BISMUTH OXYBROMIDE-BASED COMPOSITES INTEGRATED BIOCHAR FROM PALM OIL MILL EFFLUENT SLUDGE FOR PHOTOCATALYTIC REMEDIATION OF CIPROFLOXACIN IN AQUEOUS MEDIUM

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UNIVERSITI SAINS MALAYSIA

2025

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by

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Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

September 2025

ACKNOWLEDGEMENT

Alhamdulillah, all praises and gratitude are due to Almighty Allah, the Lord of the universe. I thank Allah for granting me strength, knowledge, wisdom, health, and provision to complete this research. May the peace and blessings of Allah be upon Prophet Muhammad (Sallallahu alayhi wa sallam), his companions, his household, and those following his path till the day of resurrection (Aameen).

Firstly, I acknowledge my supervisors, Assoc. Prof. Noor Haida Mohd Kaus and Prof. Dr. Rohana Binti Adnan, for their invaluable intellectual guidance and contributions, words of encouragement, and financial support towards the successful completion of this research thesis. May Allah bless you and ease your affairs.

I extend my gratitude to the Institute of Postgraduate Studies, USM, for the financial support through GRA-ASSIST and PGRA funds. I also appreciate my abroad advisor, Prof. Sirikanjana Thongmee, and the Faculty of Science team at Kasetsart University, Bangkok, Thailand, for their financial support during my attachment. I appreciate the staff of the School of Chemical Sciences, USM, my mentors, Prof. N. Abdus-Salam and Prof. H. I. Adegoke, my colleagues and friends at USM, particularly Hafsat, Zainab, Rukayyat, Dr. Ismail, Dr. Olaoye, Dr. Idris, Dr. Halimah, Dr. Amina, and others who have contributed to this journey. May Allah reward you all abundantly.

To my parents and siblings, I deeply appreciate your prayers and encouragement. Finally, to my husband, Dr. Ridhwanullah Oyekunle, your patience, sacrifices, and unwavering support have been my pillar of strength. Thank you for your support and for believing in me even when the hope of achieving this dream (PhD) seemed to vanish. May Allah continue to bless you with His everlasting bounties.

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LIST OF ABBREVIATIONS

$\bullet O_2^-$	Superoxide Radical
•OH	Hydroxyl Radical
AA	Ascorbic Acid
BBC	Bismuth oxybromide/Biochar
BBC-B	Bismuth Oxybromide/Biochar/Bismuth Oxide
BBC-G	Bismuth Oxybromide/Biochar/Graphitic Carbon Nitride
BBC-SA	Bismuth Oxybromide/Biochar/Sodium Alginate
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
CB	Conduction Band
CIP	Ciprofloxacin
DRS	Diffuse Reflectance Spectroscopy
e^-	Negatively Charged Electron
EDS	Energy Dispersive X-ray
ETDA	Ethylenediamine Tetraacetic acid
eV	Photon Energy
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infra-Red
g-C_3N_4	Graphitic Carbon Nitride
h^+	Positively Charged Hole
HR-TEM	High-Resolution Transmission Electron Microscope
IPA	Isopropyl Alcohol
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
pH_{PZC}	pH of Point of Zero Charge

PL	Photoluminescence
POMES	Palm Oil Mill Effluent Sludge
PZC	Point of Zero Charge
SA	Sodium alginate
SAED	Selected Area Electron Diffraction
TEM	Transmission Electron Spectroscopy
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
UV-Vis	Ultraviolet and Visible
VB	Valence Band
XRD	X-Ray Diffraction

KOMPOSIT BERASASKAN BISMUT OKSIBROMIDA BIOCHAR BERSEPADU DARIPADA ENAP CEMAR EFLUEN KILANG KELAPA SAWIT UNTUK PEMULIHAN FOTOKATALIK BAGI CIPROFLOXACIN DALAM MEDIUM AKUEUS

ABSTRAK

Bismut oksibromida (BiOBr) merupakan semikonduktor yang menjanjikan tenaga jurang jalur sempit (~2.7–2.9 eV), menjadikannya sebagai fotopemangkin untuk pelbagai aplikasi. Walau bagaimanapun, penggunaan secara praktikal terhad disebabkan luas permukaan yang rendah, penyerapan cahaya nampak yang rendah dan penggabungan lubang elektron dengan kadar yang cepat dan sukar untuk diguna semula. Dalam kajian ini, isu ini ditangani dengan membangunkan sistem komposit berasaskan BiOBr yang mempunyai prestasi fotopemangkin yang lebih baik untuk rawatan air buangan farmaseutikal, menggunakan ciprofloxacin (CIP) sebagai model pencemar. Komposit BiOBr-bio arang (BBC) yang mampan disintesis melalui kaedah hidrotermal tanpa pelarut dengan bio arang yang diperoleh daripada enapcemar efluen industri minyak sawit (POMES) sebagai matriks sokongan. Pembentukan hetero-simpang dengan bismut oksida (Bi_2O_3) dan karbon nitrida grafit (g-C_3N_4) menghasilkan komposit ternari BBC-B dan BBC-G. Bagi meningkatkan pengendalian dan kebolehgunaan semula, komposit BBC telah dikapsulkan dalam alginat natrium (SA) untuk membentuk manik komposit BBC-SA. Pencirian struktur dan fiziko kimia mengesahkan kejayaan penyediaan semua komposit. BBC yang dioptimumkan (nisbah jisim 1:1) menunjukkan luas permukaan yang lebih tinggi (267 m^2/g) dan jurang jalur tenaga yang lebih rendah (2.42 eV) berbanding BiOBr asli (2.85 m^2/g,

