الجمهورية الجزائرية الديمقراطية الشعبية

DEMOCRATIC AND POPULAR REPUBLIC OF ALGERIA

وزارة التعليم العالي والبحث العلمي

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH

Dr Moulay Tahar University - Saida
Faculty of Technology
Department of Process Engineering

جامعة د الطاهر مولاي سعيدة
كلية التكنولوجيا
قسم: هندسة الطرائق

A Dissertation

For Master Degree in:

Process Engineering

***Option:* Materials Process Engineering**

Presented by:

Ikram Asmaa MOKADEM

Coupling of photocatalysis with another treatment process for the elimination of a pesticide in an aqueous medium

Defended on 20/06/2023

In front of the jury members:

Mrs O. BELARBI	**MAA**	**University of Saida**	**President**
Mr. S. MERAH	**MCB**	**University of Saida**	**Examiner**
Mr. Y. AIMER	**MCB**	**University of Saida**	**Supervisor**

Academic Year: 2022-2023

Dedication

In the first place, I express my gratitude to Allah, the Almighty, for making the path easy for me and granting us the perseverance to accomplish this modest work.

This study is wholeheartedly dedicated to my beloved parents, who have been my source of inspiration and gave me strength when I thought of giving up.

To the tireless architect of my dreams, this is for you. Your hard work and dedication have brought you this far, and the journey continues. Keep believing in yourself, for there are no limits to what you can achieve.

To my siblings Badie Abdelkader, Mohamed Imad edine, Amel Achegane and Haithem Fouad.

In living memory of my loving grandmother,

And lastly to my dear friends Amel Achegane, Fatima Zohra Nana and Haythem Nour el islam who have been there for me throughout this challenging process.

Ikram Asmaa

Acknowledgments

This work was carried out in the laboratory of Process Engineering Department at MOULAY TAHAR University in Saida.

We thank the Almighty Allah (SWT) for giving us the health and the will to begin and complete this dissertation.

First and foremost, I want to express my deep gratitude to Mr. Y. AIMER, whose invaluable guidance and supervision were crucial in making this work comprehensive and achievable. I sincerely appreciate his exceptional supervision, remarkable patience, meticulousness, and unwavering support throughout the preparation of this project.

We are aware of the honour that Mrs. BELARBI has done us by being president of the jury and Mr. MERAH to have accepted to examine this work.

We would like to thank Pr. O. BENALI and all the members of the Process Engineering laboratory of the University of Moulay Tahar and in particular Mrs. S. LAHRECH and Mrs. Z. DJELLOULI, that they find in this space our sincere thanks for having been always helpful.

Our thank also goes to all our professors in the Process Engineering department in particular Mr N. GHALI responsible of our specialty and Mr B. GUEZZEN head of the department.

Our deep thank also goes to all the people who have helped and supported us from near and far and mainly Mrs S. BOUDALI and Mr F. BOUDOU.

TABLE OF CONTENTS

CHAPTER I: Water pollution by pesticides

CHAPTER II: Advanced Oxidation Process for Water Treatment

CHAPETR III: EXPERIMENTAL DEVICES

CHAPTER IV: RESULTS AND DISCUSSION

List Of Abbreviations

UN	United Nations
FAO	Food and Agriculture Organization
FDA	Food and Drug Administration
EPA	Environmental Protection Agency
BOD_5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
THB	Thiabendazole
WWT	Wastewater Treatment
AOP	Advanced Oxidation Processes
SCE	Saturated Calomel Electrode
SC	Semiconductor Catalyst
EG	Bandgap Energy
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
MW	Microwave
pH	Potential Hydrogen
LPML	Low-Pressure Mercury Lamp
CB	Conduction Band
VB	Valence Band
NHE	Normal Hydrogen Electrode
UV	Ultraviolet
Vis	Visible
C / C_0	Concentration / initial concentration
PI	Permanganate Index

List Of Figures

List Of Tables

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Water is a vital resource that is essential for all forms of life on earth. It is an odourless, tasteless, and colorless substance that covers approximately 71% of the Earth's surface. [1]

Water plays a critical role in various biological, physical, and chemical processes that support life on earth. It is involved in many functions such as digestion, metabolism, transportation of nutrients, temperature regulation, and waste removal. In addition, water is also used for various purposes such as irrigation, industry, recreation, and energy production. [2]

The importance of water has been recognized throughout history, and it has been the subject of many scientific studies. It is an essential resource for life on Earth, and plays a critical role in preserving the planet and people.

It is essential for the survival of all living things, including humans, and a vital resource for agriculture, which provides food for the world's population as well as its necessity in maintaining ecosystems and biodiversity. It provides habitats for aquatic plants and animals and supports a range of ecological processes such as nutrient cycling and wetland maintenance.

Water is a vital resource for industrial and commercial activities. It is used in the production of goods and services such as electricity, transportation, and manufacturing.

However, despite its importance, water resources are under increasing pressure due to population growth, climate change and pollution. It is therefore imperative that we sustainably manage this valuable resource to ensure that it continues to support life on Earth for generations to come.

In the last decades, contamination of drinking water and growing public concern about the health risks of contaminants have gained much publicity and initiated many research efforts, as well as political and legal activities.

The majority of the recent problems related to drinking water contamination are associated with pollution of surface and ground water resources.

Water pollution has become a global problem now a day's ongoing evaluation of water resource policy is needed to counter this problem. Deaths and diseases are caused worldwide due to water pollution and approximately 14000 people die every day due to water pollution. [3-5]

Both developed as well as developing countries are facing water pollution problems [6]. Water quality is influenced by many factors like precipitation, climate, soil type, vegetation, geology, flow conditions, ground water and human activities. The greatest threat to water quality is posed by point sources of industries and municipalities. Activities like mining, urban development and Agriculture also effect water quality. Non-point source pollution also includes nutrients, sediments and toxic contaminants [7]

This research is structured around four chapters in the following manner:

- The first chapter encompasses an overview of water pollution caused by pesticides, including their impact on both the environment and human health.
- The second chapter provides an in-depth literature review of the primary advanced oxidation processes employed for the purification of various wastewater types.
- The third chapter delves into an examination of diverse investigative approaches, encompassing the substances utilized, experimental setups, and analytical methodologies.
- Lastly, chapter four concentrates on the test monitoring aspect, presenting the obtained results along with their interpretations.

The study culminates with a comprehensive conclusion.

CHAPTER I:

WATER POLLUTION BY PESTICIDES

CHAPTER I

WATER POLLUTION BY PESTICIDES

Water pollution caused by pesticides has become a significant environmental concern worldwide. Pesticides, extensively employed in agricultural practices, Have the potential to infiltrate aquatic ecosystems through multiple routes, posing risks to human health and potentially leading to detrimental effects on aquatic ecosystems. Understanding the extent of water pollution by pesticides, along with their impacts, is essential for developing effective mitigation strategies and safeguarding water resources.

This chapter intends to provide a comprehensive overview of water pollution caused by pesticides, and the ecological consequences of pesticide contamination, focusing on the disruption of aquatic ecosystems, effects on aquatic organisms.

I.1 Generalities:

Water pollution is the contamination of water sources by substances which make the water unusable for drinking, cooking, cleaning, swimming, and other activities. Pollutants include chemicals, trash, bacteria, and parasites. All forms of pollution eventually make their way to water.

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources.

Sewage is correctly the subset of wastewater that is contaminated with feces or urine, but is often used to mean any waste water. "Sewage" includes domestic, municipal, or industrial liquid waste products disposed of, usually via a pipe or sewer or similar structure, sometimes in a cesspool emptier.

I.2 Types and sources of water pollutants

Wastewater can come from different sources, from ordinary living processes (domestic and residential sources), Commercial wastewater, comes from non-domestic sources, such as commercial buildings, taxidermy, furniture refinishing, musical instrument cleaning, or auto body repair shops, and Industrial wastewater is generated by industrial or commercial manufacturing processes, such as agriculture, and is typically more difficult to treat than household waste. The composition of industrial wastewater differs by industry.

Water can be polluted by a wide variety of substances, including pathogenic microorganisms, putrescible organic waste, fertilizers and plant nutrients, toxic chemicals, sediments, heat, petroleum (oil), and radioactive substances.

a. Domestic sewage

Domestic sewage is the primary source of pathogens (disease-causing microorganisms) and putrescible organic substances. Because pathogens are excreted in feces, all sewage from cities and towns is likely to contain pathogens of some type, potentially presenting a direct threat to public health. Putrescible organic matter presents a different sort of threat to water quality. As organics are decomposed naturally in the sewage by bacteria and other microorganisms, the dissolved oxygen content of the water is depleted. This endangers the quality of lakes and streams, where high levels of oxygen are required for fish and other aquatic organisms to survive. Sewage-treatment processes reduce the levels of pathogens and organics in wastewater, but they do not eliminate them completely (see also wastewater treatment).

Domestic sewage is also a major source of plant nutrients, mainly nitrates and phosphates. Excess nitrates and phosphates in water promote the growth of algae, sometimes causing unusually dense and rapid growths known as algal blooms. When the algae die, oxygen dissolved in the water declines because microorganisms use oxygen to digest algae during the process of decomposition (see also biochemical oxygen demand). Anaerobic organisms (organisms that do not require oxygen to live) then metabolize the organic wastes, releasing gases such as methane and hydrogen sulfide, which are harmful to the aerobic (oxygen-requiring) forms of life. The process by which a lake changes from a clean, clear condition with a relatively low concentration of dissolved nutrients and a balanced aquatic community—to a nutrient-rich, algae-filled state and thence to an oxygen-deficient, waste-filled condition is called eutrophication. Eutrophication is a naturally occurring, slow, and inevitable process. However, when it is accelerated by human activity and water pollution (a phenomenon called cultural eutrophication), it can lead to the premature aging and death of a body of water.

b. Solid waste:

The improper disposal of solid waste is a major source of water pollution. Solid waste includes garbage, rubbish, electronic waste, trash, and construction and demolition waste, all of which are generated by individual, residential, commercial, institutional, and industrial activities. The problem is especially acute in developing countries that may lack infrastructure to properly dispose of solid waste or that may have inadequate resources or regulation to limit improper disposal. In some places solid waste is intentionally dumped into bodies of water. Land pollution can also become water pollution if the trash or other debris is carried by animals, wind, or rainfall to bodies of water. Significant amounts of solid waste pollution in inland bodies of water can also eventually make their way to the ocean. Solid waste pollution is unsightly and damaging to the health of aquatic ecosystems and can harm wildlife directly. Many solid wastes, such as plastics and electronic waste, break down and leach harmful chemicals into the water, making them a source of toxic or hazardous waste.

c. Toxic waste:

Waste is considered toxic if it is poisonous, radioactive, explosive, carcinogenic (causing cancer), mutagenic (causing damage to chromosomes), teratogenic (causing birth defects), or bioaccumulative (that is, increasing in concentration at the higher ends of food chains). Sources of toxic chemicals include improperly disposed wastewater from industrial plants and chemical process facilities (lead, mercury, chromium) as well as surface runoff containing pesticides used on agricultural areas and suburban lawns (chlordane, dieldrin, heptachlor). (For a more-detailed treatment of toxic chemicals, see poison and toxic waste.)

d. Sediment:

Sediment (e.g., silt) resulting from soil erosion or construction activity can be carried into water bodies by surface runoff. Suspended sediment interferes with the penetration of sunlight and upsets the ecological balance of a body of water. Also, it can disrupt the reproductive cycles of fish and other forms of life, and when it settles out of suspension it can smother bottom-dwelling organisms.

e. Thermal pollution:

Heat is considered to be a water pollutant because it decreases the capacity of water to hold dissolved oxygen in solution, and it increases the rate of metabolism of fish. Valuable species of game fish (e.g., trout) cannot survive in water with very low levels of dissolved oxygen. A major source of heat is the practice of discharging cooling water from power plants into rivers; the discharged water may be as much as 15 °C (27 °F) warmer than the naturally occurring water. The rise in water temperatures because of global warming can also be considered a form of thermal pollution.

f. Petroleum (oil) pollution:

Petroleum (oil) pollution occurs when oil from roads and parking lots is carried in surface runoff into water bodies. Accidental oil spills are also a source of oil pollution—as in the devastating spills from the tanker Exxon Valdez (which released more than 260,000 barrels in Alaska’s Prince William Sound in 1989) and from the Deepwater Horizon oil rig (which released more than 4 million barrels of oil into the Gulf of Mexico in 2010). Oil slicks eventually move toward shore, harming aquatic life and damaging recreation areas. [8]

I.3 Agriculture water pollution

Agriculture has played a critical role in human civilization, enabling the development of settled societies and the advancement of economies. In the latest centuries it has increased due to population growth.

Agriculture has gone through significant transformations over time; from traditional farming methods to modern, high-tech agricultural practices, and those transformations has an impact on water quality, one of the major concerns about pesticide use is the possibility of these chemicals leaving agricultural lands and polluting other areas, which can pose serious health risks and costs to human and environmental health. The aim of this article is to address the mechanisms behind pesticide pollution, as well as the impacts this pollution has on soil, ecosystem biodiversity and human health. Hydrological leaching and aerial drift will be the categories of pollution of focus, and the overall impacts of pesticide pollution on economic, environmental and social sustainability will be assessed.

While essential for providing food and raw materials, it can also contribute to water pollution. The use of fertilizers, pesticides, and other chemicals in agricultural practices, as well as the management of animal waste, can result in contamination of water sources such as rivers, lakes, and groundwater, and that can lead to serious diseases in humans. The whole ecosystem of water bodies is disturbing due to water pollution.

Due to population growth, urbanization and climate change, competition for water resources is expected to increase, with a particular impact on agriculture. The population is expected to increase to more than 10 billion by 2050, and whether urban or rural, these populations will need food and fiber to meet their basic needs. Combined with the increased consumption of calories and more complex foods, which accompany income growth in the developing world, it is estimated that agricultural production will need to expand by about 70% by 2050 [9].

Water pollutants may cause disease or act as poisons. Hazardous chemicals, pesticides, and herbicides from industries, farms, homes and golf courses can cause acute toxicity and immediate death, or chronic toxicity that can lead to neurological problems or cancers. Many water pollutants enter our bodies when we use water for drinking and food preparation. The pollutants enter the digestive tract. From there, they can reach other organs in the body and cause various illnesses. Chemicals come in contact with the skin from washing clothes, or from swimming in polluted water and may lead to skin irritations. Hazardous chemicals in water systems can also affect the animals and plants which live there. Sometimes these organisms will survive with the chemicals in their systems, only to be eaten by humans who may then become mildly ill or develop stronger toxic symptoms. The animals and plants themselves may die or not reproduce properly [10].

I.4 Pesticides:

According to the Food and Agriculture Organization (FAO), pesticides are substances or mixture of substances intended to prevent, destroy or control any pest, including vectors of human or animal disease, unwanted species of plants or animals, causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances that may be administered to animals for the control of insects, arachnids, or other pests in or on their bodies.

Table I.1: Chronology of pesticide development [11]

Period	Example	Source	Characteristics
1800–1920s	Early organics, nitro-phenols, chlorophenols, creosote, naphthalene, petroleum oils	Organic chemistry, by-products of coal gas production, etc.	Often lack specificity and were toxic to user or nontarget organisms
1945–55	Chlorinated organics, DDT, HCCH, chlorinated cyclodienes	Organic synthesis	Persistent, good selectivity, good agricultural properties, good public health performance, resistance, harmful ecological effects
1945–70	Cholinesterase inhibitors, organophosphorus compounds, carbamates	Organic synthesis, good use of structure–activity relationships	Lower persistence, some user toxicity, some environmental problems
1970–85	Synthetic pyrethroids, avermectins, juvenile hormone mimics, biological pesticides	Refinement of structure–activity relationships, new target Systems	Some lack of selectivity, resistance, costs, and variable persistence
1985	Genetically engineered organisms	Transfer of genes for biological pesticides to other organisms and into beneficial plants and animals, genetic alteration of plants to resist nontarget effects of pesticides	Possible problems with mutations and escapes, disruption of microbiological cology, monopoly on products

I.4.1 *Types of pesticides:*

Pesticides are referred to by the type of pest they control. Pesticides can be either biodegradable pesticides that break down into harmless compounds by bacteria and other living organisms or persistent/non-biodegradable pesticides, which can take months or years to break down.[12]

a. Grouped by the pest types they control:

1/ Insecticides:

Insecticides are chemicals used to control insects by killing them or preventing them from engaging in undesirable or destructive behaviors. They are classified based on their structure and mode of action.

Many insecticides act upon the insect's nervous system (e.g., cholinesterase inhibition), while others act as growth regulators or endotoxins. [13]

Insecticides are commonly used in agricultural, public health and industrial applications, as well as household and commercial uses (e.g., control of roaches and termites). The most commonly used insecticides are the organophosphates, pyrethroids and carbamates. [14]

2/ herbicides:

Herbicides are chemicals used to manipulate or control undesirable vegetation. Herbicide application occurs most frequently in row-crop farming, where they are applied before or during planting to maximize crop productivity by minimizing other vegetation. They also may be applied to crops in the fall, to improve harvesting.

Herbicides are used in forest management to prepare logged areas for replanting. The total applied volume and area covered is greater but the frequency of application is much less than for farming. [15]

They may cause biological impairments of water bodies if they occur in water or sediment at sufficient concentrations. Most commonly, they enter surface water in runoff or leachate, but, because they have relatively low toxicity to fish and invertebrates. Acute toxicity is likely only when they are deliberately or accidentally applied directly to water bodies. [16]

3/ Rodenticides:

Rodenticides are pesticides that kill rodents. Rodents include not only rats and mice, but also squirrels, woodchucks, chipmunks, porcupines, nutria, and beavers.

4/ Bactericides:

Bactericides are chemical substances that helps to prevent the formation of bacteria, whether pathogenic or not such as disinfectants, antiseptics and antibiotics

5/ Fungicides:

Fungicides are pesticides that kill or prevent the growth of fungi and their spores. They can be used to control fungi that damage plants, including rusts, mildews and blights. They might also be used to control mold and mildew in other settings. Fungicides work in a variety of ways, but most of them damage fungal cell membranes or interfere with energy production within fungal cells. [17]

6/ larvicides:

A larvicide is a type of insecticide used to control mosquitoes. They work by killing mosquito larvae before they can grow into adults. Some formulations are activated when ingested by the mosquitoes, and some formulations work when they come into contact with the larvae. When used according to product label instructions, larvicides do not harm people, pets, or the environment. [18]

b. Grouped by their biodegradability:

1/ Biodegradable Pesticides

Biodegradable pesticides are those that can be broken down into harmless compounds by microbes and other living organisms within less period of time.

2/ Non-Biodegradable Pesticides

Few pesticides are known as non-biodegradable, also called persistent pesticides. The most long-lived pesticide materials include aldrin, parathion, DDT, chlordane, and endrin, they take a long period of time to break down. These pesticides can survive in the soil for over 15 years or more.

Considering the chemical pesticides extracted from a common source or some production method:

c. Chemical pesticides:

1/ Organophosphates:

Many organophosphates are insecticides that impact on the nervous system by compromising the enzyme that regulates the neurotransmitter.

2/ Carbamate:

Carbamate pesticides affect the nervous system by compromising the enzyme that regulates the neurotransmitter similar to the organophosphates, but carbamate enzyme effects are usually reversible.

3/ Organochlorine Insecticides:

This type was common in the early years when pesticides came into the market. Many countries have banned organochlorine insecticides from their markets because of their impacts and persistence on health and the environmental factors (e.g., DDT, chlordane and toxaphene).

4/ Pyrethroid:

There are synthetic variants of pyrethrin, a naturally occurring pesticide present in chrysanthemums (Flower). Their development is such a way they can maximize their environmental resilience.

5/ Sulfonylurea herbicides:

The commercial production of sulfonylureas herbicides was for weed control like flupyrsulfuron-methyl-sodium, ethoxysulfuron, chlorimuron-ethyl, bensulfuron-methyl, azimsulfuron, and amidosulfuron, rimsulfuron, pyrazosulfuron-ethyl, imazosulfuron, nicosulfuron, oxasulfuron, nicosulfuron, flazasulfuron, primisulfuron-methyl, halosulfuron-methyl, pyrithiobac-sodium, cyclosulfamuron, bispyribac-sodium, terbacil, sulfometuron-methyl Sulfosulfuron.

6/ Biopesticides:

The biopesticides are a type of pesticides obtained from natural resources such as animals, plants, bacteria, and certain minerals.

I.4.2 Impact of pesticides:

Many pesticides can pose risks to people, although pesticides are designed to (in most cases) kill pests. Generally, however, people are likely to be exposed to only very small amounts of pesticides – too small to pose a risk.

1/ Pesticide Impacts on Human Health:

Just as with organisms in natural ecosystems, humans can also be adversely affected by pesticide exposure. Some of the first pieces of work on human pesticide response are often personal stories of serious drift incidents. These anecdotes are visceral accounts of various symptoms, and often present the fear in those afflicted [19]. Behind these experiences, there are documented symptoms of acute illness from pesticide exposure, including vision changes, cognitive problems [20], nausea, vomiting and difficulty breathing [19]. In the long term, repeated exposure to pesticides like glyphosate can cause cancer, neurological decline and other serious diseases [21]. In these cases, some demographics are at heightened risk for serious harm from pesticide pollution, including children, women, older people; individuals exposed to multiple pesticides at once and farm workers [19, 20]. The common causes of these illnesses are either aerial drift of recently applied pesticides [19] or through contamination of groundwater [22].

In records of exposure to pesticide pollution in California, some accounts have indicated the lack of response by emergency medical staff since pesticide pollution does not have obvious signs compared to gas leaks and other sources [19].

