POME-derived Ag/TiO_2-based ternary nanocomposites for oxytetracycline degradation under visible light and membrane integration

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DECLARATION

I hereby declare that the work presented in this thesis was conducted in full compliance with the regulations of Universiti Malaysia Sarawak (UNIMAS). Except where proper acknowledgment is given, this work is solely the effort of the author. This thesis has not been accepted for the award of any other degree and is not being **concurrently** submitted for any other academic qualification.

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POME-derived Ag/TiO_2-based photocatalyst for oxytetracycline degradation under visible light and membrane integration

ABSTRACT

The rise of emerging pollutants demands efficient and sustainable water treatment technologies. Ag/TiO_2-driven photocatalysis is a viable solution due to its durable visible-light activity and antimicrobial properties, yet stability, recovery, and overall synthesis sustainability remain major challenges that hinder its practical application. Therefore, the need to develop a green, durable, and easily recoverable Ag/TiO_2-based photocatalyst is crucial to advance photocatalysis as an eco-friendly solution for the treatment of complex pollutants. To overcome these drawbacks, this study explored the green synthesis of Ag/TiO_2-based ternary nanocomposites using palm oil mill effluent (POME) as a natural reducing and stabilizing agent. Two ternary photocatalysts, Ag/Bi_2MoO_6/TiO_2 (ABMOT) and Ag/g-C_3N_4/TiO_2 (AGCNT), were synthesized via a microwave-assisted method and extensively characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffractometry (XRD), Scanning Electron Microscopy with Energy-Dispersive X-ray (SEM-EDX), and UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS). Their photocatalytic activities were evaluated against oxytetracycline hydrochloride (OTC). Under visible-light irradiation, ABMOT achieved 97.2% OTC degradation at an optimal dosage of 0.6 g/L, while AGCNT reached 81.3% under the same conditions. ABMOT demonstrated stronger dark-adsorption capacity and greater tolerance to increasing pollutant concentrations than AGCNT, indicating better surface affinity and active-site accessibility. Regardless, both nanocomposites showed good stability over four consecutive recycling cycles, indicating superior stability and reusability potential. Additionally, both nanocomposites further demonstrated antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, confirming their multifunctional potential. To address the limitation of powder recovery in slurry photocatalysis, both nanocomposites were immobilized in polyacrylonitrile (PAN) membranes via the phase-inversion method. Structural and surface analyses confirmed successful integration, with nanocomposite-loaded membranes exhibiting enhanced hydrophilicity and porosity. Permeation studies revealed that AGCNT@PAN (2 wt%) achieved the highest pure water flux (170.94 $L \cdot m^{-2} \cdot h^{-1}$) and rejection rate (90.34%) compared to bare PAN membranes with 149.51 $L \cdot m^{-2} \cdot h^{-1}$ pure water flux and 44.88 % rejection rate. Consequently, ABMOT@PAN also showed improvements. Overall, this study demonstrates a novel, eco-friendly approach for synthesizing multifunctional photocatalysts by valorizing agro-industrial waste. These findings provide valuable insights into advancing green nanotechnology for sustainable water treatment applications.

Keywords: Palm oil mill effluent, green synthesis, titanium dioxide, silver, photocatalysis, antibacterial, membrane.

Fotopemangkin berasaskan Ag/TiO_2 daripada POME untuk degradasi oksitetrasiklin di bawah cahaya nampak dan integrasi dalam membran