2.87 eV). Pengubahsuaian lanjut dalam menghasilkan BBC-B dan BBC-G dapat mengurangkan jurang jalur tenaga masing-masing kepada 1.84 eV dan 2.15 eV. Penambahbaikan ini meningkatkan sifat penjerapan BiOBr, memudahkan pemisahan elektron-lubang yang lebih baik, dan meningkatkan penyerapan cahaya nampak dan menghasilkan prestasi fotopemangkin yang unggul. Dalam keadaan optimum, BBC mendegradasi ~97 % CIP pada kepekatan 20 mg/L dengan 85 % mineralisasi dalam 120 minit, mencapai pemalar kadar tindak balas 0.0156 min^{-1}, iaitu 40 % lebih tinggi daripada BiOBr. BBC mengekalkan kecekapan degradasi 77 % selepas tujuh kitaran, menunjukkan satu kestabilan yang baik. Komposit ternari menunjukkan prestasi yang lebih tinggi: BBC-B mendegradasi 95.18 % CIP dengan kadar mineralisasi 61.06 % serta mengekalkan kecekapan 84.63 % selepas tujuh kitaran dengan pemalar kadar tindak balas 0.0376 min^{-1}. BBC-G pula mencapai tahap degradasi 94.89 % dan mineralisasi 57.42 % dalam 60 minit, dengan kadar tindak balas kinetik 0.0324 min^{-1}. Pengkapsulan dalam SA membolehkan pemulihan fotopemangkin yang cekap, dengan BBC-SA mencapai degradasi 80.16 % dalam 120 minit dan mengekalkan kecekapan 68.11 % selepas 10 kitaran. Hasil ini menyerlahkan potensi komposit berasaskan BiOBr untuk mendegradasi antibiotik dan bahan pencemar yang lain, serta menawarkan penyelesaian mesra alam, boleh diguna semula, dan diskalakan bagi rawatan air buangan.

BISMUTH OXYBROMIDE-BASED COMPOSITES INTEGRATED BIOCHAR FROM PALM OIL MILL EFFLUENT SLUDGE FOR PHOTOCATALYTIC REMEDIATION OF CIPROFLOXACIN IN AQUEOUS MEDIUM

ABSTRACT

Bismuth oxybromide (BiOBr) is a promising semiconductor with a narrow band gap (~2.7–2.9 eV), making it an attractive photocatalyst for various applications. However, its practical use is limited by low surface area, high electron-hole recombination rate, restricted visible light absorption, and difficulty in reuse. This study addresses these issues by developing BiOBr-based composite systems with enhanced photocatalytic performance for the treatment of pharmaceutical wastewater, using ciprofloxacin (CIP) as a model contaminant. A sustainable BiOBr-biochar composite (BBC) was synthesized via a solvent-free hydrothermal method using biochar derived from palm oil mill effluent sludge (POMES) as a support matrix. Heterojunction formation with bismuth oxide (Bi_2O_3) and graphitic carbon nitride (g-C_3N_4) produced ternary composites BBC-B and BBC-G, respectively. To enhance handling and reusability, the BBC composite was encapsulated in sodium alginate (SA) to form BBC-SA composite beads. Structural and physicochemical characterization confirmed the successful preparation of all composites. The optimized BBC (mass ratio 1:1) exhibited a higher surface area (267 m^2/g) and a reduced band gap (2.42 eV) compared to pristine BiOBr (2.85 m^2/g, 2.87 eV). Further modifications to create BBC-B and BBC-G reduced the band gap to 1.84 eV and 2.15 eV, respectively. These enhancements improved BiOBr's adsorption properties, facilitated better electron-hole separation, and increased visible light harvesting, resulting in

superior photocatalytic performance. Under optimized conditions, BBC degraded ~97 % of 20 mg/L CIP with 85 % mineralization within 120 min, achieving a reaction rate constant of 0.0156 min^{-1}, which was 40 % higher than pristine BiOBr. BBC maintained 77 % degradation efficiency over seven cycles, demonstrating good stability. The ternary composites showed even greater performance: BBC-B degraded 95.18 % of CIP with a mineralization rate of 61.06 % and maintained 84.63 % efficiency over seven cycles, with a reaction rate of 0.0376 min^{-1}. BBC-G achieved 94.89 % degradation and 57.42 % mineralization within 60 minutes, with a degradation rate of 0.0324 min^{-1}. Encapsulation in SA enabled efficient photocatalyst recovery, with BBC-SA achieving 80.16 % degradation in 120 min and retaining 68.11 % efficiency after 10 cycles. These results highlight the potential of BiOBr-based composites for visible-light-driven degradation of antibiotics and other persistent pollutants, offering scalable, environmentally friendly solutions for wastewater treatment.

CHAPTER 1

INTRODUCTION

1.1 Background

Water is one of the Earth's most important components, sustaining life. However, the number of industrial activities on a global scale increases, as does rapid urbanization and other human activities. Hence, water sources become contaminated or polluted when the effluents containing various toxic organic and inorganic pollutants from these activities enter water bodies. As a result, freshwater is no longer available for human consumption and other aquatic species that depend on it.

With the rapid development of the pharmaceutical and medical industry, the consumption of antibiotics over the years has increased among humans and animals (Wei et al., 2023). This leads to frequent detections in groundwater and surface water, which can be traced to their slower disintegration rate, improper disposal, misuse, mass production, and waste (Roy et al., 2021). Fluoroquinolones, a class of pharmaceutical products, are considered persistent organic pollutants (POPs) due to their highly stable halogenated heterocyclic structure. CIP, a second-generation fluoroquinolone antibiotic that is frequently employed to treat infections caused by pathogens (Zeng et al., 2017). Among antibiotics, CIP is one of the major pharmaceutical pollutants entering the aquatic environment globally. It is ingested by humans and animals and mainly released into the environment via pharmaceutical waste, and can be very harmful to the environment, disrupting the natural balance and exacerbating the problem of antibiotic resistance. Surface water and wastewater contain CIP in amounts ranging from 100 ng/L to μg/L

(Tran et al., 2022), while the amount in hospital waste and drug-producing industries could be as high as 42.8 µg/L (Lien et al., 2016) and 50 mg/L (Ahmadzadeh et al., 2017) respectively. Meanwhile, it is difficult for the various pharmaceutical industries to comply with a specific concentration (waste) due to the lack of information on the standard discharge limits for pharmaceuticals discharged into the water body by any recognized related bodies such as World Health Organization (WHO) or Environmental Quality Standard (EQS). The reason is partly attributed to the absence of standardized experimental techniques that can consistently produce data on the minimum concentration of an antibiotic (Hayes et al., 2022).

