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Review Article

Evaluating the Efficiency of Photocatalytic Degradation in Tetracycline Removal: A Comprehensive Review

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ABSTRACT

Tetracycline (TC) is a widely used antibiotic in both human and veterinary medicine. However, its extensive use has led to the accumulation of TC in the environment, making it one of the most common and persistent environmental pollutants. The photocatalytic degradation of TC has been extensively studied over the past few decades using various photocatalysts. This review aims to provide a comprehensive overview of the research conducted on the photocatalytic degradation of TC, highlighting its significance as an environmental pollutant and its impact on aquatic life, including plants and microbes in groundwater. Therefore, finding efficient methods to remove TC from water sources is crucial. Photocatalysis has emerged as a promising approach for TC degradation due to its ability to utilize light energy to generate reactive species that can oxidize and degrade organic pollutants. Several operating parameters significantly influence the photodegradation process including light wavelength, initial concentration of TC in solution, pH level, dissolved oxygen content, and presence of reactive species. To achieve maximum efficiency in the photocatalytic degradation of TC, these operating parameters need to be optimized.

KEYWORDS: Tetracycline, Photodegradation, Dissolved oxygen, Photocatalysts, Valence band, Conduction band, Solar Light

INTRODUCTION

Antibiotics are frequently integrated into animal feed and treatment because they promote efficiency, control the spread of disease, and promote growth [1]. Tetracycline is a common broad-spectrum antibiotic used in both veterinary and human medicine. Unfortunately, due to its widespread use, soil and water bodies have become contaminated, among other environmental compartments. Due to possible adverse effects on human health and the potential for microbial populations to evolve antibiotic resistance, the presence of antibiotics in the environment presents a serious hazard [2].

Tetracycline (TC) is the most widely used antibiotic for treating and preventing bacterial infections in both human and veterinary medicine. Figure (1) shows the structural formula of tetracycline [3], The harmful effects of TC on nontarget species, wastewater sludge microorganisms, and plants have been documented by certain researchers [4,5], The persistence and possible ecological impact of tetracycline have been highlighted by its discharge into the environment through aquaculture, agricultural runoff, and incorrect disposal of pharmaceutical waste [5,6,7], Effective ways to reduce tetracycline contamination and its environmental impact are therefore becoming increasingly necessary [3,7].

According to recent studies, photocatalysis can oxidize TC in brief amounts of time, eliminating its antibacterial properties at the

same time [8]. Determining a sustainable, effective method for wastewater treatment requires careful consideration of how different parameters affect the photocatalytic degradation efficiency from both the design and operational perspectives [9,10].

In this review, we examine the impact of important operating parameters on the degradation of TC in wastewater by photocatalysis, along with some recent successes [10,11].

Properties of Tetracycline

TC is synthesized as an odorless yellow crystalline powder. Tetracycline's complex molecular structure is made up of four six-membered rings that are linearly bonded together. It has a dimethylamino group at position 4 of the A ring and a tetracyclic nucleus with a "cyclohexane" ring. A keto group is also included in the chemical structure at position 2 of the C ring, and a phenolic hydroxyl group is present at position 7 of the D ring [12].

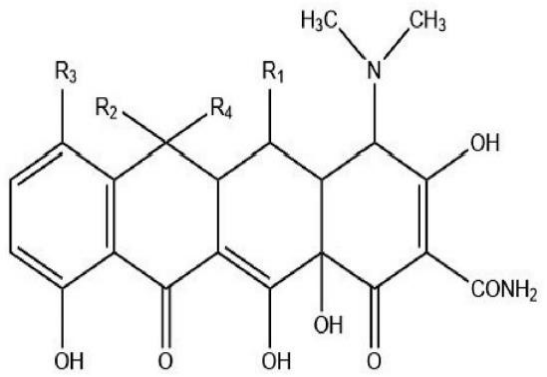

Figure 1: The Structural Formula of Tetracyline [3]

Tetracycline's molecular weight is roughly 444.44 g/mol, and its formula is $C_{22}H_{24}N_2O_8$. Tetracycline is only sporadically soluble in water; at 25°C, its solubility is estimated to be about 100 mg/L. Its solubility is, nevertheless, sensitive to pH, with increased solubility noted in acidic environments [13].