Additionally, the people most dangerously exposed to these chemicals are farm workers, who are marginalized as immigrants and low-income individuals. As a source of cheap labor for commercial growers, these workers have limited rights and enfranchisement to protect them from these risks [19]. Likewise, people of color and low-income groups generally face higher risks of exposure to pesticide pollution [23], implying systemic environmental discrimination towards communities near agricultural lands. Similar trends have been seen in Hawaii, where there are multiple incidents of aerial pesticide pollution drifting towards schools [24]. More advocacy for these marginalized people is needed among activist organizations protesting the health risks associated with pesticide exposure [25], since the increased exposure and negligence of emergency care contributes to the unsustainable social practices of oppression. Additionally, advocates and governments need to consider the costs of health care for patients harmed by pesticide pollution and for cleaning up exposed areas. These costs can pose serious economic problems in terms of perpetuating poverty via health care expenses, and using taxpayer dollars for preventable pollution.

2/ Pesticide Impacts on Soil Properties:

Because of the role of pesticides in biological control, the major concern surrounding pesticide soil pollution is the potential damage of microbial communities [26-28]. Soil microorganisms are crucial to soil health through their contributions to nutrient cycling and plant function [29]. In research on the soil microbes and pesticides, the two main focuses are on microbial diversity and activity. Moorman (1989) found while these communities are generally resilient to repeated pesticide applications, microbial diversity is impacted as certain species decline.

This is due to the fact that while many microbes are stable in the presence of pesticides, certain individual taxa may be lost [26]. Additionally, the amount of different pesticides in the soil can also alter the metabolic rates and pathways of microbes [28], such as the photosynthesis rates of algae [30]. This is key to note given that at least 99.99% of pesticides applied to target pests actually end up contaminating the soil ecosystem and potentially altering its function [31]. Despite these concerns, recent research is also finding that some microbes may use pesticides as an energy source [30], increasing soil respiration and the functional diversity of these soil communities. Since much of the work to track soil microbial communities in the presence of pesticides focuses on changes in nutrient cycling [32], and the results are often inconsistent [33] more research needs to be done on the long-term effects on microbes not directly involved in these processes, such as plant symbionts.

Among the different groups of these plant symbionts, arbuscular mycorrhizal fungi (AMF) are vital to the growth and survival of 90% of plant species, and are most often found in grasslands and managed ecosystems [34]. In a study of the effects of glyphosate on these fungi, Druille et al. (2013) found that application of the pesticide reduced the viability of AMF spores at low soil application levels and that root colonization was reduced when glyphosate was applied on the plant or the soil. This presents potential challenges to plant nutrient access and the continued survival of these fungi in grassland ecosystems. Similarly, studies into the effects of pesticides on Rhizobia bacteria have found that the nitrogen-fixing capabilities of these symbionts decline [30], again hindering plant access to nutrients. There are, however, some contradictions between different studies on whether Rhizobia bacteria are harmed by pesticide pollution or if they contribute to remediation of these chemicals in the environment without said harm [35]. On a larger community scale, alterations in the microbial community composition can cause shifts in the plant-soil feedbacks controlling plant populations, shifting the natural biological controls that limit the spread of invasive species [36]. Across these three examples, there are direct ties between the structure and function of soil microbial communities and the plant communities that rely on them, implying how the negative impacts of pesticide pollution on soil can extend to the organisms above ground.

In the long-term, the presence and persistence of pesticides can limit the ability of plants to grow in soils, reducing the usability of land for agricultural and ecological purposes [37]. However, both older and more recent research has found that pesticides like glyphosate leave minimal effects on soil microbial activity in the field [33, 38, 39]. This indicates that future research on the effects of pesticides on microbial communities needs to have a more applied focus to better understand how these microbes are impacted by a combination of factors. Additionally, research into the microbe-associated risks of pesticides need to also account for microbe-substrate interactions, which can enhance pathogen damage to crops through effects like green bridges [33]. In general, these findings are also a testament to the resilience of the soil ecosystem, as well as the design of pesticides like glyphosate to be quickly degraded in the environment [40]. Since many of these studies on soil microbes track diversity through the resulting nutrient cycling processes [32], more research also needs to be done on the long-term effects of pesticide pollution of taxa not directly involved in said processes, especially with respect to repeated exposure in different ecosystem types [41].

3/ Pesticide Impacts on Ecosystem Structure and Function:

Just as with soil microorganisms, there are multiple direct and indirect effects of pesticide pollution on the health and function of ecosystems surrounding agricultural lands. These effects arise either with the direct toxicity of the specific pesticide, or through the cascading effects of declines in biodiversity across food webs. In terms of direct toxicity, the mode of transport influences which groups of organisms are exposed to pesticide pollution. One of the major concerns with air-borne pesticide pollution is the toxicity to native wild bee populations, which provide important pollination services to fruit trees [42]. Similarly, pesticide exposure is one of the contributing factors to colony collapse syndrome among domesticated honeybees, which are also vital to pollinator-dependent plants [43]. Air-borne pesticide pollution is also a major driver in the decline of amphibians in California, which is compounded by ongoing habitat destruction [44]. In both of these cases, the losses of certain organisms pose risks to the larger ecological community. Amphibians act as indicators of general ecosystem health, and pollinators are pivotal to plant regeneration and food production. Additionally, aerial pesticide pollution creates dangerous problems for critically endangered species, such as the Lange’s metalmark butterfly [45]. Ultimately, the losses of these rare or important organisms lead to a decline in ecosystem biodiversity, which in turn impacts human access to ecosystem services.

In aquatic ecosystems, the leaching of pesticides into water contributes to similar losses in biodiversity, namely in populations of aquatic invertebrates [46]. What’s significant about the findings from Beketov et al. (2013) is that these losses even occurred at pesticide doses designated as safe by the government, indicating the need for further assessment of pesticide toxicity for aquatic systems. Pesticide leaching into streams can also have toxic effects on larger animals, such as salmon [47]. These findings show the importance of re-evaluating how we determine the risks of pesticides in the greater landscape, and how we develop regulatory policies based on those risks.

Apart from the effects of direct contact with pesticide pollution, organisms across trophic levels can be affected by the loss of food sources and shifts in ecosystem processes. Hypothetically, the loss of certain taxa due to pesticide exposure can lead to loss of taxa in other trophic levels from a decline in available resources, leading to cascading drops in biodiversity. One example of this is the decline of insectivorous bats due to a combination of pesticides and tillage in their hunting grounds [48]. Among herbivorous animals, another major example has been the decline in monarch butterfly populations because of milkweed losses in their Midwest range through increased applications of glyphosate [49]. Reviews of the literature also indicate overall declines in abundances of insects and birds surrounding agricultural lands [50], and chronic exposure to glyphosate can create negative health effects in mammals [21]. At the ecosystem level, the long-term presence of pesticides contributes to decreasing abundance of both plant and animal communities, as well as slowing of nutrient cycling [52]. There is also the risk of increased animal and plant diseases that are pesticide resistant [21], or that of pathogens that benefit off of the death of target pests [33]. Through both the direct and indirect effects of pesticides on ecosystems, the reports of declining biodiversity present an alarming picture of ecosystem degradation. Biodiversity is a key part of environmental sustainability, providing resilience through niche redundancy to ecosystems and offering a plethora of ecosystem services to humans. Addressing the consequences of pesticide pollution on biodiversity, through both research and environmental management, is a major component to understanding the overall causes in biodiversity loss and future protection.

The following chapter gives a comprehensive and detailed study of the principal advanced oxidation processes employed in wastewater treatment, and their application, efficacy, and suitability in addressing water pollution challenges. Furthermore, this chapter also includes a brief review of microwave and ultrasound technologies in relation to wastewater treatment. By synthesizing the available research and knowledge in this field, this chapter aims to enhance our understanding of the potential of advanced oxidation processes and related technologies for effective wastewater purification and environmental remediation.

CHAPTER II:

ADVANCED OXIDATION PROCESSES (AOPs) FOR WATER TREATMENT

CHAPTER II

ADVANCED OXIDATION PROCESS FOR WATER TREATMENT

Water treatment methods have undergone significant development over the years, driven by the increasing need for clean and safe water supplies. The development of water treatment methods has played a crucial role in improving public health, protecting the environment, and enabling sustainable water management practices. Such as water treatment processes. Advanced Oxidation (POA). The purpose of the treatments is to reduce the COD and the toxicity of the effluents. (Indicator for the mass concentration of organic compounds).

II.1 Advanced Oxidation Processes:

Advanced oxidation processes (AOPs) were first proposed in the 1980s for drinking water treatment and later were widely studied for treatment of different wastewaters. During the AOP treatment of wastewater, hydroxyl radicals ($^{\cdot}OH$) or sulfate radicals ($SO4^{\cdot}$) are generated in sufficient quantity to remove refractory organic matters, traceable organic contaminants, or certain inorganic pollutants, or to increase wastewater biodegradability as a pre-treatment prior to an ensuing biological treatment. [52]

The advantage of AOPs over all chemical and biological processes is that they are totally “environmental-friendly” as they neither transfer pollutants from one phase to the other (as in chemical precipitation and adsorption) nor produce massive amounts of hazardous sludge. AOPs are capable of degrading nearly all types of organic contaminants into harmless products and almost all rely on the production of reactive hydroxyl radicals ($^{\bullet}OH$) with a redox potential of 2.8 V. •OH is the second most reactive species next to fluorine atom, they attack the most part of organic pollutants molecules with rate constants usually in the order of 106-109 M^{-1} s^{-1}, which is 106 -1012 times faster than ozone. In these processes, $^{\bullet}OH$ initiate a series of oxidation reactions then leading to the ultimate mineralization products of CO_2 and H_2O. [53]

Generally, the treatment efficiencies rely heavily upon the selected AOP type, physical and chemical properties of target pollutants, and operating conditions. It would be noted that other mechanisms, besides hydroxyl radical or sulfate radical-based oxidation, may occur during the AOP treatment and contribute to the reduction of target pollutants. [52]

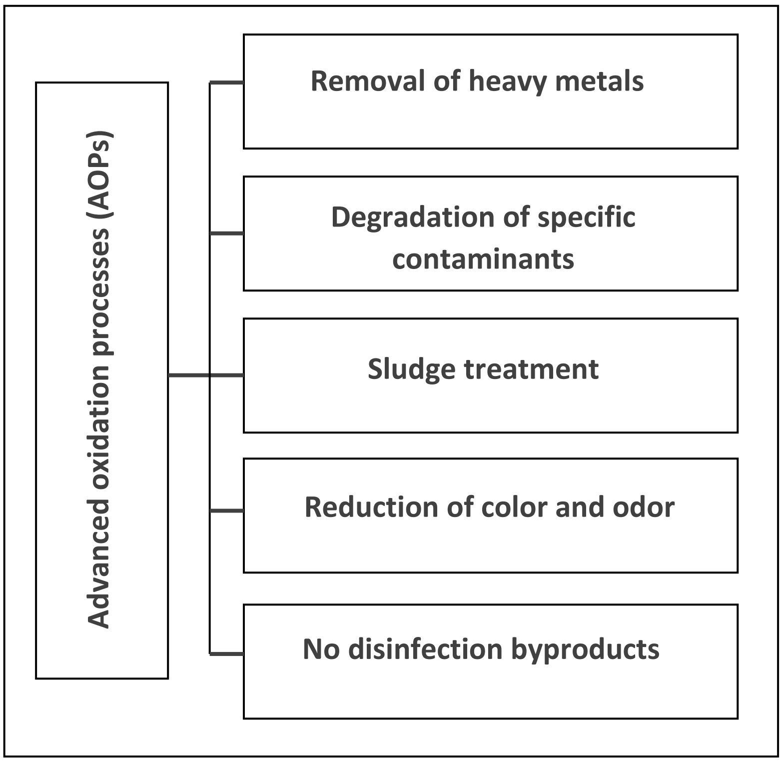


Fig. II.1 Applications of AOPs

II.1.1 Types of AOPs:

a. Homogeneous AOP:

Homogeneous processes that use light as an energy source. In general, ultraviolet (UV) radiations and other sources such as ultrasound (sono-catalysis), electrical energy, and microwave irradiation are used to degrade compounds. UV/H_2O_2, UV/Ozone, UV/Photolysis, and Photo-Fenton are all processes based on this approach. [54]

b. Heterogeneous AOP:

Among the AOPs, heterogeneous photocatalysis with semiconductor catalysts has demonstrated its efficacy in degrading a wide range of toxic contaminants into biodegradable compounds, which are then mineralized to carbon dioxide and water [55]. "Heterogeneous" denotes a state where there are two distinct phases involved: a solid phase for the catalyst and an aqueous phase for the contaminants. When a semiconductor catalyst is present, multiple phases are combined along with a light source. (UV/solar radiation) (TiO_2, ZnO, ZnS, CdS, etc.).

1. Hydroxyl Radical-Based AOPs:

Hydroxyl radical is the most reactive oxidizing agent in water treatment, with an oxidation potential between 2.8 V (pH 0) and 1.95 V (pH 14) vs. SCE (saturated calomel electrode, the most commonly used reference electrode) [56]. $^{\cdot}OH$ is very nonselective in its behavior and rapidly reacts with numerous species with the rate constants on the order of 10^8 10^{10} M^{-1} s^{-1}. Hydroxyl radicals attack organic pollutants through four basic pathways: radical addition, hydrogen abstraction, electron transfer, and radical combination [57]. Their reactions with organic compounds produce carbon-centered radicals ($R\cdot$ or $R\cdot$–OH). With O_2, these carbon-center radicals may be transformed to organic peroxyl radicals ($ROO\cdot$). All of the radicals further react accompanied with the formation of more reactive species such as H_2O_2 and super oxide ($O_2^{\bullet}$), leading to chemical degradation and even mineralization of these organic compounds. Because hydroxyl radicals have a very short lifetime, they are only in situ produced during application through different methods, including a combination of oxidizing agents (such as H_2O_2 and O_3), irradiation (such as ultraviolet light or ultrasound), and catalysts (such as Fe^{2+}) [58].

2. Ozone-Based AOPs:

Ozone (O_3) is a strong oxidant itself with an oxidation potential of 2.07 V vs. SCE. However, direct O_3 oxidation is a selective reaction, with typical reaction rate constants of 1.0×100–10^3 M^{-1} s^{-1} 8, in which O_3 preferentially reacts with the ionized and dissociated form of organic compounds, rather than the neutral form. Under certain conditions, $^{\cdot}OH$ is produced from O_3 to initiate the indiscriminate oxidation (indirect mechanisms). Different detailed mechanisms have been proposed to explain the complex $OH\cdot$ generation, and the overall reaction involving $^{\cdot}OH$ generation is expressed as below [59].

$$3O_3 + H_2O \rightarrow 2\ ^{\cdot}OH + 4O_2 \qquad (1)$$

In the presence of other oxidants or irradiation, the $^{\cdot}OH$ yield can be significantly improved. For example, in the so called peroxone (O_3/H_2O_2) system, the O_3 decomposition and $^{\cdot}OH$ production are enhanced by hydroperoxide (HO^{2-}) produced from H_2O_2 decomposition.

$$H_2O_2 \rightarrow HO_2^{-} \qquad (2)$$

$$HO_2^{-} + O_3 \rightarrow\ ^{\cdot}OH + O_2^{-} + O_2 \qquad (3)$$

In the O_3/ultraviolet (UV) irradiation, H_2O_2 is generated as an additional oxidant primarily through O_3 photolysis (Eq. 4)

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \qquad (4)$$

As a consequence, $^{\cdot}OH$ can be generated, at a minimum, through three pathways: (1) ozonation (Eq. 1); (2) O_3/H_2O_2 (Eqs. 2 and 3); and (3) photolysis of H_2O_2, as shown in Eq. 5.

$$H_2O_2 + hv \rightarrow 2\, ^{\cdot}OH \qquad (5)$$

3. UV-Based AOPs:

Hydroxyl radicals can be initiated by photons in the presence of catalysts or oxidants. The most common catalyst is titanium dioxide (TiO_2), a RO-type semiconductor. TiO_2 particles are excited to produce positive holes in the valence band (hv+ vb) with an oxidative capacity, and negative electrons at the conduction band (e− cb) with a reductive capacity, as follows:

$$TiO_2 + hv \rightarrow e^{-}_{cb} + hv^{+}_{vb} \qquad (6)$$

With the reactions of OH− , H2O, and O2·− at the surface of TiO2, these holes and electrons can further form hydroxyl radicals [60].

$$Hv^{+}_{vb} + OH^{-}_{(surface)} \rightarrow {}^{\cdot}OH \qquad (7)$$

$$Hv^{+}_{vb} + H_2O_{(absorbed)} \rightarrow {}^{\cdot}OH + H^{+} \qquad (8)$$

$$e^{-}_{cb} + O_{2\,(absorbed)} \rightarrow O_2^{\cdot -} \qquad (9)$$

In the presence of oxidants such as H_2O_2 or O_3, additional $^{\cdot}OH$ may be yielded under the UV irradiation. For example, a H_2O_2 molecule is cleaved by UV irradiation to generate two OH·.

$$H_2O_2 + hv \rightarrow 2\, ^{\cdot}OH \qquad (10)$$

In addition, at a wavelength less than 242 nm, $^{\cdot}OH$ can also be produced possibly through photolysis of H_2O.

$$H_2O + hv \rightarrow {}^{\cdot}OH + H\cdot \qquad (11)$$

4. Fenton-Related AOPs:

Among these metals that are able to activate H_2O_2 and produce hydroxyl radicals in water, iron is the most frequently used. In the so-called Fenton process, H_2O_2 reacts with Fe^{2+} to generate strong reactive species. The reactive species produced are traditionally recognized as hydroxyl radicals, though other substances such as ferryl ions are proposed. The Fenton-related chemistry for water and wastewater treatment has been discussed in detail elsewhere [61]. The classical Fenton radical mechanisms primarily involve the following reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \qquad (12)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO\cdot_2 + H^+ \qquad (13)$$

$$OH\cdot + H_2O_2 \rightarrow HO\cdot_2 + H_2O \qquad (14)$$

$$OH\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (15)$$

$$Fe^{3+} + HO\cdot_2 \rightarrow Fe^{2+} + O_2H^+ \qquad (16)$$

$$Fe^{2+} + HO\cdot_2 + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad (17)$$

$$2HO\cdot_2 \rightarrow H_2O_2 + O_2 \qquad (18)$$

$^{\cdot}OH$ is generated from Eq. 12 through electron transfer. However, $^{\cdot}OH$ produced can be scavenged by either of Fenton reagents as shown in Eqs. 13 and 14. Therefore, the optimal molar ratio of iron ion to hydrogen peroxide needs to be experimentally determined for minimization of the unwanted scavenging. Although Eq. 13 indicates that the produced Fe^{3+} from Eq. 12 can be reduced to Fe^{2+}, the iron cannot be a catalyst in the Fenton system because the rate constant in Eq. 13 is several orders of magnitude less than that in Eq. 12.

Consequently, Fe^{3+} forms iron sludge at typical water and wastewater treatment conditions. The sludge needs to be separately disposed of, thus increasing the treatment complexity and operational costs. Of note, the generation of hydroxyl radicals during the Fenton reaction is the most effective only at an acidic pH condition. As a result, the application of Fenton reaction for wastewater treatment is restricted in practice. Based on the classical Fenton treatment scheme, three modified Fenton processes are proposed, including the Fenton-like system, photo-Fenton system, and electro-Fenton system. In the Fenton-like reaction, Fe^{2+} is replaced by ferric ion (Fe^{3+}), namely, the series of reactions in the Fenton system are initiated from Eq. 13 in the Fenton-like system, rather than from Eq. 12 in the traditional Fenton treatment. In the photo-Fenton reaction, UV irradiation is applied with the traditional Fenton system with a major purpose of enhancing the UV-induced reduction of dissolved Fe^{3+} to Fe^{2+}. In the electro-Fenton reaction, either or both of the Fenton reagents may be generated through electrochemical methods.

5. Sulfate Radical-Based AOPs:

$S_2O_8^{2-}$ itself is a strong oxidant with a standard oxidation potential (E^o) of 2.01 V. Once activated by heat, ultraviolet (UV) irradiation, transitional metals, or elevated pH, $S_2O_8^{2-}$ can form more powerful sulfate radicals ($SO_4^{\cdot}$, E_o =2.6 V) to initiate sulfate radical based advanced oxidation processes [52].

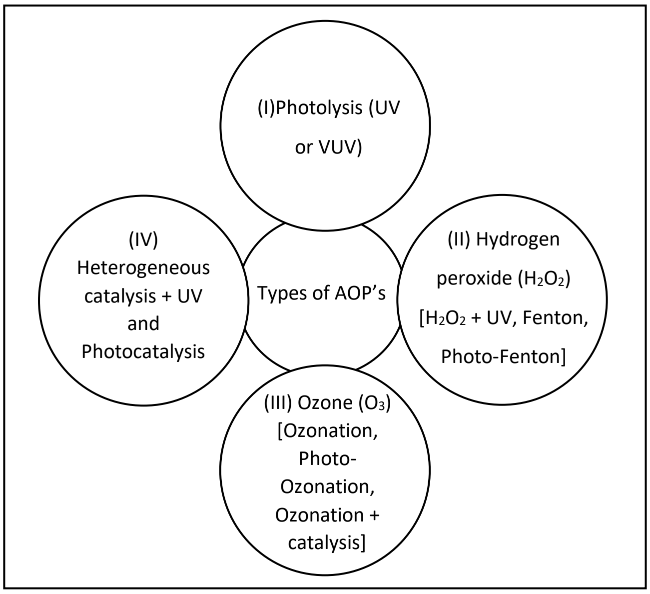


Fig.II.2 Types of AOPs.

