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Light-driven photocatalysis as an effective tool for degradation of antibiotics

 Praveen P. Singh,^a Geetika Pandey,^b Yogesh Murti,^c Jagriti Gairola,^{de} Shriya Mahajan,^f Harsimrat Kandhari,^g Shraddha Tivari,^h and Vishal Srivastava^{id *h}

Antibiotic contamination has become a severe issue and a dangerous concern to the environment because of large release of antibiotic effluent into terrestrial and aquatic ecosystems. To try and solve these issues, a plethora of research on antibiotic withdrawal has been carried out. Recently photocatalysis has received tremendous attention due to its ability to remove antibiotics from aqueous solutions in a cost-effective and environmentally friendly manner with few drawbacks compared to traditional photocatalysts. Considerable attention has been focused on developing advanced visible light-driven photocatalysts in order to address these problems. This review provides an overview of recent developments in the field of photocatalytic degradation of antibiotics, including the doping of metals and non-metals into ultraviolet light-driven photocatalysts, the formation of new semiconductor photocatalysts, the advancement of heterojunction photocatalysts, and the building of surface plasmon resonance-enhanced photocatalytic systems.

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1. Introduction

Since antibiotics have the ability to affect humans and natural ecosystems, as well as to cause pathogenic bacteria to acquire antibiotic resistance at microconcentrations, the issue of water contamination *via* antibiotic residues is of concern globally.¹ Treatment for infectious diseases and agricultural productivity^{2–5} have significantly improved as a result of the widespread use of antibiotics. On the basis of pharmacological characteristics, antibiotics are mainly divided into aminoglycosides, sulfonamides (SAs), glycopeptides macrolides, β -lactams, quinolones and tetracyclines.⁶ Antibiotics are more difficult to remove because of their strong chemical stability. The parent structure of various antibiotics, classification and their characteristics have been summarized in Table 1.

Pharmaceutical antibiotics usually get poorly absorbed and metabolised by humans as well as animals. The release of polluted water, faeces, and urine from the aforementioned

contact spots along with an escalated concentration of antibiotic residues, poses possible risks to the ecosystem (Fig. 1).¹⁷ Consequently, the advancement of an affordable and efficient antibiotic decontamination technique is required. Until lately a variety of strategies, including photoelectric Fenton, biological elimination, photocatalytic degradation, membrane filtering, and adsorption, have been used to remediate antibiotic wastewater contaminants.^{18a–h} In the realm of environmental remediation, photocatalytic technology is widely employed to oxidise antibiotics into molecules that are easily biodegradable, less hazardous, and even harmless due to which it has received much concern from scientists.^{18i,j} As we continue our work on photocatalyzed organic synthesis,^{19,20} this article provides an overview of current developments in the state-of-the-art design and production of photocatalysts with visible light sensitivity for the photocatalytic degradation of wastewater containing antibiotics.

2. Methods for antibiotic degradation

There are now multiple techniques to remove antibiotic residues in water and wastewater before releasing them back into the environment. The primary approaches employed as of right now includes both long-standing methods and more contemporary ideas.^{21–24} Unfortunately, substantial mineralization is either extremely difficult to attain or would take excessively prolonged. Because of their poor selectivity, these techniques can have the unintended consequence of killing non-target creatures that leads to unintended damages.^{25,26} This approach also has significant operating and capital expenditures. When removing antibiotic residues from water,

^aDepartment of Chemistry, United College of Engineering & Research, Prayagraj, U.P.-211010, India. E-mail: ppsingh23@gmail.com

^bDepartment of Physics, Faculty of Science, United University, Prayagraj-211012, India

^cInstitute of Pharmaceutical Research, GLA University, Mathura-281406, India

^dSchool of Pharmacy, Graphic Era Hill University, Clement Town, Dehradun, 248002 Uttarakhand, India

^eDepartment of Allied Sciences, Graphic Era (Deemed to be University) Clement Town, Dehradun, 248002 Uttarakhand, India

^fCentre of Research Impact and Outcome, Chitkara University, Rajpura-140417, Punjab, India

^gChitkara Centre for Research and Development, Chitkara University, Himachal Pradesh-174103, India

^hDepartment of Chemistry, CMP Degree College, University of Allahabad, Prayagraj, U.P.-211002, India. E-mail: vishalgreenchem@gmail.com


Table 1 Classification and characteristics of antibiotics

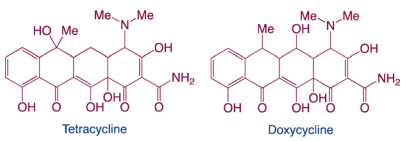
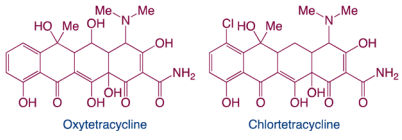
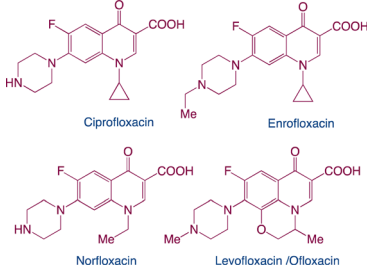
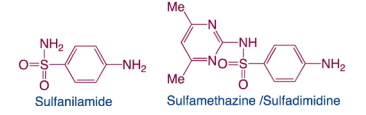
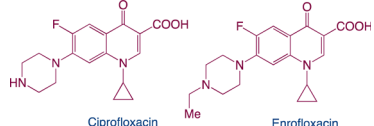
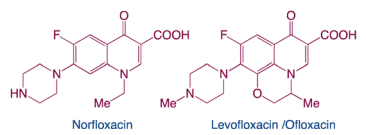
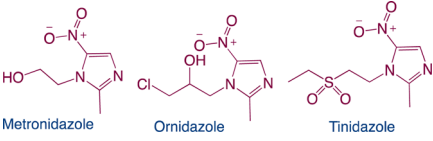
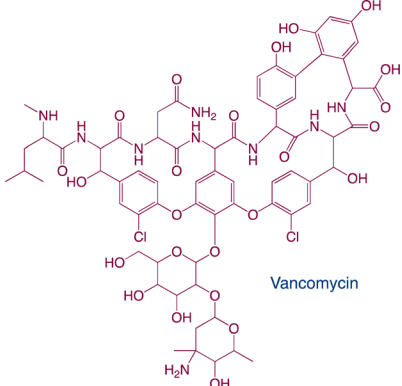
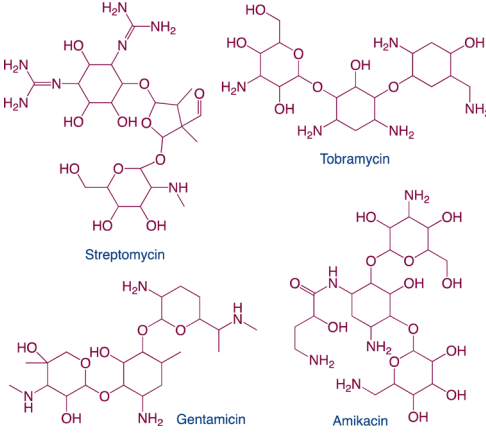

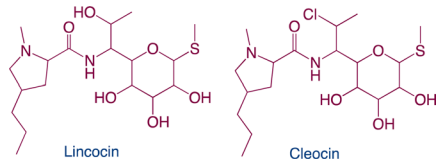
Antibiotic type	Representative	Function/hazard	Ref.
Tetracyclines	 <p>Tetracycline, Doxycycline, Oxytetracycline, Chlortetracycline</p>	<p>Function: tetracyclines prevent livestock illness and promote growth</p> <p>Hazard: result in significant persistence in the aquatic environment; increase the risk of certain infections, which may cause a negative effect on human; disturb the endocrine of aquatic species <i>etc.</i></p>	7
Sulfonamides	 <p>Sulfadiazine, Sulfamethoxazole, Sulfanilamide, Sulfamethazine/Sulfadimidine</p>	<p>Function: sulfonamides are used in human and veterinary medicine as antibacterial, especially in animal husbandry</p> <p>Hazard: the toxicity of sulfonamides is not high to vertebrates. However, it can alter the function of microorganisms living in the environment. Additionally, the toxic effects of sulfonamides and other pollutants could show a synergism</p>	8
Fluoroquinolones	 <p>Ciprofloxacin, Enrofloxacin, Norfloxacin, Levofloxacin/Ofloxacin</p>	<p>Function: fluoroquinolones can kill bacteria or inhibit bacterial growth. Their primary function is to block the replication of DNA by inhibiting the function of DNA helicase. For humans, fluoroquinolones are an essential antibiotic for the treatment of severe invasive infections such as anthrax or plague</p> <p>Hazard: promote resistance formation on microbial populations and induce toxic effects on aquatic organisms</p>	9
Macrolides	 <p>Tylosin, Erythromycin, Clarithromycin, Spiramycin, Azithromycin</p>	<p>Function: macrolides can inhibit bacterial protein synthesis and use to treat upper respiratory tract infections and soft-tissue infections</p> <p>Hazard: it may cause liver damage using for a long time and result in macrolide resistance</p>	10
β -lactams	 <p>Amoxicillin, Ampicillin, Cephalaxin, Ceftriaxone sodium, Cefotiofur sodium</p>	<p>Function: β-lactams are used to treat a variety of infections caused by susceptible bacteria, treat human genital tract infections, and serious infections. For animals, they can cure respiratory tract infections and intramammary disturbs</p> <p>Hazard: it may cause an allergic reaction in sensitive person and influent plastid division in lower plants</p>	11
Nitroimidazoles	 <p>Cefotiofur sodium, Ceftriaxone sodium</p>	<p>Function: nitroimidazoles have antiprotozoal and antibacterial activities as well as strong anti-anaerobic effects</p> <p>Hazard: potential nephrotoxicity, carcinogenesis, and neurotoxicity in human</p>	12



Table 1 (Contd.)

Antibiotic type	Representative	Function/hazard	Ref.
	 <p>Metronidazole Ornidazole Tinidazole</p>		
Glycopeptides	 <p>Vancomycin</p>	<p>Function: glycopeptides are commonly used to treat infections caused by streptococcus or enterococcus Hazard: ototoxicity, nephrotoxicity, allergic reactions <i>etc.</i></p>	13
Aminoglycosides	 <p>Streptomycin Tobramycin Gentamicin Amikacin</p>	<p>Function: aminoglycosides can promote the growth of animals Hazard: high toxicity and nephrotoxicity in human</p>	14
Chloramphenicol	 <p>Chloramphenicol</p>	<p>Function: chloramphenicol is used for several infectious diseases such as flu bacillus infection Hazard: may cause aplastic anemia and agranulocytosis</p>	15
Lincomycin	 <p>Lincocin Cleocin</p>	<p>Function: lincomycin is applied in food animals for the therapy of dysentery porcine proliferative enteropathies in pig <i>etc.</i> Hazard: allergic reactions <i>etc.</i></p>	16

a combination of chemical and physical degradation methods can greatly lower the toxicity of treated effluents. However, these techniques are expensive and complicated.²⁷

Conversely, having a distinct advantages of photocatalysis, makes it a viable option for environmental remediation because of its (1) easily attainable reaction conditions (*i.e.*, almost ambient temperature and pressure), its ability to use air oxygen as a potent oxidant, and its ability to use solar radiation as an energy source; (2) the potential complete breakdown of organic

pollutants into harmless inorganic molecules like carbon dioxide and water; and (3) its strong redox ability, low cost, lack of adsorption saturation, and long durability. As a result, photocatalysis has attracted attention from all around the world and been widely used in innovative methods of energy extraction and environmental control. Several methods^{28–47} for antibiotic degradation have been reported incorporating materials, operating conditions and disadvantages of antibiotics.