Various environmental factors, such as heat, light, and an alkaline pH, might cause tetracycline to break down [14]. Maintaining the stability and efficacy of tetracycline formulations requires storage that shields them from these elements [15].

As a common salt form of tetracycline, tetracycline hydrochloride is claimed to have a melting point between 185 and 195°C. Approximately 356 nm in acidic conditions and 365 nm in alkaline conditions are the absorption maxima of tetracycline's distinctive UV absorption spectra [16]. Tetracycline in pharmaceutical formulations is frequently quantitatively analyzed using this characteristic. Diverse crystalline forms of tetracycline can affect its solubility and stability, among other physical characteristics [17].

Effect of TC on Aquatic Life

Although it is rare for TC to cause acute toxicity, long-term environmental exposure to antibiotics may have the potential to cause chronic toxicity to organisms that are not the intended target. The extensive use of TCs has impacted plant development and the presence of microorganisms in the terrestrial environment. Tetracycline can bioaccumulate in the tissues of aquatic creatures after it enters aquatic habitats. Tetracycline is absorbed by aquatic organisms from water or sediments, resulting in this bioaccumulation [18,19,20]. Tetracycline can also go through a process called biomagnification, in which it concentrates as it goes up the food chain. This suggests that tetracycline exposure may be higher for predators at the top of the aquatic food chain than for those at lower trophic levels [19].

Tetracycline can have toxicological effects on aquatic creatures when it is present in water settings [20]. According to studies, tetracycline exposure can have negative consequences on a variety of aquatic species, including fish, amphibians, and

invertebrates, including behavioural changes, reproductive problems, and anomalies in fish development. The overall biodiversity of aquatic ecosystems may be threatened by these consequences, which have the potential to upset their ecological equilibrium [21].

Beyond certain organisms, tetracycline has an effect on aquatic ecosystems. Tetracycline exposure can change the microbial populations in aquatic habitats, which can interfere with nitrogen cycling and other vital ecological functions. Moreover, species that live in sediments and benthic invertebrates may have long-term consequences from the buildup of tetracycline residues in sediments [22]. The impact of tetracycline contamination on aquatic ecosystems has become a growing concern for regulatory bodies due to the possible risks involved [15,23]. Strict laws on the disposal of waste from pharmaceutical production facilities, enhanced wastewater treatment systems, and public awareness campaigns about appropriate medicine disposal techniques are some of the steps taken to lessen these effects [24].

Effect of TC on Plants

Holling-Sorenson et al. [15] and Holten et al. [25] performed toxicological experiments on *Microcystis aeruginosa* and Chlorella algae in various fisheries, employing TC antibiotics. Compared to green algae, *M. aeruginosa* had a greater TC content. Holling-Sorenson demonstrated that TC medications were either highly toxic or moderately toxic compounds in aquatic algae [15]. Jiang et al. also investigated the harmful effects of TC on antioxidant enzyme activity and photosynthesis of *M. aeruginosa* [26]. The authors hypothesized that TC may prevent *M. aeruginosa* from photosynthesis [26]. The inhibitory impact rises concurrently with the TC concentration. Eventually, TC will stop the growth of algae by destroying the antioxidant enzymes.

Effect of TC on microbes

Dijek et al. (1976) investigated the effects of 21 antibiotics, including TC, on 36 common waterborne microorganisms [27]. The findings demonstrated that just seven types of microbes were susceptible to antibiotics, whereas the remaining 29 species naturally exhibited resistance to popular antibiotics. Using the long-term bioluminescence inhibition test of *Vibrio spp.*, Backhaus et al. (1999) investigated the five widely used antibiotics [28]. The findings demonstrated the extreme toxicity of the aforementioned antibiotics, with the majority of EC_{50} values being less than 1 mg/L. Of the 20 studied antibiotics, tetracycline hydrochloride had the highest potency. The concentrations of TC hydrochloride were 0.0738 ng/L, 0.025 mg/L, and 0.0046 mg/L, respectively, for the 90%, EC_{50}, and EC_{10} maximal effect levels [29].