II.2 Photocatalysis:

The word "photocatalysis" is comprised of two parts: the prefix "photo," which means "light," and "catalysis," which is the process to decompose a reactant using a catalyst that modifies the rate of a chemical reaction. A catalyst does not directly take part in the reaction, but it accelerates the rate of transformation. The method of activation is the major difference between a conventional catalyst and a photocatalyst. A conventional catalyst is activated by heat, whereas a photocatalyst is activated by photons of suitable energy. [62]

Photocatalytic reactions can occur homogeneously or heterogeneously. Heterogeneous photocatalysis is more intensively studied due to its potential applications in different sectors. In heterogeneous photocatalysis, the reaction scheme implies the development of an interface between a strong metal photocatalyst and a liquid containing the reactants and products of the reaction. [63]

Pesticides are eliminated in the photocatalytic process via chemical interactions between oxidant species and pesticides in wastewater on the catalyst surface. With sufficient light irradiation, such oxidizing species are produced during the catalyst activation process. In general, the complexity of the photocatalytic process necessitates the consideration of several operational factors, such as pH, catalyst or oxidant concentration, light intensity, and substrate concentration (e.g., anion interference) that influence the oxidation of organic compounds in order to find optimal operating conditions. [64]

II.2.1 Basic principles and mechanism of photocatalysis:

Photocatalysis utilizes light to enact the substance that helps increase the rate of a chemical without participating in the reaction. Photocatalysis can be carried out either by direct irradiation or by the irradiation of a catalyst, which lowers the activation energy needed for primary reaction. Photocatalysis initiates reduction and oxidation (redox) reactions in the presence of the irradiated semiconductors [65] represents the similarities and differences between natural and artificial photocatalysis. In natural photocatalysis, chlorophyll arrests sunlight to convert water and carbon dioxide into oxygen and glucose, whereas artificial photocatalysis utilize photocatalysts to create strong oxidizing agents and electronic holes that break the organic matter into carbon dioxide and water. [63,66]

Photocatalytic reaction primarily depends on photon energy and properties of the catalyst. Absorption of light and the resultant photoexcitation of electron-hole pairs takes place as the energy of the incident photons matches or surpasses the band gap. Radiations prompt the progress of electrons from the valance band (VB) to the conduction band (CB), leaving an equivalent number of empty destinations (gaps). [68]

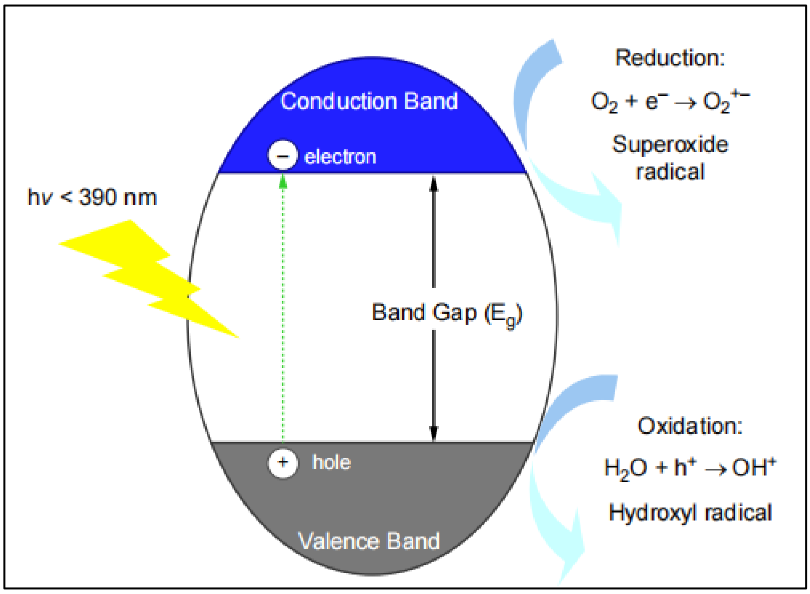


Fig.II.3 Illustration of natural and artificial photosynthesis. [67]

Fig.II.4 shows schematic representation of photocatalytic mechanism using TiO_2 photocatalyst. When titanium dioxide (TiO_2) absorbs ultraviolet (UV) radiation from sunlight or another source, it produces electron-hole pairs. The electron of the VB of titanium dioxide becomes energized when lit by light. The excess energy of this electron helps to promote it to the CB of TiO_2 by creating a negative electron (e) and positive hole (h+) pair. This stage is known as the semiconductor's "photoexcitation" stage, and the energy difference between the VBs and CBs is known as the band gap [69]

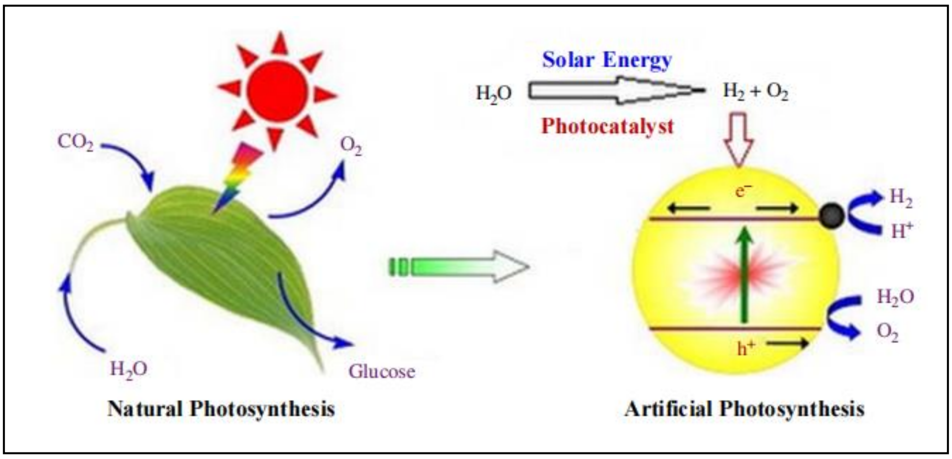


Fig.II.4 Schematic diagram of photocatalytic mechanism of Ti^{3+} self-doped TiO_2 for the visible-light response. [72]

The positive hole of titanium dioxide breaks a water molecule to generate hydrogen gas and hydroxyl radical. Hydroxyl radicals are responsible for degradation of pollutants due to their strong oxidizing power. The negative electron reacts with an oxygen molecule to form a superoxide anion. These electrons actuate the redox reactions, and the holes and electrons undergo progressive oxidation and reduction reactions adsorbed on the surface of the semiconductor to produce the desired products continuing until the availability of light. The mechanism of photocatalytic reaction of TiO_2 lies behind the strong oxidation strength of the hydroxyl radical. Photocatalytic oxidation can effectively disinfect, deodorize, and purify air, water, and any surface area. TiO_2 semiconductor is initiated by a system including radical receptive species through the accompanying series reactions. The active radical species formed were often found to be $^{\bullet}O_2$, $^{\bullet}HO_2$, and $^{\bullet}OH$. [73]

The photocatalyst surface contains absorbed water that is oxidized by positive holes made in the VB because of the electrons shifting toward the CB due to light irradiation that forms hydroxyl ($^{\cdot}OH$) radicals [74-76]. These hydroxyl ($^{\cdot}OH$) radicals react with organic material present in the dye. In presence of oxygen, the intermediate radicals in the organic compounds give rise to radical chain reactions by consuming the oxygen leaving the organic matter to decompose to produce carbon dioxide and water [77]. The reduction of oxygen contained in the air occurs because of the pairing reaction that takes place as an alternative to hydrogen generation due to oxygen being an easily reducible substance [68]. Superoxide anions are formed by the reaction of CB electrons with dissolved oxygen species that become attached to the intermediate products in the oxidative reaction to hydrogen peroxide and then to water. The reduction is more favorable in organic matter than in water. In this manner, a high concentration of organic matter leads to the formation of a larger number of positive holes resulting in reduction of the carrier recombination, thus consequently enhancing the photocatalytic activity [77].

II.2.2 Advantage of Photocatalysis:

(i) Almost all organic and inorganic pollutants can be efficiently degraded and can be mineralized by photocatalysis.

(ii) Photocatalysis is considered as *green technology* because its end products are environmentally friendly compounds such as CO_2, water, simpler salts, and minerals.

(iii) Atmospheric oxygen is used as an oxidant and no any oxidant is required for the process.

(iv) The photocatalysts are non-toxic, economic, highly stable, chemically and biologically inert, insoluble under most conditions, recyclable and reusable.

(v) Artificial light, as well as sunlight, can be utilized for photocatalyst activation.

(vi) Photocatalysis is also compared to activated carbon adsorption method for the large-scale operations [78].

The advantage of using semiconductors as photocatalysts:

(i) inexpensive,
(ii) non-toxic,
(iii) having high surface area to volume ratio,
(iv) having broad absorption spectra with high absorption coefficients,
(v) exhibits size tunable properties (can be modified by doping, size reduction, and sensitizers)
(vi) affording facility for multi-electron transfer process,
(vii) capable of extended use without significant loss of photocatalytic activity. [78]

II.2.3 Modification of photocatalysts:

Modifications of semiconductor surfaces by the addition of metals, doping, or combinations with other semiconductors are beneficial in slowdown the electron-holes recombination rate and thereby increasing the quantum yield of the photocatalytic process. The most successful approach for the modification of photocatalyst is doping, in which the addition of other metal oxide tailored the band gap and induce some significant changes in the native structure of the material.

a. Doping:

Usually, doping involves the use of metals or non-metals and is intended to extend the photocatalytic activity of a semiconductor lower energy excitation. Doping of semiconductors is the process of locally manipulating their charge-carrier density and conductivity [79]. It is the introduction of “foreign elements” into the parent photocatalyst without giving rise to new crystallographic forms, phases or structures with the aim of enhancing the net separation of photo-generated charges. Doping of photocatalyst creates new energy levels between the valance and conduction band of the catalyst, which in turn reduces its band gap. Metallic dopant attracts electrons from the conduction band and slows the charge recombination reaction. A material is doped to extend the life of charge carriers when the dopant material has energy level below the CB or above the VB, which acts as charge trapping center resulting in the extension of wavelength towards the visible region of the spectrum. [78]

Types of Doping:

There are two types of doping, i.e., n-type and p-type, for n-type [80]. Depending on their number of valence electrons, the dopants (as donors) can either donate excess electrons as negative free charge carriers to the semiconductor conduction band at moderate temperature (*n-type doping*), or they (as acceptors) can accept additional electrons from surrounding atoms to complete the covalent chemical bonding, leaving positively charged holes as charge carriers in the semiconductor valence band (*p-type doping*) [78]. In doped semiconductors weather, it is p-type or n-type, the Fermi level is shifted (blue shift & redshift) by the impurities, illustrated by their band gaps [81]. The electron and hole can recombine very fast which is called charge-recombination; it is undesirable for the photocatalyst as it releases the energy of the electron in the form of heat ultimately causing termination of the reaction. To separate the charge from the recombination, doping with the metal ions is suggested which prevents the electron to recombine with the hole. The lifespan of e$^-$ h$^+$ is femtosecond, but enough to promote the redox reaction at the surface of the catalyst [82].

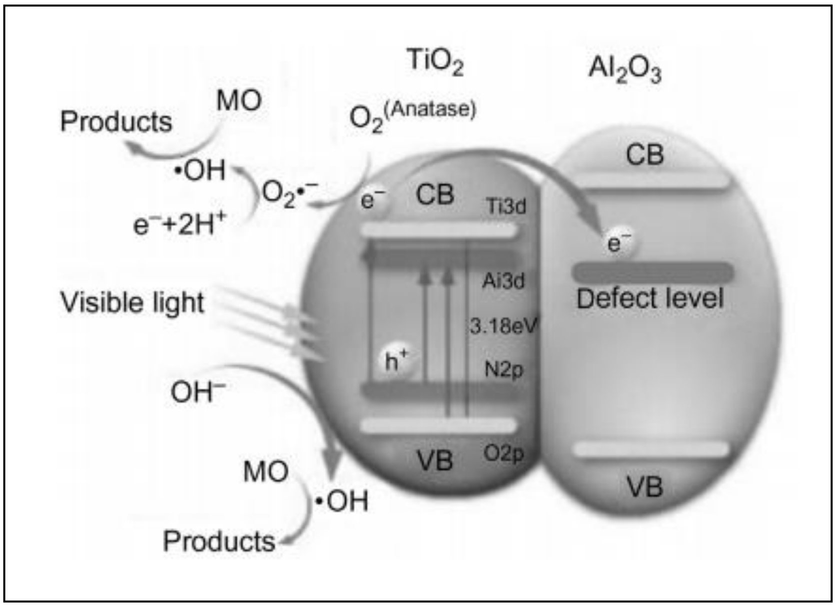


Fig.II.5 Effect of metal doping on conduction band. [77]

Table II.1 Band Gaps of Different Semiconductors. [83]

Semiconductor	**Band Gap (eV at 300K)**	**Semiconductor**	**Band Gap (eV at 300K)**
Zns (wurtzite)	3.91	Fe_2O_3	2.20
Zns (Zinc blende)	3.54	CdO	2.10
SnO_2	3.60	Cu_2O	2.10
TiO_2	3.20	CDSe	1.70
ZnO	3.03	AlSb	1.58
WO_3	2.60	CdTe	1.56
CdS	2.42		

b. Doping of TiO_2:

To extend the visible light response of TiO_2 and improve its photocatalytic activities, various modification strategies, such as dye sensitization, impurity or intrinsic doping or semiconductor coupling, have been developed. Among them, introducing impurity ions into the TiO_2 crystal lattice to substitute the host anions and/or cations has earned much attention in the past decade. By means of physical or chemical methods, researchers have been able to introduce a variety of ions into the TiO_2 matrix, where they change the band structure of TiO_2 by inducing impurity states within the bandgap. In general, ion doping contributes to the improved activities of TiO_2 in three ways:

(1) by narrowing the bandgap and promoting the adsorption of the main region of the solar spectrum, such as doping with N, S, C, B, etc.;

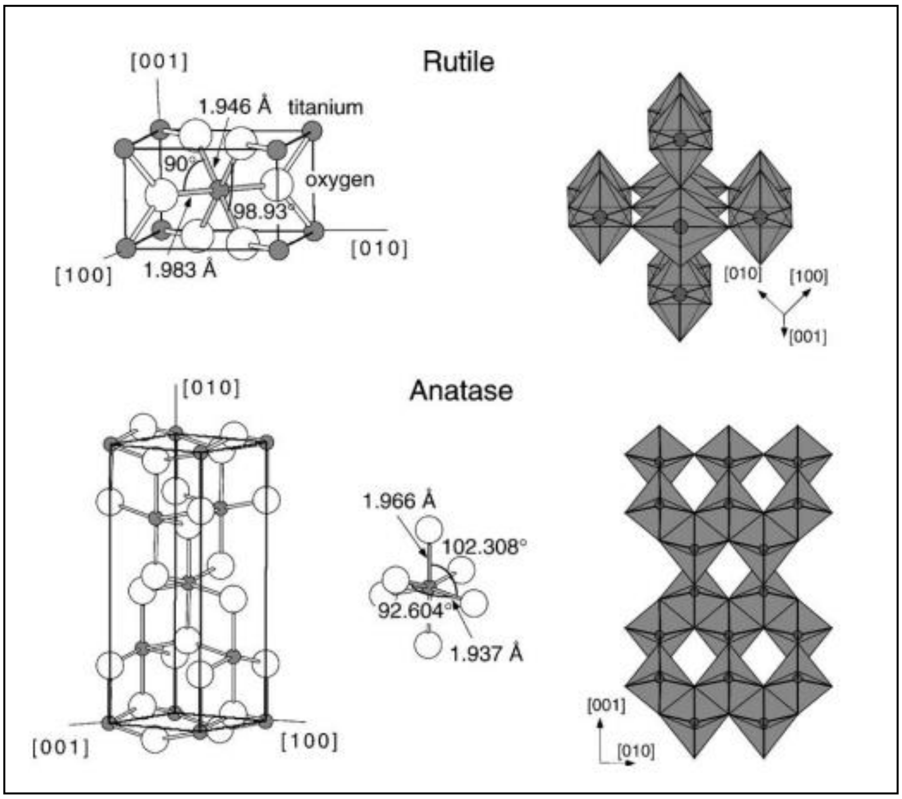
(2) by improving the conductivity of TiO_2 and the mobility of charge carriers, the increased charge traps can reduce bulk recombination and separate photogenerated electrons and holes more efficiently (e.g., Zn, Fe, and Y);

(3) by altering the conduction band position of TiO_2 with certain metal ion dopants, such as Zr^{4+}, Nb^{5+}, and W^{6+}, which further affects the carrier transfer properties. [83]

II.2.4 Photocatalysts:

a. TiO_2:

Titanium dioxide crystallizes in three major different structures; Rutile (tetragonal,D_{4h}^{14} –$P4_2$/mnm, a= b = 4.584°A, c = 2.953 °A), Anatase (tetragonal, D_{4h}^{19}-14$_1$/amd, a = b = 3.782A°, c = 9.502A°) and Brookite (rhombohedrical, D_{2h}^{15}-Pbca, a=5.436°A, b= 9.166°A, c = 5.135°A), the basic building block consists of a titanium atom surrounded by six oxygen atoms in a more or less distorted ochtahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the aspices of the octahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the aspices of the octahedron are slightly longer. A sizable deviation from a 90° bond angle is observed in anatase. In rutile, neighboring octahedral share one corner along ‹ 1 1 0 ›---type directions, and are stacked with their long axis alternating by 90° (see FigII.6 as well as Fig.II.7). In Anatase the corner-sharing octahedral from (0 0 1) planes. They are connected with their edges with the plane of octahedral below. In all three TiO_2 structures, the stacking of the octahedral results in threefold coordinated oxygen atoms. [84]



FigII.6 Bulk structure of the Rutile and Anatase. [84]

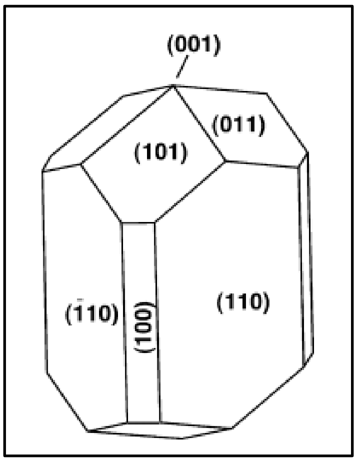


Fig.II.7 The equilibrium shape of a macroscopic TiO_2 crystal using the Wulff construction and the calculated surface energies. [84]

b. ZnO:

ZnO has been shown to be promising because of its various interesting properties. Despite their good performances and stabilities, ZnO-based photocatalysts have limited applications because of a wide band gap energy (3.37 eV) and high recombination rate. Hence, various research groups have tried to improve its photocatalytic activity using different approaches such as element doping, sensitization with a visible band gap semiconductor, and use of gold (Au) nanoparticles. [85]

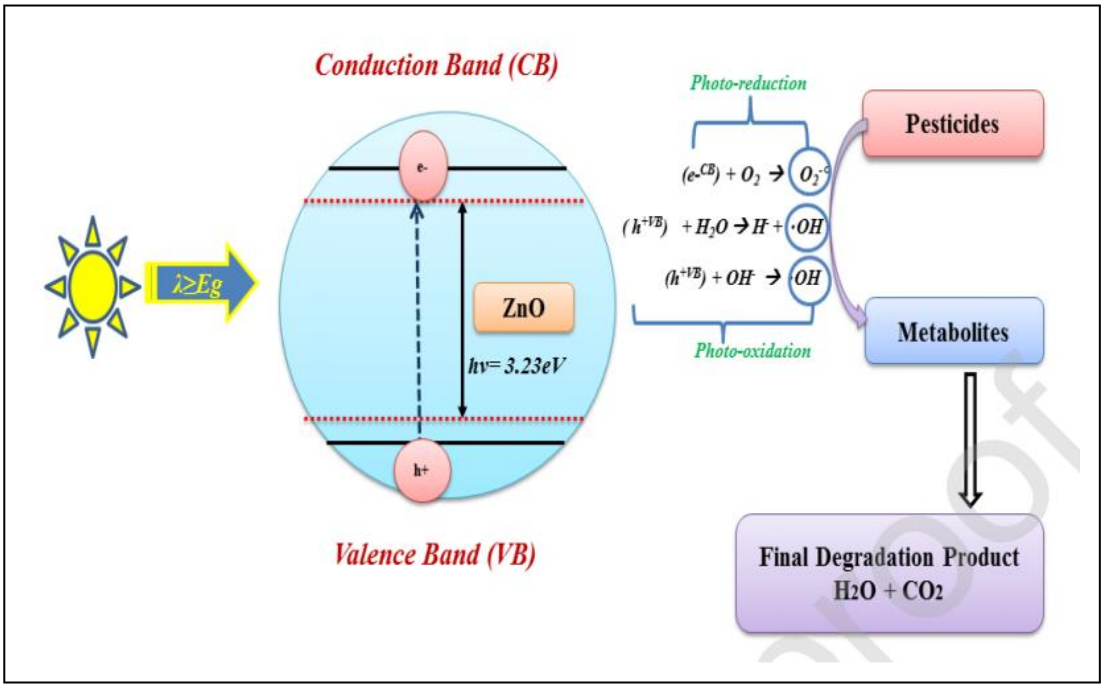


Fig.II.8 Mechanism of Photocatalytic Degradation Process at the surface of catalyst

Zinc oxide (zincite) has the well-known wurtzite structure with lattice parameters at room temperature and ambient pressure of a = 3.25 ˚A, c = 5.207 ˚A, and u = 0.3825, and space-group P63mc (no. 186 in crystallographic tables).5,6 The structure may be understood as two interpenetrating hexagonal lattices, with each Zn (resp. O) sitting at the centre of a distorted O (resp. Zn) tetrahedron. [86]

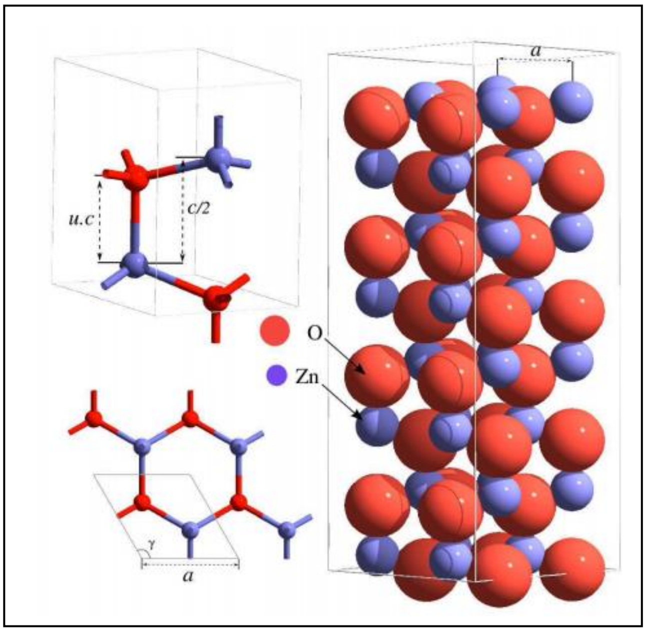


Fig.II.9 Zinc oxide (zincite) has the well-known wurtzite structure with lattice. [86]

II.3 Microwave:

Microwave (MW) radiation has become one of the more popular technologies, both domestically and industrially. It describes the low-energy electromagnetic radiation that spans the frequency range from 30GHz to 300MHz; that is the wavelengths from 100cm to 1cm.

