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TiO_2-assisted photodegradation of pharmaceuticals – a review

Review Article

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Abstract: Pharmaceutical compounds have been detected in the environment and potentially arise from the discharge of excreted and improperly disposed medication from sewage treatment facilities. In order to minimize environmental exposure of pharmaceutical residues, a potential technique to remove pharmaceuticals from water is the use of an advanced oxidation process (AOP) involving titanium dioxide (TiO_2) photocatalysis. To evaluate the extent UV/TiO_2 processes have been studied for pharmaceutical degradation, a literature search using the keywords 'titanium dioxide', 'photocatalysis', 'advanced oxidation processes', 'pharmaceuticals' and 'degradation' were used in the ISI Web of Knowledge TM, Scopus TM and ScienceDirect TM databases up to and including articles published on 23 November 2011. The degradation rates of pharmaceuticals under UV/TiO_2 treatment were dependent on type and amount of TiO_2 loading, pharmaceutical concentration, the presence of electron acceptors and pH. Complete mineralization under particular experimental conditions were reported for some pharmaceuticals; however, some experiments reported evolution of toxic intermediates during the photocatalytic process. It is concluded that the UV/TiO_2 system is potentially a feasible wastewater treatment process, but careful consideration of the treatment time, the loading and the type of TiO_2 (doped vs. undoped) used for a particular pharmaceutical is necessary for a successful application (198 words).

Keywords: *Pharmaceuticals • Titanium dioxide • Photocatalysis • Advanced oxidation process • UV*

1. Introduction

Pharmaceuticals have been detected in trace concentrations in the natural aquatic environment at concentrations of ng L^{-1} to µg L^{-1} [1-6]; and this has been a global phenomenon [7-10]. The presence of these compounds occur in sites as diverse as surface water [11-14], drinking water [15-18] and sewage influent and effluent from water treatment plants [19-34]. Pharmaceuticals persist in the environment due to their inability to be degraded by natural physical processes such as sunlight photolysis or microbial processes [35]. Many compounds that have been detected, such as paracetamol, carbamazepine, diclofenac, and ibuprofen, are entirely synthetic and classed as xenobiotics [34]. As a result, pharmaceuticals detected in natural waters systems must have arisen from their medicinal usage prior to their appearance in urine or faeces. More worrying, their appearance may also be due to unused medications which have been disposed of improperly down the toilet, *via* the sewage system [36] or dumped into rubbish as landfill waste, leading to excessive discharge of leachate into environmental waters [37].

The observed discharge of pharmaceuticals into the environment from sewage treatment plants suggests many conventional treatment processes are often not effective in reducing their levels in the wastewater stream. For instance, it has been reported that carbamazepine is poorly removed in the wastewater stream by primary sedimentation and secondary microbial degradation treatment processes [38]. Furthermore, the removal efficiencies of a pharmaceutical at a particular

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sewage treatment facility may vary depending on the sedimentation tank retention time, and the use of activated sludge treatment or membrane biofilters [39-42].

To improve the removal efficiencies, novel methods of treating pharmaceutically-rich sewage influent have been developed. Such treatment methods include advanced oxidation processes (AOPs) [43] involving ultraviolet (UV) irradiation alone [44,45], combining UV irradiation with hydrogen peroxide to generate hydroxyl ($HO^{\cdot}$) radicals as an effective oxidising agent [46-49] and incorporating hydrogen peroxide with Fe^{2+} ions (photo-Fenton) which increases the efficiency of $HO^{\cdot}$ radical generation [50-54]. More recently, heterogenous photocatalysts such as suspended titanium dioxide (TiO_2) have been used to generate $HO^{\cdot}$ radicals [55]. The success of TiO_2 as a photocatalyst is dependent on its physicochemical properties as a semiconductor [56].

Although the two most common forms of crystalline TiO_2, anatase and rutile, show similar band gap energies, it has been reported that the photocatalytic activity of anatase is greater than that of rutile due to differences in the band gap position in these two polymorphs [57,58]; and thus TiO_2 photocatalysts generally have a high proportion of anatase. Many studies on the TiO_2 photocatalysed conversion of pesticides, dyes and synthetic compounds [59-68] have used photocatalysts with a high anatase content (such as Aeroxide P25, which is also known as Aeroxide P25 and typically consists of a 80:20 or 75:25 ratio of anatase:rutile, or pure anatase photocatalysts such as Hombikat UV100). Most of these studies have shown that the use of TiO_2 photocatalysts for the production of hydroxyl radicals from UV irradiation significantly increased degradation rate constants relative to homogenous direct UV photolysis. And compared with other homogenous AOPs, such as $UV/H_2O_2/Fe^{2+}$ (photo-Fenton), the photocatalyst can be easily separated from the reaction solution and recycled without the addition of extra reagents such as H_2O_2 or iron salts [69]. Thus from the current literature, the use of TiO_2 as a photocatalyst may be an industrially-feasible tertiary sewage treatment process for the degradation of pharmaceuticals in wastewater.

Therefore, the aim of this review is to survey the extent of the use of TiO_2 mediated photocatalysis for the photodegradation of pharmaceuticals in aqueous solution. The removal efficiency obtained from various experimental parameters and the safety of TiO_2 photocatalysis as observed from current ecotoxicity data on different classes of pharmaceuticals and their photoproducts will be reported. In addition, the feasibility of using TiO_2-assisted photodegradation processes in wastewater treatment of pharmaceuticals will also be evaluated.

2. Results and discussion

2.1. Influence of pharmaceutical and TiO_2 concentration on photocatalytic degradation

Many of the studies reported an inverse relationship between the rate of TiO_2-assisted photodegradation and the concentration of the substrate pharmaceutical due to the saturation of active sites on the TiO_2 surface [70-75]. Furthermore, since pharmaceuticals or photoproducts produced from TiO_2 photocatalysis may themselves absorb UV radiation, their presence decreases the amount of incident radiation available to create valence hole-conduction band electron pairs in the TiO_2 material which mediates photocatalysis [70,76]. For example, the apparent UV-A assisted TiO_2-photocatalytic degradation rate constant for a 5 mg L^{-1} aqueous solution of diclofenac in deionized water was 0.1 min^{-1} but was decreased to an initial rate of 0.03 min^{-1} for a 20 mg L^{-1} diclofenac solution [70]. Moreover, 85% of a 5 mg L^{-1} aqueous atenolol solution in Milli-Q water was photoconverted during 240 minutes irradiation with Aeroxide P25 TiO_2 and UV-A; however only 54% of a 20 mg L^{-1} solution was degraded under the same conditions [71]. Similar decreases in photocatalytic degradation rates (from 0.0195 min^{-1} to 0.0037 min^{-1}) were observed with 2 – 10 mmol L^{-1} aqueous paracetamol solutions with UV-C irradiation and oxygen saturation in Milli-Q water at 26°C [77]. In addition, a decrease in the pseudo-first order degradation constant (from 0.229 min^{-1} to 0.078 min^{-1}) for the UV-A/TiO_2 photocatalytic treatment of propanolol in Milli-Q water (pH = 7.0) was observed when a 200 µM solution of propanolol was irradiated as opposed to a 50 µM solution.

The amount of TiO_2 used may also significantly affect the degradation rate. The apparent first-order rate constant for amoxicillin degradation (10 mg L^{-1}) increased from 0.0172 min^{-1} to 0.0237 min^{-1} when the suspended TiO_2 catalyst concentration was increased from 0.2 g L^{-1} to 0.8 g L^{-1} [78], and this was accompanied by an increase in mineralization kinetics measured by total organic carbon experiments (0.0182 min^{-1} to 0.0235 min^{-1} for 0.2 g L^{-1} and 0.8 g L^{-1} TiO_2 loadings respectively). This phenomenon is predicted, because an increase in TiO_2 loading provides more binding sites for substrate molecules to adsorb to the TiO_2 surface [79]. However, an increase in TiO_2 loading from 0.2 to 0.8 g L^{-1} did not significantly increase the apparent

degradation rate contant (k_{app}) of carbamazepine (k_{app} = 0.0311 min^{-1} and 0.037 min^{-1} respectively) [78]. Furthermore, no increase in the paracetamol degradation rate was observed with experiments using TiO_2 loadings > 0.8 g L^{-1} and the same initial pharmaceutical concentration [77]. With excessive TiO_2 loadings, It has been suggested that the TiO_2 particles in the centre of an irradiating vessel may be shielded from the incident UV by other TiO_2 particles, and thus particles in the centre do not contribute significantly to the production of (h^+, e^-) pairs [80]. As observed with the data collected in these previous studies, it is often not possible to predict the optimal loading of TiO_2 for the removal of a certain concentration of a particular pharmaceutical without the use of computer-aided modelling to determine optimal conditions for the photocatalytic reaction which one study has used and addressed [106]. Such modelling is necessary to determine the optimal quantity of TiO_2 needed for efficient photocatalysis in any particular sewage treatment facility, given that the expected concentration of a certain pharmaceutical in the wastewater is known.

2.2. Influence of pH on photocatalytic degradation

The pH of the solution can affect TiO_2-assisted photodegradation rates. The surface of the photocatalyst may become positively or negatively charged depending on the ambient pH. TiO_2 has a point of zero charge at around pH = 6 [72]; thus, the surface of the photocatalyst will be positively charged in solutions below this pH and negatively charged above. Therefore, the pH will impact the adsorption of pharmaceuticals onto the TiO_2 surface depending on their chemical structure. An *et al.* (2010) [81] investigated the pH dependence of TiO_2-assisted photodegradation of ciprofloxacin and found the photocatalytic process to be most efficient at pH = 9 (k = 0.38 min^{-1}), whereas more extreme pH conditions significantly affected the degradation rates (k = 0.06 min^{-1} and 0.07 min^{-1} at pH = 3 and 11 respectively). This is due to the chemical structure of ciprofloxacin: at high pH, both the basic nitrogen on the piperazinyl moiety (pK_a = 8.6) and the carboxyl group (pK_a = 6.1) are deprotonated with the overall charge being negative. Therefore, the molecule is repelled by the negative surface charge of the TiO_2 and minimal adsorption occurs. Similarly, at low pH, both these functional groups are protonated, and hence, the overall positive charge of ciprofloxacin repels the postively-charged surface of the photocatalyst. Similar variations in degradation rates have also been reported for other pharmaceuticals [82,83]. However the acid-base properties of a pharmaceutical only partially account for the observed degradation rates. It has been proposed by Yang *et al.* 2010 [74] that the increased degradation rate observed with propanolol when treated with the UV-A/TiO_2 system at pH = 5 relative to photodegradation at pH = 7 is because of the favourable adsorption of the electron-dense rings in propanolol onto the positively-charged surface of the photocatalyst at this pH. This phenomenon, however, was not observed with other beta-blocker pharmaceuticals which lack the electron-rich naphthyl rings, such as metoprolol and atenolol.

Given that the pH of wastewater is variable, it is again virtually impossible to evaluate the degradation of a particular pharmaceutical based solely on experiments carried out at one particular pH. Even if sewage water from one particular sewage facility is used as the matrix, it may not be representative of sewage water from another facility. Most sewage water is near neutral pH [84], however, a pH = 8.2 has been reported for tertiary treated wastewater [96]. Therefore, to characterize more fully the degradation behaviour of a particular pharmaceutical by TiO_2 photocatalytic mechanisms, a detailed analysis of how pH changes affect photocatalysis is necessary.