ABSTRAK

Peningkatan bahan cemar muncul yang semakin membimbangkan memerlukan teknologi rawatan air yang cekap dan lestari. Fotopemangkinan yang berasaskan Ag/TiO_2 berpotensi menjadi salah satu kaedah untuk mengatasi isu ini kerana keupayaannya untuk diaktifkan di bawah cahaya nampak serta sifat antibakterianya. Namun demikian, aplikasi fotopemangkin berasaskan-Ag/TiO_2 masih terhad disebabkan oleh isu kestabilan, kesukaran untuk perolehan semula dan cabaran dalam kaedah sintesis yang lestari. Oleh itu, terdapat keperluan untuk membangunkan fotopemangkin berasaskan-Ag/TiO_2 yang hijau, lestari dan mudah untuk diperoleh semula agar teknologi fotopemangkinan dapat dikembangkan sebagai solusi mampan untuk rawatan air serta degradasi bahan cemar muncul. Kajian ini meneroka sintesis hijau nanokomposit pertigaan berasaskan Ag/TiO_2 dengan menggunakan efluen kilang kelapa sawit (POME) sebagai agen penurun dan penstabil semula jadi. Dua fotopemangkin pertigaan iaitu, Ag/Bi_2MoO_6/TiO_2 (ABMOT) dan Ag/g-C_3N_4/TiO_2 (AGCNT), disintesis melalui kaedah mikrogelombang dan dicirikan menggunakan FTIR, XRD, SEM-EDX dan UV-Vis DRS. Ujian terhadap oksitetrasiklin hidroklorida (OTC) menunjukkan ABMOT dapat mencapai degradasi sebanyak 97.2% dengan dos optimum 0.6 g/L, manakala AGCNT mencatatkan 81.3% di bawah cahaya tampak. Selain itu, kapasiti penjerapan dalam keadaan gelap untuk ABMOT lebih tinggi jika dibandingkan dengan AGCNT. Ini menunjukan bahawa ABMOT mempunyai toleransi yang lebih tinggi untuk kepekatan bahan cemar yang lebih tinggi kerana afiniti permukaan yang lebih sesuai terhadap oksitetrasiklin. Walau bagaimanapu, kedua-dua nanokomposit menunjukkan kestabilan yang baik untuk empat kitaran degradasi secara berterusan yang menjadi penanda aras kepada keupayaan pengitaran semula. Kedua-dua nanokomposit turut menunjukkan keberkesanan antibakteria terhadap Escherichia coli dan Staphylococcus aureus. Bagi menangani kekangan pemulihan serbuk, nanokomposit telah dimuatkan ke dalam membran poliakrilonitril (PAN) melalui kaedah kensongsangan fasa. Membran yang tersekatgerak dengan nanokomposit menunjukkan peningkatan hidrofilisiti dan porositi, dengan AGCNT@PAN (2 wt%) mencapai fluks air tulen tertinggi (170.94 $L \cdot m^{-2} \cdot h^{-1}$) dan kadar penyingkiran sebanyak 90.34% berbanding dengan membran PAN tanpa pengubahsuaian yang hanya mempuntai fluks air tulen sebanyak 149.51 $L \cdot m^{-2} \cdot h^{-1}$ dan kadar penyingkiran sebayank 44.88%. Secara keseluruhan, kajian ini membuktikan pendekatan mesra alam dan baharu untuk menghasilkan fotopemangkin pelbagai fungsi melalui pemanfaatan sisa industriagro POME. Penemuan ini memberikan perspektif yang bermakna ke arah kemajuan nanoteknologi hijau bagi aplikasi rawatan air yang lestari.

Kata Kunci: *Efluen Kilang Kelapa Sawit (POME), sintesis hijau, titanium dioksida, argentum, fotopemangkinan, antibakteria, membran*

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LIST OF ABBREVIATIONS

ABMOT	$Ag/Bi_2MoO_6/TiO_2$
AGCNT	$Ag/Bi_2MoO_6/TiO_2$
ATR	Attenuated Total Reflectance
DRS	Diffuse Reflectance Spectroscopy
EDC	Endocrine-Disrupting Chemical(s)
EDX	Energy Dispersive X-ray
FTIR	Fourier Transform Infrared Spectroscopy
GAE	Gallic Acid Equivalent
NCs	Nanocomposite(s)
NPs	Nanoparticle(s)
OTC	Oxytetracycline hydrochloride
PAN	Polyacrylonitrile
PBS	Phosphate Buffer Solution
POME	Palm Oil Mill Effluent
PPCPs	Pharmaceutical and Personal Care Products
PWF	Pure Water Flux
QE	Quercetin Equivalent
RR	Rejection Rate
SEM	Scanning Electron Microscopy
SPR	Surface Plasmon Resonance
TEM	Transmission Electron Microscopy
TPC	Total Phenolic Content
TFC	Total Flavonoid Content
UV-Vis	Ultraviolet-Visible
XRD	X-ray Diffractometry

CHAPTER 1:

INTRODUCTION

1.1 Background of Study

As population growth and industrialization continue to progress around the world, the inevitable fate of water contamination from the penetration of various emerging pollutant sources poses a threat to both human well-being and the environment. Among various emerging pollutants, pharmaceutical and personal care products (PPCPs) have been recognized as an environmental concern due to their persistence, bioaccumulation potential, and adverse effects on aquatic ecosystems and human health Hena et al. (2021). Despite lacking regulatory status, the European Union (EU) announced that at least 33 compounds were prioritized for removal over the next 2 decades (Arumugam et al., 2025). Some of the compounds that were listed include anti-inflammatory drugs (e.g. ibuprofen, diclofenac) and antibiotics (Kumar et al., 2023). These compounds are well known to be endocrine-disrupting chemicals (EDCs) or carcinogenic. Although they are typically found in trace amounts (~0.1 ng/L to 200 ng/L), the concentrations of these compounds have been increasing in recent years, raising concerns about potential environmental risks (Hena et al., 2021; Kanakaraju et al., 2025; Ślósarczyk et al., 2021).

Despite the existence of conventional technologies in wastewater treatment, such as coagulation, flocculation and biological methods, they are limited in their ability to completely remove decontamination of the said emerging pollutants, including persistent organic/inorganic pollutants, and heavy metals (Ahmed & Haider, 2018; Anvari et al., 2021; Della Rocca et al., 2021). Generally, these processes end up producing secondary pollutants, which require further processing (Kweinor Tetteh & Rathilal, 2021). Therefore, there is a need to develop advanced wastewater treatment methods that efficiently purify contaminated water in a more sustainable way.

Advanced oxidation processes (AOPs) have emerged as effective wastewater treatment technologies for removing persistent, non-biodegradable organic pollutants. AOPs

operate by generating highly reactive oxygen species (ROS), particularly hydroxyl radicals ($HO\bullet$), which have a strong oxidation potential (~2.8 eV) and can degrade a wide range of organic contaminants into simpler and less harmful compounds (Kumari & Kumar, 2023). Unlike conventional treatment methods, AOPs can mineralize recalcitrant pollutants rather than merely transferring them from one phase to another. Common AOPs used for the degradation of organic contaminants include ozonation, Fenton and photo-Fenton processes, electrochemical oxidation, and photocatalysis, the latter of which has gained increasing attention due to its operational simplicity and environmental compatibility.

In recent years, advances in nanotechnology have highlighted the use of AOPs as a promising tool for wastewater treatment across various settings (Kweinor Tetteh & Rathilal, 2021). Photocatalysis has been extensively studied for water treatment because it uses semiconductor materials and light energy to drive redox reactions. In a typical photocatalytic process, irradiation with light energy equal to or greater than the semiconductor's band gap excites electrons from the valence band (VB) to the conduction band (CB), generating electron–hole pairs. The photogenerated holes oxidize water or hydroxide ions to form hydroxyl radicals ($HO\bullet$), while the excited electrons reduce dissolved oxygen to generate superoxide radicals ($O_2\bullet$) These reactive species play a crucial role in the degradation and mineralization of organic pollutants in aqueous systems.

Among numerous nano-based materials, titanium dioxide (TiO_2) is widely applied as a nanocatalyst in the wastewater treatment method known as photocatalysis (Celebi et al., 2021; Dahl et al., 2014). This is primarily due to TiO_2 being non-toxic, chemically stable, and possessing efficient charge separation, which contributes to its high photocatalytic activity (Zoubi et al., 2021). However, pristine TiO_2 has some drawbacks due to its high bandgap, which leads to rapid recombination of photogenerated electron-hole pairs. This limits the photocatalytic effectiveness of TiO_2, as its photoexcitation is primarily confined to the ultraviolet (UV) spectrum, with minimal functionalization in the visible light region (Lin et al., 2006). Therefore, extensive research has been conducted to address the limitations of pristine TiO_2 by incorporating dopants (e.g. metals and non-metal elements) or co-catalysts (e.g. perovskites, semiconductors, etc.) in the fabrication process (Zhang et al., 2021).

Past researchers have successfully fabricated TiO_2 with plasmonic metals like gold (Au) and silver (Ag) using various methods including sol-gel, photoreduction and solvothermal (Wang et al., 2019; Wu et al., 2021; Yang et al., 2022). These materials can