Photocatalysis

Photocatalysis is the process in which the rate of chemical transformation is enhanced by a chemical substance under light irradiation. In photocatalysis, organic contaminants are degraded into CO_2, H_2O, and acids on the surface of the photocatalyst, by irradiation of solar light. When a photocatalyst is illuminated with solar light of energy higher or the same as the band gap energy of the catalyst, electrons from the valance band are migrated to the CB, creating holes in the valance band. This process generates charge carriers or hole-electron pairs (e-/h+), on the surface of the photocatalyst. On the surface of the catalyst, charge carriers react with the adsorbed species to produce superoxide anion radicals and hydroxyl radicals. $OH^{\cdot}$ and $O^{\cdot}-$, by redox reaction, degrade the contaminants into harmless species. Oxygen (O_2) at the surface acts as electron scavenger and prevents loss of energy in the form of heat by reducing the recombination of photo-exited holes and electrons [30].

Fundamental and Mechanism of Photocatalysis

In a photocatalytic process, light and catalyst are used to boost up a chemical reaction. Photocatalysts are the materials that absorb light and speed up the reaction [31].

Photocatalysis is categorized into:

Homogenous photocatalysis: Reactions in which reactants and photocatalysts have the same phases. For homogeneous photocatalysis, mostly high oxidation state transition metal complexes are used. These metal complexes generate hydroxyl radicals which react with organic matter to degrade it into harmless substances [32].

Heterogenous Photocatalysis: Reactions in which reactants and photocatalysts are in different phases. In heterogeneous photocatalysis, semiconduction materials are used as photolyases because of their electronic structures [33].

Photocatalytic Degradation of Tetracycline

Photocatalysis depends on the catalyst and wavelength of light. Semiconducting materials act as photosensitizers. The substance which is activated by light and induces changes in the other molecule in photoreaction [34]. The photocatalytic reaction starts when a photocatalyst absorbs solar radiation of energy equal to or greater band gap of the photocatalyst. On this irradiation, electrons from the valance band migrate to the conduction band leaving positive holes behind. These electrons and holes take part in the degradation of organic pollutants into CO_2, H_2O, and mineral acids [35].

Factors Affecting Photocatalytic Degradation of Tetracycline

Various factors may significantly affect the photocatalytic degradation of tetracycline and will be discussed in this section.

Effect of TC Concentration

The concentration of antibiotics has been demonstrated to have a major impact on the photodegradation efficiency of tetracycline (TC). First, as TC concentration increases, more active sites on the photocatalyst are occupied and TC molecules absorb more light. These two processes reduce the amount of photons that reach the catalyst and, as a result, the production of reactive species for TC photodegradation [36]. Moreover, more organic intermediates and final products will be produced, which could compete with the parent TC molecules for the limited adsorption of catalyst and photocatalytic sites and prevent the degradation of TC through photocatalysis [37].

Furthermore, some intermediates might scavenge the photogenerated active species. Due to the increased competition between the increased intermediates and final products for adsorption and photocatalytic sites on the catalyst surface, an increase in the concentration of TC typically harms their photocatalytic degradation [38].