Existing wastewater treatment technologies, such as activated carbon adsorption (Adegoke et al., 2017; Dimbo et al., 2024; Fito et al., 2023; Soker et al., 2023) biological treatment (Dubey et al., 2023; Singh et al., 2023), (Phan et al., 2024) and conventional chemical methods (Kadadou et al., 2023; Metin & Çifçi, 2023; Zahmatkesh et al., 2024), have notable limitations. For instance, activated carbon adsorption, while effective for certain contaminants, often requires frequent replacement or regeneration, which can be costly and environmentally challenging (Pui et al., 2019). Biological treatment on the other hand can be limited by the complexity of the wastewater and potential incomplete degradation of certain pollutants, requiring controlled conditions to maintain microbial activity, and large space for equipment setup and longer duration for the degradation process (Musa & Idrus, 2021). Chemical methods, such as oxidation and reduction, can effectively treat pollutants but may involve hazardous chemicals and generate toxic by-products (Bello et al., 2019). Hence, it is necessary to develop sustainable, low-cost,

effective, and efficient techniques that can unselectively eliminate these antibiotics from the water system.

Heterogeneous photocatalysis offers several advantages over traditional technologies, including environmental sustainability, efficiency in degradation, minimized waste generation, and cost-effectiveness (Goodarzi et al., 2023). Bismuth oxybromide (BiOBr) has emerged as a highly effective photocatalyst for various environmental applications, notably in the degradation of organic pollutants and the treatment of wastewater (Bárdos et al., 2019; Fu et al., 2020). BiOBr belongs to the class of bismuth halide oxides (BiOX, X = Br, Cl, and I), which are renowned for their photocatalytic properties due to their unique electronic structures and optical characteristics (L. Xu et al., 2024). Among BiOX, BiOBr in particular, is distinguished by its moderate bandgap (~2.7–2.9 eV), enabling visible-light-driven photocatalysis with balanced redox potential (Li et al., 2022). This gives it an advantage over BiOCl (~3.2 eV), which has a wider band gap (~3.2–3.4 eV) and primarily absorbs UV light (Sharma et al., 2021) and BiOI, with a lower band gap of about 1.8 eV (Haile et al., 2023), with which its visible light absorption response is weak, leading to rapid recombination of charge carriers. Moreover, BiOBr internal $[Bi_2O_2]^{2+}$ layers interleaved with Br^- anions facilitate efficient charge separation, mitigating electron–hole recombination (I. Ahmad et al., 2022; Prabhakar Vattikuti et al., 2022). In addition, BiOBr easily forms effective composites with other materials, leading to superior charge separation, increased surface area, and improved overall photocatalytic activity (Deng et al., 2021; Tie et al., 2022; Zheng et al., 2020). These unique properties make BiOBr advantageous for photocatalytic applications under sunlight or artificial visible light sources (Bárdos et al., 2020), which are more accessible and cost-effective compared to UV light.

Despite these advantages, one notable issue is the relatively high rate of recombination of electron-hole pairs of BiOBr (Ouedraogo et al., 2022). This recombination issue can significantly impact the photocatalytic activity and the effectiveness of BiOBr in degrading pollutants. Additionally, BiOBr photocatalytic performance can be limited by its relatively low specific surface area compared to other photocatalysts, which can limit its adsorption capacity and subsequent pollutant degradation performance. To address the highlighted limitations, researchers have explored various strategies such as elemental doping (Wang et al., 2023), modification with semiconductor (to form heterojunction) (Shi et al., 2019), polar molecule modification (Zhou et al., 2021), among others to enhance BiOBr photocatalytic performance. For instance, Zhang et al., (2021), in their study reported a low surface area for BiOBr (6.48 m^2/g), prior modified with UiO-66-NH_2 metal-organic frameworks (MOFs), resulting in a significant increase in the surface area reaching 92.88 m^2/g. Other studies on the fabrication of BiOBr composites with carbon source include biochar/BiOBr (Geng et al., 2020), and carbon/BiOBr (Zhang et al., 2022). The formation of heterojunction between carbon-based semiconductor photocatalysts and other bismuth-based semiconductor BiOBr/g-C_3N_4/Ti_3C_2Tx (Wu et al., 2023) and Bi_2S_3/BiOBr/reed straw biochar (Li et al., 2020a) were receiving significant attention due to their low toxicity and better optical absorption. These were reported to improve the photosensitivity activity of the photocatalyst while enhancing charge separation and preventing agglomeration.

Strategies of development of BiOBr composites integrated carbon-based materials like biochar can be of great importance in improving its photocatalytic efficiency and stability by enhancing its surface area and facilitating charge separation through the

conductive effect of biochar (El Gaini, 2024; L. Meng et al., 2021) The functional characters such as oxygen-containing group in biochar also facilitate the binding of pollutants onto the surface of the composites' catalyst for better pollutant removal efficiency (Bhattacharjee & Ahmaruzzaman, 2024). These can be achieved through surface modification and effective electron transfer from BiOBr by its internal electric field to the conductive carbon component of biochar, thus, preventing the recombination of electron-hole pairs (Luo et al., 2022). The synergistic interaction between these two components can improve the overall photocatalytic process.

On the other hand, the heterojunction approach of BiOBr via the integration of two semiconductors having different electronic structures to construct an interface for enhanced charge separation can be another strategy to improve the photocatalytic activities of BiOBr (Qin et al., 2024). This strategy could increase the optical absorption range, ease the separation and migration of photoexcited electrons, and as well enhance chemical stability (Wang et al., 2024). This involves aligning the valence band and the conduction bands of the semiconductors to facilitate electron-hole migration. The procedure suppresses recombination and ensures that the holes and electrons actively participate in oxidation-reduction reactions that is crucial for pollutant degradation.