2.3. Influence of experimental apparatus and matrix conditions on degradation rate

Photocatalytic rates for the degradation of pharmaceuticals may be dependent on the type of matrix and experimental apparatus used. For instance, the apparent degradation rate of carbamazepine was reduced from 0.28 min^{-1} to 0.16 min^{-1} in distilled water compared to bog lake water with 0.5 mg L^{-1} natural organic matter (NOM) [84]. The NOM not only acted as an inner filter which absorbed an estimated ~3.5% of the incident radiation, but effectively scavenged valence holes, and therefore, reduced the production of HO·radicals. Furthermore, the NOM used in this study had an overall negative charge and thus was attracted to the positively-charged surface of TiO_2 under the experimental pH range (5.0 – 6.5). Similar results were reported in a recent study concerning the degradation of ranitidine in effluent water [85]. The pseudo-first order degradation constant of ranitidine in distilled water was over ten times greater than degradation in effluent water. In addition, only 8% of the degraded ranitidine achieved complete mineralization in an effluent water matrix after 55 min irradiation compared with 37% in distilled water after 73 min irradiation. Many studies have also involved photodegradation experiments in oxygen-saturated or anoxic conditions [86-89]. The TiO_2-assisted photodegradation of statin drugs undertaken in the

Table 1. Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
17α- ethinylestradiol	57–63–6	[111]	0.01	-	Immobilized TiO_2 on titanium alloy surface.	UV-A Philips 126W High pressure Hg lamp.	k_{app} = 0.086 min^{-1}	Complete loss of estrogenic activity after 1 h.
		[114]	0.89	400	Aeroxide P25	UV-A lamp max 355 nm, 8W, I_o = 116.6 W m^{-2}.	~3% remaining 180 min	-
			0.90	400	Aeroxide P25	UV-C lamp max 254 nm 8W, I_o = 114.5 W m^{-2}	~14% remaining 50 min	-
		[115]	5.00	500	Aeroxide P25	8W low pressure Hg lamp, 365-370 nm. $I_o = 7.38 \times 10^{-8}$ einstein s^{-1}	<10% remaining 121 min.	Intermediates predominantly present 40 min.
17β-estradiol	50–28–2	[111]	0.01	-	Immobilized TiO_2 on titanium alloy surface	UV-A Philips 126W High pressure Hg lamp.	k_{app} = 0.106 min^{-1}	Complete loss of estrogenic activity after 1 h
		[116]	10.00	500	Aeroxide P25	Low pressure Hg UV-A lamp, $I_o = 7.38 \times 10^{-8}$ einstein s^{-1}.	Complete degradation 50 min.	Complex intermediates including. 2-hydroxyestradiol, 10e-17b-dihydroxy-1,4-estradien-3-one 10e-hydroperoxide-17b-hydroxy-1,4-estradien-3-one and 17b-hydroxy-1,4-estradien-3-one.
		[117]	0.27	1000	Aeroxide P25	Xenon lamp with 365 nm band pass filter, 200W. I_o = 6 mW cm^{-2}.	99% degradation 30 min.	10e-17b-dihydroxy-1,4-estradien-3-one, androsta-4,16-dien-3-one, testosterone
		[114]	0.66	400	Aeroxide P25	UV-A lamp max 355 nm, 8W, I_o = 116.6 W m^{-2}.	~5% remaining 180 min	-
			0.69	400	Aeroxide P25	UV-C lamp max 254 nm 8W, I_o = 114.5 W m^{-2}	~8% remaining 50 min	-
		[118]	0.10	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.84 h^{-1}	-
			0.25	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.82 h^{-1}	-
			0.50	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.79 h^{-1}	-
			1.00	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.83 h^{-1}	-
			0.10	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.31 h^{-1}	-
			0.25	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.28 h^{-1}	-
			0.50	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.30 h^{-1}	-
			1.00	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.29 h^{-1}	-
Amiloride	2609-46-3	[112]	15.00	200	Aeroxide P25	Xenon solar lamp> 340 nm, I_o = 30 W cm^{-2}	k_{app} = 0.231 min^{-1}	Guanidine. Increased toxicity up to maximum 40% inhibition (*Vibrio fischeri* 4 h).

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Amoxicillin	26787-78-0	[78]	10.00	800	Aeroxide P25	Blacklight 126W 300-420 nm. $I_o = 4.7\times10^{-7}$ einstein s^{-1}.	k_{app} = 0.0237 min^{-1}	TOC removal > 80%. Incomplete toxicity reduction (121 min).
		[80]	104.00	500	Fluka 100% Anatase	6W UV-A lamp 365 nm.	42% degradation 300 min (pH = 5.0)	-
			104.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	55% degradation 300 min (pH = 5.0)	-
			104.00	1500	Fluka 100% Anatase	6W UV-A lamp 365 nm.	56% degradation 300 min (pH = 5.0)	-
			104.00	2000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	55% degradation 300 min (pH = 5.0)	-
			104.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	61% degradation 300 min (pH = 3.0)	-
			104.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	55% degradation 300 min (pH = 5.0)	-
			104.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	59% degradation 300 min (pH = 8.0)	-
			104.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	71% degradation 300 min (pH = 11.0)	-
		[91]	25.00	1000	Aeroxide P25	Natural solar irradiation; 16 mW cm^{-2}	> 80% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			50.00	1000	Aeroxide P25	Natural solar irradiation; 16 mW cm^{-2}	80% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			100.00	1000	Aeroxide P25	Natural solar irradiation; 16 mW cm^{-2}	< 60% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			25.00	1000	Iron (0.42%) doped TiO_2	Natural solar irradiation; 16 mW cm^{-2}	~70% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			25.00	1000	Iron (0.89%) doped TiO_2	Natural solar irradiation; 16 mW cm^{-2}	~65% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			25.00	1000	Iron (1.33%) doped TiO_2	Natural solar irradiation; 16 mW cm^{-2}	~62% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			25.00	1000	Iron (2.2%) doped TiO_2	Natural solar irradiation; 16 mW cm^{-2}	~75% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			25.00	1000	Iron (3.0%) doped TiO_2	Natural solar irradiation; 16 mW cm^{-2}	70% conversion 2 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			10.00	1000	Aeroxide P25	Artificial UV 15W low pressure 365 nm lamp, 0.5 mW cm^{-2}.	>60% conversion 6 h irradiation (pH = 3.0)	First intermediate p-hydroxybenzoic acid.

