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Review Article

Photocatalysis for Environmental Remediation: Degradation of Pharmaceutical Pollutants

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ABSTRACT

Pharmaceuticals, used in human and veterinary medicine, pose a significant environmental and health threat due to their ecotoxicity and microbial resistance. Conventional treatment methods are ineffective, leading to research on advanced oxidation processes like visible-light-assisted semiconductor photocatalysis. This technology, which can use solar energy as a clean and sustainable light source, has significant potential for efficient, low-cost, and green remediation. This review paper aims to provide an overview of pharmaceutical pollution in aquatic environments, discussing its effects, sources, and mitigation strategies. It also reviews heterogeneous photocatalysis technology, which has been extensively studied and applied in wastewater treatment for the remediation of persistent pollutants like pharmaceuticals. The review paper also identifies barriers and gaps that need to be resolved shortly.

KEYWORDS: Heterojunctions; Photocatalysis; Pharmaceutical pollutants; Semiconductor; Water treatment,

INTRODUCTION

The world's water resources face a constant threat of contamination by both traditional and emerging pollutants stemming from human activities. Among these, "emerging pollutants" are particularly concerning due to their persistence and adverse effects on the environment and living organisms, even in trace amounts (μg L^{-1} to ng L^{-1}). Many of these emerging contaminants, including pharmaceuticals, remain unregulated. Pharmaceuticals, widely used to enhance human and animal health, pose significant environmental and health risks, such as ecotoxicity and microbial resistance. Conventional treatment methods have proven insufficient in addressing pharmaceutical pollution, prompting increased research into advanced technologies for their removal [1].

Among these advanced technologies, semiconductor photocatalysis has gained significant attention, with a notable rise in research publications between 2009 and 2017 [2]. Following the groundbreaking study by Fujishima and Honda on water splitting via semiconductor photocatalysis, this technology has been widely applied in various fields[3]. These applications include water splitting, CO_2 reduction for energy production, water treatment for disinfection, and degradation of persistent organic pollutants. In the context of increasing global energy and environmental concerns, visible-light-assisted photocatalysis emerges as a promising green technology. It utilizes efficient, low-cost, and eco-friendly photocatalysts, with sunlight serving as a clean and sustainable energy source [4].

A brief overview of pharmaceuticals and their removal technologies

Pharmaceuticals, designed to treat diseases and promote growth in both humans and animals, have become a significant concern regarding environmental contamination. The presence of these substances in surface and groundwater was first detected in Europe and the United States during the 1960s. However, it wasn't until the 1990s that the detrimental impacts of pharmaceuticals on aquatic organisms and their terrestrial consumers became evident through various studies[5]. Despite being present in extremely low concentrations, pharmaceuticals still pose a considerable threat to the environment [6]. This ongoing issue is exacerbated by the continuous introduction of these substances into aquatic systems, leading to their pseudo-persistence, even though they might have relatively short half-lives.

The complexity of pharmaceuticals is reflected in their varied nature, encompassing different chemical structures, purposes, dosages, and metabolic processes within human and animal bodies, as well as their behavior in the environment. Each pharmaceutical compound interacts differently with environmental elements, which complicates the understanding and mitigation of their effects. The diverse usage patterns and breakdown mechanisms of these substances contribute to the challenge of managing their presence in water systems. As pharmaceuticals are metabolized and excreted, they enter wastewater and eventually find their way into natural water bodies, perpetuating their presence and impact on the ecosystem. This intricate interplay between pharmaceuticals and the environment underscores the necessity for advanced research and innovative solutions to address the persistent threat posed by these emerging contaminants [7].

Pharmaceuticals in the aquatic environment

The global production and use of pharmaceuticals for both human and veterinary purposes reach thousands of tons annually. Pharmaceuticals enter the environment through various channels, including residential areas, hospitals, agricultural activities, aquaculture, and livestock farming. After consumption, pharmaceuticals are not completely metabolized and are excreted by humans and animals in both their original (parent pharmaceuticals) and altered (transformed products) form [8]. Wastewater treatment plants (WWTPs) primarily receive these pharmaceuticals through human excretion, the disposal of unused medications and untreated effluents from pharmaceutical industries.

Numerous studies have highlighted that, although WWTPs are effective at removing certain pharmaceuticals, such as analgesics and anti-inflammatory drugs, their efficiency in removing other therapeutic classes like antiepileptics, antibiotics, and trimethoprim is often very low or nonexistent. Consequently, WWTP effluents containing residual pharmaceuticals are discharged into surface waters, while sludge containing sorbed pharmaceuticals is either landfilled or applied as manure in agriculture [9]. Waste from pharmaceutical industries is also disposed of in municipal solid waste landfills. Additionally, excretory products from livestock, often used as fertilizers, can result in pharmaceuticals running off into surface waters or leaching into groundwater from farms and landfills.

Advancements in analytical techniques have enabled the detection of pharmaceuticals in the environment at concentrations as low as ng L^{-1}. Numerous global studies have documented the presence of these contaminants in various aquatic environments, including surface and groundwater sources used for drinking water supplies [10].

Impacts on the environment and human health

Pharmaceuticals are typically bioactive, resistant to degradation, and capable of accumulating in organisms [11]. These traits contribute to significant adverse effects, such as endocrine disruption, reproductive abnormalities, bacterial resistance, and eco-toxicity, even at low concentrations. Moreover, their metabolites can be more hazardous than the parent compounds [12]. Numerous studies, including comprehensive reviews, have documented the toxic effects of pharmaceuticals on living organisms.

Beyond their environmental toxicity, the extensive use of human and veterinary antibiotics fosters bacterial resistance. A notable study identified 56,000 resistance genes against nearly all classes of antibiotics, including those that facilitate genetic material transfer, in an Indian lake contaminated by pharmaceutical industry effluent[12]. This antibiotic resistance poses a significant threat to human health as environmental bacteria transfer resistance genes to human pathogens. The rapid escalation of antibiotic resistance remains a critical challenge for global healthcare.