Some biocompatible polymers can be used as an encapsulating agent due to their ability to form hydrogels, consequently enhancing the stability of the composite. Previous studies have reported the successful encapsulation of some biopolymers such as chitosan (Ramírez et al., 2024; Sadjadi et al., 2023), cellulose (Cheng et al., 2024; Yan et al., 2023), (Zheng et al., 2024) and sodium alginate (Ben Ayed et al., 2023; Chkirida et al., 2024; Xu et al., 2024; Zhao et al., 2024), among others, support in photocatalysis. Conversely, sodium alginate offers easier gelation than other polymers due to its unique structural

arrangement. Sodium alginate structurally consists of alternating blocks of guluronic acid and mannuronic acid residues (Abka-khajouei et al., 2022). In the presence of Ca^{2+} ions (through $CaCl_2$ cross-linker), guluronic acid regions cross-linked to form a network of porous and stable matrix suitable as an encapsulating agent for photocatalysts (Kumar et al., 2024). Meanwhile, engulfing BiOBr composites into sodium alginate requires the interaction of sodium alginate and cross-linking agents. This enables the BiOBr particles to be entrapped within this network and maintain uniform distribution and porosity. The encapsulation also stabilizes the photocatalyst and enhances recyclability.

In this study, biochar (BC) from palm oil mill effluent (POMES) has been utilized as a novel supporting carbonaceous material for BiOBr-based composite that is rich in oxygenated functional groups, larger surface area, good conductivity, and easy separation from the aqueous medium. The idea behind composites and heterojunction formation aims to enhance photocatalytic performance by improving its light visibility, and/or promoting charge separation efficiency, and regeneration ability while the structure remains intact. More so, the choice of appropriate polymer support is important to prevent the blockage of the surface of the photocatalysts. The immobilization/encapsulation of photocatalysts into sodium alginate polymer support would be of great importance in enhancing the separation and easy recovery of photocatalysts after application.

1.2 Problem Statement

Among the antibiotics, CIP is one of the major pharmaceutical pollutants being fed into waterbodies across the globe. This is because it is largely consumed by humans and animals and passed into the environment mainly through hospital waste, industrial waste and pharmaceutical activities. The occurrence of CIP detection in wastewater is a

sign that using conventional treatment methods to clean up antibiotic-polluted water is not sufficient. Even at low concentrations, the buildup of CIP molecules in water will result in the emergence of drug-resistant bacteria, which could be extremely harmful to people and even the ecological environment. (Weng et al., 2022). Therefore, CIP pollutants in wastewater from industrial activities are significant environmental issues and demand urgent attention.

Researchers have shown significant interest in developing effective methods for removing these highly toxic persistent organic pollutants from water. Among the potential techniques such as adsorption (Ahmed et al., 2015; Alnajrani & Alsager, 2020; Mangla et al., 2022), membrane filtration (Nasrollahi et al., 2022; Nusrat Aman et al., 2023; Song et al., 2023), chemical coagulation (Guo et al., 2023; Lv, Chen, et al., 2023), ozonation (Abromaitis et al., 2024; Adamek & Baran, 2024), advanced oxidation processes (Brillas, 2023; Brillas & Peralta-Hernández, 2024; S. Li et al., 2023), and combined methods (Audino et al., 2023; Nghia et al., 2023; Titchou et al., 2021) among others employed in wastewater treatment, advanced oxidation processes (AOPs) have been considered one of the most effective wastewater treatment techniques due to their higher removal efficiency (Rayaroth et al., 2022). Meanwhile, heterogeneous photocatalysis is preferable to other AOPs wastewater treatment due to its ease of separation, cost-effectiveness, environmental friendliness, ease of operation, and capability to completely degrade/mineralize pollutants under appropriate conditions into environmentally safe products such as carbon dioxide and water (Issaka et al., 2024; Sibhatu et al., 2022; Zheng et al., 2024). Moreover, it is solar light-driven friendliness. Meanwhile, for efficient heterogeneous photocatalysis in AOPs wastewater treatment, a promising potential

photocatalyst with intrinsic features including good sensitivity to visible light absorption, narrow band gap, good charge separation, and cost-effectiveness is required.

Recently, among the bismuth oxyhalide photocatalysts, bismuth oxybromide (BiOBr) has been extensively investigated as a preferred alternative to conventional metal oxide semiconductors due to its moderate band gap and light-harvesting capability. However, BiOBr's relatively low surface area, fast recombination rate of photogenerated electron-hole, and partial visible-light absorption often experienced in the utilization of BiOBr for AOPs are its major challenges. These constraints are considered severe drawbacks to its photocatalytic performance and preference.

Therefore, the development of BiOBr-based composite photocatalysts to improve the photocatalytic performance of BiOBr featuring the use of BiOBr/carbonaceous materials has been attempted (Luo et al., 2022). Carbonaceous material has the potential to facilitate charge separation of BiOBr efficiency and increase the surface area which can be beneficial to its adsorptive properties.

Meanwhile, various BiOBr/carbonaceous materials composites such as BiOBr/activated carbon (Nethaji et al., 2018), BiOBr/carbon quantum dots (Ji et al., 2018), CQDs/Clay@BiOBr (Chuaicham et al., 2022), graphene-Fe_2O_3/BiOBr (Wu et al., 2019), and BiOBr/biochar have been developed and reported to have enhanced the charge transfer and charge separation of BiOBr. Among these various carbonaceous materials, biochar-based sources stand out as efficient, low-cost, and sustainable sources that also contribute to waste reduction in the environment. Some of the common basic sources of biochar include agricultural wastes such as rice husks (Agassin et al., 2023; Bose et al., 2024), wheat straw (Hamid et al., 2024; K. Yang et al., 2023), corn stover (Fu et al., 2024;

Ma et al., 2024), and oil palm wastes (Nusrat Aman et al., 2023; Promraksa & Rakmak, 2020; Savitri et al., 2023; Su et al., 2023; Zakaria et al., 2023). Meanwhile, oil palm wastes including palm fronds, palm kernel shells, and palm oil mill effluents effluent (POME) have drawn more attention from researchers due to their generation in enormous quantities.