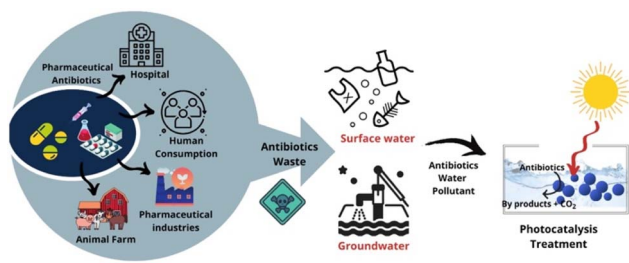


Fig. 1 Schematic representation of antibiotics consumption routes and impact on water bodies along with proposal of treating the same with solar energy-driven photocatalysis technique. Reproduced with permission from ref. 17. Copyright 2021 Elsevier Publishers.

3. General mechanism of photocatalytic antibiotics degradation

Techniques have been developed to treat contaminated water and waste water with organic pollutants. Fig. 2 depicts the mechanism of the photocatalytic degradation. An equivalent number of positively charged holes are produced in the valence band (VB) of a semiconductor when it is subjected to radiation with energy greater than its optical band gap. This is caused by excited electrons that are moved from the VB to the CB. When the potential of VB vs. NHE is more positive than H₂O/OH[•] (+2.72 V vs. NHE) or OH⁻/OH[•] (+1.89 V vs. NHE) and the potential of CB vs. NHE is more negative than O₂/[•]O₂⁻ (-0.33 V vs. NHE), the semiconductor will be able to generate OH[•] and [•]O₂⁻. After that, the photoinduced electrons and holes separate out and go to the semiconductor's surface, where redox reactions take place at the reactive site (Fig. 2).^{21,48} The reaction mechanisms of semiconductor photocatalysis are typically expressed by the following equations:⁴⁹

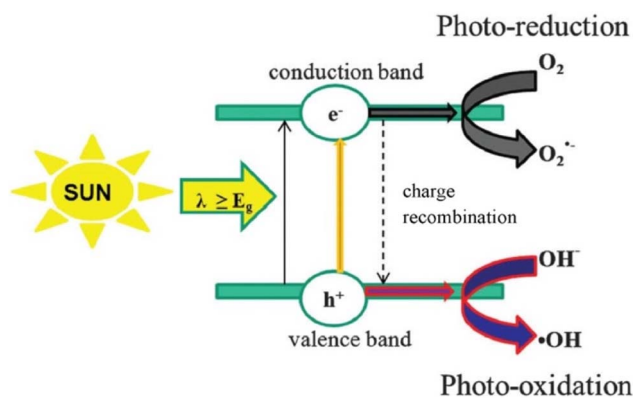
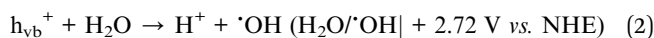
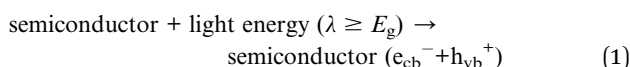


Fig. 2 General mechanism of the semiconductor photocatalytic degradation of organic pollutants. Reproduced with permission from ref. 21. Copyright 2020 Elsevier B.V. All rights reserved.



By these chemical processes solar energy can be directly converted and utilized. The consequences of photocatalytic activity are, however, lessened by restricted optical usage and the rapid annihilation of photoexcited electron-hole pairs. If photocatalysts satisfy the following requirements, they can overcome these deficiencies: (1) suitable spectral absorption range; (2) appropriate band energy structure for sufficient electron-hole pair separation and transport; and (3) sufficient active sites for adsorption or reaction.⁵⁰ To increase photocatalytic efficiency, it is imperative to meet the three previously mentioned requirements. Several attempts have been made to methodically design photocatalysts and enhance photocatalytic dynamics.

An acceptor is reduced by this excited electron, and donor molecules are oxidised by the acceptor's hole. The redox levels of the substrate⁵¹⁻⁶⁴ and the respective locations of the semiconductor's valence and conduction bands determine what happens to the excited electron and hole.

While considering photoabsorption capability and photocatalytic efficiency, optical bandgap (E_g) plays a crucial role in predicting the applicability and efficacy of a particular type of photocatalytic material. Polyfluorene co-polymers acting as photocatalysts^{65,66} are classified as photonic and electrochemical bandgaps by Ghaedi *et al.*, who also proposed a method and criterion for bandgap measurement. Furthermore, they came to the conclusion that by keeping charges from recombining, the active holes' lifetime would increase and their ability to degrade antibiotics would be improved. This approach to the interfacial charge transfer from a distinct energy surface to a molecular continuous surface from solids^{65,66} turned out to be highly effective in increasing the activity of photocatalysts under visible light.

Overall, the process of photocatalysis for the degradation of antibiotics can be broken down into five primary steps: (1) the antibiotics are transferred from the fluid phase to the surface; (2) they are adsorbed; (3) a reaction occurs in the adsorbed phase; (4) the products are desorption; and (5) the products are removed from the interface region.^{67,68} However, when the electrons that had been excited to CB quickly recombine with the separated holes in the VB before producing free radicals, photocatalytic degradation suffers from the issue of electron-hole recombination in the photocatalyst.⁶⁸ Adoption of particular photocatalysts with a low CB-VB bandgap energy and photocatalyst modifications are proposed as solutions for these issues, however this depends on numerous variable alternatives, such as tailored experimental conditions.^{69,70}

4. Synthesis techniques of nanostructured photocatalysts

Several synthesis techniques have been used as summarised in Fig. 3. It is noteworthy that the following characteristics are essential for an efficient photocatalyst: (a) robust absorption of visible and UV light (*i.e.*, a suitable bandgap value, typically less



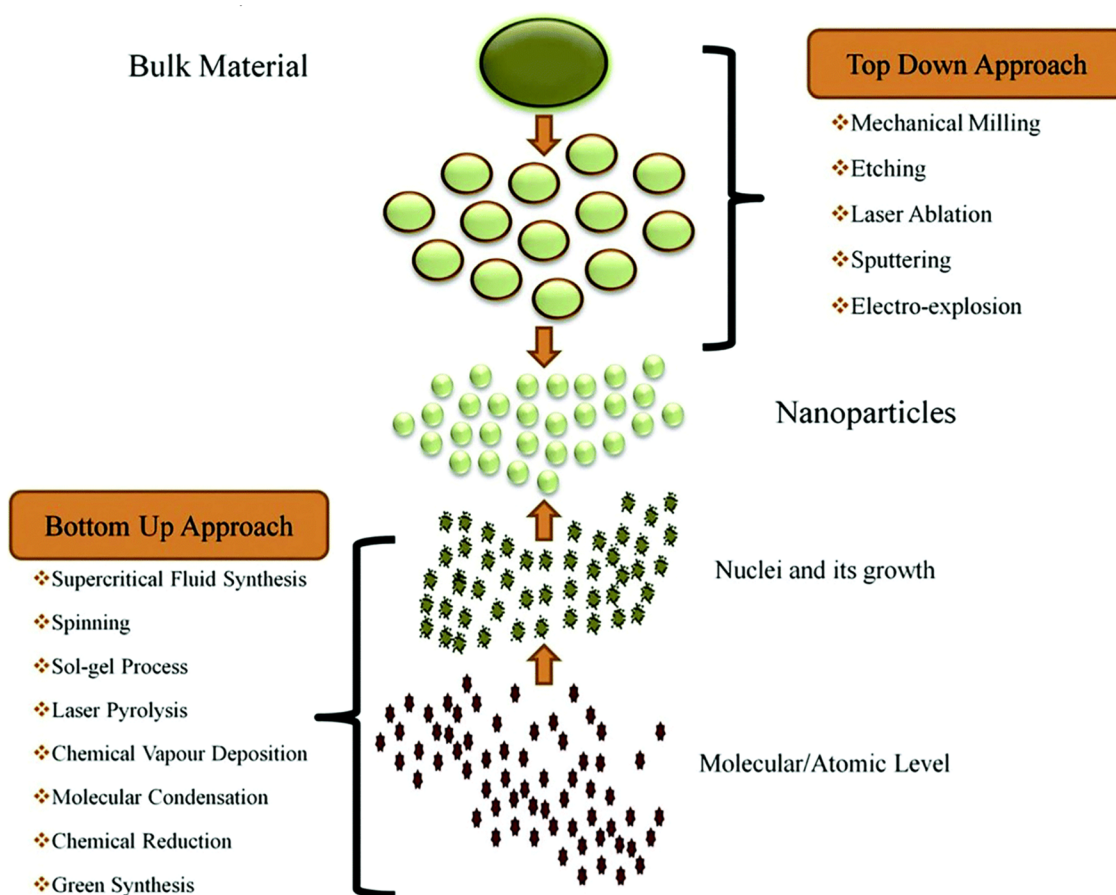


Fig. 3 Synthesis techniques of nanostructured photocatalysts. Reproduced with permission from ref. 75a. Copyright ©2019 Elsevier B.V. All rights reserved.

than 3.0 eV); (b) stability against photocorrosion in terms of temperature, chemical composition, and mechanical properties; (c) high efficiency in quantum conversion; (d) rapid generation and efficient transfer of photocarriers (e^- and h^+); and (e) slow recombination rate of photogenerated charge

carriers. Additionally, the nanopowder photocatalysts must be able to rapidly and easily recover from the solution while maintaining a sufficient level of reusability, or without noticeably losing effectiveness. To achieve the listed attributes, many tactics are now employed, such as tuning of particle

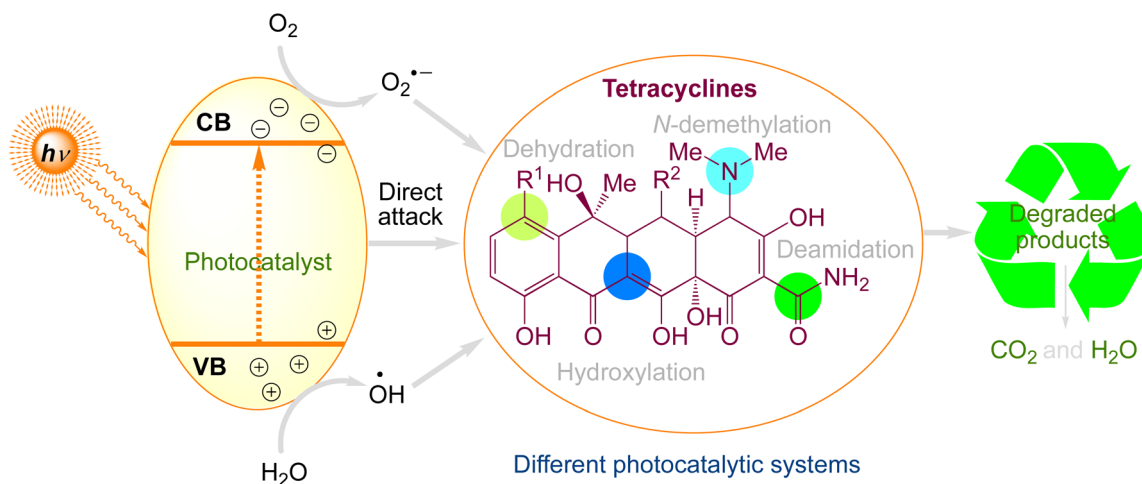


Fig. 4 The proposed photocatalytic degradation pathways of tetracyclines.