The microwave-induced acceleration of photocatalytic reactions was discovered serendipitously in the late 1990s. The activity of photocatalysts is enhanced significantly by both microwave radiation and UV light. Particularly relevant, other than as a heat source, was the enigmatic phenomenon of the non-thermal effect(s) of the microwave radiation that facilitated photocatalyzed reactions, as evidenced when examining various model contaminants in aqueous media. [87]

With the advantages of fast and uniform heating, MW has been successfully utilized to tackle various environmental challenges such as wastewater treatment, sludge disposal and soil remediation. Unlike the inefficiencies of conventional heating (CH), the heat is generated directly within the material and transferred to the outside in the MW system, with a higher transformation efficiency (80–85%) of electrical energy into heat, thereby reducing processing times and lowering energy demands. Apart from the thermal effect, some researchers believe that there is a non-thermal effect of MW, which leads to the possible breaking of hydrogen bonds, and helps to degrade complex organic components into smaller forms. The unique advantages of MW contribute to its high value, and its effectiveness in environmental remediation has been investigated since the 1990s. However, MW has a limited effect in degrading organic matter without the combination of other treatment processes. Normally, the introduction of MW into AOPs for wastewater treatment increases the reaction rate of AOPs and exerts a stronger integrated treatment effect. [88]

The number of reports on the use of microwaves as an energy source to drive chemical reactions has witnessed an astronomical growth since the early 1990s [87] as shown in Fig.II.10.

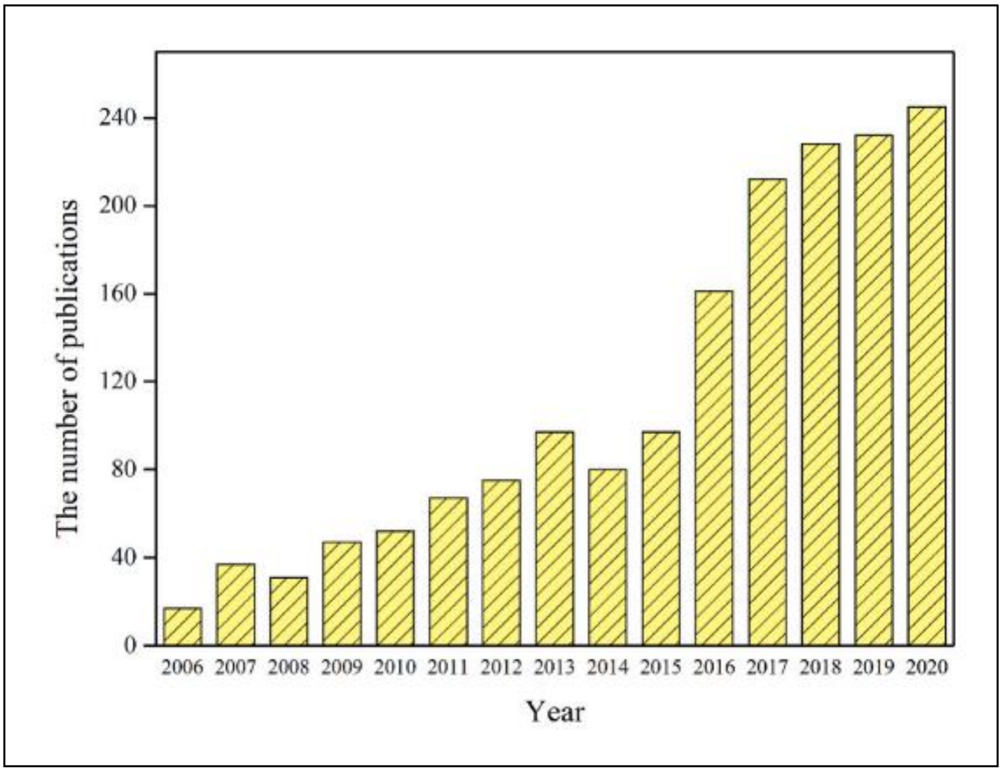


Fig.II.10 The number of publications of MW technology for wastewater treatment during 2006–2020. [88]

Theory and mechanism of MW:

MW consists of electric and magnetic fields perpendicular to each other and their interaction with materials, causing dielectric and magnetic losses, which lead to heat generation. MW heating on non-metallic materials is dominated by dielectric losses, mostly due to two mechanisms: dipole polarization and ionic conduction. In the absence of anelectric field, the orientation of polar molecules with dipole moments is random. The water molecule, for example, has a dipole moment of 1.85D, pointing from the hydrogen atom (electronegativity of 2.2) to the oxygen atom (electronegativity of 3.44).

Exposed to MW radiation, the dipoles of water molecules attempt to align with the alternating electric field and rotate at speeds of up to a million times per second, as shown in Fig.II.11.

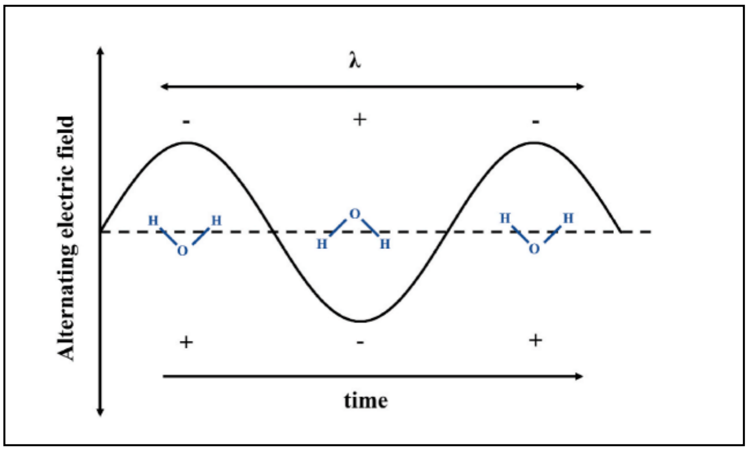


Fig.II.11 The effect of the alternating electric field of MW on water molecules. [88]

The reorientation of the dipole molecules produces heat, which is known as dipolar polarization. Ionic conduction means that ions migrate under the influence of alternating electric fields. Nevertheless, their motion cannot follow the frequency of the electric field oscillations, thus inducing random collisions and generating heat energy. When materials that absorb MW are placed in an alternating electromagnetic field, some MW energy is irreversibly absorbed. Heat is created in the entire volume of the material, and rapid “volumetric heating” occurs, making the internal temperature of the material higher than the surface. In the conventional heating system, heat is diffused from the external heat source (surface) of material to the centre through conduction, convection, and radiation. The different mechanisms of conventional heating and MW heating are shown in Fig.II.12. [88]

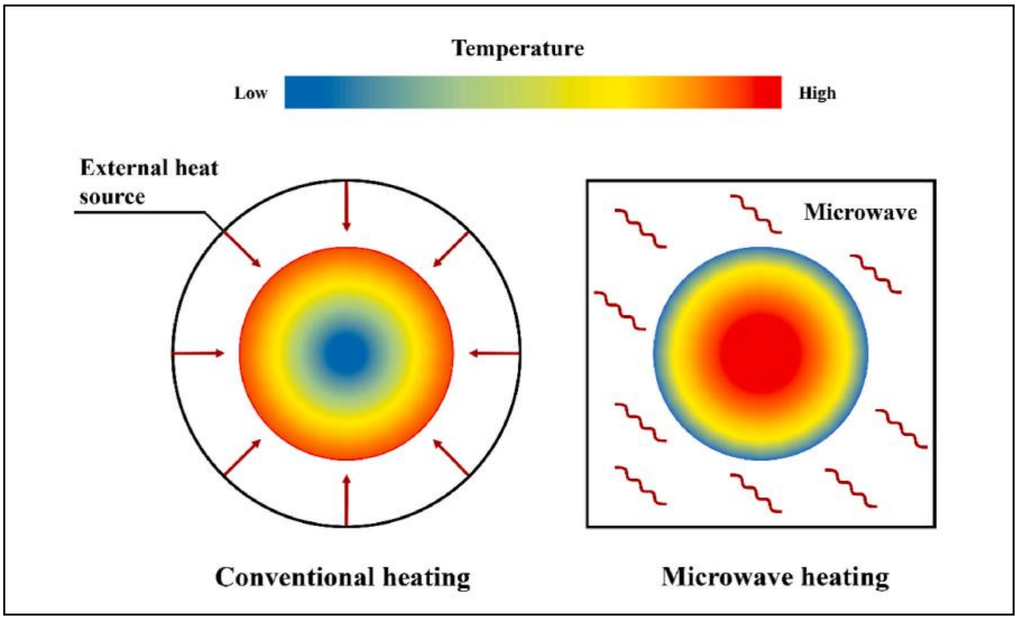


Fig.II.12 The different mechanisms of conventional heating and MW heating.

This unique reverse heating mode brings about further advantages of MW heating, such as rapid and efficient heating, non-contact heating, the ability to control on/off instantly, higher level of safety, and automation. The non-thermal effects of MW are normally referred to as effects independent of temperature increase, i.e., the chemical, physical, or biochemical changes in materials induced by MW when the system temperature is kept constant. These effects are likely to arise from the increased polarization of the dipole transition state and the interaction between MW and the material. [88]

II.4 Sonolysis:

Since the early 20th century, the ultrasound has gained considerable attention due to the enhancement of chemical and physical effects in many processes. In the 1930s, it was discovered that sonication induces polymers degradation. The first experimental evidence for the formation of hydroxyl radicals in aqueous solution was reported by Parke and Taylor (1956). Spin trapping techniques allowed for verification of the formation of hydrogen and hydroxyl radicals from water sonication. Then the “hot spot” theory was proposed to explain the thermal and radical phenomena promoted by ultrasound. This theory was widely accepted and consequently, the proliferation of ultrasound applications to the removal of organic pollutants from water considerably increased.

Due to the ability to produce radical species (mainly hydroxyl radical, $^{\bullet}OH$) that promote the degradation of refractory substances in water, ultrasound was considered an advanced oxidation process (AOP). Currently, this process is an alternative AOP with potential to eliminate chemical and microbiological pollutants in wastewaters as a tertiary treatment technology. Ultrasound has unique advantages compared to other AOPs, such as no addition of reagents, ease in handling, and differential or selective degradation according to the pollutant nature. [89]

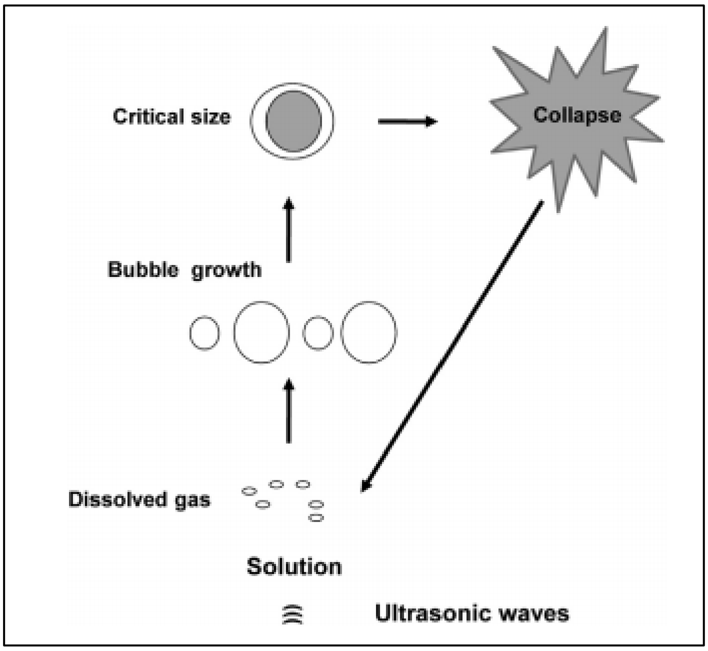


Fig.II.13 Cavitation phenomenon induced by ultrasound.

In the sonochemical process the main mechanism for the destruction of the organic pollutants is the formation of hydroxyl radicals, oxygen atoms and hydrogen atoms as a result of water pyrolysis. Ultrasonic pressure waves, made by ultrasonic irradiation (20−500 kHz) of aqueous solutions, result in the formation of vapor bubbles. These bubbles collapse violently after reaching a critical resonance size and create transient high temperatures (>5000 K) [90], high pressures (>1000 bar) and highly reactive radicals [90]. Thermal decomposition and numerous radical reactions take place during the degradation of water contaminants [91]. The critical parameters in sonolysis include pH, initial pesticide concentration, frequency, electric power and treatment time. Factors influencing the sonolytic degradation of azinphos-methyl and chlorpyrifos [92] and the degradation of insecticide diazinon by the Fenton and Fenton-like processes combined with ultrasound [93] were investigated. It was reported [92] that the initial concentration of pesticides had a strong effect on the removal efficiency of azinphos-methyl and chlorpyrifos. It was also observed that the degradation of pesticides decreased with the increase of the initial concentration of pollutant, while the pH variation did not affect the degradation of pesticides [92]. The use of ultrasound requires high-energy consumption, which results in a very low electrical efficiency compared to other AOPs technologies. Because of this, the hybrid technology, which combines ultrasound with other AOPs, can provide more efficiency and additional benefits. Wang and Shih [93] considered the effects of oxidants, such as persulphate ions ($S_2O_8^{2-}$) and hydrogen peroxide (H_2O_2), transition metal (including Co^{2+}, Ag^+ and Fe^{2+}), the initial concentrations of iron/H_2O_2 in the Fenton process and the temperature on the degradation of diazinon. The diazinon was effectively degraded, and enhanced the toxicity reduction, by the combination of the ultrasonic irradiation with the Fenton and Fenton-like processes [93].

In the following chapter, the experimental devices as well as procedures applied are presented.

CHAPTER III :

EXPERIMENTAL DEVICES

CHAPTER III – EXPERIMENTAL DEVICES

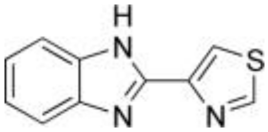
The objective of this chapter is to provide an overview of the experimental equipment employed in researching the photo-degradation of pesticides, along with the analysis techniques used. Initially, we will introduce and describe the characteristics of the selected products. Subsequently, we will discuss the experimental apparatus utilized and the corresponding protocols. Furthermore, we will present a range of analytical methods employed to assess the pesticides under examination and evaluate the experiments' effectiveness.

III .1 Products used:

a. The studied molecule:

Thiabendazole (4-1(1H-benzimidazol-2-yl)-1,3-thiazole (THB)) is a benzimidazole pesticide. It is also known as the food additive E233 from the class of preservatives. It is an antifungal and anthelminthic drug approved by the United States Food and Drug Administration (FDA). Preharvest and post-harvest treatment of fruit and vegetables with THB can reduce mold, pests and rot, and deterioration during storage and transport. Despite the fact that THB possesses low toxicity with a toxicity category of 4 (least toxic), the US Environmental Protection Agency (EPA) classified it as likely to be carcinogenic at doses high enough to cause disturbance of the thyroid hormone balance.[94]

Table III.1 Structure of the pesticides studied.

Pesticides (Purity%)	**Formula**	**Molar mass g/mol**	**Structure**	**Supplier**
Thiabendazole **(+98%)**	$C_{10}H_7N_3S$	201,248		Alfa Aesar Johnson Matthey

Tecto 500 SC, is a commercially available solution from the Benzimidazoles chemical family, contains 500 g/L of Thiabendazole as the active ingredient, while the remaining components consist of emulsifiers, developed by Syngenta for agricultural use. It is commonly referred to as 500 SC Tecto.

Fig III.1 Tecto 500 SC.

b. Photocatalysts:

In this research, we used Biochem Chemopharma's commercial Zinc Oxide (ZnO) powder (purity: 99 %) and TiO_2 (80% anatase and 20% rutile). This work entails studying the photodegradation of pesticides by coupling photo-reactor and microwave.

Table. III.2 Physicochemical characteristic of zinc oxide and titanium dioxide

Name	Zinc oxide	Titanium dioxide
Chemical formula	ZnO	TiO_2
Appearance	White solid (granules)	White Powder

The reaction mixture is stirred for 30 minutes before the photoreactor treatment (UV-A) to homogenize the solution. All of the (0, 10,20,30,60,90,120,150,180 min) samples are made in 5 ml increments. We proceeded with the filtration of the supernatant as it was hydrophilic and difficult to separate using centrifugation alone.

Preparation of ZnO–TiO_2 photo-catalysts :

The composite ZnO:TiO_2 was synthesized by solid-state reaction method. Pure ZnO and pure TiO_2 were measured in a molar ratio of 3:1. The starting compounds were not sensitive to moisture. The compounds were placed in an agate mortar and grounded for 2 h to achieve the homogeneity. After this, samples were calcined in a programmable furnace at different temperatures: 400 °C and 600 °C for a fixed period of time (2 hours) to accelerate the possible solid-state reactions. The calcined photo-catalyst samples were quickly placed in the desiccators to prevent absorption of moisture and further cooled down at room temperature. The calcined photo-catalyst samples were again grounded in agate mortar for characterization and photocatalytic measurements.

c. Other products:

Throughout this study, we utilized various analytical grade chemical reagents as shown in Table III.3.

Table III.3 List of the chemical products used.

Products (purity%)	**Formula**	**Molar mass (g/mol)**	**Supplier**
Sulfuric acid **(95-97%)**	H_2SO_4	98.08	Ridel-de Haen
Sodium oxalate **(98.8%)**	$Na_2C_2O_4$	133.99	Kokusan Chemical Works Ltd
Permanganate potassium **(99.4%)**	$KMnO_4$	158.03	Ridel-de Haen
Nitric acide (65%)	HNO_3	63.01	Ridel-de Haen
Soduim hydroxide pellets	NaOH	39.997	Biochem Chemopharma

III .2 Devices:

a. Photo-reactor (UV-A)

The UV-A irradiation has been realised by a **Vilbert Lourmat™ BLX-E365** photo-reactor **(**figure III.2**)** includes 6 lamps, The device has a wavelength interval [λ_{Min}=355 nm, λ_{Max}=375 nm] and an adjustable timer for up to 180 minutes.

Fig III.2 Vilbert Lourmat ™ BLX-E365 photo-reactor

b. Furnace

The calcination is preformed using a Nabertherm L3/11/C6 furnace.

Fig III.3 Furnace Linn High Term

c. Microwave:

The first coupling with the microwave was done using a SEVERIN MW-7825, its microwave power is 900 W with 5 levels (10%, 25%, 50%, 80% and 100%).

Fig III.4 Microwave SEVERIN MW-7825

d. Ultrasonics:

The second coupling with the ultrasound was done using a ATU GAT 600.

Fig III.5 Ultrasonics "ATU GAT 600"

III.3 Methods of Analysis:

III.3.1 The Permanganate index (Oxidability): [95]

This is the oxygen that is utilized to reduce potassium permanganate. The goal of this traditional test is to estimate the amount of organic matter in the water.

Experimental protocol:

The protocol is divided into four steps: After acidifying the sample and heating it to 98 ° C, add the potassium permanganate and continue boiling for 10 minutes (15 seconds): during this phase, the potassium permanganate will be consumed by the oxidizable materials in the sample; after 10 minutes (15 seconds), add excess sodium oxalate to reduce the potassium permanganate that has not been consumed, and measure the result. As a consequence, it is a potassium permanganate return dosage that has not been consumed by oxidizable materials.

$$\mathbf{MnO^{4-} + 8\,H^{+} + 5\,e^{-} \longrightarrow Mn^{2+} + 4\,H_2O}$$

Reduction of the excess permanganate by an excess of oxalate, then determination of the excess oxalate by permanganate, according to the following reactions:

$$\mathbf{C_2O_4^{2-} + MnO4^{-} + 8\,H^{+} + 5\,e^{-} \longrightarrow Mn^{2+} + 2\,e^{-} + 4\,H_2O + 2\,CO_2}$$

The overall titration equation being:

$$\mathbf{2\,MnO^{4-} + 5\,C_2O_4^{2-} + 16\,H^{+} \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O}$$

Place a 25 ml test portion in the test Beaker. Add 5 ml of 2 mol / L sulfuric acid, mix carefully. Placing the Beaker in the heating system for 10 min then add 5 ml of the potassium permanganate solution 0.01 N. At the end of 10 minutes (± 15 seconds), add 5 ml of 0.01N sodium oxalate solution and wait the discoloration of the solution. Titrate the still hot solution with 0.01 N potassium permanganate solution until the appearance of a pale pink colour that persists for about 30 s. Note the volume of permanganate solution consumed, either:

V_0: the volume of potassium permanganate used, V_0 must be less than 0.3 ml.