Oil palm plays a crucial role in Malaysia's economy, with high volume of waste generated (mainly palm fronds, palm kernel shells, and palm oil mill effluent) from its utilization for various industrial and agricultural purposes. Despite the advantages, oil palm wastes including palm fronds, palm kernel shells, and palm oil mill effluents effluent (POME) have drawn more attention from researchers due to their generation in enormous quantities. Improper disposal or management of this generated waste poses environmental challenges including contamination of water bodies and emission of greenhouse gases (Ahmad et al., 2023)

Research and development initiatives focus on exploring and implementing innovative technologies for converting waste into valuable materials, thereby contributing to effective waste reduction and promoting environmental sustainability (Samuel Olugbenga et al., 2024a). Palm fronds, palm kernel shells (PKS), and POME have been utilized to prepare biochar (Iberahim et al., 2019; Lawal et al., 2020; Seow et al., 2024). These various biochar offers distinct properties that influence their performance in a variety of applications, particularly concerning environmental remediation such as wastewater treatment. The characteristics of oil palm wastes from various sources influenced their performance for various wastewater treatment techniques featuring adsorption applications and photocatalyst support (Daud et al., 2024; Fatimah et al., 2024; Jagaba et al., 2023). For instance, palm oil brunch biochar (POBB) contains moderate

levels of oxygenated functional groups, such as phenolic (-OH), cellulose and hemicellulose (C-H) bond, and aromatic carbon (-O-C) (Awoh et al., 2024). It is also reported to have a lower surface area, which may hinder its adsorptive properties (Sari et al., 2014). PKS biochar, on the other hand, possesses high surface area (Dechapanya & Khamwichit, 2023; Ming-Twang et al., 2017) and high fixed carbon content (Kong et al., 2019). However, its oxygen-containing groups, such as -C=O (aldehyde) and -C-O (ketone) may also be destroyed after carbonization due to its thermal instability (Hamza et al., 2016). In contrast, POME sludge biochar is exceptionally rich in functional groups, including carboxyl (-COOH), hydroxyl (-OH), -C-O-C, and relatively partly nitrogen-based groups, resulting from the organic content of the sludge (Iberahim et al., 2018). These functional groups can significantly enhance its hydrophilicity, and adsorption of pollutants potential (Gasim et al., 2022). Furthermore, comparing POME sludge biochar with PFB and PKSB, it contains high levels of oxygen-rich functional groups, which make it particularly more effective for adsorption through its high porosity and surface area. Moreover, it can enhance charge transfer through the conducive power of biochar in the composite photocatalyst by improving the electrical conductivity (Kong et al., 2024) and facilitating better interaction. These properties can thereby enhance the overall photocatalytic performance of BiOBr (Ye et al., 2019). In addition, POMES can perform trio functions by improving the surface area and minimizing the cost of production of BiOBr photocatalyst composites, limiting faster recombination of photogenerated electron-hole pair rate and the process of recycling the sludge waste into biochar can reduce pollutants in the environment.

Additionally, construction of heterojunction photocatalysts using BiOBr with another semiconductor photocatalyst such as bismuth oxide (Bi_2O_3) and graphitic carbon

nitride (g-C_3N_4) can help facilitate high optical response for better semiconductor quantum efficiency, ease of separation, and migration of photoexcited electrons, which in turn prevent the electron-hole recombination rate, and improve the chemical stability of the BiOBr. Meanwhile, in an attempt to develop a potent BiOBr/biochar-based photocatalyst with ease of separation and recovery from the aqueous medium, the powdered BiOBr/biochar-based photocatalyst was further fabricated into beads by encapsulation into sodium alginate as polymer support, thus addressing the challenge encountered during the recovery process in photocatalysis.

1.3 Research Objectives

i. To fabricate and characterize BiOBr-biochar-based (BBC) binary photocatalyst composites via the free-solvent hydrothermal method as a potential photocatalyst towards the photodegradation of CIP antibiotic.

ii. To fabricate and characterize BiOBr-biochar-based ternary heterojunction composites (BBC-B and BBC-G) as potential photocatalysts toward the photodegradation of CIP under visible light.

iii. To prepare and characterize BiOBr-biochar-alginate beads and investigate their potential toward the degradation of CIP under visible light irradiation and potential of recovery from aqueous medium

1.4 Scope of the Study

The scope of this research work involves the preparation of biochar from palm oil mill effluent sludge and the fabrication of BiOBr-biochar-based photocatalyst composites,

their characterization, and application for the photocatalytic degradation of CIP antibiotic from aqueous solution under solar simulated visible light.

1.5 Organization of the Thesis

This thesis consists of eight (8) chapters. Chapter one (1) provides detailed information about the background of the study, the problem statements highlighting the research gaps, and the contribution of the research to the field of study. The objectives and the scope of the study were also inclusive. Chapter two (2) presents the literature review on the past work that highlighted the related topic. Chapter three (3) highlights the experimental methodology adopted including the instrumentations employed in the characterization of the prepared photocatalyst composite. The information on the chemical reagents were also highlighted. Chapter four (4) detailed the results and discussion of the BBC composites application. Chapters five (5) and six (6) focused on the results and discussion from heterojunction ternary photocatalyst composites (BiOBr/BC/Bi_2O_3, (BBC-B), and BiOBr/BC/g-C_3N_4 (BBC-G) respectively while the result of the BiOBr/BC/SA (BC-SA) composite beads is detailed in chapter seven (7). The details of results and discussion in chapters 4, 5, 6, and 7 include the structural, morphological, surface property, functional group, thermal and optical characterization, and the findings on the performance of BBC, BBC-B, BBC-G, and BBC-SA for the removal of CIP were extensively discussed. Lastly, chapter eight (8) summarizes the key findings of the research and suggests some recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Pharmaceuticals

Pharmaceuticals, increasingly recognized as persistent organic pollutants (POPs), represent a significant and emerging threat to environmental and human health due to their persistence, bioaccumulation, and potential for long-range transport (Ghazal et al., 2022; Guo et al., 2019). Like traditional POPs, such as pesticides and industrial chemicals, pharmaceuticals can resist environmental degradation, allowing them to persist in water bodies, soils, and even the atmosphere for extended periods. Their persistence is primarily due to their chemical stability and resistance to breakdown processes (Samal et al., 2022), such as photolysis, hydrolysis, and biodegradation which means they can remain active in the environment long after their intended use. When pharmaceuticals enter water bodies whether through improper disposal, excretion, or industrial effluents they do not simply dissipate. Instead, they accumulate, leading to concentrations that can have severe effects on both ecosystems and human populations. The bioaccumulation of these compounds can lead to toxic effects, such as endocrine disruption, behavioral changes, and reproductive impairments in wildlife, which can ripple through ecosystems, causing declines in biodiversity and altering ecological balance (Papaioannou et al., 2023). Furthermore, the persistence of pharmaceuticals in drinking water sources, combined with their potential to bioaccumulate, raises serious concerns about long-term exposure to low doses of these substances, which can lead to chronic health issues, including antibiotic resistance, hormonal imbalances, and even carcinogenic effects (Letsoalo et al., 2023). The classification of pharmaceuticals as persistent organic pollutants called for urgent

action to develop more effective waste management strategies, advanced treatment technologies, and regulatory frameworks to prevent their release into the environment. The common source in which pharmaceutical waste can find its way to water bodies is presented in Figure 2.1.