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
			10.00	1000	Aeroxide P25	Artificial UV 15W low pressure 365 nm lamp, 0.5 mW cm^{-2}.	90% conversion 6 h irradiation (pH = 6.0)	First intermediate p-hydroxybenzoic acid.
			10.00	1000	Aeroxide P25	Artificial UV 15W low pressure 365 nm lamp, 0.5 mW cm^{-2}.	>80% conversion 6 h irradiation (pH = 9.0)	First intermediate p-hydroxybenzoic acid.
Ampicillin	69–53–4	[80]	105.00	500	Fluka 100% Anatase	6W UV-A lamp 365 nm.	33% degradation 300 min (pH = 5.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	52% degradation 300 min (pH = 5.0)	-
			105.00	1500	Fluka 100% Anatase	6W UV-A lamp 365 nm.	54% degradation 300 min (pH = 5.0)	-
			105.00	2000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	52% degradation 300 min (pH = 5.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	78% degradation 300 min (pH = 3.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	52% degradation 300 min (pH = 5.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	74% degradation 300 min (pH = 8.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	91% degradation 300 min (pH = 8.0)	-
Atenolol	29123–68–7	[71]	20.00	250	Aeroxide P25	9W UV-A lamp (350 – 400 nm). $I_o = 3.37\times10^{-6}$ einstein s^{-1}.	Conversion > 60%	Less toxic photoproducts 15-30 min irradiation (*Daphnia magna*)
		[74]	26.63	2000	Aeroxide P25	High pressure Hg lamp 365 nm (126 W)	k_{app} (pH = 7) 0.075 min^{-1}	TOC < 10% (250 min). Aromatic Hydroxylated Intermediates.
Bezafibrate	41859–67–0	[119]	1.00	100	Aeroxide P25	1500 W Xenon lamp > 290 nm. I_o = 750 W m^{-2}	$k_{app} = 2.81\times10^{-2}$ min^{-1}	21 degradation products. 4 chlorobenzoic acid and 4-chlorobenzamide.
Caffeine	58–08–2	[120]	0.10	-	Modified SiO_2 TiO_2 mix	Natural Sunlight 10 am – 5 pm	k_{app} =0.416 s^{-1} (distilled water)	-
		[121]	0.10	5	Aeroxide P25	Solar pilot plant, average I_o = 30 W m^{-2}.	Undetectable 114 min.	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable 25 min	-
			0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.054 min^{-1}	-
			0.10	-	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.053 min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
			0.10	-	Used Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.079 min^{-1}	-
Carbamazepine	298–46–4	[96]	10.00	100	Aeroxide P25	9 W UV-A lamp, (350-400 nm). $I_o = 3.37\times10^{-6}$ einsteins s^{-1}.	Conversion = 74% (121 min)	40% DOC removal (121 min)
		[84]	4.20	100	Aeroxide P25	Xenon Solar simulator > 290 nm.	k_{app} (pH = 6.5) 0.28 min^{-1}	-
			4.20	100	Aeroxide P25	Xenon Solar simulator >290 nm.	k_{app} (0.5 mg L^{-1} DOM) = 0.16 min^{-1}	-
			4.30	100	Aeroxide P25	1000W Xenon Solar lamp. I_o> 400 nm = 1.35×10^{-4} einstein m^{-2} s^{-1}.	k_{app} = 4.7×10^{-3} s^{-1}.	10,11-dihydro-carbamazepine-10,11-epoxide, Acridine. Potentially ecotoxic mutagenic and carcinogenic photoproducts.
		[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 0.13 h^{-1}	-
		[89]	10.00	0.1	Titanate nanofibres i..	8W UV-A lamp 360 nm.	k_{app} = 0.15 h^{-1} (membrane bioreactor matrix)	-
			10.00	0.5	Titanate nanofibres	8W UV-A lamp 360 nm.	k_{app} = 0.8 h^{-1} (membrane bioreactor matrix)	-
			10.00	1.0	Titanate nanofibres	8W UV-A lamp 360 nm.	k_{app} = 1.00 h^{-1} (membrane bioreactor matrix)	-
			10.00	0.1	Aeroxide P25	8W UV-A lamp 360 nm.	k_{app} = 0.5 h^{-1} (saline matrix)	-
			10.00	0.1	Titanate nanofibres.	8W UV-A lamp 360 nm.	k_{app} = 5.0 h^{-1} (saline matrix)	-
			10.00	0.1	Aeroxide P25.	8W UV-A lamp 360 nm.	k_{app} = 4.7 h^{-1} (saline matrix)	-
		[82]	5.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp (Helios Italquartz Milan)	k_{app} (pH= 3) 1.52×10^{-1} min^{-1}	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	30% remaining 50 min	-
			0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.029 min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
			0.10	5	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.083 min^{-1}	-
			0.10	5	Used Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.085 min^{-1}	-
		[78]	5.00	200	Aeroxide P25	126 W Blacklight 300-420 nm $I_o = 4.7\times10^{-7}$ einstein s^{-1}	k_{app} = 0.0317 min^{-1}	Incomplete reduction in toxicity 121 min TOC removal > 80%
			5.00	400	Aeroxide P25	126 W Blacklight 300-420 nm $I_o = 4.7\times10^{-7}$ einstein s^{-1}	k_{app} = 0.0311 min^{-1}	As above
			5.00	800	Aeroxide P25	126 W Blacklight 300-420 nm $I_o = 4.7\times10^{-7}$ einstein s^{-1}	k_{app} = 0.037 min-1	As above
		[124]	5.00	100	Aeroxide P25	Medium Pressure Hg lamp > 300 nm. $I_o = 5.1\times10^{-6}$ einsteins s^{-1}.	k_{app} (pH = 7.5) 0.022 min^{-1}	-
Chloramphenicol	56–75–7	[125]	50.00	1000	Aeroxide P25	UV-A lamp 365 nm, $I_o = 1.12\times10^{-4}$ einstein min^{-1}.	Complete removal 90 min	<10% DOC 240 min
			50.00	1000	Tronox 100% Anatase	UV-A lamp 365 nm, $I_o = 1.12\times10^{-4}$ einstein min^{-1}.	50% removal 90 min	50% DOC 240 min
		[126]	15.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~55% degradation 30 min (pH = 3)	-
			15.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~75% degradation 30 min (pH = 5)	-
			15.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~65% degradation 30 min (pH = 7)	-
			15.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~60% degradation 30 min (pH = 9)	-
			15.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~40% degradation 30 min (pH = 11)	-
			15.00	500	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~60% degradation 30 min (pH = 5)	-
			15.00	750	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~60% degradation 30 min (pH = 5)	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
			15.00	1260	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~65% degradation 30 min (pH = 5)	-
			15.00	1500	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~50% degradation 30 min (pH = 5)	-
			5.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~75% degradation 30 min (pH = 5)	-
			10.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~70% degradation 30 min (pH = 5)	-
			15.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~65% degradation 30 min (pH = 5)	-
			20.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~60% degradation 30 min (pH = 5)	-
			25.00	1000	Nano-TiO_2 (100% anatase)	300W medium-pressure Hg lamp, > 365 nm.	~55% degradation 30 min (pH = 5)	-
Ciprofloxacin	85721–33–1	[81]	33.18	1500	Aeroxide P25	365 nm High-pressure Hg lamp. I_o= 0.38 mW cm^{-2}	k_{app} (pH = 3) 0.06±0.01 min^{-1}	Hydroxylation, decarboxylation, and piperazine ring cleavage
			33.18	1500	Aeroxide P25	365 nm High-pressure Hg lamp. I_o= 0.38 mW cm^{-1}	k_{app} (pH = 5) 0.14±0.01 min^{-1}	As above
			33.18	1500	Aeroxide P25	365 nm High-pressure Hg lamp. I_o= 0.38 mW cm^{-1}	k_{app} (pH = 7) 0.25±0.02 min^{-1}	As above
			33.18	1500	Aeroxide P25	365 nm High-pressure Hg lamp. I_o= 0.38 mW cm^{-1}	k_{app}(pH = 9) 0.38±0.01 min^{-1}	As above
			33.18	1500	Aeroxide P25	365 nm High-pressure Hg lamp. I_o= 0.38 mW cm^{-}	k_{app} (pH = 11) 0.07 ± 0.01 min^{-1}	As above
		[95]	33.18	500	Aeroxide P25	450 W Xenon arc lamp.> 324 nm I_o = 9×10^{-5} einstein min^{-1}	k_{app} = 1.53×10^{-1} min^{-1}	Cleavage of piperazine ring. No decrease in TOC >3 h
			33.18;	500	Hombikat UV 100 (100% anatase)	450 W Xenon arc lamp > 400 nm I_o= 1.6×10^{-4} einstein min^{-1}	k_{app} (pH = 3) 3.72×10^{-2} min^{-1}	As above
		[127]	33.18	500	Hombikat UV100	450 W Xenon arc lamp > 324 nm. I_o = 1.83×10^{-7} einstein cm^{-2} s^{-1}	Ciprofloxacin undetectable at 20 min	Cleavage of the piperazine ring. Loss of antibacterial activity proportional to irradiation time.
		[128]	15.00	500	Aeroxide P25	UV-A lamp 365 nm, I^o= 485 μW cm^{-2}, 300-440 nm	k_{app} (pH = 3) 0.097 min^{-1}	-
			15.00	500	Aeroxide P25	UV-A lamp 365 nm, I^o= 485 μW cm^{-2}, 300-440 nm	k_{app} (pH = 7) 0.137 min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
			15.00	500	Aeroxide P25	UV-A lamp 365 nm, I^o= 485 μW cm^{-2}, 300-440 nm	k_{app} (pH = 10) 0.068 min^{-1}	-
			15.00	500	Aeroxide P25	UV-C lamp 254 nm , I_o = 389 μW cm^{-2}.	k_{app} (pH = 3) 0.129 min^{-1}	-
			15.00	500	Aeroxide P25	UV-C lamp 254 nm , I_o = 389 μW cm^{-2}.	k_{app} (pH = 7) 0.163 min^{-1}	-
			15.00	500	Aeroxide P25	UV-C lamp 254 nm , I_o = 389 μW cm^{-2}.	k_{app} (pH = 10) 0.089 min^{-1}	-
		[129]	0.20	571	Aeroxide P25	126W medium pressure Hg lamp (Philips Brazil).	Complete degradation (pH = 3 effluent) 60 min	60% Chemical Oxygen demand remaining 60 min
Clarithromycin	81113–11–9	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 0.32 h^{-1}	-
Clofibric acid	882-09-7	[93]	0.53	500	Aeroxide P25	Xenon short-arc lamp solar simulator. I_o< 400 nm = 1.35×10^{-4} einsteins m^{-2} s^{-1}.	k_{app} = 17×10^{-3} s^{-1}	4-chlorophenol, isobutyric acid, hydroquinone. Presence of unidentified intermediates 45 min.
			0.53	500	Hombikat UV100	Xenon short-arc lamp solar simulator. I_o< 400 nm = 1.35×10^{-4} einsteins m^{-2} s^{-1}.	k_{app} = 22×10^{-3} s^{-1}	As above
		[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 4.98 h^{-1}	-
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app}(pH = 3) 3.28×10^{-2} min^{-1}.	-
			10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app}(pH = 11) 5.93×10^{-2} min^{-1}	-
		[94]	18.00	1000	Aeroxide P25	Medium pressure Hg lamp 366-578 nm. I_o = 2.38×10^{-6} einstein s^{-1}	k_{app} = 9.45×10^{-2} min^{-1}	4-chlorophenol, isobutyric acid, hydroquinone, benzoquinone, 4-chlorocatechol.
			18.00	1000	Anatase	Medium pressure Hg lamp 366-578 nm. I_o = 2.38×10^{-6} einstein s^{-1}	k_{app} =1.11×10^{-1} min^{-1}	As above
			18.00	1000	Rutile	Medium pressure Hg lamp 366-578 nm. I_o = 2.38×10^{-6} einstein s^{-1}	k_{app} =1.02×10^{-2} min^{-1}	As above
		[124]	5.00	100	Aeroxide P25	Medium Pressure Hg lamp > 300 nm. I_o = 5.1×10^{-6} einsteins s^{-1}	k_{app} = 0.025 min^{-1}.	-
Cloxacillin	61–72–3	[80]	105.00	500	Fluka 100% Anatase	6W UV-A lamp 365 nm.	47% degradation 300 min (pH = 5.0)	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	58% degradation 300 min (pH = 5.0)	-
			105.00	1500	Fluka 100% Anatase	6W UV-A lamp 365 nm.	59% degradation 300 min (pH = 5.0)	-
			105.00	2000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	60% degradation 300 min (pH = 5.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	95% degradation 300 min (pH = 3.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	58% degradation 300 min (pH = 5.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	82% degradation 300 min (pH = 8.0)	-
			105.00	1000	Fluka 100% Anatase	6W UV-A lamp 365 nm.	100% degradation 300 min (pH = 11.0)	-
Diclofenac	15307–86–5	[70]	5.00	250	Aeroxide P25	9W UV-A lamp (350 – 400 nm). I_o = 3.37×10^{-6} einstein s^{-1}.	k_{app} = 0.1 min^{-1}	121 min, crude photoproduct mixture more toxic than diclofenac (*Daphnia magna*).
			10.00	500	Aeroxide P25	9W UV-A lamp (350 – 400 nm). I_o = 3.37×10^{-6} einstein s^{-1}	k_{app} = 0.03 min^{-1}	As above
		[120]	0.10	-	Modified SiO_2 TiO_2 mix	Natural Sunlight 10 am – 5 pm.	k_{app} = 0.4057 s^{-1} (distilled water)	-
			0.10	-	Modified SiO_2 TiO_2 mix	Natural Sunlight 10 am – 5 pm	k_{app} = 0.3238 s^{-1} (wastewater)	-
		[106]	15.00	200	Aeroxide P25	1500 W Xenon arc lamp > 290 nm. I_o = 750 W m^{-2}.	k_{app} = 0.058 min^{-1}	Complete mineralization 2h. Maximal toxicity 72 min (*Vibrio fischeri*)
		[130]	20.00	200	Aeroxide P25	Hg vapour lamp 126W	100% degradation 10 min.	~20% TOC remaining 80 min.
		[105]	29.62	1500	Aeroxide P25	High-pressure Hg lamp, > 297 nm. I_o(313 nm) = 3×10^{-5} einstein s^{-1}.	$t_{1/2}$ =~ 3 min	30% TOC remaining (1 h)
		[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 16.00 h^{-1}	-
		[121]	0.10	5	Aeroxide P25	Solar pilot plant, average I_o = 30 W m^{-2}.	Undetectable 60 min.	-
		[73]	200.00	1000	Aeroxide P25	Xenon lamp, 290 – 400 nm. I_o = 6.9×10^{-6} einstein s^{-1}.	k_{app} = 9.6×10^{-3} min^{-1}.	38% TOC Removal. Minimal toxicity *Vibrio fischeri* 4h

