineering design and modeling, before full scale application. In addition to the experimental and modeling work, the performance of complete economic studies is needed. The integration of the processes as well as their combination with other treatment technologies was found to be considerable effective, overcoming simultaneously some drawbacks. In general, both homogeneous and heterogeneous photocatalysis can be efficient applicable technologies in the near future with the use of solar irradiation to be the main advantage. The design of new reactor systems as well as the development of improved photocatalysts can contribute to this direction. The current state of TRL scale varied between 5 and 7 thus pilot scale validation, system completion and standardization in full scale can been highlighted as the next steps for the application of the technology. In this direction, EEO value can be a useful metric for assessing photocatalytic activity and identifying the key chemistry and engineering factors.

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Declaration of competing interest

All authors disclose any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, the submitted work.

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