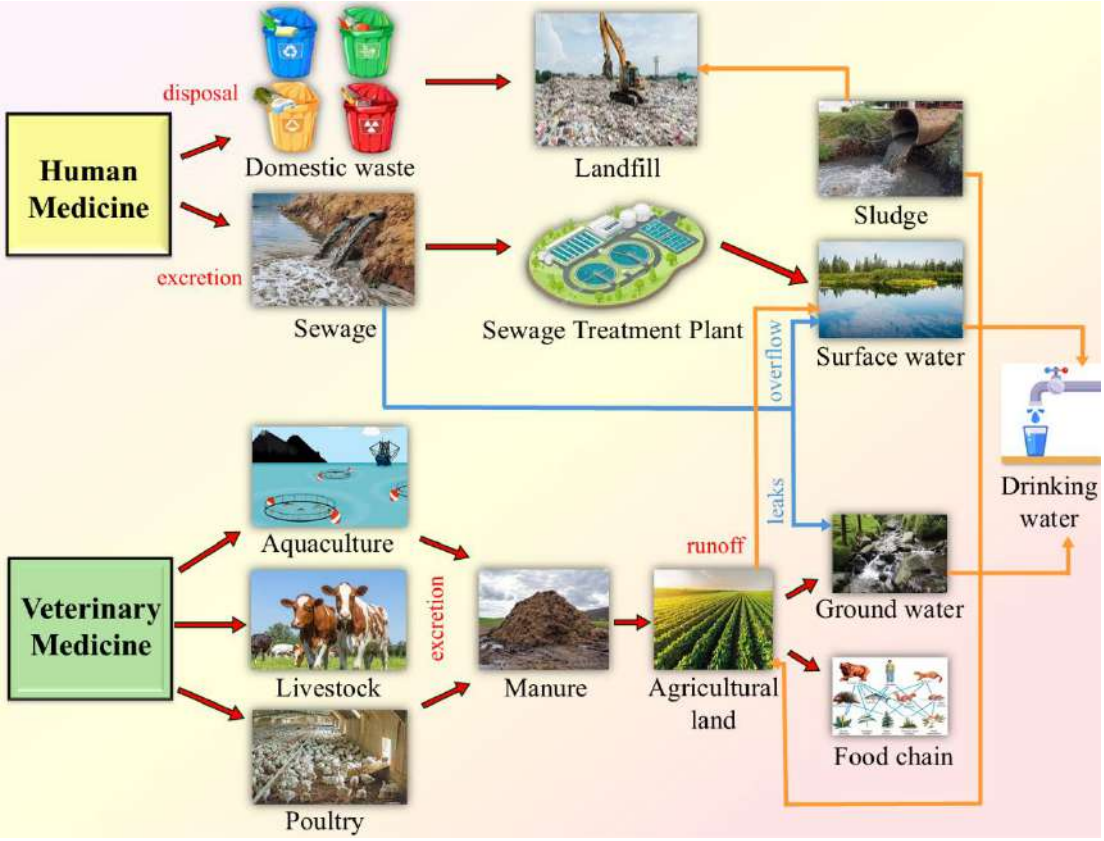


Figure 2.1 Some sources of pharmaceutical pollutants and their pathway to the environment

2.1.1 Antibiotics

Antibiotics are a critical class of pharmaceuticals that have revolutionized medicine by effectively treating bacterial infections. They are designed to combat bacterial infections by killing or inhibiting the growth of bacteria. Common antibiotics

include penicillin, fluoroquinolones, tetracyclines, macrolides, and cephalosporins (Uddin et al., 2021; Van et al., 2020), each with specific mechanisms of action targeting different aspects of bacterial cell function, such as cell wall synthesis, protein synthesis, or DNA replication.

Despite the importance of antibiotics in healthcare, the widespread and sometimes indiscriminate use has led to significant environmental concerns. Antibiotics often enter the environment through various pathways, including human and veterinary excretion, improper disposal of unused medications, and effluents from pharmaceutical manufacturing plants and healthcare facilities (Barathe et al., 2024; Saeed et al., 2024). Once in the environment, antibiotics can persist for extended periods, as many are resistant to natural degradation processes. This persistence is of great concern, especially in aquatic environments, where antibiotics can accumulate and exert selective pressure on bacterial communities, leading to the development and proliferation of antibiotic-resistant bacteria (ARB) (Bobate et al., 2023; Ding et al., 2023).

The rise of ARB is a major global health challenge, as it can render existing antibiotics ineffective, making infections harder to treat and increasing the risk of severe illness and death. In addition to the development of resistance, antibiotics in the environment can also have direct toxic effects on non-target organisms. For example, fluoroquinolone antibiotics have been shown to disrupt the growth and reproduction of aquatic species, including algae, invertebrates, and fish (Thai et al., 2023).

