

Chapter 3

Heterogeneous Photocatalysis for Pharmaceutical Wastewater Treatment

Devagi Kanakaraju, Beverley D. Glass, and Michael Oelgemöller

Abstract Environmentally sustainable solutions for wastewater management including the improvement of water quality and water recycling are considered key priority areas globally. The challenges facing our water resources are unprecedented due to the presence of organic and inorganic pollutants derived from numerous anthropogenic activities. This situation has been further complicated by emerging persistent contaminants such as pharmaceuticals which possess low biodegradability and resistance to chemical and biological treatments. Excretion of pharmaceuticals and their metabolites via human waste, improper disposal and veterinary applications is recognized as the principal sources of pharmaceuticals ending up in various compartments of the environment. Heterogeneous photocatalysis using semiconductor titanium dioxide (TiO_2) has proven to be a promising treatment method for the degradation of pharmaceuticals.

Here, we review recent research concerning the application of TiO_2 photocatalysis for the removal of selected pharmaceuticals belonging to different therapeutic drug classes. These classes of pharmaceuticals were chosen based on their environmental prevalence and potential adverse effects. The highlighted conclusions from this review are that (1) TiO_2 photocatalysis may play a major role in the degradation of pharmaceuticals; (2) various factors such as catalyst loading, initial concentrations, and water matrices significantly influence both the degradation rate and kinetics of degradation; (3) mineralization remains incomplete, despite complete abatement of the parent pharmaceutical due to the formation of stable by-products; (4) structures or number of intermediates formed differ due to the variation of photocatalytic experimental parameters, and (5) laboratory-scale experiments with artificial pharmaceutical solutions, in particular single compounds, are more common than pilot-scale or real wastewater samples. The main conclusion is

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that the use of heterogeneous photocatalysis can be considered a state-of-the-art pharmaceutical wastewater treatment. Further studies are needed to optimize the operating conditions for maximum degradation of wastewater containing multiple pharmaceuticals under realistic conditions and on industrial scales.

Keywords Pharmaceutical pollutants • TiO₂ photocatalysis • Wastewater • Antibiotic • Analgesic • Drugs • Advanced oxidation processes

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Abbreviations

AAS	Atomic absorption spectrometry
AMX	Amoxicillin
AN	Analgesic
AOP	Advanced oxidation processes
API	Active pharmaceutical ingredient
BOD	Biochemical oxygen demand
CBZ	Carbamazepine
CIP	Ciprofloxacin
COD	Chemical oxygen demand
CPC	Compound parabolic collector
DCF	Diclofenac
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
E _g	Band gap energy
ESI-MS	Electrospray ionization mass spectrometry
FIA	Flow injection analysis
FQ	Fluoroquinolone
GC-MS	Gas chromatography mass spectrometry
HPLC	High performance liquid chromatography

IBP	Ibuprofen
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
IUPAC	International union of pure and applied chemistry
LC/ESI-MS-MS	Liquid chromatography-electrospray ionization tandem mass spectrometry
LC/ESI-TOF-MS	Liquid chromatography-electrospray ionization time-of-flight mass spectrometry
LC-MS	Liquid chromatography mass spectrometry
LED	Light emitting diode
L-H	Langmuir-Hinshelwood
Log K_{ow}	Octanol/water partition coefficient
MOX	Moxifloxacin
NHE	Normal hydrogen electrode
NOM	Natural organic matter
NOR	Norfloxacin
NPX	Naproxen
NSAIDs	Non-steroidal anti-inflammatory drugs
OTC	Oxytetracycline
OX	Oxolinic acid
QTOF-MS	Quadrupole time of light-mass spectrometry
SMX	Sulfamethoxazole
$t_{1/2}$	Half-life time
TC	Tetracycline
TOC	Total organic carbon
TOF-MS	Time-of-flight mass spectrometry
UPLC-ESI/MS	Ultra performance liquid chromatography-electrospray mass spectrometry
USEPA	United States environmental protection agency
UV	Ultraviolet
WWTP	Wastewater treatment plant

3.1 Introduction: Advanced Oxidation Processes

Since water is essential to life, it is not surprising that there are a number of issues related to this essential resource. Poor sanitation, water scarcity, deteriorating water quality, waterborne diseases and lack of clean water supply are all posing global challenges due to the rising demand by an increasing world population. Further pressure on water resources has resulted from the introduction of emerging recalcitrant contaminants or xenobiotics, such as pharmaceuticals, endocrine disruptors, surfactants and personal care products. These substances display much more complex characteristics and resistance to degradation. Numerous studies highlighting the prevalence of pharmaceuticals in water environments has increased

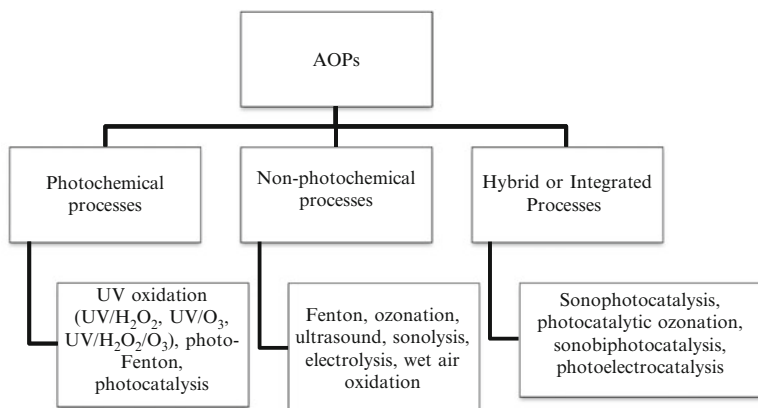


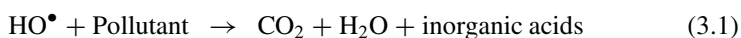
Fig. 3.1 Types of destructive advanced oxidation processes (AOPs) for wastewater purification

significantly since 2000, Heberer (2002a), Tixier et al. (2003), Fent et al. (2006), Choi et al. (2008) and Miège et al. (2009). This development has raised widespread concern of poorly known potential effects of pharmaceutical compounds and their metabolites on human and aquatic organisms, despite occurring in trace quantities ranging from ng/L to $\mu\text{g/L}$, Kümmerer (2009) and Mompelat et al. (2009).

Currently existing sewage treatment technologies can only be considered as a compromise for emerging micropollutants, although they have proven efficient for microbial, carbon, heavy metals and nitrogen removal. Complex pharmaceuticals with various physical and chemical properties in wastewater, lead to inadequate removal by existing wastewater treatment technologies which are not designed to handle this specific class of pollutants, Suárez et al. (2008). Incomplete removal of pharmaceutical residues clearly supports the urgent need for innovative technologies that can deal with their presence, either by improving existing or engaging in alternative technologies. Advanced Oxidation Processes (AOPs) are regarded to be appropriate to degrade pollutants which are known to be non-biodegradable or have low biodegradability, persistent, and possess high chemical stability. AOPs for water and wastewater treatment include photolysis and photocatalysis, ozonation, Fenton and photo-Fenton, ultrasound radiation, sonolysis, electrochemical oxidation, and wet air oxidation. These advanced technologies can be grouped into photochemical, non-photochemical and hybrid techniques (Fig. 3.1).

In principle, all AOPs are characterized by a common chemical feature known as reactive oxygen species which can react with non-biodegradable or recalcitrant compounds in water or wastewater, Dalrymple et al. (2007). Reactive oxygen or free radical species are strong oxidants required to initiate AOPs in order to mineralize pollutants to simpler and nontoxic molecules. These free radical species are based on atoms or molecules consisting of one or more unpaired electrons such as the hydroxyl radical (HO^{\bullet}), superoxide anion radical ($\text{O}_2^{\bullet-}$), hydroperoxyl radical (HO_2^{\bullet}) or alkoxy radical (RO^{\bullet}). Of these, the HO^{\bullet} has attracted the most

attention. The appealing characteristics of HO• radicals are its non-selective nature, high oxidation potential (2.8 V) when compared to other oxidants and its ability to react with a wide range of contaminants without any additives, with rate constants normally in the order of 10^6 – 10^9 mol L⁻¹ s⁻¹, Andreozzi et al. (1999). When HO• radicals reacts with organic molecules, they can either abstract a hydrogen atom or add to multiple bonds yielding oxidized intermediates or, in the case of complete mineralization, produce carbon dioxide, water and inorganic acids (3.1).



During an ideal treatment by AOPs, contaminants are structurally altered forming smaller and more biodegradable compounds until complete mineralization is achieved. For the application of AOPs in wastewater treatment, the objectives can be either to (i) increase the biodegradability of wastewater before applying conventional biological process, (ii) reduce the level of toxicity and micropollutants in the effluent or (iii) disinfect the wastewater instead of applying traditional disinfection methods such as chlorination, which is known to generate carcinogenic and mutagenic by-products such as trihalomethanes and haloacetic acids, Rizzo (2011). AOPs have been proven to be efficient for the treatment of industrial wastewater; however, due to the high chemical oxygen demand (COD) levels in industrial wastewater, AOPs are only considered efficient for a low COD level of <5 g/L. When dealing with high levels of COD, techniques such as incineration or wet oxidation are preferred, Malato et al. (2002). Semiconductor material mediated photocatalysis in particular with titanium dioxide (TiO₂), is distinctive compared to other AOPs for the removal of persistent pollutants from wastewaters.

3.2 Heterogeneous Photocatalysis

The IUPAC defines photocatalysis as a “change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance, the photocatalyst that absorbs light quanta and is involved in the chemical transformation of the reaction partners”, Braslavsky (2007). Heterogeneous photocatalysis may be also termed as a process which uses a semiconductor metal oxide as catalyst and oxygen as an oxidizing agent, Andreozzi et al. (1999).

In 1972, Fujishima and Honda discovered the possibility of water splitting by means of a photoelectrochemical cell consisting of a rutile TiO₂ photoanode and a Pt counter electrode, Fujishima et al. (2008). This discovery opened ways for new applications such as air purification, self-cleaning surfaces application, organic synthesis, disinfection, and anti-cancer therapy. An interesting application of this breakthrough is in water purification. Water purification by means of illuminating TiO₂ was first proposed by Frank and Bard for cyanide and sulfite removal,

Fujishima et al. (2008). Since then, degradation of various organic target compounds such as dyes, pesticides and pharmaceuticals has been demonstrated.

A conventional heterogeneous photocatalysis process can be divided into five individual steps, Herrmann (1999):

- i. Diffusion of the reactants from the bulk phase to the surface of the catalyst;
- ii. Adsorption of at least one of the reactants;
- iii. Reaction in the adsorbed phase;
- iv. Desorption of the product(s);
- v. Removal of the product(s) from the interface region.

An ideal photocatalyst should be chemically and biologically inert, photoactive, photostable, inexpensive, non-toxic, and should be excited with visible and near/or ultraviolet (UV) light. Despite the existence of various chalcogenide semiconductor photocatalysts (oxides and sulfides) such as zinc oxide (ZnO), zinc sulfide (ZnS), ferric oxide (Fe_2O_3), cadmium sulfide (CdS), cerium dioxide (CeO_2), tungsten trioxide (WO_3), tin dioxide (SnO_2) and titanium dioxide (TiO_2), none of these fulfils all the characteristics of an ideal photocatalyst. The choice of catalyst in photocatalytic studies is frequently narrowed to TiO_2 , CdS and ZnO. Most studies involve TiO_2 as a semiconductor candidate despite its limitations, such as a low efficiency and a narrow light response factor, Leary and Westwood (2011). CdS and ZnO are known to undergo self-oxidation, which leads to lower photoactivity, and also the release of potentially dangerous metals such as Cd^{2+} , which makes these photocatalysts unattractive, Fox and Dulay (1993). Notably, ZnO has been reported to be a better photocatalyst in photocatalytic degradation than TiO_2 due to its broader absorption within the solar spectrum, Elmolla and Chaudhuri (2010a).

3.2.1 Mechanisms of TiO_2 Photocatalysis

Mechanistic processes of TiO_2 induced photocatalytic degradation of organic pollutants have been well described in the literature, Fox and Dulay (1993), Hoffmann et al. (1995), Gaya and Abdullah (2008), Chong et al. (2010) and Augugliaro et al. (2012). Photocatalysis occurs due to absorption of a photon with sufficient energy either equal or higher than the band gap energy (E_g) of the catalyst. The E_g represents the difference between the valence band (vB) and the conduction band (cB) of TiO_2 . The vB and cB energies of TiO_2 are about +3.1 eV (vs. NHE) and -0.1 eV (vs. NHE), respectively. Consequently, the E_g between the vB and cB is 3.2 eV for anatase TiO_2 . When TiO_2 is excited with UV light ($\lambda < 380$ nm for anatase TiO_2 which is more common or $\lambda < 400$ nm for rutile TiO_2), an electron (e^-) is promoted from the vB to the cB of TiO_2 generating a hole (h^+) in the vB and an electron (e^-) in the cB (3.2). The photogenerated e^- - h^+ pair or charge carriers can either migrate to the surface of the TiO_2 , where they can actively perform their roles in oxidation-reduction reactions with the adsorbed pollutant (P) or recombine in the

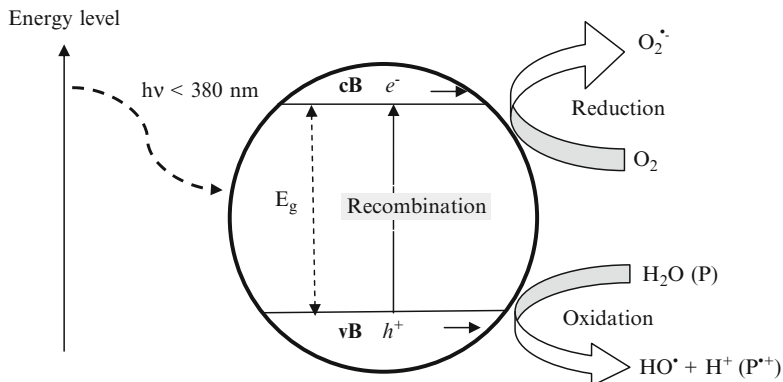
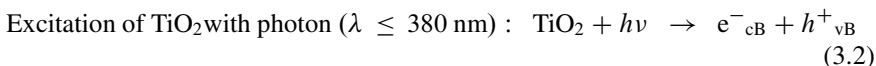
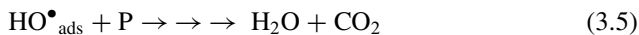
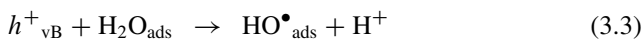


Fig. 3.2 Photogenerated e^- - h^+ pair on the TiO_2 surface and oxidation-reduction reactions

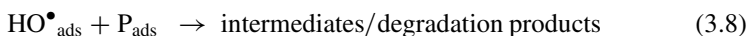
bulk or on the surface of the TiO_2 . The schematic representation of photogeneration of the e^- - h^+ pair and of the subsequent oxidation-reduction is presented in Fig. 3.2.



A series of oxidation-reduction reactions may occur during TiO_2 photocatalysis (3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 3.10, and 3.11). A generated h^+ can react with an adsorbed water molecule, which is an essential process in TiO_2 photocatalysis, or reacts with OH^- anions to form powerful HO^\bullet radicals (3.3 and 3.4). The HO^\bullet radicals can subsequently oxidize water pollutants P to complete mineralization (3.5). When molecular oxygen is available, it is adsorbed onto the surface of TiO_2 and can scavenge an electron to form the superoxide anion radical ($\text{O}_2^{\bullet-}$) (3.6).

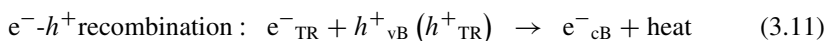
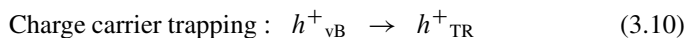
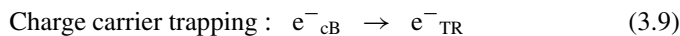


Holes can also directly oxidize pollutants P by electron transfer (3.7 and 3.8).



The photogenerated e^- - h^+ pairs can undergo rapid recombination within nano seconds in the absence of electron scavengers, such as oxygen, releasing heat

without favouring any reactions (3.9, 3.10, and 3.11). The e^-_{TR} and h^+_{TR} (3.9, 3.10, and 3.11) represent the surface trap valence band electron and conduction band hole, respectively.



Wavelengths between 300 and 400 nm (near UV range) are of interest in TiO_2 photocatalysis, which are provided either by artificial UV lamps or by a small section of the solar spectrum. Sunlight-induced photocatalytic processes have been the characteristic domain of TiO_2 as a photocatalyst candidate. Demonstration-scale solar treatments of emerging contaminants using compound parabolic collectors (CPC) underpin this, Pérez-Estrada et al. (2005) and Miránda-García et al. (2011). However, a limitation of solar photocatalysis is the poor overlap of the solar spectrum with the absorption spectrum of TiO_2 (<5 %). Thus, only 5 % of solar irradiation comprises the UV light that can be harvested by TiO_2 photocatalysis. TiO_2 doping with non-metals, metal-ion implantation, co-doping and sensitizing TiO_2 with dyes has been applied to address this limitation and to improve the TiO_2 photocatalytic efficiencies, Kumar and Devi (2011). The main objective of employing doping is to increase absorption in the visible region as it induces an optical response change i.e. decrease in band gap. One major drawback of doping is significant increase in the cost of the photocatalyst due to expense of ion implantation facilities, Zhang et al. (2009).