Effect of pH

The adsorption of antibiotics onto the surface of photocatalysts and the corresponding photodegradation efficiency are influenced by the various charges that the surfaces of the catalysts and antibiotic molecules may have under varying pH conditions [39]. Tetracycline, for example, is an amphoteric compound due to the tricarbonyl system, phenolic diketone moiety, and dimethylammonium group. It gives pKa values at 3.3, 7.68, and 9.7 as a result [40]. The point of zero charge (pzc) of TiO_2 is 6.25. Tetracycline and TiO_2 exhibit positive charges at pH values less than 3.3, which creates a repulsive effect that prevents the antibiotics from adhering to the TiO_2 surface and further lowers photocatalytic effectiveness. Their negative charge further strengthens the repelling action at pH >7.68, and the double negative charge of

tetracycline increases the impact even more at pH >9.7. As a result, acidic and alkaline pH settings result in poor photocatalytic performance for tetracycline degradation over TiO_2, suggesting that neutral pH might be a better setting for the degradation process. For the photodegradation of sulfamethoxazole and ciprofloxacin, similar results were also reported [41]. However, Chen and Chu observed that the best norfloxacin degradation was seen at pH >10.5, when both the norfloxacin and Bi_2WO_6 displayed negative charges [42]. It could be explained by a higher amount of OH^- acting as a source of OH·, which may increase the concentration of OH· to enhance the degradation of tetracycline. Moreover, pH may have an impact on the existing form of photocatalyst. It was noted that when pH was around pH_{pzc}, particle agglomerations and rapid precipitation of RGO-WO_3 composites happened. Particle aggregation and poor dispersion could reduce the photocatalyst's reactive sites, which might lower light absorption and tetracycline adsorption and severely hinder the photocatalytic process. In short, pH influences the adsorption and photodegradation of tetracycline over photocatalysts [43].

Effect of Light Wavelength

The ability of the photocatalyst to be stimulated by a light source is directly determined by the wavelength of the light. The sulphanilamide degradation and mineralization efficiencies under LED-white light and blue light irradiations were higher than those under LED-green light and yellow light irradiations, according to research by Lim and colleagues [44]. This was explained by the fact that shorter wavelengths of light can produce photos with more energy, which can lead to an increase in the quantity of e^-/h^+ pairs that are produced by photos. Nonetheless, excessively high-energy photon light may result in light waste. As a result, it can be said that the wavelength of light affects the photocatalytic degradation efficiency of TC [45].

Effect of Dissolved Oxygen

To assess the impact of dissolved oxygen on the effectiveness of TC removal by nanosized TiO_2, the suspension was purged with nitrogen and air, respectively [46].

This suggested that when dissolved oxygen content rose, so did the elimination effectiveness of TC [47]. The aforementioned factors were identified as the cause: the generation rate of reactive oxygen species increased with the concentration of dissolved oxygen, which could lead to the formation of hydroxyl radical and singlet oxygen; and the recombination of photogenerated e^-/h^+ pairs was inhibited because conduction band electrons could be trapped by dissolved oxygen molecules [47,48].

Reactive species

The active species created by photoexcitation of semiconductors is, in principle, what initiates and completes the photocatalytic degradation of antibiotics. The intermediate products and degradation efficiency of antibiotic photodegradation are determined by the active species. Electron is stimulated from the valence band (VB) of semiconductors to the conduction band (CB) when a single component of photocatalyst is photoexcited [49]. This is followed by electron migration to the surface of the semiconductor. Next, the reduction of O_2 by e- on the semiconductor surface and the oxidation of H_2O or OH- by the left h^+ in VB produce reactive species, such as hydroxyl radicals (OH·), superoxide radicals (·O_2−), and holes (h+), which are dependent on their band structures and the reduction potentials (for O_2/·O_2−, OH·/H_2O and OH^-/ OH·) [50]. Some modifications, like changing the size and shape of the single component photocatalysts, adding metals to them, and supporting them with mesoporous materials,

may only alter the active sites for the generation of reactive species, which would delay the recombination of photogenerated e^-/h^+ pairs and enhance the photocatalytic performance. However, these adjustments don't alter the redox capacity of single-component photocatalysts. Figure 2. depicts the schematic illustration of the e^-/h^+ separation on photocatalysts under light irradiation [51]. When two semiconductors are illuminated under light irradiation, photogenerated electrons from CB of the semiconductor with lower reduction potential can migrate to VB of the semiconductor with lower oxidation potential which shows the electrostatic attraction between electrons and holes.