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable <5 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.029 min^{-1}	-
		[122]	0.10	-	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.128 min^{-1}	-
		[122]	0.10	-	Used Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.085 min^{-1}	-
		[51]	50.00	200	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	Complete degradation 200 min	~12% remaining DOC 200 min
		[78]	2.50	800	Aeroxide P25	126 W Blacklight 300-420 nm Io = 4.7×10^{-7} einstein s^{-1}	k_{app} = 0.1244 min^{-1}	Less toxic intermediates with higher TiO_2 loadings
Enrofloxacin	93106-60-6	[95]	35.94	500	Hombikat UV100	450 W Xenon arc lamp > 400 nm I_o= 1.6×10^{-4} einstein min^{-1}	k_{app}(pH 3.0). 19×10^{-1} min^{-1}	Cleavage of piperazine ring. No decrease in TOC > 3 h
Erythromycin	115-07-8	[131]	10.00	250	Aeroxide P25	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	90% mineralization (TOC) 121 min.
		[131]	10.00	250	Hombikat UV (anatase)	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	~80% mineralization (TOC) 121 min.
		[131]	10.00	100	Aeroxide P25	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	~80% mineralization (TOC) 121 min.
		[131]	10.00	500	Aeroxide P25	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	Complete mineralization (TOC) 90 min (pH = 5-5.4).
		[131]	10.00	500	Aeroxide P25	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	60% mineralization (TOC) 90 min (pH = 7-7.4).
		[131]	2.50	500	Aeroxide P25	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	90% mineralization (TOC) 30 min
		[131]	5.00	500	Aeroxide P25	9W UV-A lamp, 350-400 nm, I_o= 4.69×10^{-6} einstein s^{-1}	-	90% mineralization (TOC) 40 min
Estrone	53–16–7	[111]	0.01	-	Immobilized TiO_2 on titanium alloy surface.	UV-A Philips 126W High pressure Hg lamp.	k_{app} = 0.086 min^{-1}	Complete loss of estrogenic activity after 1 h.
		[114]	1.00	400	Aeroxide P25	UV-A lamp max 355 nm, 8W, I_o = 116.6 W m^{-2}.	~5% remainng 180 min	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[114]	0.78	400	Aeroxide P25	UV-C lamp max 254 nm 8W, I_o = 114.5 W m^{-2}	~8% remaining 180 min	-
		[118]	0.10	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.86 h^{-1}	-
		[118]	0.25	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.82 h^{-1}	-
		[118]	0.50	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.84 h^{-1}	-
		[118]	1.00	1000	Aeroxide P25	TQ-150 reactor, 238-579 nm, 150 W	k_{app} = 0.86 h^{-1}	-
		[118]	0.10	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.34 h^{-1}	-
		[118]	0.25	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.40 h^{-1}	-
		[118]	0.50	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.45 h^{-1}	-
		[118]	1.00	1000	Aeroxide P25	TQ-15-32 15W 254 nm lamp.	k_{app} = 2.50 h^{-1}	-
Estriol	50-27-1	[114]	1.00	400	Aeroxide P25	UV-A lamp max 355 nm, 8W, I_o = 116.6 W m^{-2}	~8% remaining 180 min	-
		[114]	1.10	400	Aeroxide P25	UV-C lamp max 254 nm 8W, I_o = 114.5 W m^{-2}	~5% remainng 180 min	-
Famotidine	76824–35–6	[132]	33.00	-	TiO_2 integrated with activated charcoal, stationary support (0.5% w/w TiO_2)	126W medium pressure lamp 248-579 nm, λ_{max} = 366 nm.	k_{app} = 0.0045 min^{-1}	-
		[132]	32.00	-	TiO_2 integrated with activated charcoal, stationary support (1% w/w TiO_2)	126W medium pressure lamp 248-579 nm, λ_{max} = 366 nm.	k_{app} = 0.0881min^{-1}	-
		[132]	29.00	-	TiO_2 integrated with activated charcoal, stationary support (2.5% w/w TiO_2)	126W medium pressure lamp 248-579 nm, λ_{max} = 366 nm.	k_{app} = 0.0965 min^{-1}	-
		[132]	27.00	-	TiO_2 integrated with activated charcoal, stationary support (5% w/w TiO_2)	126W medium pressure lamp 248-579 nm, λ_{max} = 366 nm.	k_{app} = 0.1324 min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[132]	25.00	-	TiO_2 integrated with activated charcoal, stationary support (7.5% w/w TiO_2)	126W medium pressure lamp 248-579 nm, λ_{max} = 366 nm.	k_{app} = 0.1445 min^{-1}	-
		[132]	25.00	-	TiO_2 integrated with activated charcoal, stationary support (10% w/w TiO_2)	126W medium pressure lamp 248-579 nm, λ_{max} = 366 nm.	k_{app} = 0.1739 min^{-1}	-
Fenoprofen	31879–05–7	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 4.85 h^{-1}	-
Flumequine	42835-25-6	[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable 10 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.141 min^{-1}	-
		[122]	0.10	5	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.460 min^{-1}	-
		[133]	20.00	1.6	TiO_2 prepared by sol-gel technique	Suntest Solar XLS+ Reactor, I_o = 500 W m^{-2}.	k_{app} = 0.03 min^{-1}	-
		[133]	20.00	1.6	TiO_2 prepared by sol-gel technique doped with thiourea	Suntest Solar XLS+ Reactor, I_o = 500 W m^{-2}.	k_{app} = 0.07 min^{-1}	-
		[133]	20.00	1.6	TiO_2 prepared by sol-gel technique doped with thiourea	Suntest Solar XLS+ Reactor, I_o = 500 W m^{-2}.	k_{app} = 0.08 min^{-1}	-
		[134]	20.00	0.5	Aeroxide P25	Suntest Solar XLS+ Reactor, I_o = 500 W m^{-2}.	80% degradation 1 h	Complete mineralization 60 min.
		[95]	26.13	500	Hombikat UV100	450 W Xenon arc lamp > 400 nm I_o= 1.6×10^{-4} einstein min^{-1}	k_{app} = 1.37×10^{-2} min^{-1}	Cleavage of piperazine ring. No decrease in TOC > 3 h
Fluoxetine	54910-89-3	[158]	34.00	100	Aeroxide P25	75W high pressure Hg lamp, I_o= 2-4 mW cm^{-2}, 360 nm	k_{app} (pH = 5) = 0.075 ± 0.002 min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[158]	34.00	100	Aeroxide P25	75W high pressure Hg lamp, I_o= 2-4 mW cm^{-2}, 360 nm	k_{app} (pH = 11) = 0.77 ± 0.09 min^{-1}	-
		[158]	34.00	50	Aeroxide P25	75W high pressure Hg lamp, I_o= 2-4 mW cm^{-2}, 360 nm	k_{app} (pH = 11) = 0.55 ± 0.04 min^{-1}	50% mineralization 60 min irradiation
		[158]	34.00	10	Aeroxide P25	75W high pressure Hg lamp, I_o= 2-4 mW cm^{-2}, 360 nm	k_{app} (pH = 11) = 0.38 ± 0.05 min^{-1}	-
Furosemide	54–31–9	[82]	5.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app} (pH = 3) 3.21×10^{-2} min^{-1}.	-
		[82]	5.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app} =1.13×10^{-1}	-
Gemfibrozil	25812-30-0	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 0.64 h^{-1}	-
		[86]	47.00	400	Aeroxide P25	126 W Medium pressure Hg lamp 360 nm, I_o = 10 mW cm^{-2}	Complete degradation 0.5 h	Complete mineralization 3.2 h
		[86]	47.00	400	Hombikat UV 100	126 W Medium pressure Hg lamp 360 nm, I_o = 10 mW cm^{-2}	Complete degradation 3 h	Complete mineralization 15 h
Glimepiride	93479–97–1	[120]	0.10	-	Modified SiO_2 TiO_2 mix	Natural Sunlight 10 am – 5 pm.	k_{app} =0.2771 s^{-1} (distilled water)	-
		[120]	0.10	-	Modified SiO_2 TiO_2 mix	Natural Sunlight 10 am – 5 pm.	k_{app} =0.2203 s^{-1} (wastewater)	-
Ibuprofen	15687–27–1	[96]	10.00	250	Aeroxide P25	9W UV-A lamp, 350-400 nm. I_o = 3.37×10^{-6} einsteins s^{-1}.	62% removal by 121 min	-
		[96]	10.00	500	Aeroxide P25	9W UV-A lamp, 350-400 nm. I_o = 3.37×10^{-6} einsteins s^{-1}.	65% removal by 121 min	46% DOC removal
		[96]	5.00	250	Aeroxide P25	9W UV-A lamp, 350-400 nm. I_o = 3.37×10^{-6} einsteins s^{-1}.	80% removal by 121 min	-
		[96]	10.00	250	Aeroxide P25	9W UV-A lamp, 350-400 nm. I_o= 3.37×10^{-6} einsteins s^{-1}.	70% removal by 121 min	-
		[96]	20.00	250	Aeroxide P25	9W UV-A lamp, 350-400 nm. I_o = 3.37×10^{-6} einsteins s^{-1}.	65% removal by 121 min	-
		[120]	0.10	-	Modified SiO_2 TiO_2 mix	Natural sunlight 10 am – 5 pm.	k_{app} = 0.2411 s^{-1} (distilled water)	-
		[120]	0.10	-	Modified SiO_2 TiO_2 mix	Natural sunlight 10 am – 5 pm.	k_{app} = 0.2802 s^{-1} (wastewater)	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 1.33 h^{-1}	-
		[73]	200.00	1000	Aeroxide P25	Xenon lamp, 290 – 400 nm. $I_o = 6.9\times10^{-6}$ einstein s^{-1}.	k_{app} = 9.1×10^{-3} min^{-1}	-
		[135]	6.60	10	Aeroxide P25	UV-vis Xenon Arc lamp with Ultrasound Sonolysis at 300 Hz, 80W	k_{app} = 1.84×10^{-3} min^{-1}	DOC removal = 55%
		[136]	200.00	100	Aeroxide P25	Solar pilot plant photoreactor,	Complete removal with solar energy 70 kJ L^{-1}	80% TOC remaining after solar energy 80 kJ L^{-1}
		[136]	100.00	100	Aeroxide P25	Solar pilot plant photoreactor,	Complete removal with solar energy 30 kJ L^{-1}	-
		[136]	50.00	100	Aeroxide P25	Solar pilot plant photoreactor,	Complete removal with solar energy 10 kJ L^{-1}	-
		[136]	20.00	100	Aeroxide P25	Solar pilot plant photoreactor,	Complete removal with solar energy 5 kJ L^{-1}	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable 30 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.013 min^{-1}	-
		[122]	0.10	-	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.048 min^{-1}	-
		[122]	0.10	-	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.128 min^{-1}	-
Imipramine	50–49–7	[137]	15.00	200	Aeroxide P25	Xenon arc lamp > 290 nm, I_o = 750 W m^{-2}.	Complete degradation ~ 1.5 h.	Complete mineralization 24 h.
Indomethacin	53–86–1	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 5.11 h^{-1}	-
Iomeprol	78649-41-9	[124]	5.00	100	Aeroxide P25	Medium Pressure Hg lamp > 300 nm. $I_o = 5.1\times10^{-6}$ einstein s^{-1}.	k_{app} (pH = 7.5) 0.032 min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Iopromol	73334-07-3	[93]	5.20	500	Aeroxide P25	1000W Xenon solar short-arc lamp I_o< 400 nm = 1.35×10-4 einstein m^{-2} s^{-1}.	k_{app} = 5.25×10^{-3} s^{-1}	Deiodination of iopromol occurs. .
		[93]	5.20	500	Hombikat UV100	1000W Xenon solar short-arc lamp I_o< 400 nm = 1.35×10^{-4} einstein m^{-2} s^{-1}.	k_{app} = 9.24×10^{-3} s^{-1}	Deiodination of iopromol occurs
Isopropylantipyrine	479–92–5	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 4.37 h^{-1}	-
Ketoprofen	22071–15–4	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 31.09 h^{-1}	-
Ketorolac	74103-06-3	[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable 20 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.035 min^{-1}	-
		[122]	0.10	5	Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.086 min^{-1}	-
Levofloxacin	100986–85–4	[138]	36.14	2000	Aeroxide P25	365 nm High-pressure Hg lamp, I_o = 0.38 mW cm^{-2}	k_{app} (pH = 7.0) = 0.18 min^{-1}	Elimination of piperazinylic ring, loss of fluorine atom, multiple hydroxylations. .
Lamivudine	134678-17-4	[156]	0.10	250	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 7.0) = 0.0395 min^{-1}	6 hr irradiation: 83% mineralization.
		[156]	0.10	1000	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 7.0) = 0.0542 min^{-1}	6 hr irradiation: 83% mineralization
		[156]	0.10	3000	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 7.0) = 0.0412 min^{-1}	6 hr irradiation: 83% mineralization
		[156]	0.10	1000	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 3.0) = 0.0571 min^{-1}	6 hr irradiation: 83% mineralization
		[156]	0.10	1000	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 5.0) = 0.0472 min^{-1}	6 hr irradiation: 83% mineralization
		[156]	0.10	1000	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 9.0) = 0.0597 min^{-1}	6 hr irradiation: 83% mineralization
		[156]	0.10	1000	Aeroxide P25	365 nm High-pressure Hg lamp. I_o = 0.38 mW cm^{-2}	k_{app} (pH = 11.0) = 0.0322 min^{-1}	6 hr irradiation: 83% mineralization