3.3 Titanium Dioxide: Structure and Properties

One most prevalent application of TiO_2 is as a white pigment in paints, plastics, paper, fibres, foods, pharmaceuticals, and personal care products mainly due to its light scattering properties and high refractive index. Worldwide production of TiO_2 powder has been reported as five million tons in 2005, with projections up to a 10 % increase by 2015, Skocaj et al. (2011). Additionally, production of nano-sized TiO_2 which permits more applications such as anti-fogging and self-cleaning coatings has also increased from 2,000 t in 2005 to 5,000 t in 2010, Weir et al. (2012). However, the concern on safety and health aspects which arise from the usage of nano- TiO_2 needs to be addressed. A recent study was conducted to assess the amount of TiO_2 in various food, personal care products and pharmaceuticals and predict adverse effects of TiO_2 nanoparticles on the environment, Weir et al. (2012).

TiO_2 exists in three crystalline forms namely anatase, rutile and brookite with the anatase form more commonly used as an active photocatalyst than pure rutile phase. In contrast, brookite TiO_2 is not commonly applied in photocatalysis. The

anatase form tends to be the most photoactive and the most stable form at low temperatures ($<700\text{ }^{\circ}\text{C}$). Anatase and brookite are however, thermodynamically metastable and they can be irreversibly converted to the rutile form, the most stable form at high temperatures, Silva and Faria (2009). Surface and structural properties such as crystal structure, surface area, particle size distribution, porosity, band gap and surface hydroxyl density control the efficiency of TiO_2 as photocatalyst. Of these, crystallinity and specific surface area have great effect on the photocatalytic activity of TiO_2 .

The more common application of pure anatase compared to the pure rutile TiO_2 is attributed to a higher density of superficial hydroxyl groups, which leads to an improved capacity of anatase to adsorb oxygen, a larger specific surface area compared to pure rutile samples, and a lower recombination velocity of e^-h^+ pairs in anatase, Hoffmann et al. (1995) and Achilleos et al. (2010a). Combinations of anatase and rutile have demonstrated better photocatalytic activity due to the promotion of charge pair separation and inhibition of e^-h^+ recombination, Pelaez et al. (2012).

The most prominent TiO_2 photocatalyst, Degussa P25 (now known as AEROXIDE[®] TiO_2 P25) contains 80:20 anatase to rutile weight ratio and has demonstrated good performance in photocatalytic applications due to its large surface area of $50\text{ m}^2/\text{g}$, with a particle size range of 20–30 nm. Although TiO_2 P25 has been widely used as a benchmark photocatalyst, its effectiveness has been limited by poor light absorption in the visible region, as a result of its large band gap.

The sol–gel method has been one of the widely used synthetic methods for the preparation of TiO_2 nanocrystalline forms. Several synthetic pathways are available for the preparation of the photocatalyst from precursor chemicals, for example, titanium alkoxide or titanium halogenide. The precursors are normally calcined at very high temperatures to obtain the desired crystal form and strong adhesion to surface materials or solid support such as activated carbon, zeolite, silica and glass. Hydroxyl groups from the catalyst surface and the support can react upon loss of a molecule of water, creating an oxygen bond thus increasing the adherence of the catalyst to the support during calcinations, Shan et al. (2010). The rate of hydrolysis is difficult to control due to the affinity of the TiO_2 precursors for water leading to poor modification of TiO_2 's intrinsic properties such as surface structure, structural properties and porosity. Nitric acid, hydrochloric acid and complexing reagents such as oxalate and citrate have also been commonly used in the sol–gel synthesis. Weak acids such as acetic acid also exhibit excellent control of the hydrolysis rate of TiO_2 , as they maintain pH due to the chelating effects of anions formed (e.g. acetate ion), generation of pH buffer, and stabilization of the sol, Shamaila et al. (2010).

3.4 Pharmaceuticals in the Environment

The United States Environmental Protection Agency's (USEPA) priority pollutants such as volatile organics, semivolatile, pesticides and polyvinylchloride biphenyls, metals and inorganics have been the main focus of water pollution over the past

30 years. However, in recent years, concerns in water pollution have shifted towards emerging contaminants. In particular, pharmaceutical and personal care products have become pollutants of interest due to their notable detection and potential detrimental impact on aquatic environments, Khetan and Collins (2007). Pharmaceuticals, classified as environmental emerging contaminants because of their endocrine-disrupting properties are either of natural origin or are produced synthetically, Oller et al. (2011).

The term 'pharmaceutical' or active pharmaceutical ingredient (API) for the purpose of this review refers to chemicals used for diagnosis, treatment, alteration, and prevention of disease, health conditions or functions of the human body and also includes veterinary pharmaceuticals and illicit or recreational drugs, Daughton and Ternes (1999). APIs are complex molecules with various functionalities and physicochemical and biological properties, balanced in terms of hydrophilicity and lipophilicity with molecular weights ranging from 200 to 1,000 Da, Kümmerer (2009). Pharmaceuticals are generally designed with high stability for their intended effects on humans and are eventually metabolised in the body by biochemical processes. They can be eliminated from the human body either after being partially or completely converted to water soluble metabolites or, in some cases, without being metabolized, Khan and Ongert (2004). Their classifications are generally based on their therapeutic uses and those of environmental interest can be categorized into eight groups, namely non-steroidal anti-inflammatory drugs, antibiotics, beta-blockers, antiepileptics, blood lipid-lowering agents, antidepressants, hormones and antihistamines, Khetan and Collins (2007).

Inappropriate disposal and excretion of consumed medications by households, pharmaceutical manufacturers, hospitals, pharmacies and animal farming or aquaculture have been identified as the major sources of pharmaceuticals either as the parent drug or their metabolites in water courses (Fig. 3.3). Wastewater treatment plants (WWTPs) are thus a major source of the presence of this class of micropollutants in the environment. Various studies have reported on the discrepancies in efficiency and variation of WWTPs in the removal of pharmaceuticals due to their stability and differences in physicochemical properties. In fact, studies have also confirmed the detection of pharmaceuticals in effluents and influents from WWTP samples collected, in trace concentrations, Rodil et al. (2012).

A significant contribution of pharmaceuticals in surface water also comes from inappropriate disposal of expired or unused medications from households. Occurrence of pharmaceuticals in groundwater is related to a leaching process from landfills and soil and from sludge or manure spreading. Groundwater, being the extraction source of drinking water, has also been affected by pharmaceutical pollution, which can cause long term accumulation of trace amounts in humans. Finally, the accumulation of pharmaceuticals can be also expected in aquatic and terrestrial organisms via the food chain, Hoeger et al. (2005) and Deegan et al. (2011).

Monitoring studies conducted thus far have verified the occurrence of pharmaceutical in trace amounts in surface waters, groundwater and also sewage effluents, Andreozzi et al. (2003), Carballa et al. (2004), Lishman et al. (2006) and Moldovan

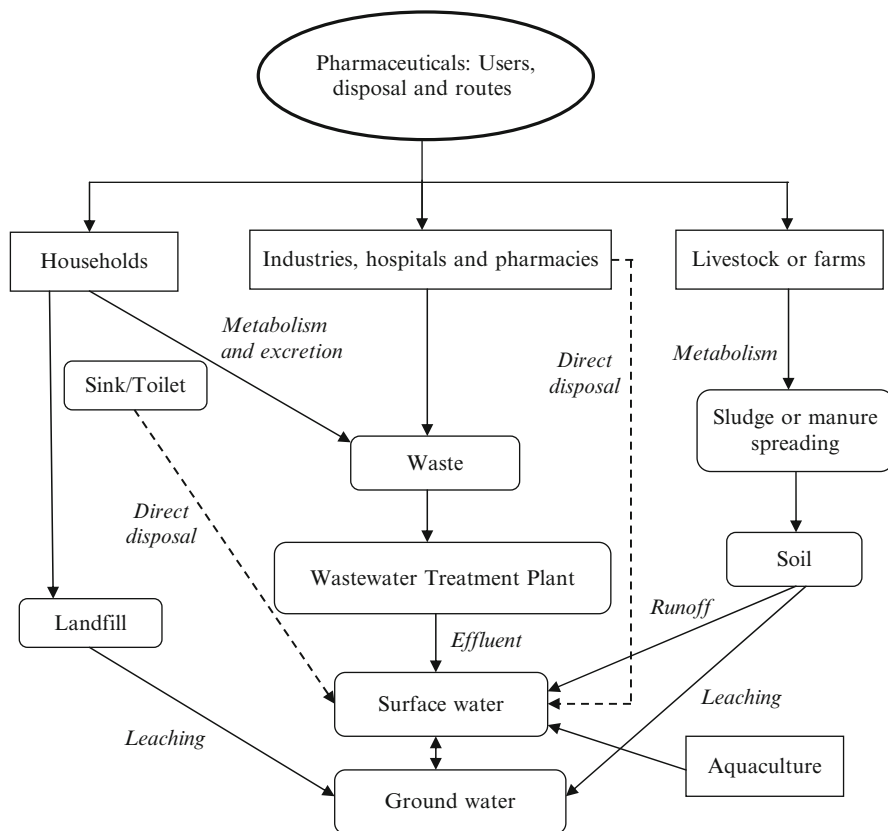


Fig. 3.3 Sources and routes of pharmaceuticals in water (Modified from Nikolaou et al. (2007) and Mompelat et al. (2009))

(2006). Moreover, concentrations of pharmaceuticals in the water environment have also been established based on their therapeutic use, Nikolaou et al. (2007), Pal et al. (2010) and Ziylan and Ince (2011). The occurrence of pharmaceutical residues in drinking and tap water has also been reported, Ternes et al. (2002) and Rodil et al. (2012). A study reported levels of numerous pharmaceuticals and endocrine disruptors in the finished water of 19 full-scale water utilities in the United States, Benotti et al. (2009).

Once released into the environment, APIs are exposed to different natural conditions and resulting transformations, which is not only affected by their physicochemical properties, but also their structure. These changes create further complexities and concerns regarding the identity, toxicity and potential risk of any new products, which may be formed.

Although studies are generally focused on a wide spectrum of pharmaceuticals, those frequently prescribed have gained importance amongst researchers.

Table 3.1 Relative annual per capita consumption (in mg/cap/y) of selected pharmaceuticals in Australia and some European countries, data taken from Carballa et al. (2008)

Pharmaceuticals	Australia (1998)	France (1998)	Germany (2001)	Spain (2003)	Sweden (2005)
Ibuprofen	720.6	2,841.0	1,553.4	6,391.2	7,864.3
Naproxen	1,159.9	646.2	n.a	986.1	n.a
Diclofenac	222.8	254.7	594.7	747.7	375.9
Sulfamethoxazole	n.a	382.9	571.4	294.0	160.4
Trimethoprim	136.8	n.a	n.a	85.6	n.a
Metoprolol	313.5	n.a	631.1	53.2	n.a
Carbamazepine	506.3	601.7	946.6	463.0	820.2
Diazepam	371.7	6.8	5.3	20.8	19.8
Bezafibrate	n.a	589.7	315.5	92.6	66.7

n.a not available

For example, acidic pharmaceuticals such as ibuprofen, ketoprofen, bezafibrate, and naproxen have been frequently monitored in receiving waters and WWTPs, Lindqvist et al. (2005) and Wang et al. (2010). Selected therapeutic classes such as antibiotics, NSAIDs and analgesics have also been reviewed, Kümmerer (2009) and Ziylan and Ince (2011). Accurate statistics on sales and consumption of pharmaceuticals present a challenge, due to difficulty in monitoring of prescription medication, in addition to non-prescription medicines, which can be obtained over-the-counter or through the internet. Statistics on global consumptions and production of pharmaceuticals are not available in the literature. In addition, about 3,000 new APIs are introduced each year as a result of advancements in medicine, Beausse (2004).

The annual per capita consumption of selected pharmaceuticals in some European countries and Australia are presented in Table 3.1. The consumption patterns vary according to countries and demand or popularity of a drug. In Australia, 262 million prescriptions were dispensed via community pharmacies in 2008 which accounts for about 12 prescriptions per person, AIHW (2011). This figure represents an increase of 24 % over prescriptions dispensed in 2001. Among the mostly prescribed medicines are cholesterol-lowering drugs, antibiotics and drugs for the treatment of high blood pressure. Amoxicillin (3.9 %), an antibiotic, emerged in the top 10 most commonly prescribed medicines in 2009–2010 followed by paracetamol (3.2 %), an analgesic and cephalexin (3.2 %), a cephalosporin antibiotic. The presences of amoxicillin and cephalexin were confirmed in WWTP influents and surface water (ng/L) in a monitoring study of 28 antibiotics in watersheds of south-east Queensland. None of these drugs was, however, detected in drinking water, Watkinson et al. (2009).

Although the fate of many pharmaceuticals released into the environment remains unknown, three possible scenarios have been proposed: (i) the pharmaceutical is mineralized to carbon dioxide, water, and other inorganic ions or acids such nitrate, sulfate and phosphate ions, (ii) the pharmaceutical is not readily degradable

and will be retained in sludge due to its lipophilic nature or (iii) the pharmaceutical will be metabolized to a more hydrophilic form than the parent compound, Halling-Sørensen et al. (1998) and Klavarioti et al. (2009).

The main concern from the presence of pharmaceuticals and their metabolites is the potential adverse effects that they may pose on human health and to other living organisms, which thus far remains unknown and unclear. Due to their complex physicochemical properties as a result of mixtures of various pharmaceuticals and other pollutants in the environment, advanced treatment such as TiO₂ photocatalysis undoubtedly can be applied for their degradation and a substantial amount of work has been published in this field, Abellán et al. (2007), Yurdakal et al. (2007), Giraldo et al. (2010) and Tong et al. (2012).

3.5 Degradation, Mineralization and Transformation Pathways of Pharmaceuticals Through Heterogeneous Photocatalysis

Positive developments in the photooxidation efficiency of TiO₂ based photocatalysis (UV/TiO₂) of pharmaceuticals have led to an increasing interest in its application for the removal of micropollutants in spiked wastewaters and also real wastewater such as wastewater effluents, river water and drinking water. Determination of optimal operating conditions to yield the highest performance in terms of degradation and mineralization has been investigated in various heterogeneous photocatalytic studies on pharmaceuticals. The disappearance of the parent API over the treatment time has been the primary focus. However, studies have reported that kinetic assessment of APIs during UV/TiO₂ degradation can often be complex, due to the formation of various transformation products. Interferences between the disappearance of the parent API and newly formed transformation products may also occur. The non-selective nature of hydroxyl radicals contributes to this complexity, Oller et al. (2011).

Another general observation is that while high removal rates of the parent API can be accomplished by UV/TiO₂, mineralization remains incomplete in most cases. The degree of mineralization also tends to vary according to the nature of the water matrices. In general, a solution of the API prepared in the laboratory with distilled water or deionized water generally yields higher mineralization compared to that of doped effluent or influent samples from WWTPs, groundwater or river water.

The interference provided by the presence of organic matter such as humic and fulvic acids and radical scavengers such as carbonate species, HCO₃⁻ and CO₃²⁻ cannot be ruled out, as these species retard photocatalysis by competing for active sites and radiation attenuation. Organic matter present in water can be classified into two major classes namely dissolved organic matter and particulate organic matter. The existence of organic matter can be naturally occurring organic matter, such as humic and fulvic acids, or that derived from anthropogenic activities, Oppenländer (2003).

The ultimate aim of TiO₂ photocatalysis (and also for other AOPs) is threefold, to degrade pollutants, to reduce toxicity and to enhance the biodegradability of the treated wastewater. Global parameters such as total organic carbon (TOC), COD, biochemical oxygen demand (BOD), dissolved organic carbon (DOC) and BOD/COD ratio are also often measured. The ratio of BOD₅/COD is commonly used in this context and ratio values of above 0.4 are regarded as highly biodegradable in wastewater, Abellán et al. (2007). Toxicity assays are used to indicate the toxicity of photocatalytically treated wastewater and various types of bioassays based on microorganisms, plants and algae, invertebrates and fish have been applied to measure the response, Rizzo (2011).

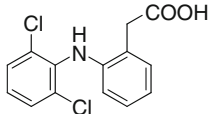
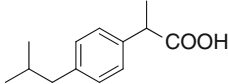
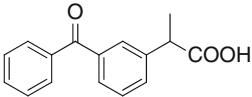
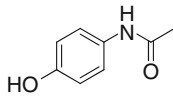
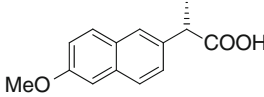
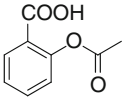
In terms of the API selection, it is either driven by their consumption which can correlate to the high probability of detection in the environment or due to an existing gap of information on the degradation rate of the particular API. Frequently investigated operational parameters include catalyst load, initial concentration, type of photocatalysts, pH of the solution, wavelength and light intensity. Other operational parameters for enhancement of the degradation rate by the addition of co-oxidants and the effect of the concentration of dissolved oxygen (DO) have also been incorporated in various TiO₂ photocatalysis studies. These variables are chosen in order to establish their relationship with respect to the API degradation. However, it is also widely accepted that the design and geometry of the photoreactor dictates the optimal degradation rate of APIs, Malato et al. (2009) and Friedmann et al. (2010).

3.5.1 Non-steroidal Anti-inflammatory and Analgesic Drugs

Non-steroidal anti-inflammatory drugs (NSAIDs) primarily reduce inflammation, while analgesic (AN) drugs are widely used to relieve pain, Ziylan and Ince (2011). Examples of NSAIDs include naproxen, ketoprofen, diclofenac, fenoprofen, indomethacin, and ibuprofen, whereas ANs are acetaminophen (paracetamol), acetylsalicylic acid (aspirin) and the opioid analgesics such as morphine. Chemical structures of selected NSAIDs and ANs are presented in Table 3.2. One of the most prominent characteristics of NSAIDs is the carboxylic acid moiety which contributes to both its activity and side effects.

Photocatalytic degradation of NSAIDs and ANs has been conducted by various researchers primarily aiming to explore the degradation kinetics and degradation efficiency of APIs under selected experimental conditions. Among the most frequently studied NSAIDs and ANs are diclofenac, ketoprofen, ibuprofen, naproxen and paracetamol. Photocatalytic studies of NSAIDs and ANs are summarized in Table 3.3 and detailed discussions of selected studies are provided to highlight both the significant findings and differences in the experimental conditions.

