Synthesis and Characterization of Heteronuclear Inorganic Complexes for the Photodegradation of Persistent Organic Pollutants

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SYNTHESIS AND CHARACTERIZATION OF HETERONUCLEAR INORGANIC COMPLEXES FOR THE PHOTODEGRADATION OF PERSISTENT ORGANIC POLLUTANTS

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B.S. University of Maine, 2017

A THESIS
Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science (in Ecology and Environmental Sciences)

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An Abstract of the Thesis Presented in Partial Fulfillment of the Requirements for the Degree of Master of Science (in Ecology and Environmental Sciences)

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The focus of this thesis is to investigate the structural modification and characterization potential of common photocatalysts that have various uses for environmental remediation purposes. Pollution involving organic chemicals is one of the most common scenarios found in communities throughout the country. Efforts to rid contaminated drinking water supplies of these chemicals include physical and chemical filters, which have limited ability and efficacy. This lack of efficient filtration services has led to an increased demand for more effective treatment methods. Chemical species that react in the presence of light are known as photocatalysts and have been used in previous studies involving chemical reduction of pollutant species. Photocatalytic semiconductors have been investigated for their photochemical responses and ability to mineralize organic pollutants into unreactive species such as carbon dioxide. These photochemical responses have shown favorable in water treatment applications that utilize high energy irradiation sources.
Previous studies have indicated complexes that contain bismuth were more efficient at photochemical reduction of organic pollutants as opposed to titanium centered species.

In this study, well known photocatalytic complexes were modified through the addition of d-block metallic species. Complexes comprised of primarily Bi(III) centers were synthesized due to their non-toxic properties and presence in environmental remediation studies. Concerns over the long-term environmental presence of these catalysts led to the development of complexes such as the ones listed in this study that remain environmentally benign. Mechanistic investigations of catalysis pathways revealed the distribution of electrons was facilitated through single electron transfer (SET) mechanisms. Oxidation-reduction reactions involving molecules of the surrounding medium generated free radical species that facilitated the hydrolyzation of the target pollutants. Novel findings in this study include the “electron trap” effect of photophysically active d-block elements in the presence of a known catalyst. The modified compounds of TiO2 and BiOCl have demonstrated remarkable efficacy and durability in photocatalytic applications yet continue to encounter serious drawbacks in continual wastewater treatment efforts.

Several investigations were conducted throughout this study that determined the effectiveness of novel compounds in photocatalytic applications. To measure how these complexes react in the presence of various excitation sources, photoluminescence studies were performed to determine energetic pathways. Photodegradation experiments were conducted in aqueous solutions using both visible and ultraviolet irradiation sources. X-ray diffraction measurements on single crystal and powder samples were performed to corroborate the photophysical observations and physical structure. Transmission electron microscopy was used to measure photocatalyst size and morphology. Several visible light experiments were conducted throughout this study and only one compound, a halogenobismuth species, produced sufficient degradation results. The primary
motivation for these studies were industrial drawbacks that led to the synthesis and design of photophysically active complexes which permitted solar utilization of ultraviolet and visible light. The addition of d10 metallic ions permitted increased proliferation of charge transfer mechanisms and formation of reactive radical species, which are the primary contenders in degradation through photocatalysis. These increased charge transfer mechanisms lead to sustained photodegradation and mineralization of organic species present. Our findings throughout this study enhance the experimental and mechanistic understandings of these metallic photocatalytic species in the use of environmental and wastewater treatment efforts.
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CHAPTER 1
INTRODUCTION

Exposure to chemical pollutants in the environment is one of the most serious threats to the well-being of the developed world.\textsuperscript{1} Reports on application rates nationwide indicated over 5.2 billion pounds of chemical pesticides are used each year to treat crops, most of which are likely to persist in the environment over time.\textsuperscript{2} Industrial runoff from facilities near bodies of water are a main source of pollutant discharge into community water systems. The types of polluting compounds include herbicides and pharmaceuticals, which increase the likelihood of human exposure as commercial consumption increases annually.\textsuperscript{2-5} The lack of proper filtration and regulatory procedures enable increased pollution of communities due to the wastewater generated by utility industries. Chemicals distributed by abandoned industrial mills throughout the nation have high potentials for persistence and are detected readily\textsuperscript{7}. Environmental contamination has been one of the country’s most challenging problems due to regional agricultural and industrial practices.

Over time, this has resulted in increased pollutant concentrations and community exposure throughout Maine and surrounding northeastern states. Efforts to remove these compounds from the environment focus primarily on chemical additives that respond to irritation by various light sources, yet these are limited in their overall efficacy.\textsuperscript{6-10} While these chemical efforts may be beneficial for immediate relief, there is high potential for chemical mutation of the persistent pesticides present which can lead to further ailments.\textsuperscript{8} Efforts to establish environmentally benign treatments has led to the research and development of photocatalytic materials that resist degradation over time and facilitate the removal of these harmful substances.\textsuperscript{9-11} This research investigates the unique characteristics displayed by common organic pollutants and how these
characteristics can be manipulated to remove them using environmentally benign inorganic semiconductors.\textsuperscript{11-15} Development of novel materials that display photocatalytic abilities was demonstrated throughout this research as well as mechanistic studies to determine the active species present.

**Persistent Organic Pollutants (POP’s).**

Frequent use in commercial agriculture and landscaping applications has led to increased human consumption in rural and urban communities.\textsuperscript{6-12} Commercial food rations containing ingredients made from certain crops such as grain and corn carry the possibility of containing trace amounts of organic pollutants that resist pasteurization and chemical treatment methods.\textsuperscript{6} Several environmentally persistent compounds such as pharmaceuticals are known for their detrimental health effects due to prolonged exposure in communities through drinking water sources.\textsuperscript{7-14}

The molecular structure of commonly used pesticides permits increased resistance to drinking water treatments, allowing for possible accumulation in biological systems.\textsuperscript{3-8} Conjugated bonding found throughout the structural motif allow for complexes and their byproducts to persist in the environment while resisting biological or chemical degradation techniques.

![Figure 1.1.](image)

**Figure 1.1.** The (A) highest occupied electronic orbital (HOMO) and the (B) lowest unoccupied molecular orbital (LUMO) of carbaryl upon excitation at 285 nm.
The conjugation present in figure 1.1 is facilitated through electronic resonance within cyclic $\pi$-bonding orbitals, which distribute the electronic density throughout the molecule. This increased resonance of electron density promotes resistance to hydrolysis and oxidative ring cleavage, further contributing to molecular stability.\textsuperscript{11-16} During prolonged agricultural treatment methods such as irrigation, sources of drinking water such as streams and reservoirs can accumulate organic pollutants and resist physical filtration. As organisms are exposed to these chemicals, collection known as bioaccumulation occurs within the adipose tissue of eukaryotic cells and can lead to severe illnesses.\textsuperscript{9-11} This exposure propagates a number of negative health effects including cancer, birth defects, and endocrine system disruption.\textsuperscript{10-12}

Detection of persistent organic pesticides (POPs) involves the use of spectroscopy and other analyses in order to detect concentration levels in different mediums both terrestrial and aqueous. Biological investigations into the detection of POPs used immunoassays anchored onto cellulose that were coupled with heavy metals such as gold to react with bound compounds.\textsuperscript{13} The gold system is suspended in a colloidal solution and acts as a biomarker due to its ability to noncovalently interact with biological molecules such as proteins.\textsuperscript{13-15} These interactions do not inhibit protein function and allow gold containing antibodies to accumulate throughout the assays and produce a fluorescent image. Detection of these harmful pollutants is required for qualitative analyses, yet complete removal or mineralization of these complexes is the beneficial outcome for many of the chemical processes described.

**Current Methods of Water Treatment.**

Various methods of water treatment, primarily natural techniques, have been utilized to disrupt these persistent pollutants in aqueous environments. A study conducted by Swetha et. al proposes a mechanism of carbaryl degradation using *Pseudomonas* strains isolated from various
soil types. These bacterial strains were isolated from soil contaminated with carbaryl and incubated to produce different cell cultures, which determined the concentration levels within these soil samples. The enzymatic activity of the pseudomonas strain C4 were affected when exposed to different metabolites such as salicylate and glucose. Compounds such as 1-naphthol and 1,2-dihydroxynaphthalene are thought to inhibit the degradation of acetylcholine into choline, which can have detrimental effects on mammalian neurological systems. Microorganisms found in sea water and terrestrial sediment displayed insensitivity when exposed to 1-naphthol as opposed to other pollutants such as malathion.

A study published in the Journal of Agricultural and Food Chemistry compares the metabolism of two cultures of bacteria in the presence of carbofuran and other carbamate-based insecticides. This study provided evidence that bacterial cultures are capable of metabolizing carbaryl and other insecticides into oxidized carbon derivatives such as carbon dioxide. Insects are able to metabolize organic pesticides using similar metabolic pathways utilized by bacterial cultures. Research on plant interactions with these organic pollutants provides evidence that indicate plants do not metabolize these insecticides as efficiently as single celled organisms. Enzymatic activity is decreased significantly in plant metabolisms, which allows these organic pollutants to accumulate within lipid layers of plant cells due to their insolvability in water and lipophilic behavior. Although these biological methods have shown slight promise in mineralizing persistent pesticides, the demand for more efficient methods requiring renewable resources remains prevalent.

Current photochemical methods of pollutant removal from recycled drinking water are inefficient and demand more effective methods. Traditional methods focus on the addition of a chemical species such as chlorine for contaminant removal, yet this technique has the potential for
increased toxicity due to compound transformations. Although forward osmosis is sufficient enough in the removal of large pollutants, these processes are ineffective in removal of molecular compounds in trace concentrations. Batch reactor irradiation treatment of water systems using ultraviolet radiation has been applied extensively in water treatment municipalities and commercial irrigation systems that require efficient recycling of water. Traditional ultraviolet irradiation has shown promise in rapid removal compared to chemical treatment methods but is limited in the overall mineralization of pollutants.

Environmental Applications for Photocatalysis.

Photocatalysts have become a new alternative for wastewater treatment due to their unique reactivity with various wavelengths of light. The accompanying charge transfer mechanisms produce reactive species that facilitate increased degradation and overall mineralization. These reactions can alter the surrounding environment by producing hydroxyl or superoxide anions in aqueous media leading to cascading degradation reactions. Semiconductor compounds such as CdS or PbS have similar optical properties to most commercial photocatalysts, yet their toxicity in the environment is concerning when used outside of photovoltaic applications. These compounds provide an alternative in drinking water treatment due to their ability to degrade hazardous pollutants in a variety of mediums, including water. Photocatalysts are semiconductive chemical species composed of metallic centers that undergo sequential oxidation-reduction reactions.

Previous studies using metal-doped photoactive compounds have reported increased photodegradation behavior, especially in complexes involving divalent or trivalent species. Similarly, reports on enhancement using copper and bismuth showed promising results as opposed to other ions, such as iron. Photocatalytic degradation is regarded as an inexpensive and
sustainable solution to reduce the accumulation of toxic contaminants in the surrounding environment. These products can be used in sustainable water treatment methods in industrial and municipal facilities across Maine and other states throughout the nation. Current literature proposes degradation mechanisms that show byproducts formed through hydrolysis is the common mode of action when these compounds are present in the environment. Degradation of harmful pollutants into nontoxic byproducts is the result of these processes and can be used in the removal and mineralization of harmful compounds from drinking water.

As photocatalysts bind to a pollutant, the radical species produced by photo-induced reduction of water or other sacrificial reagents cleave the target molecule into several smaller compounds. Previous studies conducted by the Howard Patterson research group indicated superior degradation of pharmaceuticals using bismuth photocatalysts versus titanium dioxide. The results of this study indicate bismuth oxyhalide has a smaller surface area compared to titanium dioxide yet exhibited increased degradation and absorbance at a faster rate. Although these novel compounds have proven effective against various pollutants, several limitations exist that prevent their commercial usage.

A major problem that arises with photocatalysts is their duration of degradation especially dealing with harsh POPs with extended chemical half-lives. Current commercial photocatalysts such as TiO₂ and BiOCl are only able to utilize high energy light such as ultraviolet light, increasing the cost and effectiveness of degradation. Modification of commercial photocatalysts has become a topic of interest in recent studies in order to overcome situations where conventional photocatalysts are less efficient. These modifications are often observed in the form of d-block metallic species such as iron or copper, which permit increased redox activity. Modification of commercial photocatalysts has proven to be more economically feasible in
industrial development than the design of new compounds.\textsuperscript{48-52} We envision these modifications to occur within the structural or surface interfaces on these motifs to permit increased photophysical activity required for commercial applications.

**Chapter References.**


CHAPTER 2

RECENT ADVANCES ON TIO$_2$- BASED PHOTOCATALYSTS TOWARD THE
DEGRADATION OF PESTICIDES AND MAJOR ORGANIC POLLUTANTS
FROM WATER BODIES

Chapter Abstract.

Pesticides and organic waste constitute a group of environmental pollutants that are widely
distributed in our environment due to various human activities. Adsorptive removal and
photocatalytic degradation of these pollutants from water have been emerged as energy and
cost- effective technologies. However, advanced oxidation technologies are gaining attention as
an effective method for wastewater treatment capable of degrading a diverse spectrum of organic
contaminants. Photocatalysis is a promising advanced oxidation technology to alleviate the water
pollution problem. Titanium dioxide (TiO$_2$) is considered the most popular photocatalyst due to
its low cost, nontoxicity, high oxidizing abilities, which can be easy immobilization on various
surfaces. The current review aims to highlight recent advancements in photocatalytic degradation
of pesticides and major organic pollutants on TiO$_2$- based photocatalysts. Indeed, most of the
methods, which employed potent catalysts, showed and exhibited successful degradation of the
pesticides under various conditions. We believe that this topic of research is extremely vital and
will continue to grow to reach ultimate desirable results and find more applications in different
fields of study.
Introduction.

Rapid industrial growth worldwide has increased the urgency of issues such as climate change, looming water shortages, and environmental pollution \(^1,^2\). In addition to the increase in pollutant volume, the growth of specialized and high-tech industries have contributed to the diversity of pollutants entering the environment \(^3^-^6\). Of particular concern is the widespread use of pesticides and their potential to enter water supplies and cause negative effects on public health. As of 2009, more than 50 countries applied in excess of 1,000 tons of pesticides in support of agricultural efforts \(^4\).

Despite our best efforts to regulate and engineer the use of pesticides, they continue to be detected and present problems at municipal water treatment plants \(^5\). This demonstrates a need for alternative water treatment methods capable of fully degrading pesticides and preserving access to clean drinking water. Photocatalysis has emerged as one potential alternative to traditional water treatment methods such as UV irradiation.

The phenomenon of photocatalysis remains one of the most extensively studied subjects in inorganic photochemistry. Since the discovery of the photoelectrochemical water splitting abilities of TiO\(_2\) in 1972,\(^6\) it has become the most studied photocatalyst in both academic and industrial settings\(^7\). While TiO\(_2\) is considered a commodity chemical and has numerous applications throughout industry, it has attracted new attention in environmental remediation efforts for areas affected by pollution. The photocatalytic properties of TiO\(_2\) have been commercialized though formulation into materials such as self-cleaning window films and air- purifying roofing tiles \(^8\). Other semiconductors with similar bandgaps to TiO\(_2\) such as ZnO and CdS have shown promising photocatalytic properties, but also show limitations involving catalyst stability and environmental toxicity \(^9\).
Enhancement of electrochemical degradation using photocatalysis has been demonstrated in recent literature and indicates increased pollutant removal\textsuperscript{10}. The demand for photocatalytic complexes is also observed in a myriad of industries, from solar applications including solar heat\textsuperscript{11}, solar photocatalysis\textsuperscript{12}, and batteries\textsuperscript{12-14} to anti-corrosion\textsuperscript{8}. Ani et al. have discussed extensively the potential for TiO\textsubscript{2} systems to be utilized to remove harmful compounds from petroleum wastewater\textsuperscript{15}. Application of pristine TiO\textsubscript{2} photocatalysts for environmental purposes has become a popular topic of research for removal of environmental pollutants and conversion of solar energy into useful alternatives such as electricity and H\textsubscript{2}\textsuperscript{15-17}.

Photodegradation of organic pollutants has become a prominent research topic in recent years and viewed as a potential solution for widespread pollution. Organic pollutants such as pesticides tend to remain prevalent in soil and groundwater in areas with frequent chemical treatment. These recalcitrant molecules are known carcinogens categorized by WHO standards and can remain hazardous for years\textsuperscript{18}. The application of TiO\textsubscript{2} photocatalysis to the degradation of organic pollutants was initially demonstrated by Carey et al. in 1976\textsuperscript{19}. Since then, the utilization of TiO\textsubscript{2} for photocatalytic environmental remediation purposes have been thoroughly investigated. Current methods of groundwater remediation utilize high energy UV light to degrade pollutants and sterilize aqueous solutions yet fail to achieve full mineralization of certain compounds\textsuperscript{19-22}. Although the environmental applications of TiO\textsubscript{2} are promising, there are various limitations within pure TiO\textsubscript{2} complexes that hinder its use for environment and industrial purposes\textsuperscript{21}.

Photophysical limitations of TiO\textsubscript{2} complexes have made practical environmental applications of these complexes difficult, since pure TiO\textsubscript{2} complexes all have relatively high band gaps. This limitation permits pure TiO\textsubscript{2} complexes to utilize only 6\% of the solar energy irradiating the planet.
each day. To overcome these solar harvesting limitations, research efforts have investigated potential modifications and impurities that synergistically aid TiO$_2$ in photocatalytic degradation.

Characteristics of TiO$_2$ Photocatalysts.

Photocatalytic activity originates from the absorption of photons of suitable energy to overcome the band gap. Absorption of light by the complex produces an excited state electron that is promoted to the conduction band, facilitating reduction of electron acceptors such as H$^+$ and O$_2$ $^{21-23}$. The unoccupied electron states, known as electron holes, remain in the valence band of these complexes and are capable of oxidizing substrates adsorbed to the surface as illustrated in Figure 2.1 $^{24}$. Oxidation of the surrounding environment facilitates single electron interactions that promote sequential degradation reactions. Pristine TiO$_2$ is known to have a band gap energy of 3.20 eV, which is capable of absorbing photons of wavelengths less than 350 nm, primarily in the UVA, UVB, and UVC range. Due to the fundamental principles of TiO$_2$ photochemistry and photocatalysis, TiO$_2$ and other Ti$^{4+}$ complexes have been ideal candidates for scaffolding for potential catalytic enhancements. Aluminosilicate complexes, also known as zeolites, have been reported to be a beneficial scaffold for TiO$_2$ complexes due to their porous configuration that directs interaction between the catalyst and pollutants $^{23}$.

Figure 2.1. Schematic illustration of formation of photoinduced charge carriers upon absorption of UV light. Reprinted from reference $^{24}$. Copyright Elsevier 2013.
The most common crystal structures of TiO₂ complexes include anatase, rutile, brookite, and monoclinic polymorphs. These polymorphs are all composed of a Ti⁴⁺ center with bordering oxygen atoms that act as bridging ligands, as shown in Figure 2.2 ²⁵.

**Figure 2.2.** Structure models of (A) rutile (110) (r-TiO₂(110)), (B) rutile (011) (r-TiO₂(011)) and (C) anatase (101) (a-TiO₂(101)). Red and grey balls stand for oxygen and titanium ions, respectively. Reproduced from reference ²⁵. Copyright Elsevier 2010.

The unique structure of these TiO₂ complexes permit surface vacancies on the Ti⁴⁺ centers that can act as active sites for catalytic degradation ¹⁹-²⁴. Each of these distinct allotropes are synthesized based on the annealing temperature used during synthesis, a phenomenon reported extensively by Chen et al ²⁶. Anatase crystal structure is found to be a common candidate for catalyst modification for its stable configuration suitable for photodegradation studies. The anatase structure begins to revert to the rutile configurations at temperatures higher than 600 °C, indicating anatase TiO₂ is a likely candidate for environmental photocatalytic applications ²⁷.
Catalyst size modification has been viewed as a cost-efficient enhancement that increases surface area and photodegradation. Both bulk and nanoscale TiO$_2$ systems have been investigated extensively and found to have significant differences in photochemical responses and degradation activity. Recent studies have indicated increased pollutant adsorption due to surface area increases in TiO$_2$ nanosystems as opposed to bulk systems. Modification of the crystal structure facets has also become a prevalent topic of study for investigations into photoactivity enhancement of TiO$_2$ structures.

The valance and conduction bands that comprise the accompanying gap between them denote the changes in potential required to initiate a photoinduced charge transfer. Band alignment between TiO$_2$ and an additional semiconductor is a significant area of study and development for catalytic enhancement. Alignment between the band structures of anatase and rutile TiO$_2$ have been investigated and found that alignment differences as small as 0.2 eV facilitate electron transfer between two photoactive complexes. This difference in band alignment facilitates localized trap states of photoinduced electrons and accompanying vacancies. A schematic illustration of the role of the TiO$_2$ surface in removal of pollutants through the formation of photoinduced charge carriers is shown in Figure 2.3. Nanostructures of TiO$_2$ anatase have been reported containing both (101) and (001) facets although complexes containing predominantly (101) facets are thermodynamically favored. Ong et al. have discussed the effect of mixed facet ratios within anatase TiO$_2$ structures and the benefits provided to photocatalytic activity.
To extend the photophysical capabilities of both anatase and rutile TiO$_2$ into the visible light range ($\lambda = 380$ nm), photoactive scaffolding such as graphitic carbon nitride ($g$-C$_3$N$_4$) has been viewed as an environmentally benign alternative to metallic impurities $^{28}$. Both surface and interfacial defects have been reported to have significant roles in catalyst modification, although surface defects have been found to hinder adsorption capabilities $^{31}$. Modification of rutile TiO$_2$ is an investigated aspect of enhancing photocatalytic abilities by utilizing the terminal oxygen and Ti$^{4+}$ atoms present. These terminal atoms are the primary driving force for photo-induced electrons and accompanying vacancies to migrate from the irradiated bulk system to surface atoms for redox reactions occur. Interactions at the catalyst surface are a significant part of the photochemical processes and are required to facilitate interfacial charge transfer along the catalyst facets and the adsorbed complex.

