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Comparative study of the photocatalytic degradation of pesticides using different types of catalysts

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Dedication

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. Especially my father whom I could never put into words my gratitude towards him.

To my siblings Farouk, Mouhielddine and Aya Sofia.

To my loving aunts Kheira, Rekia and all my uncles

In living memory of my brother Madjid, my loving grandmother, and my late uncle.

And lastly to my dear friends Khadidja, Aliaa, and Fatima who have been there for me throughout this challenging process.

Assala

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List Of Abbreviations

UN	United Nations
BOD_5	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
THB	Thiabendazole
DIM	Dimethoate
WWTPs	Wastewater Treatment Plants
AOP	Advanced Oxidation Processes
SCE	Saturated Calomel Electrode
SC	Semiconductor Catalyst
EG	Bandgap Energy
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
BH	Bulk Hetero-Junction
LPML	Low-Pressure Mercury Lamp
CB	Conduction Band
VB	Valence Band
NHE	Normal Hydrogen Electrode
LIBs	Lithium-Ion Batteries
DSSCs	dye-sensitized solar cells
HPLC	High-Performance Liquid Chromatography
LC	Liquid Chromatography
MS	Mass Spectrometry
GC	Gas Chromatography
UV	Ultraviolet
Vis	Visible
PI	Permanganate Index
ROS	Reactive Oxygen Species

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GENERAL INTRODUCTION

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Environmental issues with the chemical and biological contamination of water have become a major concern for society, government, and the industry in the last 30 years. The majority of domestic and industrial activities result in wastewater that contains harmful pollutants.

Physical, chemical, and biological processes and operations are used in current wastewater treatment technologies. to remove soluble pollutants and insoluble particles from effluents.

"There is a water crisis today. But the crisis is not about having too little water to satisfy our needs. It is a crisis of managing water so badly that billions of people - and the environment - suffer badly". **[1]**

Water is a natural resource that is required for the development of life and human activities. Currently, its scarcity is a major source of concern in our society. The growing water scarcity problem in arid and semi-arid areas necessitates more efficient water resource management strategies.

Currently, nearly 1 billion people in the developing world do not have access to it **[2].** Yet we take it for granted, waste it, and even pay too much to drink it from small plastic bottles. Water is the foundation of all life. Even today, far too many people spend their entire day searching for it all over the world. Time spent gathering water and suffering from water-borne diseases limits people's true potential in places such as Sub-Saharan Africa. **[3]**

The consequence of pollutants on human health and their ecological impact, as well as water quality laws that have become increasingly narrow in recent years, which have led to the development of new water treatment techniques such as Water Treatment Processes. 'Advanced Oxidation (AOP). AOPs have been proposed to decrease toxicity and improve the biodegradability of effluents by modifying the structure of organic molecules.

Photocatalysis is an advanced oxidation process that catalyses a chemical reaction using electronically excited species produced by the absorption of photons. In the case of heterogeneous photocatalysis, the catalyst is a semiconductor. The objective of our work is to study the photocatalytic degradation of pesticides

This work is therefore organized around four chapters:

- The first chapter includes general information on water pollution by pesticides as well as their impacts on the environment and human health.
- The second chapter describes a bibliographic study on the main advanced oxidation processes that have been applied for the decontamination of several wastewater.
- As for the third, we discuss the different methods of investigation such as the products used, the experimental set-up and the methods of analysis.
- Finally, the fourth chapter is devoted to the monitoring of the tests, to the presentation of results obtained as well as their interpretations, we end our study with a general conclusion.

CHAPTER I:

WATER POLLUTION BY PESTICIDES AND WASTEWATER TREATMENT

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WATER POLLUTION BY PESTICIDES AND WASTEWATER TREATMENT

In this chapter, generalities on water, its pollution by pesticides and wastewater treatment are described and presented.

I. Global water situation:

According to Population Action International, based on UN Medium Population Projections from 1998, more than 2.8 billion people in 48 countries will face water stress by 2025, both in terms of scarcity and deterioration of water quality **[4]**. Forty of these countries are located in West Asia, North Africa, or Sub-Saharan Africa. Population growth and rising demand are expected to push all West Asian countries into water scarcity over the next two decades. By 2050, the number of countries experiencing water stress or scarcity could increase to 54, with a combined population of four billion people - roughly 40% of the projected global population of 9.4 billion **[5]**.

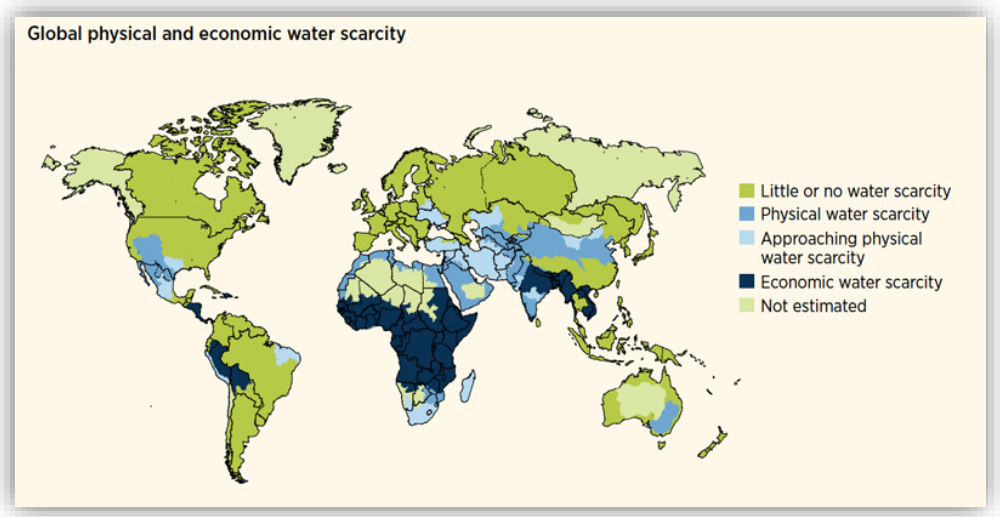


Fig I.1 World Water scarcity Assessment **[6]**

Hydrologists typically assess scarcity by looking at the population-water equation. An area is experiencing water stress when annual water supplies drop below 1,700 m^3 per person, the population faces water scarcity, and below 500 cubic metres "absolute scarcity". **[6]**

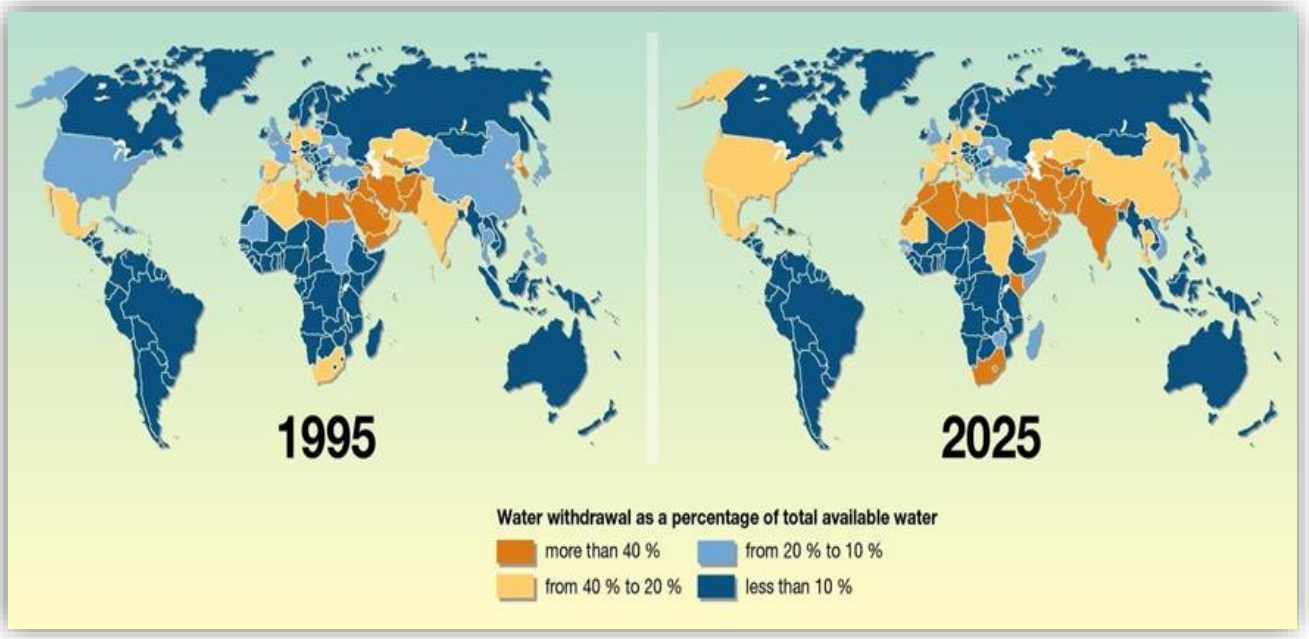


Fig I.2 Water stress situation from 1995 to 2025. **[7]**

I.1 Water quality requirement:

Table I.1 summarizes the relationship between the main quality requirements and the corresponding water uses. Water quality must meet the requirements of the various intended uses in the case of water bodies with multiple uses. The term "free" in the table is not synonymous with "absolutely free." Many contaminants cannot be guaranteed to be zero, and in most cases are not required. The acceptable concentrations are determined using risk analysis, a tool used to develop quality guidelines and standards. **[8]**

Table I.1 Association between water use and quality requirements **[8]**

General use	Specific use	Required quality
Domestic supply	–	– Free from chemical substances harmful to health – Free from organisms harmful to health – Low aggressiveness and hardness – Aesthetically pleasant (low turbidity, colour, taste and odour; absence of macro-organisms)
Industrial supply	Water incorporated into the product (e.g. food, drinks, medicines)	– Free from chemical substances harmful to health – Free from organisms harmful to health – Aesthetically pleasant (low turbidity, colour, taste and odour; absence of macro-organisms)
	Water that enters into contact with the	– Variable with the product

General use	Specific use	Required quality
	Product	
	Water that does not enter into contact with the product (e.g. refrigeration units, boilers)	– Low hardness – Low aggressiveness
Irrigation	Horticulture, products ingested raw or with skin	–Free from chemical substances harmful to health –Free from organisms harmful to health –Non-excessive salinity
	Other plantations	–Free from chemical substances harmful to the soil and plantations –Non-excessive salinity
Animal water Supply	–	–Free from chemical substances harmful to animals health –Free from organisms harmful to animals health
Preservation of aquatic life	–	–Variable with the environmental requirements of the aquatic species to be preserved
Aquaculture	Animal breeding	–Free from chemical substances harmful to animals, workers and consumers health –Free from organisms harmful to animals, workers and consumers Health –Availability of nutrients
	Vegetable growing	–Free from chemical substances toxic to vegetables and consumers –Availability of nutrients
Recreation and leisure	Primary contact (direct contact with the liquid medium – bathing; e.g.: swimming, water-skiing, surfing)	–Free from chemical substances harmful to health –Free from organisms harmful to health –Low levels of suspended solids and oils and grease
	Secondary contact (without direct contact with the liquid medium; e.g.: leisure navigation, fishing, contemplative viewing)	–Pleasant appearance
Energy Generation	Hydroelectric power plants	–Low aggressiveness
	Nuclear or thermoelectric power plants (e.g. cooling towers)	–Low hardness
Transport	–	–Low presence of course material that could be dangerous to vessels
Waste dilution And Transportation	–	–

I.2 Water pollution and reuse:

Indeed, chemical pollution of water has become a major source of concern and a priority for both society and public authorities, but more importantly, for the entire industrial world.**[9]** What exactly is water pollution? Water pollution can be defined in a variety of ways.

Water pollution occurs when one or more substances that will negatively alter the water are discharged into it. These substances can harm people, animals, and their habitats, as well as the environment. Water pollution is classified in several ways **[10]**

The two primary sources are point and non-point. The first refers to pollutants emitted from a single source, such as industrial emissions into water, while the second refers to pollutants emitted from multiple sources.

Water pollution is caused by a variety of factors, including industrial waste, mining activities, sewage and waste water, pesticides and chemical fertilizers, energy use, radioactive waste, urban development, and so on. Because water is used, it will become polluted: any activity, whether domestic or agricultural, but also industrial, produces effluent containing undesirable pollutants that can also be toxic. Water resources must be protected at all costs in this context **[11]**.

I.2.1 Definition of wastewater:

Water that has been contaminated by domestic, industrial, or commercial use is referred to as wastewater. As a result, the composition of all wastewaters is constantly changing and highly variable, making it difficult to pinpoint a single definition of the term itself.

The composition of wastewater is 99.9% water, Organic matter, microorganisms, and inorganic compounds make up the 0.1 percent removed. Wastewater effluents are discharged into a wide range of environments, including lakes, ponds, streams, rivers, estuaries, and oceans. Storm runoff is also included in wastewater because harmful substances wash off roads, parking lots, and rooftops.

I.2.2 Origins of wastewater:

- Although the terms "sewage" and "wastewater" are frequently used interchangeably, "sewage" technically refers to any wastewater that passes through a sewer. sometimes referred to as raw wastewater or raw sewage before it enters a wastewater treatment

plant.

- Domestic wastewater is produced as a result of activities such as toilet use, bathing, food preparation, and laundry.
- Commercial wastewater from non-domestic sources, such as beauty salons or auto body shops. This wastewater may contain hazardous materials and thus necessitates specialized treatment or disposal.
- 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.

I.2.3 Emerging contaminants:

It has long been assumed that sewage treatment eliminates potential polluting agents. However, standard treatments do not remove all polluting agents **[12]**. A number of compounds have been found to persist in their unaltered form through WWTPs. Among these persistent compounds is the emergent polluting agent group, which is made up of chemicals from a wide range of sources and is distinguished by its high production and consumption, implying its continuous presence in the environment **[13]**. Drugs, diagnostic products, steroids and hormones, antiseptics, personal care products, gasoline additives, heavy metals and metalloids, surfactants, endocrine disruptors, etc.

I.3 Pesticides

I.3.1 Generalities

Man has made concerted efforts throughout history to produce food for the world's ever-increasing population. Despite rapid technological advancement, the end has yet to justify the means in the field of food production. **[14]**

According to a World Health Organization report, one-third of the world's population suffers from hunger and malnutrition. This is due to the fact that agricultural production is plagued by issues caused by pests, weeds, microbial infections, and other pests. **[14]**

Pests attack stored grains and tubers in equal numbers, causing significant damage. Integrated pest management was used to completely eliminate the above-mentioned problem. Quarantine, agro-technical, mechanical, biological, and chemical methods are all included. Chemical methods of protecting agricultural products and animals were based on the use of

various organic and inorganic compounds that were synthesized and were known to be toxic to pests invading plants and animals. **[14]**

It is important to note that pesticides cannot increase plant yield but can eliminate pests that can impair plant growth. Pesticides were first used after World War II. Historically, the first pesticides were mostly inorganic compounds like $CuAs_2O_3$ (copper arsenate), sulphur compounds, and naturally occurring Rotenone and pyrethroids are two examples. $CuAs_2O_3$ has been used to eradicate colorab, an insecticide that infects tomatoes, and sulphur compounds are used as insect repellents. **[14]**

Following that are natural pesticides, some of which were derived from plant extracts, such as nicotine derived from tobacco leaves and pyrethroids derived from pyrethrin flowers. Then there are synthetic pesticides, which include: **[14]**

1. Organochlorine pesticides;

2. Organophosphorous pesticides;

3. Organocarbamates and

4. Synthetic Pyrethroids.

a. Definition:

Pesticide is derived from the English word "Pest," which refers to any animal or plant (virus, bacterium, fungus, worm, mollusc, insect, rodent, bird, and mammal) that is likely to be harmful to humans and their environment, and "Cide," which is derived from the Latin word "caedere," which means "to strike, to strike down, to kill." **[15]**

Pesticides are also referred to as "Phytosanitary Products, Plant Protection Products, or Pest Control Products for Agricultural Use" in publications relevant to European legislation. However, the English term "pesticide" is widely used around the world.

pesticides are active substances and preparations containing one or more active substances that are present in the form in which they are supplied to the user and for which they are intended **[16]**:

Protect plants or plant products from all harmful organisms; Act on plant vital processes as long as they are not nutrients (e.g. growth regulators); Ensure plant conservation, provided that the substances or products are not subject to specific provisions of the Council or the

Commission concerning preservative agents. "'Destroy undesired plants or parts of plants, slow or prevent unwanted plant growth'.

another definition of a plant protection product is "the active substance and commercial preparations containing one or more active substances in the form in which they are given to the user. **[17]**

According to the same source, the active substance, formerly known as active substance, is that which destroys or prevents the enemy of the culture from establishing itself, to which a certain number of formulations (adjuvants, solvents, anti-foams, etc.) are added in the preparation to make it usable by the farmer.

Pesticides can also be employed to control plant growth and conserve crops. They increase food quantity and quality **[18]**. They are, however, harmful compounds that pose potential risks to humans, animals, and the environment.

I.3.2 Classification of pesticides:

Pesticides are divided into two types: natural and synthetic. **[14]**

- Pyrethroids, Nicotine, and Rotenones are examples of natural pesticides.
- Organochlorines, organophosphorous, organocarbamates, and synthetic pyrethroids are examples of synthetic pesticides.

Pesticides have been classified using a variety of approaches, as indicated below: **[14]**

1. Classification according to the intended usage or target organisms;

2. Pesticide classifications based on their chemical nature or simply on their chemical composition.

Pesticides are classified chemically into three groups:

- Sulphur, $CuAs_2O_3$, and mercury are examples of inorganic compounds
- Natural pesticides, often known as botanical pesticides, are those derived from vegetable plants, bacteria, or fungi
- Organochlorine, organophosphorus, organocarbamates, and synthetic pyrethroids are examples of synthetic organic chemicals.

3. Classifications based on mode of action - this refers to how the poison penetrates or permeates the pest's body, knocking it down. The following are some sub-categories of this:

- Stomach poison pesticides: poisons insects when ingested and digested with food
- Contact poison insecticides: work by poisoning the insect when it comes into contact with the skin;

fumigants: work by infiltrating the organisms' respiratory systems in the form of gas or vapour. They are essentially vapour phase compounds that are typically used as aerosols. Systemic chemicals include stomach pesticides and fumigant pesticides. **[14]**

a. Classification according to chemical composition:

Pesticides are classified into chemical groups based on their chemical formula or active molecule, as well as their formulation.

Table I.2 Classification by chemical composition

Chemical group	**Exemples**
Organochlorine	DDT, Chlordane, Lindane, Dieldrine, Heptachlore …
Organophosphorus	Malathion, Parathion, Chlorpyrifosa, Diazinon , Dimethoate
Pyrethroids	Permethrine…
Organocarbamates	Aldicarbe, Carbaryl, Carbofuran, Methomyl Asulame, Diallate, Terbucarbe, Triallate Benthiavalicarbe
Dithiocarbamates	Mancozebe, Manebe…
Phthalimides	Folpel, Captane, Captafol
Triazines	Atrazine, Simazine…
Phenoxyherbicides	MCPA, 2,4-D, 2,4,5-T…
Chloroacetamides	Alachlore…
Pyridines,bipyridiliums	Paraquat, Diquat…
Aminophosphonates glycine	Glyphosate

b. Classification according to their activity:

Hundreds of chemical agricultural pesticides are classified based on the pest or disease they control. Table I.3

Table I.3 Agricultural chemicals including pesticides (P) and their activity

Category	*Activity*
Algicide	Kills algae, eg on wood.
Anorectic	Prevents animals from feeding on stored culture or product
Bait	Attracts plague-causing animals
Bactericide (P)	Kills or inhibits the growth of bacteria
Fungicide (P)	Disinfectant for molds and fungi
Fumigant (P)	Gas or smoke against pests or molds in stored products
Herbicide	Kills or inhibits the growth of weeds
Insect growth regulator	Modifies the development or growth phases of insects
Insecticide (P)	Kills or harms insects (e.g. aphids)
Miticide / acaricide (P)	Kills or harms mites (or spiders)
Molluscicide	Kills snails and slugs
Nematicide (P)	Kills nematodes
Junk repellents	Repels plague-causing animals
Rodenticide	Kills rats, mice, rodents
Sterilizer	Sterilizes insects chemically
Termiticide (P)	Kills or harms termites

I.3.3 **Properties or characteristics of pesticides:**

- They are hazardous and, as a result, pollute the environment, for example, organochlorine insecticides.