Table 3.2 Chemical structures of selected non-steroidal anti-inflammatory drugs (NSAID) and analgesics

		
Diclofenac (C ₁₄ H ₁₁ Cl ₂ NO ₂) 2-(2-(2,6-dichloro-phenylamino)phenyl)acetic acid	Ibuprofen (C ₁₃ H ₁₈ O ₂) (<i>RS</i>)-2-(4-(2-methylpropyl)phenyl)propanoic acid	Ketoprofen (C ₁₆ H ₁₄ O ₃) (<i>RS</i>)-2-(3 benzoyl-phenyl)propanoic acid
		
Acetaminophen (C ₈ H ₉ NO ₂) <i>N</i> -(4-hydroxyphenyl)acetamide	Naproxen (C ₁₄ H ₁₄ O ₃) (+)-(<i>S</i>)-2-(6-methoxynaphthalen-2-yl)propanoic acid	Acetylsalicylic acid (C ₉ H ₈ O ₄) 2-acetoxybenzoic acid

Diclofenac

Diclofenac (DCF) has been identified as one of the most recognized pharmaceuticals in the aquatic environment as a result of its elevated use worldwide, Heberer (2002b). The global consumption of DCF was reported to be 940 t per year with a daily dose of 100 mg. These numbers clearly demonstrate its significance as an environmentally important pharmaceutical, Zhang et al. (2008a). Threats on fish such as rainbow trout, and birds, specifically the vulture populations, have been reported, Oaks et al. (2004). NSAIDs such as DCF (and NPX) with a partition coefficient ($\log K_{ow}$) greater than 3 are generally capable of bioaccumulating in the tissues of organisms, Rizzo et al. (2009a). The concentration of DCF has been reported to be less than 10 ng/L in a drinking water sample from tap water in Berlin and ranged between 0.14 and 1.48 $\mu\text{g/L}$ in WWTPs effluents and surface water, Zhang et al. (2008a). As for the removal efficiency by WWTPs, there has been a wide range varying from 0 % to 80 % with typical ranges between 21 % and 40 %, which clearly indicates insufficient removal of this pharmaceutical, Zhang et al. (2008a).

One of the most comprehensive studies of the effect of UV/TiO₂ on DCF to date was performed by Calza and his group (2006). The study included the identification of intermediates formed, mineralization and also degradation rate controlling parameters. The photocatalytic efficiency increased with the amount of TiO₂, but high loadings (0.8–0.9 g/L) showed no positive effect on the degradation due to scattering of light. The optimum combination of TiO₂ loading/initial

Table 3.3 Highlights of the heterogeneous photocatalytic studies on non-steroidal anti-inflammatory drugs and analgesics

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
<i>Diclofenac</i>	Distilled water	Solar simulator suntest CPS + (Xe arc lamp, 1,500 W, 750 W/m ²) Initial concentration: 0.76–9.24 mg/L TiO ₂ P25 loading: 104–896 mg/L	HPLC, TOC, LC-MS, IC, toxicity measurement on bacterium, <i>Vibrio fischeri</i>	Factorial design was used to investigate effect of TiO ₂ loading and DCF initial concentration on reaction rate. Toxicity and TOC decreased. Complete DCF elimination after 1 h of irradiation	Calza et al. (2006)
	Milli-Q water	Black light fluorescent lamp (125 W, 300 and 420 nm, intensity 4.7×10^{-7} Einstein/s) Initial concentration: 5–80 mg/L TiO ₂ P25 loading: 0.2–1.6 g/L	UV-vis (254 nm, 276 nm), COD, bioassays on <i>Daphnia magna</i> , <i>Pseudokirchneriella subcapitata</i> , <i>Artemia salina</i>	Degradation data fitted pseudo-first order kinetic model. High DCF concentrations (40 and 80 mg/L) and 1.6 g TiO ₂ /L followed second-order kinetic model	Rizzo et al. (2009a)
	Deionized water, groundwater and treated municipal wastewater	UV-A lamp (9 W, 350–400 nm, intensity 3.37×10^{-6} Einstein/s) Initial concentration: 5–20 mg/L TiO ₂ loading: 50–800 mg/L Type of TiO ₂ : TiO ₂ Degussa P25, Hombikat UV 100, Aldrich, Tronox AK-1, Tronox TRHP-2, Tronox TR	UV (276 nm), TOC, toxicity measurement with <i>Daphnia magna</i>	TiO ₂ Degussa P25 performed best for DCF decomposition which was affected by water matrix and increased initial concentration. Irradiated solution, in particular after 2 h irradiation, showed high toxicity	Achilleos et al. (2010a)
		Temperature: 23 °C H ₂ O ₂ concentration: 0.07–1.4 mM			

Milli-Q water	UV (254 nm; low pressure Hg lamp; photon flux: 8.33×10^{-8} Einstein/s) and near UV-vis (366 nm; medium pressure Hg lamp; photon flux: 2.38×10^{-6} Einstein/s) Initial concentration: 8 mg/L TiO ₂ loading: 0.1–2 g/L Type of TiO ₂ : TiO ₂ Degussa P25, synthesized TiO ₂ anatase and rutile, and composite multi-walled carbon nanotube Gas flow rate: 200 mL/min O ₂ /Ar (50 % vol of oxygen) DO % (v/v): 21–100 H ₂ O ₂ concentration: 3 and 5 mM pH: 6	HPLC, UV-vis, TOC, LC-MS	Optimum degradation was obtained with synthesized anatase (0.5 g/L) and 50 % O ₂ (v/v) under UV irradiation with rate constant 0.9 min^{-1}	Martínez et al. (2011)
Urban wastewater and Milli-Q water	High pressure Hg lamp ($\lambda = 313 \text{ nm}$; intensity 3×10^{-5} Einstein/s) Initial concentration: 30–80 mg/L TiO ₂ loading: 0.5–2.5 g/L Gas flow rate: 30–50 L/h Ozone concentration: 5–30 mg/L pH: 7	HPLC, COD, BOD, dissolved ozone, TOC	Concentrations of ozone gas and initial DCF concentrations greatly affected DCF and TOC removals	Aguinaco et al. (2012)

(continued)

Table 3.3 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
	Milli-Q water	High pressure Hg lamp (313 nm; intensity 3×10^{-5} Einstein/s) Initial concentration: 10^{-4} M TiO ₂ P25 loading: 1.5 g/L Temperature: 20 °C Oxygen flow rate: 30 L/h Ozone gas concentration: 10 mg/L pH: 5, 7 and 9 (buffering conditions)	HPLC, TOC, dissolved ozone	Efficiency of TiO ₂ photocatalytic systems (O ₂ /UV-A/TiO ₂ , O ₃ /UV-A/TiO ₂ , UV-A/TiO ₂) and single ozonation were compared. DCF was completely removed under photocatalytic process and TOC removed up to 80 % which was higher than single ozonation	García-Araya et al. (2010)
<i>Diclofenac mixture</i>	Distilled water, urban wastewater effluent	Black light fluorescent lamp (125 W, 300 and 420 nm, intensity 4.7×10^{-7} Einstein/s) Initial concentration: 2.5 mg/L TiO ₂ P25 loading: 0.2–0.8 g/L	UV-vis (DCF: 276 nm), TOC, bioassays on <i>Daphnia magna</i> , <i>Pseudokirchneriella subcapitata</i> , <i>Lepidium sativum</i>	DCF degradation was examined as single compound and in mixtures with amoxicillin and carbamazepine. Degradation rate was faster in spiked distilled water compared to real wastewater	Rizzo et al. (2009b)
<i>Naproxen</i>	Milli-Q water	Solar simulator (Xe lamp, 1 kW) Initial concentration: 2–1,000 mg/L TiO ₂ P25 loading: 0.1–1 g/L Temperature: 20–40 °C DO concentration: 40 ± 2 mg/L Volumetric rate: 0.1–0.4 L/min	HPLC, DOC, COD, BOD ₅ , ESI-MS, toxicity assay on <i>Vibrio fischeri</i>	Degradation of NPX mainly contributed by photolysis although photocatalysis was more efficient for DOC removal. BOD ₅ /COD ratios were found to be below 0.05 suggesting no-biodegradable product formed during photocatalysis. The photoproducts formed through decarboxylation showed a high cytotoxicity	Méndez-Arriaga et al. (2008a)

<i>Naproxen mixture</i>									
Naproxen (Diclofenac and ibuprofen)	Milli-Q water	Solar simulator (Xe-OP lamp, 1 kW; photon flux: 6.9 μ Einstein/s) Initial concentration: 200 ppm TiO ₂ loading: 0.1–2 g/L Temperature: 20, 30 and 40 °C Circulation flow rate: 0.1, 0.2 and 0.4 mL/min DO concentration: 8, 40, 8 (initial)-2 (final) mg/L	HPLC, TOC, BOD ₅ , COD, DO, ESI/MS, toxicity assay on <i>Vibrio fischeri</i>	Increase in TiO ₂ loading showed no improvement on degradation rate and the maximum TiO ₂ loading was 0.1 g/L. Flow rate had no effect on degradation rate while increase in temperature to 40 °C yielded 99 % conversion	Méndez-Arriaga et al. (2008b)				
Naproxen (carbamazepine, clofibrac acid, phenazone, ofloxacin, furosemide, ranitidine)	Ultrapure water	Medium pressure Hg lamp (125 W) Initial concentration: 5 mg/L TiO ₂ P25 loading: 1 g/L Temperature: 30 °C Oxygen concentration: 22 mg/L pH: 3 and 11	UV-vis (NPX: 230 nm)	Adsorption of NPX increased with decreasing pH. NPX of 5 mg/L decreased with increasing radiation time and in accordance to pseudo-first order kinetics in experiments conducted in batch photoreactor without membrane	Molinari et al. (2006)				
<i>Ibuprofen</i>									
Solar photocatalysis	Water type not provided	Three solar pilot plant reactors (Two CPCs and one axis-parabolic collector) Initial concentration: 20–200 mg/L TiO ₂ loading: 0.1–1.0 g/L H ₂ O ₂ concentration: 900 and 1,028 mg/L	HPLC, TOC, BOD ₅ , COD	IBP and TOC removal increased proportionally with TiO ₂ concentration and addition of H ₂ O ₂ accelerates the degradation process. Solar photocatalysis was efficient to degrade IBP	Méndez-Arriaga et al. (2009a)				

(continued)

Table 3.3 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
Hybrid method	Milli-Q water	Initial concentration: 10 mg/L 0.024–0.044 mM Temperature: 25 °C H ₂ O ₂ concentration: 2.15 μmol/L/min	HPLC, DOC	Individual and hybrid processes of Fenton, sonolysis, and photocatalysis were compared. Combination of TiO ₂ /Fe ³⁺ /sonolysis yielded faster degradation for DOC removal (98 %) and complete degradation of IBP in 240 min	Méndez-Arriaga et al. (2009b)
Hybrid method	Milli-Q water	Initial concentration: 0.02–0.12 mM TiO ₂ P25 loading: 1 g/L Temperature: 25 ± 2 °C Ultrasonic power: 16, 35 and 55 mW/mL Fe ³⁺ concentration: 0.045 mM	HPLC, UV-vis, ESI/MS, TOC	Compared to sonolysis and photocatalysis, addition of Fe ³⁺ and TiO ₂ showed better degradation of IBP. Combination of UV, TiO ₂ and ultrasound produced highest degradation rate of 108 × 10 ⁻⁷ min ⁻¹	Madhavan et al. (2010)
<i>Ibuprofen mixture</i>					
Ibuprofen (and carbamazepine)	Milli-Q water and wastewater from WWTP	Solar simulator (1,000 W Phillip Xe lamp, intensity 272.3 W/m ²) and UV-A lamp (9 W Radium lamp, photon flux 3.37 × 10 ⁻⁶ Einstein/s) Initial concentration: 5–20 mg/L TiO ₂ loading: 50–3,000 mg/L Type of TiO ₂ : TiO ₂ Degussa P25, Hombikat UV 100, Aldrich, Tronox AK-1, Tronox TRHP-2, Tronox TR	UV (IBP: 220 nm), DOC	Simulated solar and UV-A light were efficient on IBP degradation in particular in the presence of TiO ₂ Degussa P25	Achilleos et al. (2010b)
		H ₂ O ₂ concentration: 0.07–1.4 mM pH: 3–10			

Ibuprofen (diclofenac and naproxen)	Milli-Q water	Solar simulator (Xe-OP lamp, 1 kW; photon flux: 6.9 $\mu\text{Einstein/s}$) Initial concentration: 200 ppm TiO ₂ loading: 1 g/L Temperature: 20, 30 and 40 °C Circulation flow rate: 0.1 and 0.4 mL/min DO concentration: 8, 40, 8 (initial)-2 (final) mg/L	HPLC, TOC, BOD ₅ , COD, DO, ESI/MS, toxicity assay on <i>Vibrio fischeri</i>	DO influenced the degradation of IBP and the optimum TiO ₂ loading for maximum degradation was 1 g/L	Méndez-Arriaga et al. (2008b)
Paracetamol	Milli-Q water	Black light blue UV-A (8 W) and UV-C (15 W) Initial concentration: 2.0–16.0 μM TiO ₂ loading: 0.04–5.0 g/L Temperature: 26 °C Oxygen concentration: 8.2–36.3 mg/L pH: 3.5–11.0	HPLC, TOC, GCMS	Rapid paracetamol degradation and mineralization occurred in the presence of TiO ₂ under UV-C irradiation. Also, direct photolysis under UV-C radiation was more effective compared to that of UV-A	Yang et al. (2008)
	Milli-Q water	UV lamp (254 nm) Initial concentration: 4.0 mM TiO ₂ loading: 0.4 g/L Temperature: 26 \pm 2 °C H ₂ O ₂ concentration: 48 mM Oxygen concentration: 8.2 mg/L (saturated) or 1.3–37.1 mg/L	HPLC, GCMS, IC	HO [•] radical played an important part in the degradation of paracetamol with a second-order rate constant ($1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)	Yang et al. (2009)

(continued)

Table 3.3 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
	Double-distilled water	Metal halide lamp (250 W) Initial concentration: 20–200 μM TiO_2 loading: 0.25–1.0 g/L Temperature: 15 $^\circ\text{C}$ pH: 3.0–11.0	HPLC, GCMS	Initial concentration of 100 μM was degraded by 95 % in the presence of 1.0 g/L TiO_2 within 100 min of irradiation. TiO_2 photocatalysis is efficient on paracetamol degradation without generating any toxic compound other than the parent drug	Zhang et al. (2008b)
	Milli-Q water	UV-A/LED (365 nm) Light intensity: 1–4 mW/cm ² Initial concentration: 100–385 ppb TiO_2 P25 loading: 0.005–0.06 g/L Temperature: 25 \pm 2 $^\circ\text{C}$	RP-LC, LC-MS-MS	Addition of TiO_2 accelerates the paracetamol degradation and complete conversion was obtained within 20 min. Smaller amounts of TiO_2 and stronger UV light helps for more light to penetrate into sample	Xiong and Hu (2012)

concentration, 0.6 g/L/8.17 mg/L yielded the highest degradation rate with a residual DCF percentage of 0.4 % after 30 min of irradiation. Longer irradiation times of up to 2 h were required to achieve complete mineralization. The toxicity of irradiated solutions was monitored with a microtox bioassay (*Vibrio fischeri*) and showed a decrease in the inhibition percentage to less than 1 % in 2 h, thus demonstrating the efficiency of photocatalytic detoxification. A total of 11 transformation products with four products with similar m/z ratios of 312 were generated from hydroxylation of DCF. This was attributed to the non-selective nature of the HO[•] radical. Hydroxy and bishydroxy-DCF derivatives were formed with subsequent formation of other chloro and hydroxy-phenol derivatives.

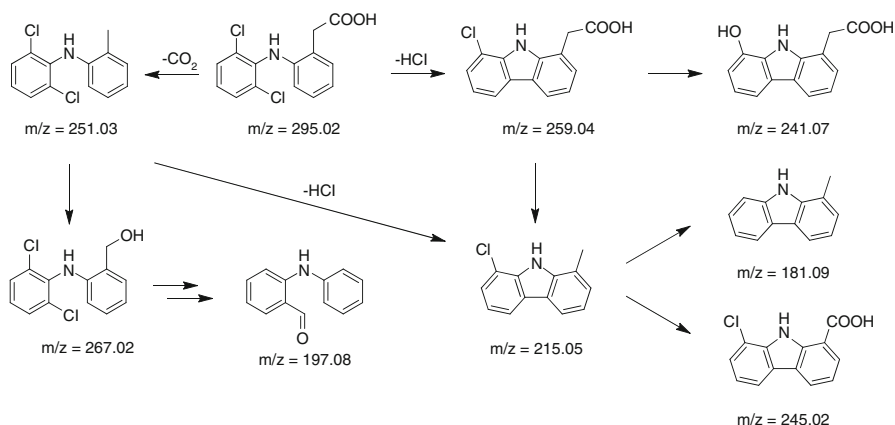
UV/TiO₂ degradation of DCF alone and in mixture solutions was examined in two studies by Rizzo et al. (2009a, b). For the investigation of DCF as a single compound in Milli-Q water, the authors investigated two operational parameters under oxygen supply, the initial concentration (5–80 mg/L) and loading of TiO₂ Aeroxide P25 (0.2–1.6 g/L) with a batch reactor. All degradation data followed pseudo-first order kinetics, but at higher initial concentrations, 40 mg/L and 80 mg/L and 1.6 g TiO₂/L, DCF degradation was reported to follow second-order kinetics. COD removal increased from 78 % to 85 % proportionally with TiO₂ loading from 0.4 to 0.8 g/L and a DCF initial concentration of 15 mg/L, but declined when DCF concentrations were increased to 40–80 mg/L, Rizzo et al. (2009a).