To establish effective monitoring policies, a study identified 40 priority pharmaceuticals, including antibiotics, analgesics/anti-inflammatory drugs, antiepileptic/psychiatric medications, lipid regulators, β-blockers, and a diuretic, along with their metabolites, based on their potential ecotoxicity in specific regions. Another study highlighted thyroid hormones, analgesics, antihypertensive drugs, antibiotics, antiulcers, bronchodilators, antidiabetics, antidepressants, diuretics, and antiasthmatics as high-priority pharmaceuticals. Additionally, research indicated that certain antibiotics, psychiatric drugs, analgesics–anti-inflammatories, lipid regulators, and beta-blockers pose medium to high risks. Experiments with combinations of various pharmaceuticals revealed more potent effects than those observed with individual pharmaceuticals. Dietrich et al. reported that pharmaceutical mixtures exhibited different toxicological effects on daphnids compared to the individual pharmaceuticals [13].

Major sources of pharmaceuticals

Every year, massive quantities of pharmaceuticals are produced and extensively utilized in both human and veterinary medicine [14]. More than 200 types of pharmaceutical compounds, including painkillers, vascular drugs, antibiotics, and antidepressants, are frequently detected in aquatic and terrestrial environments, with concentrations ranging from a few nanograms per liter (ng/L) to thousands of micrograms per liter (μg/L). Consequently, understanding the sources and fates of these pharmaceuticals in the environment is crucial for developing effective strategies to prevent their entry into water supplies [15].

Pharmaceuticals can enter aquatic ecosystems through multiple pathways. Figure 1 depicts the potential sources and pathways of pharmaceuticals in the environment. Four primary sources contribute to the presence of pharmaceuticals in aquatic environments: human use, veterinary use, agricultural and farming practices, and industrial production [16]. Pharmaceuticals can reach water sources through emissions from healthcare facilities (such as hospitals and clinics) and households (including private residences, dormitories, hotels, and residential care facilities). Among these, hospitals are a significant source of pharmaceutical contaminants, primarily through patient excretions [17].

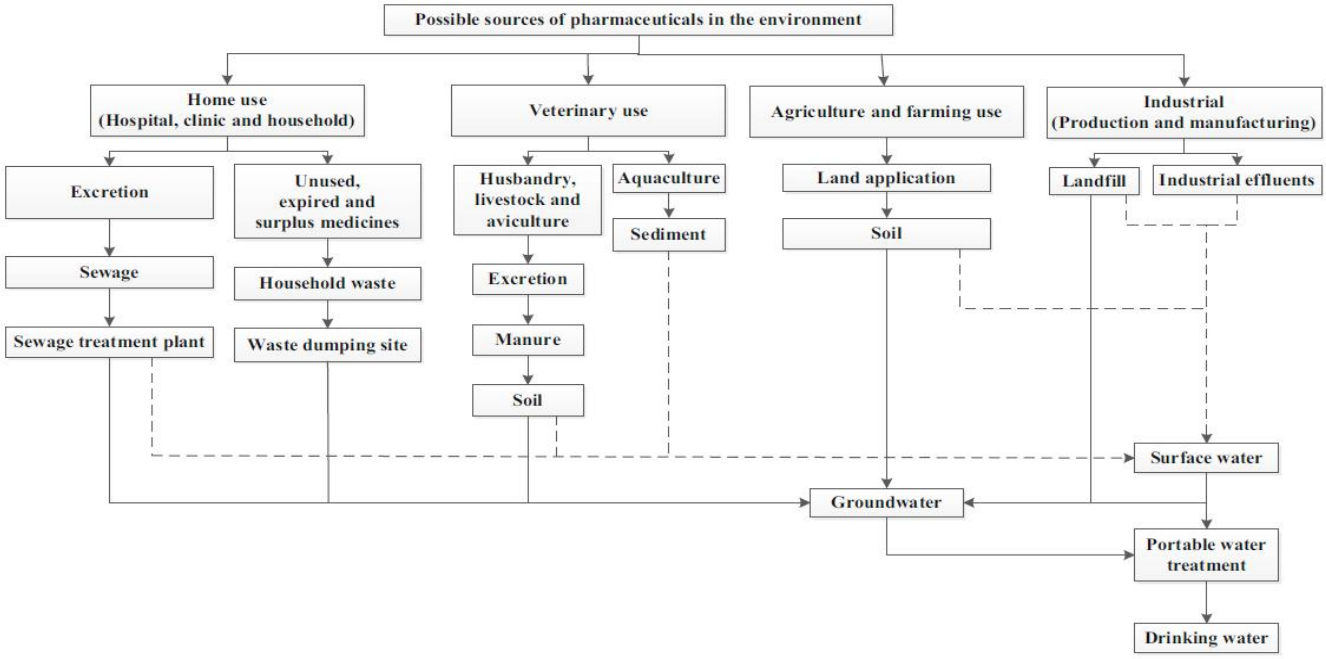

Figure 1: Possible sources of pharmaceuticals in the environment.

After human consumption, excreted residues (feces and urine) may enter the sewage system as either the original parent compound or as metabolites. Depending on their properties, only a portion of these pharmaceuticals is removed by conventional microbiological treatments in wastewater treatment plants (WWTPs), while the remaining residues are discharged and dispersed into aquatic environments [18]. As a result, WWTPs are often considered the primary route through which pharmaceuticals enter the environment, leading to widespread and continuous contamination. Additionally, the improper disposal of unused, expired, and surplus pharmaceuticals down drains or toilets represents another significant pathway for environmental contamination. These pharmaceuticals can potentially infiltrate groundwater systems depending on the local hydrology [19].