- The majority of pesticides have a basic structure and have simple biological activity.
- There is a fatal dose for each pesticide (LD50)
- Each pesticide has a chemical intermediate, which typically becomes obsolete after a certain period of time.

a. Persistence:

Pesticide persistence is frequently expressed as a half-life. This is the time required for one-half of the original quantity to degrade. For example, if a pesticide has a half-life of 15 days, half of the pesticide applied will still be present after 15 days, and half of that quantity (25 percent of the original) will be present after 30 days. In general, the larger the potential for pesticide mobility, the longer the half-life.

Pesticides are classified into three types based on their half-life: nonpersistent pesticides with a typical soil half-life of less than 30 days, moderately persistent pesticides with a typical soil half-life of 30 to 100 days, and persistent pesticides with a typical soil half-life of more than 100 days (Table I.4) **[19]**.

Table I.4 properties of certain pesticides

Pesticide	Haf-life (days)	Sorbtion coefficient Koc	Movement rating	Water Solubility mg/l*	Vapor pressure index	Henry's Law Index Kh**
Malathion	1	1800	Extremely low	130	80	1000
1,3-dichloro-propene	10	32	Moderate	2250	290billion	77 billion
Dicamba	14	2	Very high	400000	0	0
Diuron	90	480	Moderate	42	0.69	21
Bensulide	120	1000	Moderate	5.6	8	3058
Prometon	500	150	Very high	720	77.3	130
Benomyl	67	1900	Low	2	0.001	0.78

*Multiplied 107 **Multiplied 109

Photodegradation, chemical degradation, and microbiological degradation all have an impact on persistence. A single pesticide may be broken down by all three mechanisms. The pace of degradation is affected by pesticide's chemical as well as environmental factors. Pesticide persistence may be affected by the distribution of leaves and soil, as well as temperature, soil and water pH, microbial activity, and other soil properties.

b. Mobility:

Pesticide mobility may result in pesticide redistribution within the application site or migration of a small amount of pesticide away from the application site. A pesticide may:

- attach to soil particles, vegetation, or other surfaces and remain near the site of deposition;
- attach to soil particles and move with eroded soil in runoff or wind;
- dissolve in water and be taken up by plants, moved in runoff, or leached; or
- volatilize or erode from foliage or soil with wind and become airborne. The pesticide's sorption, water solubility, vapor pressure, and other environmental and site variables such as weather, topography, canopy, and ground cover all have an impact on mobility.

I.3.4 Environmental effects of pesticides:

Pesticides have an impact on the environment through both point-source and nonpoint-source pollution. The former is pollution that originates in a distinct and identifiable location, such as pesticide spills, wash water from clean-up sites, leaks from storage locations, and inappropriate pesticide and container disposal. The latter is pollution from a wide range of sources, such as pesticide drift via the air, pesticide discharge into streams, and pesticide movement into ground water **[20]**.

Pesticide-sensitive areas include:

- areas where ground water is near the surface,
- areas near surface waters,
- areas heavily populated with people,
- areas populated with livestock and pets,

- areas near the habitats of endangered species and other wildlife,
- areas near honey bees
- areas near food crops and ornamental plants **[20]**. Sensitive plants and animals, as well as the water quality of bodies of water near field margins, might be directly or indirectly impacted **[21]**.

a. Fate of pesticide in the atmosphere:

Pesticides are released into the atmosphere through application drift, post-application vapour losses, or wind erosion of pesticide-treated soil (Figure I.3). They and their photodegradation products can travel vast distances before being returned to the earth's surface by the removal processes of atmospheric wet and dry deposition **[21,22]**.

Liquid sprays are administered using nozzles that offer pesticide metering, atomization, and uniform distribution. The majority of atomizers split the liquid into droplets using hydraulic pressure as the energy source. Because small droplets are more prone to movement under windy conditions, the proportion of total spray volume contained in droplet sizes less than 150 m can be used as an indicator of drift potential.

Applications are classified into two kinds. Pre-emergence treatments, which are applied to the soil surface prior to crop emergence, may be left undisturbed on the soil surface or integrated into the upper layer of soil by some sort of soil disturbance. Post-emergence applications are applied to the crop, with a portion of the application penetrating the crop and depositing on the soil surface.

Pesticides that are frequently detected in the atmosphere are:

- organochlorine insecticides, which are resistant to environmental degradation,
- organophosphate insecticides, which are not long-lived in the environment,
- triazine herbicides, which are heavily used herbicides and are persistent in the environment
- acetanilide herbicides, which are used heavily but are not as persistent as triazine **[20]**

Hazards of atmospheric pesticides to humans and environment:

Atmospheric pesticides are a source of pesticide exposure through inhalation and a cause of pollution of surface/ground water through dry deposition and precipitation. Atmospheric movement may result in:

- pesticide transfer from application sites to sensitive regions
- pesticide build-up in the environment **[20]**.

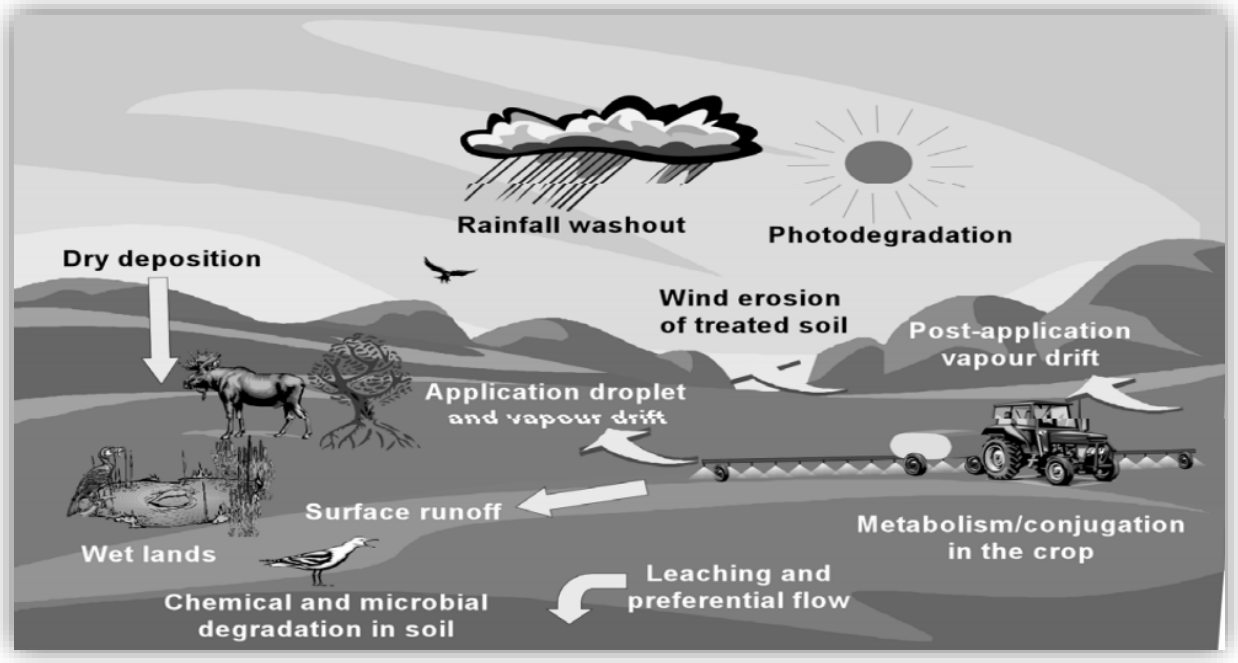


Fig I.3 Routes of entry of pesticides into the atmosphere and into surface and ground waters and mechanisms of pesticide transformation in air, soil and plants **[23]**

b. Water pollution by pesticides

Crop or livestock production accounts for more than one-third of the world's land surface and three-quarters of its freshwater resources **[24]**.

Food, feed, fiber, and bioenergy production has increased in recent decades, resulting in economic success for many industrialized countries. However, A council of hundreds of global experts has warned that these gains have come at a cost, notably to soil, water, and air quality, climate management, and habitat supply **[24]**.

Herbicides are the most common form of pesticide in agriculture, and they are used to limit weed spread and increase crop yields. Agriculture has a significant contribution to the economy.

However, it has also been identified as the leading cause of water contamination, owing to nutrient enrichment **[25]**. Indeed, land-based runoff has been recognized as having a negative influence on the seas surrounding the Great Barrier Reef that is second only to climate change **[26]**.

Pesticide residues have also been found in water resources, sediments, and groundwater**. [27]**

Pesticide contamination of water bodies can represent a serious danger to aquatic ecosystems and drinking water supplies. Pesticides can infiltrate bodies of water through diffuse or point sources. Pesticides inputs into water bodies from diffuse sources are the results of agricultural application on the field. **[27]**

Tile drain outflow, baseflow seepage, surface and subsurface runoff and soil erosion from treated fields, spray spread during application, and deposition following volatilization are examples. In contrast, point-source inputs derive from a localized situation and enter a water body at a specific or restricted number of locations. **[27]**

These primarily include farmyard runoff, sewage plants, sewer overflows, and unintentional spills. There are also non-agricultural pesticide point sources, such as application on roads, railways, or urban sealed surfaces such as parking lots **[27]**.

Many factors, such as soil and pesticide qualities, as well as crop management practices, determine the possibility for pesticide contamination of groundwater or surface water **[19]**.

Pesticides enter surface waters through run-off, wastewater discharges, atmospheric deposition and spills **[23]**.

Pesticides that enter the atmosphere through the above-mentioned pathways are prone to travel across thousands of kilometers. They are also prone to wet and dry deposition removal processes at any time during transport, both of which contaminate surface waterways. Pesticides may be trapped in snow and hail or dissolved in rain after moist deposition. Pesticides sorbed to wind-eroded soil particles in dry deposition. **[20]**

Streams, rivers, lakes, reservoirs, and seas are all examples of surface waters. Streams and reservoirs supply roughly half of the world's drinking water. A part of the water in surface waters comes from snow melt or rainfall runoff. Surface runoff pesticides are those found in the runoff-soil interaction zone, or the top 0.5 to 1 cm of soil. The amount of pesticide present

in this zone may be influenced by a number of factors. These include pesticide application method, soil type, pesticide physiochemical characteristics and formulation type, pesticide field half-life, and pesticide air deposition **[20]**.

Pesticides that drain from treated fields, mixing sites, washing sites, or trash disposal areas may contaminate groundwater.

c. Entry of pesticides into ground waters:

The movement of water over a sloping surface is referred to as runoff. It can transport pesticides dissolved in water as well as pesticides adsorbing to eroding soil. Pesticides are either mixed up with the water or attached to the eroding soil. When water is added to a field quicker than it can be absorbed by the soil, runoff occurs. Pesticides may be carried in runoff as dissolved compounds in water or as compounds bound to soil particles.

The installation of artificial subsurface drains is intended to prevent top soil saturation, which would otherwise hinder crop development, soil trafficability, and workability. Soil texture, site, drainage system, compound characteristics, weather, application rate, and season are the key factors influencing pesticide inputs into surface waterways via drainage **[27]**

The transport of pesticides in water through the soil is referred to as leaching. Leaching can occur in three directions: downhill, upward, or sideways. The qualities of the soil and pesticide, as well as their interaction with water from rain or irrigation, all influence whether pesticides will be leached into groundwater. Leaching can be accelerated if:

The pesticide is water soluble; the soil is sandy, a rain event happens shortly after spraying, and the chemical is not substantially adsorbed to the soil. Water and dissolved pesticides are leached to depth in soil via matrix flow and preferential flow. Matrix flow is a slower transport mode in which the simultaneous movement of pesticides and water is determined by the pesticide's physical-chemical properties. This movement is determined by its water solubility, vapour pressure, Kh, and Koc values **[23]**.

Spray drift is the movement of spray droplets through the air away from a treatment site during application. Spray droplet size, wind speed, and distance between nozzle and target all influence spray drift. It can harm surrounding sensitive crops, taint harvested crops, and pose a risk to people, domestic animals, and pollinating insects. It has the potential to contaminate water in ponds, streams, and ditches, as well as harm aquatic plants and animals.

Pesticide point-source inputs are discharge from hard surfaces, most commonly farmyards, storage facilities, or roadways. Contamination of hard surfaces occurs as a result of sprayer filling and cleaning, improper handling of tank mix leftovers, leaking of malfunctioning equipment, and inadequate canister storage. Of course, spills can occur as a result of leaking tanks on the way to the field to be treated **[27]**.

Water found beneath the earth's surface, usually in rock or soil, is referred to as ground water. In the United States, ground water is the primary source of drinking water for 50% of the population and 95% of rural populations. In ground water, at least 143 pesticides and 21 of their transformation products from every major chemical class have been discovered. The pesticides most commonly discovered in ground water include:

- triazine and acetanilide herbicides, which are widely used on maize and soybeans,
- carbamate insecticide aldicarb, which is widely examined for ground water pollution (Figure I.4). **[20]**

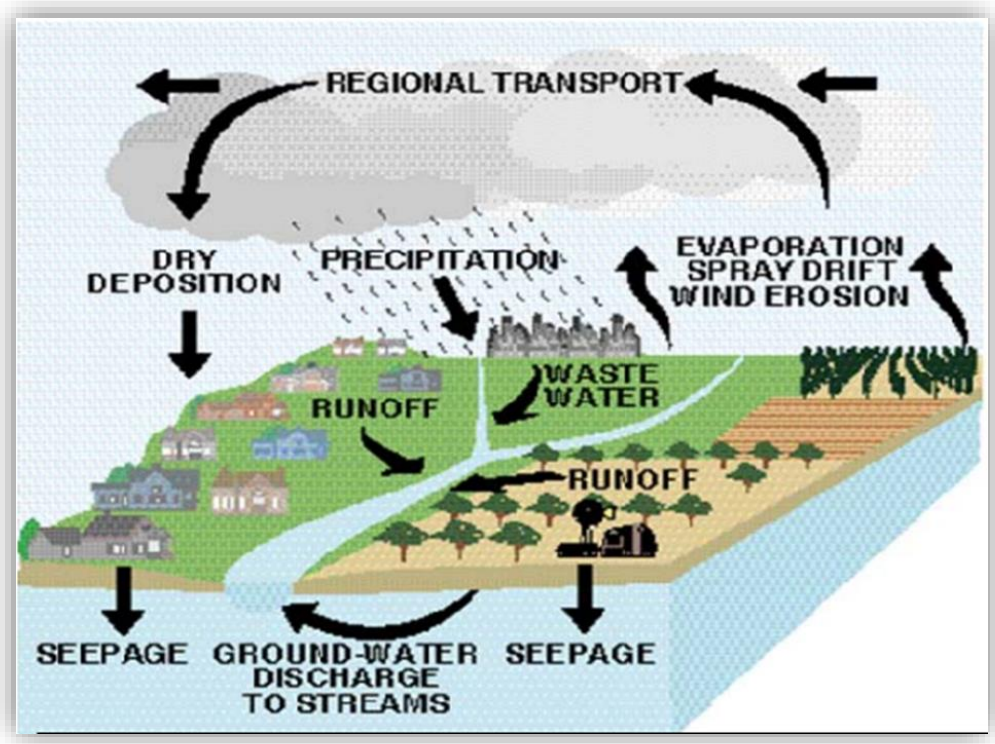


Fig I.4 Pathways of pesticide into aquatic system **[19]**.

I.4 Wastewater treatment:

Present Treatment Technologies and their Drawbacks:

Several remediation strategies are currently used for pesticide-contaminated soil and water; however, selecting the most appropriate technology is a difficult undertaking. Furthermore, if a single technique is discovered to be useless, the various technologies should be blended to provide satisfactory outcomes.

Many procedures have been proposed and are now being utilized to remove persistent pollutants. Surface adsorption **[28]**; membrane filtration **[29]**; biological degradation **[30]**; and air stripping **[31]** are the usual procedures used to remove such contaminants. Other technologies, like as adsorption and coagulation, just concentrate pollutants by moving them from one phase to the next, rather than entirely "eliminating" or "degrading" them **[32]**.

Many physiochemical technologies, including as distillation, carbon adsorption, reverse osmosis, ion exchange resins, and nano-filtration, are now employed, but their principal limitations include disposal issues, membrane deformation, sludge formation, handling, and technological constraints **[33; 34]**.

In addition, one of the most important ways of pesticide disposal is incineration, which is both expensive and unavailable in developing nations **[35]**.

Chemical oxidation is also used to remove pesticides from water **[36]**, but it is costly and pollutes the water with other harmful by-products **[37]**. Biological treatment is regarded as an environmentally beneficial method, although it is time consuming, ineffective, and has limited applicability **[38]**

Furthermore, procedures like as filtration, sedimentation, chemical, and membrane technologies have significant running costs and emit hazardous secondary pollutants into the environment **[39;40]**.

The majority of bio-recalcitrant contaminants are resistant to breakdown by traditional chemical and biological treatment approaches **[41]**.

As a result, the inability of conventional pesticide remediation procedures has considerably boosted the demand for innovative treatment technologies **[42]**.

Table I.4 summarizes the various pesticide degrading strategies now in use.

Table I.5 Present Treatment Technology for Pesticide Remediation **[43]**

Method	Technic	Advantage	Disadvantage
Physical	Adsorption Settling Membrane filtration Air stripping	Rapid	No destruction of the pesticides, By-product formation.
Chemical	Oxidation Reduction Catalysis Hydrolysis Photo-Fenton, Coagulation Ozonation Fluid extraction Solid phase extraction	Rapid and Destructive, Effective	High cost, Complex Process, Toxic by-products and end products.
Thermal	Combustion	Rapid and destructive, No by-product formed	High cost, Complex process, Not suggested for the recalcitrant compounds.
Biological	Microbial degradation	Destructive	Comparatively slow, High cost, Less effective, Toxic by-products.

The approaches described above are effective, but they have limitations in terms of effectiveness, application, time, and cost. As a result, scientists must look forward to alternate methods, such as enhanced oxidation mechanisms, for complete breakdown of persistent pesticides into environmentally beneficial molecules.

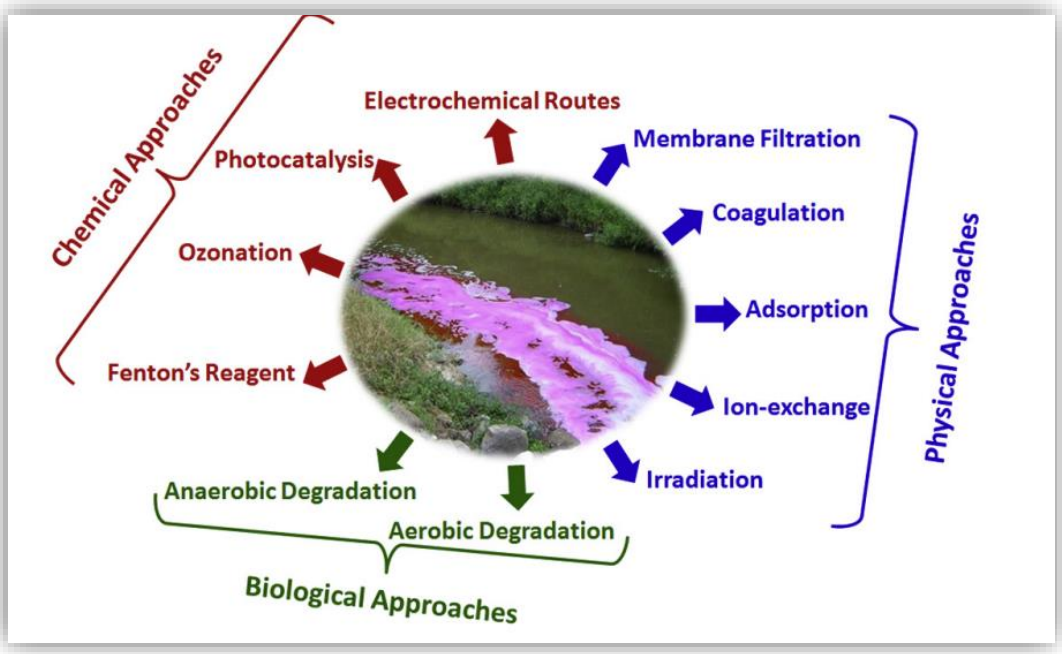


Fig I.5 Chemical, biological, and physical approaches to remove or degrade the organic pollutants in the wastewater **[43]**

I.4.1General scheme of wastewater treatment

When water is polluted and decontamination is required, the optimal purification strategy should be chosen to achieve the decontamination goals (as established by legislation). A purification process typically consists of four successive phases, as shown in Fig. I.6:**[44]**

- preliminary or pre-treatment (physical and mechanical);
- primary treatment (physicochemical and chemical);
- secondary treatment or purification (chemical and biological);
- tertiary or final treatment (physical and chemical);
- sludge treatment (supervise tipping,recycling or incineration). In general, the first two processes are referred to as pre-treatment or preliminary steps.