Table 2 Photocatalytic degradation of tetracyclines at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Tetracycline	C dots modified MoO ₃ /g-C ₃ N ₄	Visible light	20 mg L ⁻¹	0.6 g L ⁻¹	88.4% (90 min)	88
Tetracycline	g-C ₃ N ₄ /Hydroxyapatite	Simulated sunlight	50 mg L ⁻¹	1 g L ⁻¹	Almost 100% (15 min)	89
Tetracycline	β-Bi ₂ O ₃ /g-C ₃ N ₄ core/shell nanocomposites	Visible light	10 mg L ⁻¹	0.5 g L ⁻¹	80.2% (50 min)	90
Tetracycline	rGO/g-C ₃ N ₄ /BiVO ₄	Visible light	35 mg L ⁻¹	1 g L ⁻¹	72.5% (150 min)	91
Tetracycline	C-doped C ₃ N ₄ /Bi ₁₂ O ₁₇ Cl ₂	Visible light	20 mg L ⁻¹	1 g L ⁻¹	94.0% (60 min)	92
Tetracycline	CeVO ₄ /3D rGO aerogel/BiVO ₄	Visible light	20 mg L ⁻¹	0.5 g L ⁻¹	100% (60 min)	93
Tetracycline	NGQDs-BiOI/MnNb ₂ O ₆	Visible light	10 mg L ⁻¹	0.5 g L ⁻¹	87.2% (60 min)	94
Tetracycline	TiO ₂ /g-C ₃ N ₄	Simulated sunlight	20 mg L ⁻¹	1 g L ⁻¹	100% (9 min)	95
Tetracycline	Amorphous TiO ₂ /mesoporous-rutile TiO ₂	UV light	50 mg L ⁻¹	0.5 g L ⁻¹	81.1% (300 min)	96
Tetracycline	Magnetic Fe ₂ O ₃ ultrathin nanosheets/mesoporous black TiO ₂	Simulated sunlight	10 mg L ⁻¹	0.3 g L ⁻¹	99.3% (50 min)	97
Tetracycline	Bi ₅ FeTi ₃ O ₁₅	Visible light	5.0 mg L ⁻¹	0.4 g L ⁻¹	99.4% (60 min)	98
Tetracycline	Bi ₂ WO ₆ /CuBi ₂ O ₄	Visible light	15 mg L ⁻¹	0.5 g L ⁻¹	91.0% (60 min)	99
Tetracycline	AgI/BiVO ₄	Visible light	20 mg L ⁻¹	3 g L ⁻¹	94.9% (60 min)	100
Tetracycline	AgI/WO ₃	Visible light	35 mg L ⁻¹	3 g L ⁻¹	75.0% (60 min)	101
Tetracycline	Ag ₃ VO ₄ /WO ₃	Visible light	10 mg L ⁻¹	0.5 g L ⁻¹	71.2% (30 min)	102
Tetracycline	Ag ₃ PO ₄ /Zn-Al LDH	Simulated sunlight	40 mg L ⁻¹	1 g L ⁻¹	96% (90 min)	103
Tetracycline	FeNi ₃ /SiO ₂ /CuS	UV light	10 mg L ⁻¹	5 g L ⁻¹	96.7% (90 min)	104
Tetracycline	Fe-based MOFs	Visible light	50 mg L ⁻¹	0.5 g L ⁻¹	96.6% (180 min)	105
Tetracycline	Pb/MoO ₄	Simulated sunlight	20 mg L ⁻¹	1 g L ⁻¹	99.0% (120 min)	106
Tetracycline	Modified red mud	Visible light	10 mg L ⁻¹		88.4% (80 min)	107
Tetracycline	SnO ₂ /g-C ₃ N ₄	Visible light	30 mg L ⁻¹	3 g L ⁻¹	95.9% (120 min)	108
Tetracycline	RGO-CdTe	Visible light	30 mg L ⁻¹	3 g L ⁻¹	83.6% (45 min)	109
Tetracycline	Cu ₂ O-TiO ₂	Visible light	100 mg L ⁻¹	1.5 g L ⁻¹	100% (60 min)	110
Tetracycline	Bi ₂ Sn ₂ O ₇ /β-Bi ₂ O ₃	Visible light	40 mg L ⁻¹	2 g L ⁻¹	95.5% (60 min)	111
Tetracycline	MoS ₂ /TiO ₂	Visible light	10 mg L ⁻¹	0.1 g L ⁻¹	95.0% (100 min)	112
Tetracycline	Bi ₂ Sn ₂ O ₇ /Bi ₂ MoO ₆	Visible light	35 mg L ⁻¹	0.02 g L ⁻¹	98.7% (100 min)	113
Tetracycline	Ti ₃ C ₂ @TiO ₂	Visible light	20 mg L ⁻¹		90.0% (90 min)	114
Tetracycline	NiCo-S@CN	Solar light	100 mg L ⁻¹	2 g L ⁻¹	99.0% (60 min)	115a
Tetracycline	Bi ₂ Sn ₂ O ₇ /Bi ₂ MoO ₆	Visible light	20 mg L ⁻¹	0.035 g L ⁻¹	98.7% (100 min)	115b
Tetracycline	Bi ₂ WO ₆ /Ta ₃ N ₅	Visible light	20 mg L ⁻¹	0.04 g L ⁻¹	86.7% (120 min)	115c
Tetracycline	Ag/Ag ₂ S/Bi ₂ MoO ₆	Visible light	20 mg L ⁻¹	0.03 g L ⁻¹	87.3% (120 min)	115d
Oxytetracycline	Au-CuS-TiO ₂ nanobelts	Simulated sunlight	5.0 mg L ⁻¹	0.114 cm ² ml ⁻¹	96.0% (60 min)	116
Oxytetracycline	N-TiO ₂ /graphene	UV light	30 mg L ⁻¹		63.0% (160 min)	117
Oxytetracycline	Ag ₃ PO ₄ /TiO ₂ /MoS ₂	Visible light	5 mg L ⁻¹	0.5 g L ⁻¹	90.0%	118
Oxytetracycline	Ti-MCM-41	UV light	50 mg L ⁻¹	1 g L ⁻¹	92.0% (180 min)	119
Oxytetracycline	g-C ₃ N ₄	Visible light	20 mg L ⁻¹	0.3 g L ⁻¹	79.3% (60 min)	120
Oxytetracycline	Fe _{2.8} Ce _{0.2} O ₄ /GO	Visible light	30 mg L ⁻¹	0.8 g L ⁻¹	82.0% (120 min)	121
Oxytetracycline	Rhombohedral corundum-type In ₂ O ₃	UV light	10 mg L ⁻¹	1 g L ⁻¹	89.5% (120 min)	122
Oxytetracycline	SnO ₂ /BiOI	Visible light	10 mg L ⁻¹	1 g L ⁻¹	94.6% (90 min)	123
Oxytetracycline	MU-0.15	Simulated sunlight	20 mg L ⁻¹	0.5 g L ⁻¹	86.6% (120 min)	124
Oxytetracycline	CoFe@NSC-1000	Visible light	50 mg L ⁻¹	0.3 g L ⁻¹	82.7% (150 min)	125
Oxytetracycline	Fe ₃ O ₄ /rGO/Co-doped ZnO/g-C ₃ N ₄	Visible light	30 mg L ⁻¹	0.16 g L ⁻¹	82.0% (70 min)	126
Oxytetracycline	BiOI/NH ₂ -MIL125(Ti)	Visible light	10 mg L ⁻¹	0.5 g L ⁻¹	96.2% (60 min)	127
Oxytetracycline	MnFe ₂ O ₄ /g-C ₃ N ₄	Visible light	10 mg L ⁻¹		80.5% (10 min)	128
Oxytetracycline	MIL-100(Fe)	Visible light	25 mg L ⁻¹	0.05 g L ⁻¹	99.0% (240 min)	129
Oxytetracycline	Ag/BiVO ₄ /GO	Visible light	40 mg L ⁻¹	0.4 g L ⁻¹	90.43% (70 min)	130
Oxytetracycline	TiO ₂	Visible light	10 mg L ⁻¹	0.5 g L ⁻¹	95.0% (180 min)	131
Oxytetracycline	MnFe ₂ O ₄ /g-C ₃ N ₄	Visible light	10 mg L ⁻¹		90.0% (1 min)	132
Doxycline	SnO ₂ /BiOI	Visible light	10 mg L ⁻¹	1 g L ⁻¹	90.0% (60 min)	133
Doxycline	Ag/AgCl/CdMoO ₄	UV light	10 mg L ⁻¹		82.4% (60 min)	134
Doxycline	α-Bi ₂ O ₃ /g-C ₃ N ₄ + H ₂ O ₂	Visible light	25 mg L ⁻¹	0.01 g L ⁻¹	79.0% (30 min)	135
Doxycline	TiO ₂ -MCM-41	UV light	10 mg L ⁻¹	0.15 g L ⁻¹	85.0% (60 min)	136
Doxycline	In ₂ O ₃ /g-C ₃ N ₄	Visible light	10 mg L ⁻¹		99.3% (60 min)	137



Table 2 (Contd.)

Target antibiotic	Photocatalyst	Source of light	Optimum conditions		Degradation (%)	Ref.
			Initial concentration	Catalyst concentration		
Doxycycline	Cu ₂ O/SrBi ₄ Ti ₄ O ₁₅	Simulated sunlight				
Chlorotetracycline	N-TiO ₂ /graphene	Visible light	40 mg L ⁻¹		92.2% (60 min)	138
Chlorotetracycline	Bi ₂ O ₃ /MIL101(Fe)	UV light	30 mg L ⁻¹		54.0% (160 min)	139
		Visible light	20 mg L ⁻¹	0.3 g L ⁻¹	88.2% (120 min)	140

dimensions, morphology, and size. Moreover, different photocatalyst compositions result in heterojunctions, composites, core-shell structures, element substitutions, intercalation compounds, and plasmon sensitization.^{51,71-75}

5. Photocatalytic degradation of different antibiotics

5.1. Photocatalytic degradation of tetracyclines

Tetracycline is a broad-spectrum antibiotic that is commonly used to treat a wide range of illnesses. Because of its high efficacy and low cost, it is regarded as the second most frequently used antibiotic in human activities and livestock breeding.⁷⁵⁻⁷⁸ On the other hand, prolonged and excessive TC usage pollutes the environment and is a major social concern.⁷⁹ Tetracycline has been removed using a variety of methods, such as adsorption,⁸⁰ ion exchange,⁸¹ membrane filtering,⁸² biological processes,⁸³ electrolysis,⁸⁴ ozonation,⁸⁵ advanced oxidation processes,⁸⁶ and photocatalysis.⁸⁷ The most efficient, affordable, simple to implement, and environmentally benign of these processes are thought to be the photocatalysis and advanced oxidation processes. Generating charges such as holes, hydroxyl radicals, electrons, and superoxide anion radicals efficiently is

essential to the photocatalysis process. Again, the exciton creation and its subsequent dissociation into photo-induced electrons and holes are prerequisites for the production of hydroxyl radical and superoxide anion radical.