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Lincomycin	154–21–2	[75]	50 .00	400	Aeroxide P25	126W Medium pressure Hg lamp. I_o = 8.5 mW cm^{-2}	Complete degradation 3 h	~ 50% mineralization after 5 h.
		[75]	50.00	400	Merck 100% Anatase	126W Medium pressure Hg lamp. I_o= 8.5 mW cm^{-2}	Complete degradation 3 h	No significant mineralization 5 h. Thiomethyl group to sulfone and sulfoxide derivatives.
		[139]	11.50	200	Aeroxide P25	Solar Photoreactor	k_{app} = 6.23×10^{-3} M $einstein^{-1}$	-
Lomefloxacin	98019-51-7	[138]	35.13	2000	Aeroxide P25	365 nm High-pressure Hg lamp, I_o= 0.38 mW cm^{-2}	k_{app} (pH = 7.0) =0.13 min^{-1}	Elimination of piperazynilic ring, loss of fluorine atom, multiple hydroxylations
Lovastatin	75330–75–5	[87]	10.00	-	Anatase films on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps at 365 nm (Phillips CLEO model).	k_{app} (closed lactone form) = 0.046 ± 0.006 min^{-1}.	Hydroxylated derivatives. Intermediates less toxic than parent statins
		[87]	10.00	-	Anatase films on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps at 365 nm (Phillips CLEO model)	k_{app} (open hydroxy acid form with O_2) = 0.105 ± 0.004 min^{-1}.	Hydroxylated derivatives. Intermediates less toxic than parent statins
		[87]	10.00		Anatase films on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps at 365 nm (Phillips CLEO model)	k_{app} (open hydroxy acid form purged with N_2) = 0.089 ± ±0.003 min^{-1}	Hydroxylated derivatives. Intermediates less toxic than parent statins
Metamizole	68-89-3	[140]	50.00	200	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	Complete degradation of major intermediate 4-methylantipyrine 65 min	75% mineralization 30 min
Methotrexate	59–05–2	[120]	0.025	-	Modified SiO_2 TiO_2 mix	Natural Sunlight 10 am – 5 pm.	k_{app} = 3.1407 (distilled water)	-
Metoprolol	37350–58–6	[157]	2.68	1000	Aeroxide P25	125W high pressure Hg lamp, UV-A (366 nm), I_o = 8.8×10^{-9} einstein min^{-1} mL^{-1}.	k_{app}= 0.2 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	18.88	1000	Aeroxide P25	125W high pressure Hg lamp, UV-A (366 nm), I_o = 8.8×10^{-9} einstein min^{-1} mL^{-1}.	k_{app}= 0.0625 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[157]	37.76	1000	Aeroxide P25	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.03 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	2.68	1000	Wackherr TiO_2	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.35 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	18.88	1000	Wackherr TiO_2	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.14 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	37.76	1000	Wackherr TiO_2	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.11 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	13.40	1000	Aeroxide P25	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.075 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	13.40	2000	Aeroxide P25	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.07 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	13.40	5000	Aeroxide P25	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.06 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	13.40	1000	Wackherr TiO2	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.18 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[157]	13.40	2000	Wackherr TiO2	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app} = 0.16 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[157]	13.40	5000	Wackherr TiO2	125W high pressure Hg lamp, UV-A (366 nm), $I_o = 8.8\times10^{-9}$ einstein min^{-1} mL^{-1}.	k_{app}= 0 .15 min^{-1}	Hydroxyl radical attack aromatic benzene ring. Complete mineralization Aeroxide > Wackherr 4h irradiation
		[141]	133.70	1000	Aeroxide P25	15W low pressure Hg lamp, UV-C 2 54 nm, $I_o = 3.3\times10^{-6}$ einstein s^{-1}.	~40% remaining 180 min	30% mineralization 180 min (TOC)
		[142]	50.00	400	Aeroxide P25	1000W xenon lamp 290-400 nm, $I_o = 3.34\times10^{-5}$ einstein s-1;	94% removal 240 min	~55% mineralization 360 min
		[74]	26.74	2000	Aeroxide P25	High-pressure mercury lamp, 365 nm. 126W.	k_{app} (pH = 7.0) 0.072 min^{-1}	Less toxic photoproducts 15-30 min (*Daphnia magna*)
Moxifloxacin	354812-41-2	[128]	15.00	500	Aeroxide P25	UV-A lamp 365 nm, I^o= 485 μW cm^{-2}, 300-440nm	k_{app} (pH = 3) 0.069 min^{-1}	-
		[128]	15.00	500	Aeroxide P25	UV-A lamp 365 nm, I^o= 485 μW cm^{-2}, 300-440nm	k_{app} (pH = 7) 0.227 min^{-1}	-
		[128]	15.00	500	Aeroxide P25	UV-A lamp 365 nm, I^o= 485 μW cm^{-2}, 300-440nm	k_{app} (pH = 10) 0.081 min^{-1}	-
		[128]	15.00	500	Aeroxide P25	UV-C lamp 254 nm , I_o = 389 μW cm^{-2}.	k_{app} (pH = 3) 0.146 min^{-1}	-
		[128]	15.00	500	Aeroxide P25	UV-C lamp 254 nm , I_o = 389 μW cm^{-2}.	k_{app} (pH = 7) 0.236 min^{-1}	-
		[128]	15.00	500	Aeroxide P25	UV-C lamp 254 nm , I_o = 389 μW cm^{-2}.	k_{app} (pH = 10) 0.144 min^{-1}	-
Naproxen	22204–53–1	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 3.73 h^{-1}	-
		[73]	200.00	1000	Aeroxide P25	Xenon lamp, 290 – 400 nm. $I_o = 6.9\times10^{-6}$ einstein s^{-1}.	k_{app} = 7.0× 10^{-3} min^{-1}	-
		[82]	5.00	1000	Aeroxide P25	126 W medium pressure Hg lamp; Helios Italquartz, Milan.	k_{app} (pH = 3) 7.86×10^{-2} min^{-1}	-
		[82]	5.00	1000	Aeroxide P25	126 W medium pressure Hg lamp; Helios Italquartz, Milan	k_{app}(pH = 11) 4.91×10^{-1} min^{-1}	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Norfloxacin	70458-96-7	[138]	32.00	2000	Aeroxide P25	365 nm High-pressure Hg lamp, I_o = 0.38 mW cm^{-2}	k_{app} (pH = 7.0) = 0.14 min^{-1}	Elimination of piperazynilic ring, loss of fluorine atom, multiple hydroxylations
		[143]	80.00	1000	Aeroxide P25	126W medium pressure mercury lamp	Complete degradation of norfloxacin 80 min	20% TOC remaining.80 min
		[95]	32.00	500	Hombikat UV100	450 W Xenon arc lamp > 400 nm I_o= 1.6×10^{-4} einstein min^{-1}	k_{app} (pH = 3)= 7.19×10^{-2} min^{-1}	Cleavage of piperazine ring. No decrease in TOC > 3 h
Ofloxacin	83380–47–6	[71]	10.00	250	Aeroxide P25	9W UV-A lamp (350 – 400 nm). I_o = 3.37×10^{-6} einstein s^{-1}.	Conversion> 80% 250 min	Irradiation for 15-30 minutes induces higher toxicity to *Daphnia magna* than 1 h irradiation.
		[144]	10.00	250	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	< 10% conversion in pH = 8 wastewater, 121 min	Incomplete mineralization. 2% DOC removal
		[144]	10.00	500	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	~25% conversion in pH = 8 wastewater, 121 min	6% DOC removal
		[144]	10.00	1000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	~45% conversion in pH = 8 wastewater, 121 min	8% DOC removal
		[144]	10.00	2000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	~45% conversion in pH = 8 wastewater, 121 min	10% DOC removal
		[144]	10.00	3000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	~60% conversion in pH = 8 wastewater, 121 min	12% DOC removal
		[144]	10.00	4000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	~45% conversion in pH = 8 wastewater, 121 min	-
		[144]	10.00	3000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	k_{app} (pH = 2 wastewater) = 0.019 min^{-1}	-
		[144]	10.00	3000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	k_{app} (pH = 8 wastewater) = 0.009 min^{-1}	-
		[144]	10.00	3000	Aeroxide P25	1kW Solar simulator xenon lamp, I_o = 272.3 W m^{-2}.	k_{app} (pH = 10 wastewater) = 0.008 min^{-1}	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable <5 min	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	Undetectable 10 min	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[122]	0.10	5	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 1.577 min^{-1}	-
		[122]	0.10	5	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.228 min^{-1}	-
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app}(pH = 3) 2.94×10^{-1} min^{-1}.	-
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app}(pH = 11) 7.27×10^{-2} min^{-1}.	-
Oxolinic Acid	14698-29-4	[145]	20.00	1000	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	100% degradation 30 min (pH = 7.5)	50% removal DOC 60 min
		[145]	20.00	1000	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	80% degradation 10 min (pH = 7.5)	50% removal DOC 60 min
		[145]	20.00	200	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	66% degradation 15 min (pH = 7.5).	-
		[145]	20.00	200	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	42% degradation 15 min (pH = 11).	-
		[145]	20.00	1500	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	66% degradation 15 min (pH =7.5).	-
		[145]	20.00	1500	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	50% degradation 15 min (pH =11).	-
		[145]	20.00	850	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	79% degradation 15 min (pH =7.5).	-
		[145]	20.00	850	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	60% degradation 15 min (pH =11).	-
		[145]	20.00	200	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	49% degradation 15 min (pH =9.25).	-
		[145]	20.00	1500	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	63% degradation 15 min (pH =9.25).	-
		[145]	20.00	850	Aeroxide P25	Blacklight 365 nm UV-A, I_o = 14 W m^{-2}.	76% degradation 15 min (pH =9.25).	-
		[146]	18.00	-	Aeroxide P25 TiO_2 immobilized on sintered glass cylinders	Blacklight UV-A 360 nm lamp, 36W	Complete degradation 121 min	Chemical oxygen demand < 5% 160 min, TOC < 40% 180 min
		[146]	18.00	1000	Aeroxide P25	Blacklight UV-A 360 nm lamp, 36W	Complete degradation 40 min	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Oxytetracycline	79–57–2	[147]	50.00	100	Aeroxide P25 dispersed on zeolite 5A	2×254nm UV lamps, $I_o = 845\times10^{-6}$ W cm^{-2}	>90% removal (pH =7) 210 min	Inhibition (*Vibrio Qinghaiensis*) decreased to 30% after 270 min
		[147]	50.00	100	Aeroxide P25 dispersed on zeolite 13X	2×254nm UV lamps, $I_o = 845\times10^{-6}$ W cm^{-2}	>80% removal (pH = 7) 210 min.	Inhibition (*Vibrio Qinghaiensis*) decreased to 13% after 270 min
Paracetamol	103–90–2	[121]	0.10	5	Aeroxide P25	Solar pilot plant, average $I_o = 30$ W m^{-2}.	Undetectable 145 min.	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. $I_o = 765$ W m^{-2}.	Undetectable 25 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. $I_o = 30$ W m^{-2}.	k_{app} = 0.027 min^{-1}	-
		[122]	0.10	-	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. $I_o = 30$ W m^{-2}	k_{app} = 0.080 min^{-1}	-
		[122]	0.10	-	Used Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. $I_o = 30$ W m^{-2}	k_{app} = 0.045 min^{-1}	-
		[99]	604.80	400	Aeroxide P25	UV-C source 254 nm, with minor distribution 185 nm	$k_{app} = 10.5 \pm 1.6\times10^{-3}$ min^{-1}.	60% mineralization 300 min. Carboxylic acids, hydroquinone, acetamide
		[99]	604.80	400	Aeroxide P25	8 W UV-A source: blacklight 365 nm.	$k_{app} = 1.9 \pm 0.2\times10^{-3}$ min^{-1}	Slight change in TOC
		[72]	7.56	2000	Nano TiO_2: High Technology Nano Co., China	250W metal halide lamp, > 365 nm	pH = 9:~100% removal	Hydroquinone
		[72]	7.56	2000	Nano TiO_2: High Technology Nano Co., China	250W metal halide lamp, > 365 nm	pH = 9 and pH = 6.5: ~95% removal	Hydroquinone
		[72]	7.56	2000	Nano TiO_2: High Technology Nano Co., China	250W metal halide lamp, >365 nm	pH = 3:~92% removal (pH = 3)	Hydroquinone
		[72]	7.56	2000	Nano TiO_2: High Technology Nano Co., China	250W metal halide lamp, > 365 nm	pH = 11:~70% removal .	Hydroquinone