The transfer of photoinduced electrons between adsorbed molecules such as H$_2$O or an organic pollutant are the driving force that permits the redox reactions necessary for photodegradation. These chemical interactions are only permitted if the photoinduced electrons
are able to overcome the tendency to recombine with vacancies present in both bulk and surface atoms. Recombination of excited state electrons and vacancies is a problematic limitation of TiO₂ and overcoming this limitation is the primary goal of catalyst modification. Luminescence is one of the pathways that can directly result from electron-hole recombination and is detrimental to photochemical reactions due to conservation of excited state electrons. For this reason, the photoluminescence spectra of a series of similar photocatalysts may be compared to understand the effect of a structural change or dopant on overall photocatalytic potential 23. Sacrificial agents such as hole trapping species have been viewed as a potential photocatalytic enhancement that reduces the recombination of photo-induced electrons and vacancies 32. The electron trapping nature of these agents have been reported to enhance both anatase and rutile TiO₂ degradation by carrying these excited state electrons away from the catalyst surface, reducing the probability of surface recombination.

The adsorption of organic complexes such as malic acid and alkyl alcohols onto the surface of TiO₂ complexes has shown significant capabilities for transferring excited state electrons and vacancies to an organic pollutant, facilitating degradation. Oxidation-reduction reactions within the bulk system and catalyst surface are the primary electronic pathway for degradation under ultraviolet light. This generation of accompanying electrons and vacancies can facilitate the degradation of pollutants in the surrounding environment. These active chemical species originate from the catalytic splitting of water, which hydrolyze harmful pollutants through single electron transfer reactions. For an in-depth overview of previous applications of TiO₂ for water remediation, see reviews by Friedmann et al 33, Lee et al 24, Carbajo et al 34, and Horikoshi et al. 35. The remainder of this review will focus on the application of the TiO₂ photocatalytic degradation system to the remediation of organic pollutants from water.
Photocatalytic Reactor Systems.

While photocatalysis has proven to be a highly successful laboratory science, its integration into widespread water treatment applications has progressed only marginally. For this reason, a significant interest in academic and industrial research in the development of catalyst reactor systems is to implement widespread application of photocatalytic reactors in industry. The principle aspect of designing catalytic reactor systems is to maximize the interactions between the aqueous media and the catalyst to facilitate continual photodegradation. Several types of photocatalytic reactors have been developed including thin-film, packed bed, fluidized bed, swirl flow, falling film, vortex, and annular photoreactors. These reactors fall into two general philosophies of catalyst utilization where the photocatalyst is either suspended in the reaction solution or immobilized in certain fashion. Here we will briefly introduce the advantages of each type and their industrial applications for environmental purposes.

Suspended Catalyst Reactors.

The most common type of reactor employed in laboratory experiments are batch systems where the catalyst is suspended in solution. This type of reactor has been favored up to this point due to the advantage of high surface area of suspended particles which results in fast reaction rates compared to flow reactors. In such batch reactor setups, the catalyst that is introduced into a slurry must then be removed from the solution post-exposure. In these reactors, presented in Figure 2.4, the required separation and recovery of the catalyst are highly unfavorable in water treatment industries, where high volume throughput is necessary. The use of bulk catalyst systems in heterogenous solutions has significant limitations such as catalyst recovery, durability, and loss of photophysical integrity. These limitations severely hinder environmental applications on an industrial scale by increasing operating costs as well as the potential for bioaccumulation in areas
exposed to waste material. However, suspension photocatalyst reactors were found to improve the mass transfer of pollutants to the catalyst surface compared to immobilized reactors due to surface area considerations.

Figure 2.4. Schematic of a Typical Photocatalytic Experimental Set-up, suitable for immobilized reactor conditions. Reproduced from reference 47. Copyright Elsevier 2010.

Slurry reactor systems using TiO₂ as a photocatalyst were used for the degradation of chloroform in water by Pruden et al. 39. Building on this work, Kormann et al. observed an increase in chloride ion concentration during UV-TiO₂ batch reactor operations 40. Pathirana et al. reported that the catalyst concentration is an important factor for batch photocatalyst reactor systems 41. They found that the reaction rate continued to increase with photocatalyst concentration and reached equilibrium before beginning to decrease. This loss of reactivity was attributed to a reduction in the penetration depth of incident light caused by “shielding” via photocatalyst particles closer to the light source within the reactor. Light penetration depth is an important consideration for a suspended photocatalytic reactor and limits the maximum overall effectiveness of this type of reactor.
Another type of suspended photocatalyst reactor recently investigated is the drum reactor \(^{42-44}\). This system operates under a continuous flow with wastewater moving through three subsequent drums equipped with paddles to stir the solution as depicted in Figure 2.5 \(^{42}\). This reactor design allows for the reactor residence time to be tailored to the pollutant being degraded and enables system designers to employ a large effective photocatalyst concentration without losing reactivity due to shielding. McCullagh et al. reported that the drum reactor system using 30 g/L TiO\(_2\) was capable of removing 98% of methylene blue dye from solution after 60 minutes, demonstrating the high potential for this reactor be employed in wastewater treatment plants \(^{42}\). In later work, the same group reported that the same system is also effective at degrading hydrocarbons present in waste water, which includes pollutants such as decane, dodecane, and tetradecane \(^{44}\).

**Figure 2.5.** Schematic of the Novel Drum Photocatalytic Reactor. Reproduced from reference \(^{42}\). Copyright Elsevier 2010.
Fluidized bed reactors are another prominent type of suspended photocatalyst reaction system. In this type, the catalyst particles are suspended by an upward flow of fluid, thus maintaining the advantage of high surface area of a suspended photocatalytic reactor, while avoiding the need for downstream separation of catalyst. This reactor type has been confined almost exclusively to air purification for applications such as nitric oxide, methanol, and toluene vapors.

**Immobilized Catalyst Reactors.**

Due to the large costs associated with separation and handling of catalyst downstream, much research has been directed at techniques for immobilizing the catalyst within the reactor system. This reduces costs since the catalyst does not need to be removed from the solution after the reaction is complete. However, this also inherently results in a loss of surface area since the catalyst must be attached to a support for immobilization purposes. Lowering the available surface area for heterogeneous photocatalytic reactions to occur decreases the rate of the desired reaction.

Coating a surface with a thin film of TiO$_2$ is a common approach to preparing immobilized photocatalytic systems. Recent studies have found that immobilized anatase and rutile TiO$_2$ exhibit similar photocatalytic activity compared to suspension systems $^{45}$. These thin films are synthesized in variety of ways including sol-gel processing and chemical etching into a homogenous solution that produces single or multiple layers of TiO$_2$ on a surface. The hydrophilic properties of TiO$_2$ are exploited throughout catalytic investigations and permit the adsorption of aqueous atmospheric solutions containing harmful pollutants. These intrinsic properties combined with thin film technology has led to the commercialization of catalysis chambers with interior coatings containing TiO$_2$ and other scaffolding compounds. Zhuang et al. synthesized a series of TiO$_2$ bilayers containing surface and interfacial defects and demonstrated the photocatalysis using Rhodamine B, a common pollutant used in preliminary studies. $^{31}$
Two types of immobilized catalyst reactors were reported by Feitz et al. at the pilot scale using solar light. The first was a coated mesh reactor, and the other was a packed bed system. Both systems were evaluated for their ability to remove 2 mg/L phenol from water. It was found that the packed bed reactor was able to degrade phenol seven times more efficiently than the coated mesh system. This difference was explained to be due to insufficient contact between the photocatalyst on the mesh and the phenol solution. The fixed bed system was also demonstrated to efficiently degrade dichloroacetic acid in this configuration.

A rotating disk reactor has been demonstrated by Dionysiou et al. for the degradation of organic pollutants in water using TiO₂ as a photocatalyst. The schematic for this reactor is shown in Figure 2.6, with TiO₂ photocatalyst deposited as a thin film on a disk in the center of the reactor that rotates as the reaction proceeds. This design has two major advantages where the rotation of the disk generates mixing of similar intensity to suspension reactors and the use of a thin film photocatalyst enables high rates of transport of oxygen to the photocatalyst surface. This idea was further investigated by Hamill et al. who showed that the pollutant degradation rate of a rotating disk photocatalytic reactor is dependent on the rotation speed of the disk.

Figure 2.6. Schematic of the Rotating Disk Photocatalytic Reactor. Reproduced from reference. Copyright Pergamon 2000.
Although the use of TiO$_2$ complexes has gained significant interest from environmental remediation industries, modifications that permit visible light activity are required for widespread use in environmental applications. A key factor many researchers indicate during catalytic reactor setup is the need to reduce the temperature of the lamp during extended degradation periods. Efforts to reduce lamp temperature using liquid or air cooling have shown moderate success and would equate to increased operational costs in an industrial setting. Modified TiO$_2$ complexes capable of harvesting visible light are a well-studied area in recent years, yet few pilot-scale operations have been reported in the literature. The process of scaling up a photocatalytic process is complex, and many critical factors must be considered in order for the final process to be economically and technically efficient.

**Photocatalytic Degradation of Pesticides and Organic Pollutants using TiO$_2$-based Catalysts.**

The use of pesticides leads to a tremendous increase in agricultural productivity, as they provide and secure a safe and nourishing environment for plants and other living things. Pesticides are typically used to get rid of insects, mice, and other animals. They also kill weeds, fungi, bacteria, and viruses. However, despite all the benefits they bring to our environment and everyday life, they are still deemed hazardous to the mankind. It was proven that the wastes and rinsates that come from spraying those chemicals over a large area, coupled with their frequent disposal into the environment, are causing rivers, creeks, and oceans to become contaminated. Not only they are affecting water life, but also the quality of drinking water is going down because of pesticides. Thus, seeking novel strategies and methods to treat such chemicals in a way that they do not have a negative impact on the environment into which they are disposed, has become crucial over the past years. In summary, a multitude of distinct techniques were demonstrated and employed for the efficient degradation and eradication of organic pollutants in wastewater. Several variables
and parameters were controlled or varied to explore the differences in the kinetics of the reaction. Indeed, most of the methods, which employed potent catalysts, showed and exhibited successful degradation of the pesticides under various conditions as presented hereafter.

**Photocatalytic Degradation of Carbamate and Diuron Pesticides using TiO$_2$-based Catalysts.**

Carbamate pesticides are commonly used for pest control from various crops $^{49-52}$. The degradation of carbaryl was tested in the presence of TiO$_2$ aqueous suspension $^{49}$, ozone and TiO$_2$ photocatalyst $^{51}$. UV irradiated carbaryl in the presence of suspended TiO$_2$ particles provides 99% degradation of carbaryl under optimal conditions $^{49}$. Similarly, the addition of ozone, along with the photocatalyst, was found to speed up the mineralization of carbaryl owing to its relatively high reduction potential, which increases the degree of oxidation of carbaryl. The combination proved to have a strong impact on the decomposition rate of carbaryl in pesticide wastewaters with the strongest impact of the photocatalytic ozonation reached at pH 6 $^{51}$. On the other hand, the effect of photocatalyst (TiO$_2$/UV), with the aid of photosensitizers such as methyl orange, methylene blue or rose Bengal, was tested on the mineralization and toxicity degree of insecticides in wastewater $^{52,61,62}$. Photosensitizer-promoted solar photocatalysis is an innovative technique for the degradation of carbaryl rinsate to CO$_2$ $^{52}$. It was deduced that using TiO$_2$ and solar light showed 70% of the toxicity reduction efficiency of the TiO$_2$/UV process. However, when photosensitizers were added, in the scale of 1-2% of the initial carbaryl concentration, there was a 20% increase in the toxicity reduction efficiency of UV-TiO$_2$ photocatalysis.

The principal mechanisms for the decomposition of carbaryl were found to be hydrolysis, hydroxylation, and quinonation $^{52}$. This general transformation helps better understand the efficiency of photosensitizers as illustrated in the proposed photodegradation pathway presented in Figure 2.7. Moreover, applying a parabolic concentrator with TiO$_2$/UV and TiO$_2$/UV/H$_2$O$_2$
catalysts enhanced the decomposition levels by 41% and 79%, respectively. Moreover, when the sun geometric concentration ratio increases to two, the degradation levels were enhanced to 54% and 92%, respectively.

![Proposed Photodegradation Process of Carbaryl](image)

**Figure 2.7.** Proposed Photodegradation Process of Carbaryl.

A major development in the efficacy level of TiO$_2$ was observed when it was supported with a coat of granular activated carbon. The degradation of carbofuran (CBF) in the presence of TiO$_2$-Carbon modified material followed pseudo first order with the degradation of CBF slowed down when its initial concentration is increased. The modified materials showed 100% removal of CBF at optimized conditions. Further, CBF degradation was studied in the presence of TiO$_2$ and ZnO.
under 254 nm and 365 nm UV light\textsuperscript{65}. TiO\textsubscript{2} was found to be more efficient than ZnO catalyst where it gave a complete mineralization of CBF over a 5 h time interval with best catalytic activity was reached using 365 nm irradiation source\textsuperscript{65}. Moreover, Re\textsuperscript{4+} doped nano-TiO\textsubscript{2} was implemented in field on tomato leaves and soil carbofuran\textsuperscript{66}. It was determined that the degradation rate of carbofuran reached a maximum value of 54.89\% when the concentration of nano TiO\textsubscript{2} was 0.4g/L. Overall, the decomposition rates of the pesticide in the tomato leaves and soil samples were increased by 20-30\% and by 15-20\%, respectively, as compared to natural degradation procedure\textsuperscript{66}. Triadimefon and pirmicarb were photodegraded in the presence of aqueous TiO\textsubscript{2} suspension where the degradation process was four times faster than the photolysis of the target molecule without a catalyst\textsuperscript{67}.

As a different approach, diurons were treated by two different methods of solar photocatalysis, one with titanium oxide, and the other by photo-Fenton\textsuperscript{68-70}. The transformation products and toxicity levels were evaluated and compared between the two methods\textsuperscript{69}. It was found that diuron was totally disappeared in 45 min for both systems. The toxicity was reduced to a value below the threshold in a time interval that was shorter than 200 minutes, which was the time spent for 90\% of mineralization to be achieved. The transformation products were identical with variation in their relative abundance\textsuperscript{69}. Solis et al. have reported the degradation of diuron by three different approaches: single ozonation, photocatalysis, and photocatalytic ozonation\textsuperscript{70}. Compared to the single ozonation process, the total organic carbon (TOC) removal via photocatalytic ozonation was more efficient and complete where carbon dioxide and water found as final products\textsuperscript{70}. Overall, photocatalytic ozonation was deemed more effective in terms of mineralization levels and TOC percent removal, due to its great oxidizing capacity of organic pollutants\textsuperscript{70}. Moreover, boron doped TiO\textsubscript{2} was used for the degradation of four pesticides, including diuron and compared to bare TiO\textsubscript{2}
catalyst. Boron doped TiO₂ catalyst was more effective in terms of degradation and mineralization rates in contrast to the undoped TiO₂. The synergistic effect of photocatalytic ozonation led to faster mineralization rates as compared to the individual methods of treatment. Additionally, the B-doped catalyst was stable and gave reproducible results of mineralization rates up to 75% upon three successive runs. The study indicates that the doped catalyst was more active towards the removal of the organic pollutants due to the observed increase of the pore volume and surface area of the crystal compared to the bare TiO₂ sample.

The degradation of chlorotoluron in the presence of aqueous suspensions of titanium oxide under diverse conditions has been reported. The change in conditions involved the type of TiO₂ used, pH, catalyst concentration, substrate concentration, temperature, and the various types of electron acceptors, other than molecular oxygen. It was revealed that titanium oxide exhibited the highest efficiency rate for the decomposition of chlorotoluron. The temperature range used was 20-50°C, with no considerable change in the degradation rate of chlorotoluron occurred within that range. Expectedly, the decomposition rate was seen to increase with the concentration of the catalyst with three identified major products shown in Figure 2.8.
Figure 2.8. Mechanism for photodegradation of chlorotoluron irradiated with TiO₂ photocatalyst.

Fenoll et al. have reported the decomposition of methabenzthiazuran residues in leaching water in the presence of photocatalysts and amended soils ⁷³. The effect of TiO₂ and ZnO was examined on the degradation rate of the organic contaminant. The use of ZnO was found to be more effective in the degradation process of the herbicide than TiO₂, although both led to significant reduction in the amount of the herbicide ⁷³. However, ZnO had some downsides as it was dependent on the pH of the reaction medium. The study is unique in a sense that it introduced and presented innovative approaches for the eradication of a special type of herbicides ⁷³.


The activity of TiO₂, ZnO, and their mixed oxide (ZnO-TiO₂), was tested and compared towards the degradation of methylene blue and naproxene, a pharmaceutical compound ⁷⁴. While
the various photocatalysts gave approximately similar degradation rates in the case of the pharmaceutical compound, the efficacy of ZnO under UV irradiation exceeded that of the others in the degradation of methylene blue. Since zinc titanate is relatively more stable than ZnO in acidic environments and can integrate into its lattice elements that might alter the bandgap, it can be utilized in place of the more effective analogue ZnO as a candidate for advanced oxidation. Interestingly, the activity of both component oxides depends on the crystallographic alignment of the exposed surfaces. 

Azo dye solutions treated with a novel hybrid technique of hydrodynamic cavitation (HC) and photocatalysis in a pilot reactor exhibited better mineralization at 5 bar as compared to individual conditions. ZnO catalyst was found to be more efficient than TiO2 with an optimum degradation rate reached at 1.0 g/L ZnO concentration. In addition, it was found that as the initial concentration of the dye increases, the decolorization and degradation rates decrease. Also, azo dye (RR 180), as well as 2,4-dichlorophenoxyacetic acid (2,4-D) and antibiotic (enrofloxacin), were degraded using single ZnO catalyst and a 1:1 ratio of ZnO/TiO2 mixture. Irradiations using the UVC wavelength range of the UV light were found to be more effective than the UVA for all the tested chemicals, however, UVA was beneficial in a sense that it utilizes solar energy, so the energy efficiency was high. The catalysts proved to be effective and successful in terms of reusability by the consecutive degradation tests, which qualifies them as reliable methods for future applications. Furthermore, ultra-thin photocatalytically active TiO2 layers with high porosity and hydrophilic properties were utilized for the degradation of methyl orange dyes. Double-side active TiO2-modified membranes photodegraded twice the amount of photodegraded pollutant like methyl orange, when operated in the common cross-flow membrane mode under UV irradiation of both membrane surfaces.

1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, better known as atrazine, is a commonly used herbicide in the agricultural industry to limit the growth of certain weeds and grasses that prove to be an interference in the cultivation of crops such as corn, sugarcane, and sorghum. Atrazine is suspected to be an endocrine disruptor that is a potent carcinogen for humans, and can cause reproductive defects in fish. Furthermore, it is a very persistent chemical so it may remain in the environment even after several years have passed since its use. TiO$_2$ is a very effective photocatalyst for the removal of atrazine derivatives from the environment $^{78-84}$. In specific, TiO$_2$ ozonation provides a significant enhancement in the degradation rate of atrazine with a gradual increase upon the increase of the amount of catalyst and the ozonation dose. When the catalyzed ozonation process was carried out for 30 min at the ozone dose of 10 mg min$^{-1}$ and catalyst dose of 0.1 g L$^{-1}$, about 93% atrazine was removed from water. GC/MS analysis indicates the formation of five different products besides residual amount of atrazine as depicted in Figure 2.9 $^{78}$. The transformation products showed that the degradation of atrazine involved de-alkylation process followed by de-chlorination and de-amination steps. Toxicity tests based on the marine bacteria $V. Fisheri$ indicated the detoxification of atrazine by catalyzed ozonation $^{78}$.

![Figure 2.9. Atrazine degradation transformation products by catalyzed ozonation](image)

Reproduced from reference $^{78}$. Copyright Elsevier 2014.
TiO₂ synthesized using Boron Enrichment Waste (BEW), without the presence of any reducing agent, was found to be fast, efficient, and eco-friendly photocatalyst. The photocatalytic degradation of atrazine performed under UV-Vis irradiation depends heavily on the initial concentration of atrazine, the time of contact, and the amount of the catalyst 79. The TiO₂–BEW catalysts have good reusability when it comes to the elimination of atrazine from water 79. In comparison, a different technique involved modifying TiO₂ semiconductors by adding various dyes to the surface 80. While the surface modified catalyst was reacted with atrazine in the dark, it was noticed that the thionin and eosin Y dyes did not interact with the atrazine molecules 80. However, it was found that in the presence of visible light, the modified TiO₂ semiconductor particulate system could not only degrade harmful compounds like phenols and hydrocarbons, but it could also help in the decomposition of pesticides like atrazine when similar experimental conditions are regulated 80.

N-doped TiO₂ particles deposited on ZnS-based phosphors microparticle (ZSP) by a sol-gel technique showed that combination of both N doped TiO₂ as well as the ZSP gave improved results in photocatalytic activity for the removal of atrazine 81. While, 45% of the atrazine were eliminated under UVA illumination, 94% of the atrazine present in the sample was successfully removed upon illumination in the presence of the catalyst 81. Further, TiO₂ in aqueous solution as well as TiO₂ surface modified with ceramic, tetra(4-carboxyphenyl) porphyrin encapsulated various metal centers such as Fe(III), Cu(II) were used as photocatalyst towards the triazine decomposition under visible light 82, 85, 86. While, porous TiO₂ modified ceramic shows an excellent photodegradation performance toward atrazine and thiobencarb with up to 96% of the total organic carbon removal efficiency 86, it was found that these conditions were not oxidizing enough to break down the atrazine present, and as a result, hydrogen peroxide was added as an oxidizing agent 82. Under these conditions, the atrazine underwent degradation where Cu(II) porphyrin system caused the atrazine
present to degrade by 82% after one hour of irradiation. Similarly, TiO₂ deposited with metallic nanoparticles including Au, Ni, and Cu were employed for the degradation and mineralization of atrazine.

Au/TiO₂ was the most successful catalyst for the degradation of atrazine, followed by Cu/TiO₂ and then Ni/TiO₂. This is possible because Au is the most unreactive element as a result it is not being oxidized during the reaction. Studies have also been conducted on a graphene-TiO₂ catalyst. Possible theories suggest that graphene oxide (GO) combined with titanium oxide, improve the surface area for adsorption and enhance the interfacial electron transfer between the two compounds. The composite catalyst provides a better performance than the titanium oxide alone. The composite GO-TiO₂ catalyst proved to be much more efficient at photo degradation of a multitude of pesticides- atrazine, alachlor, isoproturon and diuron when compared to TiO₂-P25 system alone.

Another research involved the use of electrochemistry in the degradation of atrazine. The study uses Ti/RuTiO₂-DSA (dimensionally stable anode) electrode seeks to explore the differences in the results when a purely electrochemical method is compared to a photo-assisted electrochemical method. Results showed that when the current density was increased, the amount of atrazine removed using the combined method was much greater than the purely electrochemical method, which could possibly be due the formation of hydroxyl radicals because of interaction with the UV light. The photo-assisted method breaks down the heterocyclic ring of atrazine where the removal of atrazine from water and the chemical oxygen demand depend on the rate of deposition of organic material on the surface of the electrode. The use of an innovative, inexpensive titanium oxide that contains both the anatase and rutile phases of titanium oxide as a photoanode in conjunction with a graphite cathode removed 99.2% of the atrazine present with faster atrazine removal observed using
higher current density. The best removal took place at a pH 6 where hydroxyl radicals formed during the electrochemical process induced the dichlorination and dealkylation as depicted in Figure 2.10.