Tetracyclines are generally used worldwide. They have four linked rings with several ionizable functional groups. The most widely used tetracyclines are oxytetracycline, tetracycline, and chlortetracycline. The degradation mechanisms of tetracyclines are more intricate because of their complex molecular structure.⁷⁷ Tetracycline degradation processes under various photocatalytic systems are summarised in Fig. 4. Tetracyclines are commonly degraded *via* four different processes: hydroxylation, deamidation, *N*-demethylation, and dehydration. Table 2 comprises a summary of the information regarding the photocatalytic degradation of tetracyclines using various photocatalysts.

5.2. Photocatalytic degradation of sulfonamides

Sulfonamides are a class of synthetic pharmaceuticals that emerged in 1906 and contain the sulfonamide chemical group. Since 1940, more than 150 of these agents have been utilised as antimicrobials, making them the most commonly used antibiotics in the field of medicine with good hydrophilicity.^{141,142}

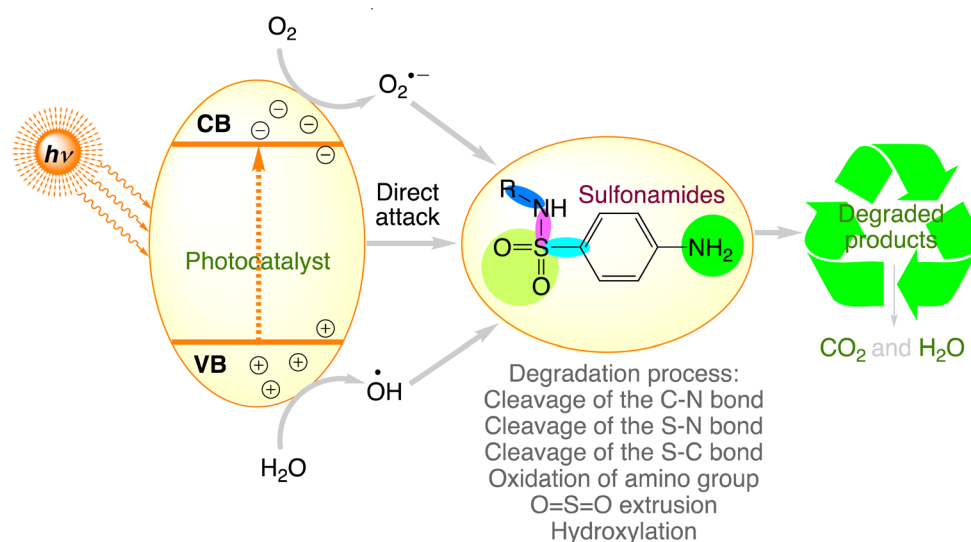


Fig. 5 The proposed photocatalytic degradation pathways of sulfonamides.



Table 3 Photocatalytic degradation of sulfonamides at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Sulfamethoxazole	Doped metals (Na, K, Ca, Mg) on g-C ₃ N ₄	Visible light	5.0 mg L ⁻¹	0.05 g L ⁻¹	g-CN-K > g-CN-Na > g-CN-Mg > g-CN-Ca > g-CN	144
Sulfamethoxazole	Ag-P co-doped-g-C ₃ N ₄	Visible light	5.0 mg L ⁻¹	1.0 g L ⁻¹	99% (30 min)	145
Sulfamethoxazole	Ag/P-g-C ₃ N ₄	Visible light	0.1 mg L ⁻¹	0.1 g L ⁻¹	100% (20 min)	146
Sulfamethoxazole	Ag/g-C ₃ N ₄ /Bi ₃ TaO ₇	Visible light	5.0 mg L ⁻¹	0.5 g L ⁻¹	98% (25 min)	147
Sulfamethoxazole	rGO/WO ₃	Visible light	10.0 mg L ⁻¹	2.0 g L ⁻¹	98.0% (180 min)	148
Sulfamethoxazole	Ag ₃ PO ₄ /N-doped rGO	Visible light	20.0 mg L ⁻¹	0.2 g L ⁻¹	93.8% (60 min)	149
Sulfamethoxazole	TiO ₂ -rGO	Simulated sunlight	0.10 mg L ⁻¹	0.1 g L ⁻¹	87.0 ± 4% (60 min)	150
Sulfamethoxazole	TiO ₂ supported on reed straw biochar	UV light	10.0 mg L ⁻¹	1.25 g L ⁻¹	91.3% (180 min)	151
Sulfamethoxazole	W Modified TiO ₂	Simulated sunlight	1.0 mg L ⁻¹	0.25 g L ⁻¹	100% (90 min)	152
Sulfamethoxazole	F-Pd co-doped-TiO ₂	Simulated sunlight	30.0 mg L ⁻¹	1.0 g L ⁻¹	94.2% (20 min)	153
Sulfamethoxazole	p(HEA/NMMA)-CuS	UV light	50.0 mg L ⁻¹	2.0 g L ⁻¹	95.9% (24 h)	154
Sulfamethoxazole	ZnO/fluoride ions	UV light	250.0 mg L ⁻¹	1.5 g L ⁻¹	97.0% (30 min)	155
Sulfamethoxazole	Mn-WO ₃	LED light	3.25 mg L ⁻¹	2.3 g L ⁻¹	100% (70 min)	156
Sulfamethoxazole	Co-CuS@TiO ₂	Solar light	5.0 mg L ⁻¹	1.0 g L ⁻¹	100% (120 min)	157
Sulfamethoxazole	ZnO/ZnIn ₂ S ₄	Visible light	2.5 mg L ⁻¹	0.20 g L ⁻¹	74.9% (6.5 h)	158
Sulfamethoxazole	TiO ₂ -based materials	Sunlight or LED	10.0 mg L ⁻¹		90.0% (30 min)	159
Sulfamethoxazole	TiO ₂ /BC	UV light	30.0 mg L ⁻¹	0.02 g L ⁻¹	89.0% (60 min)	160
Sulfamethoxazole	PAN-TiO ₂ and PAN-rGTi	Solar light	5.0 mg L ⁻¹		100% (120 min)	161
Sulfamethoxazole	Fe ₂ O ₃ /g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	0.3 g L ⁻¹	99.2% (30 min)	162
Sulfamethoxazole	P-TiO ₂ /g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	0.7 g L ⁻¹	99.0% (90 min)	163
Sulfamethoxazole	TiO ₂ @Fe ₂ O ₃ @g-C ₃ N ₄ (MFTC)	Solar light	10.0 mg L ⁻¹	0.5 g L ⁻¹	96.8% (120 min)	164
Sulfamethoxazole	Pd-BiVO ₄	Visible light	10 mg L ⁻¹		98.8% (210 min)	165
Sulfamethoxazole	CoP/BVO	Simulated sunlight	500 mg L ⁻¹	1.0 g L ⁻¹	89.0% (180 min)	166
Sulfamethoxazole	MoS ₂ @CoS ₂	Visible light	20.0 mg L ⁻¹		95.0% (80 min)	167
Sulfamethoxazole	ZrFe ₂ O ₄ @ZIF-8	Visible light	5.0 mg L ⁻¹	0.02 g L ⁻¹	100% (180 min)	168
Sulfamethoxazole	CN/N ₂ PG-0.02	Simulated sunlight	10 mg L ⁻¹		90.0% (120 min)	169
Sulfamethoxazole	g-C ₃ N ₄ /GSBC	Visible light	10.0 mg L ⁻¹		87.2% (90 min)	170
Sulfamethoxazole	Pt/PtO _x /BiVO ₄	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	99.0% (150 min)	171
Sulfamethoxazole	Fe-Co/γ-Al ₂ O ₃	UV light	10 mg L ⁻¹	1.0 g L ⁻¹	98.0% (60 min)	172
Sulfamethoxazole	Sulfur-doped-Bi ₂ O ₃ /MnO ₂ (S-BOMO)	Visible light	5.0 mg L ⁻¹	0.5 g L ⁻¹	86.0% (240 min)	173
Sulfamethoxazole	Ag ₃ PO ₄	UV light	20.0 mg L ⁻¹		99.9% (60 min)	174
Sulfamethoxazole	Cd doped γ-Bi ₂ MoO ₆ (Cd-BMO)	Visible light	5.0 mg L ⁻¹	0.05 g L ⁻¹	97.9% (210 min)	175
Sulfamethoxazole	AgNbO ₃	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	98.0% (8 h)	176
Sulfamethoxazole	Fc@rGO-ZnO	UV light	10 mg L ⁻¹		95.0% (180 min)	177
Sulfamethoxazole	CoFe ₂ O ₄ /PMS	UV light	10 mg L ⁻¹	0.1 g L ⁻¹ /0.4 g L ⁻¹	91.0% (10 min)	178
Sulfamethazine	g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	95.0% (24 h)	179
Sulfamethazine	g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	97.0% (60 min)	180
Sulfamethazine	g-C ₃ N ₄	Visible light	30.0 mg L ⁻¹	0.5 g L ⁻¹	99.7% (60 min)	181
Sulfamethazine	C Doping g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	98.0% (60 min)	182
Sulfamethazine	2D/1D g-C ₃ N ₄ /TNTs	Visible light	5.0 mg L ⁻¹	0.2 g L ⁻¹	100% (5 h)	183
Sulfamethazine	TiO ₂	UV light	20.0 mg L ⁻¹	0.5 g L ⁻¹	61.0% (120 min)	184
Sulfamethazine	AgI/Bi ₄ V ₂ O ₁₁	Visible light	10.0 mg L ⁻¹	0.1 g L ⁻¹	91.5% (60 min)	185
Sulfamethazine	Bi ₂ WO ₆ /RGO	Simulated sunlight	10.0 mg L ⁻¹		57.6% (8 h)	186
Sulfamethazine	Graphene aerogel/Bi ₂ WO ₆	Simulated sunlight	10.0 mg L ⁻¹		55.8% (120 min)	187
Sulfamethazine	W ₁₀ O ₃₂ ⁴⁻	Visible light	13.9 mg L ⁻¹	0.33 g L ⁻¹	85.0% (4 h)	188
Sulfamethazine	g-C ₃ N ₄ /Cu, N-TiO ₂	Visible light	10 mg L ⁻¹		95.8% (240 min)	189



Table 3 (Contd.)