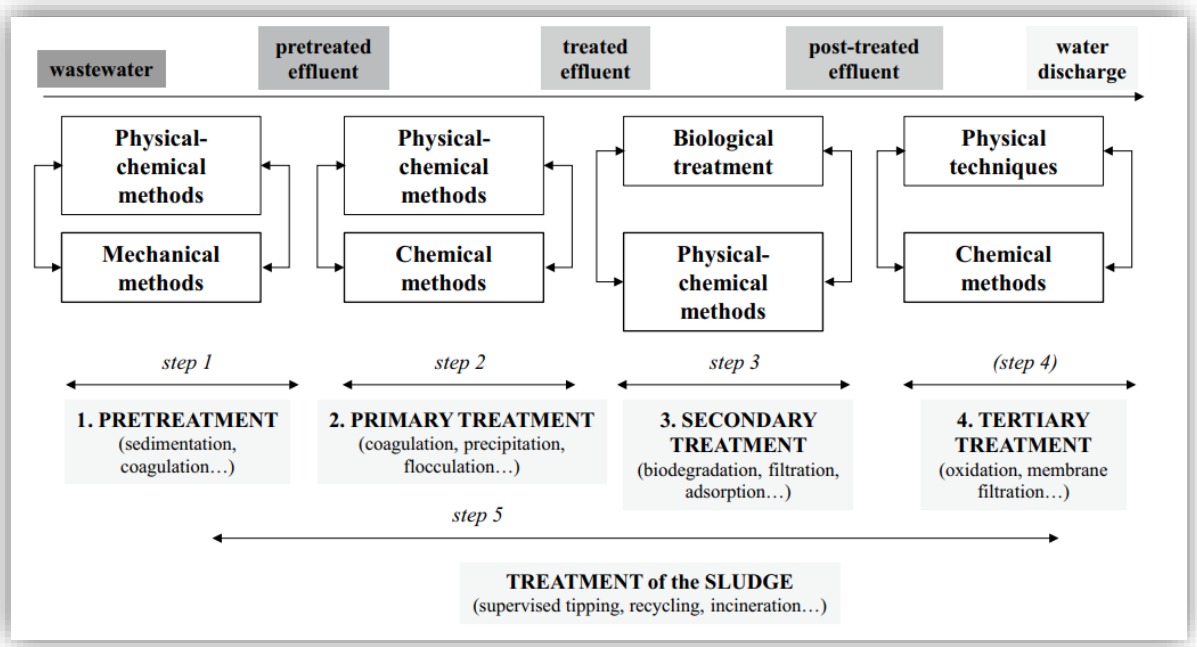


Fig I.6 Main processes for the decontamination of industrial wastewaters **[44]**

In the next chapter, we will present the main depollution and treatment processes as well as the advanced oxidation processes that have been applied for the removal of these recalcitrant organic pollutants.

CHAPTER II:

ADVANCED OXIDATION PROCESSES (AOPs) AND PHOTOCATALYSIS

CHAPTER II:

ADVANCED OXIDATION PROCESSES (AOPS) AND PHOTOCATALYSIS

New water treatment techniques were developed such as Water Treatment Processes. 'Advanced Oxidation (AOP). AOPs have been proposed to decrease toxicity and improve the biodegradability of effluents by modifying the structure of organic molecules.

II.1 Advanced Oxidation Processes (AOPs):

Organic pollutants cannot be completely degraded using conventional procedures since they simply transfer contaminants from one phase to another **[45;46]**. These findings highlight the importance of sophisticated pesticide removal methods in the environment.

To overcome the limitations associated with conventional treatment methods, researchers in the field of "Advanced Oxidation Processes" (AOPs) as advanced wastewater treatment technologies have developed an alternative way for the total conversion of pesticides into non-toxic molecules. **[47]**

In the 1980s, advanced oxidation processes (AOPs) were proposed for potable water treatment. AOPs are described as oxidation processes that generate hydroxyl radicals ($^{\bullet}OH$) in sufficient quantities to impact water purification. Later, the AOP idea was expanded to oxidative processes involving sulphate radicals (SO_4). Unlike typical oxidants such as chlorine and ozone, which serve both decontamination and disinfection functions, AOPs are used solely to destroy organic or inorganic pollutants in water and wastewater. Despite the fact that AOP inactivation of infections and pathogenic markers has been examined, **[48]**

Due to extremely low radical concentrations, the needed detention times for disinfection are prohibitively long due to their extremely short half-life (on the scale of microseconds). When AOPs are used for wastewater treatment, these radicals, as a potent oxidizing agent, are expected to sufficiently degrade wastewater contaminants and turn them into less and even non-toxic products, so giving the ultimate wastewater treatment solution.**[48]**

II.1.1 Hydroxyl Radical-Based AOPs:

The most reactive oxidizing agent in water treatment is hydroxyl radical, with an oxidation potential ranging from 2.8 V (pH 0) to 1.95 V (pH 14) vs. SCE (saturated calomel electrode, the most commonly used reference electrode) **[49]**.

•OH has a very nonselective behaviour and reacts quickly with a wide range of species, with rate constants ranging from 108 to 1010 M^{-1} s^{-1}. Hydroxyl radicals attack organic pollutants via four primary mechanisms:

Radical addition, hydrogen abstraction, electron transfer, and radical combination **[50]**. When they react with organic compounds, they produce carbon-centered radicals (R or R–OH). These carbon-center radicals can be converted to organic peroxyl radicals ($ROO^{\cdot}$) by using O_2.

All of the radicals continue to react, resulting in the formation of more reactive species such as H_2O_2 and super oxide (O_2 •-), which leads to the chemical degradation and even mineralization of these organic compounds. Because hydroxyl radicals have such a short lifetime, they are only produced in situ during application using 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+}) **[51]**.

A. Hydroxyl radical:

Many strong oxidants are “free radicals”, of which hydroxyl radical is the most powerful oxidizing species after fluorine **[52]**. A list with the most oxidizing potential species is shown in Table II.1.

Unlike many other radicals, the hydroxyl radical is non-selective, which allows it to attack a wide range of organic chemicals and convert them to less complex and less harmful intermediate products. It is practically possible to mineralize the target pollutant to CO_2, the most stable end product of chemical oxidation, with enough contact time and proper operating conditions.

Table II.1 oxidation potential of certain species **[53]**

Species	**Formula**	**Oxidation potential (V)**
Fluorine	**F_2**	**3.03**
Hydroxyl radical	***OH•***	***2.80***
Atomic oxygen	**O_2**	**2.42**
Ozone	**O_3**	**2.07**
Hydrogen peroxide	**H_2O_2**	**1.78**
Perhydroxyl radical	**HO_2 •**	**1.70**
Permanganate	**$KMnO_4$**	**1.68**
Hypobromous acid	**HBrO**	**1.59**
Chlorine dioxide	**ClO_2**	**1.57**
Hypochlorous acid	**HClO**	**1.49**
Chlorine	**Cl_2**	**1.36**

II.1.2 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.**[47]**

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 **[54]**.

The term heterogeneous refers to a dual phase, in which the catalyst is in the solid phase and the contaminants are in the aqueous phase. In the presence of a semiconductor catalyst, two or more phases are used in conjunction with a light source (UV/solar radiation) (TiO_2, ZnO, ZnS, CdS, etc.).

The AOP generated holes and electrons, which resulted in a redox reaction for contaminant degradation.**[47]**

Hydroxyl radical generation mechanisms of the major AOPs for wastewater treatment are briefly summarized below.**[47]**

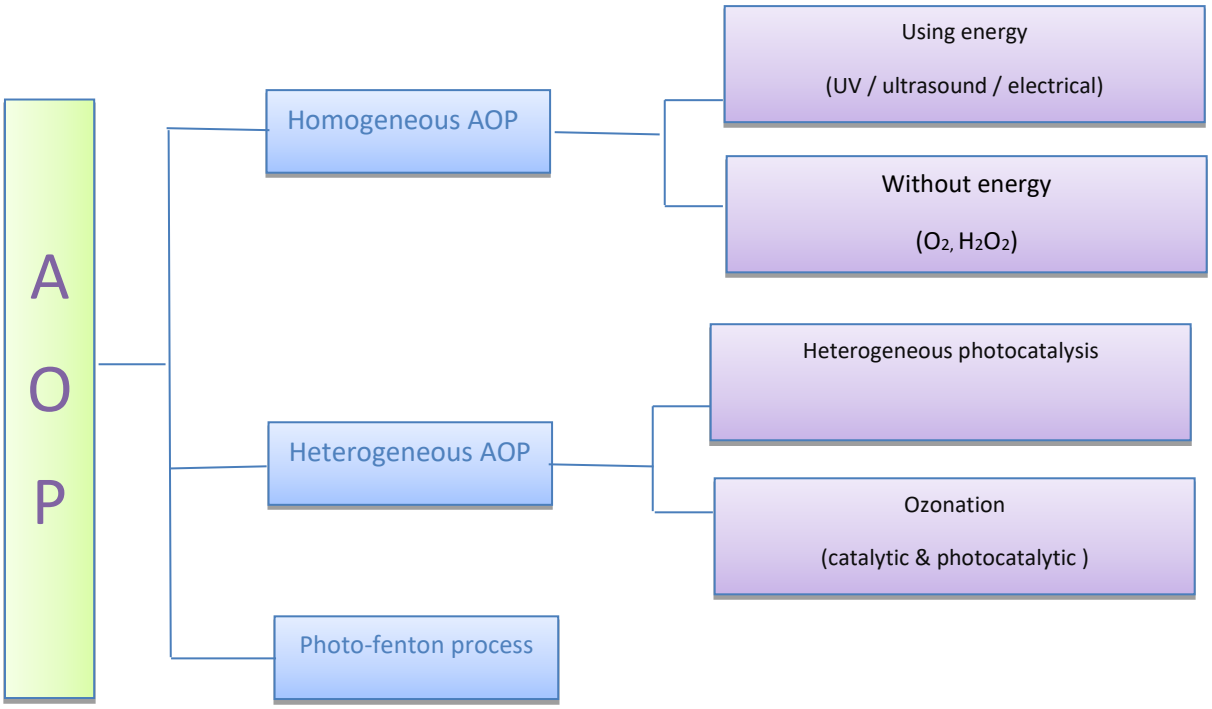


Fig II.1 Types of Advanced oxidations processes **[47]**

II.1.3 Ozone-Based AOPs:

Ozone (O_3) is a powerful oxidant in its own right, with an oxidation potential of 2.07 V vs. SCE. Direct O_3 oxidation, on the other hand, is a selective reaction with typical reaction rate constants of 1.0 x 10^0 –10^3 M^{-1} s^{-1}, in which O_3 preferentially reacts with ionized and dissociated organic compounds rather than the neutral form. Under certain conditions, O_3 produces $^{\bullet}OH$, which initiates indiscriminate oxidation (indirect mechanisms). Various detailed mechanisms have been proposed to explain the complex $^{\bullet}OH$ generation, and the overall reaction involving $^{\bullet}OH$ generation is shown below **[55]**.

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

II.1.4 UV-Based AOPs:

Photons can initiate hydroxyl radicals in the presence of catalysts or oxidants. Titanium dioxide (TiO_2), a RO-type semiconductor, is the most commonly used catalyst. When TiO_2 particles are excited, they produce positive holes in the valence band (hv^+_{vb}) with oxidative capacity and negative electrons in the conduction band (e^-_{cb}) with reductive capacity, as shown below:**[48]**

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h\nu^+_{vb} \qquad (2)$$

II.1.5 Fenton-Related AOPs:

Iron is the most commonly used of these metals capable of activating H_2O_2 and producing hydroxyl radicals in water. H_2O_2 reacts with Fe^{2+} to produce strong reactive species in the Fenton process. Although other substances, such as ferryl ions, have been proposed, the reactive species produced are traditionally recognized as hydroxyl radicals.**[56]**

II.1.6 Sulfate Radical-Based AOPs:

$S_2O_8^{2-}$ is a powerful oxidant with a standard oxidation potential (E_o) of 2.01 V **[57, 58]**. $S_2O_8^{2-}$ can form more powerful sulfate radicals (SO_4, E_o =2.6 V) when activated by heat, ultraviolet (UV) irradiation, transitional metals, or elevated pH **[59, 60].**

II.2 Photocatalysis:

Photo-catalysis is the use of light to accelerate photoreactions in the presence of a semiconductor as a catalyst. Non-toxic semiconductors are used in Photocatalysis. Such as TiO_2 and ZnO **[61]**.

Heterogeneous photocatalysis is a new approach that can be used to purify and remediate water and air. Around the last 20 years, fundamental and applied research on this topic has been conducted intensively all over the world, as evidenced by over 2000 publications. **[62]**

The number of papers published in the discipline has climbed from about 0.7 in the early 1980s to more than 23 each month in 1998. Photovoltaic conversion and energy storage were the focus of early research in the 1970s and 1980s. Later, the primary focus were the synthesis, processing, and characterization of new semiconductor materials.**[62]**

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. **[63]**

Photocatalysis, as a heterogeneous catalysis, can take place in a variety of environments, including gas phase, pure organic liquid phases, and aqueous solutions. In the case of classical heterogeneous catalysis, the total process can be divided into five independent steps:

- Reactions in the fluid phase are transferred to the surface.
- Adsorption of one or more of the reactants
- Adsorption-phase reaction
- The product's desorption.
- The products are removed from the interface region.

II.2.1 Advantages of Photocatalysis:

Photocatalysis may efficiently breakdown and mineralize almost all organic and inorganic contaminants. **[63]**

- Photocatalysis is a green technique because its end products are environmentally benign chemicals like CO_2, water, simpler salts, and minerals.
- As an oxidant, atmospheric oxygen is employed, and no other oxidant is required for the operation.
- Photocatalysts are non-toxic, cost-effective, very stable, chemically and physiologically inert, insoluble under most conditions, recyclable, and reusable.
- Both artificial and natural light can be used to activate photocatalysts.
- For large-scale processes, photocatalysis is also compared to activated carbon adsorption.

II.2.2 Principles of Heterogeneous Photocatalysis:

When a semiconductor catalyst (SC) of the chalcogenide type, oxides (TiO_2, ZnO, ZrO_2, CeO_2), or sulfides (CdS, ZnS), or nitride (Ta_3N_5, C_3N_4) is illuminated with photons whose energy is equal to or greater than their bandgap energy EG (hv EG), there is absorption of these photons and the formation within the bulk of (Fig. II.2). **[64]**

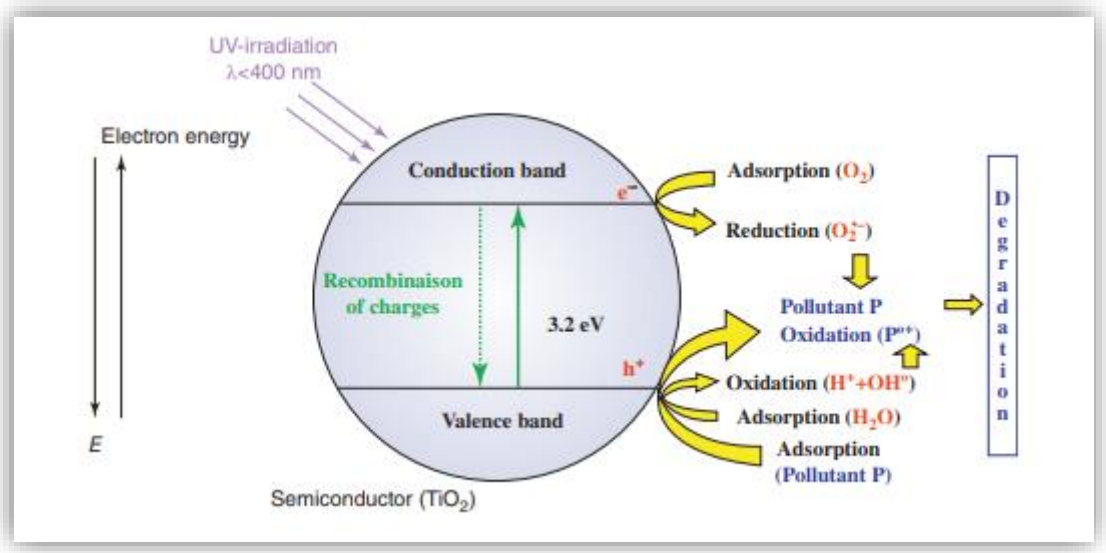


Fig II.2 Energy band diagram of a spherical titania particle **[64]**

Simultaneously, in the presence of a fluid phase (gas or liquid), spontaneous adsorption occurs, and an electron transfer proceeds toward acceptor molecules, while a positive photohole is transmitted to a donor molecule, depending on the redox potential (or energy level) of each adsorbate. In reality, the hole transfer corresponds to the donor's cession of an electron to the solid.

$$hv + (SC) \rightarrow e^- + h^+ \quad (3)$$

$$A_{(ads)} + e^- \rightarrow A^-_{(ads)} \quad (4)$$

$$D_{(ads)} + h^+ \rightarrow D^+_{(ads)} \quad (5)$$

Each generated ion then reacts to form intermediates and final products. As a result of reactions 3–5, photonic excitation of the catalyst appears as the first step in activating the entire catalytic system. As a result, the efficient photon must be regarded as a reactant, and the photon flux as a particular fluid phase known as the "electromagnetic phase." The photon energy is tailored to the absorption of the catalyst rather than the absorption of the reactants.

The action is activated by the excitation of the solid rather than the excitation of the reactants: there is no photochemical process in the adsorbed phase, only a true heterogeneous photocatalytic regime.