![Figure 2.10](image)

**Figure 2.10.** Possible Pathways of Atrazine Electrochemical Degradation. Reproduced from reference 89. Copyright Elsevier 2016.

Immobilized chitosan with TiO$_2$ thin film were used as photocatalyst for the removal of terbuthylazine (TBA) from water bodies. While the thermal degradation showed no change in TBA concentrations, both the photolytic and photocatalytic degradations have favorable results, with high removal of TBA. However, the photolytic process led to the formation of more by-products (apart from cyanuric acid), some of which were identified as toxic as TBA. In presence of the photocatalyst, the amount of cyanuric acid obtained was 37.21%, while in its absence only 16.08% was obtained, indicating that the presence of the catalyst does increase efficiency, because cyanuric
acid, although cannot be degraded using photocatalysis, it can easily be removed using microbial
degradation 90.

To assess the effect of different reaction conditions on the reaction chitosan immobilize TiO2
on a glass fiber was used for photocatalytic degradation of TBA 91. The photolytic degradation was
effective with cyanuric acid was obtained as a final product. When the rate of the reaction mixture
circulation was increased, the degradation was more successful as more cyanuric acid obtained 91.
Similar study includes the degradation of melamine (s-triazine derivative) in presence of TiO2 92.
Among several oxidation techniques with a multitude of varying experimental conditions, hydroxyl
radicals generated from hydrogen peroxide in presence of sulfate radicals were effective towards
melamine decomposition with cyanuric acid obtained as a final product 92.

The degradation of hexazinone using mixed phase crystal nano-TiO2 has been reported93. The
adsorption equilibrium of hexazinone on TiO2 was reached in 20 minutes in the dark. While
hexazinone was found to be stable in the absence of the catalyst, photodegradation occurs in the
presence of TiO2. The rate of degradation differs when the amount of nano-TiO2 is varied, but the
rate was optimum at 0.1% w/w of TiO2. The proposed degradation route fits the Langmuir –
Hinshelwood model, and the final products obtained were nontoxic 93. The adsorption of prometryn
on TiO2 also follows the Langmuir- Hinshelwood model and first order kinetics. When the reaction
proceeds in the presence of the photocatalyst, only 10% reduced after 2 hours of irradiation 94.
Adding oxidants like peroxydisulfate to the reaction mixture, improved the photodegradation due to
a synergistic effect with cyanuric acid was identified as a final product 94. Dicylanil, an insect growth
regulator derived from pyrimidine, has been also investigated 95. The rate of degradation of dicylanil
was 43 times faster in the presence of the TiO2 catalyst compared to the uncatalyzed reaction with
complete eradication occurs in less than one hour 95.
The degradation of the herbicide metamitron (4-amino-6-phenyl-3-methyl-1,2,4-triazine-5(4H)-one) was also investigated over the TiO\textsubscript{2} catalyst\textsuperscript{96}. When the photocatalyst was present, metamitron was fully degraded after 6 hours, whereas, one fifth of the initial herbicide persisted when the TiO\textsubscript{2} is absent\textsuperscript{96}. Kaniou et. al have studied the degradation of sulfamethazine (SMT), a sulfonamide drug using three n-type oxides the photocatalysts including: ZnO, TiO\textsubscript{2}-P25, and TiO\textsubscript{2} (Anatase)\textsuperscript{97}. After one hour of the exposure the percent decomposition was 100%, 65%, and 39% for the reactions occur with ZnO, TiO\textsubscript{2}-P25, and TiO\textsubscript{2}-Anatase catalysts, respectively\textsuperscript{97}.

TiO\textsubscript{2} has proved to be one of the most powerful catalysts for complete degradation of environmental pollutants\textsuperscript{98}. Using TiO\textsubscript{2} in powder form shows the most efficient catalytic activity\textsuperscript{98,99}. However, when used for water decontamination, post-treatment methods are required to collect the catalyst from the reactor. One way examined is to coat the catalyst on aluminum foam using sol-gel method which, leads to a three-dimensional structure with high surface area as it ensures sufficient flow of liquid and large interface of exchange between targeted molecules and the photocatalyst\textsuperscript{100}. While 5% of pyrimethanil went through a complete photodegradation after 19 h of exposure, 100% of the pesticide removed after 5 h upon irradiation in the presence of TiO\textsubscript{2} catalyst\textsuperscript{100}. The catalytic activities of TiO\textsubscript{2} powder immobilized with silver modified thin films in metolachlor degradation were also investigated\textsuperscript{98}. SEM image for the prepared immobilized catalyst films and silver-nanoparticle-doped films showed rough sponge-like surface in the immobilized films. The effective surface area were hundred times greater than the non-fractal surface due to ability of capturing pollutant molecule and photons and allowing higher light reflection\textsuperscript{98}.

The effect of zinc and titanium oxide photocatalysts on the degradation of the herbicide bentazon, under UV and visible light, along with effect of pH and electron acceptor groups on initial rate of catalysis were studied\textsuperscript{101}. Among ZnO and TiO\textsubscript{2} from different manufacturers, TiO\textsubscript{2}-P25
and ZnO exhibited the highest catalytic activity attributed to their different morphology as it is one of the most critical properties for high catalytic activity. ZnO and TiO$_2$ P25 have the highest catalytic activities under UVA illumination where 97 and 81% of bentazon degraded after 90 minutes, respectively $^{101}$.

The primary kinetics of degradation of pyridaben under photocatalysis of TiO$_2$ was identified $^{99,102}$. The plot of the quantity of pyridaben left in the solution versus the UV irradiation time showed that the degradation follows Langmuir-Hinshelwood kinetic model $^{102}$. The presence of TiO$_2$ particles enhances the reaction rate by 10 times compared to the uncatalyzed system, upon the exposure to wavelengths above 360 nm where a complete degradation of the pesticide has occurred $^{99}$. Further, the illumination of pyridaben was tested in a surfactant CTAB (cetyltrimethyl ammonium bromide) aqueous dispersion $^{103}$. The results indicated enhancement in the initial rate as the concentration of the catalyst increased with strong adsorption of cationic CTAB on titania particles helped co-adsorption of pyridaben which facilitated the photocatalytic degradation. The effect of pH was minimal from pH of 3-6 but overall it increased in the range of 3-10 $^{103}$.

To enhance the photocatalytic activity, TiO$_2$ was coupled with electrochemistry and doped with non-metals like nitrogen to shift the TiO$_2$ absorption to lowest level of energy $^{104,105}$. Beside the nonmetal, immobilization of transition metals is effective in enhancement of TiO$_2$ photocatalysis in visible light. Iron(III) ion has the most similar radius as Ti(IV) and can be introduced to the crystal lattice to change the electronic structure and reduce the band gap. To test the modified TiO$_2$ catalyst, photocurrent of TiO$_2$/Ti and Fe-N-TiO$_2$/Ti electrodes were used to decompose thiamethoxam pesticide $^{104}$. The effect of substrate concentration, pH, type of catalyst, catalyst dosage, and the presence of an electron acceptor such as hydrogen peroxide on the degradation of thiamethoxam were also investigated $^{106}$.
TiO₂ particles were used as photocatalyst for the photodegradation of the fungicide boscalid under different experimental conditions. A complete degradation in presence of TiO₂ occurred after 90 minutes with the degradation rate increases as the pH, photonic flux, and oxygen concentration increases. The presence of inorganic cations like Ca²⁺, Na⁺, K⁺, Mg²⁺ and anions like CO₃²⁻ tend to decrease the rate of reaction as they adsorb on the surface of TiO₂. In a similar study, complete photodegradation of pyraclostrobin was established at pH 6.2 and 0.5 g/L of TiO₂ after 60 min of UV irradiation.

Hermann and Guillard have studied a laboratory photo-reactor and a pilot solar photoreactor for photodegradation of several pesticides. The mass of catalyst required for an optimum light absorption was 2.5 g/L for the batch micro photo-reactor and only 0.2 g/L for the pilot photoreactor. Also, activated carbon coupled with titania enhanced the degradation rate by a factor of 2.5. This enhancement is due to spontaneous mass transfer of pollutant from activated carbon to titania because of concentration gradient between the two. The photolysis and photocatalysis degradation of 6-chloronicotinic acid (6CNA) was also observed under UV radiation. While 6-CNA does not degrade easily in double deionized water, the photocatalytic degradation with immobilized TiO₂ is a fast process with pseudo first order kinetics. Although the mineralization rates estimated through TOC measurements revealed absolutely no carbon removal under photolytic degradation, 46% mineralization was reached using TiO₂ as photocatalyst after 120 minutes. Major results obtained for N-based pesticides are summarized in Table 2.1.
<table>
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<tr>
<th>Catalyst</th>
<th>Preparation method</th>
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<td>UV radiation 365 nm</td>
<td>Pyrimethanil</td>
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<td>TiO$_2$ particles silver modified films</td>
<td>P-25 viscous aqueous dispersion on AgNO$_3$ solution.</td>
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<td>Pyridaben</td>
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<td>Pyridaben</td>
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<td>Pyridaben</td>
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<td>Fe-N- TiO$_2$ nanotubes</td>
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<td>Immobilized TiO$_2$ on glass slides</td>
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<td>UV radiation</td>
<td>Thiamethoxam</td>
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<td>Boscalid</td>
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<td>Cylindrical photoreactor</td>
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<td>Cylindrical photoreactor</td>
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<td>Carbofuran</td>
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<td>TiO$_2$ &amp; photo-Fenton</td>
<td>TiO$_2$ suspension in FeSO$_4$ solution</td>
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<td>HPLC, TOC anal., LC-MS</td>
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<td>LC-MS, HPLC-UV</td>
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<td>TiO$_2$</td>
<td>Degussa P-25</td>
<td>Chlorotoluron</td>
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<td>Methabenzthiazuran</td>
<td>HPLC, TOC anal.</td>
<td>73</td>
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**Table 2.1.** Major studies in photodegradation of N-based pesticides using TiO$_2$ photocatalysts.

Photocatalytic degradation of P-based pesticides generally followed pseudo first order reactions that are expressed by Langmuir-Hinshelwood model $^{85,111,112}$. The rate of degradation depends on several parameters including pH, catalyst type and concentration, substrate concentration, and the presence of electron acceptor such as H$_2$O$_2$ $^{112-118}$. Most studies include testing the use of TiO$_2$ catalysts in removing different pesticides such as malathion, dichlorvos, COD dipterex, diazinon, phorate, dimethoate, and several other organophosphorous pesticides since pesticides have been described to be harmful to the health of humans and animals $^{112-114,119,120}$.

The use of TiO$_2$ based catalysts for photolysis and degradation of malathion, isomalathion, and malaoxan has been reported $^{121-127}$. Malathion, malaoxon, isomalathion, and radotion were studied in terms of their degradation kinetics, identification of their transformation products, their toxicity, and their degree of mineralization, during UV photolysis and TiO$_2$ photocatalysis. Over 75% of theoretically expected sulfur in PQS and P–S groups was oxidized after 240 minutes of photolysis and photocatalysis. Several oxidation and isomerization products were identified by GC-MS $^{121}$. The formation of malaoxon, isomalathion or trimethyl phosphate esters correlated well with the induced toxicity (inhibition of acetylcholinesterase), which was observed in photocatalysis of malathion and radotion, and in the photolysis of malaoxon and radotion $^{121}$. N doped TiO$_2$ nanomaterials degraded malathion within 150 minutes when 1 g/dm$^3$ N-doped TiO$_2$ was added to 15 ppm malathion at pH = 6 under UV-light. The photocatalytic degraded products are less toxic as compared to malathion $^{122}$. Moreover, hierarchical porous TiO$_2$ ceramics were obtained and proved to be good for photodegradation of various pesticides including dimethoate, lindane, dipterex, malathion, and bentazone with good reproducibility $^{123,128}$. Suspended and immobilized TiO$_2$ based
catalysts were used to remove various P-based pesticides including lindane, methyl parathion, quinalphos, diazinone, and dichlorovos from water bodies\textsuperscript{129-134}.

Vela et al. have studied the photocatalyzed degradation of a mixture of six pesticides (fenitrothion, malathion, quinalphos, vinclozolin, fenarimol and dimethoate) with endocrine disrupting activity sewage wastewater effluent under natural sunlight at pilot plant scale\textsuperscript{124}. The use of TiO\textsubscript{2} alongside an electron acceptor like Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} strongly enhances the degradation rate of the studied pesticides compared with photolytic tests. The total initial concentration of pesticides (P = 1.81 mg/L) decreased to 0.39 mg/L (22\%) after 240 min of sunlight irradiation\textsuperscript{124}. After the photoperiod, malathion was totally photodegraded in the presence of TiO\textsubscript{2}-P25, while fenarimol was the most persistent pesticide. Although carbon-doped TiO\textsubscript{2} has lower band-gap energy than TiO\textsubscript{2}-P25, the latter was more efficient in all cases than TiO\textsubscript{2}, charge separation is consolidated which reduce the possibility of recombination\textsuperscript{124}.

2\% WO\textsubscript{3}/TiO\textsubscript{2} catalysts prepared by sol-gel process allowed the incorporation of very reactive WO\textsubscript{3} clusters over anatase TiO\textsubscript{2} surface\textsuperscript{125,126}. The synthesized TiO\textsubscript{2} materials exhibited a crystalline anatase phase with an average particle size of 20 nm. Results of malathion degradation using solar light indicated that 2\% WO\textsubscript{3}/TiO\textsubscript{2} showed better catalytic performance than sol-gel TiO\textsubscript{2}, achieving a complete degradation after 2 hours with 63\% TOC reduction after 5 hours. The previously mentioned results suggest that 2\% WO\textsubscript{3}/TiO\textsubscript{2} is an active material for solar photocatalytic treatment of polluted water having pesticides\textsuperscript{125}. The mineralization rate and the percentage of TOC removal were improved when the content of WO\textsubscript{3} was 2\% due to the formation of smaller clusters and a higher surface area, which reduces the recombination process and results in better contact area between the catalyst particles and the pollutant, improving the photocatalytic reactivity and the destruction efficiency against the pesticide molecule\textsuperscript{126}.

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Au–Pd co-modified TiO₂ nanotube film (Au–Pd–TiO₂) fabricated by simultaneous photo-depositing Au and Pd precursors on a self-organized TiO₂ nanotube film. The photocatalytic activity of the modified film revealed that the malathion elimination rate increased by 172% when the photocatalyst of the naked TiO₂ nanotube film was replaced by Au–Pd–TiO₂. This activity is attributed to the effective separation of photo-generated charge carriers and the higher synthesis rate of H₂O₂ as illustrated in Figure 2.11.

Figure 2.11. Diagram representing the charge-carrier transfer on Au–Pd–TiO₂ and interaction with adsorbed O₂. Reproduced from reference 127. Copyright Elsevier 2010.

Juang and Chen have reported the photocatalytic degradation rates and paths of methomyl and parathion in the presence of TiO₂ suspension using UV irradiation. Langmuir–Hinshelwood kinetic model was used to evaluate the apparent first-order rate constants of both pesticides at their initial stages of degradation processes. Under similar conditions, the degradation level of methomyl was faster than parathion as expected due to more complicated structures of parathion molecules. In similar study, titanium dioxide proved to be more efficient photocatalyst than ZnO since the oxidation and decomposition of the insecticide proceeded at higher reaction rates. Moreover, complete mineralization was achieved only in the presence of titanium dioxide. Toxicity level
was observed to be decreased during photocatalytic activity in the presence of a catalyst where eight by-products were identified during the photocatalytic activity \(^\text{136}\). It has been recently reported that anatase nanofibers act as good photocatalyst towards the degradation of methylparathion pesticide \(^\text{137}\). The modified catalyst is with high surface area that enhance the adsorption of the target pesticide and thus accelerate its degradation process \(^\text{137}\).

Several triazine derivatives and organophosphorous pesticides were investigated in aqueous TiO\(_2\) suspensions under simulated solar light \(^\text{138}\). Degradation kinetics monitored through gas chromatography followed the first-order kinetics. The degradation was fast with half-lives varying from 10.2 to 38.3 minutes depending on the nature and the structure of the compounds \(^\text{138}\). The generated transformation products were formed via oxidation, dealkylation, and dechlorination for s-triazines and via oxidation and photohydrolysis for organophosphates \(^\text{138}\).

TiO\(_2\) nanofibers containing Ag nanoparticles prepared by electrospinning were established as potential photocatalyst for the degradation of parathion. The prepared Ag/TiO\(_2\) nanoparticles provide a higher photocatalytic performance in reaction under UV photo irradiation \(^\text{139}\). The enhancement was due to the narrow size distribution, high purity, uniform distribution of doped metal and ~50 nm diameter of the prepared Ag/TiO\(_2\) nanofibers. Furthermore, the presence of metallic nanoparticles inhibits the electron-hole recombination in TiO\(_2\) by electron capture resulting in increased hole formation to produce hydroxyl radicals, which lead to an increase in the rate parathion photodegradation reaction \(^\text{139}\). It was also found that the content of Ag nanoparticles on TiO\(_2\) nanofibers performed a significant role in photocatalytic performance during the parathion degradation reaction \(^\text{139}\).

A series of bismuth-doped titania samples were prepared and applied for the photodegradation of methyl parathion under UV-A radiation \(^\text{140}\). The photocatalytic degradation of methyl parathion
in aqueous solutions was further promoted by the Bi-TiO₂ photocatalysts, compared with TiO₂ alone. It has been demonstrated that methyl parathion was degraded efficiently in aqueous Bi-TiO₂ suspension to the extent of 97% within 120 minutes.

TiO₂ photocatalyst was also used to degrade the most widely used organophosphorus pesticides, monocrotophos (MCP) and chlorpyrifos (CPS) using 16 W UV light source. The kinetic analysis of photodegradation of monocrotophos and chlorpyrifos under different initial concentration followed the Langmuir–Hinshelwood model where, TiO₂ is proved to be excellent photocatalyst for degradation of monocrotophos and chlorpyrifos. In addition, the degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil was examined in aqueous solution by TiO₂ photocatalysis under UVA (365 nm). In UV/TiO₂ photocatalysis, COD and TOC removal were 25.95 and 8.45% respectively whereas, UV/TiO₂/H₂O₂ photocatalysis revealed 53.62 and 21.54% COD and TOC removal, respectively. The study is significant regarding the application of UV/TiO₂/H₂O₂ photocatalysis as pretreatment of chlorpyrifos, cypermethrin and chlorothalonil pesticide wastewater at pH 6, for biological treatment. Batch degradation studies on Endosulphan and Chlorpyrifos were conducted in the concentration range from 5 to 25 mg/L at a pH ranging from 3.5 to 10.5 and at a catalyst loading of 0.5–2 g/L. Endosulphan removal efficiency was about 80–99% and chlorpyrifos removal efficiency was about 84–94% in the presence of TiO₂ catalyst. The obtained high removal efficiencies (80–99%) indicate the effectiveness of this process and its potential for practical application.

Photocatalytic degradation of organophosphorus compounds including organophosphonic, and organophosphinic acids by TiO₂ immobilized silica gel in a water phase was carried out. Photocatalytic degradation of organophosphorus compounds through forming various intermediates obtained via rapid absorption of acids on TiO₂ surface resulted in significant reduction in the
concentration of these compounds even under dark condition\textsuperscript{144}. Upon UV irradiation, total organic carbon (TOC) level increased indicating the elution of some organic intermediates into the aqueous phase\textsuperscript{144}.

While TiO\textsubscript{2} is commonly used for its high photodegradation activity, it is not easy to separate and reuse TiO\textsubscript{2}\textsuperscript{145}. To overcome its separation, TiO\textsubscript{2} was synthesized with supports like HZSM-11 zeolite. It was found that TiO\textsubscript{2}/ZSM-11 catalysts are suitable for the degradation of the insecticide DDVP in water, resulting in degradation percentages similar to the commercial TiO\textsubscript{2} P25\textsuperscript{145}. Similarly, TiO\textsubscript{2} supported on H\textsubscript{8} was tested on monocrotophos pesticides (MCP) where it was concluded that supporting TiO\textsubscript{2} on a zeolite makes it better for both degradation and mineralization since MCP and its intermediates were adsorbed to the supported TiO\textsubscript{2}\textsuperscript{146}. Moreover, TiO\textsubscript{2} photocatalyst removed the toxic dichlorvos pesticides present in the air indoors; but it produced a small amount of potentially harmful by-products in the gas phase\textsuperscript{147}.

The photocatalytic degradation of organophosphorous pesticide dichlorvos in suspended TiO\textsubscript{2} was also studied under solar irradiation\textsuperscript{148}. After exposure to solar irradiation, Cl\textsuperscript{-} ions were found in large quantities whereas PO\textsubscript{4}\textsuperscript{3-} was only present in small amounts due to its presence in phosphate organic compounds. Formaldehyde was also present as an unstable intermediate throughout the reaction. The presence of H\textsubscript{2}O\textsubscript{2} played a role in the reaction where it increases the rate of degradation via generating OH\textsuperscript{•} radicals\textsuperscript{148}. TiO\textsubscript{2} was found to be more effective than ZnO for the oxidation of dichlorovos that occurred at fast rate as well as the process almost reached complete mineralization\textsuperscript{149}. The comparison of both TiO\textsubscript{2} and ZnO has also been seen in another study done on dimethoate pesticide, where a similar conclusion was reached in which the rate of the oxidation and decomposition of the insecticide was faster with the use of TiO\textsubscript{2} catalyst, hence it is the more efficient
catalyst. TiO$_2$ was able to achieve mineralization with the addition of an oxidant as well as achieve complete detoxification with the addition of peroxide.

Chen et al. have discussed the treatment of Dimethoate using nanosized TiO$_2$ powder, where the concentration of the TiO$_2$ catalyst increases the degradation efficiency with an optimal concentration of 0.6 g/ml. With the right adjustment of the parameters, the efficiency of degradation could reach 99% in 160 minutes. Addition of oxidants and the use of ultrasonic irradiation (US) positively affects the degradation efficiency. Moreover, the degradation of triazophos by sunlight in the presence of TiO$_2$ has a degradation rate faster than the rate caused by direct photolysis where seventeen products were produced and projected in several transformation routes. A nanometer-sized titania coupled with a screen-printed carbon electrode (SPCE) also works as a photoelectrochemical sensor that detects the organophosphorous pesticide, dichlofenthion.