REMOVAL TECHNOLOGIES

Although traditional wastewater treatment plants (WWTPs) are effective at breaking down biodegradable organic wastes, they face significant challenges in removing pharmaceuticals, which each have unique and resistant properties. Biological processes like activated sludge are largely ineffective against many toxic and recalcitrant pharmaceuticals. Similarly, physicochemical processes such as coagulation, flocculation, sedimentation, and filtration result in minimal removal and negligible degradation. The limitations of WWTPs are highlighted by various studies that report significant concentrations of pharmaceuticals in WWTP effluents. This underlines the necessity for alternative advanced treatment methods [20].

Advanced treatment methods such as adsorption, membrane processes, and advanced oxidation processes (AOPs) are commonly employed to address a wide range of pollutants in water systems. Adsorption is an effective and cost-efficient method for removing pharmaceuticals but results in the transfer of pollutants to the adsorbent, creating new solid waste with high concentrations of pharmaceuticals [21]. Membrane processes can also remove pharmaceuticals effectively; however, they are hindered by high operating costs,

pressure requirements, membrane fouling, and limitations in handling large volumes. Furthermore, this method does not degrade pollutants but instead concentrates them on the membrane [22].

AOPs are promising methods, categorized into ozone-based, chemical, UV-based, catalytic, electrochemical, and physical processes, generating powerful oxidizing agents (such as hydroxyl radicals) capable of degrading and mineralizing pharmaceuticals. While electrochemical AOPs can handle high concentrations of pharmaceuticals, they are limited by high costs and low flow rates [23]. Ozone-based AOPs are effective in degrading many pharmaceuticals but face high operational costs, low mineralization efficiencies, and the formation of toxic intermediates. UV-based AOPs like UV photolysis are less effective without additional oxidizing agents, and processes like UV/H_2O_2 and UV/$S_2O_8^{2-}$ are not entirely clean due to the use of chemical oxidants.

Fenton processes, using iron salts and hydrogen peroxide, effectively degrade a wide range of pharmaceuticals but are limited by a narrow pH range and the need for additional treatment to remove dissolved ions [24]. Heterogeneous Fenton systems have overcome some of these drawbacks. Additionally, combining AOPs with membrane filtration and biological processes can enhance the efficiency of pharmaceutical wastewater treatment.

A recent review categorized AOPs based on energy efficiency into three groups: highly energy-efficient AOPs (median EEO values < 1 kWh/m³) like O_3, O_3/H_2O_2, O_3/UV, UV/H_2O_2, UV/$S_2O_8^{2-}$, UV/Cl_2, and electron beam; medium energy-efficient AOPs (median E_{EO} values 1–100 kWh/m³) like photo-Fenton, plasma, and electrolytic AOPs; and low energy-efficient AOPs (median E_{EO} values > 100 kWh/m³) like UV-based photocatalysis, sonolysis, and microwave-based AOPs. While sonolysis and microwave processes are energy-intensive and unsuitable for large-scale applications, visible light photocatalysis, utilizing sunlight as a renewable energy source, offers a green and self-sustaining solution despite being energy-consuming [25].

Semiconductor photocatalysis

In semiconductor photocatalysis, when photon energy (hv) exceeds the bandgap energy (E_g) of a semiconductor, it excites an electron (e^-) from the valence band (VB) to the conduction band (CB), creating a hole (h^+) in the VB. This process is expressed by the following equation:

Photocatalyst + hv → e− + h^+ (1)

h+ + H_2O → OH· + H+ (2)

Pollutant + OH· → intermediate → CO_2 + H_2O (3)

e− + O_2 → $\cdot O_2-$ (4)

$\cdot O_2-$ + H+ → $HO_2\cdot$ (5)

$HO_2\cdot$ + e− + H^+ → H_2O_2 (6)

H_2O_2 + e− → OH· + OH− (7)

$\cdot O_2-$ + pollutant → CO_2 + H_2O (8)

$HO_2\cdot$ + pollutant → CO_2 + H_2O (8)

The separated charge carriers (electrons and holes) then migrate to the catalyst surface, where they engage in redox reactions with pollutants adsorbed on the surface. The holes can oxidize OH^- or H_2O to produce hydroxyl radicals (·OH), a potent oxidizing agent. Meanwhile, the electrons reduce oxygen adsorbed on the catalyst surface to form superoxide radicals ($O_2\cdot^-$), which may subsequently generate hydroperoxyl radicals ($\cdot HO_2$) and hydrogen peroxide (H_2O_2). Hydrogen peroxide can further decompose

under light to produce additional hydroxyl radicals. These reactive oxygen species (ROS), including ·OH, $O_2{\cdot}^-$, $\cdot HO_2$, and H_2O_2, degrade and mineralize stubborn organic pollutants into harmless end products such as CO_2 and H_2O.

The photogenerated holes can also directly oxidize organic pollutants, depending on the reaction conditions and the catalyst used. Eventually, the electron-hole pairs may recombine on the catalyst surface or in the bulk medium, releasing light or heat [4].

The efficiency of a photocatalyst is determined by three key factors. Bandgap energy (Eg): A wide bandgap makes the photocatalyst sensitive to UV light, while a narrow bandgap makes it sensitive to visible light. Band edge potentials: For ROS generation, the CB potential must be more negative than the reduction potential of O_2 to $O_2{\cdot}^-$ (−0.33 eV vs. NHE), and the VB potential must be more positive than the standard oxidation potential of ·OH/H_2O (+2.68 eV vs. NHE) or ·OH/OH^- (+1.99 eV vs. NHE). If not, the holes in the VB react directly with the pollutants. More ROS generation leads to higher semiconductor efficiency. Rate of recombination of electron-hole pairs: Recombination reduces catalyst efficiency, as it causes electrons to return to the VB without performing the reduction reaction to form $O_2{\cdot}^-$. Therefore, selecting a photocatalyst involves careful consideration of these three factors to maximize efficiency [26].