enhance the photocatalytic performance of TiO_2, as plasmonic metals cause photoexcitation of the binary composite under visible light through surface plasmon resonance (SPR). Perovskite-based catalysts, such as bismuth (Bi)-based photocatalysts, on the other hand, can align the Fermi energy levels of the binary due to its narrow bandgap with a wide range of light absorption (Arif et al., 2021). Given its lower energy bandgap (E_g = 2.5 eV – 2.9 eV) in comparison to TiO_2, Bi-based perovskite, such as bismuth molybdate (Bi_2MoO_6), has suitable band structures to form heterojunctions which minimize electron-hole recombination, improve charge separation efficiency, and combine the favorable traits of the two photocatalysts (Belousov et al., 2024). Additionally, the incorporation of graphitic carbon nitride (g-C_3N_4) has also been widely studied. g-C_3N_4 is advantageous for its ability to harness visible light and for its suitable energy bandgap (E_g = 2.7 eV), which enables it to form heterojunctions with TiO_2, substantially boosting the collective photocatalytic performance of g-C_3N_4/TiO_2 heterojunction systems (Nemiwal et al., 2021).

Incorporation of g-C_3N_4 and Bi_2MoO_6 in the fabrication of Ag/TiO_2-based ternary composites has shown potential for the treatment of different pollutants (Ranjithkumar et al., 2023; Yin et al., 2021). However, there remains a need for a greener, simpler fabrication process to enhance photocatalytic performance under visible light. In most studies, the fabrication process uses harsh solvents (Aravind et al., 2021). Hence, the possibility of utilizing plant extracts, microorganisms, or agricultural waste via green synthesis can be performed to mediate the fabrication of ternary heterostructures of Ag/Bi_2MoO_6/TiO_2 and Ag/g-C_3N_4/TiO_2, providing a greener and more benign synthesis alternative.

The palm oil industry is among the largest in tropical regions such as Southeast Asia and Africa. Generally, about 10% of palm produce generates oil, and the other 90% ends up as vegetative waste such as empty fruit bunches, palm press fibers, palm kernel shells, and palm oil mill effluent (POME) (Ofori-Boateng & Lee, 2013). These wastes contain an abundance of phytochemicals such as carotenoids, phenolics, sterols, flavonoids and tocopherols, which have been previously studied and applied for the synthesis of various nanomaterials (Gan et al., 2012; Lucas-Gómez et al., 2020; Pradhan et al., 2022; Shankar & Rhim, 2016; Sowani et al., 2016). While the high organic content in POME could pose a threat to the environment, these unutilized compounds could also be a promising resource in the green synthesis of nanomaterials.

While conventional Ag/TiO_2-based NCs exhibit promising photocatalytic activity, their synthesis often relies on chemical reducing agents and surfactants that may introduce

surface defects, residual toxicity, or poor interfacial stability (Bhardwaj & Singh, 2021). In contrast, POME contains naturally occurring phenolic compounds, flavonoids, and organic acids that can act as mild reducing agents, capping agents, and stabilizers during nanocomposite formation (Imam et al., 2025). These biomolecules promote controlled nucleation, improved particle dispersion, and enhanced interfacial contact between composite components. As a result, POME-derived nanocomposites are expected to exhibit comparable or improved photocatalytic and antibacterial performance while offering a greener, more sustainable synthesis route and improved surface functionality for pollutant interaction.

1.2 Problem Statements

Previous studies have successfully demonstrated the green synthesis of Ag nanoparticles (NPs) (AgNPs) and gold nanoparticles (AuNPs) by utilizing POME as a reducing and stabilizing agent (Aliero et al., 2024; Gan et al., 2012). While these works have greatly contributed to the advancement of POME-derived nanomaterials, they largely focus on individual NPs. The fabrication of more complex ternary NCs requires more nuanced methods, especially when using an unconventional green source such as POME. Despite growing interest in sustainable synthesis routes, few studies explore the formation of ternary nanocomposites using POME as a key component. Furthermore, no comprehensive studies have investigated the photocatalytic and functional performance of POME-derived ternary systems.

Another drawback that needs to be addressed in the application of NCs in photocatalytic treatment is the difficulty of separating their powder post-treatment. One way to overcome this drawback is to immobilize the NC on materials that are easily removed or replaced, which has recently attracted research interest in integrating photocatalytic NCs with polymeric membranes (Elrasheedy et al., 2019). Amongst various membranes, polyacrylonitrile (PAN) is a well-known commercial polymer with good solubility in organic solvents, unique chemical and thermal properties, radiation stability, and low cost. However, PAN-based membranes also have disadvantages, including low chemical stability, fouling, and hydrophobicity. To enhance its properties and address its shortcomings, PAN can be modified with nanomaterials.

