

**SYNTHESIS AND MECHANISTIC STUDY OF
HETEROJUNCTION BiOBr-BASED
COMPOSITES FOR
ANTIBIOTICS PHOTODEGRADATION**

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HETEROJUNCTION BiOBr-BASED
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ANTIBIOTICS PHOTODEGRADATION**

by

SUN YANLI

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LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius
e ⁻	Electron
h ⁺	Hole
•O ₂ ⁻	Superoxide Radical
•OH	Hydroxyl Radical
eV	Electrovolt
g	Gram
mg	Milligram
L	Litre
mL	Millilitre
min	Minute
h	Hour
C	Concentration
λ	Wavelength
nm	Nanometer
k	Second Order Rate Constant
R ²	Linear Regression Coefficient
Φ	Work Function
h	Planck Constant
ν	Photon Vibration Frequency

LIST OF ABBREVIATIONS

BiOBr	Bismuth Oxybromide
BiOCl	Bismuth Oxychloride
CuFe ₂ O ₄	Copper Ferrite
ENR	Enrofloxacin
CFZ	Ceftazidime
TC	Tetracycline
EG	Ethylene Glycol
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
HRTEM	High-resolution Transmission Electron Microscopy
EDS	Energy Dispersive Spectrometer
XPS	X-ray Photoelectron Spectroscopy
UV-Vis	Ultraviolet-visible
HPLC-MS	High-Performance Liquid Chromatography-Mass Spectrometry
PL	Photoluminescence
PEC	Photoelectrochemical
EIS	Electrochemical Impedance Spectroscopy
ESR	Electron Spin Resonance
DFT	Density Functional Theory
P25	TiO ₂ Nanoparticles
RhB	Rhodamine B
PNP	P-nitrophenol
CO ₂	Carbon Dioxide
H ₂ O	Water
O ₂	Oxygen
CB	Conduction Band
VB	Valence Band
BC	BiOBr/BiOCl
CBCF	BiOCl/BiOBr/CuFe ₂ O ₄
AOPs	Advanced Oxidation Processes
E _g	Bandgap Energy

MOFs	Metal-organic Frameworks
3D	3-Dimension
2D	2-Dimension

LIST OF APPENDICES

Appendix A	Table of compounds identified by HPLC-MS during the photodegradation of ENR
Appendix B	Table of compounds identified by HPLC-MS during the photodegradation of CFZ
Appendix C	Table of compounds identified by HPLC-MS during the photodegradation of TC

**SINTESIS DAN KAJIAN MEKANISTIK HETERO-SIMPANG
KOMPOSIT BERASASKAN BiOBr UNTUK PEMFOTOURAIAN
ANTIBIOTIK**

ABSTRAK

Fotomangkin berasaskan semikonduktor semakin mendapat perhatian disebabkan potensinya dalam memanfaatkan tenaga suria dan aplikasi dalam pemuliharaan alam sekitar. Kebelakangan ini, BiOBr telah muncul sebagai calon yang berpotensi disebabkan sifatnya yang tidak toksik, kos rendah, dan ciri fizikokimia yang unik. Walau bagaimanapun, penggabungan semula pasangan elektron-lubang (e^-/h^+) yang pantas dalam bahan ini sering menghadkan aplikasi praktikalnya. Kajian ini bertujuan untuk meneroka semikonduktor berasaskan BiOBr bagi penguraian pelbagai jenis antibiotik di bawah pencahayaan cahaya tampak. Pertama sekali, dua fotomangkin BiOBr tulen (BiOBr-W dan BiOBr-EG) masing-masing telah disintesis menggunakan air dan etilena glikol sebagai pelarut. BiOBr-EG menunjukkan prestasi yang lebih baik berbanding BiOBr-W, dengan kadar penguraian terhadap Enrofloxacin (ENR) yang 7.4 kali ganda lebih tinggi, disebabkan oleh morfologi yang lebih baik, saiz kristal yang lebih kecil (~ 24.3 nm), dan pengasingan cas yang lebih berkesan. Seterusnya, heterosambungan BiOBr/BiOCl (BC(5:5)) telah dibangunkan dan menunjukkan 91.8% penguraian ENR serta 80.2% penguraian Ceftazidime (CFZ) dalam masa 180 minit. Kemudian, satu komposit terner BiOCl/BiOBr/ CuFe_2O_4 (CBCF) telah dibangunkan dan mencatatkan kecekapan fotopemangkin tertinggi, dengan penguraian sebanyak 96.4% ENR, 88.6% CFZ, dan 87.4% Tetrasiklina (TC) dalam masa 180 minit. Komposit ini juga menunjukkan keupayaan pemulihan magnetik yang sangat baik (12.35 emu/g) dan mengekalkan

lebih 89.4% kecekapan selepas empat kitaran penggunaan semula. Kajian hapus sisa dan Resonans Putaran Elektron (ESR) mengenal pasti $\bullet\text{O}_2^-$ sebagai spesies reaktif utama, manakala kajian kinetik mengesahkan bahawa semua proses fotopermangkinan mematuhi model kinetik tertib-kedua. Kedua-dua hasil eksperimen dan pengiraan Teori Fungsian Ketumpatan (DFT) mengesahkan pembentukan hetero-simpang jenis-I dan medan elektrik dalaman (IEF) dalam struktur hetero BiOBr/BiOCl, yang memudahkan pemisahan pembawa cas yang berkesan. Sebaliknya, komposit ternar BiOCl/BiOBr/CuFe₂O₄ mempamerkan mekanisme pemindahan cas hetero-simpang jenis-I/S-skim, yang seterusnya meningkatkan kecekapan pemisahan ruang dan migrasi pasangan e^-/h^+ yang dijana oleh cahaya. Analisis Kromatografi Cecair Prestasi Tinggi–Spektrometri Jisim (HPLC-MS) mengenal pasti perantaraan penguraian dan mencadangkan lintasan penguraian terperinci bagi ENR, CFZ, dan TC. Kajian ini menunjukkan kesan sinergistik antara kawalan morfologi, kejuruteraan heterosambungan, dan integrasi magnetik dalam meningkatkan prestasi fotopemangkinan dan kebolehulangan bahan nanobahan berasaskan BiOBr.