Visible light photocatalysts for pharmaceuticals removal

Various wide-bandgap semiconductors like TiO_2 and ZnO have been extensively utilized as photocatalysts for degrading a wide array of organic pollutants, including pharmaceuticals. The widespread use of TiO_2 is due to its excellent chemical stability, low cost, eco-friendly nature, and exceptional electronic and optical properties. Numerous studies have demonstrated the effectiveness of TiO_2 under UV light for photodegrading a broad spectrum of pharmaceuticals in various aqueous environments [27]. For instance, Palominos et al. achieved complete degradation and significant mineralization of tetracycline using both TiO_2 and ZnO under simulated solar light. Similarly, Pereira et al. reported complete degradation of oxytetracycline using TiO_2 under simulated solar light. However, these wide-bandgap photocatalysts face challenges such as rapid charge recombination and sensitivity only to UV light, which constitutes a mere 4-5% of the solar spectrum, thus limiting their practicality for large-scale applications. In contrast, narrow-bandgap photocatalysts, which are sensitive to visible light (constituting about 52% of the solar spectrum), offer a greener and more sustainable solution for degrading stubborn organic pollutants [28].

Unmodified semiconductor photocatalysts

Visible light photocatalysts, such as graphitic carbon nitride (g-C_3N_4), have gained popularity due to their metal-free composition, narrow bandgap (2.7 eV), high chemical stability, and effective response to visible light. Hernández-Uresti et al. demonstrated the successful use of g-C_3N_4 for photodegradation of tetracycline (TC) and ciprofloxacin (CIP) under UV-visible irradiation [29]. However, the generation of hydroxyl radicals (·OH) is limited by the more negative valence band (VB) potential of g-C_3N_4 compared to the standard redox potentials of ·OH/H_2O and ·OH/OH. Additionally, rapid recombination of photogenerated electron-hole (e^-/h^+) pairs remains a significant drawback for pure g-C_3N_4 as a photocatalyst.

Bismuth oxyhalides (BiOX, where X = F, Br, Cl, and I) are another class of visible-light-active photocatalysts known for their narrow bandgap and low electron-hole

recombination rates due to their layered structure with an internal static electric field. Among these, BiOI, with a bandgap of approximately 1.85 eV, has a high surface-to-volume ratio and anti-aggregation properties, making it an effective photocatalyst. Hao et al. synthesized mesoporous BiOI microspheres for the adsorption and subsequent degradation of tetracycline hydrochloride (TCH) [30]. Other studies have reported the use of BiOBr microspheres for the photocatalytic degradation of ibuprofen (IBP) and hierarchical $Bi_{24}O_{31}Br_{10}$ nanoflakes for efficient TCH degradation in real wastewater. Hierarchical BiOCl microspheres were also used for carbamazepine (CBZ) degradation using a solar light simulator.

Bismuth-based transition metal oxides, such as $BiVO_4$ and $BiFeO_3$, have shown potential as visible light photocatalysts for pharmaceutical degradation. $BiVO_4$, with a bandgap of ~2.4 eV, is chemically stable but suffers from poor electron-hole pair separation. $BiFeO_3$, with a bandgap of 1.97 eV, has been used for the degradation of TC. Layered perovskites like Bi_2WO_6 have been effective in inhibiting electron-hole recombination, leading to efficient degradation of norfloxacin (NOR) and TC. Hailili et al. synthesized a 3D hierarchically nanostructured $Bi_5FeTi_3O_{15}$ perovskite for TC degradation, benefiting from the efficient charge transfer between Fe^{3+} and Ti^{4+} and the individual layers, as well as an extended light absorption range and magnetic properties aided by Fe [31].

Transition metal sulfides, such as In_2S_3 and $ZnIn_2S_4$, have also shown promising visible light photocatalytic efficiency and resistance to photochemical corrosion. In_2S_3, with a bandgap of ~2.3 eV, was used for TC degradation under natural sunlight, while $ZnIn_2S_4$ was employed for visible light degradation of CBZ. To achieve efficient visible-light-induced photocatalysis, semiconductors should possess narrow band gaps, low charge recombination rates, and strong redox ability. However, a single photocatalyst rarely meets all these criteria simultaneously. For robust redox reactions and reactive oxygen species (ROS) formation, the photocatalyst's bandgap must be large enough to ensure the respective bandgap edge is sufficiently more negative than the reduction potential of $O_2{\cdot}^-/O_2$ and more positive than the oxidation potential of $\cdot OH/H_2O$. Unfortunately, a large bandgap prevents the utilization of visible light. Various modification strategies are necessary to overcome these limitations and enhance photocatalytic efficiency [32].

Semiconductor photocatalysts doped with metals and nonmetals

Doping wide-bandgap photocatalysts with metals (e.g., Sr, Bi, Fe) and nonmetals (e.g., C, N, S, B) is an effective strategy to narrow their bandgap and enhance their visible light activity and electron-hole (e^-/h^+) separation. The incorporation of dopants introduces impurity energy levels within the bandgap, enabling the utilization of visible light and reducing e^-/h^+ recombination. However, the dopant content must be optimized as excessive doping can facilitate charge recombination. For example, TiO_2 tri-doped with optimal amounts of C, N, and S has been successfully used for tetracycline (TC) degradation. This tri-doping narrows the bandgap, expanding the photocatalyst's light-harvesting capacity, while carbonaceous species act as photosensitizers, injecting electrons into the conduction band (CB) of the photocatalyst [33]. Similarly, C-sensitized and N-doped TiO_2 has been developed for the photocatalytic degradation of sulfanilamide (SNM). Additionally, C-doped g-C_3N_4, synthesized using an aqueous spray drying process, has demonstrated effective solar-light-assisted degradation of TC. This C-doping modifies the band edge potentials of g-C_3N_4, narrowing the bandgap and reducing e^-/h^+ recombination, thereby

enhancing visible light activity. Other studies include the use of N-doped TiO_2 for degrading spiramycin (SP) and B-doped TiO_2 for degrading ibuprofen (IBP) and flurbiprofen (FLU).