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Sulfamethazine	Cu-Cu _x O/TiO ₂	Simulated sunlight	10 mg L ⁻¹		98.2% (60 min)	190
Sulfamethazine	PhC ₂ Cu/Ag/Ag ₂ MoO ₄ (PAM)	Visible light	10.0 mg L ⁻¹	0.4 g L ⁻¹	97.7% (20 min)	191
Sulfamethazine	G-CDs	Simulated sunlight	10.0 mg L ⁻¹		94.0% (75 min)	192
Sulfanilamide	WO ₃ /Ag	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	96.2% (5 h)	193
Sulfanilamide	Ag/ZnFe ₂ O ₄ /Ag/BiTa _{1-x} V _x O ₄	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	100% (6 h)	194
Sulfanilamide	Mo-BiOBr	Visible light	10.0 mg L ⁻¹	0.3 g L ⁻¹	48.3% (80 min)	195
Sulfadiazine	BiOCl-Au-CdS	Simulated sunlight	20.0 mg L ⁻¹	1.0 g L ⁻¹	100% (240 min)	196
Sulfadiazine	Cu ₂ O/Bi/Bi ₂ MoO ₆	Visible light	10.0 mg L ⁻¹		98.6% (100 min)	197
Sulfadiazine	Porous g-C ₃ N ₄ with C vacancies	Visible light	5.0 mg L ⁻¹	0.02 g L ⁻¹	100% (20 min)	198
Sulfadiazine	NSFe-TiO ₂	UV light	20.0 mg L ⁻¹	0.01 g L ⁻¹	90.0% (120 min)	199
Sulfadiazine	Bi ₂ O ₃ -TiO ₂ /PAC	Visible light	20.0 mg L ⁻¹	0.2 g L ⁻¹	72.0% (30 min)	200
Sulfadiazine	TiO ₂ /ZEO	UV light	10.0 mg L ⁻¹	1.0 g L ⁻¹	90.0% (120 min)	201
Sulfadiazine	Degussa P25 TiO ₂	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	99.0% (60 min)	202
Sulfadiazine	C, N-TiO ₂ @C	Visible light	20.0 mg L ⁻¹	1.0 g L ⁻¹	99.3% (140 min)	203
Sulfadiazine	BC-TiO ₂ -MagEx	Visible light	5.0 mg L ⁻¹	1.0 g L ⁻¹	76.0% (240 min)	204
Sulfadiazine	ZIF-67/Ag NPs/NaYF ₄ : Yb,Er	Simulated sunlight	10 mg L ⁻¹		95.4% (180 min)	205

Among these, sulfanilamide, sulfadiazine, sulfamethazine/sulfadimidine, and sulfamethoxazole are frequently used. These contaminants alter the biological population, which could have an adverse effect on human health. Numerous studies indicate that the paths and capabilities of sulfonamide degradation are connected to their substituents.¹⁴³ Fig. 5 concludes the sulfonamide degradation routes in different photocatalytic systems. Sulfonamides would degrade primarily due to sulfonamide cleavage of the S-N and C-N bonds, amino group oxidation, hydroxylation, and cleavage of the S-C bond between the sulphur and benzene ring by attacking radicals, which would progressively produce the corresponding byproducts.⁷⁷ Table 3 provides an overview of the results of the efficient degradation of sulphonamides using semiconductor photocatalytic technology.

5.3. Photocatalytic degradation of fluoroquinolones

Since the late 1980s, fluoroquinolones have been used as medications for humans and animals to prevent bacterial infections.²⁰⁶ Fluoroquinolones are found in the environment in significant amounts due to animal waste from farms, human waste from residential areas and hospitals, and fertiliser dispersal in agriculture. Generally, fluoroquinolones are prepared primarily by adding fluorine and piperazine groups to form the quinolones core structure²⁰⁷ in which ciprofloxacin, norfloxacin, levofloxacin/ofloxacin, enrofloxacin are the common used fluoroquinolones.^{208,209} Since their longer half-

life (10.6 days in surface water and 580 days in sediments), more than 70% fluoroquinolones are discharged unmetabolized.²¹⁰ Moreover, due to their chemical stability, these fluoroquinolones are hard to be degraded thoroughly in the environment, which have potential harm to the ecological environment.²⁰⁹

Recent studies have demonstrated the development of highly effective photocatalytic devices for fluoroquinolone degradation. Table 4 displays the outcomes. The fluoroquinolone contaminants are discovered to be efficiently destroyed in the presence of light by employing photocatalysts. The chemical structures of fluoroquinolones and the conditions under which photocatalytic processes occur can be responsible for significant modification in the degradation capacity of fluoroquinolones by various photocatalytic processes.⁷⁷ Fig. 6, comprises the fluoroquinolone degradation pathways under various photocatalytic processes.

5.4. Photocatalytic degradation of macrolides

Macrolides are monocyclic lactones with a high substitution rate having potency to prevent the synthesis of proteins.²⁹¹ They belong to the class of large-ringed natural lactones, which typically have 12, 14, or 16 members. Examples of these lactones are tylosin, erythromycin, spiramycin, oleandomycin, clarithromycin, and azithromycin.²⁹² Macrolides are not completely eradicated in sewage treatment plants, and it has been revealed that they do not readily hydrolyze in the environment,



Table 4 Photocatalytic degradation of fluoroquinolones at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Ciprofloxacin	Ag/SiO ₂	Sunlight	10.0 mg L ⁻¹	0.12 g L ⁻¹	98.0% (180 min)	211
Ciprofloxacin	ZnO/CD	Sunlight	10.0 mg L ⁻¹	0.6 g L ⁻¹	98.0% (110 min)	212
Ciprofloxacin	NCuTiO ₂ /CQD	Visible light	20.0 mg L ⁻¹	0.8 g L ⁻¹	89.0% (180 min)	213
Ciprofloxacin	ZnO/Co ₃ O ₄	Visible light	10.0 mg L ⁻¹	2.4 g L ⁻¹	100% (30 min)	214
Ciprofloxacin	TiO ₂ /Ce	UV light	40.0 mg L ⁻¹	6.0 g L ⁻¹	93.0% (180 min)	215
Ciprofloxacin	TiO ₂ /WO ₃	UV light	20.0 mg L ⁻¹	0.5 g L ⁻¹	100% (120 min)	216
Ciprofloxacin	CuO	Visible light	10.0 mg L ⁻¹	5.0 g L ⁻¹	60.0% (300 min)	217
Ciprofloxacin	CeO ₂ /Co ₃ O ₄	Visible light	5.0 mg L ⁻¹	0.5 g L ⁻¹	87.8% (50 min)	218
Ciprofloxacin	TiO ₂ /N	UV light	30.0 mg L ⁻¹	1.0 g L ⁻¹	94.5% (120 min)	219
Ciprofloxacin	TiO ₂ /La (0.1%)	Visible light	10.0 mg L ⁻¹	0.6 g L ⁻¹	99.5% (300 min)	220
Ciprofloxacin	TiO ₂ /Sm (0.1%)	Visible light	10.0 mg L ⁻¹	0.9 g L ⁻¹	99.0% (300 min)	221
Ciprofloxacin	TiO ₂ /Er (0.1%)	Visible light	10.0 mg L ⁻¹	0.9 g L ⁻¹	99.0% (300 min)	221
Ciprofloxacin	ZnO/Nd (0.1%)	Visible light	6.0 mg L ⁻¹	0.9 g L ⁻¹	99.0% (120 min)	222
Ciprofloxacin	Fe ₃ O ₄ /Bi ₂ WO ₆	Visible light	10.0 mg L ⁻¹	0.3 g L ⁻¹	99.7% (25 min)	223
Ciprofloxacin	MMT/CuFe ₂ O ₄	UV light	32.5 mg L ⁻¹	0.78 g L ⁻¹	80.0% (47.5 min)	224
Ciprofloxacin	Au-RGO/TiO ₂	Visible light	10.0 mg L ⁻¹		96.93% (180 min)	225
Ciprofloxacin	CeO ₂ /ZnO	UV light	10.0 mg L ⁻¹	0.25 g L ⁻¹	92.0% (360 min)	226
Ciprofloxacin	MgFe ₂ O ₄ /UiO-67	Visible light	10.8 mg L ⁻¹		99.62% (90 min)	227
Ciprofloxacin	B ₂ O ₃ /N-rGO	Visible light	15.0 mg L ⁻¹	0.25 g L ⁻¹	98.0% (180 min)	228
Ciprofloxacin	rGO/Bi ₄ O ₃ Br ₂	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	97.6% (60 min)	229
Ciprofloxacin	CdS@CuS/rGO	Visible light	10.0 mg L ⁻¹	0.25 g L ⁻¹	91.5% (60 min)	230
Ciprofloxacin	NiAl LDH/Fe ₃ O ₄ -rGO	Visible light	10.0 mg L ⁻¹	0.25 g L ⁻¹	91.36% (150 min)	231
Ciprofloxacin	Ag ₂ MoO ₄	UV light	20.0 mg L ⁻¹	0.5 g L ⁻¹	98.0% (40 min)	232
Ciprofloxacin	SiC/g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	0.4 g L ⁻¹	95.0% (30 min)	233
Ciprofloxacin	B _{0.8} Ce _{0.2} TiO ₂ /EPS film	Sunlight	10.0 mg L ⁻¹	1.0 g L ⁻¹	89.17% (240 min)	234
Ciprofloxacin	rGO-ZrO ₂	Sunlight	10.0 mg L ⁻¹		93.1% (240 min)	235
Ciprofloxacin	SnO ₂	UV light	50.0 mg L ⁻¹	0.5 g L ⁻¹	99.7% (120 min)	236
Ciprofloxacin	BFO/biochar	Solar light	10.0 mg L ⁻¹	2.0 g L ⁻¹	70.4% (120 min)	237
Ciprofloxacin	g-C ₃ N ₄ /Fe ₂ O ₃	UV light	10.0 mg L ⁻¹	0.3 g L ⁻¹	100% (60 min)	238
Ciprofloxacin	Bi ₂ O ₃ CO ₃	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	76.8% (60 min)	239
Ciprofloxacin	Bi ₂ WO ₆ /BiO _{2-x}	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	91.8% (120 min)	240
Ciprofloxacin	GO@Fe ₃ O ₄ @TiO ₂	Visible light	10.0 mg L ⁻¹	0.1 g L ⁻¹	91.5% (240 min)	241
Ciprofloxacin	MIL-68(In, Bi)-NH ₂ @BiOBr	Visible light	5.0 mg L ⁻¹	0.35 g L ⁻¹	91.1% (90 min)	242
Ciprofloxacin	Sm ₂ O ₃ /In ₂ S ₃	Visible light	20.0 mg L ⁻¹	0.05 g L ⁻¹	99.4% (55 min)	243
Ciprofloxacin	ZnCrLDO/FA	Visible light	10.0 mg L ⁻¹		98.0% (120 min)	244
Ciprofloxacin	2D Bi ₂ O ₂ CO ₃	UV-vis light	10.0 mg L ⁻¹	1.0 g L ⁻¹	76.8% (60 min)	245
Ciprofloxacin	In ₂ O ₃ /BiOBr	Visible light	10.0 mg L ⁻¹		93.5% (90 min)	246
Ciprofloxacin	BiOI/MOF/F-BC	Simulated sunlight	10.0 mg L ⁻¹		94.4% (180 min)	247
Ciprofloxacin	BiOCl/diatomite	Simulated sunlight	10.0 mg L ⁻¹	0.5 g L ⁻¹	94.0% (10 min)	248
Ciprofloxacin	Ti ₃ C ₂ -Bi/BiOCl	Visible light	20.0 mg L ⁻¹	1.0 g L ⁻¹	89.0% (100 min)	249
Ciprofloxacin	3D tripyramid TiO ₂	Simulated sunlight	10.0 mg L ⁻¹	1.0 g L ⁻¹	90.0% (60 min)	250
Ciprofloxacin	ZnSnO ₃	Simulated sunlight	10.0 mg L ⁻¹	0.5 g L ⁻¹	85.9% (100 min)	251
Ciprofloxacin	ZnO-SnO ₂ -Zn ₂ SnO ₄	Simulated sunlight	10.0 mg L ⁻¹	0.5 g L ⁻¹	95.8% (80 min)	252
Levofloxacin	WO ₃ /g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹		90.8% (70 min)	253
Levofloxacin	Au@ZnONPs-MoS ₂ -rGO	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	99.8% (120 min)	254
Levofloxacin	LaFeO ₃ /CdS	Visible light	10.0 mg L ⁻¹		97.3% (100 min)	255
Levofloxacin	Fe-doped BiOCl	Visible light	15.0 mg L ⁻¹	0.5 g L ⁻¹	94.7% (60 min)	256
Levofloxacin	Mn-doped ZnIn ₂ S ₄	Visible light	10.0 mg L ⁻¹		100% (30 min)	257
Levofloxacin	g-C ₃ N ₄ /TiO ₂	Solar light and UV irradiation	5.0 mg L ⁻¹	0.5 g L ⁻¹	100% (50 min)	258
Levofloxacin	WO ₃ /TiO ₂	Solar and UV light	5.0 mg L ⁻¹	0.5 g L ⁻¹	66.0% (50 min)	258
Levofloxacin	Sb ₂ S ₃ /In ₂ S ₃ /TiO ₂	Visible light	10.0 mg L ⁻¹		86.7% (160 min)	259
Levofloxacin	Fe-ZnO/WO ₃	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	96.0% (60 min)	260
Levofloxacin	Co ₃ O ₄ /Bi ₂ MoO ₆ @ g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹		95.21%	261
Levofloxacin	Bi ₂ O ₂ CO ₃ /Ti ₃ C ₂ T _x	Visible light	10.0 mg L ⁻¹		95.4% (80 min)	262
Ofloxacin	g-C ₃ N ₄ /NH ₂ -MIL-88B(Fe)	Visible light	10.0 mg L ⁻¹	0.4 g L ⁻¹	96.5% (150 min)	263
Ofloxacin	TS-1/C ₃ N ₄	Visible light	10.0 mg L ⁻¹	1.55 g L ⁻¹	90.0% (70 min)	264
Ofloxacin	BiFeO ₃	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	80.0% (180 min)	265
Ofloxacin	Mg-Ni co-doped TiO ₂	Visible light	40.0 mg L ⁻¹	2.0 g L ⁻¹	96.0% (60 min)	266
Ofloxacin	PEB-DBT/α-Fe ₂ O ₃	Visible light	40.0 mg L ⁻¹		98.0% (50 min)	267
Ofloxacin	UiO-66/wood	Simulated sunlight	10.0 mg L ⁻¹	0.02 g L ⁻¹	80.96% (270 min)	268
Ofloxacin	ZnFe ₂ O ₄ /BiVO ₄	Visible light	20.0 mg L ⁻¹	1.0 g L ⁻¹	97.0% (30 min)	269