The electron–hole recombination, depicted in Figure II.3, can lower photocatalytic activity or the quantum yield (QY), which corresponds to the breakdown of photoelectronic energy into heat. $e^- + h^+ \rightarrow N+E$ *(6)*

where N = neutral center; E = energy (light hν′ ≤ hν or heat). **[65]**

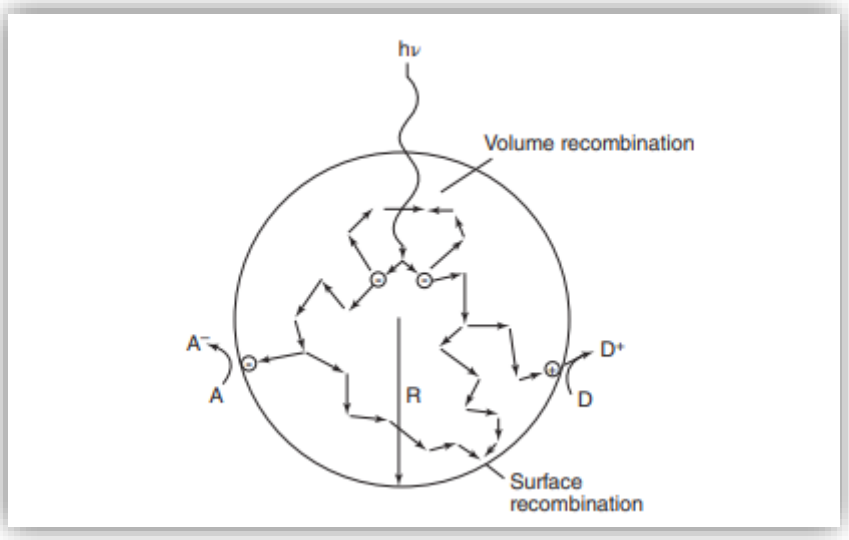


Fig II.3 Fate of electrons and holes within a spherical particle of titania in the presence of an acceptor (A) and (D) molecules (after the late Dr H. Gerisher (12)). **[64]**

a. The band gap:

The band gap is the energy difference between the valence band HOMO (highest occupied molecular orbital (valance band)) and the conduction band LUMO (lowest unoccupied molecular orbital (conduction band)) (Eg). The materials are categorized into three basic types based on band gap (Fig. II.4): **[66]**

• metal or conductor: Eg < 1.0 eV

• semiconductor: 1.5 < Eg <3.0 eV

• insulator: Eg >5.0 eV

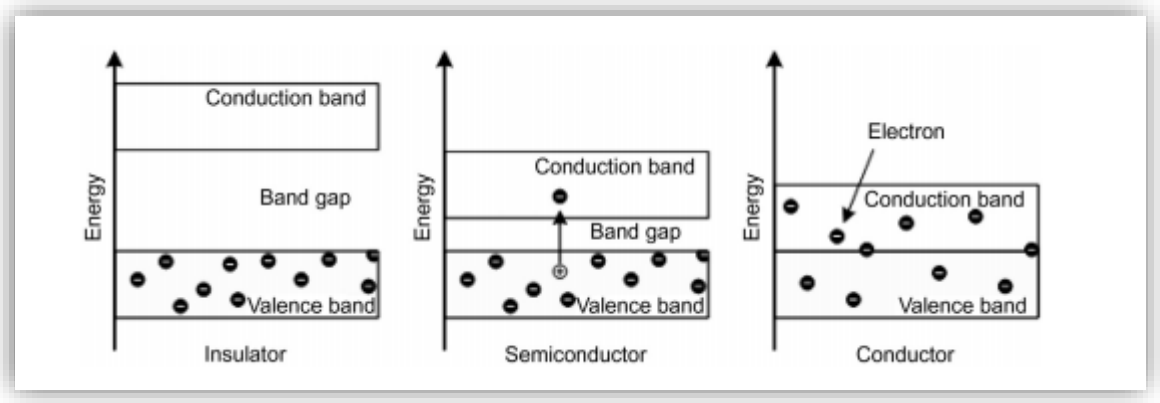


Fig II.4 band gap of different materials **[66]**

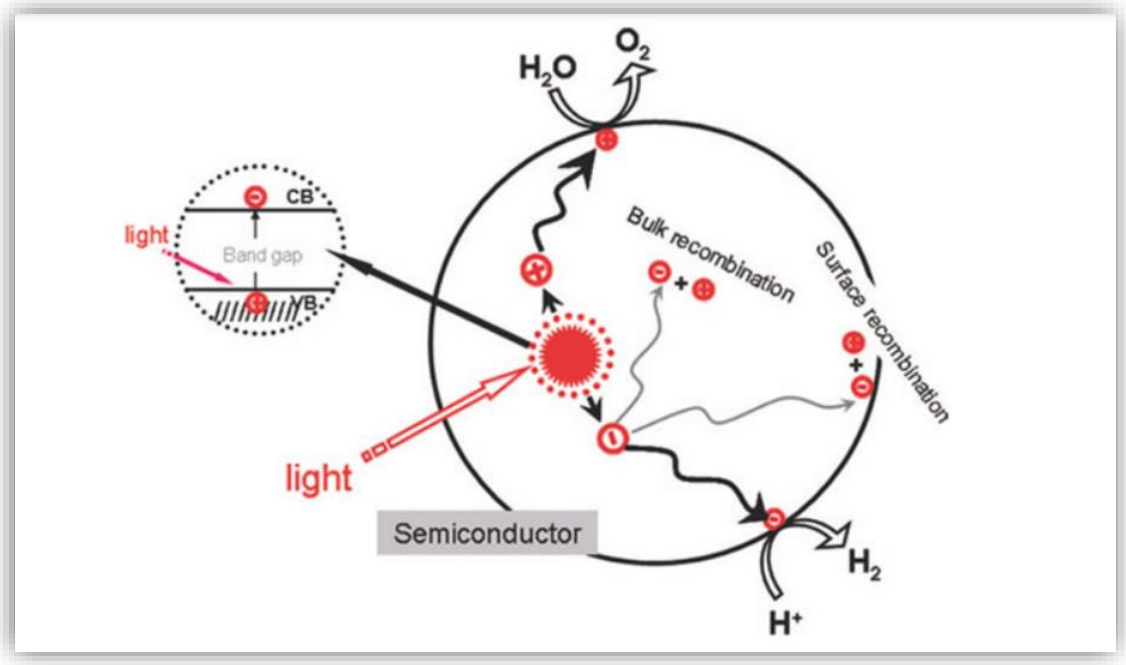


Fig II.5 Mechanism for the photocatalytic activity on the surface of the semiconductor under the irradiation of light. **[65]**

Because most photocatalysts have a large band gap (Eg) and are only active in the UV range. UV light accounts for only around 4% of the solar spectrum (wavelength less than 387 nm). Many studies have been conducted in this area to expand the photo-response of semiconductors into the visible region **[67]** and make use of 55 % of total solar radiation **[68]**.

Table II.2 Band Gaps of Different Semiconductors **[66]**

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		

Semiconductors hold the promise of providing potential solutions to environmental contamination challenges. Various strategies have been used to try to improve the photocatalytic activity of these materials. Semiconductors with a large band gap and a white hue do not absorb light in the visible spectrum.

b. Catalysts:

TiO_2, ZnO, CeO_2, ZrO_2, SnO_2, Sb_2O_4, CdS, ZnS, and other chalcogenides (oxides and sulfides) have been employed. As is commonly noticed. **[64]**

b.1Metal oxides

Because of their ability to produce charge carriers when exposed to light, metal oxides have a wide range of applications in environmental remediation and electronics.

Metal oxides have the following properties:

• necessary electrical structure

• light absorption characteristics

• charge transport properties

Semiconductor-mediated photocatalysis has received a lot of attention since it helps to solve the problem of quick charge recombination **[69]**.

c. Modifications:

There is a need to modify these photocatalysts. Surface modification, composite or coupling materials, metal and nonmetal doping, surface sensitization by organic dyes and metal complexes, and other approaches have been employed to change photocatalysts. These alterations can be accomplished using a variety of strategies such as metal or nonmetal doping **[70;71]**, co-doping, combining different metal oxides (composites), sensitization, and so on.

1. Doping:

Doping is one type of photocatalyst modification that lowers the band gap between the valence and conduction bands by adding impurities to an otherwise pure semiconductor. A semiconductor can be doped with both metals and nonmetals. Each form of dopant has a distinct effect on the semiconductor's crystal structure.**[66]**

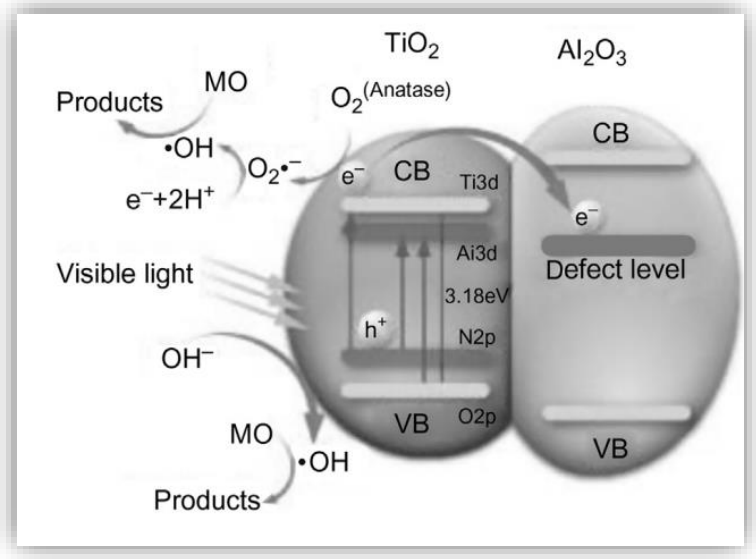


Fig II.6 Effect of metal doping on conduction band.**[66]**

2. Co-doping:

Co-doping uses various combinations of donor and acceptor species to close the band gap by elevating the valence band edge and lowering the conduction band edge. It aids in achieving activity across a wide range of the solar spectrum. In certain cases, both metal and nonmetal co-doping has been reported.**[66]**

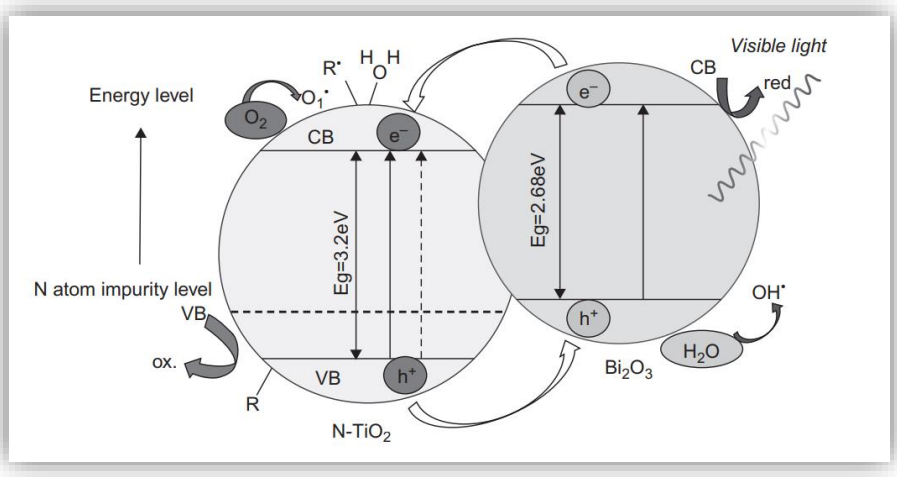


Fig II.7 Effect of co-doping **[66]**

3. Coupled Semiconductors or Composites:

Composite creation, or semiconductor coupling, is another effective way for making semiconductors photo-responsive in the visible portion of the spectrum.

Semiconductors used to make a composite must have varying band gaps.

A wide band gap semiconductor is typically paired with a small band gap semiconductor with a lower conduction band level. As a result, electrons in the conduction bands go from the small band gap semiconductor to the big band gap semiconductor. **[66]**

4. Substitution:

Another way to modify the activity of a photocatalyst is to replace one metal with another. Borse et al. (2012) **[72]** observed increased photocurrent by substituting Ti_{41} at the Fe_{41} site in a $CaFe_2O_4$-$MgFe_2O_4$ bulk hetero-junction (BH) lattice photocatalyst. Due to efficient charge separation, the Ti ion doped sample also demonstrated improved quantum yield for photodecomposition of H_2O-CH_3OH mixture.

5. Sensitization:

Sensitizers are organic and inorganic substances that are chemisorption or physisorption adsorbed on the surface of a semiconductor. Sensitization is the process of covering the surface of a semiconductor with sensitizers. Sensitizers operate as antennas, absorbing light and transferring it to a semiconductor, which aids in the excitation process.

Sensitizers are classified based on their frequency of occurrence:

• natural sensitizers

• synthetic sensitizers

• sensitizer for oneself

d. Photoreactors:

Most reactor types used for thermal or thermal-catalytic processes may accommodate photochemical reactions **[73]**. Because they are activated by light absorption, the driving force distinguishes them from other reactions. As a result, electromagnetic radiation distribution must be an intrinsic aspect of photoreactor design.

To carry out photoreactions, two types of irradiation systems can be used: artificial (lamps) and natural (the Sun). A low-pressure mercury lamp (LPML), which is a gas discharge lamp, is the oldest and most used lamp. **[74]**

II.2.3 Influence of different parameters on the degradation of pollutants:

The pH of the reaction solution, the surface area of the catalyst, the concentration of the contaminant, catalytic loading, light wavelength, intensity, and other parameters all play a role in the degradation of pollutants on the surface of the catalyst. The degradation outcomes can be affected by changes in the various parameters: **[65]**

a. Catalyst concentration:

The catalyst concentration for photoactivity in the sample is one of the important parameters that control the degradation rate of the organic compounds. This is based upon the initial concentration of the pollutant and volume of the solution being examined. It has been generally noticed that the degradation rate of the dyes and pollutants on the surface of the catalyst increases with an increase in the loading of the catalyst **[75]**. The increased loading contributes to the high activity because of the presence of more active catalyst sites at higher concentrations.

b. pH effect:

Another critical and decisive element for the degradation of pollutants in the presence of the catalyst is the pH of the reaction solution. The pH of the photocatalytic reaction mixture has a huge impact on the degradation reactions. The reaction rate is pH dependent because the pH regulates the adsorption of the organic compound onto the photocatalyst surface, and so the

degradation processes are dependent on the ionization state as well as the surface charge of the photocatalyst and the pollutant component.**[65]**

c. Surface area and morphology:

Surface and structural parameters, including as surface area, crystal composition, distribution, porosity, bandgap, particle size, and surface hydroxyl group density, all have a significant impact on semiconductor catalyst photocatalytic performance **[76]**. In heterogeneous catalysis, average crystal size is critical since it is directly connected to specific surface area, which improves a catalyst's efficiency.

d. Effect of temperature

Temperature also plays an important role in the photocatalytic degradation of organic dyes and chemicals. If the temperature of the reaction under observation fluctuates little, the temperature effect is not significant; but, if the temperature fluctuates significantly, the temperature effect is significant. will be abnormally high or low, it may alter the course of degeneration reactions. One of the essential components driving photocatalysis is dissolved oxygen. as it aids in the scavenging of CB electrons and the production of hydroxyl radicals. The percentage of changes as the temperature rises or falls. the dissolved oxygen in the samples and, as a result, alters the rate of degradation of the reaction. **[65]**

e. Effect of contaminant concentration:

Concentration in the reaction mixture is another element that might influence the degradation rate of dyes and hazardous compounds. The majority of pollutants for degradation exhibit pseudo-first-order kinetics, which can be expressed in modified formulas of the Langmuir–Hinshelwood equation for reactions occurring at the contact between liquids and solids:

$$\ln \frac{C0}{C} = kr\ Kt = k^1$$

where k^1 is the apparent first-order rate constant, t is the time necessary for the starting concentration of pollutant (C_o) to fall to (C), K is the equilibrium constant for pollutant adsorption on the catalyst surface, and K_r is the reaction limiting rate **[77]**.

f. Influence of calcination temperature:

The calcination temperature is also a significant component that contributes to the improvement of the efficiency of the manufactured photocatalyst by influencing its physical

and chemical properties. Calcination of the samples at high temperatures can boost their photoactivity because the higher temperature improves crystallization and removes undesired loosely attached contaminants. Furthermore, uncalcined samples have an overabundance of water molecules on the surface, which can lower the number of surface-active sites.**[65]**

II.2.5 The catalysts used:

1 Zno:

Zinc oxide ZnO is a semiconductor with a large band gap that has potential uses in optoelectronics, transparent electronics, and spintronics. This material's excellent UV emission efficiency could be used in solid-state white lighting devices. **[78]**

ZnO has gained a lot of attention for its ability to degrade and completely mineralize environmental contaminants **[79–80]**. Because ZnO has about the same band gap energy (3.2 eV) as TiO_2, its photocatalytic capability is expected to be comparable. However, in the case of ZnO, photocorrosion happens frequently when exposed to UV radiation, and this phenomenon is regarded as one of the primary causes of a decline in ZnO photocatalytic activity in aqueous solutions. However, certain investigations have proven that ZnO outperforms TiO_2 in photocatalytic degradation of various dyes, even in aqueous solution **[81,82]**.

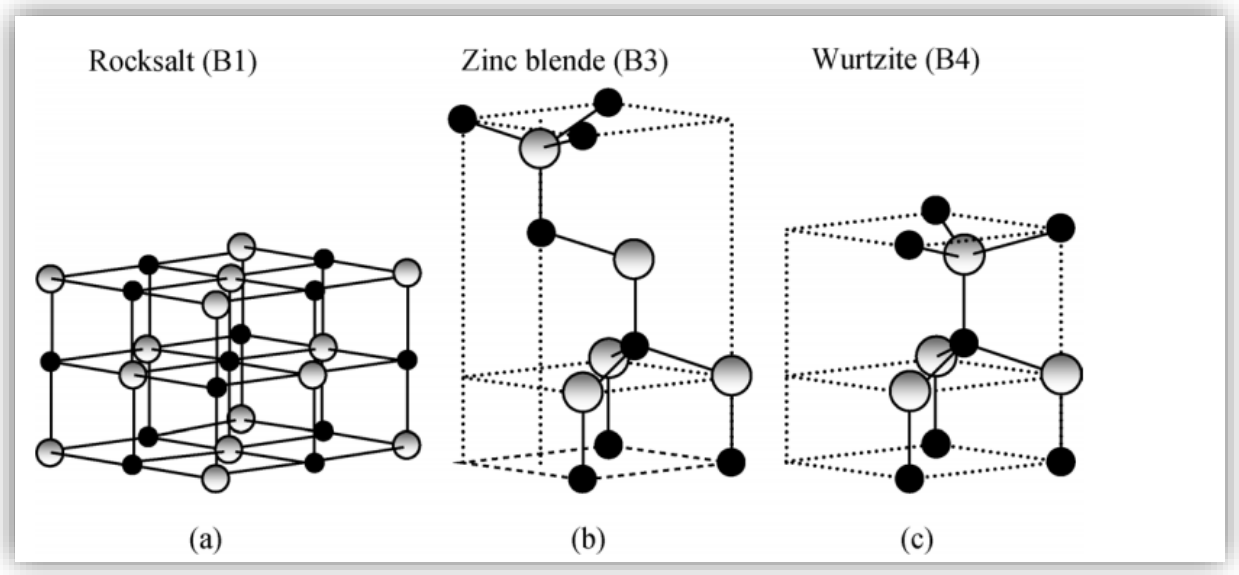


Fig II.8 Stick-and-ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). Shaded gray and black spheres denote Zn and O atoms, respectively. **[85]**

A. ZnO phases:

ZnO has three different phases: wurtzite, zinc blende, and rock salt. Generally, under ordinary conditions, the wurtzite phase (hexagonal crystal system) is the most stable **[83]**.

As shown schematically in Figure II.8, ZnO has the crystal forms wurtzite (B4), zinc blende1) (B3), and rocksalt (or Rochelle salt)2) (B1). The Strukturbericht3) designations for the three phases are B1, B3, and B4. **[84]**

B. Mechanisms of ZnO photocatalysis:

Figure II.9 depicts the photodegradation of contaminants using ZnO. Photocatalysis happens when a ZnO photocatalyst is exposed to light with an energy greater than its bandgap energy. **[84]** Light energy absorption causes charge separation by excitating electrons from the VB to the CB, leaving holes in the VB **[86]**. After that, the photogenerated e^-/h+ carriers migrate to the surface of ZnO photocatalysts.