The degradation of DCF in the presence of two other APIs, namely amoxicillin (AMX) and carbamazepine (CBZ), was investigated in a subsequent study by the same group, Rizzo et al. (2009b). In this study, spiked samples in Milli-Q water and wastewater samples collected from a WWTP in Italy downstream of the biological process were used. The experimental set-up was similar to that in their previous study. Photocatalytic oxidation displayed higher removal from the sample mixture prepared using pure water after 30 min of irradiation, than the sample mixture in real wastewater. This difference is attributed to the existence of other oxidizable species and radical scavengers such as carbonates in the wastewater samples, which are able to compete with the APIs during the photocatalytic treatment. The following Eqs. (3.12) and (3.13) show the scavenging effects of carbonate species on hydroxyl radicals:



TOC removal of up to 80 % after 2 h and a rapid increase after 30 min in the sample mixtures in pure water was observed. However, TOC $t_{1/2}$ (half-life time) was found to be significantly higher in the sample mixtures in both water matrices compared to that of the single compound samples investigated.

UV-A photocatalytic irradiation was applied to the decomposition of DCF with different types of TiO₂, water matrices, H₂O₂ concentrations, TiO₂ loadings and



Scheme 3.1 Photocatalytic degradation pathways and degradants of diclofenac (DCF), Martínez et al. (2011)

initial concentrations investigated, Achilles et al. (2010a). An immersion-well type reactor equipped with a UV-A lamp (350–400 nm, 9 W) was used in this study. All experiments were conducted at a nominal pH of 6 with continuous oxygen flow. Among six TiO₂ samples tested, the TiO₂ Degussa P25 experiment showed the highest conversion of 85 % (initial concentration 10 mg/L and TiO₂ 250 mg/L) after 4 h of irradiation due to the better photocatalytic activity of anatase. Nevertheless, the P25 TiO₂ loading resulted in no improvement of DCF conversion and in all cases only 85 % conversion was attained. The results demonstrated that UV-A/TiO₂ treatment is effective for DCF abatement as well as mineralization. Another major finding was that photocatalytically treated 10 mg/L DCF (500 mg/L TiO₂) samples taken after 120 min were highly toxic to the freshwater species *Daphnia magna*.

An attempt was made to compare the effect of the irradiation source (near UV–vis and UV) on the photocatalytic degradation of DCF with commercial TiO₂ P25 and synthesized TiO₂, Martínez et al. (2011). This study highlighted that UV radiation (254 nm) was found to be superior to near UV–vis (366 nm) for DCF photocatalytic degradation. The optimum conditions for DCF removal included 0.5 g/L of synthesized anatase in the presence of 50 % (v/v) DO. In terms of mineralization, irradiation of aqueous DCF in the presence of 1 g/L TiO₂ P25 with near UV–vis caused about 40 % reduction in TOC in 60 min where the concentration declined from 112 mg/L to 68.6 mg/L. Eight photoproducts were identified regardless of reaction conditions. The main photoproduct formed was identified as a monohalogenated carbazole with a m/z of 259 g/mol as a result of photocyclization of DCF which was also in accordance with a DCF photolysis study, Agüera et al. (2005). Another important pathway, decarboxylation generated two other intermediates corresponding to a m/z of 251 g/mol and 215 g/mol (Scheme 3.1), respectively.

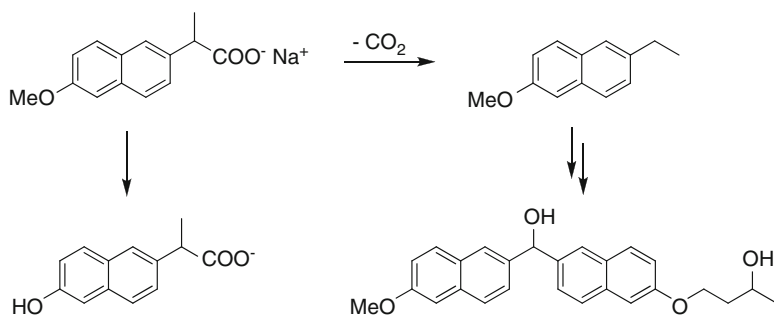
More recently, the combination of heterogeneous photocatalysis with other AOPs for DCF degradation has been studied. The effect of photocatalytic ozonation ($O_3/UV-A/TiO_2$) on DCF was assessed, Aguinaco et al. (2012). Irradiation was performed using a high pressure Hg lamp which was placed in the centre of a borosilicate-type glass photoreactor. Commercial TiO_2 Degussa P25 and ozone generated from pure oxygen were used. One interesting finding was that the wastewater sample of DCF showed no differences in terms of degradation rate and TOC removal for a DCF concentration of 30 mg/L, whereas differences were observed when Milli-Q water was used under the same conditions indicating a significant effect of the water matrix. The study reported negligible differences when investigating TiO_2 loadings (0.5–2.5 g/L) on 30 mg/L DCF and in all cases complete degradation was achieved in 5.5 min.

From the results above on the UV/ TiO_2 degradation of DCF, it is evident that attempts have been made to correlate selected operational parameters with DCF degradation in pure water and also wastewater. It can be concluded that the choice of initial concentration of DCF, TiO_2 loading and irradiation time differs between the studies. However, there is no single study which exclusively covers all the operating parameters such as pH (from acidic to basic) and TiO_2 loading (low to high range). The effects of radiant flux and wavelength are not clearly understood despite the fact that UV-A type of irradiation has been chosen for the majority of the studies reviewed.

Naproxen

The occurrence of naproxen (NPX) has been reported both in water and wastewater. A recent review has also indicated its continuous presence in the water bodies, Ziy-lan and Ince (2011). Concentrations of NPX in WWTP effluents and surface water ranged between 0.1–2.6 $\mu\text{g/L}$ and 0.01–0.1 $\mu\text{g/L}$ respectively, Boyd et al. (2005). However, there is still a considerable lack of information on its photocatalytic degradation compared to its direct photolysis which has thus far been performed with artificial UV light and direct sunlight, Felis et al. (2007) and Packer et al. (2003). NPX photodegradation products were found to be more toxic than the parent compound based on a toxicity studies conducted using *Daphnia magna* and *Vibrio fischeri*, Isidori et al. (2005).

Only one study has been conducted on the photocatalytic and photolytic degradation of NPX, Méndez-Arriaga et al. (2008a). In this study, 3 h of photolysis and photocatalysis with a solar simulator produced 90 % and 40 % NPX removal, respectively. Lower percentage removal during the photocatalytic process resulted from either low adsorption of NPX onto the TiO_2 surface or possible recombination and deactivation of the HO^\bullet radical. A higher mineralization (20 %) level was however achieved with photocatalysis compared to photolysis (5 %). Initial degradation rate of NPX increased with TiO_2 loading (0.1–1 g/L) for 0.8 mM/L NPX. The by-products formed from the 180 min of treatment were identified



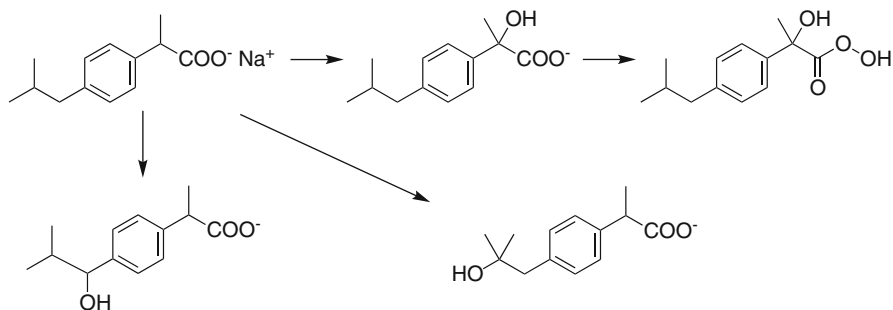
Scheme 3.2 The proposed degradation pathway of naproxen (NPX) by TiO₂ photocatalysis, Méndez-Arriaga et al. (2008a)

by means of liquid chromatography-electrospray ionization-time of flight mass spectrometry (LC/ESI-TOF-MS). Two major pathways including demethylation and decarboxylation were thus suggested to occur on the photocatalytic treatment of NPX (Scheme 3.2).

In another study, the photocatalytic degradation of NPX was evaluated together with two other NSAIDs, namely DCF and ibuprofen (IBP), Méndez-Arriaga et al. (2008b). A Duran tubular photoreactor was placed in a solar simulator and irradiated with a Xe-OP lamp (290–400 nm; photon flux 6.9 μ Einstein/s). A maximum degradation of NPX was obtained at a TiO₂ loading of 0.1 g/L for 200 mg/L NPX (30 °C and flow rate of 0.2 mL/min) with a kinetic rate constant of $7.0 \times 10^{-3} \text{ min}^{-1}$. An increase in TiO₂ (0.1–1 g/L) did not improve the degradation rate. NPX degradation and TOC conversion however showed a slight increase at 40 °C. The reaction rate for each NSAID did not vary significantly. Biodegradability (BOD₅/COD) showed no improvement after photocatalytic treatment of NPX, implying that the by-products formed affect post-biological treatment.

Another study was carried out to evaluate the feasibility of commercial nanofiltration membranes and TiO₂ P25 Degussa for NPX and six other pharmaceuticals (furosemide, rantinide, ofloxacin, phenazone, carbamazepine and clofibrac acid) degradation, Molinari et al. (2006). For irradiation purposes, a medium pressure Hg lamp (125 W) was used under continuous oxygen bubbling. NPX showed a 95 % adsorption at pH 3 and only 3 % at pH 11 due to high solubility. Degradation of NPX was only performed in a batch photoreactor without any membrane. A comparison with the membrane photoreactor for NPX removal was thus not possible. In a batch photoreactor, the concentration of NPX decreased with increasing irradiation time following pseudo-first order kinetics. The rate constants for 5 mg/L NPX at pH 3 and pH 11 were 7.86×10^{-2} and $4.91 \times 10^{-1} \text{ min}^{-1}$, respectively.

Although NPX is known to undergo direct photolysis under natural sunlight, Packer et al. (2003), various aspects of the efficiency of photocatalytic NPX degradation remain to be investigated. Further research needs to be undertaken in order to gain sufficient knowledge on the degradation kinetics and toxicity outcome of photocatalytically treated samples, in addition to the by-products generated.



Scheme 3.3 Photocatalytic degradation pathways of ibuprofen (IBP), Méndez-Arriaga et al. (2008b)

Ibuprofen

As for the other NSAIDs, ibuprofen (IBP) has been found in water, wastewater and wastewater effluents due to only partial removal in WWTPs. For example, the concentrations of IBP and one of its metabolites was recorded to be more than 500 ng/L in the effluent of a primary WWTP, Sabri et al. (2012). Elimination of IBP in WWTPs varies between 75 % and 90 %, Tixier et al. (2003). The most prominent metabolites of IBP, namely carboxy and/or hydroxy IBP, have been reported to be present after biological treatment as toxic by-products, Mozia and Morawski (2012). Despite being one of the most consumed pharmaceuticals, there has been little attention devoted to the photocatalytic oxidation of IBP thus far.

A systematic study of IBP (and CBZ) photocatalytic degradation and mineralization spiked in Milli-Q and wastewater samples was performed under UV-A and simulated solar irradiation, Achilleos et al. (2010b). The study concluded that heterogeneous photocatalysis with both, UV-A and solar irradiation, was effective for IBP removal in the presence of TiO_2 in particular Degussa P25. The study proposed that this treatment can be employed as a post-secondary treatment in WWTPs.

UV/ TiO_2 degradation of IBP and two other NSAIDs, DCF and NPX, revealed that IBP can be completely removed, Méndez-Arriaga et al. (2008b). A maximum conversion of 200 mg/L IBP was achieved in the presence of 1 g/L TiO_2 after 240 min of irradiation with a first-order kinetic rate constant of $9.1 \times 10^{-3} \text{ min}^{-1}$. A low initial concentration of IBP (25 ppm) resulted in maximum degradation within 60 min and 50 % mineralization. Further investigation showed that biodegradability (BOD_5/COD index) of IBP was enhanced in the presence of excess DO. The study thus proposed the feasibility of post-biological treatment. Electrospray ionization/mass spectrometry (ESI/MS) analysis at the end of 4 h of photocatalytic treatment revealed that hydroxylation or HO^\bullet attack on the propanoic moiety or/and isobutyl side chain is the dominant pathway for IBP degradation. Demethylation and decarboxylation processes resulted in the formation of other organic acids such as propionic, formic or hydropropionic acid or their sodium salts (Scheme 3.3).

Solar photocatalysis has proven to be an effective method for IBP degradation based on a study conducted in three solar pilot plants, Méndez-Arriaga et al. (2009a). TOC and IBP removal were enhanced in the presence of H_2O_2 . In contrast, no improvement was found on inclusion of $\text{Na}_2\text{S}_2\text{O}_8$ as the pH decreased up to 4.5 which correlates to the pK_a of IBP (4.5) and thus leads to precipitation. Improvement in the biodegradability (BOD_5/COD) of the treated solution suggested coupling potential with biological treatment.

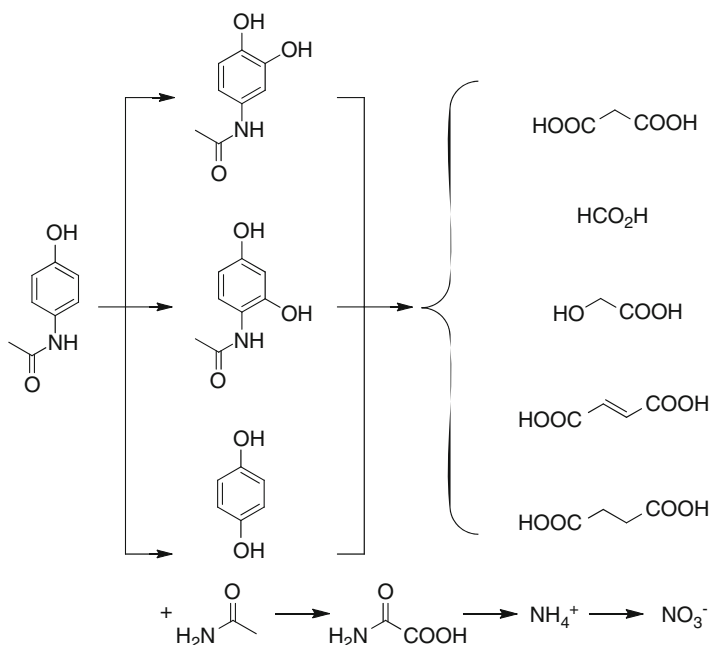
Effective photocatalytic degradation rates have also been reported when hybrid AOP methods were applied to IBP, Méndez-Arriaga et al. (2009b) and Madhavan et al. (2010). One study confirmed that AOP hybrid processes (sonophotocatalysis with TiO_2 , sonophoto-Fenton and sonophotocatalysis with TiO_2 and Fe^{2+}) improved the degree of mineralization of IBP in parallel with IBP removal. The combination of $\text{TiO}_2/\text{Fe}^{2+}$ /sonolysis turned out to be the most beneficial application, owing to its highest mineralization (98 %), Méndez-Arriaga et al. (2009b). The combination of UV and ultrasound with TiO_2 (UV/ TiO_2 /ultrasound) enhanced the degradation of 18.5 mg/L IBP (in 1 g/L TiO_2 P25) from 61 % (photocatalysis only) to 85 % after 15 min of irradiation, Madhavan et al. (2010).

Acetaminophen

Acetaminophen commonly known as paracetamol is the API in a variety of over-the-counter analgesic and antipyretic drugs. This drug is extensively used around the globe. In England, it was used in more than 400 t in 2000 while the export quantity from China was estimated to be 15,348 t in 2001, Zhang et al. (2012). Its occurrence in levels up to 6 ppb and 10 ppb, respectively, in natural waters, in European sewage treatment plant effluents and in the United States has been reported. However, only few studies deal with the removal of paracetamol by means of UV/ TiO_2 .

A study dedicated to explore the effect of various operating parameters on photocatalytic degradation for paracetamol in Milli-Q water was reported in 2008, Yang et al. (2008). Comparing UV-A/ TiO_2 and UV-C/ TiO_2 irradiation, the latter was found to be more effective to degrade 4.0 mM (0.4 g/L TiO_2) of the parent compound as well as reducing TOC to about 60 % in 300 min. Increasing TiO_2 loading from 0.04 g/L to 5.0 g/L caused the degradation rate to increase from 4.9 ± 0.5 to $14.7 \pm 1.7 \times 10^{-3} \text{ min}^{-1}$ until it levelled off to $13.7 \pm 1.2 \times 10^{-3} \text{ min}^{-1}$ at 0.8 g/L. Insignificant effects were found at 7.0 g/L due to scattering phenomena. Increase in pH from 3.5 to 9.5 also increased the degradation rates from 11.0 to $16.5 \times 10^{-3} \text{ min}^{-1}$. However, a higher pH of 11 significantly slowed down the degradation rate due to repulsion between negatively charged TiO_2 and paracetamol. A similar pH effect was also observed by Zhang et al. (2008b). Addition of oxygen showed a significant impact on paracetamol degradation compared to argon as the former inhibits $e^- - h^+$ recombination.

In order to establish the nature of the most active species (e_{cb}^- , h_{vb}^+ , HO^\bullet , HO_2^\bullet , $\text{O}_2^{\bullet-}$ and H_2O_2) for paracetamol degradation, a subsequent study was undertaken by Yang et al. (2009) using UV-A irradiation. It was proposed that the HO^\bullet radical plays a prominent role in the photocatalytic degradation of paracetamol.