Metal-doped semiconductor photocatalysts have also shown significant potential. For instance, Sr-doped β-Bi_2O_3 has been used for TC degradation. Strontium titanate ($SrTiO_3$), a wide-bandgap semiconductor (Eg = 3.2 eV), is responsive to UV light and has good photochemical stability and biocompatibility. Fe^{3+}-doped $SrTiO_3$, for example, has exhibited excellent TC degradation due to the transfer of electrons to the CB from an impurity energy level created by the dopant near the VB edge, effectively narrowing the bandgap . Additionally, Cr- and Mn-doped $SrTiO_3$ have found to be efficient photocatalysts for TC degradation. Other notable examples include Bi^{3+} self-doped $NaBiO_3$ for the degradation and mineralization of carbamazepine (CBZ) and Cu-doped TiO_2 for paracetamol (PAR) degradation [34].

Vacancy engineered photocatalysts

Surface and crystal structures significantly impact a semiconductor's physicochemical properties. Defects like vacancies introduce new energy levels in the band structure, reducing bandgap energy and broadening the light-harvesting range. Oxygen vacancies (OVs) are crystal defects that form OV states, which narrow the bandgap and make the semiconductor responsive to visible light. OVs also act as photogenerated charge-trapping sites, increasing electron-hole (e^-/h^+) pair separation. Vacancy-engineered photocatalysts have been used for visible light photocatalysis of pharmaceuticals. Figure 2. shows a general mechanism of visible-light-assisted pharmaceutical degradation by vacancy-engineered photocatalyst.

Yu et al. synthesized OV-rich $Bi_2O_2CO_3$ (OV-BOC) using a solution precipitation method, showing greater TCH degradation efficiency under visible light compared to BOC [35]. Hailili et al. synthesized OV-rich $CaCu_3Ti_4O_{12}$ photocatalyst for TC degradation, with ample OVs and surface defects making it visible light active and acting as electron capture sites [36]. However, there are few reports on vacancy-engineered photocatalysts for pharmaceutical degradation, leaving room for further research.

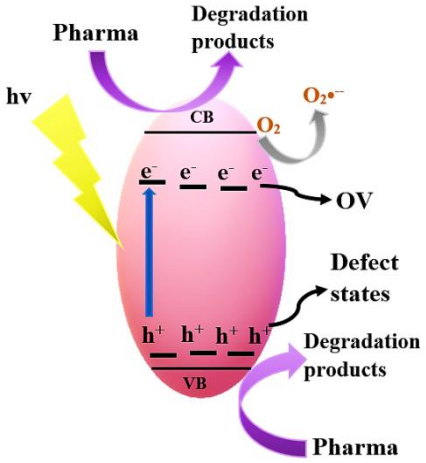

Figure 2: Mechanism of visible-light-assisted pharmaceutical degradation by vacancy-engineered photocatalyst [37].

Semiconductor photocatalysts with heterojunctions

Heterojunctions offer advantages in photogenerated electron-hole (e^-/h^+) pair separation, leveraging the combined benefits of individual semiconductors. Unlike doping methods, heterojunctions are more effective in broadening the solar light absorption spectrum. A type II heterojunction configuration, where the conduction band (CB) and valence band (VB) levels of semiconductor 1 (S1) are higher than those of semiconductor 2 (S2), is depicted in Figure 3 and described in the literature [38].

In a type II heterojunction, which can exist between a p-type and an n-type

semiconductor, the p-type has higher band edge levels and a higher work function than the n-type (Fig. 3c). Upon contact, free electrons flow from the n-type to the p-type until equilibrium is achieved (Fig. 3d), creating positively charged n-type and negatively charged p-type semiconductors at the interface. This results in an internal electric field and a potential barrier due to band edge bending [39].When exposed to light, this electric field facilitates the transport of photogenerated electrons from the CB of the p-type to the CB of the n-type and photogenerated holes from the VB of the n-type to the VB of the p-type (Fig. 3e), enhancing e−–h+ pair separation.

Heterojunctions are classified into two types based on the charge carrier flow mechanism: (1) heterojunctions with unidirectional charge flow and (2) heterojunctions with bidirectional charge flow.

Unidirectional Charge Flow in Heterojunctions

In unidirectional charge flow heterojunctions (Fig. 3a), only semiconductor 1 (S1) is photoactive under incident light, generating electron-hole (e−–h+) pairs. The photogenerated electrons on the conduction band (CB) of S1 flow to the CB of semiconductor 2 (S2), while S2, which cannot generate e−–h+ pairs under the given lighting conditions, does not transfer photogenerated holes from its valence band (VB) to the VB of S1. Thus, the charge flow is unidirectional, with electrons accumulating on the CB of S2 and holes on the VB of S1 participating in degradation reactions if the band edge potentials of the semiconductors are suitable for reactive oxygen species (ROS) formation. For example, BiOI, a p-type visible-light-active semiconductor, experiences fast recombination of photogenerated e^-/h^+ pairs, while SnO_2, an n-type semiconductor with a broad bandgap, has a poor visible light response. Their heterojunction enhances photocatalytic efficiency for OTC degradation due to increased e^-/h^+ separation, with SnO_2 acting as an electron. Wang et al. reported a core-shell In_2S_3@MIL-125(Ti) photocatalyst for TC degradation, where visible-light-active In_2S_3 was coupled with the unstable MIL-125(Ti) photocatalyst, which lacks a visible light response [40]. Similarly, In_2S_3/Zn_2GeO_4 photocatalyst showed improved visible light absorption and greater e^-/h^+ pair separation, enhancing acetaminophen (APAP) degradation.