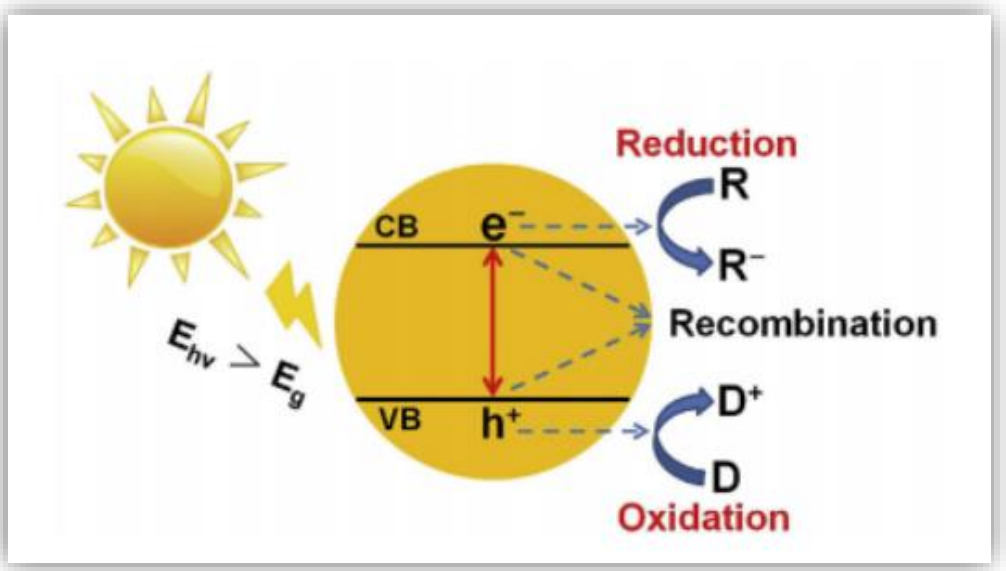


Fig. II.9 Basic mechanism of ZnO photocatalysis. Ehv is the irradiated photon energy, R is the electron acceptor, and D is the electron donor.**[84]**

Concurrently, e^- and h^+ undergo recombination, reducing quantum yield. Many parameters linked to photocatalyst architecture and surface changes influence this recombination rate **[87,88]**. Reactive e^- and h^+ arrive to the surface of ZnO to aid in oxidation

and reduction reactions that produce excess ROS, such as superoxide anion ($O_2^{-\bullet}$) and hydroxyl radical ($^{\bullet}OH$). The bottom of the ZnO CB (-0.5 V vs. normal hydrogen electrode, NHE) is more negative than the $O_2/ O_2^{-\bullet}$ redox potential (-0.33 V vs. NHE). As a result, these excited electrons can generate $O_2^{-\bullet}$. At the same time, the peak of the ZnO VB (+2.7 V vs. NHE) is more positive than the redox potential of OH/H_2O (+2.53 V vs. NHE). Consequently, H_2O molecules can be oxidized by these holes to form hydroxyl radicals. These highly reactive radical groups ($^{\bullet}OH$, $O_2^{-\bullet}$) directly oxidize organic pollutant molecules in the solutions.**[89]**

Oxidative reaction: **[47]**

$$\text{Pesticides} + h^{+VB} \rightarrow \text{Oxidation Products} \quad (7)$$

$$ZnO\ (h^{+}_{VB}) + H_2O \rightarrow ZnO + H^{-} + {}^{\bullet}OH \quad (8)$$

This reaction follows the neutralization of OH^- into $^{\bullet}OH$ by the hole-

$$ZnO\ (h^{+VB}) + OH^{-} \rightarrow ZnO + {}^{\bullet}OH \quad (9)$$

$$h^{+} + \text{organic pollutant} \rightarrow \text{Metabolites} \rightarrow CO_2 + H_2O \quad (10)$$

Reductive reaction:**[47]**

$$\text{Pesticides} + e^{-CB} \rightarrow \text{Reduction Products}$$

Here, the reaction involving the formation of superoxide anion radical by the electron-

$$ZnO\ (e^{-CB}) + O_2 \rightarrow ZnO + O_2^{-\bullet} \quad (11)$$

$$O_2^{-\bullet} + H^{+} \rightarrow HO2° \quad (12)$$

$$2HO^{\bullet} + H^{+} + ZnO\ (e^{-CB}) \rightarrow H_2O_2 + ZnO \quad (13)$$

$$^{\bullet}OH + \text{Organic pollutant} \rightarrow \text{Metabolites} \rightarrow CO_2 + H_2O \quad (14)$$

$$\text{Pesticides} + {}^{\bullet}OH \rightarrow \text{Final Degradation Product}$$

C. Methods to enhance ZnO photocatalytic activity:

The fundamental disadvantage of ZnO photocatalysts is their high band gap, which is active only when exposed to UV light but not when exposed to visible light; as a result, the effectiveness of exploiting sunlight is reduced **[90]**. To circumvent this limitation, researchers

devised a number of techniques, including metal/nonmetal atom doping, noble metal deposition, and coupling with other semiconductors or carbon materials.**[91-92]**

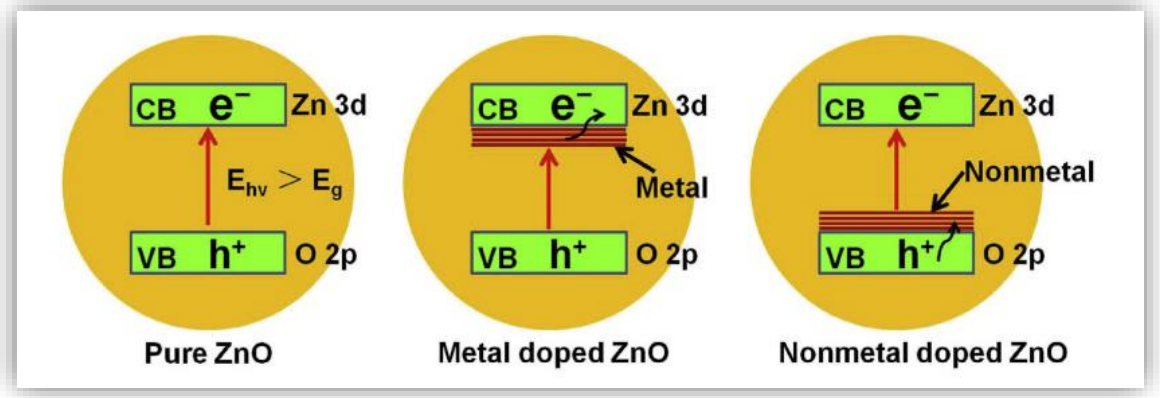


Fig II.10 Schematic of the comparison of the band structures of pure, metal-doped ZnO, and nonmetal-doped ZnO. **[84]**

2. **TiO_2**:

Titanium dioxide (TiO_2) photocatalyst has gotten a lot of attention since it was used to generate photocatalytic hydrogen from water splitting. TiO_2 is widely employed in a variety of applications due to its abundance, non-toxicity, and chemical stability. **[65]**

pigments, cosmetics, paper, plastics, catalysis, solar cells, and antibacterial agents are just a few examples.

TiO_2 has applications as a catalyst in the photodegradation of organics. pollution, water-to-hydrogen evolution, CO_2 photoreduction, lithium-ion batteries (LIBs), and dye-sensitized solar cells (DSSCs). **[65]**

TiO_2 is the most often used semiconductor for photocatalysis, and it has recently been the subject of extensive research in the field of environmental remediation using heterogeneous photocatalysis to eliminate organic molecules in polluted air and water.**[89]**

TiO_2 absorbs just a small portion of the solar energy spectrum due to its high band gap, but it has a variety of other useful properties:**[89]**

1) TiO_2 is one of the few semiconductors that are resistant to photodecomposition.
2) The reactive nature of the TiO_2 surface enables for the chemisorption of a wide range of substances.

3) The electron holes in TiO_2 have a high oxidation power and can theoretically oxidize all organic compounds in an aqueous environment.
4) TiO_2 is a low-cost, non-toxic material.

A. TiO_2 forms:

Titanium dioxide (TiO_2) has three polymorphic forms: anatase, brookite and rutile

Both anatase and brookite (which have tetragonal and orthorhombic-type crystal structures, 2.9 and 4.12 g/cm3, respectively) are unstable and transform to rutile (4.26g/cm3) when heated to 700°C and 900°C, respectively.

B. TiO_2 photocatalysis:

Semiconductor oxide photocatalysts could absorb solarlight if the energy of the incident photons matches the band gap energy (Eg) of semiconductors. Thus, when exposed to sunlight, electrons are excited from the valence band (VB) to the conduction band (CB) and begin reduction reactions on the catalyst surface. The holes left in the VB, on the other hand, participate in oxidation reactions.**[93]**

Fig II.11 Summary of main shapes and applications (i.e., lithium-ion batteries, photocatalytic hydrogen evolution, photodegradation, and solar cells) of anatase, rutile, and brookite TiO_2 crystals with their surfaces consisting of different Facets

When a photon with an energy greater than or equal to the bandgap energy is absorbed by a semiconductor particle, an electron from the vb is promoted to the cb, while a hole (h^+) is generated in the vb. The e_{cb}^- and h^+_{vb} can recombine on the surface or in the bulk of the particle in a few nanoseconds (with the energy dissipated as heat), or they can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the particle's surface. Following anodic and cathodic redox reactions can thus be initiated.

The heterogeneous photocatalytic process is a complex sequence of reactions that can be expressed by the following set of simplified equations:

$$TiO_2 \xrightarrow{h\nu}{}_{E\geq Eg} TiO_2(e^-_{cb}, h^+_{vb}) \rightarrow \text{recombination} \quad (15)$$

$$TiO_2(h^+_{vb}) + H_2O_{ads} \rightarrow TiO_2 + HO\bullet_{ads} + H^+ \quad (16)$$

$$TiO_2(h^+_{vb}) + HO^-_{ads} \rightarrow TiO_2 + HO\bullet_{ads} \quad (17)$$

$$TiO_2(h^+_{vb}) + D_{ads} \rightarrow TiO_2 + D^+_{ads} \quad (18)$$

$$HO\bullet + D_{ads} \rightarrow D_{oxid} \quad (19)$$

$$TiO_2(e^-_{cb}) + A_{ads} \rightarrow TiO_2 + A^-_{ads} \quad (20)$$

There is a lot of debate these days about the oxidative pathway, which could be performed by direct hole attack or mediated by HO• radicals, either free or adsorbed. In many cases, the oxidative pathway results in the complete mineralization of an organic substrate to CO_2 and H_2O. In general, A is dissolved O_2, which is converted into superoxide radical anion ($O_2\bullet^-$) and can result in the formation of HO•: **[62]**

$$TiO_2(e^-_{cb}) + O_{2ads} + H^+ \rightarrow TiO_2 + HO_2\bullet \leftrightarrow O_2\bullet^- + H^+ \quad (21)$$

$$HO_2\bullet + TiO_2(e^-_{cb}) + H+ \rightarrow H_2O \quad (22)$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (23)$$

$$H_2O_2 + O_2\bullet^- \rightarrow HO\bullet + O_2 + HO^- \quad (24)$$

$$H_2O_2 + h\nu \rightarrow 2HO\bullet \quad (25)$$

$$H_2O_2 + TiO_2(e^-_{cb}) \rightarrow HO\bullet + HO^- \quad (26)$$

II.3 Application of photocatalysis in water treatment:

Researchers have backed the photocatalytic decomposition process for degrading, decomposing, and eliminating hazardous or non-hazardous hard-to-biodegrade organic, inorganic, pollutants, or contaminants in industrial wastewater before they are released into larger bodies of water. The process of photocatalytic decomposition is also known as photocatalytic oxidation or photocatalysis. This method generates highly reactive hydroxyl radicals, which oxidize and mineralize the matter in solution into water, CO_2, and inorganic compounds. **[94]**

II.3.1 Organic pollutants elimination:

The studies reported here sought to demonstrate links between the molecular structure of contaminants and their photocatalytic degradability. The analyses of the numerous intermediates were performed to gain an understanding of the degradation processes as well as to identify whether harmful and stable chemicals are produced.

Pollutants such as: **[64]**

- Herbicides: atrazine, prometron, propetryne, bentazon, 2-4 D, monuron
- pesticides: parathion, lindane,
- organophosphorus: tetrachlorvinphos, phenitrothion
- dyes: methylene blue, rhodamine B, methyl orange, fluorescein, Congo Red

II.3.2 Degradation pathways of pesticides:

The primary intermediates found and identified by HPLC, LC/MS, and GC/MS of photocatalytic degradation of different aromatic pollutants relate to benzene ring hydroxylation. These intermediates have relatively low transient maximum concentrations compared to the starting pollutant, which is consistent with the fact that CO_2, acetate, and formate are generated in the early stages of breakdown. The type of the substituents influences the direction of the aromatic ring hydroxylation. For chlorophenols and dimethoxybenzenes, for example, the para and ortho positions (with respect to $^{\bullet}OH$ for the chlorophenols) are preferred. **[64]**

The degradation pathways are illustrated here by the examples of dimethoate (Fig. II.12).

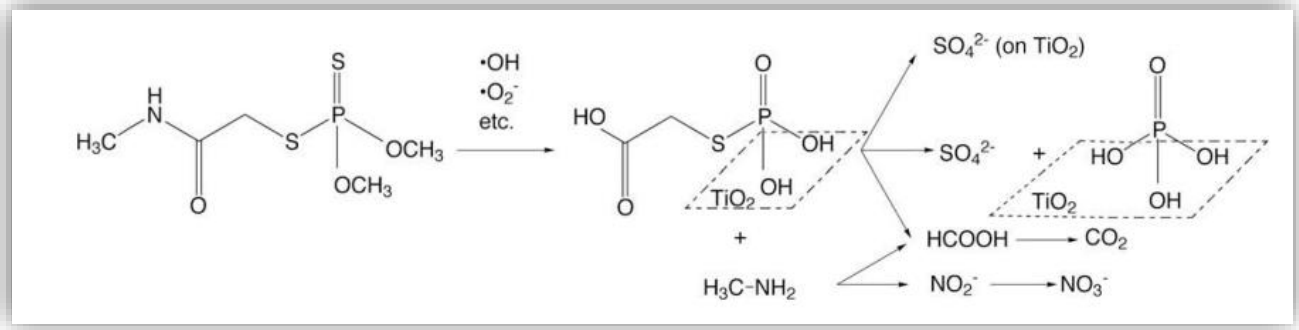


Fig II.12 Proposed tentative pathway for the photocatalytic degradation of dimethoate.**[32]**

Based on the kinetics of formation and disappearance of major byproducts, the photocatalytic decomposition of dimethoate (**Fig II.11**) is tentatively proposed to occur via rapid hydroxylation of the methyl groups borne by oxygen bonded to P and through C–N cleavage at the amide bond producing a phosphonic acid molecule, methylamine, formic acid, and mineral ions such as SO_2^{4-} , NO_2^- , and NO_3^- . Continued attack on the organic compounds eventually resulted in formation of carbon dioxide and mineral ions.**[32]**

This is why we decided to carry out an experimental study on the photo-degradation of THB in an aqueous solution and in particular a photocatalysis using ZnO because of its availability and its relatively low cost. and TiO_2 because of its efficacity.

The goal is to conduct a comparative study between the two oxides.

In the next chapter, the experimental devices used in this study are presented.

CHAPTER III :

EXPERIMENTAL DEVICES

CHAPTER III – EXPERIMENTAL DEVICES

The purpose of this chapter is to introduce the experimental devices used for the study of the photo-degradation of pesticides and methods of analysis. In the first part, the various products chosen will be presented and their characteristics described. Then, the different devices of the experiments will be exposed as well as the experimental protocols used in these experiments. Secondly, the different analytical methods used to measure the pesticides under investigation and to evaluate the performance of the experiments will be presented.

III Products used:

III.1.1 Choice of molecules studied:

In this study we will be interested in two pesticides, the first, Thiabendazole or 2- (4-thiazolyl). Thiabendazole is a fungicidal agent used to keep mold diseases like rust at bay in some plant species. It also possesses parasiticidal qualities and is used to treat disorders such as ascariasis and anguillulosis **[95].**

As a result, it is employed in agriculture, pharmaceuticals, and as a food additive. In general, it is permitted internationally for the surface treatment of fruits and vegetables, such as bananas to guarantee freshness, or citrus fruits (lemons, oranges, and so on) mixed with waxes applied to their surface.

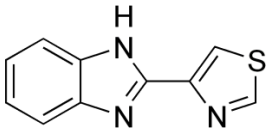
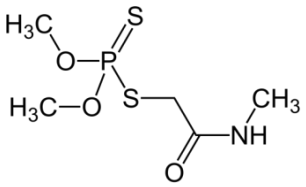
Fig III.1 Tecto 500 SC

Tecto 500 SC, a commercial solution used by farmers created by Sygenta, comprises 500 g/L Thiabendazole, with the remainder made up of emulsifiers. 500 SC Tecto.

The second is Dimethoate, an OPP organophosphate that is widely used in the Mediterranean region, notably in olive cultivation, because of its efficiency against olive fly **[95,96].**

Dimethoate is an OPP insecticide with an indirect mode of action; it is metabolized in the body to the active metabolite Demithoxon **[97]**, and it poses a significant danger of harmful health consequences from cumulative chronic exposure in fruits, particularly when fresh fruit is consumed by youngsters **[98]**.

Table III.1 Structure of the active molecules in the pesticides studied.

Active molecule (Purity%)	**Formula**	**Molar mass g/mol**	**Structure**	**Supplier**
Thiabendazole **(+98%)**	$C_{10}H_7N_3S$	201,248		Alfa Aesar Johnson Matthey
Dimethoate **(<98.5%)**	$C_5H_{12}NO_3PS_2$	229.28		Dr. Ehrenstorfer GmbH Company

Danadim Progress, a commercial solution used by farmers and manufactured by Cheminova, contains Dimethoate 400 g/L, cyclohexanone (43 % by weight), xylene (13 % by weight), and emulsifiers (5 % by weight).

Fig III.2 Danadim Progress

III.1.2. Photo-catalysts:

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 in the presence of these semiconductors.

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

Name	Zinc oxide	Titanium dioxide
Chemical formula	ZnO	TiO_2
Appearance	White solide (granules)	White Powder
Molar mass g/mol	81.38	79.866

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)minute samples are made in 5 ml increments. Then passed through the centrifuge to separate the supernatant from the Zno particles. as for the TiO_2 experiments we proceeded to filtering the supernatant as it was hydrophilic and hard to separate using only centrifugation.

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 Photo-reactor (UV-A):

UV-A irradiation was carried out with a Vilbert Lourmat ™ BLX-E365 photoreactor (figure III.3) comprising 6 lamps, the device has a wavelength interval [λ Min = 355 nm, λ Max = 375 nm] and an adjustable time of up to 180 minutes.

Fig III.3 Vilbert Lourmat ™ BLX-E365 photo-reactor.

Magnetic agitation of the suspensions examined was performed on average using an agitator from the brand Speed Safe^{TM} HANNA.

Fig III.4 Speed Safe^{TM} HANNA.

The calcination was preformed using a Nabertherm L3/11/C6 furnace

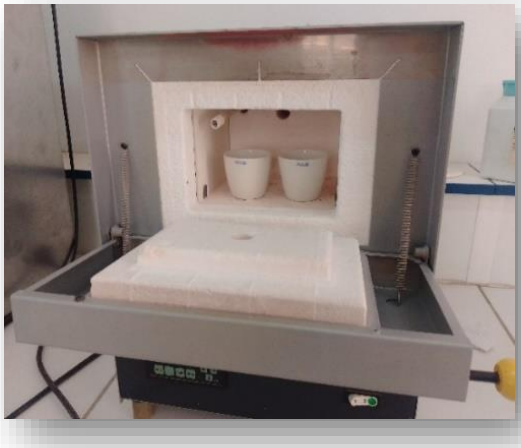


Fig III.5 Nabertherm L3/11/C6

III.3 Methods of Analysis:

III.3.1 The Permanganate index (Oxidability): [99]

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.

$$MnO^{4-} + 8\ H^{+} + 5\ e^{-} \longrightarrow Mn^{2+} + 4\ H_2O \quad (27)$$

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

$$C_2O_4^{2-} + MnO_4^{-} + 8\ H^{+} + 5\ e^{-} \longrightarrow Mn^{2+} + 2\ e^{-} + 4\ H_2O + 2\ CO_2 \quad (28)$$

The overall titration equation being:

$$2\ MnO^{4-} + 5\ C_2O_4^{2-} + 16\ H^{+} \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O \quad (29)$$

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:

$$\mathbf{PI\ (mg / LO_2) = (V_1 - V_0).\ t.\ 8.1000 / V_{sample}}$$

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).