Sonocatalytic, photocatalytic, and sonophotocatalytic degradation of diazinon were evaluated using Fe-doped TiO$_2$ nanoparticles which resulted in a faster degradation rate than TiO$_2$ alone. The rate of degradation depends on the pH, catalyst dosage, and initial concentration of diazinon and concentration of Fe doping. As the concentration of the catalysts and the Fe doping increased, the rate of degradation increased as well. TiO$_2$/Fe$_2$O$_3$ nano powder, which was present in the form of anatase and maghemite crystalline phases, respectively were used to decompose diazinon. The TiO$_2$/Fe$_2$O$_3$ catalysts was compared with a pure TiO$_2$ as a catalyst in which it was concluded that TiO$_2$/Fe$_2$O$_3$ had high absorption in both the UV region and the visible region. FeNS-TiO$_2$ has been found to be more effective than pure TiO$_2$ with diazinon pesticides in which it improved the degradation of diazinon by 53% at pH 7. Similar to other studies, the rate of degradation increases with the increase of catalyst concentration.
Studies were also done on different types of toxic pesticides that should be eliminated from the environment including phorate, diisopropyl fluorophosphate (DFP) and (DMMP) dimethylmethylphosphonate, Chemical Oxygen Demand (COD) dipterex, as well as 2-chloroethyl sulfide (CEES)\(^{157-166}\). Phorate degradation over TiO\(_2\) catalyst using UV irradiation follows first order pseudo reaction with the degradation efficiency could reach 99\% in 60 minutes \(^{158}\). Inorganic ions present in natural water systems like Cl\(^-\) and NO\(_3^-\) decreases the degradation rate of phorate. Using wet TiO\(_2\) for DFP and DMMP photodegradation reduces the number of intermediates that accumulate on the surface while still maintaining a fast degradation rate \(^{160}\). DMMP was also treated using Zr-doped TiO\(_2\)\(^{159}\).

TiO\(_2\) doped with 6.8 wt\% Zr produces the most efficient sample for the photodegradation of these pesticides \(^{159}\). Photocatalytic degradation is also used to remove pesticides such as COD dipterex using TiO\(_2\)/Ni photodegrade \(^{157}\). Under certain experimental conditions, the rate of COD dipterex degradation reached up to 82.6\% whereas the organophosphorous conversion could reach 83.5\%. This study offered a new porous nickel net photocatalyst carrier, which could inhibit the recombination of electrons and holes and enhance the efficiency of photocatalytic degradation of dipterex pesticide from wastewater, compared with the commonly used Ti metal carrier \(^{157}\). Major results obtained for P-based pesticides are summarized in Table 2.2.
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<th>Preparation method</th>
<th>Irradiation source</th>
<th>Pesticide</th>
<th>Detection method</th>
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<td>Commercial</td>
<td>Medium pressure mercury lamp of 228 W</td>
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<td>TiO₂ surface by pressing into a self-supporting pellet (80-100 g/m²)</td>
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<td>UV-vis, GC-MS</td>
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<td>Solar light</td>
<td>Diisopropyl fluorophosphate</td>
<td>DRIFT</td>
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**Table 2.2.** Major studies in photodegradation of P-based pesticides using TiO₂ photocatalysts.

Several comparative studies on the photocatalytic degradation of various benzene derivatives over TiO₂ (Phenol, Chlorobenzene and Toluene) were established in aqueous medium 167-172. The results demonstrate the existence of a relationship between organic compound photo degradation and the type of substituent on the aromatic ring. The degradation was faster for electron-donating substituents 167. Photo catalysis efficiency can be increased using Pickering emulsion in degrading non-soluble organic pollutants 169. The study showed that Pickering emulsion with TiO₂–Salicylic acid nanoparticles lead to improving the photocatalytic degradation of the chlorobenzene derivatives. The key point is having small drop size to increase the contact area between the contaminant photo catalysts 169. The photo-oxidation of 4-chloroanaline was also investigated under UV/TiO₂/H₂O₂ 168. Gas chromatography and mass spectrometry screening showed that the degradation initiated by OH radicals and the intermediates formed were able to be oxidized into benzoquinone then become carboxylic acids by ring cleavage 168. Platinum modified TiO₂ nanoparticles showed higher photocatalytic degradation efficiency for both phenol and 2-chlorophenol by 87.7 and 100%, respectively 171.

Advanced oxidation processes (AOPs) are eco-friendly for destroying non-biodegradable pollutants where solar light being used for generating hydroxyl radicals 173. TiO₂ photocatalytic degradation of chloropyridines in presence of UV light is being used in pharmaceutical industry and agricultural chemistry 173. In the presence of TiO₂ as a heterogeneous photocatalyst, 3-chloropyridine and 2-chloropyridine disappearance follow a zero-order and a first-order kinetics, respectively 173. A comparative study between homogeneous (photo-Fenton) and heterogeneous (TiO₂) photocatalytic degradation of 3-chloropyridine in presence of UV and sunlight by scaling-up solar photo-Fenton process. For Fenton, photo-Fenton and direct photolysis, the results showed that
Fe(II) ions facilitate mineralization of 3-chloropyridine in the presence of H$_2$O$_2$, but still it is a lot slower than in the presence of light. The time required for 100% mineralization in presence of UV light was 60 and 300 min for photo-Fenton and TiO$_2$ photocatalysis, respectively \textsuperscript{173}. TiO$_2$ hollow microsphere calcined at 500 °C exhibited twice higher than uncalcinated sample \textsuperscript{174}. The microstructure of the hollow microspheres leads to improvement in the efficiency of 4-chloronitrobenzene mineralization with high stability and reproducibility up to six cycles \textsuperscript{174}.

The use of nano-TiO$_2$ coated films as photocatalyst towards the decomposition of organochlorine pesticides having hexachlorobenzene (BHC), dicofol and cypermethrin has been reported \textsuperscript{175}. The results showed that photocatalytic degradation efficiency is much higher than direct photolysis with all pesticides were completely degraded over the film in 45 min \textsuperscript{175}. The potential of immobilized TiO$_2$-based zeolite composite photocatalyst (TiO$_2$-FeZ) done from commercial Aeroxide TiO$_2$ P25 and iron-exchanged zeolite of ZSM5 type (FeZ), for solar assisted treatment of diclofenac (DCF) was studied \textsuperscript{176}. TiO$_2$-FeZ composite was used in the photocatalytic treatment of DCF water solution. The DCF degradation adsorption happens on the catalyst surface by hydroxylation and ring cleavage \textsuperscript{176}. Figure 2.12 shows the photodegradation pathways that illustrates all products formed \textsuperscript{176}. The biodegradability increases when there is a decrease in the aromatic DCF by-products and enhanced dechlorination of organic structures \textsuperscript{176}.
Figure 2.12. Degradation Pathway of diclofenac. Reproduced from reference 176. Copyright Elsevier 2016.

Direct photolysis and photocatalytic degradations of chlorfenapyr in TiO$_2$ suspensions in presence and absence of hydrogen peroxide was investigated under monochromatic UV irradiations where photo catalysis rates increased 2.5 and 3 times when TiO$_2$ was used at 300 and 350 nm UV, respectively 177. Light-induced degradation of chlorfenapyr in UV was done using solution having TiO$_2$ as photocatalyst 178. The degradation goes through pseudo-first-order kinetics following two pathways: First, cleaving of aliphatic ether group and forming pyrrole-$\alpha$-carboxylic acid, then breaking the pyrrole group and forming 4-chloroglycine. Second, debromination of chlorfenapyr and cleaving ether group and forming pyrrole group that broke into 4-chlorophenylglycine. Glycine was degraded to form 4-chlorobenzoic acids, then break and form inorganic ions and CO$_2$ 178.

Photocatalytic degradation of 4-chloro-2-methylphenol (PCOC) in aqueous solutions using various TiO$_2$ catalysts have been investigated 179-185. It has been reported that 51.4% of PCOC degraded in the presence of TiO$_2$ which can be improved by different oxidants as electron scavenger 179. Having metal ions to UV/TiO$_2$/H$_2$O$_2$ leads to increase in photo degradation by inducing
Fenton/photo-Fenton type reactions and quenching photo-ejected electrons from the TiO\textsubscript{2} surface\textsuperscript{179}. Similarly, 4-chlorophenol (4-CP) was degraded through Fenton-like heterogeneous on TiO\textsubscript{2} and CuFe\textsubscript{2}O\textsubscript{4}\textsuperscript{184}. The results showed that the system goes through homogeneous route, using dissolved metal ions found in the solid phase catalysts. Ferric ions and hydrogen peroxide enhanced the degradation efficiency of combined chlorophenols in solar/TiO\textsubscript{2}\textsuperscript{185}. In addition, Ag-coated Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2} particles with a good core shell structure shows strong photocatalytic activity for the degradation of 2,4,6-trichlorophenol. The particles showed high dispersibility and stability in water so they can be reused for many cycles with convenient magnetic separability\textsuperscript{183}.

Sol–gel using titanium(IV) isopropoxide and zirconium nitrate precursors, was used for making Zr\textsuperscript{4+} doped nano titania\textsuperscript{180}. TEM results showed Zr\textsuperscript{4+} doped TiO\textsubscript{2} is nanocrystalline, so having dopants lead to the growth of TiO\textsubscript{2} grains, increasing the surface area and decreasing the transformation of anatase to rutile. This leads to having larger photocatalytic activity for Zr\textsuperscript{4+} doped nano TiO\textsubscript{2} than the undoped samples. Adding metal nitrate can control the selective crystallization of anatase phase of TiO\textsubscript{2}, and that provide high efficiency in the photocatalytic mineralization of 4-chlorophenol\textsuperscript{180}. Similarly, P loaded to TiO\textsubscript{2} via sol-gel protocol leads to slowing the growth of the anatase particle and increasing its transformation to rutile. As a result, the photocatalytic activity for 4-chloro-phenol using UV irradiation on P-modified TiO\textsubscript{2} was 4.5 times higher than TiO\textsubscript{2} alone\textsuperscript{182}. Further, sol impregnation process to fabricate Ce-TiO\textsubscript{2}/CA electrode was reported\textsuperscript{181}. Spectroscopic analyses showed that the optical absorption edge of Ce-TiO\textsubscript{2}/CA is red-shifted compared with TiO\textsubscript{2}/CA, and the density was 75 times higher than Ce-TiO\textsubscript{2}. The conductivity of Ce-TiO\textsubscript{2}/CA was shown by the spectra to be larger than Ce-TiO\textsubscript{2}/FTO. As a result, Ce-TiO\textsubscript{2}/CA improved the electrosorptive photodegradation of 4-chlorophenol\textsuperscript{181}. 

Chlorinated aromatic compounds such as dichloro$^{186-191}$, dibromo$^{192}$, and multichloro$^{193-201}$ derivatives are some of the main contaminants present in water as they are widely used as pesticides and in many chemical syntheses. They are of great health and environmental concern due to their ability to bio-accumulate, suspected carcinogenicity and potential toxicity, hence their removal is essential. Moreover, chlorophenols are currently listed in the US-EPA Clean Water Act as the primary pollutant to be removed from water. In addition to chlorinated aromatic compounds, other compounds that are potential to cause risk to humans and environment are different DDT compounds ($p,p'$-DDT, $o,p'$-DDT, $p,p'$-DDD and $p,p'$-DDE) which can also be degraded using TiO$_2$ in the form of nano tubes. Several biorecalcitrant pesticides (alachlor, atrazine, chlorfenvinfos, diuron, isoproturon, pentachlorophenol) can be degraded through oxidation processes using different form of TiO$_2$ catalysts$^{197,202-207}$.

Advanced oxidation processes for degradation of 1,4-dichlorobenzene (1,4-DCB) and mineralization are employed under photolysis, photocatalysis on TiO$_2$, and sonolysis$^{186}$. Photocatalysis on TiO$_2$ particles is kinetically faster for removal of 1,4-DCB than direct photolysis and sonolysis. Degradation and mineralization of 1,4-DCB using sono photo catalysis (combination of sonolysis and photocatalysis) was the fastest but required more energy than photocatalysis$^{186}$. Fe/TiO$_2$ catalysts prove to be more effective than the pure Fe or TiO$_2$$^{187}$. This is due to the potential of iron to reduce toxicity of the product and enhance mineralization by trapping photo-generated electrons and holes. Hence, increasing concentration of Fe further improves the effectiveness of catalyst$^{187}$. Moreover, mineralization of 2,4 –dichlorophenol (2,4 DCP) in water under UV irradiation was improved using immobilized Fe$^0$, activated carbon fiber (ACF) and TiO$_2$ as a
composite membrane. 2,4 DCP degradation improved by presence of Fe$^{0}$ and TiO$_{2}$ at an optimum pH of 6 and optimal loading of 1 wt % Fe$^{0}$ to TiO$_{2}$. ACF adsorption effect was very useful for TOC removal as it adsorbs 2,4 DCP as well as intermediates $^{188}$.

The immobilized Fe$^{0}$/TiO$_{2}$/ACF catalyst proved to be reusable, stable and durable and uses adsorption, chlorination, hydroxylation and cleavage of aromatic ring to degrade 2,4 DCP $^{188}$. Further, 2,4 DCP degradation was tested using TiO$_{2}$/UV and laccase by simultaneous photocatalytic-enzymatic process. TiO$_{2}$/UV inactivated laccase but covalent immobilizing laccase to controlled porous glass (CPG), enhanced its stability. CPG-laccase and TiO$_{2}$/UV coupling produced better results than either individual condition, especially at high concentrations of 2,4 DCP where up to 90% removal of 2,4 DCP was attained within 2 hours $^{191}$.

Varying few parameters, such as initial DCP concentration, initial pH, photocatalyst dose of TiO$_{2}$ suspensions were tested for 2,4 DCP adsorption and degradation along with effect of three co-oxidants (hydrogen peroxide, ozone and sodium peroxodisulfate) on the photo catalytic process $^{190}$. The DCP degradation was optimum at pH 5.0 and the patterns were fitted to Langmuir-Hinshelwood model. The heterogeneous photocatalysis of DCP enhanced by hydrogen peroxide, while the use of ozone did not show a significant result with sodium peroxodisulfate inhibited DCP degradation $^{190}$.

Kamble et al. have reported the solar photocatalytic oxidation of 2,4 - dichlorophenoxyacetic acid (2,4-D) using TiO$_{2}$, air and concentrated solar radiation in batch and continuous bubble column reactors. The 2,4-D adsorption on the surface of catalyst depend on the pH, the concentration, and the type of anions present. The treatment of wastewater is possible from a plant manufacturing 2,4-D using novel slurry bubble column reactor under acidic conditions $^{189}$. In addition, doped Cs on TiO$_{2}$ was used for photocatalytic ozonated degradation of bromoxynil $^{192}$. Results of 1% Cs/TiO$_{2}$ catalyst showed 100% degradation and mineralization of bromoxynil at basic pH in two
hours as confirmed by GC-MS and a possible decomposition process is given in Figure 2.13. The catalyst is fully recyclable and reusable with no loss of activity 192.

![Reaction Diagram](image)

**Figure 2.13.** Proposed reaction protocol for Bromoxynil photodegradation using TiO$_2$ photocatalyst.

Cu$_2$O/TiO$_2$/Carbon Aerogel (CA) electrode is tested for the photodegradation of 2,4,6-trichlorophenol (TCP) and removal of TOC from wastewater using visible light for its excellent electro-sorptive and highly efficient photocatalytic properties. About 96.3% removal of 2,4,6-TCP and 91.3% of TOC removal were achieved in 5.5 hours 193. Anatase TiO$_2$ nano tubes loaded with Ag nano particles (Ag/TNTs) showed significant visible light absorption and about 99% pentachlorophenol (PCP) was removed after 180 minutes of visible light irradiation while pure TNTs removed only 59.4% PCP 194. This increase of PCP removal is due to better trapping of photo generated electrons between Ag nano particles and increase in absorption of visible light by the localized surface plasmon resonance of Ag nano particles. Ag/TNTs had high catalytic activity and high stability even after being used for five cycles 194. In addition, visible light degradation of PCP was tested using TiO$_2$ with B doping and Bi$_2$O$_3$ coupling (resulting a Bi$_2$O$_3$/TiO$_{2-x}$B$_x$). The Bi$_2$O$_3$/TiO$_{2-x}$B$_x$ combination gave much higher results than using each alone. This is due to each one having their own strength (B doping produce more photo generated electron-hole pairs and
$\text{Bi}_2\text{O}_3$ inhibit the recombination of photo induced charge carriers) and combination of their strengths lead to better results. This technique has proven to be effective for removal of highly toxic halogenated aromatic compounds $^{195}$.

**Photocatalytic Degradation of Chlorinated Pesticides using TiO$_2$-based Catalysts.**

Lindane, an organochlorine pesticide, was removed using visible and solar light assisted sulfur doped TiO$_2$/peroxymonosulfate (HSO$_5^-$). Photocatalysis using visible and solar light assisted S-TiO$_2$ resulted in 31.0 and 63.4% lindane removal, respectively. Whereas, addition of 0.2 mM HSO$_5^-$ resulted in 68.2 and 99.9% lindane removal, respectively $^{196}$. The S-TiO$_2$ film remained stable even after 4 cycles and this proved its efficiency for detoxification of water contaminated with OCPs such as lindane $^{196}$. Moreover, novel TiO$_2$ nano tubes were used as a solid phase extraction adsorbent for $p,p'$-DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane], $o,p'$-DDT [1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane] and its metabolites $p,p'$-DDD [1,1-dichloro-2,2-bis(4-chlorophenyl)ethane], and $p,p'$-DDE [1,1-(2,2-dichloroethanylidene)-bis(4-chlorobenzene)] as the target analytes and then applied for analysis of real water samples $^{197}$. The detection limits for $p,p'$-DDT, $o,p'$-DDT, $p,p'$-DDD and $p,p'$-DDE were obtained as 0.0037, 0.0053, 0.0031 and 0.0025 ng mL$^{-1}$ under optimal conditions $^{197}$. In analysis of environmental water samples, recoveries were obtained in the range of 81.2-115% which proved novel TiO$_2$ nano tubes having potential in decontaminating water bodies from DDT derivatives $^{197}$.

The degree of degradation of Lindane, $p,p'$-DDT and methoxychlor was also measured using a UV/TiO$_2$/O$_2$ system where different degradation products were identified by gas chromatography either with a mass spectrometry detector (GC-MS) or electron capture detector (GC-ECD). The two different types of photo catalysts used were powdered anatase and rutile and anatase supported on glass hollow microspheres $^{202}$. Elimination of pesticides with anatase supported on glass hollow
microspheres was obtained in the range of 68 to 90% in just 30 minutes of irradiation while only 50% removal of lindane, 85% removal of DDT and 99% removal of methoxychlor was obtained with rutile in 150 minutes of irradiation. Also, due to low density of hollow microspheres, anatase supported on glass hollow microspheres was easily separated from reaction mixture. Hence, the results showed that anatase is better catalyst than rutile and activity of 5 mg/dm$^3$ anatase on hollow microspheres is equivalent to that of 500 mg/dm$^3$ powdered anatase.

Photo-Fenton/ozone (PhFO) and TiO$_2$-photo catalysis/ozone (PhCO) advanced oxidation coupled systems are used for degradation of some biorecalcitrant pesticides (alachlor, atrazine, chlorfenvinfos, diuron, isoproturon, PCP) and leads to a rapid decrease in their concentrations. This reaction goes through oxidation of organic molecules and using PhFO follows a first or using PhCO follows zero order kinetics. PhFO or PhCO with TiO$_2$ using UV irradiation enhances the removal of TOC in all pesticides except atrazine which experiences no TOC removal. PhFO was found to be better catalyst than PhCO for all studied pesticides except for alachlor and atrazine in which detoxification requires more than 2-3 hours. However, a reverse reaction could cause toxicity in alachlor to increase after 3 hours of treatment with PhFO.

**Photocatalytic Degradation of Phenol Derivatives by TiO$_2$-based Catalysts.**

Industrial wastewater is a major contributor to water pollution. Industrial processes such as petroleum refining, synthetic resins, coal tar, steel, coal gasification and liquefaction, pharmaceutical production, and surface runoff from coal mines release a massive amount of wastewater containing high levels of phenols and phenolic compounds. These organic compounds are bio-recalcitrant and toxic and have harmful effects on organism at low concentrations. Phenols and phenolic compounds pose a threat to biotic life and must be capped at a threshold concentration of 1 mg/L in inland water according to Central Pollution
Degradation of these compounds occurs at slow natural rates due to their significant water solubility.

Conventional wastewater treatment like precipitation, coagulation, chlorination, sedimentation, and combustion are inept of removing bio-recalcitrant compounds and are expensive, and therefore, new methods must be found. New technology has looked at the use of advanced oxidation processes (AOPs) that generate strongly oxidizing hydroxyl radicals that degrade bio-recalcitrant compounds into biodegradable ones. Heterogeneous photocatalysis using titanium oxide is one such process that has been widely researched. TiO₂ is a semiconductor with extensive environmental applications due to its ability to use solar UV light or catalytic function, low toxicity, biological and chemical inertness, availability, and low cost. Improvements for increased photocatalytic efficiency and recovery of titanium oxide have been extensively researched to find the optimum way to use the metal oxide catalyst in nature.

The widely used TiO₂ catalyst for phenols and phenolic-based compounds is Degussa (P-25). Saravanan et. al studied TiO₂ Anjatox as an alternative photocatalyst of phenols to the conventional photocatalyst, Degussa P-25. Degussa had a small range of catalysts loading from 1 to 4 g/L with a maximum phenol degradation of 90% at 3 g/L. This indicates the potential use of Degussa as photocatalyst for phenol degradation providing its uniform particle distribution, larger catalytic surface area, and high efficiency of phenol degradation. It is observed that photocatalytic degradation of the pollutants improved by introducing solid supports that provide better adsorbent sites. Munoz et al looked at enhancing TiO₂ photo- efficiency by modifying the surface with a high surface area material such as activated carbon (AC) for its porous structure that can encapsulate organic pollutants and provide high adsorption capacity. Different ratios of a
home-made titania catalyst (TiEt) and AC were physically mixed to find the best performance catalysts for phenol degradation. The optimum TiEt to AC concentration ratio for phenol photodegradation was found to be 500/100 TiEt/AC. Naeem et al. reported that the optimum photocatalytic degradation of phenol and 4- chlorophenol was observed when 50 mg of the solid supports, AC, SiO₂, or zeolite, were used in which activated carbon had the highest enhancement and SiO₂ had the lowest.