To check the title of the potassium permanganate solution, Add 5 ml solution of oxalate of sodium 0.01 N to the end of the blank test. If necessary, warm the solution to 80°C.

Titrate with the solution of potassium permanganate to the apparition of a persistent pink colouring about 30 s.

V_1 : At the same time as the test, carry out a blank test under the same conditions but on 25 ml of distilled water.

V_2 : the volume used. The title (or normality) of the potassium permanganate solution is then:

$$t = \frac{5 \times 0.01}{V2}$$

The title t must be very close to 0.01 N. In the case otherwise, check the cleanliness of the equipment. If it's not the cause, proceed with a new preparation of the titrated solutions (oxalate and permanganate).

Expression of results:

The permanganate Index (PI), expressed in milligrams of oxygen per litre of sample, can then be calculated as follows:

$$\mathbf{IP\ (mg\ O_2/L) = (V_1 - V_0).\ t.\ 8.1000\ /\ V_{sample}}$$

Expression in which we can replace t by its value calculated previously, with:

t : normality of the potassium permanganate solution used (close to 0.01 N).

V_1 : volume in ml of the potassium permanganate solution consumed for the sample.

V_0 : volume in ml of the potassium permanganate solution consumed for the blank test .

V_2 : volume in ml of the potassium permanganate solution used for the titration of the solution.

V_{sample} : volume in ml of sample used for the test

8 : oxygen equivalent, expressed in mg, of one millilitre of a normal solution of potassium permanganate.

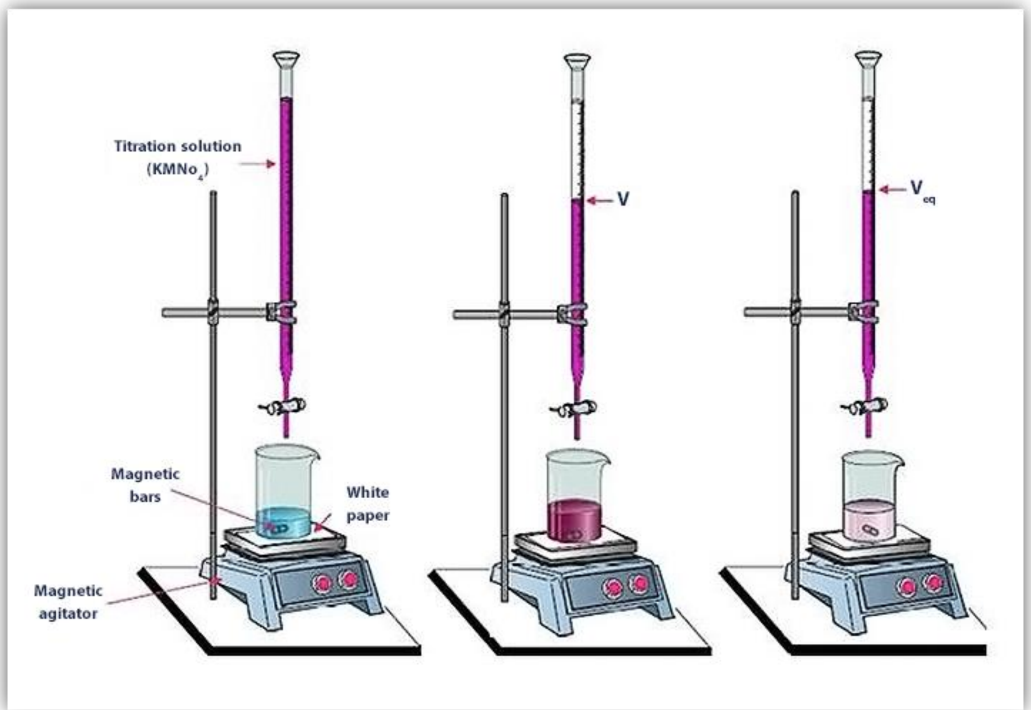


Fig III.6 Experimental protocol for the permanganate index until the pale pink colour is obtained. [96]

Note: Thoroughly wash hot glassware with an acidic solution of potassium permanganate. Check the condition of the glassware in proceeding to a blank test. Reserve glassware for the exclusive use of the permanganate index.

III.3.2 Ultraviolet-visible absorption spectroscopy (UV-Vis) :

Spectroscopy results from the interaction between matter and an electromagnetic wave [97] Spectroscopy has practically replaced the ancestral qualitative study of chemical compounds, it allows the determination of the structure on very small quantities of matter, it uses non-destructive methods, the precision of the determinations is extreme. Each of the specific areas of the electromagnetic radiation or substantially matches a type of spectroscopy which is based on an interaction specific to the material with the radiation [98].

- **Law of absorption of radiation:**

Quantitative analysis is possible by considering the intensities of the absorption bands. The absorption of the light by the sample, at a frequency determined, is in fact connected to the product concentration in a solution by the equation:

$$A = \varepsilon.C.L = -\log T = \log (Io/I)$$

With: **A**: Absorbance, **C**: Molar concentration, **ε**: Absorption coefficient, **L**: Optical path, **T**: Transmittance, **I $_0$**: incident radiation and **I**: transmitted radiation.

In a molecule, the electronic transitions have place in the region of ultraviolet (180- 200 nm) and visible (400-800nm). An electronic transition is analyzed as a change of population between an orbital molecular fundamental HOMO (Highest Occupied molecular Orbital) and an excited molecular LUMO (Lowest Unoccupied Molecular Orbital) [99]. When it takes place, matter absorbs a photon whose energy corresponds to the energy difference between the fundamental term and an excited term. But not all energetically possible transitions are allowed.

The concentration of Thiabendazole has been measured by spectroscopy absorbing ultraviolet-visible (UV-Vis). The analyses were carried out on UV-Visible systems model “Shimadzu, UV mini-1240”.

Thiabendazole is detected in the ultraviolet range, a scan is performed from 250 to 400 nm (Fig. III.7) to determine the wavelength which corresponds to the maximum absorption (λ_{max}).

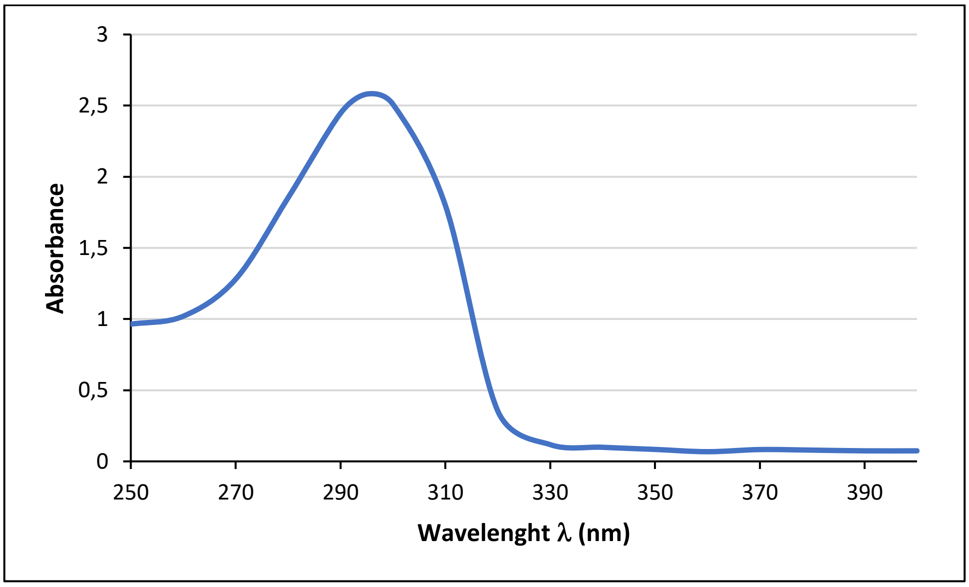


Fig III.7 Absorption curve of a solution [THB]=0.5mmol/L as a function of the wavelength λ.

λ max = 296 nm.

The calibration curve obtained is shown in figure III.8.

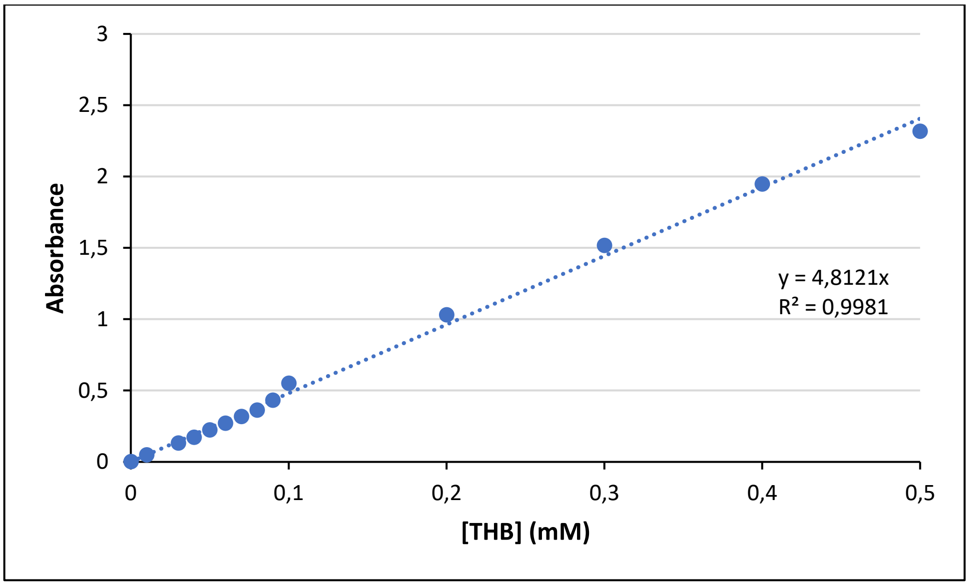


Fig III.8 Calibration line of the THB detected by UV-Vis.

In the next chapter the results of our study are presented, discussed and interpreted.

CHAPTER IV:

RESULTS AND DISCUSSION

CHAPTER IV – RESULTS & DISCUSSION

In this chapter the results of the photocatalysis of Thiabendazole in its commercial solution, using two solid catalysts (ZnO and TiO_2) and their mixture as well as coupling the process with microwave or ultrasonic treatment will be presented, discussed and compared.

The concentrations of the pesticide used in this study are chosen on the basis of their user manuals, $[THB]_0 = 0.5$ mM and $[THB]_0 = 0.1$ mM.

IV.1. THB Photodegradation:

Initially, we conducted the photodegradation of Thiabendazole using its commercial solution.

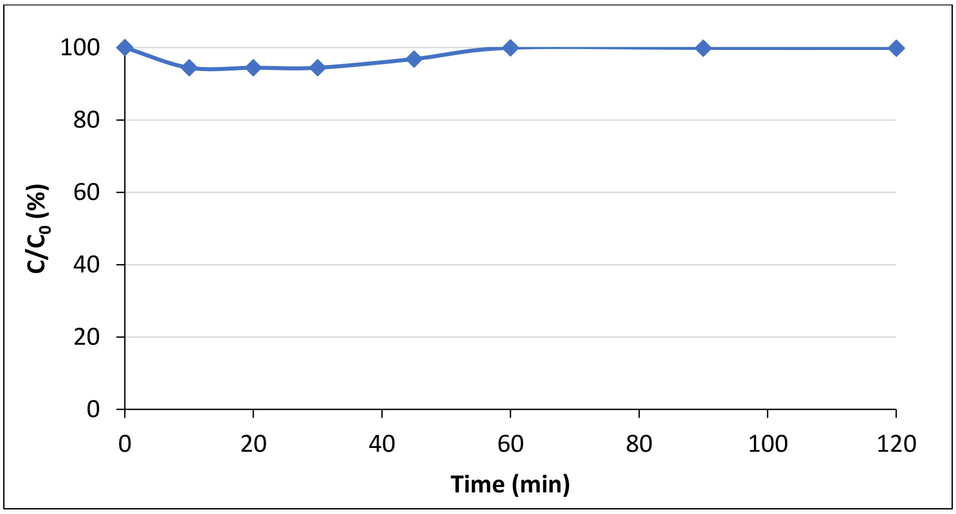


Fig IV.1 Temporal variation of the active phase [THB] of TECTO during its photodegradation. Operating Conditions: $[THB]_0 = 0.5$ mM, V=200 mL, T= 20 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

Fig IV.1 shows that THB does not degrade by photodegradation and remains stable.

IV. 2 Photocatalysis:

a - Using ZnO:

In this study, several experiments were carried out in order to optimize the operating conditions in order to eliminate the THB as much as possible, the first catalyst used is ZnO.

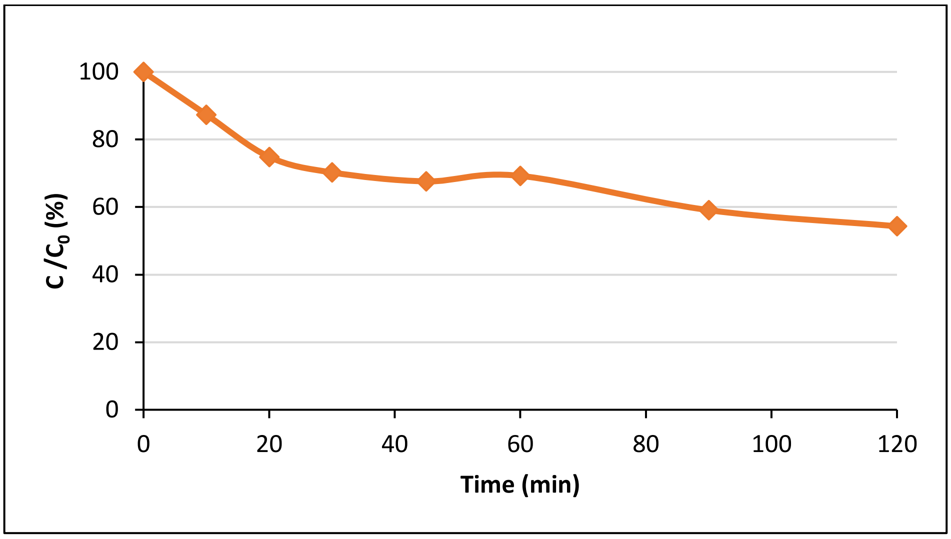


Fig IV.2 Temporal variation of the active phase [THB] of TECTO during its photocatalysis using [ZnO]= 5g/L. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 250 mL, T = 20 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

According to this figure, the degradation of THB reached 45% after 2 hours of the experience for 5 g/L of ZnO.

b - Using TiO_2:

The second catalyst used is TiO_2, its concentration was chosen $[TiO_2]$ = 200 mg/L, the results are presented below:

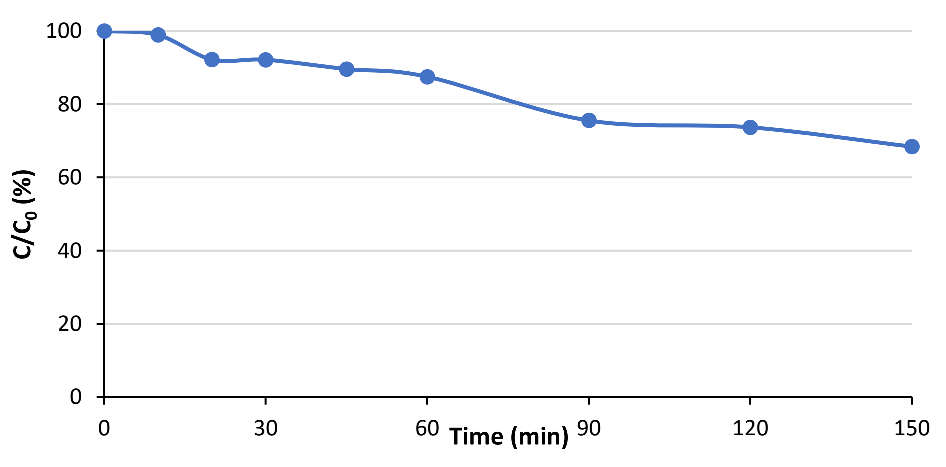


Fig IV. 3 Temporal variation of the active phase [THB] of TECTO during its photocatalysis using $[TiO_2]$ = 200 mg/L. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 200 mL, T = 20 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

The degradation of THB reached more than 30% for 200 mg/L of TiO_2, the catalytic efficiency is low but we remind that we work with the mass form which will lead us to use it in doping form in the second part of this work.

c - Using (ZnO : TiO_2) mixture :

In order to optimize our process, we opted for the mixture of our two catalysts (see the part "Preparation of ZnO-TiO_2 mixed oxides" in chapter III) in order to increase their structural properties like specific surface. which are important factors in heterogeneous catalysis.

In this work, we used the molar ratio which gave the best efficiency according to the study conducted by M. AGHAMIR and M. OUARDI last year which is: (ZnO:TiO_2) = (3:1) under two calcination temperatures 400 and 600°C.[100]

The results obtained are represented in the Fig VI.4, noting that we worked with the optimal concentration of catalysts (1 g/L) with an initial concentration of $[THB]_0 = 0.5$ mM.

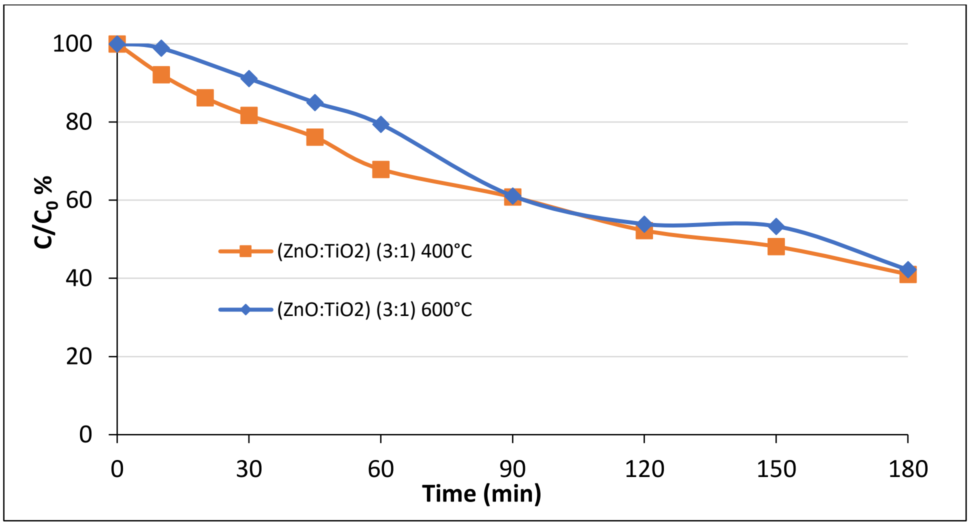


Fig IV. 4 Temporal variation of the active phase [THB] of TECTO during its photocatalysis using [ZnO:TiO_2] (3:1) = 1 g/L. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 200 mL, T = 20 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

The two photocatalysts calcined at different temperatures (400 and 600°C) gave the same efficiency 59% and 58% respectively, which confirms that the doping of the two catalysts increased the photocatalytic power of the process, the observed outcomes were found to lack satisfactory efficiency, thus necessitating the integration of a supplementary treatment through coupling in the subsequent segment

IV. 3 Coupling Photocatalysis with Microwave:

In this part, we used the time (1, 5 min) and the power of the Microwave (10, 100%), the obtained results are represented here:

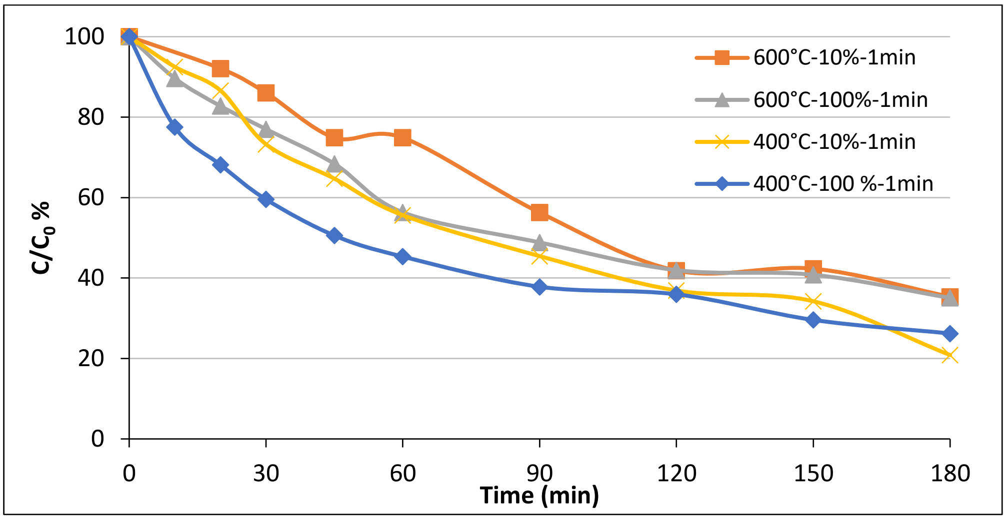


Fig IV. 5 Temporal variation of the active phase [THB] of TECTO during its photocatalysis using [ZnO:TiO$_2$] (3:1) = 1 g/L coupling with 1 min of Microwave (10, 100%). Operating Conditions: [THB]$_0$ = 0.5 mM, V=200 mL, T=20°C, UV-A [355 nm< λ < 375 nm].