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Phenacetin	62–44–2	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 0.15 h^{-1}	-
Phenazone	60–80–0	[121]	0.10	5	Aeroxide P25	Solar pilot plant, average I_o = 30 W m^{-2}.	>196 min to complete degradation	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	50% remaining 50 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.019 min^{-1}	-
		[122]	0.10	5	Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	~25% remaining 50 min	-
		[122]	0.10	5	Used Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.022 min^{-1}	-
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app} (pH = 3) 1.74×10^{-1} min^{-1}.	-
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app}(pH = 11) 1.60×10^{-1} min^{-1}	-
Phenobarbital	50–06–6	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 0.62 h^{-1}	-
Phenytoin	57–41–0	[123]	1.00	-	TiO_2 fibre catalyst on fixed support, Ube Ltd., Japan.	Low pressure 10W UV-C 254 nm lamp.	k_{app} = 2.65 h^{-1}	-
Pravastatin	81103–37–0	[87]	10.00	-	Anatase films on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps at 365 nm (Phillips CLEO model).	k_{app} (open hydroxy acid form, O_2) = 0.107 ± 0.006 min^{-1}	Hydroxylated derivatives. Intermediates less toxic than parent statins
		[87]	10.00	-	Anatase films on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps at 365 nm (Phillips CLEO model).	k_{app} (open hydroxy acid form, purged with N_2) = 0.083 ± 0.004 min^{-1}	Hydroxylated derivatives. Intermediates less toxic than parent statins
Progesterone	57-83-0	[121]	0.10	5	Aeroxide P25	Solar pilot plant, average I_o = 30 W m^{-2}.	Undetectable 145 min	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable <5 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	~20% remaining 90 min	-
		[122]	0.10	-	Fresh Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}	k_{app} = 0.071 min^{-1}	-
Propanolol	525–66–6	[142]	50.00	400	Aeroxide P25	1000W xenon lamp 290-400 nm, $I_o = 3.34\times10^{-5}$ einstein s^{-1};	94% removal 240 min	~55% mineralization 360 min
		[74]	25.93	2000	Aeroxide P25	High-pressure Hg lamp, 365 nm. 126W.	k_{app} (pH = 7)= 0.182 min^{-1}	TOC < 10% (250 min). Aromatic Hydroxylated Intermediates
Ranitidine	66357–35–5	[75]	50 .00	400	Aeroxide P25	126W Medium pressure Hg lamp. I_o = 8.5 mW cm^{-2}	Complete degradation 0.5 h	~ 60% mineralization 5 h
		[75]	50.00	400	Merck (100% anatase)	126W Medium pressure Hg lamp. I_o = 8.5 mW cm^{-2}	Complete degradation 1 h	No significant mineralization 5 h
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure mercury UV lamp; Helios Italquartz, Milan.	k_{app} (pH = 3) 9.74×10^{-2} min^{-1}.	-
		[82]	10.00	1000	Aeroxide P25	126 W medium pressure Hg UV lamp; Helios Italquartz, Milan.	k_{app} (pH = 11) 5.35×10^{-2} min^{-1}	-
		[85]	10.00	200	Aeroxide P25	Sunlight, pilot plant (latitude 37°N, longitude 2.4°W).	k_{app} (distilled water) = 0.146 min^{-1}.	37% mineralization 73 min;. propionic, oxalic and formic acids
		[85]	10.00	200	Aeroxide P25	Sunlight, pilot plant (latitude 37°N, longitude 2.4°W).	k_{app} (effluent water) = 0.00997 min^{-1}	Intermediates: Hydroxylated ranitidine ; desmethylated ranitidine.
Salbutamol	18559–94–9	[107]	15.00	200	Aeroxide P25	Xenon arc lamp 1500 W > 290 nm. I_o = 750 W m^{-2}	Complete degradation 30 min.	Complete mineralization 3 h . Intermediates more toxic than salbutamol (*Vibrio fischeri* , 15 min).
Salicylic acid	69–72–7	[89]	100.00	2500	TiO_2 fibres distributed on a glass film.	High pressure Hg lamp at 365 nm. 500 W.	k_{app} = 0.0016 min^{-1} (with oxygen bubbled).	Less than 40% mineralization. Refractory carboxylic acids

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[89]	100.00	2500	TiO_2 fibres distributed on a glass film.	High pressure Hg lamp at 365 nm. 500 W	~25% removal (without bubbled oxygen).	2,3 dihydroxybenzoic acids, muconic acid.
		[83]	50.00	500	Wackherr Standard (100% anatase).	40 W UV-B lamp, Spectrum 290 nm – 320 nm. $I_o = 2.6\times10^{-4}$ W cm^{-2}.	k_{app} (pH = 3.6) 2.9×10^{-5} s^{-1}	-
		[83]	50.00	500	Wackherr Standard (100% anatase).	40 W UV-B lamp, Spectrum 290 nm – 320 nm. $I_o = 2.6\times10^{-4}$ W cm^{-2}	k_{app}(pH = 5.2) 3.26×10^{-5} s^{-1}	-
		[83]	50.00	500	Wackherr Standard (100% anatase).	40 W UV-B lamp, Spectrum 290 nm – 320 nm. $I_o = 2.6\times10^{-4}$ W cm^{-2}	k_{app} (pH = 7.4) 3.57×10^{-5} s^{-1}	-
		[148]	13.80	1000	Aldrich (70:30 anatase: rutile).	400W high pressure Hg lamp	$k_{app} = 3.33\times10^{-8}$ mol L^{-1} s^{-1}.	-
		[149]	21.00	1000	TiO_2 prepared by a sol-gel process	450 W Hanovia High-pressure Hg lamp, > 280 nm. I_o = 193 μeinsteins L^{-1} min^{-1}.	75% removal of salicylic acid (45 min, pH= 4).	-
		[150]	10.00	-	Immobilized anatase TiO_2 prepared by an atomic layer deposition process on glass plates.	UV –C low pressure Hg lamp, 250-260 nm. I_o = 0.2 mW cm^{-2}	~ 80% removal (pH = 3) 1 hr	-
		[150]	10.00	-	Immobilized anatase TiO_2 prepared by an atomic layer deposition process on glass plates.	UV –C low pressure Hg lamp, 250-260 nm. I_o = 0.2 mW cm^{-2}	~65% removal (pH = 4.2) 1 hr	-
		[150]	10.00	-	Immobilized anatase TiO_2 prepared by an atomic layer deposition process on glass plates.	UV –C low pressure Hg lamp, 250-260 nm. I_o = 0.2 mW cm^{-2}	~70% removal (pH = 6) 1 hr	-
		[150]	10.00	-	Immobilized anatase TiO_2 prepared by an atomic layer deposition process on glass plates.	UV –C low pressure Hg lamp, 250-260 nm. I_o = 0.2 mW cm^{-2}	~50% removal (pH = 8) 1 hr	-
		[150]	10.00	-	Immobilized anatase TiO_2 prepared by an atomic layer deposition process on glass plates.	UV –C low pressure Hg lamp, 250-260 nm. I_o = 0.2 mW cm^{-2}	~65% removal (pH = 10) 1 hr	-

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Simvastatin	79902–63–9	[87]	10.00	-	TiO_2 films of anatase on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps 365 nm (Phillips CLEO model).	k_{app} (closed lactone form) = 0.052 ± 0.008 min^{-1}.	Hydroxylated derivatives far less toxic than parent (*Vibrio fischeri*)
		[87]	10.00	-	TiO_2 films of anatase on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps 365 nm (Phillips CLEO model).	k_{app} (open hydroxy acid form in the presence of O_2) = 0.114 ± 0.007 min^{-1}.	Hydroxylated derivatives far less toxic than parent (*Vibrio fischeri*)
		[87]	10.00	-	TiO_2 films of anatase on glass slides 175 ×12.5×2 mm	3×20 W UV-A lamps 365 nm (Phillips CLEO model).	k_{app} (open hydroxy acid form purged with N_2) = 0.095 ± 0.006 min^{-1}.	Hydroxylated derivatives far less toxic than parent (*Vibrio fischeri*)
Sulfacetamide	144–80–9	[108]	21.42	2500	Riedel de-Haen TiO_2 standard.	UV-A lamp λmax = 366 nm. I_o = 8.76×10-9 einstein s^{-1} cm^{-2}.	k_{app} = 0.0132 min^{-1}. Complete degradation 300 min	30-70% TOC (300 min). Toxicity of photoproducts (*Chlorella vulgaris*) lower than parent.
Sulfachlorpyridazine	80–32–0	[76]	28.47	2000	Aeroxide P25	High-pressure mercury lamp, 365 nm. 126W	Removal Efficiency: 85.2% (60 min). k_{app} (pH = 7.0) 0.031 min^{-1}.	240 min TOC levels < 20%. Clevage of S-N bond and hydroxylation.
Sulfadiazine	68–35–9	[108]	25.03	2.5	Riedel de-Haen TiO_2 standard.	UV-A lamp with λ_{max} = 366 nm. I_o= 8.76×10^{-9} einstein s^{-1} cm^{-2}.	k_{app} = 0.0131 min^{-1}. Complete degradation 300 min.	30-70% TOC (300 min)
Sulfamethazine	57-68-1	[97]	50.00	1000	Aeroxide P25	9W UV-A 350-400 nm lamp, λ_{max} = 366 nm. I_o= 2.02×10^{-4} einstein min^{-1}	65% degradation 60 min.	20% DOC 360 min. Sulfate, ammonium, nitrate ions.
		[97]	50.00	1000	Tronox 100% anatase	9W UV-A 350-400 nm lamp, λ_{max} = 366 nm. I_o= 2.02×10^{-4} einstein min^{-1}	39% degradation 60 min.	70% DOC 360 min. Sulfate, ammonium, nitrate ions.
Sulfamethiazole	144–82–1	[90]	27.00	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.033 min^{-1} (pH = 3)	-
Sulfamethoxazole	723–46–6	[151] [152]	100.00	500	Aeroxide P25	Xenon lamp > 290 nm, 1000W	80% degradation, 6 h.	25% TOC removal, 6h.
		[151] [152]	100.00	1000	Aeroxide P25	Xenon lamp > 290 nm, 1000W	88% degradation, 6 h.	88% TOC removal, 6 h.
		[151] [152]	100.00	2000	Aeroxide P25	Xenon lamp > 290 nm, 1000W	91% degradation, 6 h	40% TOC removal, 6 h.
		[108]	25.33	2500	Riedel de-Haen TiO_2 standard	UV-A lamp with λmax = 366 nm. I_o= 8.76×10^{-9} einstein s^{-1} cm^{-2}.	k_{app} = 0.0301 min^{-1}. Complete degradation 200 min	30-70% TOC (300 min)

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[109]	25.33	1500	Aeroxide P25	High-pressure Hg lamp, > 290 nm, I_o = 0.112 einstein h^{-1}	$t_{1/2}$= 5 min	Oxalic acid. Minimal toxicity reduction (*Daphnia magna*) 121 min.
		[130]	20.00	200	Aeroxide P25	Hg vapour lamp 126W	100% degradation 10 min.	~20% TOC remaining 80 min.
		[90]	25.33	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.054 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, Ammonium, nitrate ions detected.
		[90]	25.33	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.076 min^{-1} (pH = 3, O_2)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	1.27	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.36 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	2.28	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.30 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	12.00	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.11 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	58.00	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.025 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	122.00	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.015 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	25.33	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.042 min^{-1} (pH = 5)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	25.33	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.064 min^{-1} (pH = 9)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[90]	25.33	100	Aeroxide P25	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.063 min^{-1} (pH = 11)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	25.33	100	Hombikat UV Anatase	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.0054 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[90]	25.33	100	TiOxide Rutile	UV-A Xenon Arc lamp I_o = 9 x10^{-5} einstein min^{-1}	k_{app} = 0.0028 min^{-1} (pH = 3)	80% reduction DOC 6 h. Sulfate, ammonium, nitrate ions detected.
		[121]	0.10	5	Aeroxide P25	Solar pilot plant, average I_o = 30 W m^{-2}.	Undetectable 145 min.	-
		[122]	0.10	-	Immobilized TiO_2 synthesized by sol-gel process	Solar light simulator 290 – 800 nm. I_o = 765 W m^{-2}.	Undetectable 20 min	-
		[122]	0.10	5	Aeroxide P25	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.035 min^{-1}	-
		[122]	0.10	5	Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	~25% remaining 50 min	-
		[122]	0.10	5	Used Immobilized TiO_2 synthesized by sol-gel process	Compound Parabolic Collector, natural sunlight. I_o = 30 W m^{-2}.	k_{app} = 0.085 min^{-1}	-
		[153]	60.00	500	Aeroxide P25	UV-C 254 nm lamps, I_o = 1.3×10^{-3} einstein min^{-1} L^{-1}	Complete removal 60 min	Toxic photoproducts 13 h (*Daphnia magna* 48 h). Sulfanilic acid, 3-amino-5-methylisoxazole
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. I_o = 2.81×10^{-4} einstein min^{-1}.	Complete degradation 30 min	>90% reduction TOC 121 min
		[79]	10.00	250	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. I_o = 2.81×10^{-4} einstein min^{-1}.	Complete degradation ~ 45 min	>80% reduction TOC 121 min
		[79]	10.00	250	Hombikat UV anatase	9W UV-A lamp, 350 – 400 nm. I_o = 2.81×10^{-4} einstein min^{-1}.	~80% degradation 121 min	~60% reduction TOC 121 min
		[79]	30.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. I_o = 2.81×10^{-4} einstein min^{-1}.	Complete degradation 90 min	~75% reduction TOC 121 min