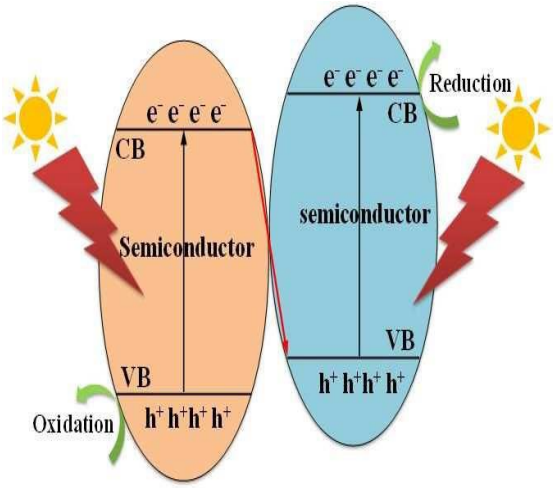

Figure 2: Schematic Illustration of the e^-/h^+ Separation on Photocatalysts under Light Irradiation[51]

The possible mechanism for photocatalytic degradation reaction can be summarized as follows [51]:

$$e^- + O_2 \rightarrow \cdot O_2^- \quad (1)$$

$$\cdot O_2^- + H^+ \rightarrow HO_2\cdot \quad (2)$$

$$HO_2\cdot + e^- + H^+ \rightarrow H_2O_2 \quad (3)$$

$$H_2O_2 + e^- \rightarrow OH\cdot + OH^- \quad (4)$$

$$h^+ + H_2O \rightarrow OH\cdot + H^+ \quad (5)$$

$$h^+ + OH^- \rightarrow OH\cdot \quad (6)$$

$$\text{Pollutant} + OH\cdot \rightarrow \text{intermediate} \rightarrow CO_2 + H_2O \quad (7)$$

Table 1: Different Photocatalysts along with the Reaction Conditions [30-51].

Photocatalyst	Initial TC Concentration (mg/L)	Light Source	Catalyst Dosage (g/L)	Time (h)	Degradation Efficiency (%)
BiOBr/BiOAc	20	Vis (500 W)	0.4	2	69.9%
g-C_3N_4/$Bi_4O_5I_2$	10	Vis (500 W)	1.0	4	≈9%
g-C_3N_4/BiOI	10	Vis (500 W)	1.0	4	≈17%
g-C_3N_4/Bi_5O_7I	10	Vis (500 W)	1.0	4	≈59%
PTI hollow tube/ ZnO	10	Vis (300 W)	0.2	1.5	97%
PVDF-TiO_2@ g-C_3N_4	50	Vis (300 W)	1.0	5.0	97%
$Bi_2W_2O_9$/g-C_3N_4	10	Sunlight (35 W)	1.0	1.5	95%
Ag/$Bi_2Sn_2O_7$-C_3N_4	20	UV (400 W)	1.0	1.5	89.1%
AgBr-TiO_2-Pal	10	Vis (300 W)	0.5	1.5	90%
$ZnIn_2S_4$/$BiPO_4$	40	Vis (300 W)	0.3	1.5	84%
$NiFe_2O_4$/SCNNR	10	Vis (40 W)	0.5	1.0	97%
AgI/$CuBi_2O_4$	10	Vis (300 W)	0.5	1.0	80%
In_2S_3/$InVO_4$	10	Vis (300 W)	0.5	1.0	71%
POPD-$CoFe_2O_4$	20	Vis (300 W)	0.5	1.0	69.9%
Ag/Ag_2S/Ag_3PO_4	20	Vis (400 W)	1.0	2.0	95%
γ-Fe_2O_3/b-TiO_2	10	Sunlight (300 W)	0.3	0.83	99.3%
Ag/Ag_2CO_3/ $BiVO_4$	20	Vis (500 W)	0.4	2.5	94.9%
Bi_4NbO_8Cl/g-C_3N_4	10	Vis (300 W)	1.5	3.0	78%
TiO_2-MIL-101(Cr)	10	Vis (300 W)	0.2	1.5	99.7%
In_2S_3@MIL-125(Ti)	46	Vis (300 W)	0.3	1.0	63.3%
β-Bi_2O_3/ $Bi_2O_2CO_3$	30	Sunlight (250 W)	1.0	1.0	98.79%
$CuBi_2O_4$/MoS_2	10	Vis (300 W)	0.5	2.0	76%
$In_{2.77}S_4$/WS_2	10	Vis (300 W)	0.5	0.33	87.5%