The Fig IV. 5 shows that the [ZnO:TiO$_2$] (3:1) mixture calcined at 400°C gives the best efficiency 80% and 74% for coupling Microwave power of 10 and 100% respectively against 65% for those calcined at 600°C after 3 hours of photocatalysis.

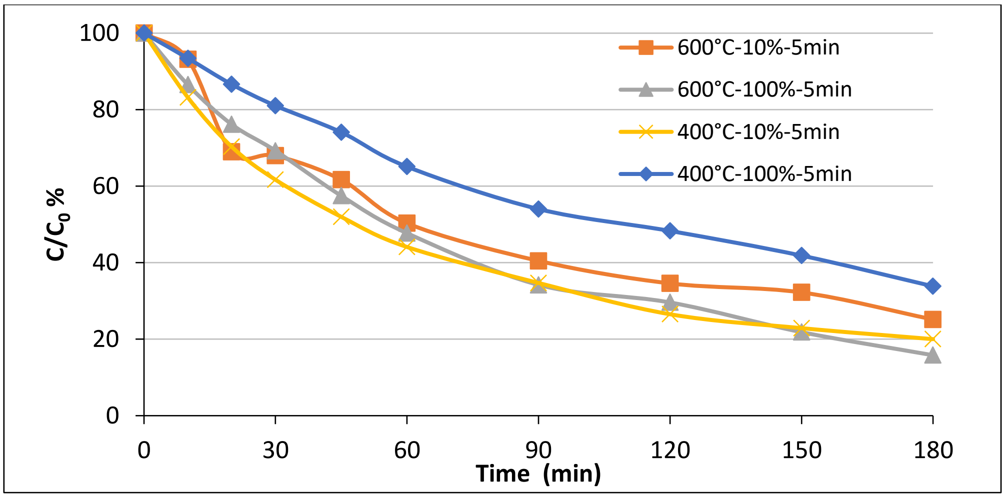


Fig IV. 6 Temporal variation of the active phase [THB] of TECTO during its photocatalysis using [ZnO:TiO$_2$] (3:1) = 1 g/L coupling with 5 min of Microwave (10, 100%). Operating Conditions: [THB]$_0$ = 0.5 mM, V = 200 mL, T = 20°C, UV-A [355< λ<375 nm].

The Fig IV. 6 indicates that the [ZnO:TiO$_2$] (3:1) mixture calcined at 600°C gives the best efficiency 85% with coupling 100% of Microwave power against those calcined at 400°C with80% coupling 10% of Microwave power then 75% for those calcined at 600°C with coupling 10% of Microwave power coupling and finally 64% for 400°C with Microwave power of 100%.

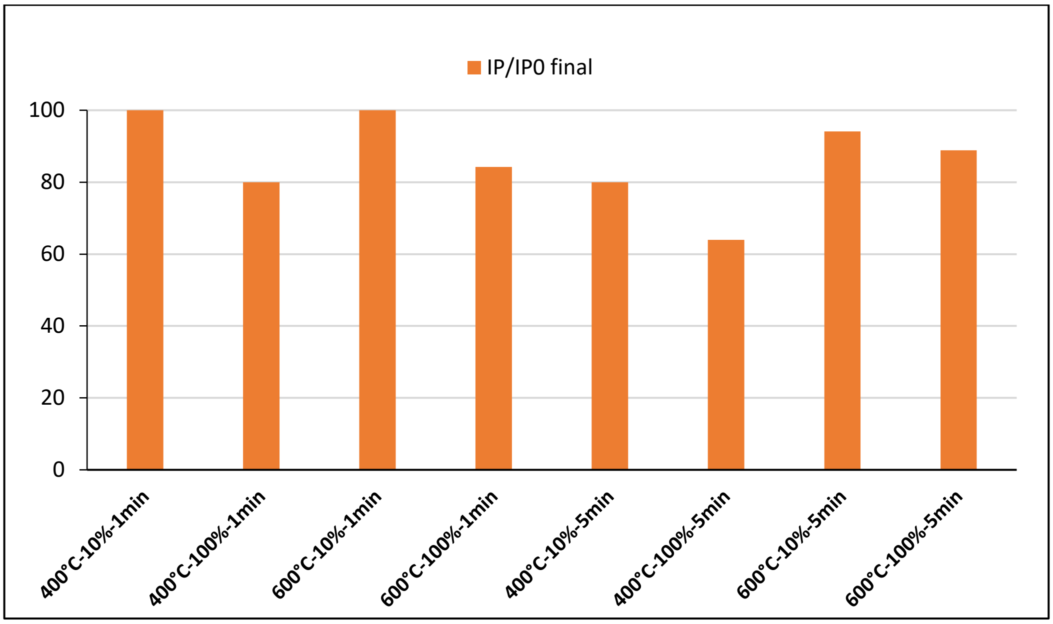


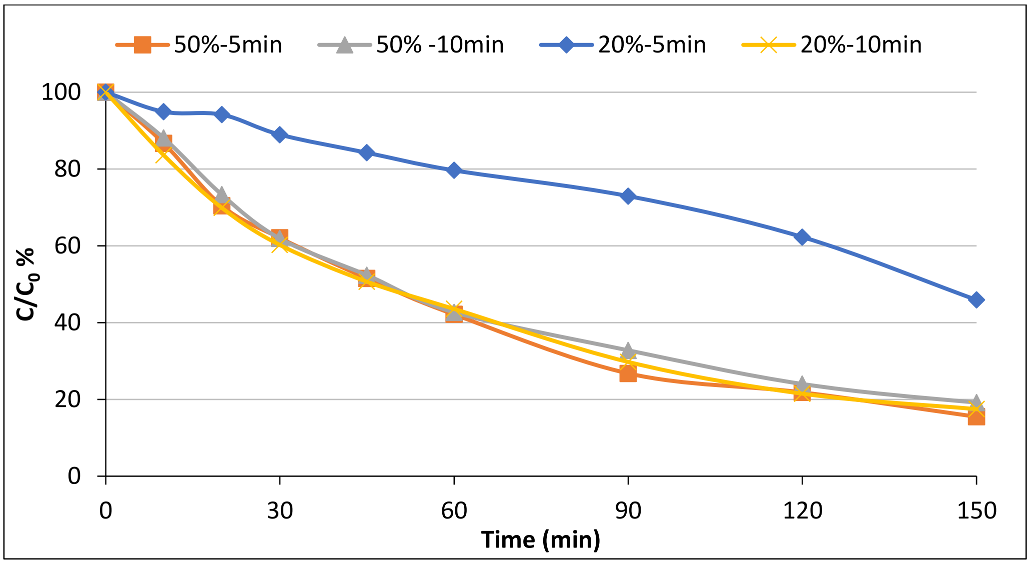
Fig IV. 7 Effect of the coupling with Microwave on temporal variation of the permanganate index during the photocatalysis of THB. Operating Conditions: $[THB]_0 = 0.5$ mM, $[ZnO:TiO_2](3:1) = 1$g/L, T=20°C, V = 200 mL, UV-A ([$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

The mineralization of the solution reaches 36% in the 5 min-100%, 20% for the 5 min-10% and 1 min-100% of microwave using the mixture [ZnO:TiO$_2$](3:1) calcined at 400°C, 15% in in the 1 min-100%, 12% for in the 5 min-100%and 6% in in the 5 min-10%of microwave using the mixture [ZnO:TiO$_2$](3:1) calcined at 600°Cafter 3 hours of photocatalysis. For the 1 min-10% of microwave, there is no variation of the IP Index.

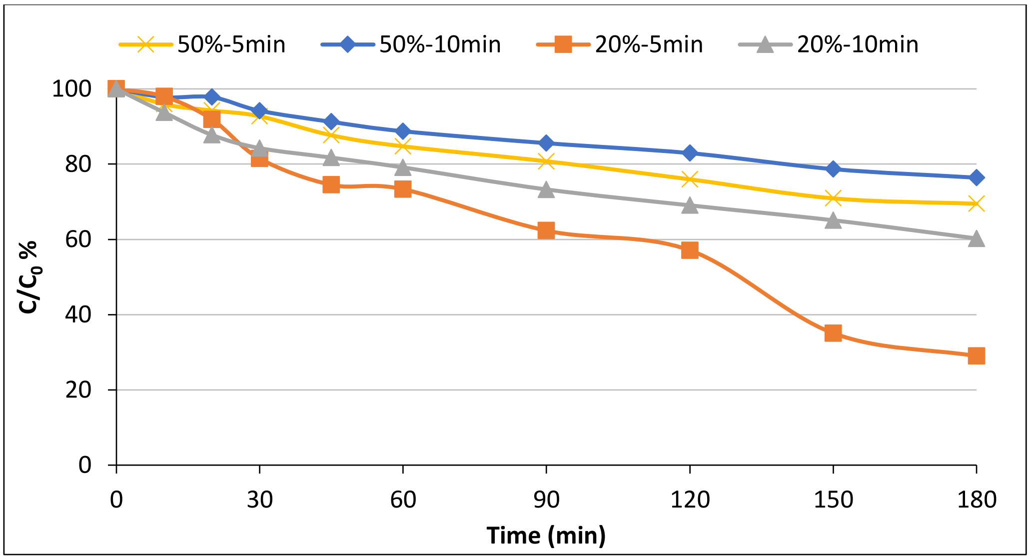
IV. 4 Coupling Photocatalysis with Ultrasonics:

In this process, the time (5, 10 min) and the power of the ultrasonics (20, 50%) are used, the obtained results are represented in Fig IV. 8.

The first figure (Fig IV. 8: A) indicates that the elimination of THB reaches 85%,83% and 81% for 50%-5min, 20%-10min and 50%-10min of ultrasonic treatment coupling after 150 minutes of photocatalysis, against 55% for 20%-5min of ultrasonic treatment after the same time of photocatalysis of $[THB]_0$ = 0.1 mM.



A : $[THB]_0$ = 0.1 mM



B: $[THB]_0$ = 0.5 mM

Fig IV. 8 Temporal variation of the active phase [THB] of TECTO during its photocatalysis using $[ZnO:TiO_2]$ (3:1) = 1 g/L calcined at 600°Candcoupling with Ultrasonics. Operating Conditions: V = 200 mL, T = 25 ° C,UV-A [λ_{Min} = 355 nm, λ_{Max} = 375 nm]. A: $[THB]_0$ = 0.1 mM, B: $[THB]_0$ = 0.5 mM

The second figure (Fig IV. 8: B) shows that the elimination of THB reaches 25%,30% and 40% for 50%-10min, 50%-5min and 20%-10min of ultrasonic treatment coupling, against 71% for 20%-5min of ultrasonic treatment after the 3 hours of photocatalysis of $[THB]_0$ = 0.5 mM.

The Fig. IV.9 indicates that the mineralization of the solution reaches 60% in the 20%-10min and 50%-5min of ultrasonics, 15% in in the 50%-10min and 20%-5min for ultrasonics using the mixture [ZnO:TiO_2](3:1) calcined at 600°C after 3 hours of photocatalysis of $[THB]_0$ = 0.1 mM and 0.5 mM. For the other experiences, there is no variation of the IP Index.

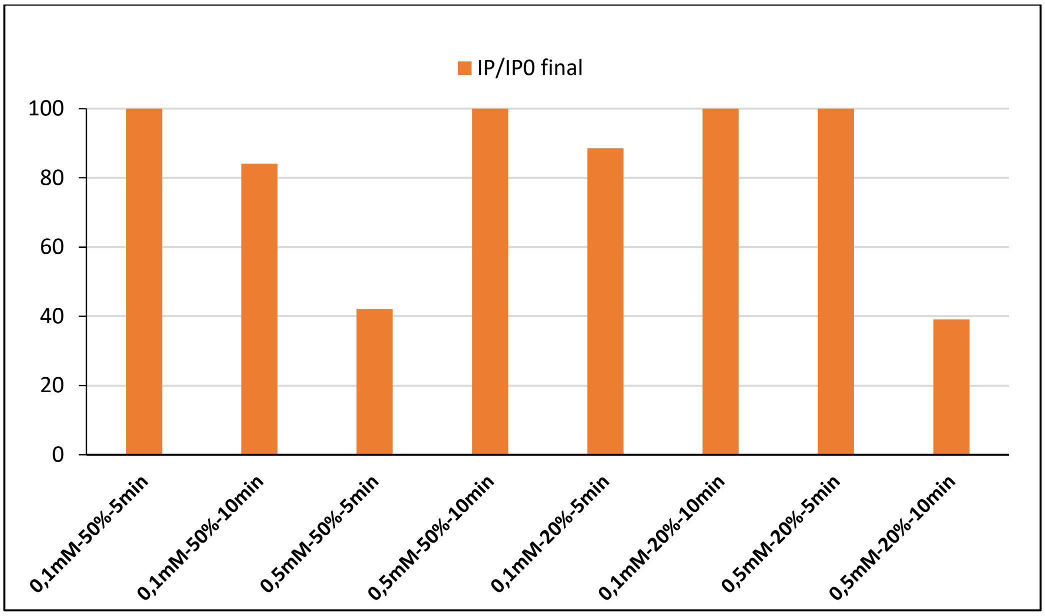


Fig IV. 9 Effect of the coupling with ultrasonics on temporal variation of the permanganate index during the photocatalysis of THB. Operating Conditions: $[THB]_0$ = 0.1 mM or 0.5 mM, [ZnO:TiO_2](3:1) = 1g/L, T=20°C, V = 200 mL, UV-A ([λ_{Min} = 355 nm, λ_{Max} = 375 nm].

IV.5 pH effect:

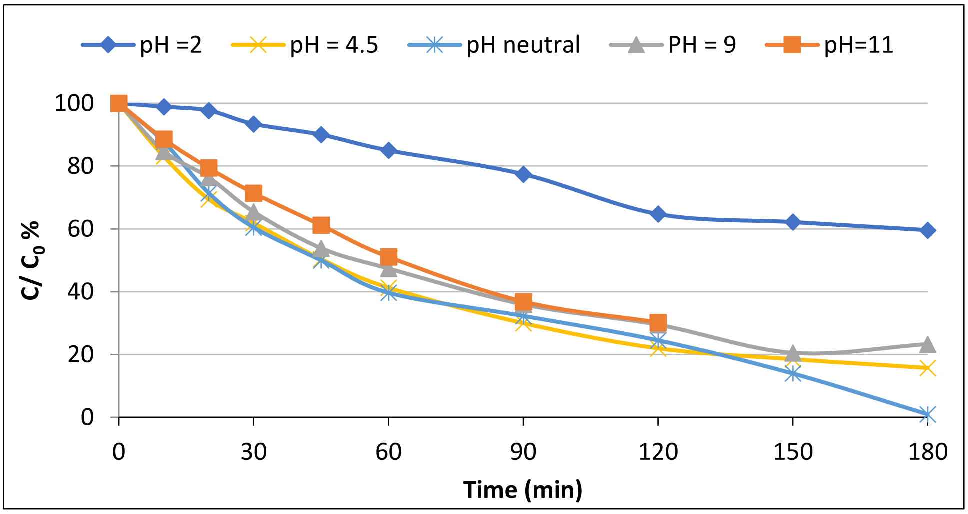


Fig IV. 10 Effect of the pH on the temporal variation of the active phase [THB] of TECTO during its photocatalysis. Operating Conditions: $[THB]_0$ = 0.1 mM, [ZnO:TiO_2](3:1) = 1g/L, T=20°C, V = 200 mL, UV-A ([λ_{Min} = 355 nm, λ_{Max} = 375 nm].

The previous experiments were all carried out under neutral pH (6.5), the change of medium has major consequences on the production of hydroxyl radicals and the behaviour of the catalyst, for this we carried out four other experiments, two of them, under an acidic medium near the addition of 8mL and 0.1 mL of HCl (0.1M) pH of the solution became 2 and 4.5 and the others were in a basic medium with a pH of 9 and 11 by adding 1.5 mL and 2.5 mL of NaOH (1M).The results are shown in figures IV.10 and IV.11.

The figure indicates that the elimination of THB is slow (40%) in very acidic (pH = 2), on the other hand it reaches 70% in a very basic medium (pH=11) after 2 hours,76% in basic medium (pH = 9),85% for pH=4.5 and 99% in the neutral medium after 3 hours of photocatalysis.

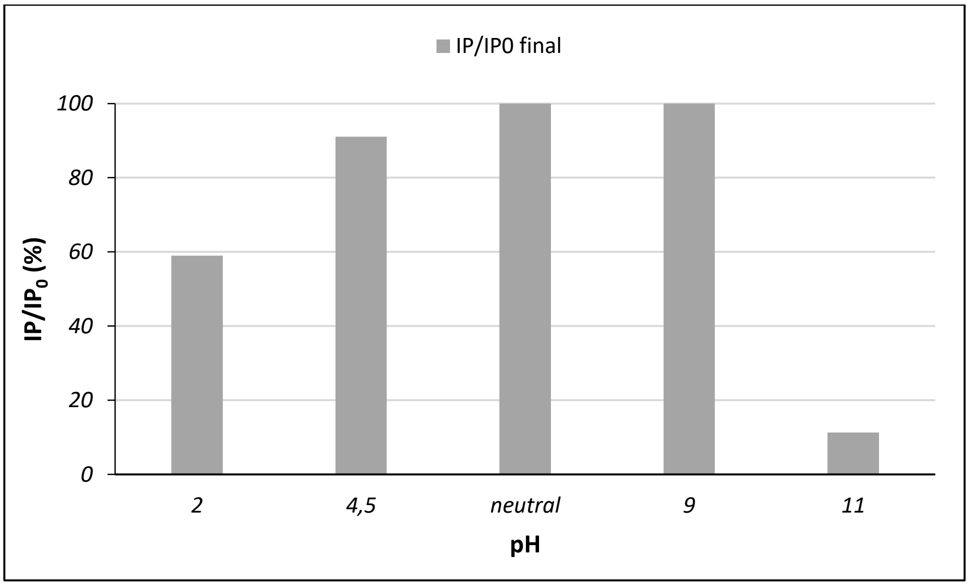


Fig IV. 11 Effect of the pH on temporal variation of the permanganate index during the photocatalysis of THB. Operating Conditions: $[THB]_0 = 0.1$ mM, $[ZnO:TiO_2](3:1) = 1$g/L, T=20°C, V = 200 mL, UV-A ([$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

The Fig IV. 11 shows us that the mineralization of the solution reaches 88% in the very basic medium and 41% in the very acidic medium after 3 hours of photocatalysis, this can be explained by the presence of hydroxyl ions in the basic medium which increases this mineralization unlike the acidic medium. For the neutral medium, there is no variation of the IP Index.

IV. 6 Kinetic Study of THB Photocatalysis:

a - Using ($ZnO:TiO_2$) mixture :

For the photocatalysis using the ($ZnO:TiO_2$) mixture calcined in 400°C and 600°C, the degradation of THB was determined using a pseudo-first-order kinetics model according to the following equation: $Ln\,\frac{C_0}{C} = kt$ (IV-1) with k: rate constant of the degradation reaction.