Therefore, this study aims to use POME extracts in the green fabrication of ternary Ag/TiO_2-based NCs, namely Ag/Bi_2MoO_6/TiO_2 and Ag/g-C_3N_4/TiO_2, and assess their effectiveness and functionality as visible-light-driven photocatalysts for degrading oxytetracycline hydrochloride (OTC), a model emerging pollutant. OTC has been chosen as the model pollutant owing to its widespread use as a veterinary and human antibiotic, especially in aquaculture. Furthermore, this study emphasizes incorporating POME-derived NCs into PAN membranes via the phase-inversion method. To develop a multifunctional membrane-photocatalyst system for potential wastewater treatment applications, a performance comparison with a powder-based photocatalytic system was also presented.

1.3 Research Hypothesis

This study hypothesizes that Ag/TiO_2-based ternary NCs synthesized using POME as a green reducing and stabilizing agent will exhibit enhanced physicochemical properties, visible-light photocatalytic activity, and antibacterial performance compared to conventionally synthesized counterparts. It is further hypothesized that immobilizing these NCs into polyacrylonitrile (PAN) membranes will improve material recovery and filtration performance without significantly compromising their functional properties.

1.4 Research Question

With respect to the aforementioned criteria, several research questions were raised:

i. How does the use of POME extracts influence the morphology, crystallinity and chemical composition of Ag/Bi_2MoO_6/TiO_2 and Ag/g-C_3N_4/TiO_2 NCs?
ii. How effective are the POME-derived ternary NCs against OTC?
iii. How effective are POME-derived ternary NCs against gram-positive and gram-negative bacteria?
iv. What are the effects of incorporating POME-derived NCs into PAN membranes on the permeability, separation efficiency and physicochemical properties?
v. Does the use of POME as a green synthesis agent present a viable alternative to chemical synthesis routes in terms of environmental and functional performance?

1.5 Research Objectives

Hence, the objectives of this study were:

i. To synthesize ternary Ag/Bi_2MoO_6/TiO_2 and Ag/g-C_3N_4/TiO_2 NCs using POME extracts as a green reducing and stabilizing agent, and characterize their physicochemical and structural properties.
ii. To evaluate the photocatalytic performance of the synthesized ternary NC in degrading OTC under visible light,
iii. To assess the antibacterial activity of the synthesized ternary NCs against gram-positive (*E. coli*) and gram-negative (*S. aureus*) bacteria,
iv. To fabricate PAN membranes embedded with POME-derived ternary NCs via the phase inversion method and determine their permeability and separation efficiency,
v. To compare the removal efficiency of bare ternary NC powders with membrane-integrated systems for the removal of OTC.

1.6 Significance of Study

This study successfully demonstrated a green and sustainable approach in synthesizing ternary Ag/TiO_2-based NCs using POME, which is an underutilized agro-industrial waste. By extending the application of POME beyond the synthesis of singular NPs to the fabrication of more complex heterostructure NC systems, this research contributed to the development of an eco-friendly photocatalyst with good functionality under visible light. In addition to evaluating the potential of POME-derived NCs in powder form, this research explored their incorporation into PAN membranes via the phase inversion method. Although the membrane systems were not applied under photocatalytic conditions, their basic filtration performance was evaluated to gain insight into how NC loading influences membrane properties, providing a basis for understanding the effectiveness of incorporating ternary NCs into membrane systems. The outcomes of this study provided useful insights into the viability of using POME as a green route for synthesizing ternary photocatalysts and the potential of integrating ternary NCs into filtration membranes for future multifunctional water treatment applications. This work supports the advancement of sustainable materials and highlights a pathway for the valorization of agro-industrial waste into high-value components in material science and environmental remediation technologies.

1.7 Research Hypothesis

This study focuses on the green synthesis of Ag/TiO_2-based ternary NCs using POME as a natural reducing and stabilizing agent. Two photocatalysts, Ag/Bi_2MoO_6/TiO_2 and Ag/g-C_3N_4/TiO_2, were synthesized via a microwave-assisted method and characterized for their physicochemical, structural, and optical properties using FTIR, XRD, SEM-EDX, and UV-Vis DRS.

The photocatalytic performance of the synthesized NCs was evaluated under visible-light irradiation for the degradation of OTC as a model emerging pollutant. The effects of catalyst dosage, initial pollutant concentration, and reusability were investigated. Antibacterial activity against gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria was also assessed.