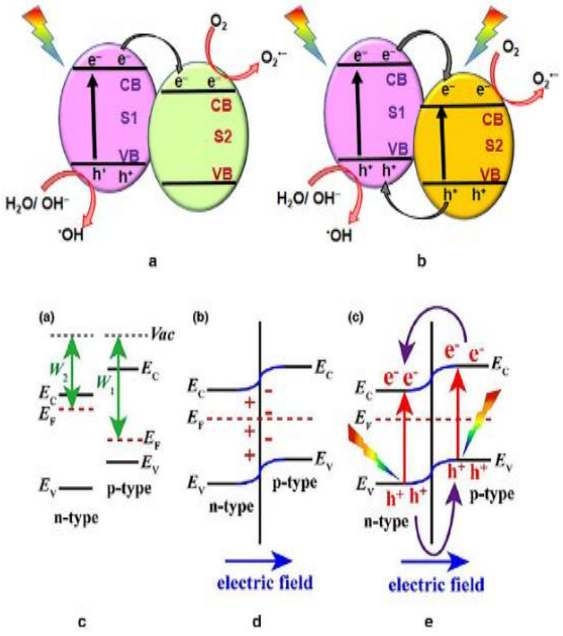

Figure 3: Schematic of (a) heterojunctions with unidirectional charge flow and (b) heterojunctions with bidirectional charge flow; schematic of p–n junction: (c) before contact (d) after contact (e) transfer of photogenerated charge carriers in p–n junction mode [38].

Graphitic carbon nitride (g-C_3N_4) has been used to form heterojunction systems with other semiconductors acting as sinks for photogenerated charge carriers, enhancing photocatalytic efficiency under visible light. For instance, Jiang et al. created a 2D–2D heterostructure with g-C_3N_4 and $K^+Ca_2Nb_3O_{10}^-$ perovskite nanosheets for efficient TCH degradation. This structure

provided a large contact area for fast interfacial charge separation and broadened the optical window for effective light harvesting compared to 0D–2D and 1D–2D heterostructures.

All the studies mentioned used visible light to activate only one semiconductor. Investigating systems containing both UV and visible-light-active photocatalysts under solar light is crucial. Hong et al. synthesized a Nb_2O_5/g-C_3N_4 heterojunction photocatalyst and studied its efficiency under both visible and solar light for pharmaceutical degradation, finding enhanced efficiency under solar light due to e^-/h^+ pair photogeneration in both semiconductors compared to single photocatalyst excitation under visible light [41]. This system demonstrates the best output under solar light.

Bidirectional Charge Flow in Heterojunctions

In bidirectional charge flow heterojunctions (Fig. 3b), both semiconductors generate electron-hole (e^-/h^+) pairs under incident light. Photogenerated electrons on the conduction band (CB) of semiconductor 1 (S1) flow to the CB of semiconductor 2 (S2), while photogenerated holes on the valence band (VB) of S2 flow to the VB of S1, resulting in bidirectional charge flow. The accumulated electrons and holes on the CB of S2 and the VB of S1 actively participate in degradation reactions, provided the band edge potentials of the semiconductors are suitable for reactive oxygen species (ROS) formation.

Several examples of this system using purely visible light have been reported. Ren et al. synthesized a magnetic $NiFe_2O_4/Bi_2O_3$ heterojunction system for the photocatalytic degradation of TC, with both semiconductors being visible light active due to their narrow bandgaps. Similarly, g-C_3N_4 has been combined with narrow bandgap semiconductors $Bi_4O_5Br_2$ and Bi_2WO_6 to form heterojunctions that effectively degrade CIP and IBP, respectively. Additionally, Shi et al. used CdS QDs/N-doped TiO_2 photocatalyst to effectively mineralize diclofenac (DCF) [42].

There are also examples of this system using solar light irradiation. Hong et al. synthesized a Nb_2O_5/g-C_3N_4 heterojunction photocatalyst for the degradation of TCH, CIP, and levofloxacin (LEV) under simulated solar light.[41] Bi_2O_3 has been coupled with wide-bandgap semiconductors such as $(BiO)_2CO_3$ and TiO_2 to form heterojunctions that utilize both the UV and visible spectra of solar radiation to efficiently degrade CIP and OFL, respectively. While heterojunctions enhance charge separation, this often comes at the expense of the redox ability of electrons and holes, potentially limiting the completion of specific photocatalytic reactions. To address this, composite semiconductor systems with or without redox mediators have been developed to overcome this limitation [38]. Table 1. depicts the efficiencies of different photocatalysts for degradation of pharmaceuticals.

Table 1: Efficiency of photocatalysts for degradation of pharmaceuticals

Photocatalyst	Pharmaceutical	Conditions	Degradation efficiency/ time (min)	References
$Bi_5FeTi_3O_{15}$	TC	TC: 4.45 mg L^{-1} Catalyst: 0.4 g L^{-1} 300 W Xe lamp with 420-nm cutoff filter	99.34%/60	43
BiOBr	IBP	IBP: 10.31 mg L^{-1} Catalyst: 1 g L^{-1} 500 W Xe lamp with UV cutoff filter pH: 4–9	80%/120	44
BiOCl	CBZ	CBZ: 2.5 mg L^{-1} Catalyst: 0.5 g L^{-1} 350 W Xe lamp Solar simulator pH: 9	100%/150	45
$ZnIn_2S_4$	CBZ	CBZ: 0.1 mg L^{-1} Catalyst: 0.03 g L^{-1} 100 W I-Ga lamp pH: 9	100%/20	46
g-C_3N_4	OFL	OFL: 10 mg L^{-1} Catalyst: 0.5 g L^{-1} Solar simulator pH: 7.7	100%/10	47
Bi_2WO_6	NOR	NOR: 10 mg L^{-1} Catalyst: 0.5 g L^{-1} 300 W Xe lamp Solar simulator	83.7%/20	48
B-doped TiO_2	IBP, FLU	IBP, FLU: 20 mg L^{-1} Catalyst: 1 g L^{-1} Visible light pH: 6.5	IBP: 79.4%/240 FLU: 71%/240	49
Cu-doped TiO_2	PAR	PAR: 50 mg L^{-1}	100%/180	50