The 500/100 TiEt/AC catalytically converted 80% of the phenol with 70% total organic carbon removal at 300 min of irradiation. Intermediates formed such as hydroquinone, p-benzoquinone, resorcinol, and catechol were also adsorbed by the TiEt/AC catalysts. An ideal photo-oxidation process occurs due to activated carbon concentrating the organic pollutants on its large surface allowing for easier access to the active sites on the titania surface. TiEt/AC catalysts showed good stability and durability of photocatalytic activity in four consecutive trials, where 60% of the total organic carbon with total phenol degradation was accomplished over 36 hours of irradiation. Dried rice husk solid support for TiO₂-P25 catalyst was found to have similar catalytic features to the three supports for the degradation of phenol and 4-chlorophenol. All solid supports mixed with TiO₂ enhanced the degradation of pollutants in comparison to the bare TiO₂ catalyst.

Carbajo et. al compared the photodegradation of TiEt-450 with the conventional TiO₂-P25 on three organic pollutants: phenol, dichloroacetic acid (DCA), and pyrimethanil along with five pharmaceutical microcontaminants: ofloxacin, sulfamethoxazole, carbamazepine, flumequine, and ibuprofen. Most importantly, the study followed the TiO₂ recovery using sedimentation, as this is a critical challenge that is limiting the application of the catalyst in wastewater. TiEt-450 presented a surface area of 43 m²/g, while TiO₂-P25 showed a slightly larger surface area.
of 54 m$^2$/g. The composition of the water matrix, deionized water or natural groundwater, influenced the phenol photodegradation for both catalysts. In deionized water, P-25 had a better phenol and TOC photodegradation performance than TiEt-450$^{214}$. However, in natural water, conversion drastically increases for both catalysts in comparison to irradiation time in deionized water.

The presence of ions such as CO$_3^{2-}$/HCO$_3^-$, NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, or Cl$^-$ in natural water that are capable of scavenging photocatalyst produced hydroxyl decreases the disappearance rates of phenol and TOC with both catalysts and irradiation time. Moreover, total photo-oxidation of pharmaceuticals by both catalysts showed that ofloxacin, fiumequine, and ibuprofen required irradiation time of 5-7 minutes respectively, while sulfamethoxazole and carbamazepine need 20-30 min irradiation time. To remove all pharmaceutical microcontaminants, TiO$_2$-P25 required 221 minutes irradiation time while TiEt-450 required only 28 minutes. TiEt-450 presented the best global photo-efficiency, both photo-oxidation and recovery steps, for photocatalytic removal of the previously mentioned contaminants$^{214}$.

Turki et. al compared the use of anisotropic TiO$_2$ nanomaterials such as nanotubes, nanowires, nanorods, and nanoparticles to the conventional TiO$_2$-P-25 on the photodegradation of phenol$^{211}$. Nanotubes, nanowires, and nanorods demonstrate different adsorption ability based on their different adsorption sites. Phenol adsorption obeys a quasi-second-order reaction model that assumes that the adsorption rate is determined by the square number of vacant adsorption sites on the surface of the catalyst$^{211}$. Among the titania nanomaterials, nanotubes calcinated at 400 °C showed the lowest phenol adsorption in both the dark and under UV by adsorbing 0.79 µmol/g and 1.25 µmol/g, respectively. The highest phenol adsorption occurred with titanate nanotube -600 adsorbing 89.34 µmol/g phenol in the dark indicating that nanomaterials poses a possible
alternative to the conventional TiO₂-P25 for phenol photodegradation. Since, nanosized TiO₂ can cause liver and heart damage on mice and could possibly affect humans if it remains in treated water, Mejia et al. studied the use of immobilized TiO₂ thick film on a compound parabolic collectors (CPC) as an alternative to TiO₂ powder. TiO₂ thick films showed a mix of anatase and rutile crystalline with nanoscopic particles. Resorcinol had a 75% removal efficiency by the film and was converted to tri-hydroxy benzenes at neutral pH.

Photocatalytic Degradation of Chlorophenols by TiO₂-based Catalysts.

Dissolving transition metal ions in heterogeneous catalysts has been extensively studied for their catalyst efficiency enhancements. Transition metal doped TiO₂ catalysts provide higher concentrations of hydroxyl ions and prevent the recombination of electron-hole pairs thus enhancing the photocatalytic activity. Lin et al studied the degradation of chlorophenol by CuSO₄-doped TiO₂. Four parameters were examined, pH, temperature, initial concentration of pollutant, catalyst dosage and oxygen concentration, to see their effect on 2-chlorophenol degradation. It was found that 100% of 20 ppm levels of 2-chlorophenol was degraded in the presence of the catalyst after six hours. Moreover, the dosage of catalyst was also examined where 3.0 g of the Cu-doped TiO₂ yielded an optimum result of degrading 100% of 2-chlorophenol under visible light in six hours. While lower mass of the catalyst did not provide sufficient active sites for photocatalytic degradation, the higher masses showed agglomeration and sedimentation, which reduces the available surface area for photon absorption. Furthermore, degradation of 2-chlorophenol was more favorable in acidic conditions over basic conditions, specifically at a pH of 5.5.
Zhao et al studied the effect of pH, catalyst and H$_2$O$_2$ concentration on the degradation of nitrophenol $^{217}$. The degradation of 4-nitrophenol by Fe-doped TiO$_2$ increased in acidic conditions similar to what is observed in 2-chlorphenol with optimum concentrations of catalyst and H$_2$O$_2$ required for degradation efficiency were 0.1 g L$^{-1}$ and 4.9 mM respectively $^{217}$. Moreover, the effect of the pollutant structure and the electronic character of the substituents, play significant roles on the degradation efficiency by TiO$_2$ catalyst.

Tolosana-Moranchel et al studied five TiO$_2$ catalysts: Evonik P25, Evonik P25.20, Evonik P90, Hombikat UV100 (HBK), and Cristal ACTIV PC105 (PC105) for their degradations on phenol, 4-chlorophenol, 4-nitrophenol, and methyl p-hydroxybenzoate $^{212}$. The efficiency of the photocatalysts followed the order: P25 > P90 > P25/20 > PC105 > HBK. This is due to the presence of mixture of anatase and rutile phases that result in improvement of electrostatic interactions between the two crystalline phases. Finally, the substituents on the phenolic compounds were studied for their influence on photodegradation, by comparing their initial degradation rates to phenol that is used as a reference. The reaction rates were observed to follow the order: phenol > 4-chlorophenol > methyl p-hydroxybenzoate > 4-nitrophenol. The reaction rate of 4-nitrophenol was reduced nearly four times in comparison to phenol $^{212}$. It is concluded that the stronger the electron withdrawing group the lower the probability of a reaction in the unsubstituted position$^{212}$. Ksibi et al supports this former finding upon studying the degradation of hydroquinone, resorcinol, 4-nitrophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol using TiO$_2$ catalyst $^{218}$. 2,4-dinitrophenol presented the highest adsorption constant due to the ortho-position of the nitro group. On the other hand,
2,4,6-trinitrophenol presented the lowest adsorption constant due to the numerous nitro groups that cause excessive hindrance of the molecule \(^{218}\).

The modification of TiO\(_2\) nanoparticles (P25) via a coating of a molecular imprinted polymer (MIP) shows increased activity and selectivity towards 2-nitrophenol (2NP) and 4-nitrophenol (4NP) \(^{219}\). The molecular imprinted polymer consists of the target molecule, 2NP or 4NP, mixed with o-phenylenediamine. The modified catalysts, 2NP-P25 and 4NP-P25 were studied for their degradation activity and selectivity in comparison to P-25 as a reference. The degradation of 2NP and 4NP occurred faster using their respective catalysts 2NP-P25 and 4NP-P25 in comparison to P25 but produced the same intermediates when using P25. However, the accumulation of the intermediates is lower in the MIP coated photocatalysts, promoting the degradation of the intermediates \(^{219}\). Herrera-Melian et al showed that P25 efficiently removes 200 ppm of 4NP, however the treated effluent must be further treated for toxicity, by constructed wetlands to achieve complete elimination and detoxification of 4NP \(^{220}\). The selectivity of MIP-coated TiO\(_2\) is primarily affected by the difference between functional groups, molecular weights, and shape of the target molecules, 2NP and 4NP, and nontarget pollutants. Nontarget molecules that exhibit similar functional groups to the target molecule show enhanced degradation by the catalyst \(^{219}\).

Perch et al studied the degradation of nitrophenols and nitroamines by TiO\(_2\)-P25 \(^{210}\). The TiO\(_2\) catalysts degraded 98.1\% and 94.6\% of Dinoterb (2-tert-butyl-4,6-dinitrophenol) and Dinoseb (2-sec-butyl-4,6-dinitrophenol) herbicides after 8 hours irradiation period. On the other hand, the explosives, ROX and HMX, were resistant to TiO\(_2\) photocatalytic treatment. The weak reactivity of the explosives with the catalyst could be due to their high chemical stability or to their incapacity to approach the catalyst surface under pH of 7.2 \(^{210}\).
Concluding Remarks.

In this review we have discussed several state of the art TiO₂ catalytic systems for decontaminating various pesticides and organic pollutants. Such systems have the potential to make a major impact on human health and safety through domestic and industrial use. Current literature has indicated the anatase crystal structure as the most stable configuration suitable for photodegradation studies. However, anatase TiO₂ still exhibits a high rate of electron-hole recombination that prevents further improvements in photocatalytic degradation efficiency. Many strategies to reduce the recombination rate of TiO₂ have been attempted including the addition of photosensitizers, nonmetal doping, morphology modification, and metal doping. Some highlighted results of these studies are summarized below.

The aid of various photosensitizers promoted solar photocatalysis for the degradation of carbaryl rinsate to CO₂. TiO₂-Carbon modified materials provided a larger active surface area for the degradation of carbofuran. Boron doped TiO₂ catalyst was more effective towards diuron pesticide in terms of degradation and mineralization rates in contrast to the undoped TiO₂ where, the B-doped catalyst is stable and gave reproducible results of mineralization rates up to 75% upon several runs. Porous TiO₂ modified ceramic shows an excellent photodegradation performance toward atrazine, thiobencarb, dimethoate, lindane, methyl parathion, dipterex, malathion, quinalphos, diazinone, dichlorovos and bentazone with good reproducibility. Au–Pd co-modified TiO₂ nanotube film (Au–Pd–TiO₂) showed photocatalytic activity towards malathion, where its elimination rate increased by 172% when the photocatalyst of the naked TiO₂ nanotube film was replaced by Au–Pd–TiO₂. Ag nanoparticles doped TiO₂ nanofibers performed a significant role in photocatalytic performance during the parathion and PCP degradation reactions. The photocatalytic activity for 4-chlorophenol using UV irradiation on P-modified TiO₂ was 4.5 times higher than TiO₂ alone. Cs/TiO₂ catalyst
showed 100% degradation and mineralization of bromoxynil in two hours at basic conditions with fully recyclable and reusable catalyst with no loss of activity. Applications of these unique TiO₂ complexes have been investigated exclusively in laboratory settings, yet limited investigations into the relevance of this technology in industry applications have been reported. Future work should build on the optimization of these systems and focus on the applications in pilot scale reactors to attract the interest of industrial partners to deliver the benefits of this technology to society.

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CHAPTER 3

THE ROLE OF COPPER (II) IONS IN COPPER-BIOCL FOR USE IN THE
PHOTOCATALYTIC DEGRADATION OF ATRAZINE

Chapter Abstract.
Photocatalysis has increasingly been used as a response to pollution by organic compounds. One pressing issue faced by photocatalytic systems is lack of activity with persistent pollutants. A strategy that has been employed by researchers in the field is to add transition metal dopants to known photocatalysts to increase their catalytic activity. Here, based on recent reports, we synthesize Cu-BiOCl to target degradation of atrazine, which represents the model organic pollutant. The prepared photocatalyst is characterized via XRD, SEM-EDAX, UV-Vis DRS, and photoluminescence measurements. Photocatalytic activity studies have been conducted to assess the potential of Cu-BiOCl to degrade atrazine in the absence of sacrificial donors such as hydrogen peroxide. The results from this investigation indicate successful synthesis of copper-modified photocatalysts which exhibit a decrease in atrazine removal when compared to pure BiOCl. Active species trapping experiments were used to propose a mechanism that suggests the copper-modified systems produce electron vacancies more efficiently than pure BiOCl systems yet are most effective in the presence of sacrificial agents.

Introduction.
Organic pollutants are the most common form of environmental contaminants detected within the United States \(^1\). These types of compounds include herbicides and pharmaceuticals, which increases the likelihood of human exposure as commercial consumption increases annually \(^{1-2}\). These compounds exist in mediums such as aqueous and gaseous solutions which are introduced into the environment through practices in the agricultural and commercial
landscaping industries. Atrazine is a model environmentally persistent compound that is known to resist natural degradation \(^3\-^4\). Reports on accumulation of atrazine in soil indicates increases in the bacterial populations in areas that have continuous applications \(^3\). The molecular structure of atrazine and other molecules allows increased resistance to current drinking water treatments, enabling possible accumulation in biological systems. This exposure propagates several negative health effects including cancer, birth defects, and endocrine system disruption\(^5\).

Traditional ultraviolet irradiation has shown promise in rapid removal but is limited in the overall mineralization of pollutants. Photocatalysts have become a new alternative for drinking water treatment due to their unique reactivity with ultraviolet radiation, producing increased degradation and overall detoxification \(^6\-^7\). Photocatalysts provide an alternative in drinking water treatment due to their ability to degrade hazardous pollutants in a variety of mediums, including water\(^8\). These compounds are semiconductors composed of inorganic compounds that accelerate chemical reactions using ultraviolet radiation present in the atmosphere.

Degradation of harmful pollutants into nontoxic byproducts is a result of this process and can be used in the removal of herbicides, such as atrazine, from drinking water \(^8\,^9\). Traditional treatment methods focus on the addition of chemical species such as chlorine for contaminant removal, yet this technique has the potential for increased toxicity due to compound transformations\(^10\). As these photocatalysts adsorb pollutants such as atrazine, photochemical oxidation-reduction reactions create reactive chemical species that cleave the molecule into smaller compounds. A previous study conducted by the Patterson research group indicated superior degradation of pharmaceuticals using bismuth photocatalysts versus titanium dioxide \(^7\). The results of Ahern et al. indicated bismuth oxyhalide has a smaller surface area compared to titanium dioxide, yet it exhibited increased degradation rates \(^7\-^11\).
Enhancement of photocatalytic compounds can be achieved through targeting the addition of metallic ions into the chemical arrangement of a known photocatalyst to act as an electron trap to prevent recombination of excited-state electrons and electron holes\textsuperscript{12-13}. Previous studies using metal-doped compounds have reported increased photodegradation behavior from this addition. Reports on the enhancement by addition of copper, specifically Cu(II), have indicated the most successful degradation rates when comparing the addition to other ions, such as iron\textsuperscript{14}. The addition of metallic impurities facilitates the transfer of excited state electrons from the conduction band of the photocatalyst\textsuperscript{15}. The transfer of electrons from the conduction band of bismuth oxyhalide to the copper ions facilitates extended lifetimes of these excited state electrons\textsuperscript{16}. Previous studies using transition elements such as nickel, copper, and gold have indicated these compounds are sufficient additives to facilitate increased degradation of pollutants\textsuperscript{17}.

In this study, we present the application of Cu-BiOCl to photocatalytic degradation of atrazine. We demonstrate the reproducibility of the earlier reported Cu-BiOCl ionic liquid synthetic method through characterization via XRD, DRS, SEM-EDS, and photoluminescence\textsuperscript{18}. The properties of the copper-modified material are characterized by DRS, FTIR, and photoluminescence measurements. The photocatalytic activity for Cu-BiOCl is measured in the absence of hydrogen peroxide and uses atrazine as a target model organic pollutant. Active species trapping experiments are used to assist in proposing a mechanism of Cu-BiOCl photocatalytic activity.
Experimental.

Synthesis of 5:1 Cu(II):BiOCl photocatalysts was first achieved by Jun Di et al. The synthesis presented in this study was achieved by mixing a 1 mmol (0.485g) solution of Bi(NO$_3$)$_3$ -5 H$_2$O in a 20ml solution of ethylene glycol. The source of copper ions was an ionic fluid consisting of 1 mmol 1-methyl-3-octylimidazolium (omim) chloride mixed with copper(II) chloride to yield ([Omim]CuCl$_3$), and a 1 mmol solution was added to the ethylene glycol solution and stirred for 30 minutes. The resulting solution was then transferred to a Teflon-lined autoclave system where it was left to bake overnight at 140°C. The remaining mixture separated into two distinct layers, with the solid product found in the aqueous teal layer. Upon separation the particles were washed twice with a 1:1 ethanol to water solution. The remaining sample was transferred to a watchglass and left to dry overnight at 50°C and collected for further characterization. Pure BiOCl (99.8%; Alfa Aesar) was used as a reference photocatalyst for both characterization and photodegradation experiments.

To characterize the surface morphology and elemental composition of the catalysts, Scanning Electron Microscopy with Elemental X-Ray Dispersive Spectroscopy (SEM-EDS) was used. SEM-EDS scans were performed using a Zeiss SII Nvision 40 SEM with Ametek EDAX Genesis EDS mounted on it. The SEM image was done at a working distance of 4.2 mm and an EHT value of 2.00 kV. The EDS was run at 10.0 kV. The results of the EDS analysis were used to determine the elemental composition of the catalyst crystal structures for Cu(II) bismuth species. X-ray diffraction (XRD) scans on the catalysts were used to verify the compositional purity and crystallinity of the compounds. XRD patterns were obtained using a PANalytical X’Pert Pro diffractometer operated with CuK$_\alpha$ radiation (45 keV and 40 mA). The samples were prepared for XRD analysis by depositing a MeOH/catalyst slurry onto a pre-cleaned glass slide
and allowing the methanol to evaporate under reduced pressure. Diffuse Reflectance Spectroscopy (DRS) experiments were used to determine the optical band gap energy of both pure BiOCl and BiOCl with copper impurities present. The light source was a Mikropack DH-2000 deuterium and halogen light source coupled with an Ocean Optics USB4000 detector. A fiber optic cable was used to gather collected light. Spectra was referenced with PTFE and potassium chloride. Data was processed using SpectraSuite software model 1.4.2_09.

Steady-state luminescence scans were run on the BiOCl and Cu-BiOCl at 78 K. Spectra were collected with a Model Quantamaster-1046 photoluminescence spectrometer from Photon Technology International. The device utilizes a 75W xenon arc lamp coupled with two excitation monochromators and one emission monochromator to adjust the bandwidth of light hitting the sample and detector, respectively. Light intensity was measured using a photomultiplier tube. The samples were mounted on a copper plate using a non-emitting copper-dust-high vacuum grease. Low-temperature scans were run on the same system coupled with a Janis ST-100 optical cryostat and used liquid nitrogen as a cooling agent.

100 parts per million (ppm) atrazine samples were prepared by dissolving 10 mg of atrazine in 10mL methanol and bringing the solution up to 100mL with deionized water. For photocatalytic activity trials, a 10-ppm solution of atrazine was prepared by adding 10mL of stock solution to 100mL of deionized water. Irradiation trials took place in a 250mL round bottom flask with 25mg of catalyst added in each trial. Catalysts were loaded into a solution held in a 250mL round bottom flask and stirred for 15 minutes to achieve adsorption-desorption equilibrium. The source of UV irradiation was a Steripen Mercury UV lamp with emission wavelength of 254 nm. The solution was sampled at five-minute intervals for a period of 30
minutes to obtain degradative information on the reaction. Each photocatalytic trial was repeated at least three different times with the averages of each trial compiling each figure.

Radical scavenging experiments were performed in a similar setup as detailed earlier (Section 2.3), except with an added component acting as a radical scavenger. The radical scavenging compounds used in these trials included potassium iodide, (KI), for electron holes, isopropyl alcohol, (IPA), for \('\text{OH}, and benzoquinone, (BQ), for O_{2}^{\cdot-}. Throughout these irradiations, the atrazine concentration was determined by referencing the characteristic 260 nm absorption peak of atrazine to an external calibration curve. Each result was statistically averaged over a period of three separate runs to limit any spectroscopic interferences. Trials measuring adsorption were run in a similar fashion yet in the absence of ultraviolet irradiation. The samples were collected and filtered through a 33-mm chromatography syringe filter (pore size = 0.25 \(\mu m\) to remove catalysts prior to analysis. UV-Vis spectra were collected using a Vernier UV-vis spectrophotometer with the corresponding Logger-Lite spectroscopy software.

Fourier Transform-Infrared Spectroscopy (FT-IR) was used to characterize the structure of the synthesized photocatalysts before and after irradiation. Spectra were collected on solid samples at 298 K using a Perkin Elmer FT-IR Spectrum Two equipped with a Universal Attenuated Total Reflectance (UATR) accessory. The UATR consists of a diamond crystal with a 2-micron pathlength. The detector is a LiTaO\(_3\) MIR detector with a range of 8,300 cm\(^{-1}\) to 350 cm\(^{-1}\). Spectra were collected using resolution of 2 cm\(^{-1}\).
Results and Discussion.

X-Ray Diffraction scans were acquired for both pure BiOCl and Cu-BiOCl samples to characterize the structure and purity of the photocatalysts. The diffraction patterns for BiOCl and Cu-BiOCl are displayed in Figure 3.1. The diffraction pattern observed for BiOCl was found to match that of tetragonal (P4/nmm) BiOCl (JCPDS 1-073-2060). The pattern obtained for Cu-BiOCl matches that reported by Di et al. (JCPDS 06-0249).

![X-ray diffraction patterns for BiOCl and Cu-BiOCl](image)

**Figure 3.1.** X-ray diffraction patterns obtained for BiOCl and Cu-BiOCl.

Consistent with their report, we do not note any characteristic patterns of copper species. Di et al. suggest that this result could be due to the chemical deposition of copper ions onto the surface of BiOCl. The diffraction pattern obtained for Cu-BiOCl is qualitatively less resolved than that obtained by Di et al., this may indicate that the size of our synthesized Cu-BiOCl microspheres are smaller. Both photocatalyst samples were determined to be of high purity based on the absence of contaminant peaks in either diffraction pattern.
Scanning electron microscopy coupled with X-Ray dispersive spectroscopy (SEM-EDS) was utilized to investigate the structural morphology and elemental composition of Cu-BiOCl. The commercial BiOCl samples imaged confirm the morphology of BiOCl as stacked 2D nanosheets (Figure 3.2). The nanosheets range from 2 to 10-μm in diameter and are ~100-nm thick. SEM images obtained (Figure 3.2) indicate that the Cu-BiOCl samples synthesized in this report are spherical formations of aggregated nanoplates, corresponding with the catalysts synthesized by Jun Di et al. From the SEM images, we determine that the diameter of the synthesized Cu-BiOCl spheres is ~0.3 μm. This diameter is smaller than that observed in previous reports 18.