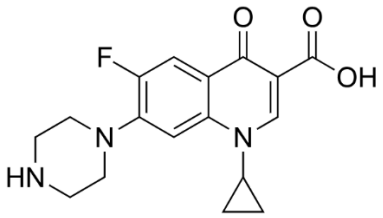
2.1.2 Ciprofloxacin (CIP)

CIP ($C_{17}H_{18}FN_3O_3$), a second-generation fluoroquinolone, is a broad-spectrum antibiotic used in treating a variety of bacterial infections. CIP, (synthetic antibiotic) was developed in the 1980s by Bayer AG, a German pharmaceutical company. It was first approved for medical use in 1987. The development of CIP was part of a broader effort to create antibiotics with broad-spectrum activity. CIP quickly gained popularity due to its effectiveness against both Gram-negative and Gram-positive bacteria, making it a versatile tool in treating various infections. It works by inhibiting bacterial DNA gyrase and topoisomerase IV, enzymes crucial for bacterial DNA replication and repair, thereby preventing bacterial growth and proliferation (Collins et al., 2024). The photochemical properties and molecular structure of CIP are presented in Table 2.1

CIP is popularly prescribed in treating a wide range of infections, including respiratory tract infections, urinary tract infections, gastrointestinal infections, skin infections, and certain types of sepsis (Thai et al., 2023). It is also used in the treatment of anthrax, particularly in the event of bioterrorism, due to its efficacy against *Bacillus anthracis*, the bacteria that cause anthrax (Heine et al., 2017). Due to its chemical stability and limited biodegradability, ciprofloxacin is resistant to conventional wastewater treatment processes. Conventional approaches such as biological degradation, sedimentation, and filtration often fail to remove CIP effectively, leading to its accumulation and detection in natural water bodies. The detection of CIP in surface water and wastewater ranges from one hundred ng/L to µg/L according to Tran et al., (2022). Meanwhile, the amount detected in hospital waste and drug-producing industries were reported to be 42.8 µg/L and 50 mg L^{-1} respectively according to Lien et al., (2016);

Ahmadzadeh et al., (2017) reports. As a result, the presence of CIP in water bodies not only disrupts microbial ecosystems but also contributes to the development and spread of antibiotic-resistant bacteria, posing severe health threats. Therefore, the development of advanced treatment methods capable of degrading CIP in wastewater is of paramount importance.

Table 2.1 Molecular structure and some physicochemical properties of ciprofloxacin

Name	Properties	Empirical formula	Chemical structure
CIP		$C_{17}H_{18}FN_3O_3$	
CAS number	85721-33-1		
Molecular weight	331.34		
pKa values	6.1 and 8.7		
Assay	≥ 98 %		
Empirical	1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-1,3-dihydroquinoline-3-carboxylic acid, ciprobay		

pKa values obtained from Hayri-Senel et al., (2024).

2.2 Wastewater Treatments

Wastewater treatment is essential for managing and mitigating pollution to protect environmental and public health. Wastewater treatment involves various methods to remove contaminants before water is released back into the environment or reused. Conventional treatment methods, including primary, secondary, and tertiary processes, address various aspects of wastewater contamination. Primary treatment focuses on removing large solids and debris through physical processes such as screening and

sedimentation (Saravanathamizhan & Perarasu, 2021). Secondary treatment, which includes biological processes like activated sludge and trickling filters, aims to degrade dissolved organic matter and pollutants using microorganisms (Sravan et al., 2024). While effective for organic waste, secondary treatment often falls short in removing persistent or complex contaminants, such as pharmaceuticals. Tertiary treatment further purifies wastewater through advanced filtration, nutrient removal, and chemical treatments but some pollutants remain challenging to address. Advanced Oxidation Processes (AOPs) offer significant advantages over conventional methods and have emerged as crucial technologies for treating persistent pollutants (Priyadarshini et al., 2022), particularly those resistant to conventional methods.

Each wastewater treatment method has its own set of techniques that vary in complexity, effectiveness, and application. An overview of these methods along with merits and limitatations are summarized in Table 2.2.

Table 2.2 Summary of general wastewater treatment methods, the advantages, and limitations

Treatment method	Merits	Limitations	References
Primary treatment	• Simple and cost-effective. • Removes large solids and sediments.	• Ineffective in removing dissolved organic matter and nutrients. • Requires large areas for settling tanks.	(Crini & Lichtfouse, 2019)
Secondary treatment (e.g Anaerobic wastewater treatment systems, activated sludge process among others	• Effective in reducing BOD and COD. • Widely used and well-understood processes. • Low installation cost	• High energy consumption. • Sludge production requires further treatment. • Less effective against emerging contaminants.	(Tran et al., 2022; Zieliński et al., 2023)
Tertiary treatment (e.g Coagulation and Flocculation, adsorption	• Produces high-quality effluent. • Removes pathogens and nutrients. • Reduces eutrophication risks.	• High operational and maintenance costs. • Requires advanced technology and skilled personnel. • Generation of sludge	(Sadegh & Ali, 2018)
Tertiary treatment (e.g Advanced oxidation processes)	• Target specific contaminants. • Suitable for water reuse and sensitive environments. • Complete mineralization of pollutants. • Effective for organic and inorganic pollutants. • Non-selectivity oxidation destruction of organic pollutants.	• Very high cost and energy-intensive. • Complex operation and maintenance. • Potential membrane fouling in filtration.	(Priyadarshini et al., 2022)

The selection of each wastewater treatment method is based on the specific needs of the wastewater being treated and the intended use of the treated water.

2.3 Advanced Oxidation Processes (AOPs) for Wastewater Treatment

Recently, AOPs have been used as promising alternative techniques in response to the traditional methods for efficiently removing organic pollutants from wastewater. AOPs are chemical treatment methods designed to remove organic pollutants from water by generating highly reactive species, primarily hydroxyl radicals ($^{\bullet}OH$) (Kumari & Kumar, 2023). These radicals are powerful oxidizing agents capable of attacking and breaking down a wide range of complex organic molecules into simpler, non-toxic, compounds such as carbon dioxide (CO_2) and water (H_2O) (Khan et al., 2023a). The ability of hydroxyl radicals to oxidize a wide range of organic contaminants rapidly and non-selectively makes AOPs effective for treating pollutants that are resistant to conventional methods (Gaur et al., 2022).

Furthermore, AOPs are highly versatile and adaptable, capable of being applied to various types of wastewaters, including industrial effluents, municipal wastewater, and contaminated groundwater. Moreover, AOPs can be effectively combined with other treatment processes, such as membrane filtration, biological treatment, or adsorption, creating hybrid systems that enhance overall treatment efficiency and performance (Babu Ponnusami et al., 2023; Rosman et al., 2018). These merits make AOPs particularly suitable for addressing the challenges posed by emerging contaminants and achieving higher levels of water purity, especially in applications where conventional treatment methods fall short.