Table 4 (Contd.)

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Ofloxacin	Ag ₂ O-g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	99.1% (15 min)	270
Norfloxacin	AgI/BiOI	Visible light	20.0 mg L ⁻¹	1.0 g L ⁻¹	98.8% (120 min)	271
Norfloxacin	Fe ₃ O ₄ @La-BiFeO ₃	Visible light	10.0 mg L ⁻¹		93.8% (60 min)	272
Norfloxacin	Y-TiO ₂ /5A/NiFe ₂ O ₄	Visible light	30.0 mg L ⁻¹	2.0 g L ⁻¹	96.55% (60 min)	273
Norfloxacin	AgI/BiOI	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	98.8% (120 min)	274
Norfloxacin	Ni ₂ O ₃ @PC	UV light	10.0 mg L ⁻¹	0.1 g L ⁻¹	59.0% (180 min)	275
Norfloxacin	ZnO/g-C ₃ N ₄	Visible light	15.0 mg L ⁻¹	1.8 g L ⁻¹	92.8% (120 min)	276
Norfloxacin	RGO-SnSe	Visible light	40.0 mg L ⁻¹	1.0 g L ⁻¹	90.7% (70 min)	277
Norfloxacin	SnS ₂	Solar light	20.0 mg L ⁻¹	0.05 g L ⁻¹	80.0% (110 min)	278
Norfloxacin	Cu ₂ O@WO ₃	Visible light	10.0 mg L ⁻¹	0.2 g L ⁻¹	90.0% (90 min)	279
Norfloxacin	Fe(III)-SrTiO ₃ -GO	Visible light	10.0 mg L ⁻¹		92.3% (120 min)	280
Norfloxacin	GCNQDs/Ni ₅ P ₄	UV light	40.0 mg L ⁻¹	0.1 g L ⁻¹	92.0% (120 min)	281
Norfloxacin	BiOCl/ZnS-V _{Zn} O	Visible light	20.0 mg L ⁻¹	0.5 g L ⁻¹	97.9% (50 min)	282a
Norfloxacin	Au/MIL-101(Fe)/BiOBr	Visible light	10.0 mg L ⁻¹	0.1 g L ⁻¹	100% (20 min)	282b
Enrofloxacin	Strontium-doped TiO ₂ /CDs	Visible light	10.0 mg L ⁻¹	0.05 g L ⁻¹	84.7% (70 min)	283
Enrofloxacin	Ag-ZnFe ₂ O ₄ -rGO	Visible light	10.0 mg L ⁻¹		99.1% (60 min)	284
Enrofloxacin	C _{ss} WO ₃ /BiOI	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	100% (60 min)	285
Enrofloxacin	Zero-valent copper (nZVC)	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	99.51% (70 min)	286
Enrofloxacin	CdS/CuAg	Visible light	10.0 mg L ⁻¹	0.02 g L ⁻¹	99.9% (45 min)	287
Enrofloxacin	Fe _{3-x} S _{4-y} /g-C ₃ N ₄	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	100% (30 min)	288
Enrofloxacin	P/O co-doped g-C ₃ N ₄ /TiO ₂	Visible light	10.0 mg L ⁻¹	1.0 g L ⁻¹	98.5% (60 min)	289
Enrofloxacin	Ball-milled biochar	Visible light	20.0 mg L ⁻¹	0.2 g L ⁻¹	80.2% (150 min)	290a
Enrofloxacin	MIL-101(Fe)/BiOBr	Visible light	10.0 mg L ⁻¹	0.1 g L ⁻¹	84.4% (40 min)	290b

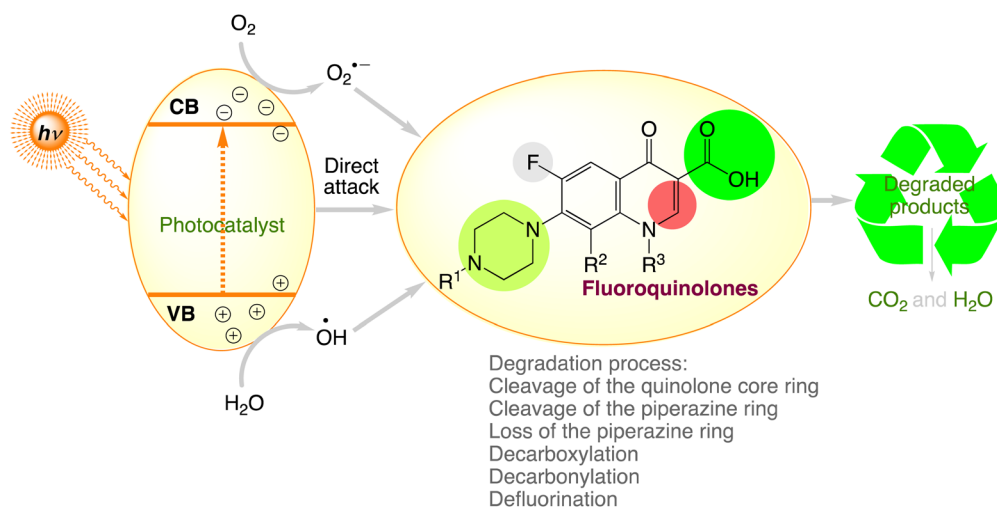


Fig. 6 The proposed photocatalytic degradation pathways of fluoroquinolones.

suggesting that they may continue to exist in the environment. Thus, it is important that we pay attention to the issue of macrolides causing environmental contamination.²⁹³ Tylosin is the most often utilised agent among macrolides, and one of the best technologies for their removal is photocatalytic oxidation.^{77,294} The photodegradation of macrolides by various photocatalysts can be briefly summarized in the Fig. 7. When a photon flows surpassing a semiconductor's band gap, an electron (e^-) moves from the valence band (VB) to the conduction band (CB), generating a photogenerated hole on the VB. The chemical reaction will then occur when the separated

charge carriers diffuse into the semiconductor/liquid interface's catalytically active regions (Fig. 7).

Three types of radicals can be formed by holes: (1) directly oxidising macrolides into certain byproducts; (2) reacting with H₂O to generate hydroxyl radicals ($\cdot\text{OH}$) with high oxidation potential; and (3) reacting with O₂ to form superoxide radicals (O₂^{·-}) with significant reducibility of electrons. In the end, these produced oxidation radicals can break down macrolides into hazardous or harmless byproducts, which can then be broken down further into CO₂ and H₂O by extending the reaction period. According to numerous research conducted recently,



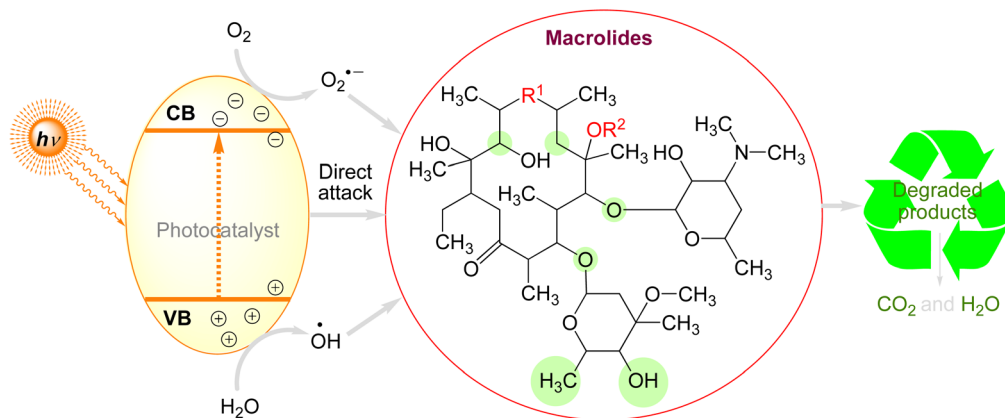


Fig. 7 The proposed photocatalytic degradation pathways of macrolides.

photocatalytic oxidation technologies are an excellent way to treat macrolides. Unfortunately, not much research has been done to fully understand how macrolides' complicated structure and enormous molecular weight affect their degradation processes. Table 5 summarises the photocatalytic degradation of macrolides under various circumstances.

5.5. Photocatalytic degradation of β -lactams

β -Lactams as broad-spectrum antibiotics that are mainly classified as penicillin and cephalosporin. Amoxicillin (AMX) and ampicillin (AMP) are examples of penicillins that are generated from penicillium and have the ability to prevent amino acid

chains in bacterial cell walls from cross-linking. The semi-synthetic antibiotic class referred to as cephalosporins, which includes ceftiofur sodium (CFS), ceftriaxone sodium, cephalixin (CLX), and other similar antibiotics, is derived from 7-aminocephalosporanic acid (7-ACA).^{77,317,318}

Investigations have shown that municipal wastewater treatment plants³¹⁹ have greater quantities of penicillin and cephalosporin. β -Lactams, on the other hand, were not expected to survive in the environment because of their strong polarity, reduced adsorption capacity, and capacity to hydrolyze to the soil. Fig. 8 summarises the processes *via* which various, β -lactam antibiotics degrade. Table 6 summarises the results of the photocatalytic degradation of β -lactams using various photocatalysts.