SYNTHESIS AND MECHANISTIC STUDY OF HETEROJUNCTION BiOBr-BASED COMPOSITES FOR ANTIBIOTICS PHOTODEGRADATION

ABSTRACT

Photocatalysis based on semiconductors has garnered increasing attention due to its potential to utilize solar energy and applications in environmental remediation. Recently, BiOBr has emerged as a promising candidate owing to its non-toxicity, low cost, and distinctive physicochemical properties. However, the fast recombination of electron-hole (e^-/h^+) pairs in these materials often limits its practical applications. This study aims to explore BiOBr-based semiconductors for the degradation of various antibiotics under visible light. First, two pristine BiOBr photocatalysts (BiOBr-W and BiOBr-EG) were first synthesized using water and ethylene glycol, respectively. BiOBr-EG outperformed BiOBr-W, exhibiting a 7.4-fold higher degradation rate for Enrofloxacin (ENR), due to improved morphology, smaller crystal size (~ 24.3 nm), and enhanced charge separation. Then, a BiOBr/BiOCl heterojunction (BC(5:5)) was then fabricated, exhibiting a 91.8% degradation of ENR and 80.2% Ceftazidime (CFZ) within 180 mins. Subsequently, a ternary BiOCl/BiOBr/CuFe₂O₄ (CBCF) composite was developed, achieving the highest photocatalytic efficiency. The ternary composite degraded 96.4% ENR, 88.6% of CFZ, and 87.4% of Tetracycline (TC) in 180 mins. It also showed excellent magnetic recoverability with a satisfactory saturation magnetization of 12.35 emu/g and retained over 89.4% efficiency after four cycles. Scavenging test and Electron Spin Resonance (ESR) spectra studies identified $\bullet O_2^-$ as the dominant reactive species, and kinetic studies confirmed second-order behavior in all the photocatalytic processes. Both experimental results and Density Functional Theory (DFT) calculations confirmed the formation of a type-I band alignment and an

internal electric field (IEF) in the BiOBr/BiOCl heterostructure, which facilitated effective charge carrier separation. In contrast, the ternary BiOCl/BiOBr/CuFe₂O₄ composite exhibited a Type-I/S-scheme charge transfer mechanism, further enhancing the spatial separation and migration efficiency of photogenerated e⁻/h⁺ pairs. High-Performance Liquid Chromatography-Mass Spectrometry (HPLC/MS) analysis identified degradation intermediates and proposed detailed degradation pathways for ENR, CFZ, and TC. This work demonstrates the synergistic effects of morphology control, heterojunction engineering, and magnetic integration in enhancing the photocatalytic performance and recyclability of BiOBr-based nanomaterials.

CHAPTER 1

INTRODUCTION

1.1 Overview

With the development of industry, antibiotics are widely regarded as one of the greatest achievements in the history of microbiology due to their remarkable therapeutic efficacy against bacterial infections (Oberoi et al., 2019; Qin et al., 2021). Antibiotics are widely utilized in personal care products, livestock farming, agriculture, and aquaculture. However, antibiotic overuse has led to elevated concentrations in surface water worldwide, often exceeding standard safe levels. According to a report from Indexbox, which is a market intelligence platform that provides market data, analysis tools, over 18,100 tons of antibiotics were consumed globally in 2023. This contamination poses significant risks, including chronic toxicity to aquatic organisms, increased antimicrobial resistance, and potential declines in human immunity (Wu et al., 2023).

Over the past decades, a range of technologies has been utilized to remove antibiotic pollutants from aqueous solutions, including adsorption (Zhao et al., 2016), microbial remediation (Hiller et al., 2019), membrane technique (Cheng et al., 2018), and advanced oxidation process (AOP) (Lu et al., 2020). Among these, photocatalytic degradation stands out due to its environmental friendliness, high degradation efficiency, versatility, and ability to utilize solar energy, making it an important approach for addressing antibiotic contamination in water (Chen et al., 2022). However, conventional photocatalysts like ZnO and TiO₂ face significant limitations. Both ZnO and TiO₂ possess wide bandgaps (ZnO: ~3.37 eV, TiO₂: ~3.2 eV), which restricts their light absorption primarily to the UV region of the solar spectrum (Jia et al., 2022; Wu et al., 2020). Therefore, various innovative semiconductor

photocatalysts, have been developed to enhance antibiotic degradation under visible light. Among these, BiOBr is particularly noteworthy for its exceptional chemical stability, unique photoelectric properties, and low toxicity (Yang et al., 2018, Ye et al., 2014).

Up to now, various strategies have been employed to enhance the photocatalytic performance of BiOBr, focusing on improving its light absorption, charge separation, and surface activity. For example, doping BiOBr with metal (e.g., Ag, Fe) or non-metal (e.g., N, S) elements can introduce new energy levels within the bandgap, enabling better utilization of visible light (Sharma et al., 2019). In particular, heterojunctions between BiOBr and other semiconductors have been explored by combining two or more semiconductors with distinct electronic structures, interconnected through closely bonded interfaces. The fabrication of BiOBr heterojunction nanocomposites can effectively suppress the rapid recombination of photo-induced charge carriers while enhancing their ability to capture visible light (Yang et al., 2020).

Besides, efficient recovery of BiOBr-based photocatalysts from aqueous solutions while preserving their effectiveness is essential for continued use and reducing secondary pollution (Liu et al., 2023). A practical strategy involves the immobilizing of the photocatalyst onto a magnetic substrate such as CuFe_2O_4 , allowing for easy recovery via magnetic attraction (Bang Truong et al., 2023). In this approach, magnetic materials are often integrated with BiOBr photocatalysts to create a composite that can be separated quickly and efficiently using external magnets (Jacinto et al., 2020). This not only improves sustainability but also reduces the operational costs associated with continuous wastewater treatment.