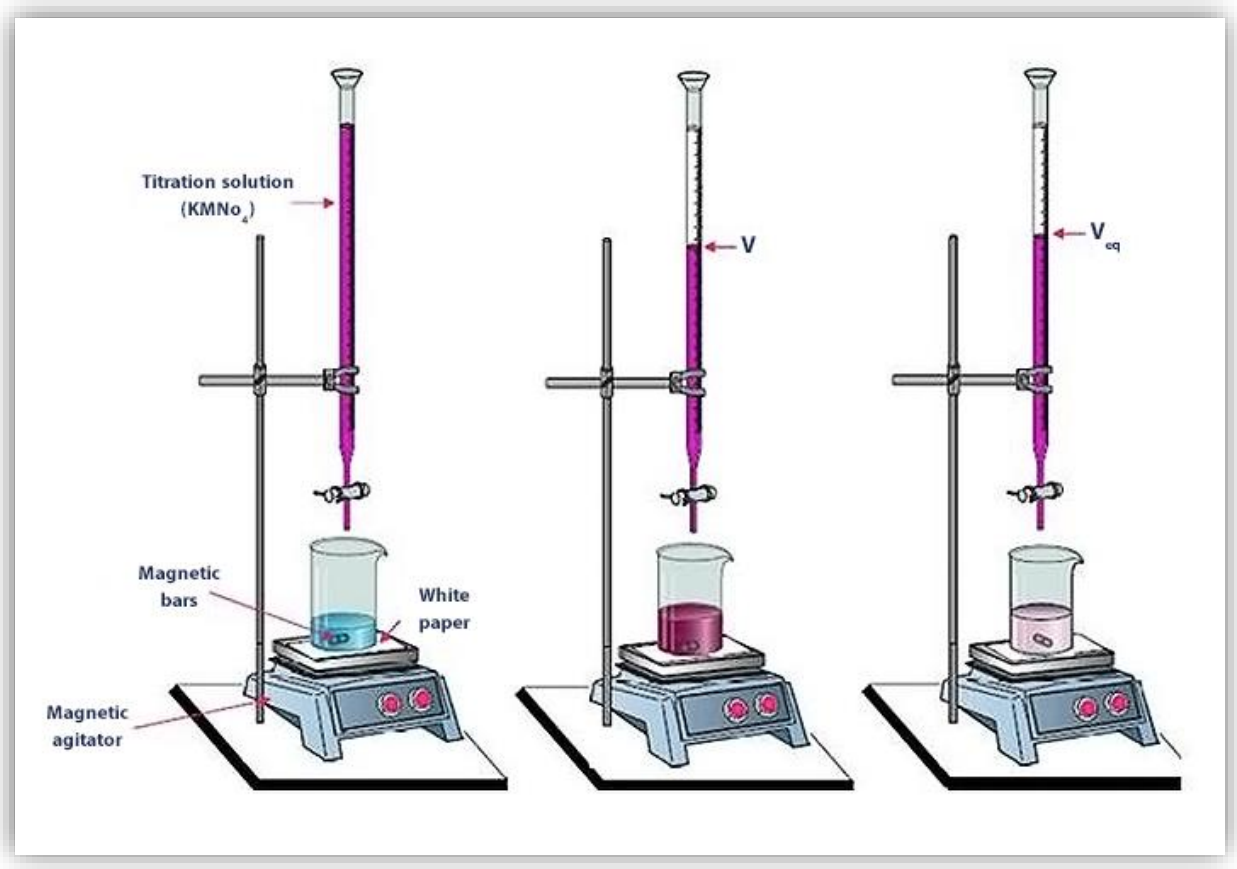
V_1 : volume in ml of the potassium permanganate solution consumed for the sample.

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.



FigIII.6 Experimental protocol for the permanganate index until the pale pink colour is obtained.

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 **[100].** 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 **[101]**.

- 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:

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

With:

- **A**: Absorbance.
- **C**: Molar concentration.
- **ε**: Absorption coefficient.
- **L**: Optical path
- **T**: Transmittance.
- **I_0**: incident radiation.
- **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 analysed as a change of population between an orbital molecular fundamental HOMO (Highest Occupied molecular Orbital) and an excited molecular LUMO (Lowest Unoccupied Molecular Orbital) **[102]**. 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 ultra violet-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 was performed from 200 to 400 nm (Fig. III.7) to determine the wavelength which corresponds to the maximum absorption (λ_{max}).

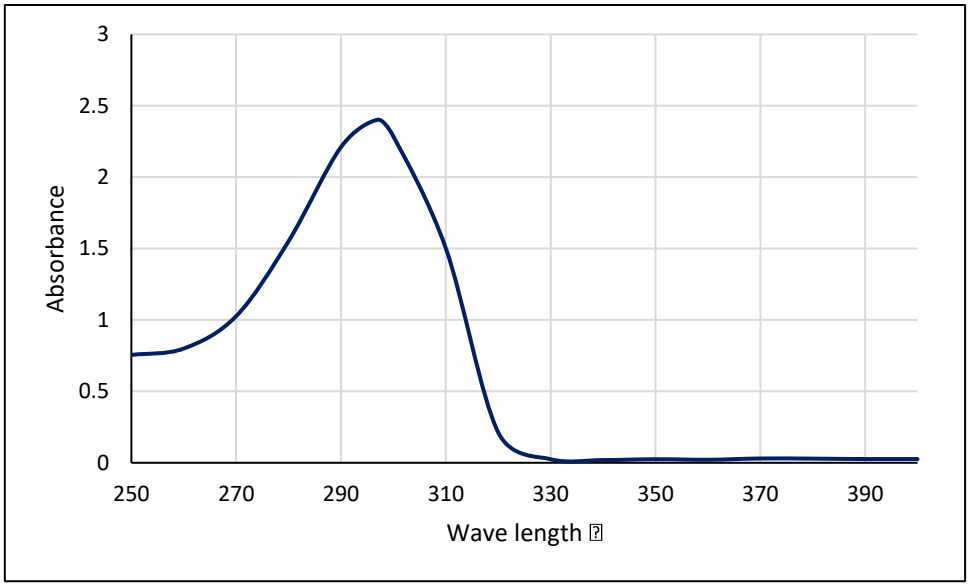


Fig III.7 Absorption curve of a solution [THB] = 0.5 mM as a function of the wavelength λ.

λ max = 296 nm

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

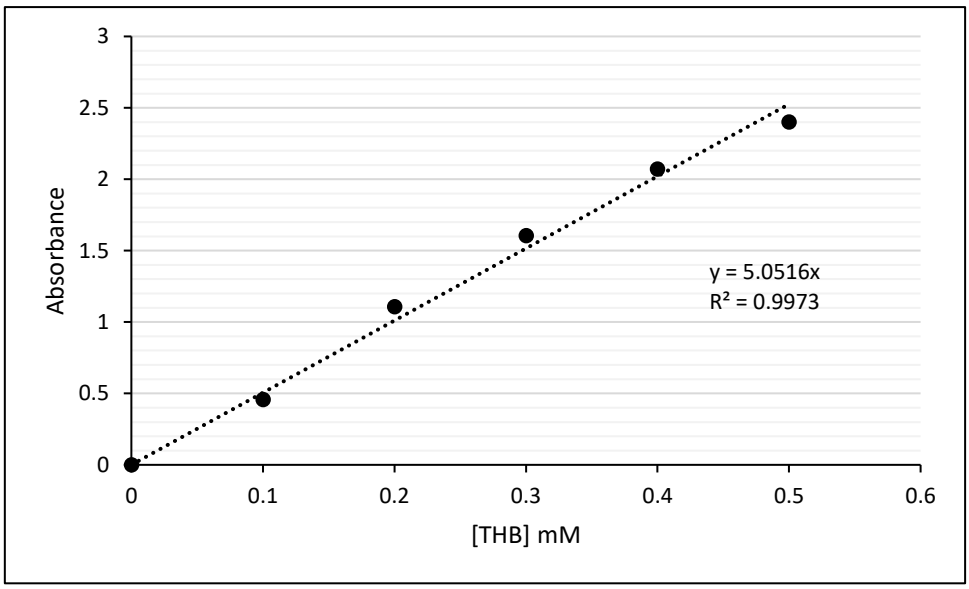


Fig III.8 Calibration line of the THB detected by UV-Vis.

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

CHAPTER IV:

RESULTS AND DISCUSSION

CHAPTER IV - RESULTS AND DISCUSSION

In this chapter the results of the photo-catalytic degradation of Thiabendazole in its commercial solution as well as in a mixture with another pesticide (Dimethoate) using two solid catalysts (ZnO and $TiO_{2)}$ will be presented, discussed and compared.

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

IV.1. Thiabendazole Photocatalysis:

IV.1. 1 Photo-degradation:

Initially, we conducted the photo degradation of Thiabendazole using its commercial solution and changing the parameter of agitation (stirring).

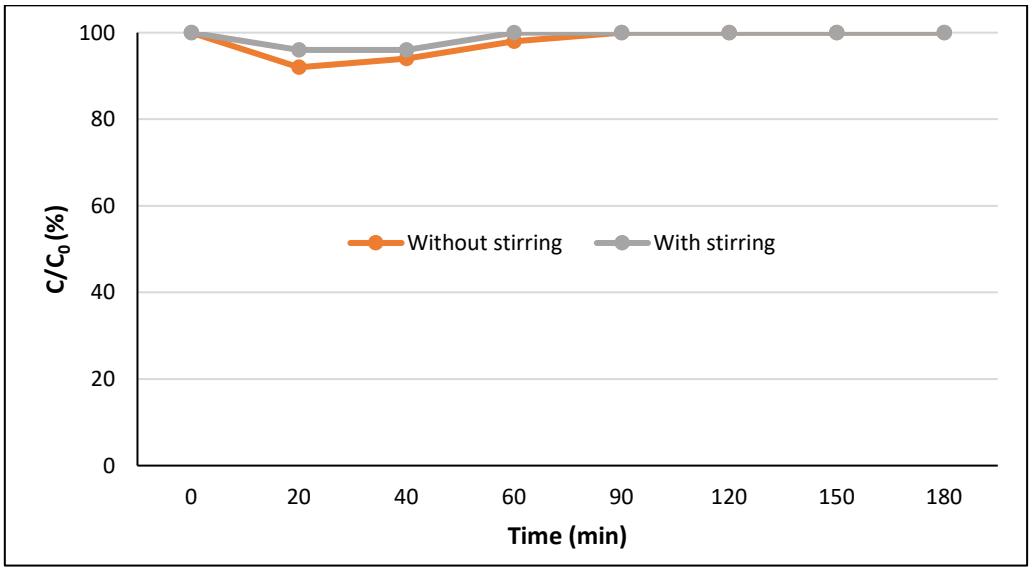


Fig IV.1 Influence of agitation on the temporal variation of the active phase [THB] of TECTO during its photo-degradation. Operating Conditions: $[THB]_0$ = 0.5 mM, V=250 mL, T = 25 ° C, UV-A [λ_{Min} = 355 nm, λ_{Max} = 375 nm].

Fig IV.1 shows that THB does not degrade by photo-degradation and remains stable.

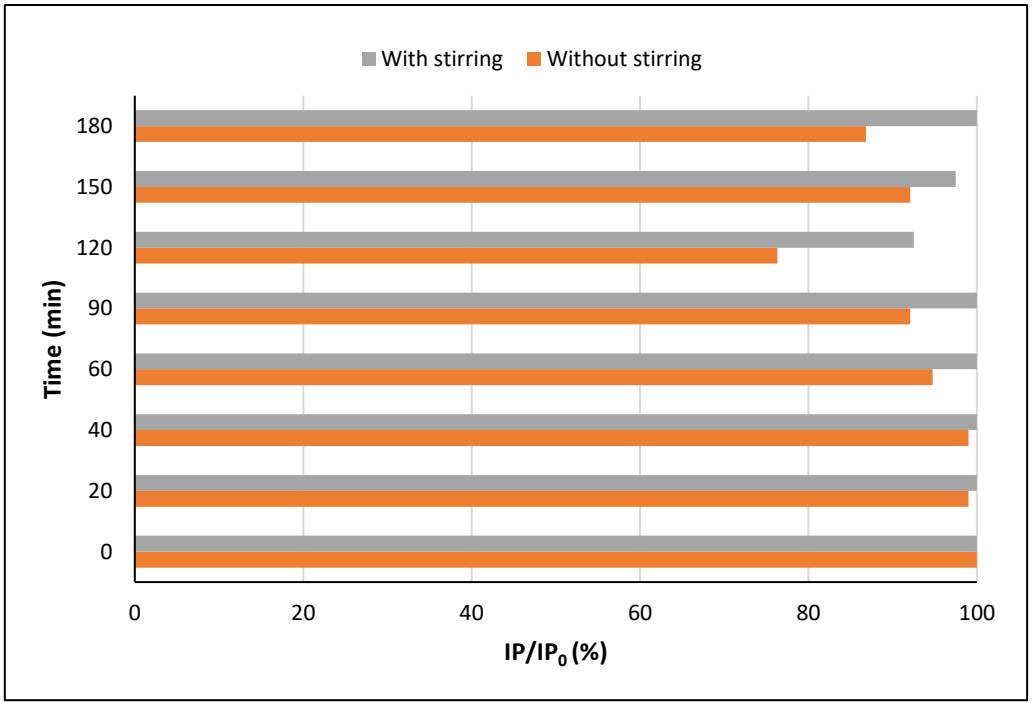


Fig IV. 2 Influence of agitation on the temporal variation of the permanganate index during the photo-degradation of thiabendazole. Operating Conditions: $[THB]_0$ = 0.5 mM, T = 25 ° C, V = 250 mL, UV-A [λ_{Min} = 355 nm, λ_{Max} = 375 nm].

From Fig IV. 2, the permanganate index drops to 76% after 2 hours of photo-degradation without stirring and remains stable when stirring is used.

In The following part we will use two catalysts in their mass form in order to proceed to the photo catalysis of the THB and its mixture with the DIM.

IV.1. 2 Photocatalysis:

a - Using ZnO:

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

- Effect of catalyst concentration:

Three concentrations of the catalyst have been selected [ZnO] = 0.5 g/L, [ZnO] = 5g/L and [ZnO] = 10 g /L, the results are presented below:

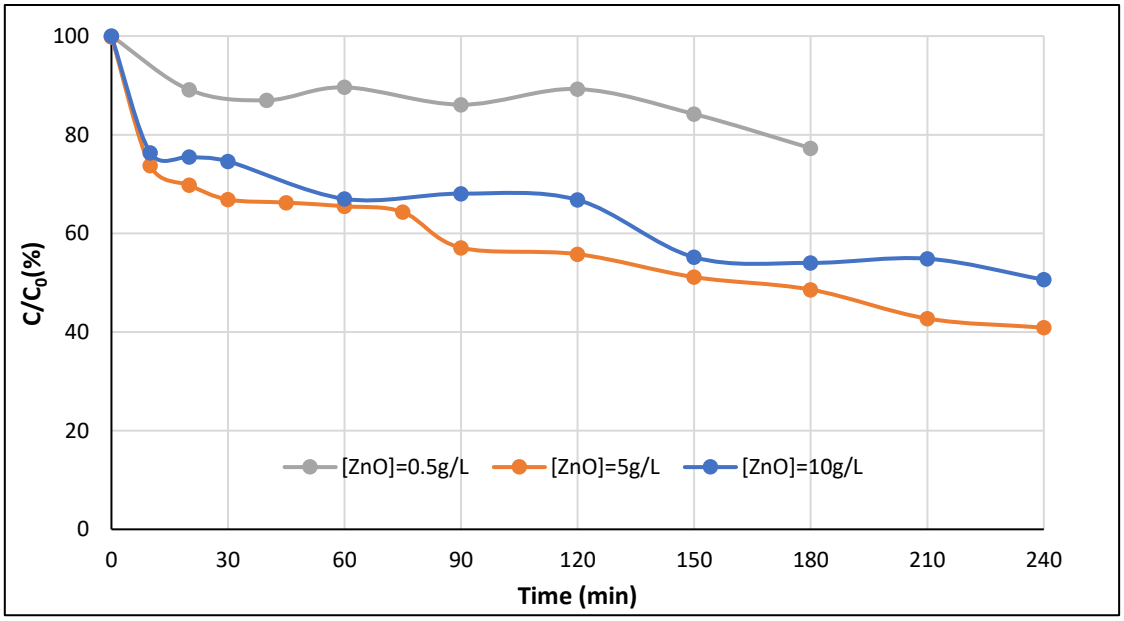


Fig IV. 3 Effect of ZnO concentration on the temporal variation of the active phase [THB] of TECTO during its photo- catalysis. Operating Conditions: [THB] $_0$ = 0.5 mM, V = 250 mL, T = 25 ° C, UV-A [λ_{Min} = 355 nm, λ_{Max} = 375 nm].

According to this figure, the degradation of THB reached 22% after 3 hours for 0.5 g/L of ZnO versus 50 and 60% elimination for 10 and 5 g/L of Zno respectively after 4 hours of the experience.

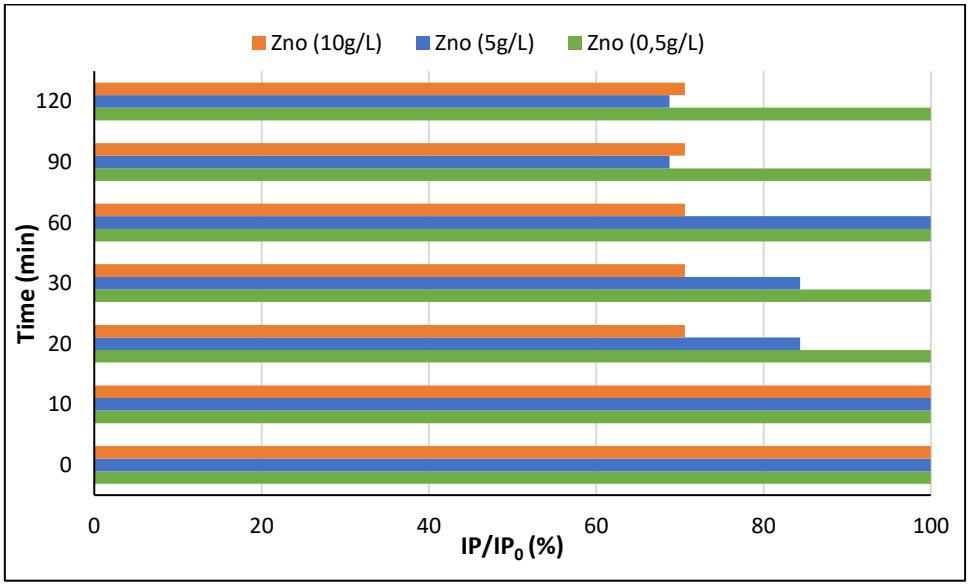


Fig IV. 4 Effect of ZnO concentration on the temporal variation of the permanganate index during the photocatalysis of THB. Operating Conditions: [THB] $_0$ = 0.5 mM, V = 250 mL, T = 25 ° C, UV-A ([λ_{Min} = 355 nm, λ_{Max} = 375 nm].

Figure IV. 4 shows that the PI remains stable for 0.5 g / L of ZnO on the other hand it decreases to 70 and 68% for 10 and 5g / L of ZnO respectively after 2 hours of photocatalysis, which leads us to continue our study with [ZnO] = 5 g/L.

- pH effect:

The previous experiments were all carried out under neutral pH (7.5) the change of medium has major consequences on the production of hydroxyl radicals and the behaviour of the catalyst, for this we carried out two other experiments, the first, under an acidic medium near the addition of 5ml of HNO_3 (0.5M) pH of the solution became 2.58 and the second in a basic medium with a pH of 11.33 was obtained after adding 2ml of NaOH (1M).