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[79]	20.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	Complete degradation 45 min	~80% reduction TOC 121 min
		[79]	10.00	100	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	Complete degradation 45 min	~80% reduction TOC 121 min
		[79]	10.00	250	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	Complete degradation 45 min	~85% reduction TOC 121 min
		[79]	10.00	750	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	Complete degradation 30 min	~90% reduction TOC 121 min
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	>90% reduction (Ultrapure water, pH = 3.9-4.1) 20 min	-
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	>80% reduction (Ultrapure water, pH = 7.2-7.8).20 min	-
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	>80% reduction (Groundwater, pH = 4.8-5.6) 20 min.	-
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	>70% reduction (Groundwater, pH = 7.8-8.3) 20 min.	-
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	>90% reduction (Wastewater, pH = 4.8-5.6) 20 min.	-
		[79]	10.00	500	Aeroxide P25	9W UV-A lamp, 350 – 400 nm. $I_o = 2.81\times10^{-4}$ einstein min^{-1}.	~80% reduction (Wastewater, pH = 7.5-8.2) 20 min.	-
Sulfapyridine	144–83–2	[76]	24.93	2000	Aeroxide P25	High-pressure mercury lamp, 365 nm. 126W	k_{app} (pH = 7.0) 0.043 min^{-1}. Removal Efficiency: 92.5%(60 min).	240 min TOC levels < 20%.
Sulfathiazole	72–14–0	[108]	25.53	2500	Riedel de-Haen TiO_2 standard	UV-A lamp λmax = 366 nm. $I_o = 8.76\times10^{-9}$ einstein $s^{-1}cm^{-2}$.	k_{app} = 0.0175 min^{-1}. Complete degradation 200 min	30-70% TOC (300 min).
		[90]	25.53	100	Aeroxide P25	UV-A Xenon Arc lamp $I_o = 9\times10^{-5}$ einstein min^{-1}	k_{app} = 0.053 min^{-1} (pH = 3)	-
Sulfisoxazole	128-69-5	[90]	26.73	100	Aeroxide P25	UV-A Xenon Arc lamp $I_o = 9\times10^{-5}$ einstein min^{-1}	k_{app} = 0.055 min^{-1} (pH = 3)	-
		[76]	26.73	2000	Aeroxide P25	High-pressure Hg lamp, 365 nm. 126W	k_{app} (pH = 7.0) 0.031 min^{-1} Removal efficiency: 85.0% (60 min)	240 min TOC levels < 20%.

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
Tamoxifen	10540-29-1	[86]	20.00	400	Aeroxide P25	126 W Medium pressure mercury lamp at 360 nm, I_o = 10 mW cm^{-2}.	Complete degradation 60 min	Complete mineralization 22 h
		[86]	20.00	400	Merck (100% anatase).	126 W Medium pressure mercury lamp at 360 nm, I_o = 10 mW cm^{-2}	Complete degradation 83 min	Complete mineralization 28 h
Tetracycline	60–54–8	[75]	50.00	400	Aeroxide P25	126W Medium pressure mercury lamp. I_o = 8.5 mW cm^{-2}	>98% decrease in concentration 2 h	Mineralization near completion 5h
		[75]	50.00	1000	Merck (100% anatase)	126W Medium pressure mercury lamp. I_o = 8.5 mW cm^{-2}	Complete degradation 2 h	50% mineralization; loss of dimethylamine group; dealkylation.
		[103]	0.50	20	Aeroxide P25	Solarium UV-A lamp, 15W	~90% degradation 60 min	-
		[103]	0.50	20	Aeroxide P25	Solarium UV-A lamp, 30W	~90% degradation 60 min	-
		[103]	0.50	20	Aeroxide P25	Solarium UV-A lamp, 60W	~90% degradation 60 min	-
		[103]	1.00	20	Aeroxide P25	Solarium UV-A lamp, 15W	~75% degradation 60 min	-
		[103]	1.00	20	Aeroxide P25	Solarium UV-A lamp, 60W	~90% degradation 60 min	-
		[103]	2.00	20	Aeroxide P25	Solarium UV-A lamp, 15W	~50% degradation 60 min	-
		[103]	2.00	20	Aeroxide P25	Solarium UV-A lamp, 60W	~70% degradation 60 min	-
		[103]	0.50	20	Aeroxide P25	Solarium UV-A lamp, 30W	~90% degradation 60 min	-
		[103]	0.50	20	Aeroxide P25	Blacklight 365 nm, 32W	~67% degradation 60 min	-
		[103]	0.50	20	Aeroxide P25	Solarium UV-A lamp, 60W	~90% degradation 60 min	-
		[103]	0.50	20	N-doped TiO_2	Solarium UV-A lamp, 60W	~53% degradation 60 min	-
		[103]	0.50	20	Fe-doped TiO_2	Solarium UV-A lamp, 60W	~52% degradation 60 min	-
		[103]	0.50	20	Zr-doped TiO_2	Solarium UV-A lamp, 60W	~69% degradation 60 min	-
		[101]	40.00	500	Aeroxide P25	UV (>254 nm) Philips HPLN 126W; I_o (360 nm) = 1220 μW cm^{-2}	k_{app} = 71.6×10^{-3} s^{-1}	90% Mineralization (2 h) CO_2, NH_3 and H_2O. No antibacterial effects 1 h

Continued **Table 1.** Pharmaceuticals reported to degrade *via* TiO_2 assisted photocatalytic processes.

Pharmaceutical	CAS Number	Ref.	[Pharmaceutical] (mg L^{-1})	[TiO_2] (mg L^{-1})	TiO_2 catalyst	Apparatus conditions	Degradation kinetics	Photoproducts and mineralization
		[101]	40.00	500	Aeroxide P25	6×20W Solarium lamps (300-400 nm) Philips HB31; Io (360nm) = 1980 μW cm^{-2}	k_{app} = 39.3×10^{-3} s^{-1}.	75% Mineralization (2 h) CO_2, NH_3 H_2O. No antibacterial effects 1 h
		[101]	40.00	500	Aeroxide P25	160 W Philips Blacklight (365 nm). I_o (360 nm) = 59 μW cm^{-2}	k_{app} = $5.53\times10^{-3}s^{-1}$.	Neglibible mineralization.
		[154]	20.00	1500	Aeroxide P25	Suntest XLS+ Solar lamp, I_o = 250 W m^{-2}.	Complete degradation 15 min, pH = 8.7	30% TOC remaining 60 min. Complete removal antibacterial activity
Trimethoprim	738–70–5	[152]	100.00	500	Aeroxide P25	Xenon lamp > 290 nm, 1000W	100% degradation 6 h.	~50% TOC removal, 6h.
		[152]	100.00	1000	Aeroxide P25	Xenon lamp > 290 nm, 1000W	100% degradation 6 h.	~50% TOC removal, 6h.
		[152]	100.00	2000	Aeroxide P25	Xenon lamp > 290 nm, 1000W	100% degradation 6 h.	~50% TOC removal, 6h.
		[130]	20.00	200	Aeroxide P25	Hg vapour lamp 126W	97.5% degradation 30 min.	~20% TOC remaining 90 min.
		[155]	20.00	200	Aeroxide P25	Compound Parabolic Collector, natural sunlight, 30 W m^{-2}.	k_{app} (Distilled water) = 0.22 min^{-1}	~30% DOC remaining 100 min
		[155]	20.00	200	Aeroxide P25	Compound Parabolic Collector, natural sunlight, 30 W m^{-2}.	k_{app} (Sewage water) = 0.081 min^{-1}	~30% DOC remaining 360 min

presence of bubbled oxygen progressed at faster rates compared with nitrogen-purged solutions [87]. Providing the dissolved oxygen content in solutions is not limiting, any increases in oxygen concentration should increase the $O_2^{\cdot-}$ production, which in turn, favors H_2O_2 and $HO^{\cdot}$ radical formation [90].

2.4. Effect of TiO_2 type on photocatalytic degradation

The form of the TiO_2 used in experiments, such as whether the TiO_2 is in a suspension or immobilized form, or whether the TiO_2 has been doped, has a significant influence on photodegradation rates [91,92], and degradation efficiencies of these TiO_2 materials vary from one pharmaceutical to another. The photocatalytic activity of various forms of TiO_2 (pure anatase, pure rutile or an anatase-rutile mixture) have been compared in many studies [71,75,86,93-96]. As predicted by the band gap differences between anatase and rutile, higher conversion rates have been observed for anatase-predominant photocatalysts [71,96]. For example, Silva and Faria (2008) [94] compared the photodegradation rates of clofibric acid using either commercial Aeroxide P25, anatase or rutile. The anatase photocatalyst degraded clofibric acid faster than the rutile potocatalyst but slower than Aeroxide P25 which has a mixed anatase:rutile composition. Another study confirmed that Aeroxide P25 is more photocatalytically efficient than pure form anatase or rutile photocatalysts probably as a result of reduced recombination of valence hole-conduction band electron events on the surface or the bulk of the photocatalyst [97].

The use of various doped TiO_2 photocatalysts has been reported to remove potential organic contaminants such as phenol and azo dyes [98]. Little research has been done on the removal of pharmaceuticals with these doped TiO_2 photocatalysts, and while commerical preparations of doped materials are available in some countries for research (*i.e.*, Japan) [100], much of the present literature focuses on the synthesis and

characterisation of these doped materials [102]. However, a previous report has observed the degradation of salicylic acid by a samarium-nitrogen doped TiO_2 under visible light [104] having a photocatalytic efficiency greater than that of extemporaneously-prepared undoped TiO_2. While doping may be an effective strategy to decrease the band gap energy of TiO_2, and thus allow visible-light photocatalysis of organic contaminants, the decrease in the band gap energy may increase the ability for recombination [102] resulting in unpredictability of the photocatalytic efficiency of doped TiO_2 materials. Klauson *et al*. [91] observed that a 0.42% iron-doped TiO_2 material increased pharmaceutical photocatalysis by 10% compared to undoped TiO_2; however, when the dopant concentration in the TiO_2 was increased, the resultant material was less efficient in photocatalysis. Indeed, Choina *et al*. [103] observed that N, Fe or Zr doping of TiO_2 did not enhance the photodegradation of tetracyclines after 60 min degradation, compared to undoped Aeroxide P25 alone. While there is some evidence to suggest that doping of TiO_2 increases photocatalytic efficiency, many of these materials are not tandardized. Therefore, it is difficult to conclude whether they are truly more efficient than Aeroxide P25 or other standardized undoped materials. In addition, it would be useful to understand the photocatalytic abilities of one standardized doped TiO_2 material on a range of pharmaceutical compounds and compare its photocatalytic efficiency with undoped TiO_2.