As such, current research efforts have focused on developing high-performance BiOBr-based photocatalysts. In Chapter 4, a high catalytic performance BiOBr is obtained through a facile precipitation method, and Enrofloxacin (ENR) is selected as the model pollutant for degradation studies. In Chapter 5, BiOBr was integrated with BiOCl to form a hetero-composite, significantly enhancing its photocatalytic performance. Both ENR and Ceftazidime (CFZ) are chosen as model pollutants to expand the application of photocatalysts. In Chapter 6, CuFe_2O_4 is employed as a magnetic substrate to create a recyclable magnetic composite photocatalyst namely BiOCl/BiOBr/ CuFe_2O_4 . The application is further expanded to Tetracycline (TC), alongside ENR and CFZ. These three antibiotics—ENR, CFZ, and TC—are selected as model pollutants due to their frequent detection in wastewater and the significant challenges they pose to wastewater treatment processes. Finally, the photodegradation mechanisms and degradation processes of the three antibiotics are thoroughly investigated.

This study presents a novel strategy for enhancing the photocatalytic degradation of antibiotics through the synthesis and optimization of BiOBr-based photocatalysts. A key innovation lies in the systematic investigation of solvent effects, which significantly influence the morphology and crystal size of BiOBr. Furthermore, binary (BiOBr/BiOCl) and ternary (BiOCl/BiOBr/ CuFe_2O_4) heterostructures were fabricated using simple methods to improve charge separation efficiency. Especially, the incorporation of magnetic CuFe_2O_4 nanoparticles into the BiOBr system not only enhances visible-light-driven photocatalytic activity but also enables convenient magnetic recovery. In addition, the integration of density functional theory (DFT) calculations with experimental findings provides valuable insights into the antibiotic degradation mechanism, making this research one of the few that combines theoretical

modelling with practical photocatalytic application in different antibiotic photodegradation.

1.2 Problems statement

Commercial photocatalysts such as TiO_2 have been widely applied in environmental remediation due to their chemical stability, non-toxicity, and strong oxidative power. However, their photocatalytic performance is primarily limited to UV light due to their wide bandgap, leading to poor solar energy utilization and low degradation efficiency under visible light. These limitations restrict their practical application in large-scale, sunlight-driven wastewater treatment (Nakata & Fujishima, 2012). As an emerging semiconductor photocatalyst in recent years, BiOBr has attracted substantial interest due to its suitable bandgap, layered structure, and easy synthesis.

However, the catalytic activity of BiOBr is not only related to the chemical composition but also to the size and morphology of the materials. These are influenced by the chosen synthetic strategies and solvent.

Despite its layered structure, pure BiOBr still suffers from the recombination of photogenerated electrons and holes, restricted absorption of visible light, and insufficient separation of electrons (e^-) and holes (h^+). This reduces the production of reactive species such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$), which are essential for driving photocatalytic reactions.

The use of powdered BiOBr -based photocatalysts in large-scale water remediation is indeed limited by the challenges of separation after treatment. The energy and time required for effective separation can make the process inefficient.

Furthermore, the degradation performance can vary depending on the molecular structure of the antibiotic. The underlying mechanisms of photocatalysis—such as reaction kinetics, charge transfer processes, and antibiotic degradation pathways—are not always fully elucidated through experiments alone, which highlights the need for complementary DFT calculations to provide theoretical insight.

1.3 Research objectives

This research aims to develop BiOBr-based photocatalytic nanomaterials with enhanced photocatalytic activity and recyclability for the degradation of environmentally hazardous antibiotics under visible light. The specific objectives, arranged according to the research flow, are as follows:

- i. To synthesize two BiOBr photocatalysts using water and ethylene glycol (EG) as different solvents to control morphology, crystallinity, and visible-light activity.
- ii. To construct BiOBr/BiOCl heterojunction photocatalysts to promote charge carrier separation and suppress recombination, thereby improving photocatalytic efficiency under visible light.
- iii. To fabricate a ternary magnetic composite (BiOCl/BiOBr/CuFe₂O₄) by immobilizing BiOBr/BiOCl onto a CuFe₂O₄ substrate to enable magnetic separation and reusability while maintaining high degradation performance.
- iv. To investigate the photocatalytic degradation kinetics, mechanisms, and reaction pathways of selected antibiotics (Enrofloxacin, Ceftazidime, and Tetracycline) through experimental analysis and density functional theory (DFT) simulations to gain molecular-level insight into the photocatalytic processes.

1.4 Significance of the study

This research contributes significantly to the field of environmental remediation by addressing the growing concern of antibiotic contamination in aquatic systems. By developing BiOBr-based photocatalysts and forming heterojunction structures with BiOCl and CuFe_2O_4 , the study enhances visible-light-driven photocatalytic activity. The inclusion of magnetic CuFe_2O_4 not only improves charge separation but also enables facile recovery and reuse of the catalyst, which is important for practical applications. Furthermore, the selection of multiple antibiotic pollutants (ENR, CFZ, and TC) reflects real environmental application. This gives a broader understanding of how the photocatalyst works with various pollutants. Additionally, the integration of DFT-based analysis introduces a theoretical dimension that helps to reveal degradation pathways and the understanding of structure–activity relationships. Overall, this research provides a foundation for designing advanced, cost-effective, and sustainable photocatalytic systems for wastewater treatment.

1.5 Outline of thesis

The thesis consists of seven chapters which are presented as follows:

Chapter 1 provides an overview of the study, highlighting the key problem statement, research objectives, and outline of the thesis.

Chapter 2 presents a comprehensive literature review, including topics such as antibiotic pollution, the fundamentals of photocatalysis, semiconductor photocatalysts, synthesis methods of BiOBr, and BiOBr-based heterostructure photocatalysts, magnetic photocatalysts.

Chapter 3 details the methodology carried out in this study. It begins with a description of the fabrication processes for pure BiOBr using different solvents, the

BiOBr/BiOCl heterostructure, and the ternary BiOCl/BiOBr/CuFe₂O₄ materials. The fundamental principles behind various instrumental characterization techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence (PL) spectra, photoelectrochemical (PEC) properties, electrochemical impedance spectroscopy (EIS), high-performance liquid chromatography-mass spectrometry (HPLC-MS), and electron spin resonance spectroscopy (ESR), are also explained. Furthermore, the methods used for the photocatalytic experiments (photodegradation experiments, scavenging study) and density functional theory (DFT) are discussed in detail.