To address limitations in catalyst recovery, the synthesized NCs were incorporated into PAN membranes via the phase-inversion method. The membrane study was limited to evaluating morphology, permeability, and rejection performance under filtration conditions. Photocatalytic membrane operation, large-scale application, and by-product toxicity analysis are beyond the scope of this study.

CHAPTER 2:

LITERATURE REVIEW

2.1 Advanced oxidation processes

Advanced oxidation processes (AOPs) are powerful chemical treatment technologies that emerged to remediate water, as they can remove a wide range of pollutants without producing secondary pollutants. This advantage addressed the limitations of conventional physicochemical and biological processes, which are further constrained by stringent environmental legislation (Liu et al., 2021). The first mentions of AOPs can be traced back to 1987 for the degradation of organic and non-biodegradable pollutants via the generation of hydroxyl radicals ($HO\bullet$) in place of oxidation with reagents such as potassium permanganate, potassium dichromate and sodium persulfate (Khan et al., 2020). This was because oxidation of pollutants with these reagents only produced partially oxidized intermediates that served as a secondary source of pollution. Instead, the generations of radicals led to the complete mineralization of pollutants into simpler products, such as carbon dioxide and water. Hence, in recent years, various AOPs have been introduced, including Fenton-based, ozone-based, and photocatalytic-based AOPs. In general, all these processes follow the same fundamental steps in which they produce either one or more species of ROS, such as $HO\bullet$ radical, superoxide radicals ($O_2\bullet$), peroxyl radical ($RO_2\bullet$), and so forth (Kumari & Kumar, 2023).

2.1.1 Photocatalysis

Among AOPs, photocatalysis has attracted considerable attention as an effective and sustainable water treatment technology. In recent years, there has been increased research interest due to its ability to generate ROS in situ (mainly OBJ and OBJ), while operating under relatively mild conditions compared with other conventional AOPs such as Fenton and ozone-based systems (Arifin et al., 2023). Fenton and ozone-based systems generally require strict pH control, continuous chemical input, and complex operational setups. In

photocatalytic systems, semiconductor materials are often employed to absorb photons with energy that is either equal to or greater than the energy band gap, E_g. This results in the excitation of electrons from the valence band (VB) to the conduction band (CB), forming electron-hole pairs (Abey et al., 2025). These charge carriers subsequently participate in surface redox reactions, thereby producing ROS. The combination of operational simplicity, the catalyst's reusability (due to the heterogeneous nature of the process), and the potential for complete mineralization has positioned photocatalysis as a promising and versatile AOP for the removal of persistent and emerging pollutants.

2.1.2 Photocatalytic reaction mechanism

Following the general principles of photocatalysis, the fundamentals of photocatalytic reaction mechanisms in water treatment involve a sequence of steps. The first step often involves charge generation, followed by transport and finally, the interfacial redox reactions of the photogenerated charge carriers on the surface of the catalyst (Chakravorty & Roy, 2024). The final step governs pollutant degradation reactions. Upon irradiation with incident photons, a semiconductor photocatalyst absorbs energy. This promotes electrons from the VB to the CB, resulting in the formation of electron-hole pairs. These charge carriers may undergo recombination or migrate to other catalyst surface, where they participate in simultaneous oxidation and reduction reactions. The photogenerated holes (h^+) can oxidize surface-adsorbed water molecules and hydroxide ions to form $HO\bullet$ radicals while excited electrons (e^-) reduce dissolved oxygen to generate $O_2\bullet$ radicals. The ROS subsequently attacks organic pollutant molecules through a series of complex reactions, which ultimately end in the mineralization of these complex pollutants to harmless by-products such as CO_2, H_2O, and inorganic ions. However, photocatalytic efficiency is strongly influenced by critical factors such as recombination rate, light absorption capacities, overall surface areas, and the availability of reactive sites on the photocatalyst surface (Bekele & Alamnie, 2025).

2.1.3 Application of photocatalyst in wastewater treatment

Metal oxide-based semiconductors are the most extensively investigated class of photocatalysts for wastewater treatment due to their chemical stability, ease of synthesis, and strong redox capability. The most widely studied metal oxides include zinc oxide (ZnO),

tungsten trioxide (WO_3), iron oxide (Fe_2O_3), and titanium dioxide (TiO_2), each exhibiting distinct band structures and photocatalytic behaviors, producing different treatment outcomes.