		Catalyst: 4 g L^{-1} Visible light pH: 6		
Bi^{3+} self-doped $NaBiO_3$	CBZ	CBZ: 4.725 mg L^{-1} Catalyst: 1 g L^{-1} 500 W Xe lamp with 420-nm cutoff filter pH: 6	99.8%/60	34
C-doped g-C_3N_4	TC	TC: 44.4 mg L^{-1} Catalyst: 0.5 g L^{-1} Sunlight	> 90%/90	26
C-sensitized and N-doped TiO2	SNM	SNM: 5 mg L^{-1} Catalyst: 1 g L^{-1} LED light	95%/300	51
$Bi_2O_2CO_3$ with OV	TCH	TCH: 10 mg L^{-1} Catalyst: 1 g L^{-1} 500 W Xe lamp with 420-nm cutoff filter	50%/300	35
Ag-doped hollow TiO_2	Metronidazole (MTZ)	MTZ: 30 mg L^{-1} Catalyst: 0.5 g L^{-1} 125 W Hg lamp	94.77%/120	52
Ag/g-C_3N_4	DCF	DCF: 100 mg L^{-1} Catalyst: 0.1 g L^{-1} 300 W Xe lamp with UV cutoff filter	100%/120	53
Ag/$AgIn_5S_8$	TCH	TCH: 10 mg L^{-1} Catalyst: 0.4 g L^{-1} 300 W Xe lamp with 400-nm cutoff filter	95.3%/120	54
Ag/Bi_3TaO_7	TC	TC: 10 mg L^{-1} Catalyst: 0.5 g L^{-1} 250 W Xe lamp with 420-nm cutoff filter	85.42%/120	55
Ag-decorated monodisperse TiO_2	OTC	OTC: 0.5 mg L^{-1} Catalyst: 0.5 g L^{-1} 2 nos. 15 W	100%/45	56

		fluorescent lamps with/without UV filter pH: 5.8		
$Cu–BiVO_4$ $Ag–BiVO_4$	IBP	IBP: 10 mg L^{-1} Catalyst: 0.8 g L^{-1} 300 W Xe lamp with 420-nm cutoff filter	$Cu–BiVO_4$: 89%/300 $Ag–BiVO_4$: 96%/300	13
$g\text{-}C_3N_4/K^+Ca_2Nb_3O_{10}^-$	TCH	TCH: 35 mg L^{-1} Catalyst: 1 g L^{-1} 500 W tungsten lamp	81%/90	57
In_2S_3/Zn_2GeO_4	APAP	APAP: 5 mg L^{-1} Catalyst: 1 g L^{-1} Xe lamp with cutoff filter pH: 9	95%/360	58
SnO_2/BiOI	OTCH	OTCH: 10 mg L^{-1} Catalyst: 1 g L^{-1} 300 W Xe lamp with 420-nm cutoff filter pH: 5.49	94%/90	39
In_2S_3@MIL–125(Ti)	TC	TC: 46 mg L^{-1} Catalyst: 0.3 g L^{-1} 500 W Xe lamp with 420-nm cutoff filte	63.3%/60	40
$g\text{-}C_3N_4/Bi_2WO_6$	IBP	IBP: 5.16 mg L^{-1} Catalyst: 0.2 g L^{-1} 300 W Xe lamp with 420-nm cutoff filter	96.1%/60	59
$Nb_2O_5/g\text{-}C_3N_4$	TCH, CIP, LEV	TCH, CIP, LEV: 20 mg L^{-1} Catalyst: 1 g L^{-1} 250 W Xe lamp Solar simulator	TCH: 90.2%/60 CIP: > 60%/60 LEV: > 70%/60	41

		pH: 3		
Bi_2O_3/TiO_2	OFL	OFL: 25 mg L^{-1} Catalyst: 0.5 g L^{-1} Sunlight pH 7	92%/120	60
g-$C_3N_4/Bi_4O_5Br_2$	CIP	CIP: 10 mg L^{-1} Catalyst: 0.5 g L^{-1} 300 W Xe lamp with 400-nm cutoff filter Solar simulator	50%/30	61
$NiFe_2O_4/Bi_2O_3$	TC	TC: 10 mg L^{-1} Catalyst: 1 g L^{-1} 150 W Xe lamp with 420-nm cutoff filter	90.78%/90	42

EFFECT OF PARAMETERS ON PHARMACEUTICAL REMOVAL

Photocatalyst dosage

The dosage of photocatalyst is crucial for the effective photocatalytic degradation of pharmaceuticals. Increasing the amount of catalyst enhances the surface area and provides more active sites, which improves adsorption and boosts photocatalytic activity [43]. However, there is a limit to this benefit. Beyond a certain point, adding more photocatalyst can actually reduce efficiency. Excessive catalyst concentration can cause the solution to become turbid, which impedes light penetration and results in only a small portion of the catalyst, typically near the reactor walls, receiving adequate light. Additionally, a high dosage can lead to agglomeration and sedimentation of the photocatalyst, reducing its effective surface area. For instance, Kumar et al. found that during sulfamethoxazole (SMX) degradation, the apparent rate constant (k_{app}) increased with photocatalyst dosage up to 400 mg L−1 but then decreased with further increases [44]. Thus, optimizing the photocatalyst dosage is essential for achieving maximum efficiency and cost-effectiveness. The optimal dosage will depend on the specific pollutant being treated [45].