$CoO/BiVO_4$	40	Vis (300 W)	0.6	1.5	87.3%
$Ag/Ag_6Si_2O_7/Bi_2MoO_6$	20	Vis (300 W)	0.5	2.67	89.8%
BiOCl/BiOCOOH	20	Sunlight (300 W)	1.0	1.0	80.4%
MIL-88B@COF-200@10%PANI	50	Vis (500 W)	0.33	2.0	97.4%
Ag_2O/Ta_3N_5	10	Vis (300 W)	0.75	3.0	78.3%
$BiFeO_3/TiO_2$	10	Vis (300 W)	1.0	3.0	72.2%
$BiFeO_3/TiO_2$	10	UV (300 W)	1.0	3.0	67.9%
p-Ag_2S/n-$BiVO_4$	20	Vis (500 W)	0.4	2.5	90.2%
$BiOBr/Bi_2SiO_5$	20	Vis (300 W)	1.0	3.0	96.1%
m-Bi_2O_4/BiOCl	30	Vis (300 W)	0.5	2.5	85.5%
$Ag_3PO_4/CuBi_2O_4$	10	Vis (300 W)	0.5	1.0	75%
$CdTe/Bi_2WO_6$	20	Vis (300 W)	0.5	2.25	91.45%
AgI/Bi_5O_7I	20	Vis (300 W)	0.5	0.67	93.81%
$CuInS_2$/g-C_3N_4	10	Vis (300 W)	0.05	1.0	83.7%
MoS_2/Eu/Bg-C_3N_4	20	Vis (400 W)	0.4	0.83	99%
C-g-C_3N_4/WO_3	10	Vis (500 W)	1.0	1.0	75%
$AgI/BiVO_4$	20	Vis (300 W)	0.3	1.0	94.9%
γ-Fe_2O_3/g-C_3N_4	10	Vis (500 W)	0.5	2.0	73.8%
Ag_3PO_4/C_3N_5	20	Vis (300 W)	1.0	1.0	90.5%
Ag-C_3N_4/SnS_2	15	Vis (500 W)	0.4	2.5	≈90%
BiOBr/CDs/g-C_3N_4	20	Vis (300 W)	0.2	1.0	82.7%
BiOBr/CDs/g-C_3N_4	20	NIR light (300 W)	0.3	1.0	17.5%
BiOI/Ag@AgI	20	Vis (300 W)	0.3	1.0	86.4%
3D PANI/PDI	20	Vis (5 W)	0.5	2.0	70%
$Bi_{12}O_{15}Cl_6/Bi_2WO_6$	10	Vis (250 W)	0.5	1.0	81.2%
$AgBr/CuBi_2O_4$	10	Vis (300 W)	0.5	1.0	90%
CO_3O_4/Ag/Bi_2WO_6	10	Vis (300 W)	1.0	1.0	57.2%

CONCLUSIONS

The photocatalytic degradation of TC has been extensively studied using a variety of photocatalysts during the past few decades as it is the most common and persistent environmental pollutants, threatening ecological and human health worldwide. This review also highlights how TC endangers aquatic life, including plants and microbes in groundwater. A few investigation have compared and

systematically evaluated the various catalysts' photocatalytic activity during photocatalytic degradation. Various operating parameters, including light wavelength, TC concentration, pH, dissolved

oxygen and reactive species can influence the photodegradation of tetracycline. For the photocatalytic degradation of tetracycline, they ought to be tuned for maximum efficiency.

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