**Figure 3.2.** SEM images of BiOCl at 5kX magnification (Left), and Cu-BiOCl at 25kX magnification (Right).

Figure 3.3 shows the same region of Cu-BiOCl visualized as in Figure 3.2; however, this image was generated using a backscatter detector instead of the secondary electron detector. This image appears uniformly bright, indicating that the surface of the synthesized Cu-BiOCl does not vary significantly in composition. Analysis of this result suggests the Cu(II) ions deposited on
BiOCl during the synthesis process are not localized in any one area but are instead evenly distributed on the surface.

**Figure 3.3.** SEM image of Cu-BiOCl at 25kX magnification with Backscatter Detector.

Figure 3.4 shows the EDS results obtained for the synthesized Cu-BiOCl. Characteristic electron dispersion peaks associated with Cu, Bi, O, and Cl are all identified and labeled in Figure 3.4. The weight percent of each element estimated based on dispersion efficiencies is 13.1% oxygen, 14.3% bismuth, 11.1% chlorine, and 56.9% copper. These estimations are roughly consistent with the 1:1:1 (bismuth:oxygen:chlorine) ratio expected, and correspond to a 5x loading of copper. The remaining weight percent is accounted for by the large bromine peak visible in the EDS spectrum. We attribute this bromine present to be an impurity potentially acquired during the synthesis process.
Figure 3.4. EDAX Spectrum acquired for the synthesized Cu-BiOCl Samples.

![EDAX Spectrum](image)

Figure 3.5. UV-Vis spectra acquired for BiOCl (Solid) and Cu-BiOCl (Dotted).

The determination of optical band gap energy was achieved using UV-Vis Diffuse Reflectance Spectroscopy (DRS). Determination of absorbance is achieved through the SpectraSuite analysis software using the equation $f(R) = \frac{(1-R)^2}{2R}$ where $R$ is equal to reflectance. Figure 3.5 shows the absorption spectra acquired for both BiOCl and Cu-BiOCl from 300-800 nm. Both spectra show a distinct absorption edge at 360 nm, while the Cu-BiOCl spectra also shows a less prominent
adsorption edge at 550 nm, consistent with previous reports. The Kubelka-Munk method was used to determine the optical band gap value for both photocatalysts based on the absorption spectra. BiOCl is determined to have an optical band gap of 3.2 eV, while Cu-BiOCl was found to have an optical band gap of 3.0 eV.

**Figure 3.6.** Photoluminescence emission spectrum of Cu-BiOCl measured at 78 K. The excitation wavelength used to acquire the spectrum was 265 nm.

Photoluminescence spectroscopy was used to further characterize the synthesized Cu-BiOCl. The luminescence spectra are shown in Figure 3.6. At 78 K we observe characteristic Cu(I) d^{10} photoluminescence. We attribute this to electron transfer from the conduction band of BiOCl to the deposited Cu(II) species. This results in the reduction of Cu(II) to Cu(I) which allows for the observed photoluminescence. Cu(I) is a d^{10} photoluminescent species, which our group has previously investigated and reported on^{19}. The photoluminescence spectra exhibit vibrational fine structure. We attribute the presence of this stretch to interaction with the Bi-O Raman mode, further indicating the close interaction of Cu(II) and BiOCl.
Trials measuring catalyst adsorptivity and degradative abilities were conducted to determine the percentage of atrazine remaining in the presence of pure and copper-modified BiOCl. The results of these trials (Figure 3.7) indicate that neither BiOCl nor Cu-BiOCl show significant adsorption of atrazine onto the surface of the catalysts. This result confirms that photocatalytic removal of atrazine from aqueous solutions is not due solely to adsorption and suggests reactive chemical species play a significant role in the degradation of atrazine.

Figure 3.7. Atrazine removal rates for photocatalytic degradation conditions monitored by UV-Vis spectroscopy.
Decreased removal of atrazine was observed in photocatalytic degradation trials in the presence of Cu-BiOCl (Figure 3.7). Initial photocatalytic studies indicate no observable degradation in the presence of visible light (λ > 400 nm). Photodegradation trials indicated that 35% of atrazine was removed during pure BiOCl photocatalysis, whereas 29% of atrazine was removed during Cu-BiOCl photocatalysis. The rate, however, of photolysis and BiOCl photodegradation is qualitatively similar when compared to the degradative rate exhibited by Cu-BiOCl. These results suggest that the addition of Cu(II) ions to this system are not beneficial for the photocatalytic degradation of organics without the aid of a sacrificial donor. The use of a sacrificial agent such as hydrogen peroxide assists in photocatalytic degradation by facilitating the splitting of peroxide species in the presence of an excitation source, such as UV light. The presence of this excited state Cu(I) species permits the transmission of electrons which cleave the oxygen bonds within peroxide and generates additional hydroxyl radicals. To better investigate radical and electron transition activity, photocatalytic trials in the presence of radical scavenging compounds were used.

Radical scavenging experiments were performed to determine the active species generated by both pure and modified BiOCl that are responsible for atrazine degradation. These investigations are used to assist in constructing a proposed mechanism that details the flow of photo-generated electrons in BiOCl in the presence of Cu(II). The results for pure BiOCl and copper modified BiOCl scavenging experiments are shown in figures 3.8 and 3.9, respectively. For BiOCl, the addition of potassium iodide (KI) resulted in no observable degradation of atrazine. When isopropanol (IPA) is added as a radical scavenger, a moderate amount of degradation is observed, with a percentage of atrazine removed to be around 23%. Addition of benzoquinone (BQ) resulted in no reduction in removal activity, indicating superoxide radicals
may not be a dominant reactive species in aqueous photocatalytic degradation. The results displayed in figure 3.8 indicate that electron holes and hydroxyl radicals play a substantial role in atrazine degradation using BiOCl, while superoxide radicals have little involvement initiating degradation. The electron vacancies formed due to ultraviolet irradiation help proliferate the oxidation of atrazine, thereby facilitating increased degradation.

![Figure 3.8](image.png)

**Figure 3.8.** Atrazine removal rates via BiOCl with KI, Isopropanol, and Benzoquinone.

The addition of Cu(II) allows for sustained photo-induced separations that generate these electron vacancies as well as the excited state radical species. A similar degradation trend is observed using Cu-BiOCl, with KI completely shutting down atrazine removal while normal degradation was still observed after the addition of either IPA or BQ, as shown in figure 3.9. The percentage of atrazine removed remained more pronounced for Cu-BiOCl in the presence of IPA than for BiOCl, indicating a lack of hydroxyl radical activity in the copper-modified systems. These results suggest that hydroxyl radicals play a more integral role in atrazine degradation for BiOCl than for Cu-BiOCl in aqueous solutions.
The results from photocatalytic and radical scavenging trials indicated both electron vacancies and superoxide radicals play a substantial role in the degradation process of copper-modified BiOCl. The results displayed in Figure 3.8 suggest superoxide radicals are not a primary active species during photodegradation, which is consistent with results using pure BiOCl. Dependence on the superoxide radical during degradation is more prominent in the copper-modified systems based on Figure 3.9, which indicates a reduction in atrazine removal during radical scavenging trials. These results suggest increased radical formation through reduction of Cu(II) is achieved through the contribution of additional electrons to the conduction band of BiOCl. The proposed electron transition mechanism for Cu-BiOCl is shown below.

Irradiation of the BiOCl catalyst by light of sufficient energy (represented by $h\nu$) excites an electron from the valence band to the conduction band of BiOCl (Equation 1), generating both an excited electron ($e^-$) and an electron hole ($h^+$). As shown in part (2) and (3) of the proposed mechanism, irradiation of Cu-BiOCl creates photo-induced separations that reduces the surface-
deposited Cu(II) species to Cu(I) via transfer of electrons originating from the conduction band of BiOCl (Equation 2). As Cu(I) oxidizes to regain charge balance, remaining electrons participate in oxidation-reduction reactions that facilitate increased radical species formation.

\[
\text{BiOCl} + h\nu \rightarrow e^- + h^+ \quad (1)
\]

\[
\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \quad (2)
\]

\[
\text{Cu}^+ + \text{O}_2 \rightarrow \text{Cu}^{2+} + \text{O}_2^- \quad (3)
\]

This electronic transition is facilitated through interactions between the Cu(II) ion and the crystal structure of the BiOCl system, which is thought to exist in a terminal Cu(OH)₂ complex as proposed in studies using bismuth oxide complexes by Sudrajat and coworkers. This configuration and catalytic stability is further suggested by the lack of degradation using hydroxyl radicals, which is also indicated in Figure 3.9. The interactions between the copper complex and the bismuth center of the catalyst allow for increased transition of electrons that allow for the increased formation of reactive chemical species, which equate to increased degradation of atrazine.

\[
\text{O}_2^- + \text{ATZ} \rightarrow \text{Degradation Products} \quad (4)
\]

\[
\text{ATZ} + h^+ \rightarrow \text{ATZ}^+ \quad (5)
\]

\[
\text{ATZ}^+ \rightarrow \text{Degradation Products} \quad (6)
\]

This radical species generation pathway may be de-emphasized in the copper-modified system, since the radical scavenging experiments showed that superoxide does not play a large role in photocatalytic degradation of atrazine. In the presence of a sacrificial donor, such as hydrogen peroxide, the excited-state electrons captured by the reduction of Cu(II) would permit
the dissociation of hydrogen peroxide into radical and anionic species. However, any superoxide radicals generated during the irradiation process will react with atrazine to form degradation products (Equation 4). The direct interaction of electron holes with the pollutant was found to be the major pathway associated with photocatalytic degradation of atrazine. We propose that this reaction may take place through an electron transfer from atrazine to the electron hole in the valence band of BiOCl to generate ATZ\(^+\) (Equation 5). ATZ\(^+\) is an electron deficient and unstable species and will then react to form degradation products (Equation 6).

The stability of the modified bismuth oxyhalide photocatalysts were investigated using Fourier-Transformed infrared spectra. Initial scans of Cu-BiOCl indicated bismuth-oxygen stretch in the fingerprint region (0-500 cm\(^{-1}\)) which is indicated in figure 3.10.

![FT-IR of Cu-BiOCl before and after 1hr of UV Irradiation Exposure.](image)

**Figure 3.10.** FT-IR of Cu-BiOCl before and after 1hr of UV Irradiation Exposure.

This stretch was determined to be the Bi-O chemical signature based on previous literature and was recorded at a wavelength of 521 cm\(^{-1}\). Di et al. indicated the presence of a Bi-O stretch at 528 cm\(^{-1}\) for pure and the copper-modified BiOCl. Upon one hour of irradiation. No shifts in the 521 cm\(^{-1}\) peaks were observed, suggesting the Bi-O stretch remained intact upon
exposure to UV irradiation. The results displayed in figure 3.10 suggest the synthesized catalyst resists photo-corrosion and other detrimental processes which can disrupt catalytic capabilities.

**Conclusion.**

Characterization results indicated successful synthesis of copper-modified BiOCl in agreement with results reported by Di. et al. The results of the photocatalytic investigations suggest a decrease in pollutant removal in the copper modified photocatalysts compared to the pure BiOCl counterparts.

![Graphical representation of photocatalytic mechanism of Cu-BiOCl.](image)

**Figure 3.11.** Graphical representation of photocatalytic mechanism of Cu-BiOCl.

This change in photocatalytic activity is thought to arise from electronic transitions between the BiOCl framework and copper (II) ions present, which facilitate increased electron transitions and radical formation. The reduction of surface deposited Cu(II) to Cu(I) promote increased electron flow from the conduction band of the BiOCl catalyst, thereby increasing photo-induced charge separations which assist in the degradation of atrazine. Enhancement of photocatalytic complexes using metallic ions such as copper have been suggested as a possible method to decrease recombination of excited state electrons and allow for increased degradation of pollutants. The electronic transition pathway purposed in this study suggest this method of modification proliferates the hole carrier capabilities in photocatalytic complexes.
Chapter Note.

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CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF (RPh₃P)₃[Bi₃I₁₂] (R = Me, Ph)

IODOBISMUTHATE COMPLEXES FOR PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS

Chapter Abstract.

Phosphonium iodobismuthates(III) (MePh₃P)₃[Bi₃I₁₂] (1) and (Ph₄P)₃[Bi₃I₁₂] (2) were prepared. X-ray crystal structures were determined for both complexes. Photophysical behavior of both complexes was determined via diffuse reflectance spectroscopy and photoluminescence measurements. Photoluminescence results for complex 2 revealed room temperature emission, which has been rarely reported by bismuth compounds. Low temperature luminescence scans further indicated a dramatic change in emission properties between the MePh₃P⁺ and Ph₄P⁺ complexes. Photodegradation studies using both ultraviolet and visible light were carried out to determine the light-absorbing capabilities of both complexes. Visible light-promoted degradation studies in the presence of catalytic amounts of 1 and 2 showed significant degradation of aqueous methylene blue (MB) and carbaryl solutions over a period of one hour. The reported photoirradiation studies indicated the phosphonium iodobismuthate salts promote visible light-harvesting and facilitate catalytic dye photosensitization. This sensitization allows for the degradation of organic pollutants in the presence of visible light and suggests coupling with fluorescence dyes is viable in photovoltaic applications.
Introduction.

The chemistry of halogenobismuthate(III) and other p-block halogenate complexes has been recently found to offer desirable properties, such as photophysical and semiconductor activity \(^1\text{-}^3\). Solar materials based on haloplumbate(II) salts are promising materials for photovoltaic applications due to their broad absorption in the visible light region, as well as their high conversion efficiencies with low manufacturing costs \(^3\text{-}^8\). These plumbate complexes have been investigated for potential use as photocatalysts, but any industrial applications would necessarily be limited due to environmental concerns.

Concerns over stability and toxicity of haloplumbate complexes have motivated research efforts to identify suitable alternatives for solid-state solar materials that are capable of continuous photochemical degradation \(^9\text{-}^{14}\). Recent studies, including those by our group, have focused primarily on photophysical and theoretical aspects of tetrabutylammonium iodobismuthates \(^2\).

Reports of amorphous and crystalline phosphorus complexes suggest that the nature of the crystal lattice formation plays a significant role in phosphorus-based photoactivity and influences p-type semiconductor behavior \(^15\text{-}^{18},^{19}\). Phosphonium-based iodobismuthate(III) complexes have been recently investigated as possible alternatives to lead-based materials such as methylammonium iodoplumbates \((\text{CH}_3\text{NH}_3)[\text{PbI}_3]\) and other haloplumbate analogs due to similarities in bandgap, charge transmission mechanisms, and redox activity \(^16\text{-}^{20}\).

In addition to possible photovoltaic applications, iodobismuthate complexes have been considered for photocatalytic applications \(^14\text{-}^{20},^{22}\). Various studies have reported on the visible light activity of BiOI and other iodide-containing catalysts for removal of methylene blue \(^18\text{-}^{19},^{23}\text{-}^{25}\). Advances in catalytic materials containing phosphonium species were reported by Golandaj et al. with discussion of their extensive use in organic synthesis processes \(^22\). The photophysical
interactions of halogenobismuthate(III) anions with alkyl phosphonium cations have been utilized extensively in these processes. These reported studies have led to the development of catalytic complexes coordinated with triphenyl phosphine (PPh₃) species. Here we report the pairing of methyltriphenylphosphonium (MePh₃P⁺) and tetraphenylphosphonium (Ph₄P⁺) cations with iodobismuthate anions to tune their photophysical properties. Iodobismuthate complexes are known with a diverse range of cations and show varying degrees of anion catenation through variations in halide bridging behavior. These factors render prediction of the particular anionic Bi(III) halide species challenging. Cation variation in halogenobismuthates is currently an area of interest, especially the use of pyridinium and viologen-like ions.

In this work we report two novel phosphonium iodobismuthate complexes, (MePh₃P)₃[Bi₃I₁₂] (1) and (Ph₄P)₃[Bi₃I₁₂] (2), which display unique photophysical properties, with the latter being one of few bismuth compounds that show luminescence emission at room temperature. Photoactivity in the presence of visible light is a necessity for industrial applications and is the central focus of recent research and development. These salts are shown to be photocatalytically active and thus to offer a simple environmentally benign alternative to traditional photocatalytic systems.

In order to further demonstrate the catalytic capabilities of compounds 1 and 2, aqueous photochemical degradation studies of organic pollutants such as carbaryl and methylene blue (MB) are reported. Carbaryl (1-naphthyl N-methylcarbamate) is a widely used pesticide throughout the world for cotton, fruit, vegetables, nuts, and other crops and is inherently toxic to humans by skin contact, inhalation, and ingestion. Methylene blue (MB) is employed as a dye model for the investigation of degradation pathways of dyes that are present in colored aqueous effluents from
textile industries due to its strong adsorption to metal surfaces, well-defined optical absorption in the visible spectrum, and good resistance to light degradation\textsuperscript{43}.

**Experimental.**

Methyltriphenylphosphonium iodide (MePh\textsubscript{3}PI) was purchased from TCI Chemical, and all other reagents from Aldrich, and all were used as received. Tetraphenylphosphonium iodide (Ph\textsubscript{4}PI) was prepared according to the literature\textsuperscript{39}. Infrared spectra were collected on solid samples at 298 K using a Perkin Elmer FT-IR Spectrum Two equipped with a Universal Attenuated Total Reflectance (UATR) accessory. The UATR consists of a diamond crystal with a 2-micron pathlength. The detector is a LiTaO\textsubscript{3} MIR detector with a range of 8,300 cm\textsuperscript{-1} to 350 cm\textsuperscript{-1}. Spectra collected at a 2 cm\textsuperscript{-1} resolution. Diffuse reflectance spectra were collected on solid samples at 298 K. The light source was a Mikropack DH-2000 deuterium and halogen light source coupled with an Ocean Optics USB4000 detector. Scattered light was collected with a fiber optic cable. Spectra were referenced with MgSO\textsubscript{4}. Data was processed using SpectraSuite 1.4.2_09.

BiI\textsubscript{3} (295 mg, 0.500 mmol) and MePh\textsubscript{3}PI (201 mg, 0.497 mmol) were added to a 100 mL round bottom flask and purged with Ar. Dry acetone (40 mL) was added to the flask and the resulting red solution was stirred for 18 h at room temperature. The solution was concentrated under vacuum to \textsim\textasciitilde20\% of its original volume. The solution was then precipitated with addition of excess anhydrous ethyl ether. The oily solid was triturated with additional ether with vigorous stirring. The resulting orange solid was then vacuum filtered, washed with ether, and dried on a vacuum line overnight, 0.406 g, 0.136 mmol, 82.1%.

BiI\textsubscript{3} (294 mg, 0.499 mmol) and Ph\textsubscript{4}PI (236 mg, 0.506 mmol) were combined in a 100 mL round bottom flask and flushed with Ar. Acetonitrile (40 mL) was added to the flask and the resulting red solution was stirred for 18 h at room temperature. The solution was filtered and
concentrated under vacuum ~20% of its original volume. The oily solid was triturated with additional ether with vigorous stirring. The resulting orange solid was then vacuum filtered, washed with ether, and dried on a vacuum line overnight, 0.422 g, 0.133 mmol, 80.0%.

All measurements were made using fine focus sealed tube Mo Kα radiation on a Bruker-AXS three-circle Apex DUO diffractometer, equipped with a SMART Apex II CCD detector. Initial space group determination was based on a matrix consisting of 36 frames. The data were reduced using SAINT+4-5, and empirical absorption correction applied using SADABS6. A crystal of 1 and 2 were mounted on a glass fiber, and full data sets were collected at 100 K. The structures were solved using intrinsic phasing. Least-squares refinement for all structures was carried out on F². The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in theoretical positions. Structure solutions were carried out using SHELXTL43 and refinements were performed using the ShelXle program44.

Steady-state luminescence scans were collected between 298 K and 78 K. Spectra were recorded using a Model Quantamaster-1046 photoluminescence spectrophotometer from Photon Technology International using a 75 W xenon arc lamp combined with two excitation monochromators and one emission monochromator. A photomultiplier tube at 800 V was used as the emission detector. The solid samples were mounted on a copper plate using non-emitting copper-dust high vacuum grease. All scans were collected under vacuum with a Janis ST-100 optical cryostat. Low temperature scans used liquid nitrogen for scans down to 78 K.

An aqueous 100 ppm rhodamine B stock solution was prepared by dissolving 10 mg of rhodamine B and filling to 100 mL with deionized water. For photocatalytic activity trials, a 10-ppm solution of rhodamine B was prepared by adding 10 mL of stock solution to 100 mL of deionized water. Irradiation trials took place in a 250 mL round bottom flask with 25 mg of catalyst
added in each trial. The source of UV irradiation was a Steripen Mercury UV lamp with emission wavelength of 254 nm. The solution was sampled at five-minute intervals for a period of 30 minutes to obtain degradative information on the reaction. To perform these experiments 8.21 mmol of (MePh3P)3[Bi3I12] were added to a 5-ppm solution of rhodamine B and allowed to stir in the dark for 15 mins, ensuring adsorption equilibrium. After 15 mins the solution was irradiated with a UV light source over 30 mins with aliquots samples taken every 5 mins. Visible light experiments using the (MePh3P)3[Bi3I12] catalysts were performed using a 75W LED lamp. To measure catalytic activity for an hour duration, a similar experimental setup to the 30-minute degradation was used, and aliquots were taken at 10-minute intervals. Each photocatalytic trial was repeated at least three different times with the averages of each trial compiling each figure.

Results and Discussion.

Both phosphonium iodobismuthate(III) salts were prepared by direct combination of BiI3 and the relevant phosphonium iodide RPh3PI (R = Me, Ph). Synthesis of the iodobismuthate complexes produced two orange solids, each being comprised of discrete Bi3I123– trimers that are charge-balanced by three phosphonium cations. These are the first reported examples of phosphonium cations paired with the anionic iodobismuthate(III) ions, although a wide variety of iodobismuthate(III) oligomers and polymers have been reported in the literature4-9.

Figure 4.1. Thermal ellipsoid drawings of 1•Me2CO•Et2O and 2•Me2CO (50% ellipsoids). Hydrogen atoms are omitted.
The methyltriphenylphosphonium and tetraphenylphosphonium iodobismuthate complexes, \((\text{MePh}_3\text{P})_3\text{[Bi}_3\text{I}_{12}]\) (1) and \((\text{Ph}_4\text{P})_3\text{[Bi}_3\text{I}_{12}]\) (2) were crystallized from acetone/ethyl ether. The X-ray crystal structures of both 1 and 2 were determined at 100 K. The crystal refinement data for both complexes are presented in Table 1 and selected atomic distances are presented in Table 2. The MePh$_3$P$^+$ structure contained a molecule of acetone and a molecule of ethyl ether, 1•Me$_2$CO•Et$_2$O, while the Ph$_4$P$^+$ structure contained a molecule of acetone only, 2•Me$_2$CO. Thermal ellipsoid pictures of both structures are shown in Figure 1, and an overlay of the [Bi$_3$I$_{12}$]$^{3-}$ anions is presented in Figure 2.