Chapter 4 presents the results and discussions about two BiOBr samples (BiOBr-W and BiOBr-EG) via a simple precipitation method. These samples were characterized in terms of their morphology, crystal structure, and photoelectric properties. Then, the BiOBr catalysts are applied to photodegrade ENR antibiotic. The superiority of BiOBr-EG compared to BiOBr-W and a commercial TiO₂ are evaluated. Finally, the degradation pathways of ENR are examined using DFT calculations and HPLC-MS analysis.

Chapter 5 discusses the BiOBr/BiOCl heterostructure composite. The composite is synthesized through an eco-friendly, one-step precipitation method by combining BiOBr and BiOCl. Then, this catalyst is used for the photodegradation of ENR and CFZ in aqueous solutions. The stability and reusability of the heterostructure are evaluated. Furthermore, a detailed analysis of the reaction mechanisms within the heterostructure is discussed. Finally, the degradation pathways of CFZ are proposed.

Chapter 6 gives the results and discussions of a magnetic ternary BiOCl/BiOBr/CuFe₂O₄ composite as a photocatalytic catalyst. Comprehensive characterizations of the synthesized samples are performed. The photocatalytic performance of the composite is evaluated through the degradation of ENR, CFZ, and TC under visible light illumination. The detailed formation mechanism of the ternary composite and the photocatalytic mechanism are thoroughly studied. Importantly, the magnetic recyclability is also evaluated.

Chapter 7 presents the conclusions and proposed future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Antibiotics

2.1.1 Usage of antibiotics

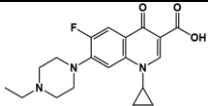
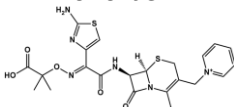
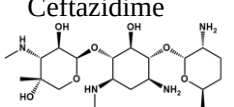
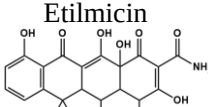
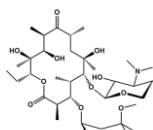
Antibiotics are organic compounds produced by microorganisms or synthesized as artificial analogues, primarily used for the prevention and treatment of diseases in animals and humans caused by microbial infections (Nicolaou & Rigol, 2018). In 1928, British scientist named Alexander Fleming made a groundbreaking discovery in antibiotic research when he accidentally identified the antibacterial properties of Penicillin in his laboratory. This marked the beginning of a new era in medicine. By the 1940s and 1950s, further research led to the discovery of additional antibiotics such as Streptomycin, Tetracycline, and Chloramphenicol, which significantly broadens the range of available treatments. These developments provided clinicians with a diverse set of tools to combat infections, making antibiotics a cornerstone of modern medical treatment and enabling the successful treatment of many infectious diseases (Durand et al., 2019).

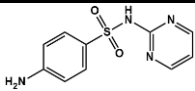
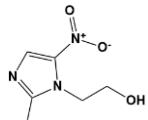
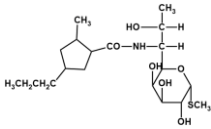
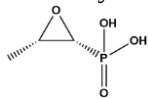
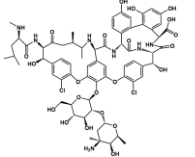
Over the past few decades, global antibiotic consumption has increased significantly and continues to grow yearly. This increase is primarily driven by population growth, rapid urbanization, and a higher prevalence of infectious diseases. In particular, the global outbreak of COVID-19 in 2020, along with the associated organ infections, resulting in a substantial surge in antibiotic use (Ali et al., 2023; Hu et al., 2022).

2.1.2 Classification of antibiotics

There are many kinds of antibiotics and different authors have described them in different ways (Ahmed et al., 2015; Kümmerer, 2009). For instance, based on their pharmacological properties, antibiotics are typically classified into five main groups: antibacterial, antifungal, antiviral, anti-tuberculosis, and antiparasitic drugs (Afifa et al., 2023; Haedenkamp et al., 2023). Additionally, the three kinds of antibiotics—narrow-spectrum, broad-spectrum, and extended-spectrum—can be categorized based on the range of activity they exhibit (Yang et al., 2021). Among the different methods of categorization, chemical structural classification is one of the most revealing, which is based on their chemical structures. For further clarification, Table 2.1 summarizes these classifications which typically highlights the different structural groups (Afifa et al., 2023; Bayan et al., 2021).

Table 2.1: Classification of antibiotics.

No	Classification	Groups	Examples	Structure example
1	Quinolone	4-Quinolone	Ciprofloxacin Moxifloxacin Enrofloxacin	 Enrofloxacin
2	β -lactams	β -Lactams ring	Amoxicillin Ceftazidime Aztreonam	 Ceftazidime
3	Aminoglycosides	Aminoglycosid-es	Streptomycin Kanamycin Etilmicin	 Etilmicin
4	Tetracyclines	Hydrogenated tetrabenzene	Tetracycline OxyTetracycline Doxycycline	 OxyTetracycline
5	Macrolides	12-16 Carbon lactone ring	Erythromycin Roxithromycin Azithromycin	 Erythromycin

6	Sulfonamides	Sulfonyl amino group	Sulfadiazine Sulfamethoxazole Sulfamethonone	 Sulfadiazine
7	Niimidazole	Nitroimidazole	Metronidazole Tinidazole Ornidazole	 Metronidazole
8	Linkamines	Amide	Lincomycin Clindamycin	 Lincomycin
9	Fosfomycins	Epoxypropylp hosphonic acid	Fosfomycin	 Fosfomycin
10	Glycopeptides	Heptapeptide skeleton	Vancomycin Norvancomycin Teicoplanin	 Vancomycin

2.1.3 Sources of antibiotic pollutant

Antibiotic consumption has surged significantly in recent years, with human antibiotic usage increasing by a staggering 65% between 2000 and 2015, and by 2030 projections indicating a potential rise of up to 200% (Polianciuc et al., 2020; Scaria et al., 2021). The widespread use of antibiotics has inevitably led to their excretion and subsequent release into the environment. Several researches have documented the existence of antibiotics across various environmental compartments, including wastewater, surface water, groundwater, and soil (Carvalho & Santos, 2016; Moreno-Bondi et al., 2009). Overall, six primary sources contribute to environmental pollution, as illustrated in Figure 2.1.