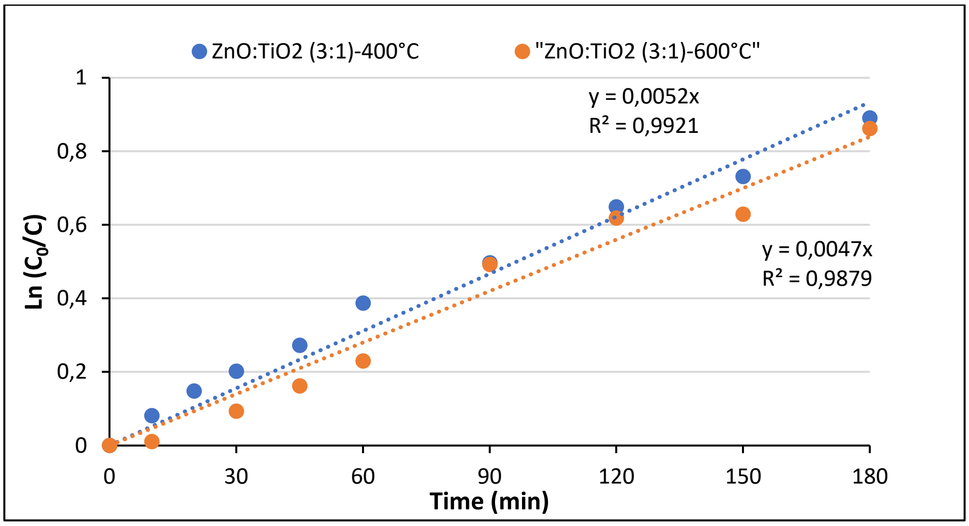


Fig IV. 12 Kinetic modeling of the THB active phase removal operation in TECTO by photocatalysis using [$ZnO:TiO_2$] (3:1) = 1 g/L. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 200 mL, T = 20 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

b. pH effect:

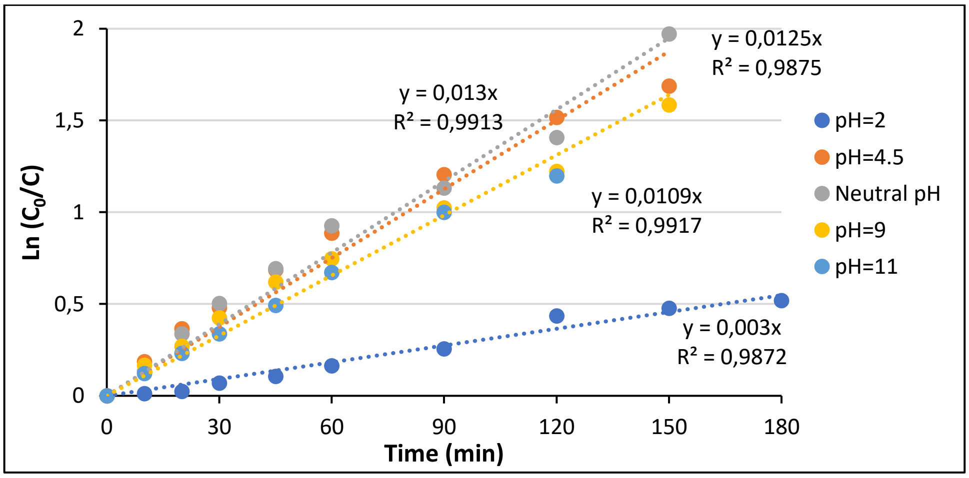
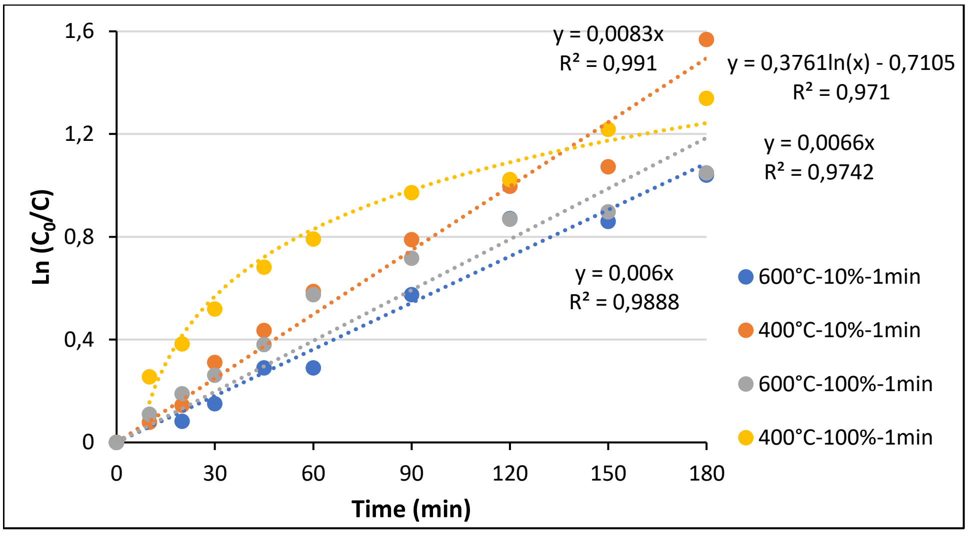


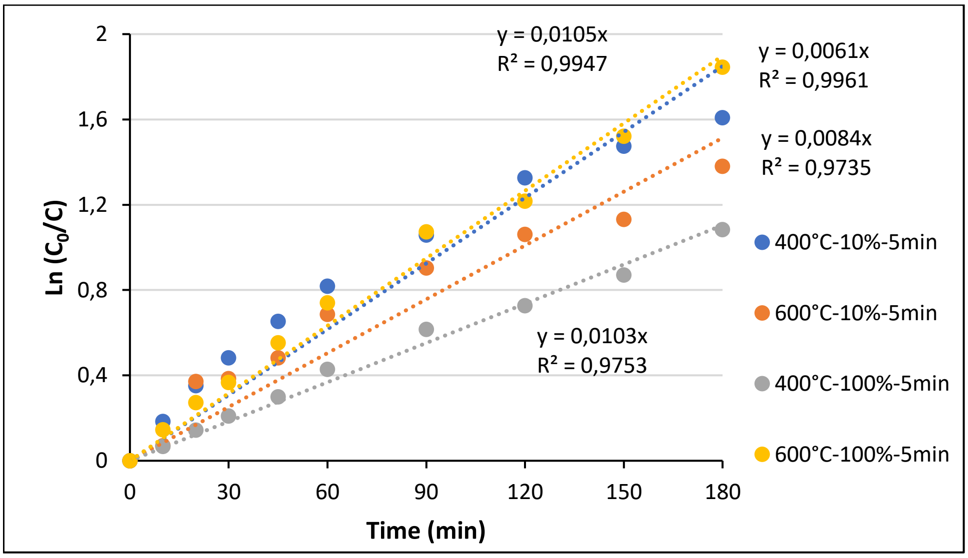
Fig IV. 13 Kinetic modeling of the THB active phase removal operation in TECTO by photocatalysis using [$ZnO:TiO_2$] (3:1) = 1 g/L in different pH. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 200 mL, T = 20 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

According to the Fig .13, the degradation of THB was determined using a pseudo-first-order kinetics model according to equation (IV-1) for all pH mediums.

c. Coupling Photocatalysis with Microwave:



A : Microwave time (1min)



B: Microwave time (5min)

Fig IV. 14 Kinetic modeling of the THB active phase removal operation in TECTO by coupling Microwave and Photocatalysis using [ZnO:TiO_2] (3:1) = 1 g/L. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 200 mL, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm], T=20°C.

The Fig VI.14 shows that all experiences of coupling Microwave and Photocatalysisusing [ZnO:TiO_2] (3:1) was determined using a pseudo-first-order kinetics model according to equation (IV-1) except the one we used 1min-100% and [ZnO:TiO_2] (3:1) calcined at 400°C, the degradation follows the kinetic model of the pseudo second order according to the following equation: $\frac{1}{C} = \frac{1}{C_0} + kt$…. (IV-2) which is represented in the Fig. IV.15.

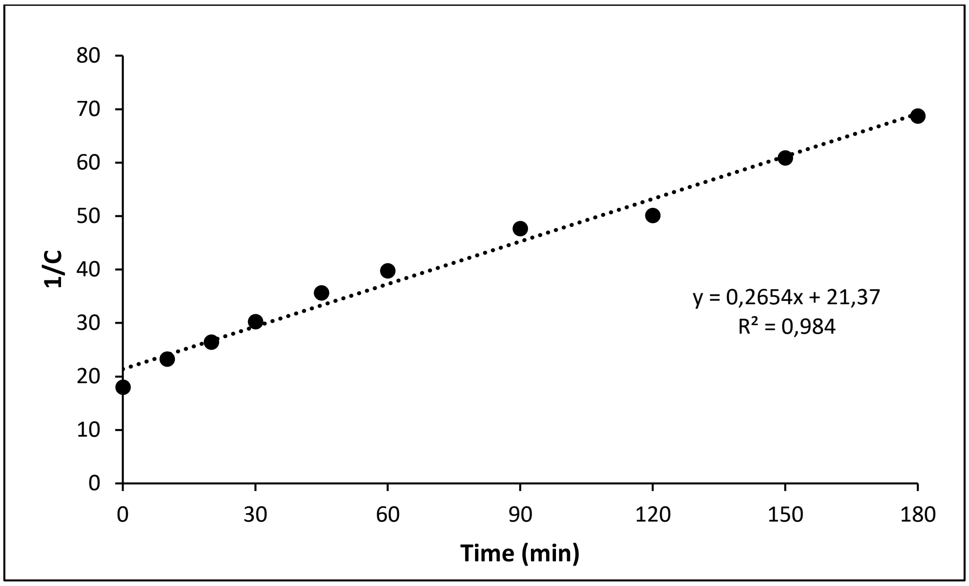
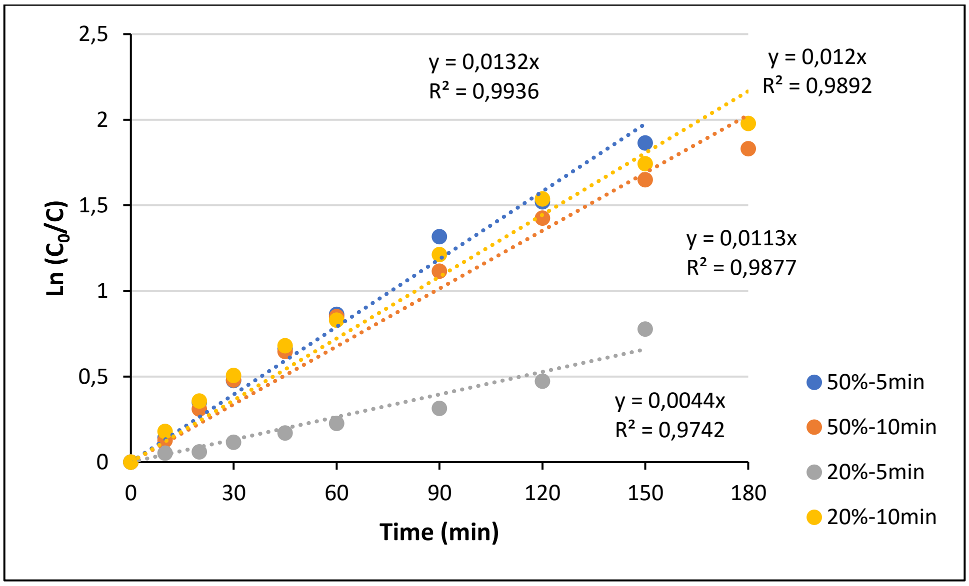
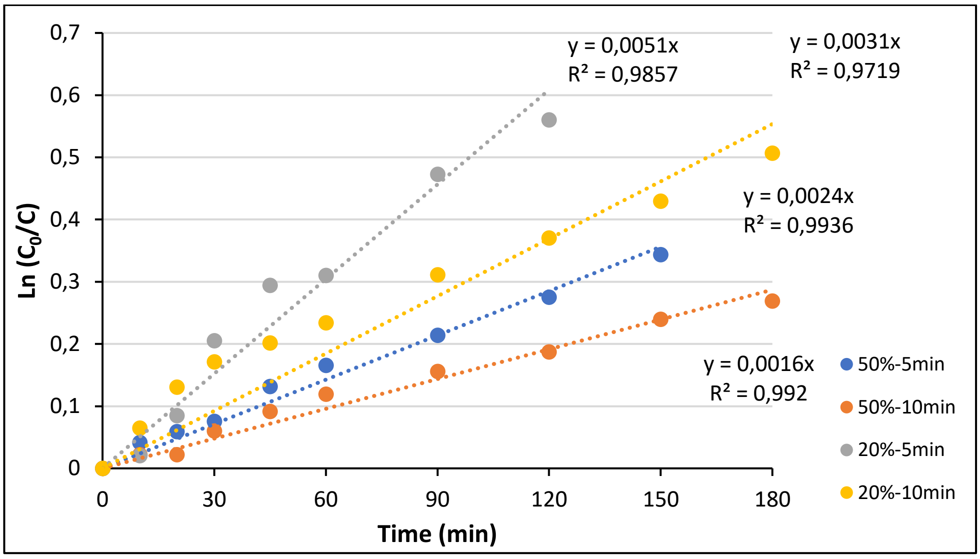


Fig. IV.15 Pseudo second order modeling of the THB active phase removal operation in TECTO by coupling Microwave (1min-100%) and Photocatalysis using (ZnO:TiO$_2$) (3:1) calcined at 400°C.Operating Conditions: [THB]$_0$ = 0.5 mM, V = 200 mL, T = 20 ° C, UV-A [λ $_{Min}$ = 355 nm, λ $_{Max}$ = 375 nm]. [ZnO:TiO$_2$] (3:1) = 1 g/L.

d. Coupling Photocatalysis with Ultrasonics:



A : [THB]$_0$ = 0.1 mM



B: [THB]$_0$ = 0.5 mM

Fig IV. 16 Kinetic modeling of THB active phase removal in TECTO by coupling Ultrasonics and Photocatalysis using [ZnO:TiO_2] (3:1) = 1 g/L.A: [THB]$_0$ = 0.1mM, B: [THB]$_0$ = 0.5mM Operating Conditions: V = 200 mL, T=20°C, UV-A [355 nm $<\lambda<$ 375 nm].

All the experiences of coupling Ultrasonics and Photocatalysisusing [ZnO:TiO_2] (3:1) are was determined using a pseudo-first-order kinetics model according to equation (IV-1).

Finally, we noted that: The coupling of Microwave or Ultrasonics with Photocatalysis of THB in aqueous medium was studied using a photoreactor and the mixture of two catalysts.

First, the degradation of THB reached 45% after 2 hours of the experience for 5 g/L of ZnO and more than 30% for 200 mg/L of TiO_2.

Then, the two photocatalysts were mixed and calcined at different temperatures (400 and 600°C), they gave the same efficiency 59% and 58% respectively, which confirms that the doping of the two catalysts increased the photocatalytic power of the process

In this study, we realize two coupling methods with photocatalysis:

The first was the Microwave treatment which we used different times (1, 5 min) and powers (10, 100%), the [ZnO:TiO_2] (3:1) mixture calcined at 600°C gives the best efficiency 85% with 100% power of Microwave against those calcined at 400°C with 80% of 10% power of Microwave then 75% for those calcined at 600°C with 10% power of Microwave and finally 80% and 74% for 10 and 100% power of Microwave respectively after 3hours of photocatalysis.

The mineralization of the solution reaches 36%, 15% and there was no variation of the IP index which is a bad result for the enhancing of the toxicity of the solution.

The second was the Ultrasonics which we used different times (5, 10 min) and powers (20, 50%), the best results were 85%,83% and 81% of elimination of $[THB]_0$ = 0.1 mM for 50%-5min, 20%-10min and 50%-10min, of ultrasonic treatment coupling after 150 minutes of photocatalysis and 71% for 20%-5min of ultrasonic treatment after the 3 hours of photocatalysis of $[THB]_0$ = 0.5 mM.

For the variation of IP, the solution reaches 60% of mineralization in the 20%-10min and 50%-5min of ultrasonics using the mixture $[ZnO:TiO_2]$(3:1) calcined at 600°C after 3 hours of photocatalysis of $[THB]_0$ = 0.5 mM.

The study of pH effect indicates that the elimination of THB is slow in very acidic, fast in basic medium and the acidic one (pH=4.5) but the best result is 99% in the neutral medium after 3 hours of photocatalysis.

The mineralization of the solution reaches 88% in the very basic medium, this can be explained by the presence of hydroxyl ions in the basic medium which increases this mineralization unlike the acidic medium. For the neutral medium, there is no variation of the IP Index.

For the kinetic study, all the experiences was determined using a pseudo-first-order kinetics model according to equation (IV-1) except the one we used 1min-100% of microwave and $[ZnO:TiO_2]$ (3:1) calcined at 400°C, the degradation follows the kinetic model of the pseudo second (equation IV-2).

Finally, we can say that the coupling of Photocatalysis with Microwave and Ultrasonics has improved the efficiency of the process from 58% to 85% of THB removal. For the mineralization only the coupling with Ultrasonics gave us a good result with 60% against 30% for Microwave treatment.

GENERAL CONCLUSION

GENERAL CONCLUSION

This work was carried out in the laboratory of the Department of Process Engineering at the University of Saida.

Its first part was devoted to the bibliographical study of treatment methods specific to pollutants that are difficult to degrade such as pesticides, in the second, the coupling of photocatalysis with other treatment to remove THB from aqueous medium was studied using a photoreactor and a mixture of two catalysts under different conditions, in the end, we noticed the following points:

- First, the degradation of THB reached 45% after 2 hours of the experience for 5 g/L of ZnO and more than 30% for 200 mg/L of TiO_2.

- Then, the two photocatalysts were mixed and calcined at different temperatures (400 and 600°C), they gave the same efficiency 59% and 58% respectively, which confirms that the doping of the two catalysts increased the photocatalytic power of the process.

In this study, we realize two coupling methods with photocatalysis:

- The first was the Microwave treatment which we used different times (1, 5 min) and powers (10, 100%), the [ZnO:TiO_2] (3:1) mixture calcined at 600°C gives the best efficiency 85% with 100% power of Microwave against those calcined at 400°C with 80% of 10% power of Microwave then 75% for those calcined at 600°C with 10% power of Microwave and finally 80% and 74% for 10 and 100% power of Microwave respectively after 3 hours of photocatalysis.

- The mineralization of the solution reaches 36%, 15% and there was no variation of the IP index which is a bad result for the enhancing of the toxicity of the solution.

- The second was the Ultrasonics which we used different times (5, 10 min) and powers (20, 50%), the best results were 85%, 83% and 81% of elimination of $[THB]_0$ = 0.1 mM for 50%-5min, 20%-10min and 50%-10min, of ultrasonic treatment coupling after 150 minutes of photocatalysis and 71% for 20%-5min of ultrasonic treatment after the 3 hours of photocatalysis of $[THB]_0$ = 0.5 mM.

- For the variation of IP, the solution reaches 60% of mineralization in the 20%-10min and 50%-5min of ultrasonics using the mixture [ZnO:TiO_2] (3:1) calcined at 600°C after 3 hours of photocatalysis of $[THB]_0 = 0.5$ mM.

- The study of pH effect indicates that the elimination of THB is slow in very acidic, fast in basic medium and the acidic one (pH=4.5) but the best result is 99% in the neutral medium after 3 hours of photocatalysis.

- The mineralization of the solution reaches 88% in the very basic medium, this can be explained by the presence of hydroxyl ions in the basic medium which increases this mineralization unlike the acidic medium. For the neutral medium, there is no variation of the IP Index.

- For the kinetic study, all the experiences was determined using a pseudo-first-order kinetics model according to equation (IV-1) except the one we used 1min-100% of microwave and [ZnO:TiO_2] (3:1) calcined at 400°C, the degradation follows the kinetic model of the pseudo second (equation IV-2).

- Finally, we can say that the coupling of Photocatalysis with Microwave and Ultrasonics has improved the efficiency of the process from 58% to 85% of THB removal. For the mineralization only the coupling with Ultrasonics gave us a good result with 60% against 30% for Microwave treatment.

The perspectives of this work are:

- Use the ZnO and TiO_2 photocatalysts in their supported form in order to reduce the cost of the process and at the same time increase the specific surface area and thus increase the number of active sites.

- Estimate the toxicity of the solution studied by measuring the COD and the BOD_5 and thus calculate the ratio of Biodegradability BOD_5/COD during the treatment to assess the risk of the process.

BIBLIOGRAPHIC REFERENCES

BIBLIOGRAPHIC REFERENCES

[1] National Geographic. (n.d.). *Water*. Retrieved from: https://www.nationalgeographic.com/environment/freshwater/water/

[2] USGS. (n.d.). *Water Science School*. Retrieved from https://www.usgs.gov/special-topic/water-science-school.

[3] Letchinger M, (2000), *Pollution and Water Quality, Neighbourhood water quality assessment*. Project oceanography.

[4] Pink DH (2006) *Investing in tomorrow's liquid gold*. World Journal of Analytical Chemistry 2: 42-46.

[5] Larry w (2006) *World water day: A billion people worldwide lack safe drinking water*.

[6] *National Water Quality Inventory Report to Congress* (2009) Washington, D.C: United States, Environmental Protection Agency (EPA). EPA 841-F-08-03

[7] Florescu, Ionete RE, Sandru C, Iordache A, Culea M (2011), *The influence of pollution monitoring parameters in characterizing the surface water quality from Romania southern area*, Rom. Journ. Phys., Vol. 56, Nos. 7–8, P. 1001–1010.

[8] https://www.britannica.com/science/water-pollution#ref286082, Accessed 08/06/2023

[9] https://www.worldbank.org/en/topic/water-in-agriculture, Accessed 08/06/2023.

[10]https://www.hsph.harvard.edu/ehep/822/#:~:text=Water%20pollution%20is%20the%20contamination,make%20their%20way%20to%20water. Accessed 08/06/2023

[11] Stephenson, G.A. and Solomon, K.R. *Pesticides and Environment*. Department of Environmental Biology, University of Guelph, Guelph; 1993. Available at https://www.fao.org/3/w2598e/w2598e07.htm, Accessed 08/06/2023.

[12] https://www.toppr.com/guides/chemistry/chemistry-in-everyday-life/pesticides/
Accessed 08/06/2023.

[13] Bloomquist, J.R. (2009) *Insecticides: Chemistries and Characteristics*. From Radcliffe's IPM World Textbook, University of Minnesota, Minneapolis.

[14] https://www.epa.gov/caddis-vol2/insecticides, Accessed 08/06/2023.

[15] James P. Shepard, Jerre Creighton, Howard Duzan Source: *Wildlife Society Bulletin*, 32(4):1020-1027. Published By: The Wildlife Society.

[16] https://www.epa.gov/caddis-vol2/herbicides, Accessed 08/06/2023

[17] http://npic.orst.edu/ingred/ptype/fungicide.html, Accessed 08/06/2023

[18] https://www.cdc.gov/mosquitoes/mosquito-control/community/larvicides.html, Accessed 08/06/2023

[19] Harrison J, *Abandoned bodies and spaces of sacrifice: Pesticide drift activism and the contestation of neoliberal environmental politics in California*. Geoforum 39(3): 1197–1214. https://doi.org/10.1016/j.geoforum.2007.02.012.

[20] Lee S-J, Mehler L, Beckman J, Diebolt-Brown B, Prado J, Lackovic M, Waltz J, Mulay P, Schwartz A, Mitchell Y, Moraga-McHaley S, Gergely R, and Calvert GM (2011) *Acute pesticide illnesses associated with off-target pesticide Drift from agricultural applications*: *11 states*, *1998–2006*. Environmental Health Perspectives 119(8): 1162–1169. https://doi.org/10.1289/ehp.1002843.

[21] Van Bruggen AHC, He MM, Shin K, Mai V, Jeong KC, Finckh MR, and Morris JG (2018) *Environmental and health effects of the herbicide glyphosate*. The Science of the Total environment 616–617: 255–268. https://doi.org/10.1016/j.scitotenv.2017.10.309.