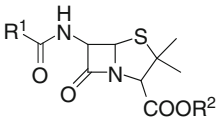

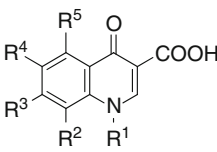
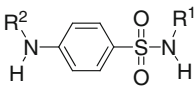
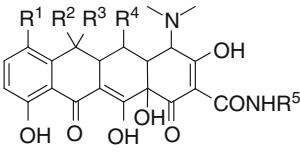
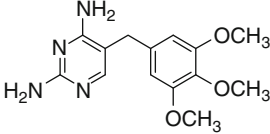


Scheme 3.4 Photocatalytic degradation pathways and degradants of paracetamol, Yang et al. (2008, 2009)

Both studies identified 11 common intermediates, including aromatic compounds, carboxylic acids, and nitrogen containing aliphatic compounds from photocatalytic degradation of paracetamol (Scheme 3.4). Two additional inorganic intermediates, namely ammonium and nitrate, were proposed as a result of successive mineralization of the intermediates. The degradation is initiated by hydroxylation through HO[•] addition onto the aromatic ring, which subsequently results in further oxidation to form carboxylic acid derivatives, Yang et al. (2009).

Recent advances in the photocatalytic degradation of paracetamol revealed that UV-A/LEDs (Light Emitting Diode) can be used instead of the traditional Hg lamps. Conventional lamps are known for their high energy cost and the incorporation of toxic mercury, Xiong and Hu (2012). Negligible amounts of paracetamol were removed with UV-A/LED photolysis. In contrast, TiO₂ P25 caused a significant level of degradation with complete degradation within 20 min. An increase in light intensity from 1 to 4 mW/cm² significantly enhanced the degradation rate of paracetamol. One important advantage demonstrated in this study is the possibility to employ low average amount of TiO₂ (0.01 g/L) due to the high light intensity from LED lamps. This finding has important implications for pursuing the applications of UV-A/LED light sources in water and wastewater treatment.

Table 3.4 Classifications of antibiotics (Adapted from Homem and Santos (2011))

Classes	Features of structures	Chemical structure
Penicillins	Thiazolidine ring connected to a β -lactam ring, to which a side chain is attached	
Imidazoles	Heterocyclic compounds of 5 member di-unsaturated ring structure with two nitrogen atoms at nonadjacent positions	
Quinolones	Two fused rings with a carboxylic acid and a ketone group. When R ⁴ is F, then it is a fluoroquinolone	
Sulfonamides	Sulfonyl group connected to amine group	
Tetracyclines	Consists of an octahydro-tetracene ring skeleton and four fused rings	
Trimethoprim	Diaminopyrimidine, analogue of the pteridine moiety of folic acid	

3.5.2 Antibiotics

In recent years, there has been an increasing amount of literature on the photocatalytic treatment of antibiotics, due to their extensive use in both humans and animals as agents to prevent and treat microbial infections. Classifications of the major antibiotics are presented in Table 3.4, according to importance attached to their chemical structure and mechanism of action.

The annual consumption of antibiotics for human and veterinary usage is estimated to be about 100,000–200,000 t, Xu et al. (2007). The first detection of antibiotics in river water was reported in 1982 in England, where macrolides, tetracycline (TC) and sulphonamides at levels of 1 $\mu\text{g/L}$ were found, Homem and Santos (2011). Since then, numerous studies have reported the presence of antibiotics in water courses around the world, Watkinson et al. (2009). The polar and non-volatile nature of antibiotics contributes significantly to their accumulation

in the environment due to their persistence either as the parent compound or metabolites after conventional water treatment. One of the major effects of the continuous accumulation is the emergence of antibiotic resistance strains of bacteria, Elmolla and Chaudhuri (2010a). Accumulation of small quantities of antibiotics in receiving water over a long term has been the main concern, as they may have adverse effects on both humans and aquatic organisms.

Studies conducted to assess the potential of UV/TiO₂ degradation on four important classes of antibiotics namely β -lactam antibiotics, quinolones, tetracyclines and sulphonamides are summarized in Table 3.5.

β -Lactam Antibiotics

Amoxicillin (AMX) (C₁₆H₁₉N₃O₅S) has been one of the most popular candidates amongst the β -lactam antibiotics selected for UV/TiO₂ treatment. This API has three pK_as namely 2.7, 7.5 and 9.6, Dimitrakopoulou et al. (2012). In water, AMX shows absorption up to 290 nm (Fig. 3.4). Oral consumption of 500 mg of AMX has resulted in 86 \pm 8 % of AMX unchanged in human urine within 2 h of consumption, Martins et al. (2009). Excretion of unchanged AMX due to a slow rate of metabolism in humans has led to its discharge into the environment. AMX has also been detected in effluents from drug manufacturing facilities with levels reaching several hundreds of milligrams per liter, Mavronikola et al. (2009). The possibilities of AMX elimination by means of UV/TiO₂ have been investigated by several research groups, Martins et al. (2009) and Dimitrakopoulou et al. (2012).

AMX spiked ultrapure water and secondary effluent water were used in a UV-A/TiO₂ degradation comparative study, Dimitrakopoulou et al. (2012). Of the various catalysts tested, TiO₂ Degussa P25 (250 mg/L) was found to be the most efficient TiO₂ catalyst, yielding complete degradation after 25 min and 93 % mineralization within 90 min of irradiation for 10 mg/L of AMX. Under the same conditions, TiO₂ (Anatase) required at least 45 min to cause a complete removal. The other six TiO₂ catalysts needed much longer reaction times and in most cases lead to incomplete degradation. In addition, the degrees of mineralization failed to rise above 75 % after 90 min of irradiation. Direct photolysis with a UV-A light source had little effect on AMX degradation (only 4 %) due to its poor absorbance within the emission spectrum of the irradiation source. The comparison between ultrapure water and secondary effluent showed that the latter hindered the degradation due to the presence of organic matter and scavenging effects of bicarbonates and chlorides.

AMX spiked hospital wastewater samples yielded complete degradation with TiO₂ Degussa P25 photocatalysis (800 mg/L at pH 4 and 30 °C) after 30 min of irradiation while only 85 % degradation was achieved using the photo-Fenton process after an extended period of 60 min, Martins et al. (2009). The lower degradation in the latter case was explained by the pH conditions as it has a significant effect on the treatment. At pH 4 and beyond, the formation of Fe²⁺ hydroxide complexes and Fe³⁺ species retard the production of HO[•]. In contrast, the

Table 3.5 Highlights of heterogeneous photocatalytic studies on antibiotics

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
<i>Amoxicillin</i>					
	Ultrapure water and treated wastewater (secondary effluent)	9 W Radium Ralutec concentration: 2.5–30 mg/L TiO ₂ loading: 100–750 mg/L Type of TiO ₂ : Degussa P25 (21 nm), Hombikat UV 100 (5 nm), Millennium PC50 (20–30 nm), Millennium PC100 (15–25 nm), Millennium PC105 (15–25 nm), Millennium PC500 (5–10 nm), Tronox AK1 (20 nm), Aldrich Anatase AA (15 nm) pH: 5 and 7.5	TOC, HPLC, toxicity on <i>Escherichia coli</i> , <i>Klebsiella pneumoniae</i> and <i>Enterococcus faecalis</i>	UV-A/TiO ₂ is an effective abatement method for AMX in water in particular with TiO ₂ Degussa P25. Antibiotic activity of irradiated solution showed that <i>Escherichia coli</i> and <i>Klebsiella pneumoniae</i> were highly resistant to AMX up to 25 mg/L	Dimitrakopoulou et al. (2012)
	Hospital wastewater	Medium pressure Hg lamp (125 W; intensity: 401 W/m ²) TiO ₂ P25 loading: 400–1,200 mg/L Temperature: 20–40 °C pH: 3–11	HPLC, COD, toxicity on <i>Artemia salina</i>	Response surface methodology was used to study the combined effect of pH and TiO ₂ loading on COD reduction and AMX photocatalysis. Maximum COD removal was achieved with 800 mg/L TiO ₂ and pH 3. Toxicity inhibition of 46.3 % was obtained	Martins et al. (2009)

	Water type not provided	15 W low pressure luminescent Hg lamp (UV, 365 nm) and 15 W daylight fluorescent lamp (Vis, 0.6 mW/cm ²) Solar radiation (16 mW/cm ²) Initial concentration: 20–100 mg/L TiO ₂ concentration: 1 g/L Temperature: 20 ± 1 °C pH: 3–9	UV-vis (230 nm), IC, UPLC-ESI/MS, QTOF/MS, COD	Carbon and iron doped titania and Degussa P25 was tested for AMX degradation under artificial visible light and solar radiation. Doped titania yielded comparable degradation with that of Degussa P25 under UV light	Klauson et al. (2010)
<i>Amoxicillin mixtures</i>					
Amoxicillin (ampicillin and cloxacillin)	Distilled water	UV lamp (6 W, 365 nm) Initial concentration: 104 mg/L TiO ₂ (Anatase) loading: 0.5–2.0 g/L ZnO loading: 0.2–2.0 g/L Temperature: 22 ± 2 °C pH: 3–11 H ₂ O ₂ concentration: 50–300 mg/L	HPLC, COD, BOD ₅ , DO, DOC	All treatments degraded the antibiotics and also improved biodegradability except for UV/ZnO which did not show any effect on the latter. Photo-Fenton showed highest rate constant (0.029 min ⁻¹) and was most cost-effective	Elmolla and Chaudhuri et al. (2010b)
Amoxicillin (ampicillin and cloxacillin)	Distilled water	UV lamp (6 W, 365 nm) Initial concentration: 104 mg/L TiO ₂ (Anatase) loading: 0.5–2.0 g/L Temperature: 22 ± 2 °C pH: 3–11 H ₂ O ₂ concentration: 50–300 mg/L	HPLC, COD, BOD, DO, DOC	Addition of H ₂ O ₂ at pH 5 with TiO ₂ 0.1 g/L led to complete degradation of all antibiotics. Mineralization was also observed through DOC removal and formation of nitrate, ammonia and sulphate	Elmolla and Chaudhuri et al. (2010c)

(continued)

Table 3.5 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
Amoxicillin (Diclofenac)	Deionized water	Solar simulator (250–765 W/m ²) Initial concentration: 200 mg/L TiO ₂ loading: 100 mg/L	HPLC, UV-vis	Degradation of AMX was more efficient in the presence of TiO ₂ where about 70 % removal was achieved after 6 h of irradiation at 400 W/m ²	Kockler et al. (2012)
<i>Sulfonamide and other sulfa antibiotics</i>					
Sulfamethoxazole	Milli-Q water	Solar simulator Xe lamp (1,000 W) Initial concentration: 100 ppm TiO ₂ concentration: 0.1–2.0 g/L Temperature: 25 ± 0.1 °C Oxygen concentration: 8 mg/L Initial pH: 5 (not buffered) pH: 2, 5, 7 and 11	HPLC, TOC, BOD ₅ /COD, FIA, IC, LCMS	Increase in TiO ₂ amount improved SMX degradation and TOC removal. Change in pH showed more effect on TOC removal than that on the degradation of SMX	Abellán et al. (2007)
Sulfamethoxazole (and trimethoprim)	Milli-Q water	Solar simulator (Xe lamp, 1,500 W) Initial concentration: 100 mg/L TiO ₂ loading: 0.1–2.0 g/L Temperature: 25 °C	HPLC, TOC, BOD, COD	Increase in the amount of TiO ₂ has great influence on the reaction rate. The optimum catalyst concentration was between 0.5 and 1.0 g TiO ₂ /L for SMX degradation	Abellán et al. (2009)
Sulfamethoxazole	Reverse-osmosis water	Hg-Ar (Germicidal UV-C) lamp Initial concentration: 3–12 mg/L TiO ₂ P25 loading: 0.5 g/L Temperature: 25 ± 0.1 °C DO concentration: 8.8 mg/L Pure oxygen concentration: 42 mg/L	HPLC, COD, DO, pH, UV-vis, LCMS, toxicity test on <i>Daphnia magna</i>	Kinetic rate constant decreased with increasing SMX concentration. DO did not favour removal of SMX	Nasuhoglu et al. (2011)

Sulfamethoxazole	Ultrapur water, municipal wastewater and ground water	UV-A Radium lamp (9 W) Initial concentration: 2.5–30 mg/L TiO ₂ loading: 100–750 mg/L Type of TiO ₂ : TiO ₂ Degussa P25, Hombikat UV 100, Millennium PC50, Millennium PC100, Millennium PC105, Millennium PC500 Temperature: 25 °C pH: 4–8	HPLC, TOC	Degradation of SMX was described by L-H model. Excess DO showed large effect on TOC removal rather compared to SMX degradation. Initial reaction rate for SMX decomposition increased from 0.428 mg/(L × min) to 1.510 mg/(L × min) when SMX concentration was increased from 2.5 mg/L to 20 mg/L	Xekoukoulotakis et al. (2011)
Sulfachlorpyridazine, sulfapyridine and sulfisoxazole	Milli-Q water	High pressure Hg lamp (125 W) Initial concentration: 50–200 μM TiO ₂ P25 loading: 0.25–3.0 g/L Initial pH: 3–11 Radical quencher: isopropanol and potassium iodine	TOC, HPLC, HPLC/MS/MS	All three sulfa drugs, sulfachlorpyridazine, sulfapyridine and sulfisoxazole can be effectively degraded in aqueous system with removals of 85.2 %, 92.5 % and 85.0 % after 1 h of irradiation respectively. Effect of pH varied between the drugs	Yang et al. (2010)
Sulfamethoxazole and sulfonamide analogues (sulfisoxazole, sulfathiazole, sulfamethizole)	Deionized water	Xe arc lamp (450 W) Initial concentration: 5–480 μM TiO ₂ P25 loading: 0.01–1.0 g/L Hombikat UV-100 loading: 0.1 g/L Temperature: 25 °C pH: 3–11	HPLC, LC/MS/MS, DOC	UV-A/TiO ₂ photocatalysis is very effective for degrading sulfonamides particularly in natural waters exhibiting either alkaline pH or low concentrations of NOM, or both conditions	Hu et al. (2007)

(continued)

Table 3.5 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
<i>Quinolones</i>					
Oxolinic acid	Water type not provided	Annular reactor with black light (36 W) Initial concentration: 18 ppm TiO ₂ ; 1 g/L (suspension) and 8.79 g for immobilized form pH: 9	Spectrophotometer, TOC, COD, antibacterial activity with <i>Escherichia coli</i>	Treated solutions showed no antibiotic activity. TiO ₂ coated on sintered glass cylinder efficient to remove OX acid	Palominos et al. (2008)
Oxolinic acid	Ultrapure water	Black lamp (14 W/m ² ; 365 nm) Initial concentration: 20 mg/L TiO ₂ P25 loading: 0.2–1.5 g/L pH: 7.5–11	LC with fluorescence detector, HPLC-MS DOC, COD, antimicrobial activity on <i>Escherichia coli</i>	Experimental conditions of pH 7.5 and 1.0 g/L of TiO ₂ favoured between 80 % and 100 % of OX acid degradation. About 20 % of OX acid was adsorbed on TiO ₂ under dark conditions	Giraldo et al. (2010)
Ciprofloxacin	Double distilled water	High pressure Hg lamp (0.38 mW/cm ²) Initial concentration: 100 µM TiO ₂ P25 loading: 1.5 g/L Temperature: 25 °C pH: 3.0–11.0	HPLC, LC/MS/MS	Oxidative and reductive processes are important for CIP degradation. Hydroxyl and azide radicals can react with CIP at high rate constants, (2.15 ± 0.10) × 10 ¹⁰ and (2.90 ± 0.12) × 10 ¹⁰ m ⁻¹ s ⁻¹ respectively	An et al. (2010)

Ciprofloxacin	Deionized water	O ₃ free Xe arc lamp (450 W) Initial concentration: 100 μM TiO ₂ and Hombikat UV 100 loading: 0.5 g/L Temperature: 25 °C pH: 6	HPLC, HPLC/UV/FLD, LC/MS/MS, antibacterial activity with <i>Escherichia coli</i>	Degradation rate of CIP under comparable solution conditions (100 mM CIP, 0 or 0.5 g/L TiO ₂ , pH 6, 25 °C) followed the trend UV-A/TiO ₂ > Vis-TiO ₂ > UV-A	Paul et al. (2010)
Ciprofloxacin	Hospital wastewater	Medium pressure Hg lamp (125 W) Initial concentration: 200 μg/L TiO ₂ P25 loading: 400 mg TiO ₂ /700 mL	LC/FLD, UV-vis, COD	Heterogeneous photocatalysis and ozonation were compared for CIP degradation in hospital wastewater. Both treatments produced complete degradation in 60 min and degradation products generated were similar	Vasconcelos et al. (2009)
Moxifloxacin	Deionized water	UV-A (485 μW/cm ²) Initial concentration: 12.5–124.6 μM TiO ₂ P25 loading: 0.25–8 g/L Temperature: 25–65 °C Oxygen concentration: 0–100 % pH: 7 Stirring speeds: 2.3, 7.9 and 13.2 rps Effect of radical inhibitors: isopropanol and potassium iodide	HPLC	Degradation kinetics was affected by the variables investigated. Oxidative holes play more important role than hydroxyl radicals as it led to 63 % MOX degradation	Van Doorslaer et al. (2012)

(continued)