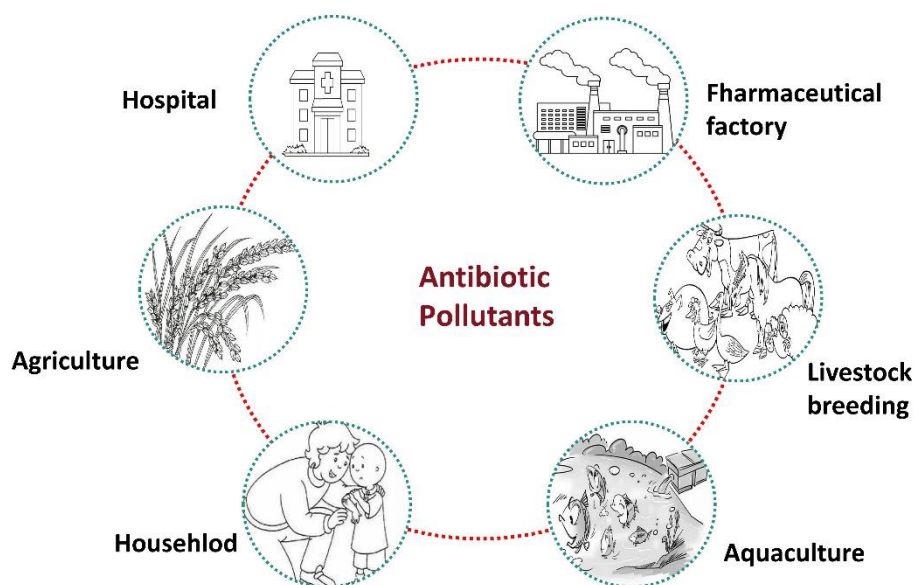


Figure 2.1: Sources of antibiotic pollutants

The release of antibiotics into the environment has contributed to the growing issue of drug resistance, which has become a significant global concern over the past few decades (Ben et al., 2019; Zhang et al., 2022). Antibiotic resistance complicates infection treatment, increases healthcare costs, prolongs hospital stays, and raises mortality rates. Therefore, it is crucial to remove antibiotic residues from the environment. Developing efficient methods for antibiotic wastewater treatment is critical in relieve the development and spread of antibiotic resistance, which are discussed in the following sections.

2.2 Treatment technologies for antibiotics wastewater

Numerous methods have been developed to eliminate antibiotics from aqueous solutions, so as to reduce their harmful environmental and health impacts. Some of the approaches are adsorption, membrane processes, biological treatment, phytoremediation, and AOP.

2.2.1 Adsorption

Adsorption is recognized as a potent method to purify antibiotic wastewater due to the strong binding ability of adsorbents for organic compounds. Adsorbent materials are highly diverse, encompassing carbon-based materials (Biswal & Balasubramanian, 2022; Scaria et al., 2022), polymers (Ajala et al., 2023; Rasoulzadeh et al., 2019), metal-organic frameworks (Mukhtar et al., 2020), and mineral materials (Tumrani et al., 2021; Zide et al., 2018). Consequently, the performance of adsorbents for removing antibiotics from wastewater warrants comprehensive evaluation. The interaction mechanism between adsorbent and adsorbate is highly diverse, and it includes electrostatic interaction, electron-donor-acceptor interactions, hydrogen bonding, hydrophobic, van der Waals forces (Yang et al., 2020). The interactions depend on the adsorbent's and adsorbate's properties; surface functional groups like hydroxyl, carboxyl, and amine on the adsorbent surface can facilitate various interactions with antibiotics. However, the adsorbents become saturated over time, which requires frequent regeneration or replacement. This regeneration process can be costly, energy-intensive, and potentially harmful to the environment.

2.2.2 Membrane processes

Membrane technology is utilized in various aspects of the process, involving the separation of chemical components using synthetic membranes. It has been acknowledged as a vital technology for the removal of pollutants from contaminated sources, particularly for the purification of original waters. In recent years, membrane technology has undergone significant enhancement, leading to improved capabilities and widespread adoption in commercial markets worldwide (Ye et al., 2023). One significant advantage of membrane separation processes is the physical separation of chemicals without a change of phase, and without introducing additional substances.

However, the membrane systems are still limited due to high cost, limited lifespan, selectivity limitations, etc.

2.2.3 Biological treatment

Biological treatment is another useful approach to treating antibiotic wastewater apart from physical and chemical treatment. Aerobic (activated sludge, AS) and anaerobic digestion are recognized for their cost-effectiveness and environmental friendliness in biological treatments (Melo-Guimarães et al., 2013). Aerobic treatment generally shows faster degradation rates for most pharmaceutical drugs compared to anaerobic treatment. The removal mechanisms in aerobic treatment include biodegradation and sorption (Changotra et al., 2019). However, active sludge can only remove certain antibiotics by restricted biotransformation possibilities because most chemicals are not digested by microorganisms as a source of carbon and can even inhibit their activity.

2.2.4 Phytoremediation

Phytoremediation, a green *in situ* remediation technology, involves the use of plants to remove, break down, or immobilize antibiotics, in soil or water body (Date & Jaspal, 2023). Plants have the ability to convert organic pollutants into less harmful or non-toxic substances, thereby minimizing the risk of secondary pollution more effectively than other methods. In cases where pollutants accumulate excessively in plants, regular harvesting can be carried out, and secondary pollution can be managed through composting (Zhou et al., 2024). Consequently, phytoremediation offers advantages such as minimal environmental disruption, low cost, and aesthetic benefits. However, phytoremediation processes can take a long time (months to years) to achieve significant contaminant removal, making it less suitable for urgent cleanup needs.

2.2.5 Advanced oxidation processes

In the past decades, AOPs have become prominent techniques for removing organic pollutants in wastewater. AOPs encompass various technologies such as persulfate (PMS), Fenton, ozonation (O_3), ultrasonic, photo-Fenton, and photocatalytic oxidation, which have been effectively employed for wastewater treatment (Table 2.2). They involve the generation of highly reactive species (e.g., $\bullet OH$, $\bullet O_2^-$, and $SO_4^{\bullet -}$), which can facilitate the oxidation and mineralization of antibiotics into CO_2 and H_2O (Preethi et al., 2024).