[22] Hallberg GR (1989) *Pesticides pollution of groundwater in the humid United States*. Agriculture, Ecosystems and Environment 26(3): 299–367. https://doi.org/10.1016/0167-8809(89)90017-0.

[23] Moses M, Johnson ES, Anger WK, Burse VW, Horstman SW, Jackson RJ, Lewis RG, Maddy KT, Mcconnell R, Meggs WJ, and Zahm SH (1993) *Environmental equity and pesticide exposure*. Toxicology and Industrial Health 9(5): 913–959. https://doi.org/10.1177/074823379300900512.

[24] Center for Food Safety (2015) *Pesticide Disclosure and Buffer Zones*. https://www.centerforfoodsafety.org/issues/3859/hawaii-center-for-food-safety/pesticide-disclosure-andbuffer-zones. Accessed March 2018.

[25] Harrison J (2008b) *Lessons learned from pesticide drift: A call to bring production agriculture, farm labor, and social justice back into agrifood research and activism*. Agriculture and human Values 25(2): 163–167. https://doi.org/10.1007/s10460-008-9121-5.

[26] Moorman TB (1989) *A review of pesticide effects on microorganisms and microbial processes related to soil fertility*. Journal of Production Agriculture 2(1): 14–23. https://doi.org/10.2134/jpa1989.0014.

[27] Druille M, Omacini M, Golluscio RA, and Cabello MN (2013) *Arbuscular mycorrhizal fungi are directly and indirectly affected by glyphosate application*. Applied Soil Ecology 72: 143–149. https://doi.org/10.1016/j.apsoil.2013.06.011.

[28] Álvarez-Martín A, Hilton SL, Bending GD, Rodríguez-Cruz MS, and Sánchez-Martín MJ (2016) *Changes in activity and structure of the soil microbial community after application of azoxystrobin or pirimicarb and an organic amendment to an agricultural soil*. Applied Soil Ecology 106: 47–57. https://doi.org/10.1016/j.apsoil.2016.05.005.

[29] USDA Natural Resource Conservation Service (USDA-NRCS) (2018) *Principles for High Functioning Soils.* https://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/national/soils/health/?cid¼stelprdb1049236. Accessed March 2018.

[30] Hussain S, Siddique T, Saleem M, Arshad M, and Khalid A (2009) *Chapter 5 impact of pesticides on soil microbial diversity, enzymes, and biochemical reactions*. Advances in Agronomy, pp. 159–200. Academic Press.

[31] Pimentel D (1995) *Amounts of pesticides reaching target pests: Environmental impacts and ethics*. Journal of Agricultural and Environmental Ethics 8(1): 17–29. https://doi.org/10.1007/BF02286399.

[32] Johnsen K, Jacobsen CS, Torsvik V, and Sørensen J (2001) *Pesticide effects on bacterial diversity in agricultural soils—A review*. Biology and Fertility of Soils 33(6): 443–453. https://doi.org/10.1007/s003740100351.

[33] Paulitz T (2018) *Glyphosate and soil microbial communities: Fake news vs. Facts*. Or. State Univ. Media. https://media.oregonstate.edu/media/t/0_nonp7i8r. Accessed 4 March 2018.

[34] Blount R (2017) '*Zygomycetes' or 'Zygomycota'*. BOT461: Mycology. Oregon State University: Lecture.

[35] Aynalem B and Assefa F (2017) *Effect of glyphosate and Mancozeb on the rhizobia isolated from nodules of Vicia faba L. and on their N2-fixation, north Showa, Amhara regional state, Ethiopia*. Advances in Biology. https://doi.org/10.1155/2017/5864598.

[36] Klironomos JN (2002) *Feedback with soil biota contributes to plant rarity and invasiveness in communities*. Nature 417(6884): 67. http://proxy.library.oregonstate.edu/login?url¼http://search.ebscohost.com/login.aspx?direct ¼true&db¼aph&AN¼6800762&site¼ehost-live. Accessed 18 May 2017

[37] McKay M (2017) *Oregon Hops and Brewing Archives oral history interview*. OSU MediaSpace. https://media.oregonstate.edu/media/t/0_o6yckpzl. Accessed 14 February 2018.

[38] Bromilow RH, Evans AA, Nicholls PH, Todd AD, and Briggs GG (1996) *The effect on soil fertility of repeated applications of pesticides over 20 years*. Pesticide Science 48(1): 63–72. https://doi.org/10.1002/(SICI)1096-9063(199609)48:1<63::AID-PS442>3.0.CO;2-I.

[39] Busse MD, Ratcliff AW, Shestak CJ, and Powers RF (2001*) Glyphosate toxicity and the effects of long-term vegetation control on soil microbial communities*. Soil Biology and Biochemistry 33(12): 1777–1789. https://doi.org/10.1016/S0038-0717(01)00103-1.

[40] Haney RL, Senseman SA, Hons FM, and Zuberer DA (2000) *Effect of glyphosate on soil microbial activity and biomass*. Weed Science 48(1): 89–93. https://doi.org/10.1614/0043-1745(2000)048[0089:EOGOSM]2.0.CO;2.

[41] Druille M, García-Parisi PA, Golluscio RA, Cavagnaro FP, and Omacini M (2016) *Repeated annual glyphosate applications may impair beneficial soil microorganisms in temperate grassland*. Agriculture, Ecosystems and Environment 230: 184–190. https://doi.org/10.1016/j.agee.2016.06.011.

[42] Park MG, Blitzer EJ, Gibbs J, Losey JE, and Danforth BN (2015) *Negative effects of pesticides on wild bee communities can be buffered by landscape context*. Proceedings of the Royal Society B 282(1809): 20150299. https://doi.org/10.1098/rspb.2015.0299.

[43] Sagili R (2017) *Honey Bee Genetics. ENT322: Honey Bee Biology and Beekeeping*. Oregon State University: Lecture.

[44] Davidson C, Shaffer HB, and Jennings MR (2002) *Spatial tests of the pesticide Drift, habitat destruction, UV-B, and climate-change hypotheses for California amphibian declines*. Conservation Biology 16(6): 1588–1601. https://doi.org/10.1046/j.1523-1739.2002.01030.x.

[45] Stark JD, Chen XD, and Johnson CS (2012) *Effects of herbicides on Behr's metalmark butterfly, a surrogate species for the endangered butterfly, Lange's metalmark*. Environmental Pollution 164: 24–27. https://doi.org/10.1016/j.envpol.2012.01.011.

[46] Beketov MA, Kefford BJ, Schäfer RB, and Liess M (2013) *Pesticides reduce regional biodiversity of stream invertebrates*. Proceedings of the National Academy of Sciences 110(27). https://doi.org/10.1073/pnas.1305618110.

[47] Charles D (2018) *Government Scientists Say A Controversial Pesticide Is Killing Endangered Salmon*. NPR.org. https://www.npr.org/sections/thesalt/2018/01/11/577178180/government-scientists-say-a-controversial-pesticide-is-killing-endangered-salmon. Accessed 7 February 2018

[48] Barre K, Le Viol I, Julliard R, Chiron F, and Kerbiriou C (2018) *Tillage and herbicide reduction mitigate the gap between conventional and organic farming effects on foraging activity of insectivorous bats*. Ecology and Evolution 8(3): 1496–1506. https://doi.org/10.1002/ece3.3688.

[49] Freese B and Crouch M (2015) *Monarchs in Peril: Herbicide-Resistant Crops and the Decline of Monarch Butterflies in North America*. Center for Food Safety Executive Summary. http://www.centerforfoodsafety.org/files/monarch_es_82936.pdf.

[50] Goulson D (2013) *An overview of the environmental risks posed by neonicotinoid insecticides*. Journal of Applied Ecology 50(4): 977–987. https://doi.org/10.1111/1365-2664.12111.

[51] Neary DG, Bush PB, and Michael JL (1993) *Fate, dissipation and environmental effects of pesticides in southern forests: A review of a decade of research progress*. Environmental Toxicology and Chemistry 12(3): 411–428. https://doi.org/10.1002/etc.5620120304.

[52] Yang Deng & Renzun Zhao, *Advanced Oxidation Processes (AOPs) in Wastewater Treatment*, Water Pollution (S Sengupta, Section Editor) Curr Pollution Rep (2015) 1:167–176. DOI: 10.1007/s40726-015-0015-z

[53] M. Cheng, G. Zeng, D. Huang, C. Lai, P. Xu, C. Zhang, Y. Liu, *Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: a review*, Chemical Engineering Journal (2015).
DOI: http://dx.doi.org/10.1016/j.cej.2015.09.001

[54] Khan SH, Pathak B, *ZnO based Photocatalytic Degradation of Persistent Pesticides: A Comprehensive Review*, Environmental Nanotechnology, Monitoring and amp; Management (2020), doi: https://doi.org/10.1016/j.enmm.2020.100290

[55] Turchi, C.S., Ollis, D.F., 1990. *Photo-catalytic Degradation of organic water contaminants: mechanisms involving hydroxyl radical attack*. J. Catal. 122, 178–192.

[56] Tchobanoglous G, Burton F, Stensel H. *Wastewater engineering*. New York: Metcalf & Eddy Inc; 2003.

[57] System SE. *The UV/oxidation handbook*. In 1994.

[58] Huang C, Dong C, Tang Z. *Advanced chemical oxidation: its present role and potential future in hazardous waste treatment*. Waste Manag. 1993;13(5):361–77.

[59] Gottschalk C, Libra JA, Saupe A. *Ozonation of water and wastewater: a practical guide to understanding ozone and its applications*. John Wiley & Sons; 2009.

[60] Tang WZ. *Physicochemical treatment of hazardous wastes*. CRCPress; 2003.

[61] Pignatello JJ, Oliveros E, MacKay A. *Advanced oxidation processes for organic contaminant destruction based on the Fenton reactionand related chemistry*. Crit Rev Environ Sci Technol. 2006;36(1):1–84.

[62] Prasad Mandade, *CHAPTER 5 Introduction, basic principles, mechanism, and challenges of photocatalysis*, Bioenergy and Energy Planning Research Group, EPFL, Lausanne, Switzerland, Handbook of Nanomaterials for Wastewater Treatment. https://doi.org/10.1016/B978-0-12-821496-1.00016-7

[63] D.I. Kondarides, *Photocatalysis*, in: Encyclopedia of Life Support System (EOLSS) Website: Http://Www. eolss.net/Sample-Chapters/c06/e6-190-16-00.pdf, Encyclopedia of Life Support Systems, 2010, pp. 1–11.

[64] Mohammad Malakootian, Armita Shahesmaeili, Maryam Faraji, Hoda Amiri, Susana Silva Martinez. *Advanced oxidation processes for the removal of organophosphorus pesticides inaqueous matrices: A systematic review and meta-analysis*. Process Safety and Environmental Protection Volume 134, February 2020, Pages 292-307.

[65] R. Saravanan, M.M. Khan, V.K. Gupta, E. Mosquera, F. Gracia, V. Narayanan, A. Stephen, *ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents*, J. Colloid Interface Sci. 452 (2015) 126–133.). (Fig. Illustration of natural and artificial photosynthesis

[66] D. Gust, T.A. Moore, A.L.M. Moore, *Realizing artificial photosynthesis*, Faraday Discuss. 155 (2012) 9–26.

[67] Y. Zheng, Z. Pan, X. Wang, *Advances in photocatalysis in China*, Chin. J. Catal. 34 (2013) 524–535. Copyright (2013) Elsevier.

[68] J. Hagen, *Industrial Catalysis: A Practical Approach*, second ed., Wiley, Weinheim, 2006.

[69] K. Rajeshwar, M.E. Osugi, W. Chanmanee, C. R. Chenthamarakshan, M. Zanoni, P. Kajitvichyanukul, R. Krishnan-Ayer, *Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media*, J. Photochem. Photobiol. C 9 (4) (2008) 171–192.

[70] X. Qu, P.J.J. Alvarez, Q. Li, *Applications of nanotechnology in water and wastewater treatment*, Water Res. 47 (2013) 3931–3946.

[71] M.M. Khan, S.F. Adil, A. Al-Mayouf, *Metal oxides as photocatalysts*, J. Saudi Chem. Soc. 19 (5) (2015) 462–464.

[72] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K. O'Shea, M.H. Entezari, D.D. Dionysiou, *A review on the visible light active titanium dioxide photocatalysts for environmental applications*, Appl. Catal. B: Environ. 125 (2012) 331–349. Copyright (2012) Elsevier.

[73] V. Augugliaro, M. Bellardita, V. Loddo, G. Palmisanoa, L. Palmisano, S. Yurdakal, *Overview on oxidation mechanisms of organic compounds by TiO2 in heterogeneous photocatalysis*, J. Photochem. Photobiol. C: Photochem. Rev. 13 (2012) 224–245.

[74] M.M. Khan, D. Pradhan, Y. Sohn, *Nanocomposites for Visible Light-Induced Photocatalysis*, Springer Series on Polymer and Composite Materials, Springer, Cham, 2017.)

[75] F. Huang, A. Yan, H. Zhao, *Influences of doping on photocatalytic properties of TiO2 photocatalyst*, in: Semiconductor Photocatalysis – Materials, Mechanisms and Applications, IntechOpen, 2016.

[76] A. Hernandez-Ramırez, I. Medina-Ramirez, *Photocatalytic Semiconductors: Synthesis, Characterization, and Environmental Applications*, Springer, New York, 2014.

[77] A. Fujishima, K. Honda, *Electrochemical photolysis of water at a semiconductor electrode*, Nature 238 (5358) (1972) 37–38.

[78] Samreen Heena Khan& Bhawana Pathak, *ZnO based Photocatalytic Degradation of Persistent Pesticides: A Comprehensive Review*, Environmental Nanotechnology, Monitoring and amp; Management (2020), doi: https://doi.org/10.1016/j.enmm.2020.100290.

[79] Chen, W. et al. **2009**. *Progress in Surface Science Surface transfer doping of semiconductors*. Progress in Surface Science. 84(9-10), 279–321. http://doi.org/10.1016/j.progsurf.2009.06.002.

[80] Lee, W., Kang, J. and Chang, K. J. **2008**. *p-Type Doping and Compensation in ZnO*, Journal of the Korean Physical Society. 53, 1; 196-201.

[81] Reynolds, J. G. and Reynolds, C. L. **2014.** *Progress in ZnO Acceptor Doping : What Is the Best strategy?* Advances in condensed matter phyisics. 457058, 15. http://dx.doi.org/10.1155/2014/457058.

[82] Reza, M. et al. **2017.** *Application of Doped Photocatalysts for Organic Pollutant Degradation- A Review*. *J. Environ. Manage.* 198, 78–94.

[83] Rakshit Ameta, Meenakshi S. Solanki, Surbhi Benjamin and Suresh C. Ameta. *Photocatalysis. Advanced Oxidation Processes for Wastewater Treatment*. Emerging Green Chemical Technology, 1st Edition - February 19, 2018.

[83] Xiaolan Kang , Sihang Liu, Zideng Dai, Yunping He, Xuezhi Song and Zhenquan Tan, *Titanium Dioxide: From Engineering to Applications*, Catalysts **2019**, *9*, 191; doi:10.3390/catal9020191, www.mdpi.com/journal/catalysts.

[84] Ulrike Diebold*, The surface science of titanium dioxide,* surface science reports 48 (2003) 53-229.

[85] Rajendra C. Pawar, Caroline Sunyong Lee, *Heterogeneous Photocatalysts Based on Organic/Inorganic Semiconductor*, In book: Heterogeneous Nanocomposite-Photocatalysis for Water Purification 10.1016/B978-0-323-39310-2.00003-5

[86] H. Meskine, P. A. Mulheran, *Simulation of reconstructions of the polar ZnO (0001) surfaces***,** Physical review. B, Condensed matter, June 2010.
DOI: 10.1103/PhysRevB.84.165430.

[87] Satoshi Horikoshi, and Nick Serpone, *Coupled Microwave/Photoassisted Methods for Environmental Remediation,* Molecules 2014, *19*, 18102-18128;
DOI:10.3390/molecules191118102, www.mdpi.com/journal/molecules).

[88] Huiling Xia, Chengwei Li, Guoying Yang, Zhiang Shi, Chenxi Jin, Wenzhi He,
Jingcheng Xu, Guangming Li, *A review of microwave-assisted advanced oxidation processes for wastewater treatment*. Chemosphere, volume 287, Part 2, January 2022, 131981.
DOI: https://doi.org/10.1016/j.chemosphere.2021.131981)

[89] Ricardo A. Torres-Palma and Efraim A. Serna-Galvis, *Advanced Oxidation Processes for Wastewater Treatment,* Chapter 7 – Sonolysis.
DOI: https://doi.org/10.1016/B978-0-12-810499-6.00007-3

[90] Flint, Edward B., and Kenneth S. Suslick. "*The temperature of cavitation*." Science 253.5026 (1991): 1397-1399.

[91] Kamyar Yaghmaeian, Susana Silva Martinez, Mohammad Hoseini & Hoda Amiri (2016) *Optimization of As(III) removal in hard water by electrocoagulation using central composite design with response surface methodology,* Desalination and Water Treatment, 57:57, 27827-27833, DOI: 10.1080/19443994.2016.1177735.

[92] Shilpi Agarwal, Inderjeet Tyagi, Vinod Kumar Gupta, *Degradation of azinphos-methyl and chlorpyrifos from aqueous solutions by ultrasound treatment*, Journal of Molecular Liquids volume 221, September 2016, Pages 1237-1242.

[93] Chi-Kang Wang, Yi-Heng Shih, *Facilitated ultrasonic irradiation in the degradation of diazinon insecticide*, Sustainable Environment Research, volume 26, Issue 3, May 2016, Pages 110-116.

[94] Budetic, M.; Kopf, D.; Dandic, A.; Samardžic, *M. Review of Characteristics and Analytical Methods for Determination of Thiabendazole*. Molecules **2023**, *28*,3926. https://doi.org/10.3390/molecules28093926.

[95] RODIER, J., LEGUBE, B., MERLET, N., et coll, *Analyse de l’eau*, 9ème Edition. Dunod (2009) Paris.

[96] http://leonardvinci.e-monsite.com/medias/files/11.dosage-colorimetrique.pdf, Accessed 28/06/2023

[97] Rafael Escribano Torres, *The Structure and Spectroscopy of Cyanate and Bicarbonate Ions*. Astrophysical Implications; J. Phys. Chem. A, (2013), 117, 39, 9564–9573.

[98] Jack Yarwood, Richard Douthwaite, Simon Duckett, *Spectroscopic Properties of Inorganic and Organometallic Compounds: Techniques, Materials and Applications*, Royal Society of Chemistry, 1 juil. 2012.

[99] Challa S.S.R. Kumar, *UV-VIS and Photoluminescence Spectroscopy for Nanomaterials Characterization*, Springer Science & Business Media, 19 février 2013.

[100] AGHAMIR M, OUARDI M, *Etude de la dégradation photocatalytique de pesticide à l'aide de nanostructures d'oxydes mixtes (ZnO, TiO2)*, 2022, Master Theisis, University of Saida.

التحفيز الضوئي مقرونًا بعملية معالجة أخرى للتخلص من المبيدات في الوسط المائي

الملخص:

أصبحت حماية موارد المياه العذبة مصدر قلق كبير للعديد من البلدان في العالم، وحماية البيئة عاملاً اقتصاديًا وسياسيًا مهمًا للغاية. من بين المصادر الرئيسية لتلوث المياه الملوثات العضوية، ولا سيما المبيدات أو منتجات الصحة النباتية، عن طريق الزراعة لتحسين غلة المحاصيل. تشكل هذه الممارسات تهديدًا مباشرًا للبيئة والكائنات الحية وصحة الإنسان على وجه الخصوص. لذلك تم تطوير تقنيات إزالة بقايا هذه المبيدات للحد من هذا النوع من التلوث. في هذا العمل، دراسة تحلل المبيد Tecto 500 SC الذي جزيئه النشط هو Thiabendazole وهو مبيد فطري يستخدم على نطاق واسع في زراعة الأشجار، عن طريق اقتران عملية الميكروويف أو الفوق صوتي مع التحفيز الضوئي باستخدام مفاعل ضوئي. باستخدام محفزات مختلفة مثل TiO_2 و ZnO وتعاطي المنشطات عن طريق قياس اختفاء الجزيء النشط باستخدام مقياس الطيف الضوئي UV / Vis بالإضافة إلى المعلمات العالمية المتعلقة بالحمل العضوي.

الكلمات المفتاحية: التحفيز الضوئي، الميكروويف، الفوق صوتي، جذور الهيدروكسيل، المبيدات.

Coupling of photocatalysis with another treatment process for the elimination of a pesticide in an aqueous medium

Abstract:

The protection of freshwater resources has become a major concern for many countries in the world, and the protection of the environment, a very important economic and political factor. Among the main sources of water pollution, organic contaminants, in particular pesticides or phytosanitary products, are introduced by agriculture to improve crop yields. These practices constitute a direct threat to the environment, living beings and in particular human health. Therefore, pesticide residue removal techniques have been developed to reduce contaminated areas and matrix. In this work, a study of the degradation of a pesticide, Tecto 500 SC whose active molecule is Thiabendazole is a fungicide widely used in arboriculture, by coupling Microwave or Ultrasonic treatments processes with photocatalysis using a photoreactor. using different catalysts such as TiO_2 and ZnO and their doping by measuring the disappearance of the active molecule using a UV/Vis spectrophotometer as well as global parameters concerning the organic load.

Keywords: Photocatalysis, Microwave, Ultrasonic, Hydroxyl Radicals, Pesticide.