2.5. UV-C vs UV-A photodegradation of pharmaceuticals

The radiation source used to generate the (h^+-e^-) pairs in the TiO_2 photocatalysts may also affect photodegradation. Yang *et al*. (2009) [99] reported that TiO_2-assisted paracetamol degradation rates using UV-C were significantly faster than UV-A. Furthermore, the photodegradation of tetracycline [101] was reportedly faster using UV-B (>254 nm) and Solarium lamps, in contrast to blacklight (365 nm) assisted photodegradation. In addition, the power of the lamps used for irradiation processes may significantly affect removal of pharmaceutical compounds as observed with the photocatalytic degradation of the antibacterial tetracycline [103]. While the ability to generate (h^+-e^-) pairs is independent of the wavelength of radiation used if the radiation is higher-energy than the TiO_2 band gap, other processes, such as direct photolysis, may further increase the apparent degradation rates observed as with the UV-C induced TiO_2-assisted degradation of paracetamol [99] In contrast, no significant degradation was found for the drug when irradiated with UV-A alone, thus the observed degradation kinetics from the UV-A/TiO_2 process was solely derived from the TiO_2 photocatalysis of the pharmaceutical.

2.6. Effect of electron acceptors on the photocatalytic degradation of pharmaceuticals

The addition of electron acceptors to the photodegradation mixture significantly enhances photodegradation rates of substrates. As noted previously, oxygen saturation increases degradation rates. Paul *et al*. (2007) [95] observed a marked improvement in degradation of ciprofloxacin and other fluoroquinolones when bromate ion (BrO_3^-) was added as an electron acceptor. BrO_3^- - promoted degradation when used in conjunction with visible light irradiation, whereas the absence of BrO_3^- or molecular oxygen (anoxic conditions) prevented any significant photodegradation. Since the band gap energy of TiO_2 [57] does not permit the formation of electron-hole pairs using visible light, the authors suggest that the photocatalytic oxidation of fluoroquinolones is mediated by the transfer of electron(s) to the electron acceptor resulting in the formation of unstable radical fluoroquinolone species which are further oxidized. Furthermore, the addition of hydroxyl radical scavengers (such as methanol) and superoxide scavengers (such as superoxide dismutase) decreased the degradation rate of ciprofloxacin under UV but not visible light irradiation. Such results suggested that the visible light-induced photocatalysis of ciprofloxacin is not mediated by electron-hole pairs as there are no significant changes to the photodegradation rate as a result of $HO^{\cdot}$ or $O_2^{\cdot -}$ quenching.

Other systems utilized to increase photodegradation and mineralization rates have included the addition of ozone or hydrogen peroxide to the TiO_2 system [105] which may lead to the formation of additional hydroperoxyl or hydroxyl radicals, respectively, when irradiated by UV [89]. However, these experimental variations have led to variable results. Diclofenac mineralization (*i.e.*, the conversion of the pharmaceutical completely to inorganic compounds such as CO_2, H_2O and NH_3) was improved with the addition of ozone to the UV/TiO_2 system [105] and only 10% of the total organic carbon content (TOC) remained in the irradiated suspension compared with 30% TOC remaining in the absence of ozone. As TOC measures the concentration of parent pharmaceuticals and any intermediate photoproducts, the parameter is a good indicator of mineralization achieved by the photocatalytic process. Since the intermediate photoproducts formed *via* diclofenac photodegradation and photocatalysis are more

toxic than the parent pharmaceutical, adding ozone improves the efficiency and acceptability of the UV/TiO_2 system as a feasible wastewater treatment process. However, the addition of a high concentration of H_2O_2 (> 20 mmol L^{-1}) to a UV/TiO_2 photocatalytic fibre system inhibited the degradation of salicylic acid [89] while lower H_2O_2 concentrations promoted salicylic acid degradation. It was suggested in the study that H_2O_2 may also act as an electron acceptor for conduction band electrons and may compete with molecular oxygen for adsorption sites on the surface of the TiO_2 photocatalyst.

2.7. Degradation pathways for pharmaceuticals and ecotoxicity of photoproducts

The photodegradation pathways and extent of mineralization for TiO_2 - photocatalysed pharmaceuticals have been reported widely with some reports observing complete mineralization of pharmaceuticals [86,103,108]. Significant decreases in toxicity to the test organism has been observed for many studies after treatment with UV/TiO_2 [71,87,104]. Piecha *et al*. (2010) [87] observed that the photoproducts derived from UV/TiO_2 treatment of statin drugs were of significantly lower toxicity to Vibrio fischeri compared to the parent statins. In addition, the degradation of sulfa drugs was observed to produce a mixture of photoproducts with reduced toxicity [108] after 300 minutes irradiation.This is consistent with another study [109] which reported some toxicity even after treatment of sulfamethoxazole with UV/TiO_2 for 121 minutes. In contrast, UV/TiO_2 treatment of atenolol (TiO_2 loading = 150 mg L^{-1}) in aqueous suspension for 15-30 minutes resulted in a significant reduction in toxicity to Daphnia magna [71], and no antibacterial effects were observed after a 1 hr UV/TiO_2 treatment of an aqueous tetracycline suspension [101].

Many studies have evaluated the ecotoxicity from the photoproducts of non-steroidal anti-inflammatory drug (NSAIDs) during the photocatalytic process, particularly diclofenac and ibuprofen [70,73,78,102]. Previous experiments on the direct UV photolysis and the UV/H_2O_2 and photoFenton mediated degradation of diclofenac has shown that identified photoirradiation intermediates, including 8-chlorocarbazoleacetic acid, were more toxic than diclofenac [110], and indeed, some of these intermediates may also be formed by UV/TiO_2 systems. Calza *et al*. (2006) [106] observed that the toxicity of a 20-minute irradiated solution of diclofenac had a 72% growth inhibition of the luminescent bacterium Vibrio fischeri, whereas only 24% growth inhibition was observed with unirradiated suspensions. Several hydroxylated and chlorophenol derivatives, including 2,6-dichlorophenol and 4-chlorocatechol were identified in the study, along with the toxic compound hydroquinone. Rizzo *et al*. (2009) [78] reported that a 121-minute irradiation of diclofenac in aqueous solution lead to insignificant reductions in toxicity to Daphnia magna with a TiO_2 loading of 0.2 g L^{-1}. However, irradiated suspensions were less toxic than the unirradiated suspension when the TiO_2 concentration was increased to 0.4 g L^{-1} and 0.8 g L^{-1}. These results suggest that chloroderivative intermediates formed in the photodegradation pathway for diclofenac are clearly more toxic than diclofenac and an extended irradiation time (> 2 h) or an increase in TiO_2 concentration must be employed to ensure an efficient removal of diclofenac to form non-toxic and presumably mineralized products. Similar toxic intermediates were identified from the TiO_2-assisted photodegradation of ibuprofen [73]. However, again it is important to note that sewage effluent and environmental concentrations of ibuprofen are likely to be much lower than those used in these experiments, and thus, the behaviour of the UV/TiO_2 photocatalytic system to such lowered concentrations may vary from these experimental results.

The production of intermediates which are more toxic than the parent pharmaceutical have also been reported for the TiO_2 – assisted degradation of amiloride [112], the selective beta-2-adrenergic agonist salbutamol [107], the antiepileptic agent carbamazepine [78,93] and the antibacterial agent ofloxacin [71]. Unirradiated amiloride solutions were not shown to be toxic to Vibrio fischeri, but there was a 40% increase in toxicity to this organism after 4 h treatment with UV/TiO_2. Identified photoproducts after prolonged photocatalysis included small molecules such as guanidine which was resistant to UV/TiO_2 treatment and not fully mineralized to nitrogenous by-products until > 45 h photocatalysis [112]. It is possible that the toxicity of the irradiated amiloride was attributed to the formation of smaller, unknown molecules. Similarly a solution of salbutamol [107] that had been irradiated in the presence of TiO_2 for 15 minute was observed to be more toxic than the unirradiated suspension, and a decrease in toxicity to Vibrio fischeri was only observed after irradiating the salbutamol suspension for 60 minutes. A potentially mutagenic and carcinogenic compound, acridine, was elucidated in the UV/TiO_2 treatment of carbamazepine [93].

These findings clearly suggest that UV/TiO_2 processes successfully remove pharmaceuticals in aqueous suspension if an appropriate treatment timeframe is applied, and this parameter is especially important to consider when treating wastewater suspected of being rich in pharmaceuticals. The treatment timeframe should

ideally be derived from bioassays which can provide information on whether certain timeframes are adequate to prevent the production of toxic intermediates and ensure the complete removal of toxic intermediates [113].

3. Conclusions and future developments

The literature suggests that TiO_2 - assisted degradation systems may be potentially feasible wastewater treatment processes for the degradation of pharamceuticals, given that some studies have reported on the complete mineralization of particular pharmaceuticals. However, several questions need to be answered before such technique can be employed successfully in any wastewater treatment facility:

- What pharmaceuticals are expected to appear in the influent of a wastewater treatment facility? This question can be answered at least in part from a knowledge of the particular medications used and disposed by a population served by the particular wastwater treatment plant. Such information can be obtained from studies which identify and quantify the type and amount of particular pharmaceuticals, or modelled from prescription data relating to the population served by a wastewater treatment facility.

-What pharmaceutical concentrations are expected? The removal of pharmaceuticals at higher concentrations may benefit from increased TiO_2 loadings (for example, in the range of 1-2 g L^{-1}).

-What potential effects does the wastewater matrix have on photocatalysis? As noted in this review, natural organic matter may act as inner filters or adsorb / trap radical species and inhibit TiO_2 photocatalysis mechanisms, thereby leading to decreased degradation of pharmaceuticals in the wastewater compared to solutions involving pure water which are the most likely situation in the laboratory.

-What are the operating conditions of the plant (pH, type and intensity of UV-irradiation available)? Such operating conditions may drastically affect the photocatalytic rates or types of photoproducts produced.

In addition, much of the current literature concerning the photocatalytic degradation of pharmaceuticals use undoped TiO_2 materials such as Aeroxide P25. While it has been observed that the use of doped TiO_2 materials has enhanced the photodegradation of various organic contaminants such as dyes and pesticides, little is known about the photocatalytic behaviour of these materials in the degradation of pharmaceutical compounds. Patents concerning the characterisation and synthesis of doped materials are abundantly available; however, the photoactivity of these novel materials on pharmaceutical compounds is poorly defined. Also, while there are standardized methods on the preparation of doped TiO_2 photocatalytic materials, commercially-prepared doped materials are less available as research reagents. Furthermore, while theoretically feasible, there are limitations to undoped TiO_2 which may render it impractical for sewage treatment after treatment times and loadings for the optimal removal of a particular pharmaceutical is considered. As the band gap of undoped TiO_2 requires UV to create valence hole-electron pairs, the cost of installing UV lamps and the energy required to run these lamps in some sewage treatment facilities may render the technique economically unfeasible. The use of TiO_2 at concentrations of 1-2 g L^{-1} to achieve optimal effects in the removal of a particular pharmaceutical may also be cost-inhibitive. Therefore, in order to establish effective strategies in the removal of pharmaceuticals from sewage water, further research comparing the photocatalytic abilities of both doped and undoped materials on the photodegradation of pharmaceutical compounds should be carried out. Because of the unpredictable efficiency of doped TiO_2 materials, such research is neccessary to determine whether these doped materials are truly more viable as photocatalysts than undoped TiO_2 for the photocatalytic degradation of pharmaceuticals. The use of inexpensive materials for the synthesis of doped TiO_2 photocatalysts would increase the sewage treatment feasibility of these materials. Once studies are completed on the ability of these doped TiO_2 photocatalysts to remove pharmaceutical compounds from water, it would be of benefit to commercialize an effective doped photocatalyst for sewage treatment use.

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