Overall, the combination of high efficiency, ease of operation, safety, and environmental compatibility makes AOPs an attractive option for the decontamination of antibiotic wastewater (Elkacmi & Bennajah, 2019). They provide a promising approach to address the challenges posed by complex organic contaminants in industrial wastewater streams.

Table 2.2: Summary of AOPs methods.

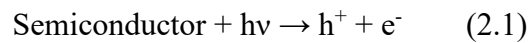
Types of AOPs	Model pollutant	Reactive species	References
O_3	p-nitroaniline	$\bullet OH$	(Wang et al., 2022)
Fenton	Methylene blue	$\bullet OH$	(Wang et al., 2021)
Electro-Fenton	Methylene blue	$\bullet OH$	(Ma et al., 2016)
Photo-Fenton	Tetracycline	1O_2 and $\bullet O_2^-$	(Liu, et al., 2022)
Photo-Fenton	Tetracycline	$\bullet O_2^-$, $\bullet OH$, h^+	(Lu et al., 2023)
Ultrasonic	Methyl orange	$\bullet O_2^-$, $\bullet OH$, h^+	(Kang et al., 2020)
Ultrasonic-PMS	Tetracycline	$SO_4^{\bullet -}$, $\bullet O_2^-$, $\bullet OH$, h^+	(Zeng et al., 2023)
Ultrasonic-photo	Ciprofloxacin, Norfloxacin, Ofloxacin	$\bullet O_2^-$, $\bullet OH$, h^+	(Yu et al., 2020)
PMS	Atrazine	$SO_4^{\bullet -}$	(Li et al., 2018)
Photo-PMS	Ofloxacin	$SO_4^{\bullet -}$, 1O_2	(Chen et al., 2020)
Photodegradation	Enrofloxacin	$\bullet O_2^-$, $\bullet OH$, h^+	(Chen et al., 2017)
Photodegradation	Methyl orange	$\bullet O_2^-$, $\bullet OH$, h^+	(Kite et al., 2021)
Photodegradation	O-xylene	$\bullet O_2^-$, $\bullet OH$, h^+	(Rao et al., 2021)

2.3 Photocatalysis

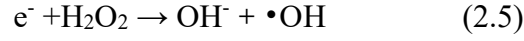
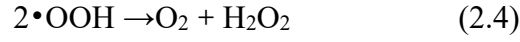
Solar energy is a renewable, clean, and cost-effective energy source, and the efficient utilization, conversion, and storage of solar energy have become a major focus of contemporary research. Fujishima and Honda made groundbreaking advancements by demonstrating the photocatalytic decomposition of water using TiO₂, marking the beginning of modern photocatalysis technology (Sari et al., 2024). Photocatalytic technology harnesses solar energy in combination with the unique physical and chemical properties of semiconductors to degrade toxic pollutants which offers a powerful approach for environmental purification. Photocatalytic reactions come with several advantages, including an abundance of catalytic materials, mild reaction conditions, ease of operation, low risk of secondary pollution, and high efficiency in pollutant degradation (Doña-Rodríguez & Pulido Melián, 2021; Perathoner et al., 2017).

2.3.1 Principles of Photocatalysis

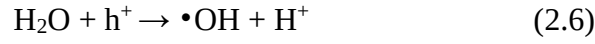
According to Energy Band Theory, the semiconductor band consists of an empty CB (conduction band) and a VB (valence band) filled with electrons (Figure 2.2). In the absence of light (in the dark), no electronic transitions occur within the semiconductor. However, when the material is exposed to UV or visible light, and the photon energy ($h\nu$) exceeds the bandgap energy (E_g), e^- (electrons) in VB are excited and transition to CB, leaving behind photo-generated h^+ (holes) in VB (Equation 2.1), initiating the photocatalytic reactions (Chong et al., 2010).



e^- , can react with O₂ adsorbed on the surface of semiconductors, generating a series of reactive oxygen species (ROS), like $\bullet\text{O}_2^-$, $\bullet\text{OH}$ (Jiang et al., 2022; Ren et al., 2022). As shown in (Equation 2.2)-(Equation 2.5):



h^+ , due to their strong oxidizing properties, can directly react with H_2O molecules (Equation 2.6) adsorbed on semiconductor surfaces to generate highly oxidizing $\cdot\text{OH}$ radicals (Chong et al., 2010; Kuk et al., 2023).



h^+ , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ undergo photochemical reactions with antibiotics on semiconductor surfaces, degrading antibiotics into CO_2 and H_2O (Figure 2.2).

In summary, the photocatalytic process consists of three key steps: (1) the generation of e^- and h^+ , (2) the carriers migrate to the photocatalyst surface, and (3) redox reactions of antibiotic pollutants.

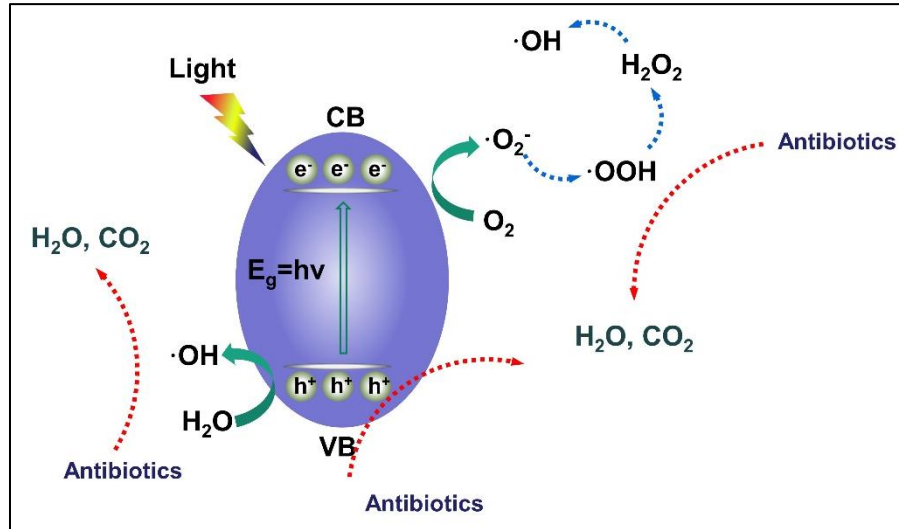


Figure 2.2: Process of photocatalytic degradation of antibiotics on semiconductor.