Table 5 Photocatalytic degradation of macrolides at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Tylosin	ZnCrNi/GO	Visible light	10.0 mg L ⁻¹		90.0% (80 min)	295
Tylosin	Au/TiO ₂ -CCBs	Visible light			92.0% (180 min)	296
Tylosin	TiO ₂	UV light	20 mg L ⁻¹	0.1 g L ⁻¹	80.0% (300 min)	297
Tylosin	g-C ₃ N ₄	Simulated sunlight	5 mg L ⁻¹	0.05 g L ⁻¹	99.0% (30 min)	298
Tylosin	Sm-doped gC ₃ N ₄	Simulated sunlight	25 mg L ⁻¹	0.5 g L ⁻¹	78.4% (90 min)	299
Tylosin	Er-doped g-C ₃ N ₄	Simulated sunlight	25 mg L ⁻¹	0.5 g L ⁻¹	70% (90 min)	300
Tylosin	Goethite-modified C ₃ N ₄ /ZnFe ₂ O ₄	Simulated sunlight	5 mg L ⁻¹	0.5 g L ⁻¹	99.0% (30 min)	301
Erythromycin	SnO ₂ -doped TiO ₂	Visible light	50 mg L ⁻¹	0.5 g L ⁻¹	67.0% (240 min)	302
Erythromycin	CaCO ₃ (nano-calcite)	Sunlight	30 mg L ⁻¹	0.5 g L ⁻¹	93.0% (360 min)	303
Erythromycin	Graphene-based TiO ₂	Simulated sunlight	0.10 mg L ⁻¹	0.1 g L ⁻¹	84.0% (60 min)	304
Erythromycin	TiO ₂	UV light	10 mg L ⁻¹	0.25 g L ⁻¹	90.0% (250 min)	305
Erythromycin	g-C ₃ N ₄ /CdS	Simulated sunlight	50 mg L ⁻¹	0.5 g L ⁻¹	81.02% (60 min)	306
Erythromycin	ZnIn ₂ S ₄	Visible light	10 mg L ⁻¹	0.05 g L ⁻¹	100% (180 min)	307
Spiramycin	TiO ₂	UV light	25 mg L ⁻¹	0.25 g L ⁻¹	100% (180 min)	308
Spiramycin	TiO ₂ and ZnO	UV/Visible light	10 mg L ⁻¹	0.05 g L ⁻¹	100% (120 min)	309
Spiramycin	N-doped TiO ₂	Visible light	40 mg L ⁻¹	3.0 g L ⁻¹	74.0% (240 min)	310
Spiramycin	g-C ₃ N ₄ /ZnFe ₂ O ₄	Visible light	20 mg L ⁻¹	1.0 g L ⁻¹	95.0% (240 min)	311
Clarithromycin	Graphene-based TiO ₂	Simulated sunlight	0.10 mg L ⁻¹	0.1 g L ⁻¹	86.0 (60 min)	312
Azithromycin	ZrO ₂ /Ag/TiO ₂	Visible light	20 mg L ⁻¹	0.2 g L ⁻¹	90% (9 h)	313
Azithromycin	GO/Fe ₃ O ₄ /ZnO/SnO ₂	UV light	30 mg L ⁻¹	1.0 g L ⁻¹	90.06% (120 min)	314
Azithromycin	Doped TiO ₂ /fberglass-rubberized silicone	UV light	250 mg L ⁻¹	0.02 g L ⁻¹	70.0% (15 min)	315
Azithromycin	PAC/Fe/Ag/Zn	UV light	40 mg L ⁻¹	0.04 g L ⁻¹	99.5% (120 min)	316



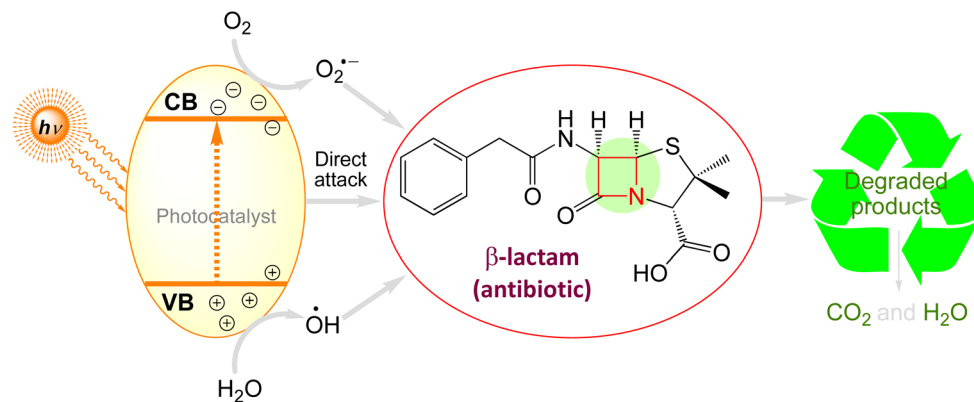


Fig. 8 The proposed photocatalytic degradation pathways of β -lactams (antibiotics).

Table 6 Photocatalytic degradation of β -lactams (antibiotics) at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions			Ref.
			Initial concentration	Catalyst concentration	Degradation (%)	
Amoxicillin	$Fe_3O_4@void@CuO/ZnO$	Visible light	10.0 mg L^{-1}		100% (70 min)	320
Amoxicillin	Iron nanoparticle (IPP)	Visible light	10.0 mg L^{-1}	2.5 g L^{-1}	60.0% (60 min)	321
Amoxicillin	TiO_2-Cr	Visible light	10 mg L^{-1}	0.33 g L^{-1}	100% (90 min)	322
Amoxicillin	$CuI/FePO_4$	Visible light	10 mg L^{-1}		90.0% (60 min)	323
Amoxicillin	GO/TiO_2	UV light	50 mg L^{-1}	0.6 g L^{-1}	99.84% (60 min)	324
Amoxicillin	CN-T	Visible light	50 mg L^{-1}	0.3 g L^{-1}	100% (48 h)	325
Amoxicillin	Magnetite/SCB biochar	Visible light	100 mg L^{-1}	0.12 g L^{-1}	73.51% (240 min)	326
Amoxicillin	$TiO_2@nZVI/PS$	Visible light	20 mg L^{-1}	1.0 g L^{-1}	99.0% (60 min)	327
Amoxicillin	Ni doped ZnO	UV-visible light	10 mg L^{-1}		86.21% (120 min)	328
Amoxicillin	ZnONPs	UV light	100 mg L^{-1}	0.2 g L^{-1}	90.0% (120 min)	329
Amoxicillin	TiO_2/Fe_2O_3	Solar light	50 mg L^{-1}	1.0 g L^{-1}	100% (180 min)	330
Amoxicillin	MIL-53(Al)/ZnO	Visible light	10 mg L^{-1}	1.0 g L^{-1}	100% (60 min)	331
Amoxicillin	Mn-doped Cu_2O	Sunlight	15 mg L^{-1}	1.0 g L^{-1}	92.0% (180 min)	332
Amoxicillin	WO_3	Simulated sunlight	20 mg L^{-1}	0.104 g L^{-1}	99.99% (180 min)	333
Amoxicillin	TiO_2	UV light	10 mg L^{-1}	0.25 g L^{-1}	65.0% (150 min)	334
Amoxicillin	$ZnO@TiO_2$	Visible light	10 mg L^{-1}	0.1 g L^{-1}	80.0% (70 min)	335
Amoxicillin	Mesoporous $g-C_3N_4$	Visible light	2 mg L^{-1}	1.0 g L^{-1}	99% (60 min)	336
Amoxicillin	Ag/TiO_2 /Mesoporous $g-C_3N_4$	Visible light	5 mg L^{-1}	1.0 g L^{-1}	99% (60 min)	337
Amoxicillin	$BiVO_4$	Visible light	5 mg L^{-1}		97.45% (90 min)	338
Amoxicillin	C-dots/ $Sn_2Ta_2O_7/SnO_2$	Simulated sunlight	20 mg L^{-1}		88.3% (120 min)	339
Ceftiofur sodium	$CdFe_2O_4/g-C_3N_4$	Visible light	30 mg L^{-1}		68.6% (60 min)	340
Ceftiofur sodium	$Ag-ZnO$	Visible light	10 mg L^{-1}		89.0% (6 h)	341
Ceftiofur sodium	$Ag-TiO_2$	Visible light	10 mg L^{-1}		92.0% (90 min)	342
Ceftriaxone sodium	$g-C_3N_4-ZnO$	UV light	10 mg L^{-1}		100% (60 min)	343
Ceftriaxone sodium	$ZnO/ZnIn_2S_4$	Visible light	10 mg L^{-1}	0.4 g L^{-1}	83.5% (150 min)	344
Ceftriaxone sodium	$CdS-g-C_3N_4$	Visible light	15 mg L^{-1}	0.06 g L^{-1}	92.55% (81 min)	345
Ceftriaxone sodium	$CdSe \text{ QDs}@MoS_2$	UV light	20 mg L^{-1}	0.012 g L^{-1}	85.47% (180 min)	346
Cephalexin	ZnO	Simulated sunlight	20 mg L^{-1}	0.1 g L^{-1}	96.0% (25 min)	347
Cephalexin	Sodium persulfate (SPS) and fenton	UV light	10 mg L^{-1}	0.1 g L^{-1}	100% (60 min)	348
Cephalexin	$g-C_3N_4/Zn$ doped Fe_3O_4	Visible light	10 mg L^{-1}		91.0% (5 h)	349
Cephalexin	$CeO_2@WO_3$	Visible light	20 mg L^{-1}	0.019 g L^{-1}	98.8% (95 min)	350



5.6. Photocatalytic degradation of nitroimidazoles

Nitroimidazoles are widely utilised in both human and veterinary medicine, mostly for the treatment of infectious illnesses. Nitroimidazoles are easily accumulated in hospitals, fish and

poultry farms, animal husbandry, and the meat industry due to their high solubility, limited degradability, and carcinogenicity, all of which pose a major concern to human health and the ecosystem. As a result, creating effective strategies for the removal of nitroimidazoles^{77,351–354} is crucial. One popular