Table 3.5 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
Norfloracin	Double distilled water	Medium pressure Hg lamp (125 W) Initial concentration: 0.15–0.50 mM TiO ₂ loading: 1 g/L Type of TiO ₂ : Degussa P25, Hombikat UV100, PC500 H ₂ O ₂ concentration: 10 mM pH: 4.2, 6.3, 8.1 and 10.4	UV-vis, TOC	TiO ₂ Degussa P25 was found to be more efficient than other catalysts. Degradation rate increased with initial concentrations at optimum pH 10.4 from 0.009 × 10 ⁻³ mol L ⁻¹ min ⁻¹ (0.15 mM) to 0.017 × 10 ⁻³ mol L ⁻¹ min ⁻¹ (0.50 mM)	Haque and Muneer (2007)
Levofloxacin	Reverse osmosis water	Hg-Ar Germicidal UV-C lamp (254 nm; intensity: 1.3 × 10 ⁻³ ± 0.3 Einstein/min/L) Initial concentration: 20 mg/L TiO ₂ P2.5 loading: 0.05–0.5 g/L	HPLC, COD, antibacterial activity on <i>Escherichia coli</i> and <i>Pseudomonas fluorescens</i>	First study to report photocatalysis and ozonation under UV-C radiation for levofloxacin removal. About 97 % levofloxacin was removed after 2 h under photocatalysis. No antibacterial activity found under both treatments	Nasuhoglu et al. (2012)
<i>Fluoroquinolone mixtures</i> Ofloxacin norfloxacin, ciprofloxacin and enrofloxacin	Distilled water	Solar irradiation (800 W Xe lamp) Initial concentration: 0.028 mM (ofloxacin), 0.031 mM (norfloxacin), 0.027 mM (ciprofloxacin) and 0.028 mM (enrofloxacin) TiO ₂ loading: 0.1–1.5 g/L pH: 2–9 H ₂ O ₂ concentration: 41.25–330 mg/L	HPLC, TOC, antibacterial activity with <i>Bacillus subtilis</i>	Photocatalytic reactions of the four FQs could be described by a pseudo-first order kinetic model. Complete removal of all FQs at 0.5 g/L TiO ₂ and 82.5 mg/L of H ₂ O ₂ at pH 6 after 90 min of irradiation	Li et al. (2012)

Ciprofloxacin, danofloxacin, enrofloxacin, levofloxacin, marbofloxacin and moxifloxacin	River water	Natural sunlight (290–470 W/m ²) Phosphorus-covered low pressure Hg lamp (12 W/m ² , 310 nm) Initial concentration: 20–50 µg/L TiO ₂ P25 loading: 0.5 g/L	HPLC with fluorescence detector, ESI-MIS/MS	About 15 min sufficient to remove the FQs under natural sunlight	Sturini et al. (2012)
Ciprofloxacin and moxifloxacin	Deionized water	UV-A (485 µW/cm ²) and UV-C (389 µW/cm ²) Initial concentration MOX: 37.4 µM Initial concentration CIP: 45.3 µM TiO ₂ P25 loading: 0.5 g/L Temperature: 25 °C pH: 3–10	HPLC	The highest removal rates were obtained at pH 7 in the presence of TiO ₂ (0.5 g/L) as a photocatalyst were as follows: k_1 , CIP, UV-A = 0.137 min ⁻¹ , k_1 , CIP, UV-C = 0.163 min ⁻¹ , k_1 , MOX, UV-A = 0.227 min ⁻¹ , k_1 , MOX, UV-C = 0.236 min ⁻¹	Van Doorslaer et al. (2011)
<i>Tetracyclines</i> Tetracycline	Water type not provided	Solar simulator (300–800 nm, Xe lamp, 250 W/m ²) TiO ₂ P25 loading: 0.5–1.5 g/L ZnO loading: 0.2–1.5 g/L pH range for TiO ₂ : 3–10 pH range for ZnO: 6–11	Spectrophotometer, TOC, AAS, antibacterial activity with <i>Staphylococcus aureus</i>	Irradiation in the presence of catalyst completely removes the solution's antibacterial activity. The catalytic activity of both catalysts indicates that ZnO presents a slightly higher oxidation rates than TiO ₂	Palominos et al. (2009)

(continued)

Table 3.5 (continued)

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
Tetraacycline	Deionized water	UV lamp (125 W), UV-A lamp (black light, 160 W), solarium device (6 W × 20 W lamps, 300–400 nm) Initial concentration: 40 mg/L TiO ₂ P25 loading: 0.5 and 1 g/L Oxygen gas flow: 200 mL/min	HPLC, TOC, UV-vis, antibacterial activity on <i>Staphylococcus aureus</i> strain	In the absence of TiO ₂ , no degradation was observed. Degradation of TC up to 50 % was obtained after 10, 20 and 120 min under UV lamp, solarium device and UV-A lamp respectively	Reyes et al. (2006)
Tetraacycline	Water type not provided	Medium pressure Hg lamp (700 W) Initial concentration: 67 mg/L TiO ₂ loading: 30 mg/L	HPLC, DOC, LC-ESI/MS/MS, toxicity on <i>Pseudomonas</i>	Toxicity test carried out on <i>Pseudomonas</i> showed decrease in toxicity during tetracycline photocatalysis. Irradiation of 90 min is not sufficient to generate biodegradable by-products	Mboula et al. (2012)
Oxytetracycline	Deionized water	Solar simulator (Xe-OP lamp 1 kW) and CPC reactor Initial concentration: 20 mg/L TiO ₂ P25 loading: 0.1 and 0.5 g/L pH: 3, 9, 11 and free initial pH 4.4	HPLC, TOC, BOD, COD, UV-vis, LC-MSD-TOF, ESI-MS, toxicity test on <i>Vibrio fischeri</i>	Combination of 0.5 g/L TiO ₂ at nominal pH (pH ~4.4) showed complete removal after 40 min of irradiation with 7.5 kJ/L of UV dose	Pereira et al. (2011)

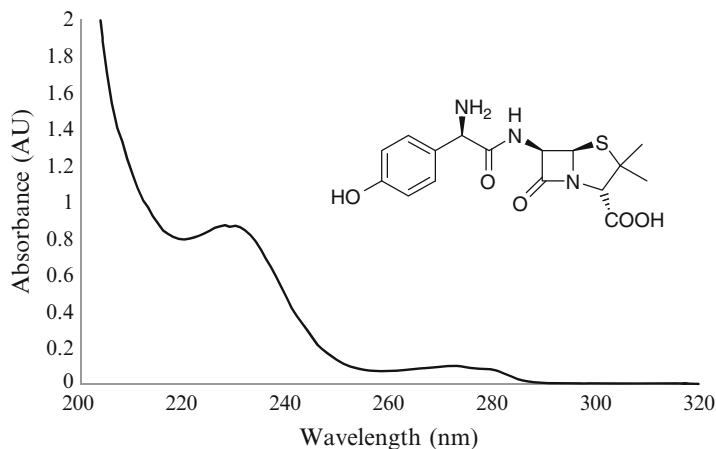
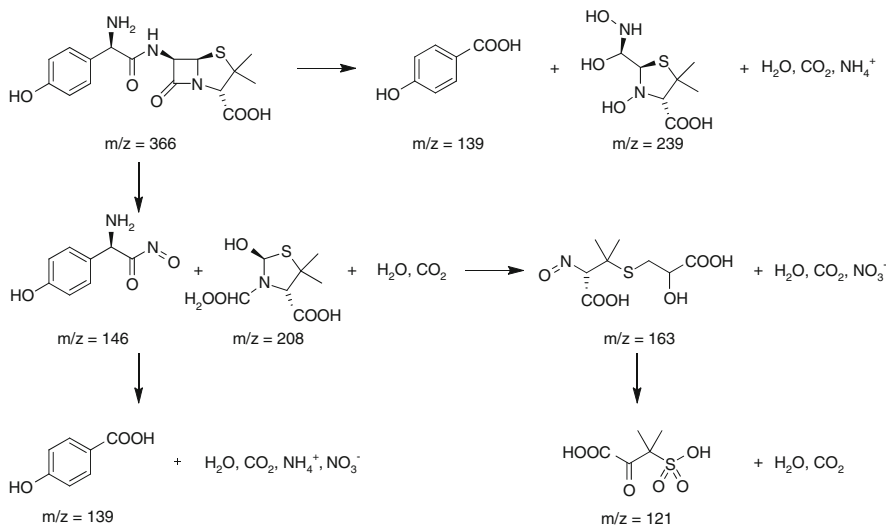


Fig. 3.4 Absorbance spectrum of amoxicillin in water

percentage COD removal was higher for photo-Fenton than for photocatalysis with 64.6 % versus 44 %, respectively. Toxicity inhibition studies with *Artemia salina* showed that both treatments were efficient in removing toxicity and reductions of 43.5 % and 46.3 % were obtained in photo-Fenton and UV/TiO₂ processes, respectively.

Another study compared the efficiency of four AOPs, namely Fenton, photo-Fenton, TiO₂ photocatalysis (UV/TiO₂ and UV/TiO₂/H₂O₂) and ZnO photocatalysis (UV/ZnO) on AMX (104 mg/L) in distilled water in combination with two other antibiotics, ampicillin (105 mg/L) and cloxacillin (103 mg/L) under UV-A irradiation (365 nm), Elmolla and Chaudhuri (2010b). Based on the pseudo-first order rate constants under optimum operating conditions, photo-Fenton demonstrated the highest rate constant of 0.029 min⁻¹, followed by Fenton with 0.0144 min⁻¹ with t_{1/2} of 49.5 min and 69.3 min, respectively. Although the performances of UV-A/TiO₂/H₂O₂ and UV/ZnO were similar in terms of the reported rate constants of 0.0005 min⁻¹ and 0.00056 min⁻¹, respectively, the rate constant for UV/TiO₂ was not reported therefore preventing a meaningful comparison. With the exception of UV-A/ZnO, biodegradability (BOD₅/COD) was improved for all treatment methods investigated.

A separate study reported the efficacy of TiO₂ (Anatase with purity >99 %) on AMX (and ampicillin and cloxacillin) degradation in distilled water, irradiated with UV-A lamp (365 nm, 6 W) which was further enhanced by the addition of H₂O₂, Elmolla and Chaudhuri (2010c). These results, somewhat contradictory with those reported by Martins et al. (2009), may be due to differences in the photocatalytic activity of the different TiO₂ used, the irradiation source, addition of H₂O₂ and also the water matrix. None of these studies described the degradation products formed during the photocatalytic treatment.





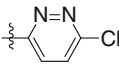


Scheme 3.5 Proposed photocatalytic degradation pathway for amoxicillin (AMX) (10 mg/L AMX; pH 6; 20 °C), Klauson et al. (2010)

A comparison between photocatalysis using doped and undoped titania with artificial UV-A and sunlight showed that the latter produced a three times faster degradation for AMX than artificial UV, Klauson et al. (2010). The improved efficiency of 2 h of solar (16 mW/cm²) photocatalytic illumination with TiO₂ Degussa P25 over 6 h irradiation with artificial UV-A light (365 nm, 0.5 mW/cm²) for AMX was apparent. The faster degradation occurred at pH 6 (20 °C) and a concentration of 50 mg/L and yielded the highest photocatalytic efficiency of 80 %. Doped catalysts with Fe and C also showed comparable efficiencies to that of Degussa P25. With artificial UV light, COD was removed to a percentage between 10 % and 40 % in all experiments. This study revealed the superiority of solar photocatalysis for AMX conversion. Photocatalytic degradation pathways were proposed to occur for different AMX concentrations, 10, 25 and 100 mg/L (pH 6, 20 °C) at three different reaction rates of control. The majority of the degradation products differed under these three reaction conditions, with only a few common products identified. Only small amounts of ammonia, nitrate and sulphate were detected, which implies that the heteroatoms N and S remained in the organic by-products. *p*-Hydroxybenzoic acid (*m/z* 139) was a common degradation product found under all photocatalytic conditions. It is proposed to form through the fragmentation of the peptide bond, which is in close proximity to the aromatic ring in AMX. Scheme 3.5 shows the proposed degradation pathway for AMX.

It can be concluded that artificial UV and solar photocatalysis with TiO₂ facilitated efficient AMX degradation. ZnO was also effective, albeit only one study used this photocatalyst. As a result of this, more research is needed to evaluate the

Table 3.6 Selected sulfonamides and their structures

Common name	-R
Sulfathiazole	
Sulfisoxazole	
Sulfapyridine	
Sulfamethoxazole	
Sulfachloropyridazine	

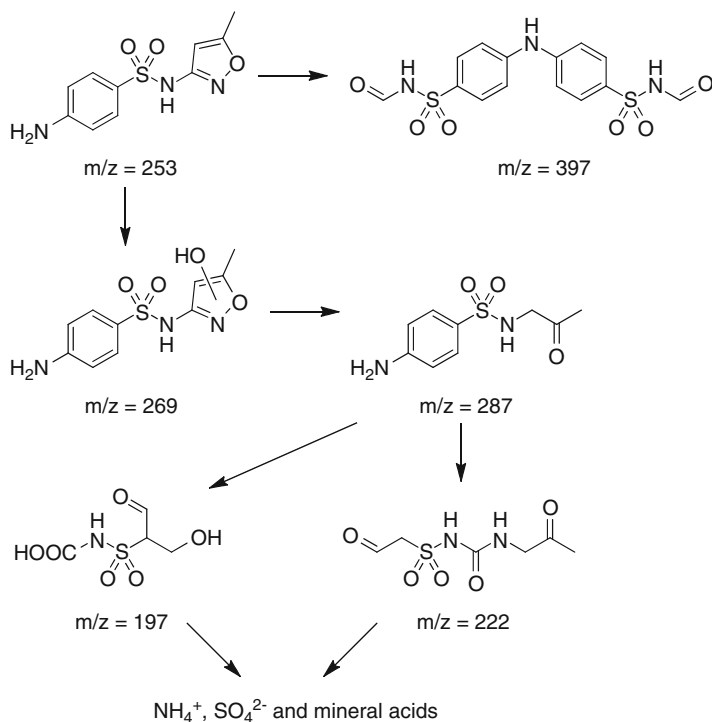
potential of ZnO for AMX degradation by optimizing the parameters influencing its degradation as this catalyst has higher photocatalytic activity than TiO₂. There are also similarities expressed between studies where the UV-A type of irradiation was sufficient to cause AMX degradation.

Sulfonamide and Other Sulfa Antibiotics

Sulfonamides and sulfanilamides are derived from sulfanilic acid and their common features are the sulfanilamide group and a five or six member heterocyclic ring (shown as R in the general structure) and are represented in Table 3.4. Selected sulphonamides, with their common names and the nature of their R groups are shown in Table 3.6. Sulfonamides and sulfanilamide derivatives are antibacterial agents used both in animals and humans for the treatment of infections. Almost 80 % of all sulfonamides have been detected in the environment, which could easily infiltrate groundwater, and have shown high toxicity to microorganisms, algae and plants, Baran et al. (2011).

Sulfamethoxazole (SMX) (C₁₀H₁₁N₃O₃S), being the most commonly used member of the group of sulfonamide antibiotics, is prescribed for urinary tract infections and has been detected in the environment. This synthetic antibiotic is used either alone or in combination with trimethoprim. SMX has been detected in plant effluents at concentrations ranging between 0.01 and 2.0 µg/L in countries such as Germany, Spain and Italy and in surface waters between 0.03 and 0.48 µg/L, Trovó et al. (2009). SMX has two pK_a values, pK_{a1} = 1.6 and pK_{a2} = 5.7, and thus exists predominantly in the cationic form at pH < 1.6 and in the anionic form at pH > 5.7. There have been reports on UV/TiO₂ treatment of this pharmaceutical using various lamp sources, Abellán et al. 2009 and Nasuhoglu et al. (2011).

SMX has been reported to be susceptible to direct photolysis with a Xe lamp resulting in significant degradation, but poor mineralization, Abellán et al. (2007, 2009). In water, SMX is capable of absorbing light up to 310 nm. When irradiated



Scheme 3.6 Degradation pathways of sulfamethoxazole (SMX) with TiO_2 photocatalysis, Abellán et al. (2007)

without the use of a filter and photocatalyst, SMX degraded up to 80 % but only resulted in a reduction of 14 % of TOC, Abellán et al. (2007). In contrast, the photocatalytic degradation of 100 ppm SMX (irradiation of 6 h) in the presence of 1.0 g/L TiO_2 yielded 88 % reduction in SMX. With 2.0 g/L TiO_2 , the degradation marginally increased to 91 %. The optimum TiO_2 P25 concentration was found between 0.5 and 1.0 g/L. Variations in pH (2–11) resulted in very minor changes and the degradation remained almost constant at 85 %, with a very small increase at lower pHs. A total of five intermediates were identified using mass spectrometry. Of these, the intermediate with a molecular weight of $m/z = 397$ was found to be the major product and was assigned to a dimer product of the parent SMX. Other intermediates possessed molecular weights of 222 in ES positive ion mode and 197, 269 and 287 in ES negative ion mode, Abellán et al. (2007) (Scheme 3.6).

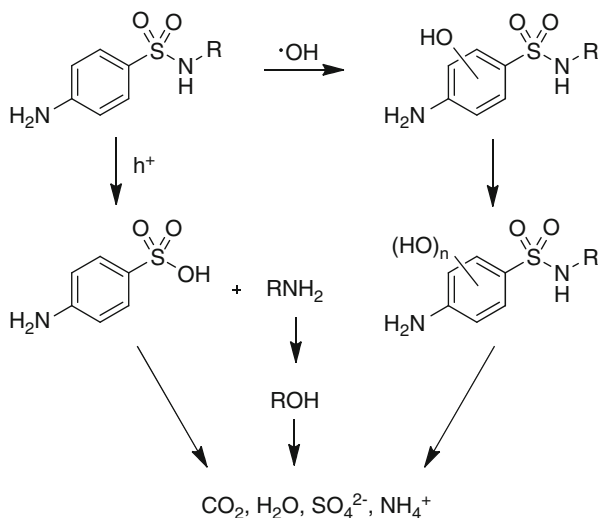
UV-C irradiation (254 nm) was employed to study the photolytic and photocatalytic degradation of SMX in pure water, Nasuhoglu et al. (2011). Irradiation was carried out in a cylindrical acrylic photoreactor equipped with an Hg-Ar lamp source. The results suggest that photolysis is an important removal mode for SMX (12 mg/L) which corroborates the findings of Abellán et al. (2007). The high tendency for direct photolysis was explained based on the matching of the SMX

absorbance with the highest intensity emission of the UV-C lamp. UV-C radiation yielded complete degradation of 12 mg/L SMX within 10 min, while UV/TiO₂ required 30 min to achieve a similar level of degradation. However, mineralization measured as COD was more efficient on photocatalysis treatment with 87 % removal, compared to only 24 % removal upon photolysis. Photoproducts generated as a result of both treatments were reported to be more toxic than the parent SMX, as demonstrated by the acute toxicity *Daphnia magna* testing.