The results are shown in the following Figures:

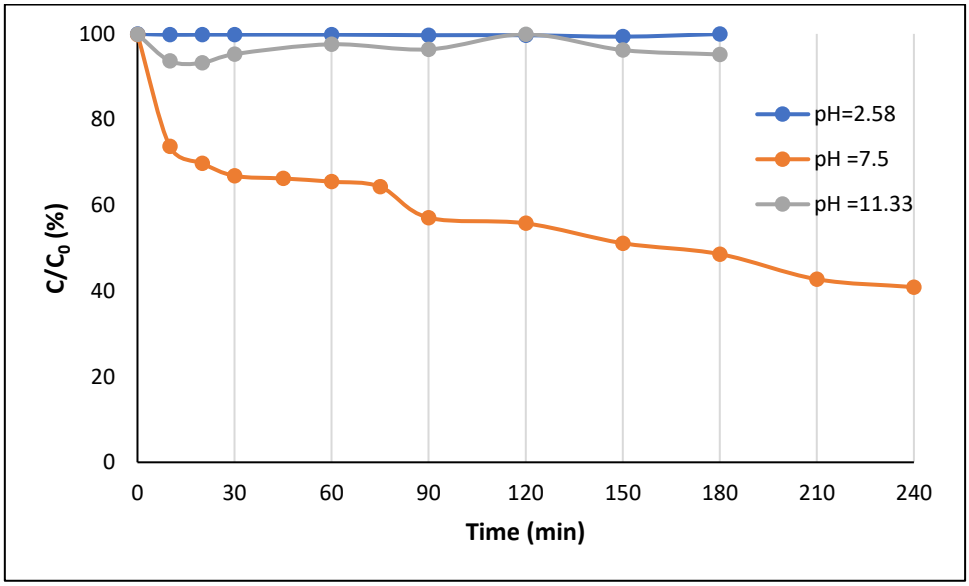


Fig IV. 5 Effect of the pH on the temporal variation of the active phase [THB] of TECTO during its photocatalysis. Operating Conditions: $[THB]_0$ = 0.5 mM, [ZnO] = 5 g/L, T=25°C, V = 250 mL, UV-A ([λ_{Min} = 355 nm, λ_{Max} = 375 nm].

The first figure indicates that the elimination of THB is non-existent in acidic (pH = 2.58) and basic (pH = 11.33) medium after 3 hours, on the other hand it reaches 60% in a neutral medium after 4 hours of photocatalysis.

The second figure shows us that the mineralization of the solution reaches 78% after 2 hours of photocatalysis in the basic medium and 62.5% in the acidic medium after only 30 min but decreases to reach 16% then, 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, 31.25% is the maximum value after 90 min.

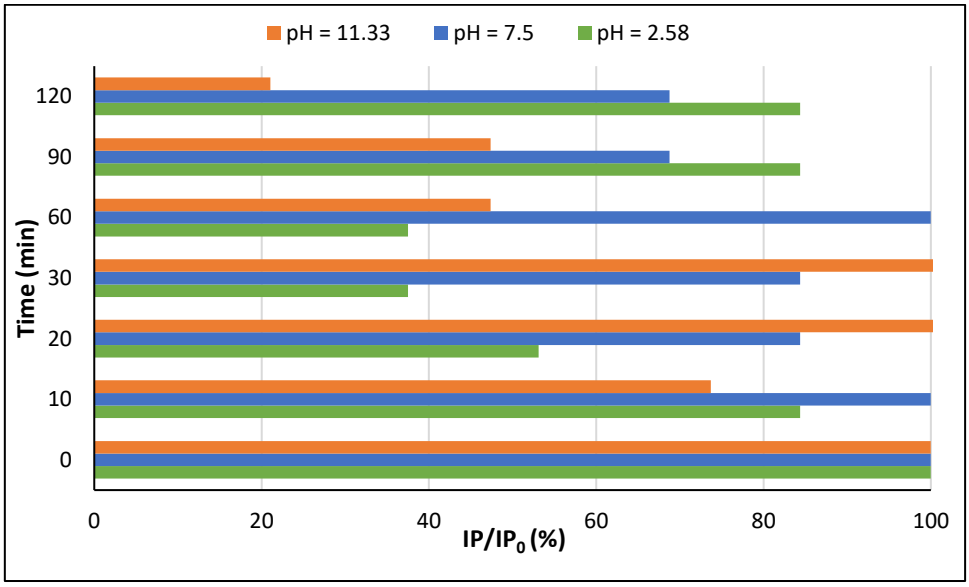


Fig IV. 6 Effect of pH on the temporal variation of the index permanganate for photo catalysis of THB. Operating Conditions: $[THB]_0$ = 0.5 mM, [ZnO] = 5 g / L, T = 25°C, V = 250 mL, UV-A ($[\lambda_{Min}$ = 355 nm, λ_{Max} = 375 nm].

- Influence of the actual effluent (presence of another pesticide):

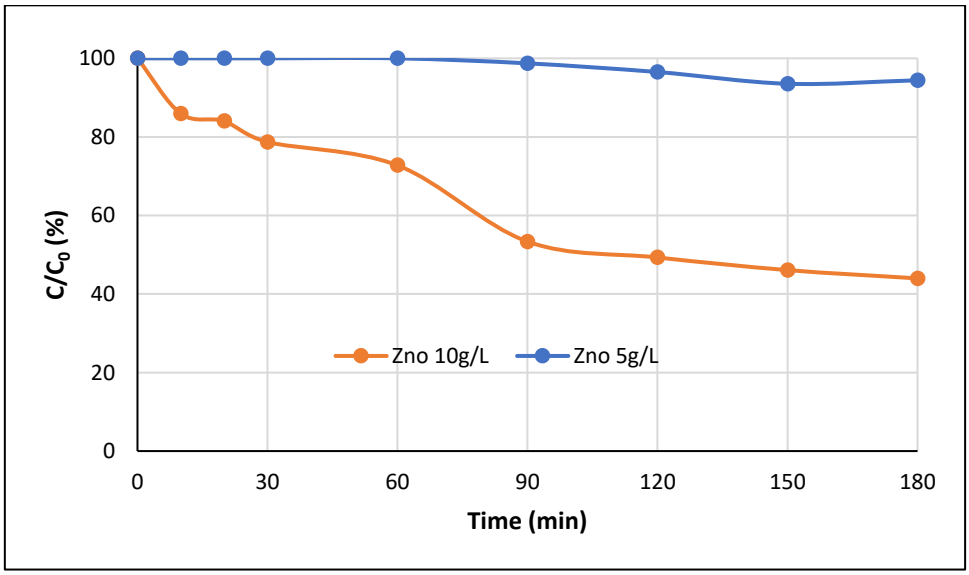


Fig IV.7 Temporal variation of the active phase [THB] of TECTO during its photocatalysis in the mixture with the Danadim. Operating Conditions: $[THB]_0$ = 0.5 mM, V = 250 mL, T = 25 °C, UV-A ($[\lambda_{Min}$ = 355 nm, λ_{Max} = 375 nm].

We used a mixture of two commercial solutions: Tecto (THB) and Danadim (DIM) in order to understand the influence of the presence of other active molecules in the solution and thus get closer to the "real effluent" label.

From the results (Fig. IV. 7), it can be seen that the photo- degradation of THB in the mixture is almost non-existent for 5g /L of ZnO, on the other hand it reaches 56% after 3 hours for 10 g/L of ZnO. This is due to the doubled organic load (mixing) and its need for more catalyst (specific surface and active sites). Compared with Fig IV.3, degradation of THB in the mixture (56%) is a little faster than only in its commercial solution (46%), as a result we found that the presence of the DIM in the active molecule mixing positively influences the reaction rate of degradation of THB in the mixture.

A result which confirms what has already been found by other works such as the one carried out by SD BABA which studied the Photo-degradation in aqueous medium of three pesticides: Thiabendazole, Dimethoate and Diazinon, (PhD in Science and Management of the Environment, University of Abobo-Adjamé, November 2012) **[103]**.

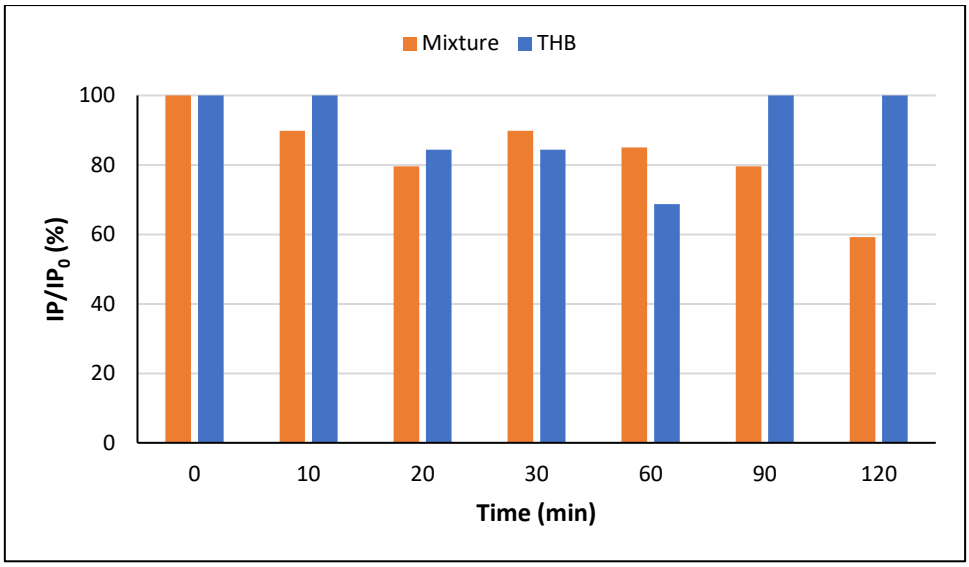


Fig IV. 8 Temporal variation of the permanganate index during the photocatalysis of THB and its mixture with DIM. Operating Conditions: $[THB]_0$ = 0.5 mM, [ZnO] = 5 g/L, T=25°C, V = 250 mL, UV-A ($[\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

- The degree of reuse of the catalyst (ZnO):

In order to reduce the cost of catalytic processes, the catalyst is often regenerated and reused, in this experiment we reused our catalyst after a simple washing with distilled water

and drying in the oven at 150 ° C in order to understand its influence on THB photocatalysis, the results are shown in the following figure:

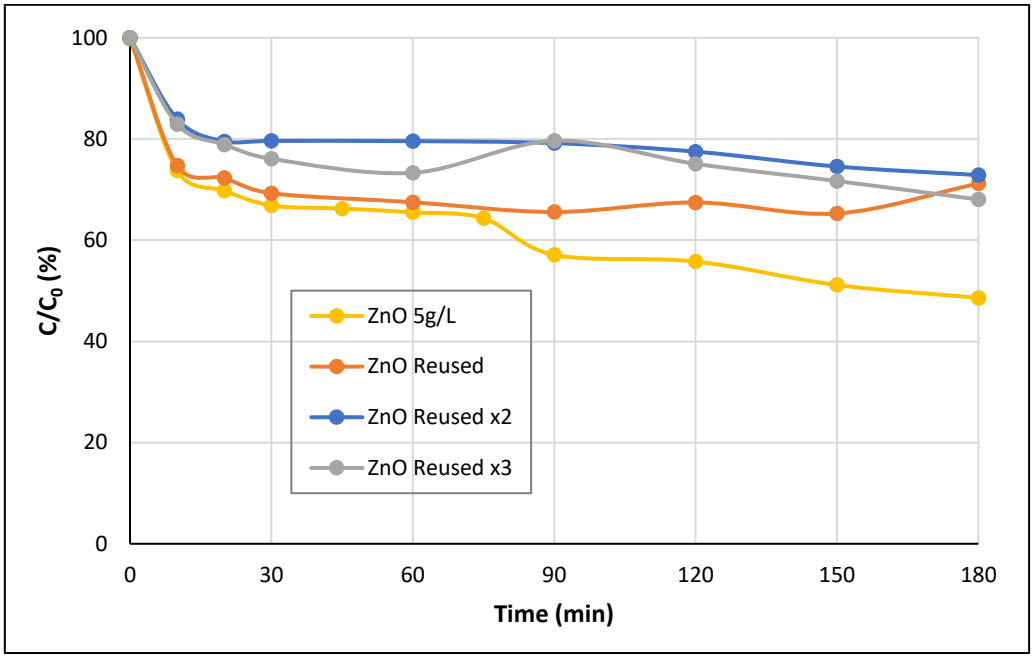


Fig IV. 9 Temporal variation of the active phase [THB] of TECTO during the photocatalysis using ZnO several times. Operating Conditions: $[THB]_0$ = 0.5 mM, [ZnO] = 5 g/L, V = 250 mL, T = 25 ° C, UV-A [λ_{Min} = 355 nm, λ_{Max} = 375 nm].

From these results, we notice that the more ZnO is reused, the more its catalytic efficiency decreases, after 1h30, ZnO (50%), ZnO x1 (35%), ZnO x2 (30%) and ZnO x3 (28%) is this is normal because its structure is influenced by the catalytic act and the number of its active sites decreases.

- Influence of the calcination temperature:

In order to understand the influence of the calcination temperature on the structure and thus on the photocatalysis, three temperatures were chosen [..] 400, 500 and 600 ° C, the catalyst was put in a porcelain crucible is calcinated for 1 hour using a Nabertherm L3 / 11 / C6 furnace.

The degradation of THB reached more than 30% for ZnO calcined at 400 and 500°C, on the other hand it did not exceed 17% for ZnO calcined at 600°C, this result is confirmed by several works, in particular those of I. Sugihartono et al [104] and AM.Ismail et al [105].

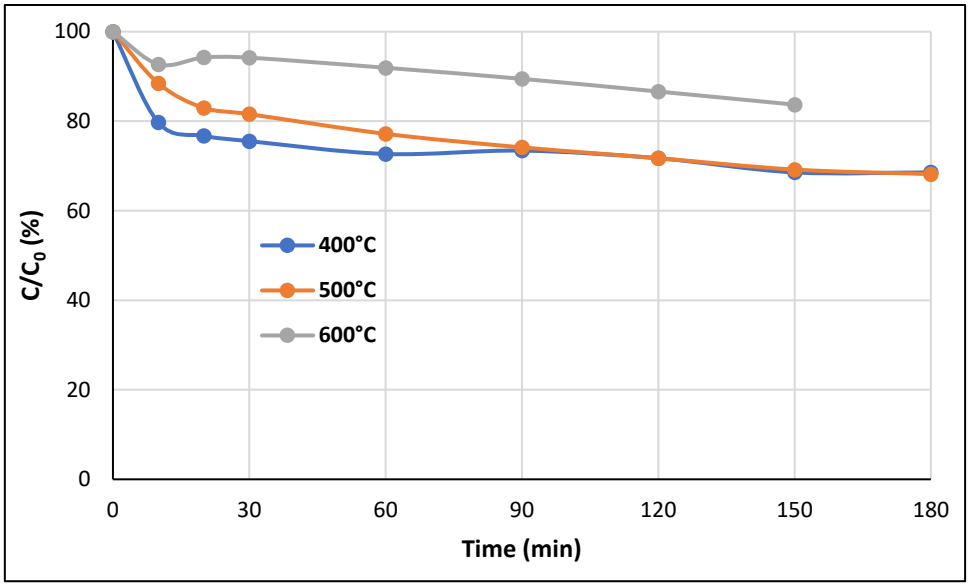


Fig IV. 10 Temporal variation of the active phase [THB] of TECTO during its photocatalysis with ZnO calcined under different temperatures. Operating Conditions: $[THB]_0 = 0.5$ mM, [ZnO] = 5 g / L, V = 200 mL, T = 25 ° C, UV-A ($[\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

b - Using TiO_2:

The second catalyst used is TiO_2, several experiments were carried out in order to optimize the operating conditions with the aim of eliminating the THB as much as possible.

- Effect of catalyst concentration:

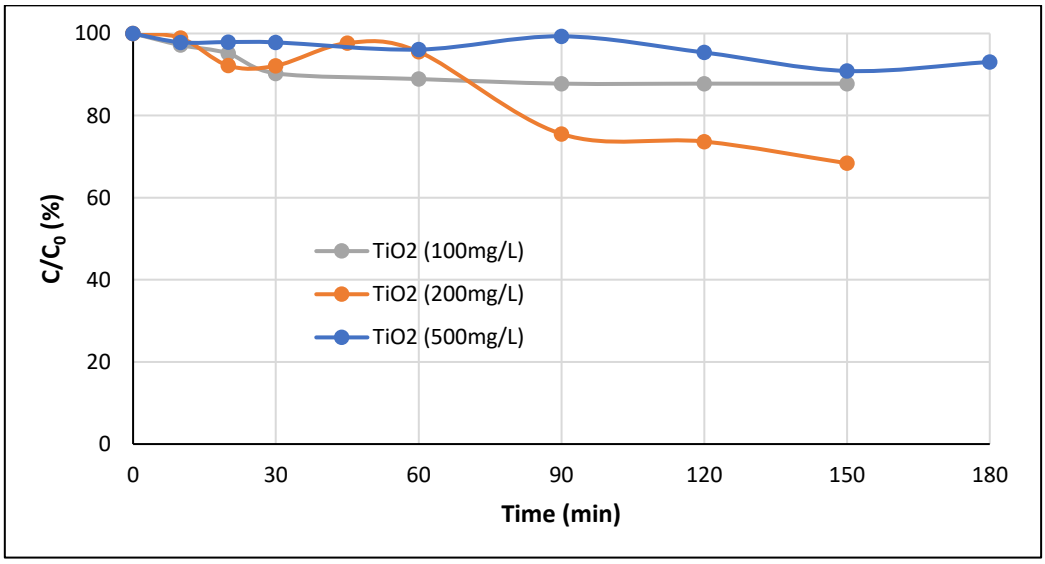


Fig IV. 11 Effect of the TiO_2 concentration on the temporal variation of the active phase [THB] of TECTO during its photocatalysis. Operating Conditions: $[THB]_0 = 0.5$ mM, V = 250 mL, T = 25 ° C, UV-A [$\lambda_{Min} = 355$ nm, $\lambda_{Max} = 375$ nm].

Three catalyst concentrations were chosen [TiO_2] = 100 mg/L, [TiO_2] = 200 mg/L and [TiO_2] = 500 mg/L, the results are presented in Fig IV. 11.

The degradation of THB reached more than 30% for 200 mg/L of TiO_2 on the other hand it did not exceed 10% for 100 and 500 mg/L of TiO_2, the catalytic efficiency is low compared to the literature but we remind that we work with the mass form which will lead us to use it in supported form in the perspectives of this work.

- Influence of the calcination temperature:

In order to understand the influence of the calcination temperature on the structure and thus on the photocatalysis, three temperatures were chosen [..] 400, 500 and 600 ° C, the catalyst was put in a porcelain crucible is calcined for 1 hour using a Nabertherm L3 / 11 / C6 furnace.