Figure 4.2. Atomic overlay of [Bi$_3$I$_{12}$]$^{3-}$ anionic chains in compounds 1 (red) and 2 (blue).

Anionic iodobismuthate(III) trimers in complexes 1 and 2 both showed local approximate octahedral symmetry at each Bi center. The essentially identical [Bi$_3$I$_{12}$]$^{3-}$ clusters seen in complexes 1 and 2 are both composed three Bi atoms bridged by two trios of $\mu_2$-I atoms with two trios of terminal iodides, similar to trimers reported by Adonin et al.$^{14-16}$ Thus, the [Bi$_3$I$_{12}$]$^{3-}$ anions belong to the point group $D_{3d}$. Slight distortion from octahedral geometry at the Bi(III) centers was revealed by comparison of bridging vs. terminal I–Bi–I angles (Table 2), with angles ranging from 78.8 to 88.2° for bridging and 92.7 to 98.3° for terminal. In both structures, the cations constitute nearly perfect tetrahedra. One of the three crystallographically independent MePh$_3$P$^+$ cations in 1 shows positional disorder for one phenyl ring.
Table 4.1. Crystal and Structure Refinement Data.

<table>
<thead>
<tr>
<th></th>
<th>(1), (MePPh₃P)₃[Bi₃I₁₂]</th>
<th>(2), (Ph₄P)₃[Bi₃I₁₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC deposit no.</td>
<td>1938207</td>
<td>1938208</td>
</tr>
<tr>
<td>Color</td>
<td>Orange</td>
<td>Orange</td>
</tr>
<tr>
<td>Size, mm</td>
<td>0.441 × 0.386 × 0.184</td>
<td>0.308 × 0.266 × 0.152</td>
</tr>
<tr>
<td>Formula</td>
<td>C₆₄H₇₀Bi₃I₁₂O₂P₃</td>
<td>C₇₅H₆₆Bi₃I₁₂OP₃</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>3113.85</td>
<td>3225.92</td>
</tr>
<tr>
<td>Space Group</td>
<td>Cc</td>
<td>P–1</td>
</tr>
<tr>
<td>a, Å</td>
<td>22.0374(19)</td>
<td>13.4584(6)</td>
</tr>
<tr>
<td>b, Å</td>
<td>14.6083(13)</td>
<td>17.1466(8)</td>
</tr>
<tr>
<td>c, Å</td>
<td>26.758(2)</td>
<td>19.3741(9)</td>
</tr>
<tr>
<td>α, °</td>
<td>90</td>
<td>82.2000</td>
</tr>
<tr>
<td>β, °</td>
<td>100.571</td>
<td>84.6600</td>
</tr>
<tr>
<td>γ, °</td>
<td>90</td>
<td>77.6320</td>
</tr>
<tr>
<td>Volume, Å³</td>
<td>8467.9(13)</td>
<td>4317.2(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>ρcalc, cm⁻³</td>
<td>2.442</td>
<td>2.482</td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>5600</td>
<td>2908</td>
</tr>
<tr>
<td>μ(Mo Kα), mm⁻¹</td>
<td>10.687</td>
<td>10.485</td>
</tr>
<tr>
<td>Temp., K</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Residuals: a R; R_w</td>
<td>0.0183, 0.0406</td>
<td>0.0181, 0.0396</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>0.935</td>
<td>1.122</td>
</tr>
</tbody>
</table>

The linear axis of the anionic chain runs parallel to the c-axis for both compounds 1 and 2. In compound 1 there is a relatively short contact between I3 and I10 on adjacent anions (I…I = 3.853
Å), running roughly along the b-axis. In contrast to this chain formation-like behavior, the anions in 2 show a dimer-like interaction between pairs of I8···I10 atoms, but also running parallel to the b-axis. The bridging versus terminal Bi–I bond lengths for both 1 and 2 were starkly different, with the former being 3.32 Å and the latter being about 2.92 Å.

**Table 4.2.** Selected Bond Distances (Å) and Angles (°) for 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>1, (MePh₃P)₃[Bi₃I₁₂]</th>
<th>2, (Ph₄P)₃[Bi₃I₁₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi···Bi</td>
<td>4.1347(6), 4.1417(5)</td>
<td>4.0653(2), 4.1484(3)</td>
</tr>
<tr>
<td>Bi—I Bridging</td>
<td>3.0621(6)-3.3820(6)</td>
<td>2.9992(3)-3.3415(3)</td>
</tr>
<tr>
<td>Bi—I Terminal</td>
<td>2.8929(6)-2.9129(7)</td>
<td>2.8767(3)-2.9451(3)</td>
</tr>
<tr>
<td>I–Bi–I a</td>
<td>77.890(15)-97.24(2)</td>
<td>75.823(6)-106.679(7)</td>
</tr>
<tr>
<td>Bi–I–Bi</td>
<td>78.496(15)-80.351(14)</td>
<td>78.352(6)-80.899(7)</td>
</tr>
<tr>
<td>C–P–C</td>
<td>106.0(10)-111.8(4)</td>
<td>106.01(15)-112.31(16)</td>
</tr>
</tbody>
</table>

*Cis* angles (only) given.

Solid samples of 1 and 2 display a rich orange color under ambient light. To investigate the optical properties, we have performed diffuse reflectance UV-Visible measurements of solid samples at 298 K, as shown in Figure 3. Both compounds show strong absorption band in the UV and high energy visible regions, with absorption falling off sharply around 540 nm for both. The spectra of 1 and 2 are nearly identical with reflection edges of 521 nm and 536 nm, respectively, suggesting both compounds are capable of harnessing similar irritation wavelengths. This distinction between these reflection edge values is due to the replacement of an alkyl group in 1 with a conjugated phenyl system in 2 leading to a red shift in the absorbance band.
Figure 4.3. UV-Vis reflection spectrum of solid microcrystalline 1 and 2 at 298 K.

We assign these absorption bands to a mixed metal/halide-ligand charge transfer (XLCT) processes between the I 5p/5s to the $\pi^*$ phosphonium cations based on previous observations in related systems\(^2-12\). The similarities between our observed spectra and the previously reported studies indicate that these metal-halide transitions are responsible for the photophysical activity observed. The luminescence transitions reported for these bismuth compounds differ insofar as they do not involve the unoccupied Bi 6$p$ orbitals, which are commonly involved in bismuth oxyhalide luminescence transitions\(^18,19,23-25,38-42\). Significant changes in light absorption and emission are observed upon substitution of tetrabutylammonium with phosphonium cations. Optical band gaps of approximately 1.97 eV and 2.08 eV were calculated for 1 and 2, respectively, indicating a change in wavelength absorption and corresponding luminescence bands.

Luminescence measurements of 1 and 2 were performed at 298 K and 78 K, as depicted in Figure 4.4. At 298 K complex 1 is non-emissive; but upon cooling to 78 K a weak emission band appears at 448 nm. A corresponding excitation band is also observed in the UV region with a global maximum value at 335 nm. A less pronounced local maximum is observed at 300 nm, which did not produce an individual emission band. A calculated Stokes shift of 7,529 cm\(^{-1}\) was determined for complex 1 based on the observed luminescence spectra presented in Figure 4.4.
Unlike 1, compound 2 is emissive at 298 K with a dominant band at 594 nm and a weaker high energy band at 380 nm upon excitation at 324 nm. Cooling to 78 K results in a dramatic rearrangement of the emission spectra. At low temperature, the high energy band (~380 nm band) becomes dominant while the lower energy band (~ 594 nm) decreases in intensity with both emission modes observed a redshift to 440 nm 612 nm, respectively. A drastic change in stokes shifts was observed whereby the 14,029 cm\(^{-1}\) recorded at room temperature shifted to 8,719 cm\(^{-1}\) at 78 K. No significant changes are observed in the excitation band of 2 between 298 K and 78 K, except a minor blue shift from 320 nm to 310 nm.

![Luminescence Spectra of 1 and 2 at 298 K and 78 K.](image)

**Figure 4.4.** Luminescence Spectra of 1 and 2 at 298 K and 78 K.

Previous studies involving these complexes indicate that the HOMO is composed primarily of the halide ligand 5p/5s orbitals in the halogenobismuthate clusters\(^{26-29,48}\). The LUMO is entirely comprised of an aromatic \(\pi^*\) system on the phenyl system of the \(\text{MePPh}_3^+\) cations. Kelly et al.
utilized TD-DFT calculations to predict the transfer of electrons in iodobismuthate compounds from the I 5p/5s atomic orbitals to the π* systems of the cation species present. Inclusion of a conjugated π-system into the cationic species produces a bathochromic emission shift, producing luminescence at room temperature. This phenomenon may be caused by the additional phenyl group in complex 2, which acts as the auxochrome. These molecular orbital compositions strongly suggest a XLCT pathway in agreement with our DRS assignments. This pathway is a common phenomenon in conjugated motifs, further suggesting these complexes are capable of photophysical transitions that facilitate organic oxidation and reduction\textsuperscript{30,31,48-51}.

Based on the photophysical data observed here and the precedent for bismuth and bismuth oxyhalide catalysis, photodegradation studies were performed to determine the photocatalytic potential of both complexes. To explore this behavior, we photolyzed solutions of carbaryl and methylene blue (MB) in the presence of compounds 1 and 2 using excitation sources including a 302 nm UV lamp and a 75 W LED light source that produced wavelengths above 450 nm. The degradation kinetics for both pollutants was quantified by fitting the experimental data whereby the concentration change depends logarithmically on time: $\ln \left( \frac{C_0}{C} \right) = kt$, in which $k$ is the rate constant and $C_0$, $C$ are the analyte concentrations before and after UV irradiation, respectively.

Figure 4.5 shows the emission spectra at various time intervals for carbaryl irradiated using the LED visible lamp. As shown in Figure 4.5a, the emission intensity shows a slight reduction upon irradiation of carbaryl, with 11% of the irradiated carbaryl photodegraded after 1 hour. In contrast, in the presence of catalyst 1, the emission intensity was greatly reduced upon irradiation, with 67% of the carbaryl degraded after irradiation for one hour, as presented in Figure 4.5b. The evolution of the carbaryl photocatalytic degradation rates as a function of time for all samples under 302 nm and visible light irradiation sources are shown in Figures 4.5c and 4.5d, respectively.
Table 4.3. A summary of the observed rate constants (min$^{-1}$) for all irradiated samples.

<table>
<thead>
<tr>
<th>Studied compounds</th>
<th>UV-302 nm</th>
<th>Visible LED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbaryl</td>
<td>0.0039</td>
<td>0.0036</td>
</tr>
<tr>
<td>Carbaryl-Catalyst 1</td>
<td>0.0073</td>
<td>0.0183</td>
</tr>
<tr>
<td>Carbaryl-Catalyst 2</td>
<td>0.0057</td>
<td>0.0084</td>
</tr>
<tr>
<td>MB</td>
<td>0.0042</td>
<td>0.0029</td>
</tr>
<tr>
<td>MB-Catalyst 1</td>
<td>0.014</td>
<td>0.0158</td>
</tr>
<tr>
<td>MB-Catalyst 2</td>
<td>0.0054</td>
<td>0.0141</td>
</tr>
</tbody>
</table>

A comparison between the rate constants estimated by the fitting analysis indicates that both catalysts produce higher photocatalytic activity than occurs in the uncatalyzed system. In addition, catalyst 1 always shows considerably higher photocatalytic efficiency than that of catalyst 2. For example, the rate constant of carbaryl irradiated for 302 nm UV is 0.0039 min$^{-1}$ increased to 0.0073 and 0.0057 min$^{-1}$ in the presence of catalyst 1 and 2, respectively. Greater catalytic activity was achieved for carbaryl irradiated with the LED visible light. As shown in Figure 5d, the rate constant of carbaryl alone irradiated under visible light was 0.0036 min$^{-1}$, which is very similar to the catalytic activity observed for the irradiated carbaryl under 302 nm UV source. However, irradiated samples under LED light in the presence of catalysts 1 and 2 showed a significant enhancement in the photocatalytic activities wherein the rate constants were 0.0183 and 0.0084 min$^{-1}$, respectively. These results indicated that catalyst 1 produced sizeable degradation of carbaryl under visible light. The summary of the photodecomposition rate constants of carbaryl in the presence of the two catalysts is shown in Table 3.

In standard photocatalytic systems, surface adsorption plays a significant role in degradation activity$^{36-38}$. The surface absorption observed in this study is thought to arise from charge differences between the alkyl amine groups of the organic substrates and contact with
catalyst surfaces. Like-polarity interactions between substrates and catalyst particles are common. We furthered our degradation studies by collecting isotherm data. These suggest that degradation occurs upon initial contact between the model pollutant and active sites on the solid catalyst. Therefore, the higher photocatalytic efficiency of 1 could be attributed to the higher efficiency of generation, mobility, and separation of photoinduced electrons and holes of catalyst 1. As seen in Figure 4.5, carbaryl tends to have a higher adsorption affinity with catalyst 1 than 2 where in the former case the emission intensity has been reduced directly upon mixing for two minutes. Both catalysts are capable of absorbing visible light during irradiation to aid in visible light-harvesting and utilization, as revealed in recent literature. Such light-harvesting materials are capable of generating excited state electrons that could be transferred into the iodobismuthate conduction band via non-radiative means. These charge transfer pathways have been elucidated using theoretical and experimental studies, which indicate large extinction coefficients resulting in extended luminescence lifetimes.
Figure 4.5. Emission Spectra of Irradiated Carbaryl alone (a) monitored at $\lambda_{ex} = 285$ nm and carbaryl in the presence of catalyst 1 (b). The photodegradation profiles for carbaryl irradiated with and without catalysts upon irradiation for 302 nm UV light (c) and LED visible light (d).

The reactions were also monitored by GCMS to identify reaction products. Carbaryl solutions (30 ppm in methanol) in the presence and absence of 10 mg of catalyst 1 and catalyst 2 were irradiated after 60 minutes of light exposure. After irradiation was complete, the samples were filtered and analyzed via GCMS. Catalyst-free carbaryl solutions following UV and visible irradiation showed a strong peak at 30.5 min associated with major ion peak at 201 amu corresponding to carbaryl. In addition, two weak peaks at 4.13 and 20.7 minutes appeared and are identified in Scheme 1. It is noted that an additional GC band appears after 22.0 min associated to
a major mass ion peak at 178 amu. The products produced in the presence of complex 1 are identified and presented in Scheme 4.1. The products identified for carbaryl irradiated in the presence of complex 2 are similar to those found for irradiated carbaryl alone but with various intensities that reflect a larger number of products and lesser amount of residual carbaryl. In addition, a GC peak appears after 42 minutes is associated to a major ion peak at 277 amu indicating the formation of Ph₃PO representing minor decomposition of the catalyst upon irradiation.

Investigations into the visible light photocatalytic activity of both 1 and 2 in solution were also performed with MB with all results illustrated in Figure 4.6. After 30 minutes irradiation, 5.8% in the control was degraded, whereas, in the presence of catalyst 1 around 42% of the MB was degraded compared. Continued degradation results were observed after one-hour irradiation, wherein 62% and 55% of MB were degraded in the presence of catalysts 1 and 2, respectively, compared to 15.4% with no catalyst present, as shown in Figures 4.6a-c. Kinetic data shown in Figure 4.5 from both experiments suggest a pseudo-first order degradation mechanism, which is in agreement with other reported bismuth-based photocatalysts.
Figure 4.6. Absorption spectra irradiated methylene blue (MB) solutions under LED visible light for indicated times a) MB alone, b) MB-catalyst 2, (c) MB-catalyst 1, and the photodegradation kinetic profiles for irradiated MB samples (d).

The use of 302 nm UV irradiation source produced a similar trend. MB solutions irradiated at 302 nm for 60 minutes without a catalyst resulted in 21.7% degradation. This value is higher than that of MB under visible light due to the high energy input. However, in the presence of catalysts 1 and 2, MB irradiated with 302 nm UV source underwent 85.1% and 77.1% decomposition, respectively. Similar kinetic trends were observed for MB in all systems, as summarized in Table 3. For instance, the rate constants for MB irradiated under UV and visible light sources were 0.0042 min\(^{-1}\) and 0.0029 min\(^{-1}\), respectively, reflecting the difference in input energy. In addition, catalyst 1 produced the highest photocatalytic activity with rate constants of
0.014 min$^{-1}$ and 0.0158 min$^{-1}$ under UV and visible light, respectively. Thus, in all cases, the use of catalyst 1 combined with an ultraviolet irradiation source provides the maximum catalytic efficiency for the studied molecules. Both complexes showed catalytic activity in the presence of visible light yet degraded pollutants at a slower kinetic rate than ultraviolet irradiation. The bismuthate systems studied herein provided better catalytic activity than has been observed for ZnO, TiO$_2$, and mixed Zn-Ti oxide composites$^{52-53}$. 

Scheme 1. Carbaryl degradation products for complexes 1 and 2 identified by GCMS after irradiation for 60 min.
Conclusion.

Phosphonium iodobismuthates (MePh₃P)₃[Bi₃I₁₂] (1) and (Ph₄P)₃[Bi₃I₁₂] (2) were prepared and their X-ray structures determined. Photophysical studies suggests strong absorption of light by both complexes, primarily in the UV-A range (315-350 nm) with drastic changes in emission as temperature decreased. The visible light emission observed in complex 2 (but not in 1) is thought to be due to the additional phenyl group acting as an auxophore producing a luminescence red shift into the visible region. Our preliminary results confirm the photocatalytic activity of these complexes, facilitating chemical reactions to degrade pollutants in aqueous solutions. Because these materials are active under visible light as well as UV light, they are potentially more energy efficient in comparison to current catalyst materials. Our results supplement the current research on development of halgenobismuthate(III) salts for applications in photovoltaic and environmental fields of study.

Chapter References.


(8) Patel, Ealin N.; Arthur, Robert B.; Nicholas, Aaron D.; Reinheimer, Eric W.; Omary, Mohammad A.; Brichacek, Matthew P.; Patterson, Howard H., *Dalton Trans.* **2019**, *48*, 10288-10297.


CHAPTER 5
PHOTODEGRADATION OF THE HARMFUL PESTICIDE CARBARYL USING
BISMUTH NANOPARTICLES

Chapter Abstract.

We explored the use of bismuth nanoparticles and studied their effect on the photodegradation of the pesticide carbaryl. The literature collected prior to this research was used to review the chemistry and metabolic pathways of carbaryl metabolites in insects and humans. Current methods of water treatment are ineffective at removing this harmful contaminant. This incomplete removal leads to bioaccumulation in wildlife and in adipose tissue of humans. Use of photocatalytic compounds allow treatment facilities to operate more efficiently and at lower operating costs than compared to traditional photocatalysts such as titanium dioxide. Bismuth oxyhalides have been shown to be an alternative to titanium dioxide and a precursor for more advanced photocatalytic motifs. Thus, bismuth nanoparticles were hypothesized to have higher efficiency due to increased surface area and high oxidation potential. We synthesized a series of bismuth nanoparticles and tested their photocatalytic capacity in the photodegradation of the harmful pesticide carbaryl. Nanoparticles were characterized using TEM, DRS, and X-Ray Photoelectron Spectroscopy (XPS). To monitor the degradation of carbaryl, we utilized liquid-phase luminescence spectroscopy to measure the rate of degradation over time.

Introduction.

Persistent Organic Pesticides (POPs) are compounds that are not readily broken down by microbes or ultraviolet light and have become a problem in countries across the globe. It is estimated that over 5.2 billion pounds of POPs are used each year to treat both crops and humans¹.
Due to frequent use of POPs around homes and residential areas, human contact with broad spectrum pesticides has increased.

A study published in Chemosphere journal provides evidence that POPs are less soluble resulting in accumulation in the environment\textsuperscript{2}. As humans are exposed to these chemicals by respiration, ingestion, or absorption, collection occurs in adipose tissues of humans and animals over time which can lead to cancer and other severe illnesses\textsuperscript{3}. Demand for carbaryl has increased over the years due to its insolubility in water, which allows the insecticide to remain during precipitation. Frequent use in commercial agriculture and landscaping has led to increased human consumption and exposure\textsuperscript{4}. Bacterial metabolism of carbaryl has been the focus of toxicology as well as microbial degradation studies. The metabolic pathway of carbaryl in bacteria is similar in both insects and humans, but sensitivity to byproduct metabolism varies between organisms.

In biological systems, metabolites of carbaryl degrade into derivatives of naphthalene, which provides a scaffold for reactive functional groups such as hydroxides. The stability of carbaryl is the result of conjugated carbon bonds throughout the molecule which provides resonance through electron distribution\textsuperscript{5}. The degradation of carbaryl in the presence of bismuth nanoparticles was exclusively investigated to determine amounts of carbaryl removed as well as kinetic rates. The chemical properties of carbaryl have been observed in order to determine electronic affinity across the molecule that facilitates chemical degradation.

\textbf{Figure 5.1.} General chemical structure of carbaryl.
Carbaryl is an inexpensive insecticide that has gained popularity in recent years due to its effectiveness against a broad spectrum of insects\textsuperscript{6}. Industrial uses focus extensively on mass produced crops such as corn and cotton due to depletions caused by insect invasions. Recently, use in residential landscapes has increased due to contact with disease carrying vectors such as mosquitos and ticks\textsuperscript{7}. Compounds similar to carbaryl such as carbofuran are classified as carbamate-based molecules and are used as commercial insecticides around the world\textsuperscript{8}. This widespread use has led to increases in human exposure through retail distribution and contamination of commercial produce.

Excess industrial runoff into groundwater systems has allowed pollution caused by carbaryl to affect humans in both rural and urban settings. Recently, evidence of increased commercial use has led to increases in potential exposures in communities\textsuperscript{9}. Record of use across Maine forests has been indicated to control outbreaks of spruce budworm\textsuperscript{10}. Carbaryl and other carbamate-based pesticides are used to control the population of insects such as fruit flies that are abundant in the environment. Use of carbaryl is found primarily in cities with large agricultural industries, such as rural areas\textsuperscript{11}. This insecticide is found commonly in both solid and liquid form and distributed to retailers nationwide. These insecticides are known to produce toxic side effects in insects and humans such as nervous system inhibition and respiratory failure\textsuperscript{12}. Current methods of wastewater removal have become inefficient due to the presence of these organic pesticides which resist degradation.

Photocatalysts are a cost effective and efficient alternative to traditional wastewater treatment methods due to their reactive properties under ultraviolet light. This ability allows the nanoparticle to degrade compounds spontaneously as free radicals are generated to remove toxic
compounds such as carbaryl. Current literature proposes degradation mechanisms that show the byproducts formed through hydrolysis is the common mode of action in organisms\textsuperscript{13-15}.