Light wavelength

The generation of photogenerated charge carriers is directly proportional to light intensity. As the intensity increases, more photons strike the photocatalyst, producing a higher number of electron-hole (e−–h+) pairs, leading to increased reaction rates [46]. Research has shown that higher light intensity can accelerate the degradation rate of pharmaceuticals. Additionally, light intensity diminishes with increasing distance from the light source. Belver et al. found that the highest photonic efficiency of the catalyst was achieved at an intensity lower than that which produced the highest reaction rate. This suggests that simply increasing light intensity does not necessarily enhance the separation of e−–h+ pairs [47-49].

The wavelength of light also significantly influences the degradation rate. Wang et al. investigated the effects of different light-emitting diode (LED) strips with identical intensities but different emission wavelengths: white (W, 450 nm), blue (B,

465 nm), green (G, 523 nm), and yellow (Y, 589 nm). The study revealed that the degradation and mineralization efficacies of sulfanilamide (SNM) under various irradiations followed the order W > B > G > Y [49-50].

pH

For effective photocatalytic degradation, pollutants must come into contact with the photocatalyst surface. Pollutants adsorbed onto the photocatalyst surface degrade more rapidly than those in the bulk solution, primarily because short-lived charge carriers are less likely to be lost through migration or diffusion [51-52]. Enhanced adsorption on the photocatalyst surface generally leads to more efficient pollutant degradation. Key factors influencing this surface contact or adsorption include the solution's pH, the pollutant's pKa values, and the photocatalyst's zero-point charge (ZPC).

A photocatalyst's surface charge varies with pH relative to its ZPC: it is positively charged below the ZPC and negatively charged above it [53]. Pollutants also change their speciation depending on the solution's pH and their pKa values. For instance, tetracycline (TC) has three pKa values: 3.30, 7.68, and 9.68. Below pH 3.3, TC is fully protonated (H_3L^+); between pH 3.3 and 7.68, it exists as a zwitterionic form ($H_2L^{\pm}$); and above pH 7.68 and pH 9.68, it is found as anionic forms HL− and L−2, respectively [54-55]. Similarly, sulfamethoxazole (SMX) has two pKa values: 1.8 and 5.6. At pH ≤ 1.7, SMX is cationic (SMX^+), while at pH ≥ 5.7, it is anionic (SMX^-); it remains neutral between pH 1.8 and 5.6. Optimal conditions for electrostatic attraction occur when the pH of the solution creates opposing charges on the photocatalyst and the pollutant [56-58].

Initial concentration of pharmaceuticals

When the initial concentration of a pollutant is elevated, the competition for photon absorption between the pollutant and the photocatalyst increases. This results in fewer photons reaching the photocatalyst surface, which reduces photocatalytic efficiency. Chen et al. observed that a higher initial concentration of ciprofloxacin (CIP) led to decreased photocatalytic degradation [59-61]. Similarly, Wang et al. noted that with sulfamethoxazole (SNM) degradation, the efficiency of photocatalysis diminished at higher pollutant concentrations. They suggested that the end products and intermediate compounds formed during the photodegradation process might compete with the parent molecules for adsorption and reactive sites on the photocatalyst surface, further impeding the degradation process [62-63].

Presence of ions and natural organic matter

Natural water sources and industrial or domestic wastewater often contain various inorganic ions that can impact photocatalytic reactions. For example, inorganic anions like persulfate ($S_2O_8^{2-}$), bromate (BrO_3^-), and sulfite (SO_3^{2-}) can enhance photocatalytic degradation by scavenging electrons and thereby reducing electron-hole recombination. However, high concentrations of these ions might inhibit degradation by scavenging hydroxyl radicals (·OH). Other inorganic ions such as chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and hydrogen phosphate ($H_2PO_4^-$) can act as scavengers for both holes (h^+) and ·OH, forming ionic radicals that are less effective oxidants.[51] These ions can also adsorb onto the catalyst surface, blocking active sites and reducing degradation efficiency. The presence of these ions has been shown to decrease the photodegradation efficiency of compounds like ibuprofen (IBF) and sulfamethoxazole (SNM) [64-65].

Ionic strength plays a crucial role in photocatalytic activity. High ionic strength

can reduce the repulsive forces between contaminants, enhancing their adsorption onto the photocatalyst. For instance, while low concentrations of sodium chloride (NaCl) can inhibit the photodegradation of compounds like carbonic acid (CA), higher concentrations of NaCl can maintain or even improve degradation efficiency to levels comparable to those in pure water [66]. Similar effects have been observed with tetracycline (TC) degradation.[68] Conversely, cations such as sodium (Na^+) can compete with pollutants for adsorption sites, potentially reducing photocatalytic efficiency. For example, calcium (Ca^{2+}) and magnesium (Mg^{2+}) have been reported to significantly inhibit TC degradation, while manganese (Mn^{2+}) can enhance photo-oxidation by increasing the generation of photogenerated electrons and holes and reducing their recombination [67-68].

Natural organic matter (NOM) in water can also scavenge reactive oxygen species (ROS), impacting photocatalytic efficiency. For instance, the presence of NOM in raw water samples has been found to reduce the effectiveness of visible light degradation of ibuprofen using the UTCB-25 photocatalyst [69].

CONCLUSION

Pharmaceuticals, widely used in human and veterinary medicine, present a significant environmental and health threat due to their ecotoxicity and contribution to microbial resistance. Conventional treatment methods have proven ineffective, prompting the exploration of advanced oxidation processes, such as visible-light-assisted semiconductor photocatalysis. This technology harnesses solar energy as a clean and sustainable light source, offering considerable potential for efficient, low-cost, and eco-friendly remediation. This review has provided an overview of pharmaceutical pollution in aquatic environments, discussing its effects, sources, and mitigation strategies. It has also highlighted heterogeneous photocatalysis technology, which has been extensively studied and applied in wastewater treatment to remediate persistent pollutants like pharmaceuticals. Despite its promise, there are still barriers and gaps that need to be addressed. Resolving these challenges is crucial for the future development and application of this technology in environmental remediation.

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