ZnO has been reported to exhibit photocatalytic activity comparable to that of TiO_2 under UV irradiation. For example, ZnO yielded degradation efficiencies of 99% for Tartrazine (TRZ), and 98% for naproxen (NAP) after 120 minutes of exposure under UV (Balu et al., 2019; Mohamed et al., 2023). However, its practical application is often limited by photocorrosion and dissolution. Another candidate photocatalyst, WO_3, has a narrower band gap (approximately 2.4 eV) and therefore exhibits strong visible-light-driven activity. For instance, Manganese and Copper (Mn-Cu) doped WO_3 nanostructures achieved 86.7% degradation of methylene blue (MB) within 175 minutes and 75.9% of levofloxacin (LVF) within 120 minutes under visible light (Rizvi et al., 2024). Similarly, Ag-doped WO_3 composites have shown enhanced performance in degrading chloramphenicol (CLP) (Truong et al., 2025). Fe_2O_3, despite being abundant and absorbing visible light, its efficiency is often limited by rapid charge carrier recombination, though it can be improved through heterojunction formation (Hitam & Jalil, 2020).

Among the afore-mentioned semiconductors, TiO_2 remains as the benchmark material due to its high chemical stability, non-toxic nature and resistance to photocorrosion. Modified TiO_2 systems, such as black TiO_2, have achieved 100% degradation of ciprofloxacin (CIP) under LED irradiation in 70 minutes (Samy et al., 2024). While TiO_2 primarily exhibits UV activity due to its wide band gap (3.2 eV), its consistent performance and environmental compatibility make it the reference material in research on heterogeneous photocatalytic wastewater remediation. A summary of various photocatalysts used for the degradation of organic pollutants is presented in Table 2.1.

Table 2–1: Summary of selected metal oxide-based photocatalysts for the removal of organic pollutants

Semiconductor	Dopant/Co-catalyst	Target Pollutant	Conditions	Removal Efficiency	Reference
TiO_2	Nitrogen	CIP	• Visible light • 70 minutes	100.0%	Samy et al. (2024)
WO_3	Mn-Cu	MB	• Visible light • 175 minutes • pH 11	86.7%	Rizvi et al. (2024)

WO_3	Ag	CLP	• Visible light • 120 minutes	~80.0%	Truong et al. (2025)
ZnO	g-C_3N_4/α-Fe_2O_3	TRZ	• Visible light • 120 minutes • pH 7 (Neutral)	99.34%	Balu et al. (2019)

ZnO	Pristine	NAP	• UV light • 120 minutes	98.7%	Mohamed et al. (2023)
Fe_2O_3	Carbon quantum dots	MB	• Visible light (Xenon) • 180 minutes	~90%	Hitam and Jalil (2020)

2.2 Titanium dioxide, TiO_2 as a photocatalyst

The adaptation of TiO_2 as a photocatalyst has been widely studied ever since the discovery of its water-splitting abilities under the irradiation of UV light by Fujishima and Honda (1972). Following this revelation, a study by Frank and Bard (1977) paved the way for the incorporation of TiO_2 in the photocatalytic oxidation of aqueous sulphite and cyanide ions. This study was one of the earliest mentions of the application of TiO_2 in water purification technology. Subsequently, further studies on the properties and mechanism of TiO_2 single crystals were established by Wang et al. (1999), which paved the path for numerous other studies with a variety of applications in photocatalysis. To date, various studies on the application of TiO_2 photocatalyst have been established, such as its application in water purification, cancer therapy, green energy generation, energy storage and so forth (Çeşmeli & Biray Avci, 2019; Demir et al., 2019; R. Li et al., 2020; Singh et al., 2020). The versatility of TiO_2 in the aforementioned areas is attributed to the properties of TiO_2 being environmentally friendly, non-toxic, non-corrosive, highly stable, cost-effective and reusable (Qamar et al., 2023).

2.2.1 Crystalline properties of TiO_2

There are three main polymorphs ascribed to TiO_2, which are anatase, rutile and brookite. These crystalline phases of TiO_2 are widely available in nature and are caused by the distortion of the TiO_2 octahedral forms (Eddy et al., 2023). Based on Figure 2.1, rutile and brookite phase octahedrons exhibit a slight orthorhombic distortion, whereas in anatase, a more significant distortion is observed, making anatase less symmetrical than the other two variations (Chen & Mao, 2007). The Ti−Ti distances in anatase are larger, whereas the Ti−O distances are shorter than those in rutile. In the rutile structure, each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms), while in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). Differences in lattice structures