AOPs can be classified based on the primary mechanism of hydroxyl radical generation. The classification typically revolves around the type of chemical, physical, or electrochemical process involved. The major types of AOPs include ozone-based, Fenton, photocatalysis, and combined methods. Each technique generates highly reactive hydroxyl radicals (•OH) capable of degrading a wide range of organic contaminants.

2.3.1 Ozone-Based

Ozonation has gained significant attention in AOP research due to ozone's high oxidative potential (2.07 V vs. SHE) (Zhang et al., 2024). This powerful oxidant has been widely used for drinking water disinfection and wastewater treatment. Ozone-Based Processes AOPs utilize ozone (O_3) as the primary oxidant. Ozone generates hydroxyl radicals through various mechanisms when combined with hydrogen peroxide (H_2O_2) or ultraviolet (UV) light (Jamali et al., 2024; Liu et al., 2021a). The O_3/H_2O_2 process involves injecting ozone and hydrogen peroxide into the wastewater, where the latter (H_2O_2) reacts with ozone to produce radicals. Similarly, the O_3/UV process uses UV light to activate ozone, enhancing its oxidative capacity. The primary advantages of ozone-based processes include their high efficiency in oxidizing organic pollutants and their ability to address a broad spectrum of contaminants (Cuerda-Correa et al., 2020; Liu et al., 2021). However, the high operational costs associated with ozone generation and the need for effective ozone destruction in treated effluents pose significant disadvantages (Jamali et al., 2024). Equations 2.1, 2.2, and 2.3 describe the mechanism of ozone-based degradation processes corresponding to O_3/H_2O_2 and O_3/UV, respectively.

$$H_2O_2 + 2O_3 \rightarrow 2HO^{\bullet} + 3O_3 \quad (2.1)$$

$$O_3 + UV \rightarrow O_2 + O^{\bullet} \quad (2.2)$$

$$O^{\bullet} + H_2O \rightarrow O_2 + 2OH^{\bullet} \quad (2.3)$$

2.3.2 Fenton Oxidation

In recent times, studies have highlighted the photo-Fenton reaction as a highly effective and promising method for the removal of pollutants from wastewater (Liang et al., 2023). Fenton oxidation is known for its effectiveness in degrading complex organic contaminants through the generation of highly reactive •OH. The Fenton process involves the reaction of H_2O_2 with ferrous iron (Fe^{2+}) to produce •OH, which can rapidly oxidize and decompose a wide range of organic pollutants (Pimentel Prates et al., 2023). This process operates optimally under acidic conditions (Lima Santos Klienchen Dalari et al., 2020), where the reaction kinetics are enhanced, leading to the efficient removal of contaminants. One of the significant advantages of Fenton oxidation is its ability to treat pollutants with high efficiency, making it suitable for a variety of industrial and municipal wastewater applications (Pimentel Prates et al., 2023). The process can be further optimized by incorporating UV light, creating the photo-Fenton process, which enhances radical generation and improves treatment performance. Despite its strengths, the Fenton process faces challenges such as the need for careful pH control and the production of iron sludge by-products (Lima Santos Klienchen Dalari et al., 2020).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + HO^- \quad (2.4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \bullet + HO^+ \quad (2.5)$$

2.3.3 Photocatalysis

With rapid advancements in the development of novel nano-photocatalysts, photocatalysis has gained global recognition as a sustainable solution for wastewater treatment (Mishra & Sundaram, 2023). This is due to its great promise as an affordable and eco-friendly approach to water purification (Ali et al., 2023).

Photocatalysis involves the use of semiconductor materials, such as titanium dioxide (TiO_2), under UV or visible light to produce hydroxyl radicals. When a semiconductor photocatalyst is illuminated, it absorbs photon energy and generates electron-hole pairs which interact with water and oxygen to form radicals (Chakravorty & Roy, 2024). These radicals can oxidize a wide range of organic pollutants, including pharmaceuticals, dyes, and pesticides (Imohiosen et al., 2024; Khan et al., 2023b). Photocatalysis offers several advantages including environmental sustainability, low chemical consumption, and operation under mild conditions (Hassaan, El-Nemr, et al., 2023; Zheng et al., 2024). Furthermore, its ability to degrade a wide range of organic contaminants that are resistant to other methods and typically generate non-toxic by-products, makes it environmentally friendly (Hassaan, El-Nemr, et al., 2023; Zheng et al., 2024).

2.3.4 Combined AOPs

Combined AOPs are the integration of multiple advanced oxidation techniques to enhance treatment performance. For instance, combining ozone with photocatalysis or Fenton can synergistically improve pollutant removal efficiency. These combined methods leverage the strengths of each AOP, offering improved degradation of complex

contaminants and greater flexibility in addressing various types of pollution. However, the complexity and cost of implementing and managing combined AOP systems can be a challenge.

Overall, while each type of AOP has its own set of advantages, including high efficiency and broad applicability, they also come with disadvantages such as high operational costs, the need for specific conditions, and potential by-product management issues. The choice of AOP depends on the specific requirements of the wastewater treatment, including the type and concentration of contaminants, treatment goals, and economic considerations. Below are some efficiencies recorded using different AOPs in the literature for wastewater treatment.

For instance, Wang et al., (2021) reports the successful degradation of Rhodamine B (RhB) and tetracycline hydrochloride (TH) using a novel ternary heterojunction of $Bi_2WO_6/BiFeO_3/g\text{-}C_3N_4$ via a heterogeneous photo-Fenton process. The study demonstrated that the heterojunction possessed enhanced photocatalytic activity due to the effective separation of photogenerated electron-hole pairs. This separation was facilitated by the good conductivity of $BiFeO_3$ and $g\text{-}C_3N_4$, which also contributed to enhanced photo-Fenton activity. As a result, the system achieved significant degradation efficiencies, with 99.85 % degradation of RhB in 30 min and 83.68 % degradation of TH in 45 min. The study confirmed the feasibility of using the $Bi_2WO_6/BiFeO_3/g\text{-}C_3N_4$ heterojunction for the highly efficient degradation of persistent organic pollutants in wastewater.