Table 7 Photocatalytic degradation of nitroimidazoles at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions		Degradation (%) Ref.
			Initial concentration	Catalyst concentration	
Metronidazole	Ag-doped- Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ (Ag-d-NZF)	UV light	50.0 mg L ⁻¹	0.01 g L ⁻¹	99.9% (360 min) 355
Metronidazole	Ag-N-SnO ₂	Visible light	10.0 mg L ⁻¹	0.4 g L ⁻¹	97.03% (120 min) 356
Metronidazole	TiO ₂ decorated magnetic reduced graphene oxide	Visible light	20.0 mg L ⁻¹	0.75 g L ⁻¹	100% (120 min)
Metronidazole	Co-TiO ₂ /sulphite	Visible light	20.0 mg L ⁻¹	0.8 g L ⁻¹	94.0% (18 min) 357
Metronidazole	ZEO/HDTMA-Br/CuS	Simulated sunlight	10.0 mg L ⁻¹	0.01 g L ⁻¹	100% (180 min) 358
Metronidazole	Co/g-C ₃ N ₄ /Fe ₃ O ₄	Visible light	5.0 mg L ⁻¹	0.7 g L ⁻¹	100% (60 min) 359
Metronidazole	UiO-66-NH ₂	Solar light	5.0 mg L ⁻¹	0.125 g L ⁻¹	68.0% (360 min) 360
Metronidazole	PAC/Fe ₃ O ₄	UV light	30.0 mg L ⁻¹	0.6 g L ⁻¹	99.87% (90 min) 361
Metronidazole	ZnFe ₂ O ₄ @UiO-66	UV light	90.0 mg L ⁻¹	0.05 g L ⁻¹	93.7% (120 min) 362
Metronidazole	ZnO/biochar	Visible light	10.0 mg L ⁻¹		97.1% (40 min) 363
Metronidazole	CN-PPy-MMT	Visible light	10.0 mg L ⁻¹	0.8 g L ⁻¹	99.3% (40 min) 364
Metronidazole	TiO ₂ -Fe ₃ O ₄	Visible light	20.0 mg L ⁻¹	1.0 g L ⁻¹	96.0% (180 min) 365
Metronidazole	SBA-15/TiO ₂	UV light	10.0 mg L ⁻¹	0.5 g L ⁻¹	87.7% (200 min) 366
Metronidazole	ZnO-ZnAl ₂ O ₄	Sunlight	20.0 mg L ⁻¹	0.4 g L ⁻¹	50.0% (120 min) 367
Metronidazole	CuS/NiS	Visible light	150.0 mg L ⁻¹	0.2 g L ⁻¹	23.31% (120 min) 368
Metronidazole	MoS ₂ /Bi ₂ S ₃	NIR light	10 mg L ⁻¹		91.54% (40 min) 369
Metronidazole	HKUST-1-based SnO ₂	UV/Visible light	40.0 mg L ⁻¹	2.0 g L ⁻¹	98.0% (240 min) 370
Metronidazole	Fe ₃ O ₄ @SiO ₂ @TiO ₂ /rGO	UV light	10.0 mg L ⁻¹	0.1 g L ⁻¹	94.0% (60 min) 371
Metronidazole	TiO ₂	UV light	80.0 mg L ⁻¹	0.7 g L ⁻¹	100% (600 min) 372
Metronidazole	FeNi ₃ /chitosan/BiOI	Simulated sunlight	20.0 mg L ⁻¹	0.04 g L ⁻¹	100% (200 min) 373
Metronidazole	Ag ₂ S/BiVO ₄ @α-Al ₂ O ₃	Visible light	30.0 mg L ⁻¹	1.0 g L ⁻¹	90.5% (120 min) 374
Tinidazole	rGO/BiOCl	UV light	18.0 mg L ⁻¹	0.001 g L ⁻¹	97.0% (5 min) 375
Tinidazole	Co/NCHPs	UV/Visible light	20.0 mg L ⁻¹		99.99% (6 min) 376
Tinidazole	Ag/HAp/In ₂ S ₃ QDs	Visible light	20.0 mg L ⁻¹	0.24 g L ⁻¹	96.32% (30 min) 377
Ornidazole	TiO ₂	UV light	50.0 mg L ⁻¹	1.0 g L ⁻¹	66.15% (180 min) 378
Ornidazole	Y ³⁺ -Bi ₅ Nb ₃ O ₁₅	Visible light	20.0 mg L ⁻¹	2.0 g L ⁻¹	90.5% (180 min) 379

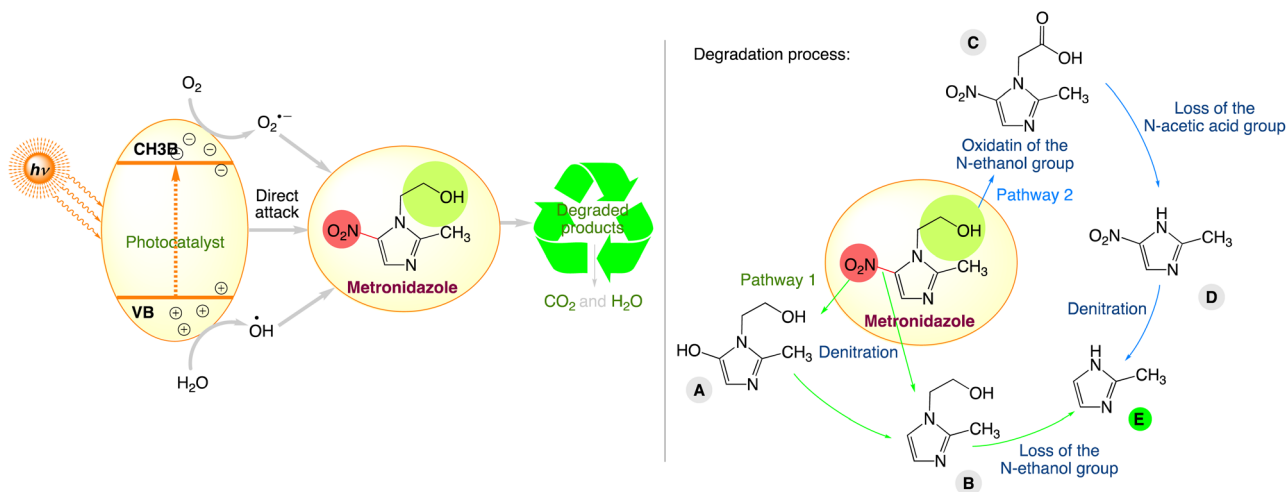


Fig. 9 The proposed photocatalytic degradation pathways of metronidazole.



Table 8 Photocatalytic degradation of other antibiotics at different conditions

Target antibiotic	Photocatalyst	Source of light	Optimum conditions		Degradation (%)	Ref.
			Initial concentration	Catalyst concentration		
Chloramphenicol	Fe/TaON/ β -Si ₃ N ₄ / β -Si ₃ Al ₃ O ₃ N ₅	Visible light	20.0 mg L ⁻¹	0.01 g L ⁻¹	98.0% (30 min)	380
Chloramphenicol	SmVO ₄ /g-C ₃ N ₄ (SM/CN)	Visible light	10.0 mg L ⁻¹	0.5 g L ⁻¹	94.35% (105 min)	381
Chloramphenicol	BiOI/ZnO/rGO	Visible light	10.0 mg L ⁻¹		100% (180 min)	382
Chloramphenicol	CuInS ₂	Visible light	10.0 mg L ⁻¹	0.2 g L ⁻¹	94.3% (120 min)	383
Chloramphenicol	Bi ₂ S ₃ /ZrO ₂ and Bi ₂ WO ₆ /ZrO ₂	Visible light	10.0 mg L ⁻¹	0.2 g L ⁻¹	96.0% (15 min)	384
Chloramphenicol	PbS/TiO ₂	Sunlight	10.0 mg L ⁻¹	0.06 g L ⁻¹	76.0% (240 min)	385
Chloramphenicol	rGO-ZnO	UV light	10.0 mg L ⁻¹	0.5 g L ⁻¹	90.0% (100 min)	386
Gentamicin	TiO ₂ nps	Visible light	10.0 mg L ⁻¹		95.0% (80 min)	387
Gentamicin	ZnO	UV light	20.0 mg L ⁻¹	0.2 g L ⁻¹	93.0% (30 min)	388
Lincomycin	O-g/C ₃ N ₄	Visible light	100.0 mg L ⁻¹		99.0% (180 min)	389
Lincomycin	TNWS/TNAs	Visible light	500.0 mg L ⁻¹		85.0% (20 min)	390
Vancomycin	TNWS/TNAs	Visible light	500.0 mg L ⁻¹		100% (20 min)	390
Vancomycin	TiO ₂	UV light	58.2 mg L ⁻¹	0.23 g L ⁻¹	93.0% (36.3 min)	391
Vancomycin	TiO ₂ -clinoptilolite	UV light	30.0 mg L ⁻¹	0.2 g L ⁻¹	97.0% (50.9 min)	392

method for treating nitroimidazoles is photocatalysis. The three most used nitroimidazoles are ornidazole, tinidazole, and metronidazole. The photocatalytic degradation and routes associated with metronidazole have been the subject of the greatest research among them. Table 7 provides an overview of the data from current investigations on the photocatalytic degradation of nitroimidazole.

Further observation from these investigations shows that the nitroimidazole degradation routes are comparable and may be summed up as denitration and the removal of their unique substituents. For instance, Fig. 9 illustrates the various stages of the metronidazole degradation process during the majority of the photocatalytic oxidation process. Three different reaction products were suggested for each of the two metronidazole degradation pathways. In pathway 1, metronidazole undergoes denitration and then loss of *N*-ethanol group, with the generation of products A, B, and E, respectively. In pathway 2, the *N*-ethanol group is first oxidized to carboxyl to produce C, which converts to D through loss of the *N*-acetic acid group. Besides, product D further transforms to E by denitration.

5.7. Photocatalytic degradation of other antibiotics

Apart from the previously stated antibiotic, some research continues to concentrate on the photocatalytic breakdown of antibiotics such as lincomycin, glycopeptides, aminoglycosides, and chloramphenicol. Table 8 provides an overview of the data regarding photocatalytic degradation of these antibiotics.

6. Conclusions and perspective

The extensive discovery and application of antibiotics in recent decades has impacted human health and environmental systems to some extent. Antibiotic contamination has become a more significant scientific and practical issue overall. Since previous research has already acquired significant fundamental scientific and technical expertise, the photocatalytic technique represents an intriguing promise for attaining the elimination of antimicrobial contaminants. We are able to choose this

technology for both indoor and outdoor water treatment systems owing to the freedom in selecting light sources. In addition, it is an industry-friendly technology because it is feasible to use sunlight. Photocatalysis is a cost-effective method since it requires less space and maintenance than biodegradation. This review therefore provides an overview of the most recent advancements in the photocatalytic degradation of different antibiotics including tetracycline, sulfonamide, fluoroquinolones, macrolides, β -lactams, nitroimidazoles as well as miscellaneous antibiotics in aqueous solution under various reaction circumstances and critically examines recent methods for photocatalytic antibiotic degradation by involving the doping of metal and non-metal into ultraviolet light-driven photocatalysts, the generation of new semiconductor photocatalysts, the development of heterojunction photocatalysts, the building of surface plasmon resonance-enhanced photocatalytic systems that offers a basic understanding of the photocatalytic water treatment process. Utilising solar energy to reduce antimicrobial contaminants through photocatalytic technologies is promising from an industrialization and commercialization standpoint. A useful strategy for increasing photocatalytic activity, decreasing photogenerated carrier recombination, and improving charge separation and transfer efficiency at the photocatalyst interface is the development of heterojunctions. Building several heterojunctions with various semiconductors is therefore a typical tactic. As a result, due to their exceptional photocatalytic activity and acceptable redox ability, heterojunction photocatalysts have gained a lot of interest recently. The development of these photocatalysts on a wide scale and the formation of more efficient photocatalytic water purification systems will be greatly facilitated by future advancements.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.



Conflicts of interest

There are no conflicts to declare.

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