SMX was reported to undergo UV-A (350–400 nm) induced photocatalytic degradation with TiO₂ Degussa P25, Xekoukoulotakis et al. (2011). A 9 W lamp (photon flux 2.81×10^{-4} Einstein/min) in an immersion well batch photoreactor was used under continuous oxygen sparging. Complete degradation of 10 mg/L SMX with 250 mg/L TiO₂ P25 was achieved in 30 min. Likewise, a TOC reduction of up to 90 % was observed. The photocatalytic degradation at different initial concentrations (2.5–30 mg/L) followed the Langmuir-Hinshelwood (L-H) kinetic model.

The behaviour of three sulfa pharmaceuticals, namely sulfachlorpyridazine, sulfapyridine and sulfisoxazole with similar structures towards UV/TiO₂ treatment were investigated by Yang et al. (2010). A Pyrex reactor with a high pressure Hg lamp ($\lambda_{\max} = 365$ nm) was chosen. Photocatalytic treatment proved generally effective on these sulfa drugs, with removal efficiencies varying between 85.2 % and 92.5 % after 60 min of irradiation. TOC was concomitantly removed in high percentages (81.5–90.8 %) within 240 min with all three drugs showing complete mineralization to CO₂, H₂O and inorganic ions. Photocatalytic degradation rate constants of these three sulfa drugs also increased with the amount of TiO₂ from 0.25 to 3 g/L. It was proposed that h^+ and HO• play the most important role in the disappearance of sulfa pharmaceuticals. Remarkably, different photocatalytic degradation rate constants for the three drugs were obtained at different pH values despite their similarity in structure. This was attributed to changes in their zwitterionic nature in different pH environments. Various intermediates formed rapidly within 15 or 20 min of irradiation and then slowly disappeared. The two major pathways for photocatalytic degradation of the sulfa drugs were hydroxylation and cleavage of the S-N bond by the photohole (Scheme 3.7).

Another study employed a UV-A light source to determine the degradation of SMX and a few other sulphonamides, namely sulfamethizole, sulfathiazole and sulfisoxazole, Hu et al. (2007). The effects of natural organic matter (NOM) and bicarbonate ion on the degradation of SMX were investigated. The occurrences of NOM and bicarbonate ions in water are known to impede the degradation of compounds by scavenging HO•. However, the results showed that an increase in bicarbonate concentrations generated a higher degradation rate for SMX. This was attributed to considerably higher HCO₃⁻ and CO₃²⁻ concentrations compared to SMX, which is likely to induce a stronger interaction with Ti (IV) than between SMX and Ti (IV). As a result, these ions efficiently scavenged the adsorbed HO• radicals, which in turn reduced the recombination of the charge carriers. The CO₃^{-•} radicals generated were proposed to react with SMX in the bulk rather than on the



Scheme 3.7 Photocatalytic degradation pathways of sulfa pharmaceuticals, Yang et al. (2010)

surface because they are more stable and possess longer lifetimes. In contrast, an increase in NOM concentrations (2–20 mg/L) inhibited the SMX degradation, in particular at higher concentrations of NOM.

Quinolones and Fluoroquinolones

Quinolones are synthetic antibacterial agents which are widely used in both humans and livestock. The basic structure of quinolones contains two fused rings with a carboxylic acid and a ketone group (Table 3.4). First and second generation quinolones are active against gram-negative bacteria, while the third and fourth generations have extended activity against gram-positive bacteria as well, Nasuhoglu et al. (2012). Fluoroquinolones (FQs) have attracted substantial attention due to their incomplete metabolism and frequent detection in the environment. A FQ compound contains a fluorine substituent in position R⁴ of the quinolone ring as shown in Table 3.4.

FQs are excreted to between 20 % and 80 % and their persistence has led to detection in surface waters, municipal wastewaters and tertiary treated effluents, Michael et al. (2010). As with other synthetic antibiotics, FQs are not fully metabolized and thus excreted unchanged. The persistent nature of FQs is associated with the quinolone ring, which results in high chemical stability and contributes additionally to their resistance towards hydrolysis, Sturini et al. (2010). Only a few studies dealing with the degradation of FQs by TiO₂ mediated photocatalytic treatment have been reported thus far. In general, incomplete mineralization of FQs results in the generation of a range of intermediates which still contain the quinolone ring structure and as a result continue to exhibit antibacterial activity.

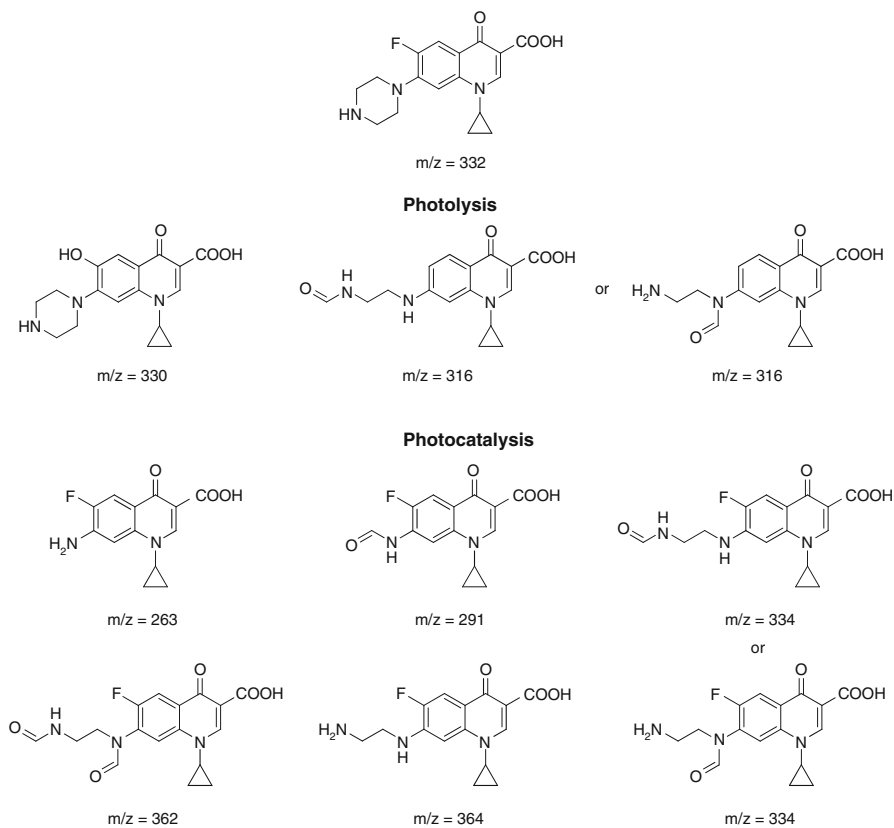
The performance of immobilized TiO_2 integrated into an annular reactor was tested with black light (360 nm) using 18 ppm oxolinic acid (OX) at pH 9 under oxygenated conditions. A comparison was made with a 1 g/L titania suspension, using the same reactor. The coated titania was capable of removing OX acid to over 90 % after 60 min, while TOC was reduced by 50 % after 100 min of irradiation. In suspension, 90 % removal was achieved after 20 min whereas total removal took 40 min. The superior performance of the suspended TiO_2 was explained by the superior adsorption, which subsequently increased the reaction rate, Palominos et al. (2008).

A systematic evaluation of OX acid removal in ultrapure water was conducted by Giraldo et al. (2010). The optimum conditions for complete degradation of 20 mg/L OX acid after 60 min of irradiation were with 1.0 g/L TiO_2 and pH 7.5. COD was reduced by 50 % and the degradation followed pseudo-first order kinetics. The study also revealed that OX acid intermediates, which were identified by high performance liquid chromatography-mass spectrometry (HPLC/MS) exhibited lower toxicity than the parent compound in addition to a loss of antimicrobial activity based on an *Escherichia coli* assay.

UV-A/ TiO_2 is also an effective technology for oxidation of ciprofloxacin (CIP) in pure water, An et al. (2010) and Paul et al. (2010). UV-A and Vis light sources were employed to study the photolytic and photocatalytic treatment of CIP, Paul et al. (2010). Based on the pseudo-first order rate constants, the efficiency of CIP degradation increased in the order UV-A/ TiO_2 > Vis/ TiO_2 > UV-A only. Degradation of CIP by UV-A/ TiO_2 is proposed to occur via three mechanisms: direct UV-A photolysis, charge transfer and charge separation involving the semiconductor. Various piperazine ring transformation products were formed upon UV-A/ TiO_2 and Vis/ TiO_2 treatment and their proposed structures are shown in Scheme 3.8. Energy efficiencies for the three treatment protocols were compared and the UV-A/ TiO_2 turned out to be the most energy efficient process.

Degradation of 100 μM CIP and a short $t_{1/2}$ of 1.9–10.9 min were furthermore achieved at different pH ranges (3.0–11.0) using 1.5 g TiO_2 /L Degussa P25 and UV-A irradiation (365 nm) emitted from a high pressure Hg lamp. The degradations followed pseudo-first order kinetics and the rate constant increased from $0.06 \pm 0.01 \text{ min}^{-1}$ at pH 3 to $0.38 \pm 0.01 \text{ min}^{-1}$ at pH 9. At a higher pH value of 11, the degradation rate decreased to $0.07 \pm 0.01 \text{ min}^{-1}$ due to the repulsive effect between the negatively charged compound and the negatively charged TiO_2 surface. Addition of hydroxyl radicals to CIP and photohole attack were established as the two predominant reaction pathways, An et al. (2010).

Photocatalytic degradation of four FQs, namely ofloxacin, norfloxacin, ciprofloxacin and enrofloxacin, was examined simultaneously using a solar simulator, Li et al. (2012). Alkaline conditions (pH 9) resulted in almost complete degradation (98–100%) for all four FQs after 150 min of irradiation. Likewise, TOC was reduced by 58 %. The threshold TiO_2 load was found to be 0.5 g/L at pH 9 to achieve 96–100% of degradation of the four FQs. An increase in the TiO_2 load from 0.1 g/L to 1.5 g/L did not produce a direct correlation with TOC removal. The effects of pH changes on these four FQs were rather complex, due



Scheme 3.8 Possible degradation products of ciprofloxacin (CIP) from photolysis and TiO_2 photocatalysis, Paul et al. (2010)

Table 3.7 Molecular formulas and $\text{p}K_a$ values of four fluoroquinolones (FQ), Li et al. (2012)

	Ofloxacin	Norfloxacin	Ciprofloxacin	Enrofloxacin
Chemical formula	$\text{C}_{18}\text{H}_{20}\text{FN}_3\text{O}_4$	$\text{C}_{16}\text{H}_{18}\text{FN}_3\text{O}_3$	$\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3$	$\text{C}_{19}\text{H}_{22}\text{FN}_3\text{O}_3$
$\text{p}K_{a1}$	6.05	6.20	6.00	6.03
$\text{p}K_{a2}$	8.11	8.70	8.80	8.70

to different ionization states of the catalyst and the substrates (two $\text{p}K_a$ values for each). In particular, these FQs can either exist in their cationic ($\text{pH} < \text{p}K_{a1}$), or anionic ($\text{pH} > \text{p}K_{a2}$) or in zwitterionic form ($\text{p}K_{a1} < \text{pH} < \text{p}K_{a2}$) (Table 3.7) due to the presence of a carboxylic acid group in the quinolone structure and an additional amine group from the piperazinyl ring.

A third generation FQ, moxifloxacin (MOX) was subjected to UV/TiO₂ and the influence of various parameters was examined using a batch photoreactor equipped with a UV-A lamp (300–440 nm, 485 μW/cm²), Van Doorslaer et al. (2012). A catalyst loading of 5 g/L, temperature of 25 °C and air sparging at 60 mL/min were found optimal for removing 37.4 μM of MOX. The initial degradation rate and the t_{1/2} were determined to be 16.2 ± 0.3 μM/min and 1.6 min, respectively. A stirring speed of 13.2 rps produced a higher degradation rate. The TiO₂ P25 loading ranged from 0.1 to 5.0 g/L.

An independent study highlighted that TiO₂ Degussa P25 was more effective than two other common photocatalysts, Hombikat UV 100 and PC 500 for the degradation of 0.25 mM of norfloxacin (NOR) (pH 6.3) with 1 g/L of photocatalyst, Haque and Muneer (2007). Almost complete degradation was achieved in 80 min of irradiation from a medium pressure Hg lamp (125 W) under oxygen purging. Likewise, the TOC content was depleted as a function of irradiation time. The efficiency of the photocatalytic degradation of NOR was subsequently correlated with pH, substrate concentration, catalyst concentration, and the addition of electron acceptor, H₂O₂. The results revealed that addition of 10 mM of H₂O₂ significantly enhanced the degradation rate and mineralization of 0.25 mM NOR (pH 6.3 and 1 g/L TiO₂ P25).

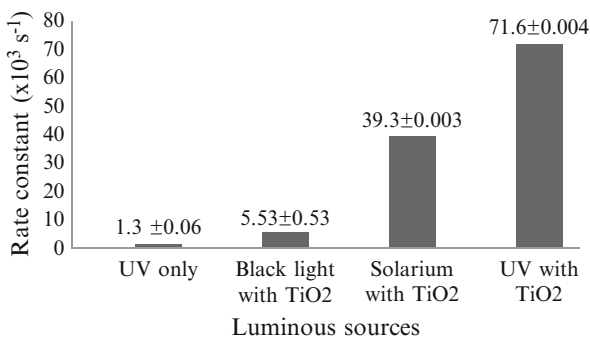
A recent study was conducted with unfiltered river water to explore the photocatalytic decomposition of six FQs, namely ciprofloxacin, danofloxacin, enrofloxacin, levofloxacin, marbofloxacin and moxifloxacin, under natural sunlight. Compared to direct photolysis under natural sunlight, all of the tested drugs except CIP underwent faster degradation with degradation rate constants ranging from 0.22 to 2.78 min⁻¹ in the presence of TiO₂ (0.5 g/L). The results demonstrated the effectiveness of solar TiO₂ photocatalysis for the removal of FQs from river water matrix despite the presence of other non-target matrix components, Sturini et al. (2012). CIP in hospital wastewater was also satisfactorily removed with UV/TiO₂ using a medium pressure Hg lamp. For comparison, ozonation was used as an alternative AOP. Both processes generated similar degradation products and oxidation of the piperazine group was found to be the major degradation pathway, Vasconcelos et al. (2009).

The results presented for quinolones and FQs are significant and demonstrate the potential removal from wastewaters not only for single compounds but also for mixtures.

Tetracyclines

A comparison of photocatalytic degradation and mineralization of oxytetracycline (OTC) in a laboratory and at pilot-scale was reported by Pereira et al. (2011). Laboratory scale experiments with a solar simulator showed that photocatalysis of 20 mg/L OTC with 0.5 g/L TiO₂ at free initial pH produced 95 % degradation. In contrast, only 36 % degradation was achieved upon direct photolysis after 60 min of irradiation. Solar photocatalysis in a CPC pilot plant reactor showed complete

Fig. 3.5 Comparison of pseudo-first order constant for tetracycline (TC) degradation (TC: 40 mg/L; TiO₂ P25: 0.5 g/L) (Data taken from Reyes et al. (2006))



removal of OTC with energy consumption 10 times less than solar photolysis which was also performed by means of CPC reactor. Solar photocatalysis in the pilot plant reactor yielded 80 % mineralization. All experiments followed pseudo-first order kinetics, but the rate constants increased from the photolytic to photocatalytic operation modes. Solar photocatalysis in a CPC reactor produced the highest pseudo-first order rate constant of $2.63 \pm 0.03 \text{ L/kJ}$, indicating the efficiency of such a photoreactor to harvest and utilize solar photons.

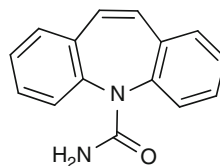
Several studies involving tetracycline (TC) have been carried out to determine its photocatalytic degradation, Reyes et al. (2006), Palominos et al. (2009) and Mboula et al. (2012). Catalyst performance and biodegradability or antibacterial efficiency arising from the treated solutions differed for all studies reported. Using a multivariate and response surface method approach, the optimum degradation rate for each catalyst was investigated. ZnO exhibited a slightly higher oxidation rate than TiO₂ P25. The optimum oxidation conditions for TiO₂ were established as 1.5 g/L and at pH 8.7. For ZnO, the most appropriate conditions were 1.0 g/L and pH 11, Palominos et al. (2009).

The TC disappearance over the irradiation time, at different pH values and with three different light sources, namely UV lamp ($\lambda > 254 \text{ nm}$), UV-A lamp ($\lambda = 365 \text{ nm}$) and a solarium device ($\lambda = 300\text{--}400 \text{ nm}$), was carried out by Reyes et al. (2006). Based on the pseudo-first order rate constants, direct photolysis was regarded negligible for TC. In contrast, faster degradation rates were achieved with the solarium and UV light in the presence of TiO₂ (Fig. 3.5). These findings were supported by the high irradiance intensities measured from the UV lamp ($1,210 \mu\text{W}/\text{cm}^2$ at 365 nm) and the solarium lamp ($1,980 \mu\text{W}/\text{cm}^2$ at 365 nm), respectively. Rapid disappearance of TC and subsequent complete mineralization was achieved after 2 h of irradiation.