**Experimental.**

A 1:1 ratio of bismuth chloride to soluble starch solution was synthesized by adding 0.0315 grams of BiCl\textsubscript{3} and 0.2 grams soluble starch to an erlenmeyer flask. Ten milliliters of acetonitrile were then added under nitrogen gas and stirred vigorously for ten minutes. A ten-milliliter solution of 30.0 mm sodium borohydride was made by diluting 0.0113g NaBH\textsubscript{4} with 10 milliliters of water, which was added to an Erlenmeyer flask and stirred for 15 minutes under nitrogen gas. Ten milliliters of NaBH\textsubscript{4} was transferred to the ten-milliliter solution of bismuth chloride and mixed vigorously. The solution turned from clear to black and mixed for an additional five minutes. The solution was then centrifuged at 3,000 rpm for approximately 2 minutes. The particles were washed the bismuth compounds with ten milliliters of water. UV-Vis spectroscopy was used to determine structural composition.

\[
\text{Bi}^{\text{III}} \text{Cl}_3 + 3\text{NaBH}_4 \rightarrow \text{Bi}^0 + 3\text{NaCl} + 1.5\text{H}_2 + 1.5\text{B}_2\text{H}_6
\]

**Figure 5.2.** Chemical equation for the synthesis of bismuth nanoparticles

Due to the low solubility of carbaryl in water, stock 0.2 mM solutions of carbaryl were synthesized by dissolving 1.0 mg of carbaryl with 10 mL of methanol and diluting to 100 mL with deionized water. The final 0.2 mM solution of carbaryl was used for experimentation. Solutions were stored at 37 °C and were stable for 5 days. A series of dilutions were created using several amounts of stock solution that were separated into 100 mL volumetric flasks.

Luminescence measurements were collected using a Jobin Yvon Fluorolog 3 spectrophotometer powered by a 75W Xenon Arc Lamp. This device utilizes a dual excitation
monochromator as well as a single emission monochromator. Carbaryl solution samples were scanned with an integration time of 0.3 seconds and a slit width of 5 nm for all monochromators. Emissions were scanned from 302 nm to 450 nm with an excitation of 296 nm. Three scans were recorded for each sample with the averages reported.

A 100 mL carbaryl solution was used to contained dissolved carbaryl and as the medium to conduct photodegradation. The solutions were irradiated with a Steripen for a two-hour period with constant mixing. Aliquots of samples were taken at timed intervals. The Steripen uses a mercury UV lamp which emits at a wavelength of 254 nm. The reaction occurred in a 250 mL round bottom flask at atmospheric conditions. Aliquots were centrifuged for two minutes at 3000 RPM to separate the catalysts from aqueous solutions.

A Vernier model VSP-UV UV-Vis spectrophotometer was used with a deuterium (UV) and incandescent (VIS) light source to confirm the synthesis of pure and doped bismuth nanoparticles. Samples were placed inside a 1 cm quartz cuvette using water as a blank. Nanoparticles in an aqueous solution were scanned at room temperature. Absorbance wavelength was measured from 220 nm to 800 nm. The software used with the spectrophotometer was Logger Pro.

Images of nanoparticles were collected using the University of Maine’s Electron Microscopy Laboratory’s Philips/FEI CM 10 TEM with a point resolution of 0.5 nm and lattice resolution of 0.3 nm. TEM was used to confirm core shell sizes and confirmation of silver shell thickness on gold nanoparticles. Magnification power in the range of 25X to 450,000X with an accelerating potential of 100 kV was used. For imaging, nanoparticles were deposited from sample solution onto copper TEM grids coated with a layer of amorphous carbon. To deposit nanoparticles
a small drop of nanoparticle solution was pipetted onto a grid surface and allowed to air dry at ambient temperature.

**Results & Discussion.**

Diffuse reflectance spectroscopy was performed on the pure elemental bismuth complexes. This instrumentation was utilized in order to measure the physical properties of the nanoparticles when exposed to visible light. Figure 5.3 displays the wavelengths at which the pure bismuth nanoparticles absorb light that ranges from 220-800 nm. This figure suggests the bismuth particles absorb all visible light within the visible light spectrum, which is confirmed by the black pigmentation of the outer surface. The highest rate of absorbance was observed at 298 nm and indicates photophysical excitation is present at this wavelength. Although soluble starch was used as a surfactant throughout the synthesis process, Bi$_2$O$_3$ is thought to be the active species on the surface of the bulk bismuth substrates. This oxide is a thermodynamically favored configuration of elemental Bi(III) species and is reported to display a band gap of 2.23 eV$^{34-37}$. The bismuth species reported in this study displayed an optical band gap of 2.14 eV which is in agreement with recent literature.

![Figure 5.3. DRS absorbance spectra of elemental bismuth photocatalysts.](image)

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Bismuth nanoparticles doped with silicon and terbium were also examined and exhibited a similar absorption of all visible light as shown in figure 5.4. Efforts to deconvolute the spectra revealed no prominent absorption bands in either pure or doped bismuth compounds. Bandgap calculations were achieved through determining the adsorption edges and sequentially converting these wavelengths into electrovolts (eV). By determining the wavelengths needed to induce an emission band, this determines the energy needed to cross the fermi level within the band gap toward the conduction band. These differences in energy required are proportional to the excitation wavelength as well as the wavelength reflected. This relationship between band gap size is what causes changes in the color between the dark pigmented Bi⁰ complexes and bismuth oxyhalide species. Observation of these photophysical properties provides evidence of the photocatalytic properties when exposed to ultraviolet or visible light.

The luminescence spectra of 0.2 mM aqueous solution of carbaryl, summarized in Table 5.1, shows two dominant emission peaks at 322 nm and 332 and a shoulder at 347 nm. Excitation spectra display a distinct maximum peak at 296 nm with a prominent shoulder at 258 nm. A less distinct small shoulder is observed at 310 nm. A stoke’s shift between the maximum excitation peak at 296 nm and maximum emission peak at 332 nm was calculated at 3,620 cm⁻¹. The black pigmentation of pure bismuth nanoparticles indicates absorption of all wavelengths of within the visible light range. Upon luminescence studies at both 293K and 78K, no luminescence measurements were detected within the elemental bismuth species, suggesting a strong resistance to electronic recombination. The recombination of excited state electrons and their respective vacancies are detrimental to photocatalytic processes due to loss of redox active species within the environment. A strong potential for recombination in photocatalytic systems is evident though prominent luminescence bands with large extinction coefficients.
Table 5.1. Luminescence features of 0.2 mM aqueous solution carbaryl at 298K.

<table>
<thead>
<tr>
<th></th>
<th>Excitation</th>
<th></th>
<th>Emission</th>
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<tbody>
<tr>
<td>Peak</td>
<td>296 nm</td>
<td>Peak</td>
<td>322 nm</td>
</tr>
<tr>
<td>Shoulder</td>
<td>310 nm</td>
<td>Peak</td>
<td>332 nm</td>
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<tr>
<td>Shoulder</td>
<td>258 nm</td>
<td>Shoulder</td>
<td>347 nm</td>
</tr>
<tr>
<td>Stoke’s Shift</td>
<td>3,620 cm(^{-1})</td>
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Figure 5.4. Luminescence spectra of 0.2 mM carbaryl aqueous solution at 298 K.
X-ray photoelectron spectroscopy was utilized to determine the elemental composition of various bismuth particles. This spectroscopy measures the energy of an emitted photoelectron to determine the binding affinity of an atom as well as its elemental identity. Photoelectron spectroscopy is achieved through the excitation of electrons within a surface using X-rays. The wavelengths used to irradiate the samples are adjusted throughout the irradiation trials in order to determine which wavelength the samples respond to. The peaks observed in a photoelectron spectrum correspond to the atoms detected within a compound and are indicated by the vertical lines on each figure.

This analysis is also utilized to identify binding affinity corresponding to other elements, which indicated what ligands would be most likely to coordinate with the bulk bismuth complexes. Results from this spectroscopy indicated bismuth atoms were present in both pure and doped nanoparticles with high affinity for oxygen species present. Affinity for oxygen species is commonly seen in heavy p-block elements such as bismuth and further suggests bismuth oxide (Bi₂O₃) is the dominant species along the substrate surface.

**Figure 5.5** XPS Spectroscopy of bismuth nanoparticles.
Figure 5.5 shows spectroscopic tests of pure bismuth nanoparticles that indicate the presence of all corresponding molecular orbitals in a bismuth atom. The silicon detected in the second region of the bismuth nanoparticles is present due to the microscope the sample was placed on. Spectroscopic analysis of bismuth oxyhalides as reference indicated both oxygen and chlorine atoms were present as shown. The addition of dopants such as silicon and terbium are indicated and suggest inclusion within the bulk substrates.

The photodegradation of carbaryl with different nanoparticles show distinct differences in rates of degradation. Irradiation of carbaryl without a catalyst results in no photodegradation over time. This lack of degradation is in agreement with previously published data suggesting conjugates of the naphthalene backbone are primary byproducts. Addition of gold nanoparticles for degradation reference resulted in a dramatic increase the rate of degradation to 0.21 % per min. After 150 min, the total degradation was 39.0%. Substitution of gold nanoparticles for bismuth nanoparticles increases the rate of degradation to 0.33%, an increase of 86%. Doping bismuth nanoparticles with trace amounts of terbium result in no change to the degradation rate compared to pure bismuth nanoparticles.
Figure 5.6. (A) Percent of carbaryl that remained after irradiation with no catalyst. (B) Emission spectra of carbaryl irradiated over time.

Figure 5.7. (A) Percent carbaryl after irradiation. (B) Emission of carbaryl with bismuth compound irradiated.
The first trial used pure bismuth particles that were irradiated for 140 minutes. The second contained bismuth nanoparticles that contained terbium as an enhancing agent and were irradiated for 140 minutes. The bismuth nanoparticles were compared to both titanium dioxide and bismuth oxychloride and were twice as efficient as both compounds during the degradation of carbaryl. The use of luminescence spectroscopy in vitro allowed the concentration of carbaryl in aliquot, which was determined using the maximum intensity of each solution and multiplied with the instantaneous rate.

**Figure 5.8.** (A) Percent carbaryl after irradiation and (B) Emission spectra of carbaryl with terbium doped bismuth nanoparticles.
Conclusion.

The results collected from luminescence spectroscopy and other instrumentation suggest bismuth photocatalysts are potential alternatives to current industry standards. This observation is seen in the irradiation that calculate the decreases in carbaryl concentration over time. The addition of elements such as terbium did not contribute enough to band gap stabilization to cause a significant change in degradation rate. These results were observed after comparing the concentrations of carbaryl observed during two different irradiation experiments. Irradiation of carbaryl without nanoparticles present indicated 82% of carbaryl remained after one-hour irradiation. Both the elemental bismuth and terbium doped nanoparticles exhibited 53% of carbaryl remained after one-hour irradiation time. Bismuth nanoparticles containing oxyhalide ligands had 59% of carbaryl remaining after similar time intervals. Luminescence spectroscopy indicated 39% of carbaryl remained after irradiation using colloidal gold-core nanoparticles. Gold core nanoparticles were hypothesized to degrade at a rate similar to the bismuth nanoparticles. The results of these irradiations suggest pure bismuth is an efficient catalyst that removes carbaryl without the use of enhancing species. The findings from these trials support the null hypothesis that indicating pure bismuth nanoparticles are a sufficient photocatalyst in removing organic pollutants from wastewater systems.

Chapter References.


CHAPTER 6
CONCLUSIONS

This chapter attempts to summarize the achievements and future directions of this thesis. Two major projects have been investigated: The involvement of transition and post-transition metal species such as Cu(II) and Bi\(^0\) in electronic proliferation and photosensitization using organic complexes such as rhodamine or coumarin species was studied extensively. We believe that the work described here significantly adds to the fields of metal-coordination chemistry, network chemistry, photophysics, crystallography, analytical/environmental analysis, spectroscopy. Two novel materials have been discovered that show favorable photophysical properties for prototype devices: (MePh\(_3\)P)\(_3\)[Bi\(_3\)I\(_{12}\)] and (PPh\(_4\))\(_3\)[Bi\(_3\)I\(_{12}\)]. The studies presented in this thesis also provide foundations for visible light utilization in photocatalytic systems using photosensitizing compounds. In addition, future possible research directions are also discussed based on current results.

Metallic chemical species found in the d-block periodic sections are common candidates for photocatalytic applications based on their photophysical activities. The activity of titanium(IV) centered complexes have been reported exclusively due to oxidation-reduction reactions facilitated through high energy wavelengths of light. Utilization of this high energy radiation is practical in benchtop applications yet proves inadequate in real world environmental applications. Regions throughout the world receive varying intensities of solar irritation thus equating to a decrease in photosynthetically active radiation (PAR) that could be utilized by catalytic systems. Band gap alignment between the titanium(IV) center and an accompanying metal species contributes significantly to charge transfer proliferation and light utilization. Alignment between the conduction band of a titanium center and the valence band of a metallic species has been reported
to proliferate pollutant mineralization and degradation. Modification of catalytic motifs involving 
this alignment are not likely to drive visible light utilization due the large band gap (2.72 eV) of 
TiO₂ catalytic systems. Presence of this large band gap is difficult to overcome due to conduction 
band potentials being greater than the minimal threshold. Analysis of optical activity continues to 
be a key factor in modification during photocatalytic investigations to include pollutant 
mineralization as well as lower energy irradiation.

Coupling titanium-based systems with d-block elements such as zirconium or hafnium 
have been reported to facilitate increased charge transfer mechanisms which directly influence 
photodegradation kinetics. Although these properties are favorable in certain aspects of pollutant 
degradation, utilization of visible light using TiO₂ systems. Both zirconium and hafnium display 
similar properties as titanium such as tetravalent and oxyphilic activity. Hafnium is unique due to 
the presence of full f orbitals, which lead to a dramatic increase in band gap activity (eV = 5.2) and 
zero utilization of solar radiation. The presence of insulator activity in f-block elements was 
determined in various modification studies involving TiO₂ complexes and lanthanide series 
elements. Throughout recent years, studies have suggested that inclusion of metal-organic 
frameworks (MOF) coupled with anatase or rutile species are capable of facilitating visible light 
absorption.

Carbon-based materials have gained significant interest in photocatalytic applications due 
to its charge carrying capabilities and nontoxic properties. Materials such as graphene and 
graphitic carbon nitride (g-C₃N₄) are two materials that have been reported to pair well with 
photocatalytic systems such as TiO₂. Modification of these materials to accommodate TiO₂ and 
exterior species such as transition metals is ineffective due to chemical constraints such steric and 
charge imbalances. Further studies that focus on improving the light harvesting abilities of these
carbon materials could prove beneficial to TiO$_2$ impurities along the surface. To sustain continual mineralization with any organic pollutants present in wastewater systems, alternative materials coupled with TiO$_2$ motifs have been investigated extensively in recent years.

The addition of actinide series species in photocatalytic complexes is an underrepresented field of study due to obvious health and environmental concerns. Recent reports have focused on the addition of uranyl ions across the surface of bulk TiO$_2$ systems. These uranium species exist primarily in the tetravalent or hexavalent state which help proliferate charge transfer mechanisms via emissive decay pathways. These mechanisms arise from the partially filled $5f$ orbitals that enable uranyl cations and respective oxides to form under irradiation from lower wavelengths. Efforts to replicate the antennae charge transfer effect observed in lanthanide-based materials has been the main focus of these actinide research efforts for fuel and energy conservation.

Photocatalytic systems that bear Bi(III) centered chemical species have been viewed as viable alternatives to titanium based systems. Due to the nontoxic properties of various bismuth analogs these materials are well sought in industrial and commercial applications. Recently, bismuth complexes coordinated with oxyhalide species have been a popular topic of interest in environmental and inorganic photochemical studies. These materials have an optical band gap that is capable of utilizing ultraviolet wavelengths up to 350 nm, which is not observed in pure anatase and rutile titanium motifs. Elemental bismuth species have been reported to display increased photodegradation rates with minimal overall mineralization. Spectrochemical placement of halogen species indicates species with larger atomic radii such as iodine contribute weakly to charge transfer mechanisms within the crystal fields of the bulk bismuth substrates. These changes in spectrochemical series promote a small array of wavelengths past 350 nm that are utilized by species such as bismuth oxyiodide (BiOI).
Recent investigations have centered on motif modification have focused primarily on BiOI due to possessing the smallest band gap (eV = 1.93) between the bismuth oxyhalide species. Coupling of the BiOI structures with fluorescent dyes such as rhodamines or coumarins have shown to facilitate the harvesting of visible light in a process known as photosensitization. This process involves the coupling of an organic compound with large extinction coefficients to the inorganic photocatalytic structure. These fluorescent compounds possess extended luminescent lifetimes which are able to facilitate intersystem crossing between the singlet states of the organic dye and triplet states of the photocatalysts. Synthesis of these coupled complexes has been achieved through hydrothermal methods involving autoclaved enclosures.

Exposure to ambient air throughout synthesis allows for oxidation of the organic species, which detrimentally affects their luminescence capabilities. These oxidation processes can also facilitate the formation of covalent linkage between dopants and active sites along the surface. Presence of these bonds and other surface impurities can lead to severe reduction in catalyst productivity. As indicated throughout investigations involving titania species, surface area can often be affected through modification of photocatalytic systems. Inclusion of these dopants are often not covalent yet may present increases in steric hinderance which make interactions between catalyst surface and pollutants difficult. Utilization of light within the crystal structure can also be affected by surface modification, since inclusion of large organic species can disrupt charge transfer processes between adjacent substrate facets.

Zeolites are an aluminosilicate compound that acts as a molecular sieve for molecules of varying sizes. These inorganic complexes were early candidates for catalytic motifs since they remain benign both chemically and photophysically. Addition of anionic species to the crevasses present within the zeolite is achieved mostly through ion exchange reactions, suggesting these
reactions are capable of anchoring Bi(III) analogs along bulk zeolite substrates. Recent investigations focusing on promoting oxygen vacancies within BiOCl anchored to monoclinic substrates have shown to promote singlet oxygen production in aqueous media. Inclusion of various dopants within bismuth oxyhalides aims to utilize the natural photocatalytic properties these materials possess.

The phenomenon of transition metal complexes with mixed valencies has been discussed extensively in recent work involving d-block and post-transition metals. Bismuth is unlikely to exist outside of the trivalent state due to the stability of the fully occupied 5d and vacant 6p orbital shells. Because of this stability, modification involving other metallic species have been viewed as the most likely route for mixed valence charge transfer. Efforts to implement mixed valence complexes stem from desirable band structures that arise from interactions between adjacent metal centers. These interactions lead to a series of intervalent charge transfer (IVCT) mechanisms that promote oxidation-reduction reactions to coordinated ligands. These IVCT mechanisms are often observed under visible or infrared excitation wavelengths and are reported to favor band gap alignments capable of utilizing visible light (eV < 2.0).

Vanadyl species are a popular candidate for dopants in photocatalytic motifs and are reported to pair well with BiOX complexes. Inclusion of vanadyl sulfate (VOSO4) into (110) BiOCl facets showed significant response to UVC and visible light excitation. The primary species during photodegradation studies were indicated to be V^{+3} and V^{+5} and contributed additional excited state electrons onto the conduction band of the BiOCl systems. Vanadium and other 4d metal species are known to possess lower reduction potentials that allow for continual oxidation when coordinated with accompanying ligands and are relatively non-toxic in environmental
settings. Due to these favorable properties, future research involving BiOX complexes should involve anchoring of catalytic structures to photophysically active motifs during degradation trials.

The involvement of bismuth centered species in photocatalytic systems has evolved rapidly to include elements with similar atomic radiiuses. According to Pearson theory, soft acids with accompanying bases are capable of extensive polarizability in comparison to chemical species with smaller radiiuses. The inclusion of this principle has led to the development of an anionic iodobismuth(III) chain in various reported complexes. This anionic chain exhibits remarkable photophysical properties when coordinated with specific cationic species. First reports of this iodobismuth complex were observed as early as 1984, yet their photophysical properties have only been extensively studied in recent years. Investigations into the photophysical behavior of iodobismuthate(III) species arises from the use of haloplumbate(II) species in various photovoltaic and solar applications.

The origins of their photophysical properties have been elucidated through the use of density functional theory calculations (DFT) to calculate the orbital transitions responsible. DFT is the study of electronic distribution throughout a molecule using the density present as a function of increasing electron count. These calculations use these electron densities to calculate the lowest ground state the molecule can exist in under absolute zero. Once the ground state densities have been calculated the excited state orbital transitions that equate to photophysical excitation can be determined and observed. Early reports indicated a series of halide-ligand charge transfer mechanisms arising from the I 5p/5s orbitals facilitate excitation into the π* orbitals of the accompanying ligand. Due to these observed phenomena, efforts to design iodobismuthate(III) complexes for photocatalytic use revolve around lowering of cationic LUMO to facilitate these charge transfers.
Initial synthesis and theoretical investigations utilized tetrabutyl ammonium cations as the species adjacent to the anionic chain. Efforts to locate a suitable cation for visible light utilization has shifted to the use of phenyl species coordinated with non-metallic centers. Investigations into metallic cationic species have indicated π-backbonding significantly reduces the transfer of excited state electrons into the surrounding environment. The backbonding present arises from the coordination of the $d$ orbital of the metal centers with the $p$ orbitals of a coordinated ligand. Through these interactions extensive studies have shifted to the inclusion of phosphorus-based species due to their high coordination and photoluminescent properties. In organic synthesis, phosphonium analogs have been used extensively in thermal catalytic reactions that lead to stereospecific attachments of alkyl groups. Inclusion of additional lone pairs into the $p_z$ orbital of the phosphorus center presents an occupied frontier orbital that is capable of orbital overlap.

Overlapping of adjacent $p_x$ orbitals from the bridging halide ligands drive the XLCT mechanisms thought to result in the photoluminescence bands of the iodobismuthate(III) structures presented in previous chapters. Phosphine species in the cationic form coupled with alkyl anions present themselves with rich luminescence when irritated with UVC radiation ($\lambda = 365$ nm). The radiative transfers observed during luminescence measurements suggests these properties can be utilized for photocatalytic purposes. Radical scavenging experiments suggests the presence of hydroxyl and superoxide radical species, indicating reduction of the surrounding environmental into excited state species. Because of these desirable properties, investigations into the photodegradation properties of iodobismuthate species are beginning to emerge extensively in recent inorganic and environmental chemical literature. Future investigations should focus on visible light utilization within these complexes by the addition of fluorescent dyes or photoactive dopants.
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