2.3.2 Photocatalyst

Anatase-type TiO_2 , a first used traditional photocatalytic material, has a relatively large bandgap (~ 3.2 eV). As a result, this material has a low solar energy utilization rate and is unable to harness approximately 43% of the visible light (400-750 nm) present in the solar spectrum (Baker & Kamat, 2009; Lei et al., 2015). For many years, researchers have been dedicated to developing new semiconductor photocatalytic materials with higher activity and broader spectral response, aiming to improve the efficiency of solar energy conversion and utilization. Following are some commonly used photocatalysts.

2.3.2(a) Metal oxides

As one of crucial photocatalysts, metal oxides play a crucial role in photodegradation due to their ability to generate charge carriers upon exposure to suitable energy. Metal oxide nanostructures, such as TiO_2 , ZnO , CuO , WO_3 , CeO_2 , AgO , and SnO_2 , possess unique properties, including favourable electronic structures, strong light absorption capabilities, and excellent charge transport characteristics (Khan et al., 2015). These attributes have made them ideal candidates for use as photocatalysts, and have been widely employed to assist in the degradation of organic pollutants, including pesticides, dyes, and pharmaceuticals (Pascariu et al., 2023, Wan et al., 2024). However, certain metal oxides may experience photo corrosion or instability under prolonged illumination or in specific pH environments. These limitations often require modification strategies, such as doping, heterojunction formation, or coupling with other materials, to enhance their performance.

2.3.2(b) Metal sulfides

Metal sulfides are a type of visible light-responsive catalytic material, known for their suitable bandgap widths and strong photocatalytic degradation abilities for

environmental pollutants. Sulfide photocatalysts, such as CdS and ZnS, have been developed with promising results. Wang et al. developed a sulfur-vacancy CdS photocatalyst that not only mineralizes organic pollutants but also converts CO₂ into CO, offering a potential solution for both environmental pollution and the energy crisis (Wang et al., 2023). However, despite their good visible light catalytic activity, metal sulfides are prone to oxidation or reduction during photocatalytic reactions, leading to photo-corrosion, which compromises their stability in reaction systems (Ren et al., 2024).

2.3.2(c) Metal-organic frameworks (MOFs)

MOFs are indeed versatile materials owing to their tunable structures and exceptional surface properties (Alkhatib et al., 2020). The ability to modify both the metal clusters and organic linkers provides substantial control over their optical and electronic properties, making them suitable for advanced applications like photocatalytic water splitting, degradation of organic pollutants, CO₂ reduction (Zeng et al., 2016). MOFs' bandgaps, which range from 1.0 to 5.5 eV, offer flexibility in terms of which part of the electromagnetic spectrum they can absorb, making them viable for use under visible or UV light (Younis et al., 2020). Moreover, their intrinsic structural properties uniform pore size, channels, and large surfaces also contribute to faster mass transfer and diffusion, improving reaction kinetic in photocatalytic processes.

However, most MOFs exhibit poor stability in water or under humid conditions, which limits their long-term use in aqueous photocatalytic applications. Additionally, they often show low electrical conductivity, which hinders efficient charge transport and increases the recombination of photogenerated e^-/h^+ pairs.

2.3.2(d) Non-metal photocatalysts

Non-metal photocatalysts are indeed an emerging class of materials, attracting attention due to their unique advantages such as affordability, environmental compatibility, and diverse applications (Tang et al., 2023). Commonly used non-metal photocatalysts include carbon quantum dots (CQDs), graphitic carbon nitride (g-C₃N₄), black phosphorus (BP), and boron nitride (BN), among others.

g-C₃N₄ is a typical non-metallic organic semiconductor photocatalytic material with visible light responsiveness (Han et al., 2021). It has a CB made up of C 2p orbitals and a VB composed of N 2p orbitals. This unique electronic configuration endows g-C₃N₄ with excellent thermal and chemical stability, great photocatalytic activity, and cost-effective synthesis. It also benefits from readily available raw materials, a simple and non-toxic synthesis process, and the absence of metal elements. These advantages have attracted significant global attention from researchers, and g-C₃N₄ shows great potential for applications in catalysis, sensors, and drug delivery systems.

However, they also face several drawbacks. A major limitation is their low charge carrier mobility, which can lead to rapid recombination of photogenerated electrons and holes, reducing photocatalytic efficiency. Many non-metal photocatalysts also have a limited surface area or poor crystallinity, which weakens pollutant adsorption and active site availability. Additionally, their optical absorption range may be narrow, and they often require modification (e.g., doping or forming heterojunctions) to enhance light harvesting and redox capability. Some materials may also degrade under strong irradiation or in harsh environments, limiting their long-term stability in practical applications.

2.3.2(e) Bismuth-based photocatalyst

Bismuth-based photocatalytic materials represent a novel class of photocatalysts that can directly harness visible light and demonstrate excellent performance in degrading persistent organic pollutants. As a result, they have become a central focus in new catalytic semiconductors. This category includes various compounds such as Bi_2O_3 , $\text{Bi}_2\text{Ti}_2\text{O}_7$, BiVO_4 , Bi_2WO_6 , Bi_2MoO_6 , AgBiO_3 , and bismuth halide oxides (BiOX , $\text{X} = \text{Cl, Br, I}$) (Qin et al., 2021b) .

Among these, BiOX have garnered significant attention due to their unique electronic structures, highly anisotropic layered morphologies, and exceptional photocatalytic stability (Yuan & Jiang, 2023). BiOBr , particularly, has been extensively utilized recently because of its relatively narrow bandgap and excellent photocatalytic performance (Zhang et al., 2008).

2.4 BiOBr photocatalyst

2.4.1 Structure and chemical properties

BiOBr (bismuth oxybromide) has garnered substantial attention due to its excellent photocatalytic performance and low toxicity, which make it a highly desirable material for wastewater treatment. With a bandgap ranging between 2.7 and 2.9 eV, BiOBr absorbs visible light effectively and is highly suitable for photocatalytic reactions under sunlight, distinguishing it from other photocatalysts that primarily rely on UV light (Kim & Jo, 2019).