3.5.3 Antiepileptics

The most commonly investigated antiepileptic is the dibenzazepine derivative, carbamazepine (CBZ) (Fig. 3.6). CBZ is also used as sedative for numerous mental

Fig. 3.6 Chemical structure of carbamazepine ($C_{15}H_{12}N_2O$) (*5H*-dibenzo [*b,f*]azepine-5-carboxamide)



disorders, can cause toxic effects in the liver and is a haematopoietic. Only 72 % of CBZ is absorbed when orally administered, while 28 % remains unchanged and is finally excreted through faeces. CBZ has been known to persist in the environment and studies have reported the removal efficiency of CBZ in WWTPs as below 10 %, Andreozzi et al. (2002) and Zhang et al. (2008a). Thus far, CBZ has been detected in various water compartments around the world. In Germany, CBZ was detected in surface water samples at a concentration up to 1,075 ng/L, Heberer (2002b) and also in groundwater and rivers in the USA, Canada and Germany, Khetan and Collins (2007). These observations clearly confirm the CBZ presence in the aquatic environment. Although the effects of CBZ are not clearly known or confirmed, its toxic effect on aquatic organisms has been already published. There is also evidence of specific chronic effects of CBZ on the oligochaete *Chironomus*, Oetken et al. (2005). These facts show that this antiepileptic needs to be removed with effective remediation technology. In this context, photocatalysis has been shown to be effective for CBZ degradation. A summary of UV/TiO₂ studies of CBZ is tabulated in Table 3.8.

There has been an insufficient amount of information available pertaining to photocatalytic degradation of CBZ. Photocatalytic degradation of CBZ has however been examined in deionized water, Dai et al. (2012) and Im et al. (2012), real wastewater samples from WWTPs, Achilleos et al. (2010b) and formulated hospital wastewater, Chong and Jin (2012). In general, there are some discrepancies in the photocatalytic efficiency on CBZ.

A comparative study on the effect of different on CBZ (4.2 μ M) degradation efficiencies showed the following trend: UV/Fenton (86.9 %) > UV/TiO₂ (70.4 %) > Fenton (67.8 %) > UV/H₂O₂ (40.6 %) > UV (14.2 %). On the basis of operating costs, the Fenton process was the most cost-effective in comparison with the other four AOPs (Table 3.9), Dai et al. (2012). As shown in Table 3.9, UV/TiO₂ and UV can be considered as costly approaches for wastewater treatment. However the authors reported that this statement can be challenged on the grounds that the cost of photocatalytic treatment can be reduced by applying sunlight as the irradiation source.

The removal efficiency by UV-A (350–400 nm) and solar irradiation provided by a solar simulator on CBZ was investigated along with another API, IBP, Achilleos et al. (2010b). Greater degradation was attained with UV-A irradiation than with artificial solar radiation for both APIs. Degradation of CBZ in pure water was found to be more dependent on changes in the loading of Degussa P25 TiO₂ compared to IBP. Conversion of 74 % CBZ was achieved after 120 min of reaction with 100 mg/L

Table 3.8 Highlights of heterogeneous photocatalytic studies on antiepileptics

Compound(s)	Water matrix	Experimental features	Analytical methods	Findings	Reference
<i>Carbamazepine</i>					
	Deionized water	Medium pressure Hg lamp (30 W) Initial concentration: 4.2 μ M TiO ₂ loading: 0.5–2.0 g/L Temperature: 25 °C pH: 6.5	HPLC	Comparison of UV/TiO ₂ with UV, UV/H ₂ O ₂ and UV/Fenton showed the UV/TiO ₂ yielded 70.4 % degradation which was slightly lower than UV/Fenton at 86.9 % degradation. All processes followed pseudo-first order kinetics	Dai et al. (2012)
	Hospital wastewater	Annular slurry photoreactor UV-A black light (8 W) Initial concentration: 5,000 μ g/L TiO ₂ Anatase particles	HPLC, COD	Photodegradation at high concentration of CBZ in synthetic hospital wastewater was fitted to the L-H kinetics model	Chong and Jin (2012)
	Milli-Q water	UV-A lamp: 2.17 mW/cm ² UV-C lamp: 3.56 mW/cm ² Initial concentration: 0.021 mM TiO ₂ loading: 0.5 g/L pH: 5.4	HPLC, IC, TOC	UV-A and UV-C irradiation efficient to degrade CBZ	Im et al. (2012)
<i>Carbamazepine mixtures</i>					
Carbamazepine (and ibuprofen)	Milli-Q water and wastewater from WWTP	Solar simulator (1,000 W Phillip Xe lamp) and UV-A lamp (9 W Radium lamp) Initial concentration: 5–20 mg/L TiO ₂ loading: 50–3,000 mg/L Type of TiO ₂ : Degussa P25, Hombikat UV100, Aldrich,	UV-vis (CBZ: 284 nm), DOC	Degradation under UV-A irradiation in pure water was sensitive to TiO ₂ P25 loading. Solar and UV-A photocatalysis appears to be efficient on CBZ degradation	Achilleos et al. (2010b)

Carbamazepine (Clofibric acid, ioneprol)	Milli-Q water	Tronox AK-1, Tronox TRHP-2, Tronox TR H ₂ O ₂ concentration: 0.07–1.4 mM pH: 3–10 Solar simulator Xe short arc lamp (1,000 W) (cut-off 296 nm) Initial concentration: 1–5.5 mg/L TiO ₂ loading (P25 and Hombikat UV100): 500 mg/L	UV-vis, HPLC, DOC	Degradation of CBZ dependent on the concentration of NOM as it greatly influences its kinetics	Doll and Frimmel (2005a)
	Ultrapure water	Solar simulator Xe short-arc lamp (1,000 W) Initial concentration: 4.3 mg/L TiO ₂ and Hombikat UV100 loading: 0.1 g/L Temperature: 20 ± 2 °C	HPLC, DOC, ICP-AES, HPLC/TQMS	Pseudo-first order degradation rate of CBZ for TiO ₂ P25 and UV100 were 4.7×10^{-3} and $0.13 \times 10^{-3} \text{ s}^{-1}$	Doll and Frimmel (2005b)
Carbamazepine (Clofibric acid, ioneprol, iopromide)	Milli-Q water	Solar simulator Xe short arc lamp (1,000 W) Initial concentration: 1.0 and 4.3 mg/L TiO ₂ P25 loading: 0.01–1,000 mg/L Temperature: 20 ± 2 °C Hombikat UV100 loading: 0.1–1,000 mg/L	HPLC, DOC, ICP-AES, HPLC/ESMS, DOC	Degradation of CBZ was faster with TiO ₂ P25 due to higher adsorption	Doll and Frimmel (2004)

Table 3.9 Comparison of operating costs of advanced oxidation processes (AOP) studied (Data taken from Dai et al. (2012))

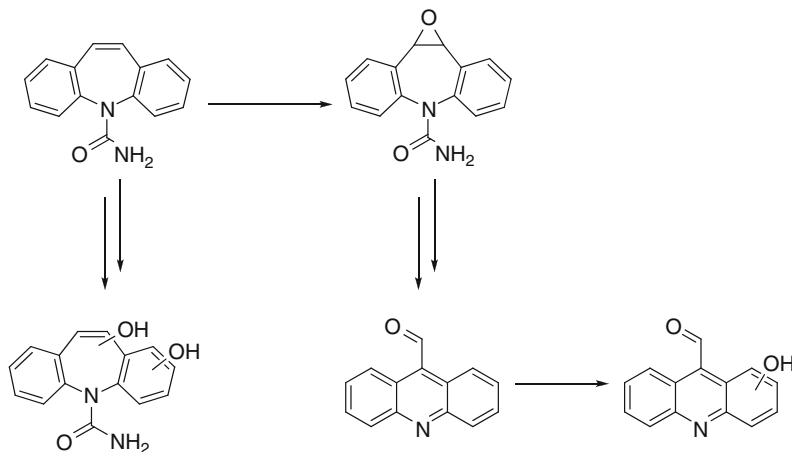
Process	Treatment cost (US\$/kg)
UV	210.4
UV/H ₂ O ₂	42.6
Fenton	5.4
UV/Fenton	26.7
UV/TiO ₂	70.2

P25 under UV-A irradiation, but it decreased to 35 % upon solar irradiation, which was attributed to completely different reactor set-ups. Wastewater samples spiked with 10 mg/L CBZ had a detrimental effect on DOC removal, due to the presence of scavengers of HO[•] radicals and naturally occurring DOC in the raw wastewater sample. Nevertheless, the study proved that UV-A and solar irradiation can be applied to CBZ removal (and also for IBP). Direct photolysis with a UV-A lamp produced negligible degradation and DOC removal for CBZ.

The results from another study confirmed that direct photolysis supplied by a UV-C irradiation source is not effective for CBZ elimination, Im et al. (2012). An important contribution of the study is that UV-C irradiation increased the removal efficiency compared to that of UV-A irradiation employed on the 0.021 mM CBZ in the presence of 0.5 g/L TiO₂ P25. Addition of radical scavengers decreased the removal rate, implying that HO[•] has a crucial role to play in the photocatalytic degradation of this compound. Addition of oxygen also enhanced the mineralization.

A TiO₂ nanofiber was evaluated as a pre-treatment option and for improvement of biodegradability of 5,000 µg/L CBZ in synthetic hospital wastewater, Chong and Jin (2012). This application was found to be efficient for CBZ abatement in synthetic hospital wastewater and also for COD removal. High CBZ degradation rate of 48.33 µg/L min was obtained, which also resulted in 40 % COD reduction after 4 h of treatment. The study highlighted the fact that the TiO₂ based system has a good potential as a sustainable pre-treatment system for hospital wastewater.

Doll and Frimmel (2004, 2005a, b) conducted multiple photocatalytic studies on CBZ under various conditions, which revealed that TiO₂ photocatalysis is a promising abatement method for CBZ degradation. When a comparison was made with Hombikat UV100, CBZ was degraded more efficiently with TiO₂ P25 under simulated solar irradiation (1,000 W), Doll and Frimmel (2004). In the subsequent study, photocatalytic degradation of CBZ was investigated with two types of TiO₂ photocatalysts in the presence and absence of NOM under simulated solar UV light, Doll and Frimmel (2005a). It was noted that different concentrations of NOM had different effects on the kinetics of CBZ degradation. In general, NOM retarded the photocatalytic degradation rate of CBZ. This was attributed to competitive inhibition as NOM scavenged the holes. The research group also suggested possible photocatalytic degradation products for CBZ, Doll and Frimmel (2005b) (Scheme 3.9).



Scheme 3.9 Photocatalytic degradation pathways of carbamazepine (CBZ), Doll and Frimmel (2005b)

3.6 Conclusion

A typical UV/TiO₂ investigation is shown in Fig. 3.7. After one or more model compounds have been chosen, the next step is the photocatalytic experimental set-up or the choice of the photoreactor and light source, which will have a significant effect on the outcome of the degradation rate, Legrini et al. (1993). There are various factors that need to be taken into consideration with respect to photoreactors, namely the material it is made of, shape, geometry, radiation path lengths, and the cooling apparatus. Similar issues have been highlighted in a review which has commented on this lack of information, when explaining photoproducts formed from the photocatalytic and photolytic studies, Fatta-Kassinos et al. (2011a).

When considering light sources, artificial light sources have been employed in most studies. These can be grouped into monochromatic light sources such as low pressure Hg lamps and polychromatic light source namely medium pressure Hg lamps and high pressure Hg lamps. Other irradiation devices include Xe, Xe-arc, Hg and Ra lamps. Solar simulators have been commonly applied to simulate solar irradiation. LED based light sources are also emerging as an alternative light source, due to advantages which include no mercury waste, longer life time compared to Hg based lamps and improved flexibility in terms of reactor design, Landgraf (2001) and Chen et al. (2007). Very few studies have made a comparison between the lamp's spectral domain and the absorption spectrum of the reactant. Photon flux, intensity and irradiance emitted from the light source also need to be clearly stated as these values determine the rate of photons emitted, which has a direct correlation to the degradation rate. Selection of a radiation source (shape and dimension) is also greatly influenced by the type of photoreactor.

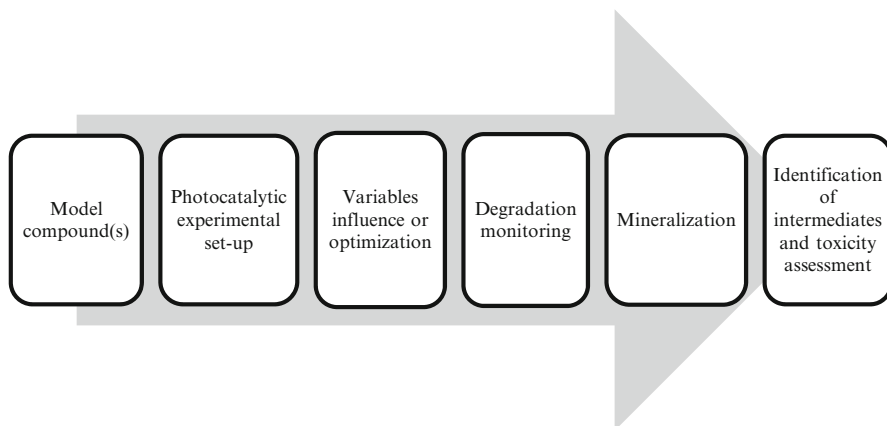


Fig. 3.7 Typical steps involved in heterogeneous photocatalytic degradation

Reaction rates are known to be dependent on operation conditions. Optimization of these variables thus allows for maximum degradation. Statistical approaches such as multivariate analysis and response surface methodology have also been applied to establish the optimal degradation rate. One of the most commonly investigated and important factors is the TiO_2 loading. It has been shown that the degradation rate is not always proportional to the catalyst load, but an optimum load needs to be determined. Difficulty arises when comparing studies for a particular compound of interest. In general, optimal catalyst load is influenced by the photoreactor design including its diameter and source of irradiation. Commercially available TiO_2 such as Degussa P25, Hombikat UV 100, PC 500 and Aldrich have been used in various photocatalytic degradation studies of pharmaceuticals. Among them, TiO_2 Degussa P25 has demonstrated its superiority in removing various APIs. A concentration below the optimum catalyst loading is typically chosen for further investigation, due to the fact that catalyst deposition might occur during the experiment. For example, 0.4 g/L TiO_2 was chosen instead of 0.5 g/L which gave the best results for metoprolol and propranolol degradation, Romero et al. (2011).

Initial concentrations of APIs applied in photocatalytic studies tend to be higher than the environmental level. Furthermore, in most cases single pharmaceuticals are investigated despite the fact that real wastewaters contain complex mixtures of pharmaceuticals. Although most studies have demonstrated efficiency for API in spiked distilled water or ultrapure water, real wastewater samples are rarely used. The presence of radical scavengers such as HCO_3^- , CO_3^{2-} ions and NOM in real wastewater typically impacts on degradation efficiencies. Radical scavengers or inhibitors are frequently studied to determine the role of reactive intermediates, e.g. the HO^\bullet radical, $\text{O}_2^{\bullet-}$ anion and holes in the photocatalytic degradation. Isopropanol, benzoquinone and iodide ions are commonly used for this purpose.

In general, laboratory scale experiments are more common than pilot scale operations due to a more controllable environment. There is usually no direct

correlation between the effectiveness of photodegradation in the laboratory with that under real environmental conditions. Conducting photodegradation studies on pilot scales will provide more realistic environmental conditions such as season, latitude, and hardness of water. These are generally not encountered when working in the laboratory. Trials using solar energy have been reported for pharmaceutical degradation, although the results thus far vary between compounds of interest. Commercial and industrial scale applications of solar energy have been established in a few European countries, the USA and Canada.

In the subsequent step, degradation monitoring of pharmaceuticals is generally carried out by using HPLC detection or UV-vis spectrophotometry. The latter has been reported to be a fast and useful tool of monitoring although it is not the state-of-the-art technique for API detection. The kinetics of degradation in terms of percentage API removed or API disappearances versus irradiation time or concentration change versus irradiation time (C/C_0 vs time) are commonly reported. The L-H model has been often applied to describe photocatalytic mineralization of pharmaceutical degradation.

Apart from determining the removal rate of APIs with photocatalytic treatment, the degree of mineralization is a critical parameter in heterogeneous photocatalysis. DOC has been frequently measured as an indication of the formation of CO_2 . In most cases, complete degradation of the pharmaceutical does not correspond directly with the mineralization rate mainly due to the formation of more stable compounds or transformation products during the degradation. A non-biodegradable fraction frequently remains in the treated solution. Mineralization can be also determined by measuring the formation of inorganic ions such as chlorine, sulphate and nitrate.

Although the ultimate goal of heterogeneous photocatalysis is to achieve complete mineralization of parent compounds, it is also important to evaluate the by-products generated to ensure that there are no toxic or more persistent compounds produced during the treatment. This will contradict the ultimate goal of the application of such an AOP. However, photodegradation products are not commonly studied. A few possible reasons for this are: (i) difficulties in separating and identifying a large number of these transformation products formed; (ii) lack of or non-existent analytical standards to determine the identity of these transformation products; and (iii) requirement for more than one analytical technique or sample preparation technique due to their diverse physicochemical properties, Agüera et al. (2005) and Fatta-Kassinos et al. (2011b). Moreover, studies have also assessed the toxicity of the photocatalytically treated samples by applying toxicity assays on various microorganisms and invertebrates.

In conclusion, despite most promising findings reported, the lack of compatibility in terms of degradation schemes and photoproducts formed, removal rates and degree of mineralization of APIs highlights the complex behaviour of the various APIs towards UV/TiO₂. Meaningful comparison between studies for scaling-up and application to real wastewater treatment at a pilot scale is limited by all these factors. Additional studies are thus urgently required to eliminate these shortcomings.

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