BiOBr has a structure consisting of $[\text{Bi}_2\text{O}_2]^{2+}$ and Br^- layers (Figure 2.3) (Xue et al., 2018). The $[\text{Bi}_2\text{O}_2]^{2+}$ layers are tightly bound within each monolayer through covalent bonds, and help it forming a stable framework. The connection between adjacent $[\text{Bi}_2\text{O}_2]^{2+}$ and Br^- layers is much weaker due to van der Waals forces. These

forces are non-covalent and arise from the electrostatic attractions between molecules, resulting in relatively weak interlayer bonding (Li et al., 2020; Xue et al., 2018). This facilitates charge separation, as the photogenerated e^- and h^+ can migrate more easily through the layers without being trapped (Yang et al., 2018). Furthermore, the crystal structure of BiOBr is favorable for the formation of layered shapes, which consist of multiple BiOBr monolayers and alternating $[\text{Bi}_2\text{O}_2]^{2+}$ and Br^- layers.

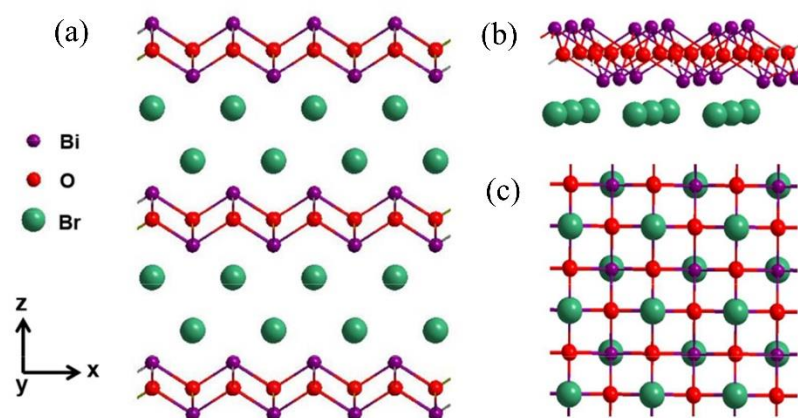


Figure 2.3: The laminar crystalline structure of BiOBr (a) the front view, (b) the side view, and (c) the top view of BiOBr crystal unit cells (Xue et al., 2018).

2.4.2 Preparation methods

Presently, the demand for BiOBr with particular characteristics including particle size, morphology, surface area, and crystallinity has prompted the laboratory's development of various synthesis techniques. By using these techniques, the characteristics of BiOBr can be adjusted to match particular needs for photocatalysis and other applications. To date, many different methods prepare or synthesize BiOBr, such as precipitation, solvothermal/hydrothermal approaches, microwave-assisted synthesis, and hydrolysis.

2.4.2(a) Solvothermal/hydrothermal methods

Solvothermal and hydrothermal methods are closely related synthesis methods that involve subjecting a precursor solution to high temperatures and pressures inside an autoclave (Shi et al., 2013). This thermal treatment creates autogenous pressure, facilitating reactions that are difficult to achieve under ambient conditions. The primary distinction between the two lies in the solvent used: hydrothermal synthesis utilizes an aqueous solution, while solvothermal synthesis allows for a range of solvents, such as methanol, ethylene glycol, and glycerol (Sasikala et al., 2017). These solvent variations in solvothermal synthesis can influence the growth direction of BiOBr crystals. A key feature of both methods is their ability to precisely control crystal phase, morphology, and size by adjusting kinetic and thermodynamic parameters such as temperature and reaction time (Imam et al., 2021). Consequently, hydrothermal and solvothermal methods are commonly employed for synthesizing BiOBr photocatalysts.

Using a hydrothermal method, Wang and co-workers synthesized BiOBr nanosheets with various exposed crystal facets at 160°C for 12 h (Wu et al., 2015), while Lv and co-researchers synthesized BiOBr flowers through a solvothermal method (Lv et al., 2020). In another study, BiOBr nanoplates and VO-BiOBr (oxygen vacancy BiOBr) nanosheets were achieved using a simple hydrothermal method (Xue et al., 2018).

However, they also have drawbacks, including high energy consumption, pressure-related safety risks, scalability challenges, complex parameter optimization, and potential nanoparticle agglomeration. Despite these limitations, these methods remain popular for achieving well-defined BiOBr structures with enhanced photocatalytic properties.

2.4.2(b) Hydrolysis method

The hydrolysis method involves the breakdown of precursors by solvents to prepare novel materials (Pandi et al., 2021). The study of Li and co-workers highlighted the preparation of a series of BiOBr photocatalysts with tunable morphology, crystallinity, and crystal facet orientation through hydrolysis, utilizing BiBr₃ as the precursor in different solvents (water, ethanol, or isopropyl alcohol) (Sivakumar et al., 2014). Also, Duresa and co-workers synthesized indium (In)-doped BiOBr nanosheets enriched with oxygen vacancies using a straightforward hydrolysis method at room temperature, free from capping agents or toxic precipitation chemicals (Duresa et al., 2021).

However, disadvantages of hydrolysis method include poor crystallinity, potential impurity formation, and limited control over particle size and shape compared to solvothermal/hydrothermal methods. The hydrolysis method is useful for rapid synthesis but may require post-treatment steps (e.g., calcination) to improve crystallinity and photocatalytic performance.

2.4.2(c) Microwave-assisted process

Nowadays, microwave-assisted process is acknowledged as a powerful technique that combines speed, efficiency, and reproducibility in the synthesis of photocatalysts with tunable shapes and sizes (Yan et al., 2013). This approach provides significant advantages, including rapid and uniform dielectric heating without thermal gradient effects, which greatly enhances the reaction rate and results in high throughput capacity and reproducibility of nanostructures. Miao and co-workers adopted a microwave-assisted self-assembly technique to manufacture bismuth oxybromide (BiOBr) (Miao et al., 2018). The obtained BiOBr sample had a hierarchical microcube morphology which was made up of regular multi-layered nanosheets.