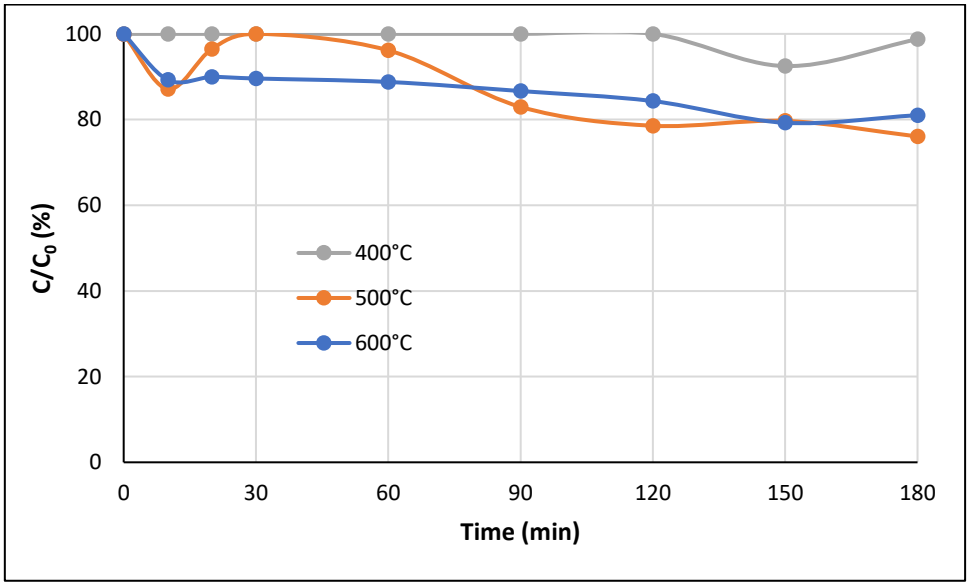


Fig IV. 12 Temporal variation of the active phase [THB] of TECTO during its photocatalysis with TiO_2 calcinated under different temperatures. Operating Conditions: $[THB]_0$ = 0.5 mM, [TiO_2] = 200 m g / L, V = 250 mL, T = 25 ° C, UV-A ([λ_{Min} = 355 nm, λ_{Max} = 375 nm].

Degradation THB has reached less than 10% by TiO_2 calcinated at 400°C versus 20 % for the TiO_2 calcinated at 600°C and 25% for the TiO_2 calcinated at 500°C.

In this part devoted to TiO_2 we note that its catalytic power is very reduced and this because of the form used which is the mass form, it is very interesting to test it in the supported form in order to exploit its photocatalytic activity to the maximum.

In the end of this chapter, we noted that: The photocatalysis of THB in aqueous medium was studied using a photoreactor and two catalysts in mass form under different conditions:

For ZnO, the concentration effect of the catalyst revealed that [ZnO] = 5g/L is the most efficient with a THB elimination rate of more than 60% and almost 70% mineralization (IP), as to the nature of the medium, neutral pH is by far the best condition for eliminating the pesticide.

The addition of another pesticide which is the DIM to have the cocktail effect or the real effluent influenced the operating conditions and forced us to double the quantity of the catalyst ([ZnO] = 10g/L) have a better yield of almost 60% but with less time than when the THB is alone which leads us to deduce that the presence of DIM has positively influenced the degradation reaction rate of the THB in the mixture.

The comparison of the reduction in the permanganate index shows us that it reaches more than 40% for the mixture after 2 hours of photocatalysis against 31% for THB alone, this can be explained by the accumulation of intermediate products in the mixture.

The reuse of the catalyst has shown us that the more the ZnO is reused, the more its catalytic efficiency decreases, after 1h30, ZnO (50%), ZnO x1 (35%), ZnO x2 (30%) and ZnO x3 (28%) which is normal because its structure is influenced by the catalytic act and the number of its active sites decreases.

For TiO_2, the degradation of THB has reached its best level of more than 30% for 200 mg/L, the catalytic efficiency is low compared to the literature but we remind that we are working with the mass form which takes us to using it in its supported form in the perspectives of this work.

And finally, the effect of the calcination temperature is studied and the degradation of THB reached its best level for ZnO calcined in 400 and 500°C, on the other side it reached 20% for TiO_2 calcinated in 600°C and 25% for the TiO_2 calcinated at 500°C.

By comparing the two catalysts, ZnO is more efficient in mass form than TiO_2 with more than 60% against 30% removal of THB respectively, although the masses are not the same (5g/L > 0.2 g/L), their cost too, TiO_2 is very expensive compared to ZnO.

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 photocatalysis of THB with DIM in an aqueous medium was studied using a photoreactor and two catalysts in mass form under different conditions and in the end, we noticed the following points:

- For ZnO, the concentration effect of the catalyst revealed that [ZnO] = 5g/L is the most efficient with a THB elimination rate of more than 60% and almost 70% mineralization (IP), as to the nature of the medium, neutral pH is by far the best condition for eliminating the pesticide.

- The addition of another pesticide which is the DIM to have the cocktail effect or the real effluent influenced the operating conditions and forced us to double the quantity of the catalyst ([ZnO] = 10g/L) have a better yield of almost 60% but with less time than when the THB is alone which leads us to deduce that the presence of DIM has positively influenced the degradation reaction rate of the THB in the mixture.

- The comparison of the reduction in the permanganate index shows us that it reaches more than 40% for the mixture after 2 hours of photocatalysis against 31% for THB alone, this can be explained by the accumulation of intermediate products in the mixture.

- The reuse of the catalyst has shown us that the more the ZnO is reused, the more its catalytic efficiency decreases, after 1h30, ZnO (50%), ZnO x1 (35%), ZnO x2 (30%) and ZnO x3 (28%) which is normal because its structure is influenced by the catalytic act and the number of its active sites decreases.

- For TiO_2, the degradation of THB has reached its best level of more than 30% for 200 mg/L, the catalytic efficiency is low compared to the literature but we remind that we are working with the mass form which takes us to using it in its supported form in the perspectives of this work.

- And finally, the effect of the calcination temperature is studied and the degradation of THB reached its best level for ZnO calcined in 400 and 500°C, on the other side it reached 20% for TiO_2 calcinated in 600°C and 25% for the TiO_2 calcinated at 500°C.

By comparing the two catalysts, ZnO is more efficient in mass form than TiO_2 with more than 60% against 30% removal of THB respectively, although the masses are not the same (5g/L > 0.2 g/L), their cost too, TiO_2 is very expensive compared to ZnO.

The perspectives of this work are:

- The study of the influence of the structural parameters of the photocatalyst, thus optimizing the process by combining it with other processes such as adsorption in order to recover the catalyst and proceed to its regeneration.

- 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.

- Coupling of these two oxides to form a ZnO/TiO_2 nanocomposite. The development of mixed oxide nanostructures is another approach for the photocatalytic degradation.

- 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.

REFERENCES

REFERENCES

[1] Frank R. Rijsberman, William J. Cosgrove World Water Vision: Making Water Everybody's Business (2000) DOI:10.4324/9781315071763

[2] World Helth Organization, (n.d.). http://www.who.int/en/ (accessed 09/12/2021).

[3] The Water Project, (n.d.). http://thewaterproject.org/ (accessed 09/12/ 2021).

[4] D. Bixio, C. Thoeye, J. De Koning, D. Joksimovic, D. Savic, T. Wintgens, et al., Wastewater reuse in Europe, Desalination. 187 (2006) 89–101. doi:10.1016/j.desal.2005.04.070

[5] An Overview of the State of the World's Fresh and Marine Waters - 2nd Edition, United Nations Environment Programme 2008.

[6] WWAP (World Water Assessment Programme). 2012. The United Nations World Water Development Report 4: Managing Water under Uncertainty and Risk. Paris, UNESCO.

[7] United Nations Environment Programme (UNEP, 2008).

URI: https://wedocs.unep.org/20.500.11822/7742 (accessed 09/12/ 2021).

[8] Marcos von Sperling, Carlos Augusto de Lemos Chernicharo, Biological wastewater treatment in warm climate regions, volume one, Department of Sanitary and Environmental Engineering federal University of Minas Gerais, Brazil 2006

[9] Ashok K. Rathoure, Vinod K. Dhatwalia, Toxicity and Waste Management Using Bioremediation (2016) DOI: 10.4018/978-1-4666-9734-8

[10] Grégorio Crini, Eric Lichtfouse. Wastewater treatment: an overview. Green Adsorbents for Pollutant Removal, 18, Springer Nature, pp.1-22, 2018, Environmental Chemistry for a Sustainable World, 978-3-319-92111-2. ff10.1007/978-3-319-92111-2_1ff. ffhal-02065607f

[11] Khalaf MN (ed) (2016) Green polymers and environmental pollution control. CRC Press, Oakville.

[12] A. Ginebreda, I. Muñoz, M.L. de Alda, R. Brix, J. López-Doval, D. Barceló, Environmental risk assessment of pharmaceuticals in rivers: Relationships between hazard indexes and aquatic macroinvertebrate diversity indexes in the Llobregat River (NE Spain), Environ. Int. 36 (2010) 153–162. doi:http://dx.doi.org/10.1016/j.envint.2009.10.003.

[13] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, et al., A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment., Sci. Total Environ. 473-474 (2014) 619–41.

doi:10.1016/j.scitotenv.2013.12.065.

[14] Hideo Ohkawa, Philip W. Lee, Hisashi Miyagawa, Pesticide Chemistry: Crop Protection, Public Health, 2007, Willy-VCH.

[15] Gatignol C., & Etienne J.C., Rapport sur pesticides et santé, Sénat : Assemblée nationale Collection : Les Rapports de l'OPECST, 2010, Paris.

[16] Calvet R., Barriuso E., Benoit P., Bedos C., Charnay M.P., Coquet Y., Les pesticides dans le sol. Conséquences agronomiques et environnementales. Editions France Agricole, 2005, Paris.

[17] Association de Coordination Technique Agricole., Index phytosanitaire ACTA 2005. 41e édition, Paris: ACTA publications, 2004.

[18] Garrido Frenich, A., Martínez Vidal J.L., López López T, Cortés Aguado, S., Martínez Salvador, I., Monitoring multi-class pesticide residues in fresh fruits and vegetables by liquid chromatography with tandem mass spectrometry, Journal of Chromatography A, 1048, 2, 2004, 199-206.

[19] Kerle EA, Jenkins JJ and Vogue PA (2007). Understanding pesticide persistence and mobility for groundwater and surface water protection. Oregon State Univ Extension Service, EM8561-E.

[20] Toth, S.J. and Buhler, W.G., (2009) Environmental effects of pesticides. Department of Entomology and Horticultural Science, North Carolina State University.

[21] Cessna A J, Wolf T M, Stephenson G R, Brown R B (2005). Pesticide movement to field margins: routes, impacts and mitigation. Field boundary habitats: implications for weed. Insect and Disease Management, 1: 69-112.

[22] Cessna AJ, Larney FJ, Kerr LA, Bullock MS (2006). Transport of trifluralin on wind-eroded sediment. Canadian Journal of Soil Science, 86: 545-554.

[23] Cessna AJ (2009). Pesticides in the environment: Real or Imagined. Agriculture and Agri-food Canada, Research Centre, Lethbridge, AB. http://www.ssca.ca/conference/conference 2005/Cessna.pdf.05.02.2009).

[24] Diaz, S., Settele, J., Brondízio, E., Ngo, H., Guèze, M., Agard, J., Arneth, A., Balvanera, P., Brauman, K., Butchart, S., 2019. In: Carneiro da Cunha, M., Mace, G.M., Mooney, H. (Eds.), Summary for Policymakers of the Global Assessment Report on Biodiversity and Ecosystem Services of the Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services. IPBES, Paris, pp. 1–45.

[25] Foley, J.A., DeFries, R., Asner, G.P., Barford, C., Bonan, G., Carpenter, S.R., Chapin, F.S., Coe, M.T., Daily, G.C., Gibbs, H.K., Helkowski, J.H., Holloway, T., Howard, E.A., Kucharik, C.J., Monfreda, C., Patz, J.A., Prentice, I.C., Ramankutty, N., Snyder, P.K., 2005. Global consequences of land use. Science 309, 570–574.

[26] PL Tan, F Humphries, Adaptive or aspirational? Governance of diffuse water pollution affecting Australia's Great Barrier Reef 361-384 Water International, 2018 volume43.

[27] Reichenberger S, Bach M, Skitschak A and Frede HG (2007). Mitigation strategies to reduce pesticide inputs into groundand surface water and their effectiveness; A review. Science of the Total Environment 384: 1–35.

[28] Dhiraj Sud, Paramjeet Kaur Sidhu (2012). Photocatalytic degradation of quinalphos in aqueous TiO_2 suspension: Reaction pathway and identification of intermediates by GC/MS,

DOI:10.1016/j.molcata.2012.08.005.

[29] Islam, M. T., Castle, S. J., & Ren, S. (2010). Compatibility of the insect pathogenic fungus Beauveriabassiana with neem against sweet potato whitefly, Bemisiatabaci, on eggplant. Entomologia Experimentalis et Applicata, 134(1), 28–34.

doi: 10.1111/j.1570-7458.2009.00933.x

[30] Undeğer, U., & Başaran, N. (2005). Effects of pesticides on human peripheral lymphocytes in vitro: induction of DNA damage. Archives of Toxicology, 79, 169–176. https://doi.org/10.1007/s00204-004- 0616-6.

[31] Lea Muszkat,Leonid Feigelson,Lena Bir,Karol A Muszkat.(2002). Photocatalytic degradation of pesticides and bio-molecules in water. doi: https://doi.org/10.1002/ps.578.

[32] Echavia, G. R. M.; Matzusawa, F.; Negishi, N. (2009) Photocatalytic Degradation of Organophosphate and Phosphonoglycine Pesticides Using TiO_2 Immobilized on Silica Gel. Chemosphere, 76, 595–600.

[33] Dehghani M.H., Fadaei A.M. 2012. Photocatalytic Oxidation of Oganophosphorus Pesticides using Zinc Oxide. Research Journal of Chemistry and Environment., 16 (3) Sept (2012), 104- 109.

[34] Navarro, C., Bullock, S., Lehmann, R. (2009). Altered dynein-dependent transport in piRNA pathway mutants. Proc. Natl. Acad. Sci. U.S.A. 106(24): 9691--9696.

[35] Evgenidou, E., Fytianos, K., Poulios, I., 2005. Photocatalytic oxidation of dimethoate in aqueous solutions. J. Photochem. Photobiol. A 175, 29–38.

[36] Yehia Sayed El-Temsah,Erik J. Joner,(2011). Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil.

https://doi.org/10.1002/tox.20610

[37] Burrows, W. H., Henry, B. K., Back, P. V., Hoffman, M. B., Tait, L. J., Anderson, E. R., Menke, N., Danaher, T., Carter, J. O., and McKeon, G. M. (2002). Growth and carbon stock change in eucalypt woodlands in north-east Australia: ecological and greenhouse sink implications. Global Change Biology 8, 769–784. doi: 10.1046/j.1365-2486.2002. 00515.x

[38] Dishun Zhao,Jialei Wang,Zhigang Zhang,Juan Zhang. Photocatalytic degradation of omethoate using NaY zeolite-supported TiO_2. June 2009. Frontiers of Chemical Engineering in China 3(2):206-210 DOI:10.1007/s11705-009-0053-4

[39] Jose Colina-Márquez, Fiderman Machuca-Martínez. Enhancement of the potential biodegradability and the mineralization of a pesticides mixture after being treated by a coupled process of TiO_2 -based solar photocatalysis with constructed wetlands. July 2013. Ingeniería y Competitividad 15(2):181

[40] Ioannis K.Konstantinou,Vasilios A.Sakkas,Triantafyllos A.Albanis Photocatalytic degradation of propachlor in aqueous TiO_2 suspensions. Determination of the reaction pathway and identification of intermediate products by various analytical methods. Water Research. Volume 36, Issue 11, June 2002, Pages 2733-2742

[41] Victor Sarria, Sandra Parra, Nevenka Adlera, Paul Péringer, Norberto Benitez, César Pulgarin. Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. Catalysis Today. Volume 76, Issues 2–4, 15 November 2002, Pages 301-315.

[42] Răileanu, M., Crişan, M., Niţoi, I., Ianculescu, A., Oancea, P., Crişan, D., & Todan, L. (2013). TiO_2-based nanomaterials with photocatalytic properties for the advanced degradation of xenobiotic compounds from water. A literature survey. Water, Air, and Soil Pollution, 224(1548), 45.

[43] Rashi Gusain,Kanika Guptaa, Pratiksh Joshi ,Om P.Khatri . Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. Advances in Colloid and Interface Science. Volume 272, October 2019, 102009. https://doi.org/10.1016/j.cis.2019.102009

[44] Grégorio Crini, Eric Lichtfouse. Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters, Springer Verlag, 2019, 17 (1), pp.145-155. ff10.1007/s10311-018-0785-9ff. ffhal-02082890f.

[45] E. Evgenidou, K. Fytianos, I. Poulios. Semiconductor-sensitized photodegradation of dichlorvos in water using TiO_2 and ZnO as catalysts. Applied Catalysis B: Environmental

Volume 59, Issues 1–2, 8 July 2005, Pages 81-89. https://doi.org/10.1016/j.apcatb.2005.01.005

[46] Haque, M.M., Bahnemann, D., Muneer, M., 2012. Photocatalytic degradation of organic pollutants: Mechanisms and kinetics. Organic Pollutants Ten Years After the Stockholm Convention-Environmental and Analytical Update. IntechOpen, pp. 293–326.

[47] 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

[48] Deng, Y., & Zhao, R. (2015). Advanced Oxidation Processes (AOPs) in Wastewater Treatment. *Current Pollution Reports*, *1*(3), 167-176. https://doi.org/10.1007/s40726-015-0015-z .

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

[50] Solarchem Environmental Systems. The UV/oxidation handbook. 1994.

[51] 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.

[52] I. Gültekin, N.H. Ince, Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes., J. Environ. Manage. 85 (2007) 816–32. doi:10.1016/j.jenvman.2007.07.020.

[53] Ana Justo Llopis. Advanced technologies applied to wastewater treatment plant effluents doctoral theses. (2015)

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

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

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

[57] Kolthoff IM, Stenger VA, Belcher R. Volumetric analysis. 2. Titration methods: acid–base, precipitation, and complex formation reactions. Interscience Publ; 1947.

[58] Huling SG, Pivetz BE. In-situ chemical oxidation; DTIC Document. 2006.

[59] House DA. Kinetics and mechanism of oxidations by peroxydisulfate. Chem Rev. 1962;62(3):185–203.

[60] Kolthoff I, Miller I. The chemistry of persulfate. II. The reaction of persulfate with mercaptans solubilized in solutions of saturated fatty acid soaps1. J Am Chem Soc. 1951;73(11):5118–22.

[61] Abhishek Mahajan1, Kulbir Singh Nain2, Rajesh Kumar Lohcha. Photocatalytic Degradation of Pulp & Paper Mill WastewaterUsing ZnO Photocatalyst.

[62] Marta I. Litter∗ Unidad de Actividad Qu´ımica, Centro Atómico Constituyentes, Comisión Nacional de Energ´ıa Atómica Av. Gral. Paz1499, Gral. San Mart´ın, (1650) Buenos Aires, Argentina Heterogeneous photocatalysis Transition metal ions in photocatalytic systems.

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

[64] Craig, C. (2006). Kirk-Othmer Encyclopedia of Chemical Technology and Ullmann's Encyclopedia of Industrial Chemistry. *Issues in Science and Technology Librarianship*, (46). https://doi.org/10.5062/F4RF5S0T

[65] J. Zhang et al., Photocatalysis, 2018 Lecture Notes in Chemistry 100,

https://doi.org/10.1007/978-981-13-2113-9_1

[66] Rakshit Ameta, Meenakshi S. Solanki, Surbhi Benjamin and Suresh C. Ameta. Photocatalysis. Advanced Oxidation Processes for Wastewater Treatment.

DOI: https://doi.org/10.1016/B978-0-12-810499-6.00006-1

[67] Ali, A.M., Muhammad, A., Shafeeq, A., Asghar, H.M.A., Hussain, S.N., Sattar, H., 2012. Doped metal oxide (ZnO) and photocatalysis: a review. J. Pak. Inst. Chem. Eng. 40 (1), 11-19.

[68] Nyamukamba, P., Mamphweli, S., Petrik, L., 2017. Silver/carbon codoped titanium dioxide photocatalyst for improved dye degradation under visible light. Int. J. Photoenergy. Available from: http://dx.doi.org/10.1155/ 2017/3079276.

[69] Wang, H., Zhang, L., Chen, Z., Hu, J., Li, S., Wang, Z., et al., 2014. Semiconductor heterojunction photocatalysts: Design, construction, and photocatalytic performances. Chem. Soc. Rev. 43 (15), 5234-5244.

[70] Rajkumar, R., Singh, N., 2015. To study the effect of the concentration of carbon on ultraviolet and visible light photo catalytic activity and characterization of carbon doped TiO_2. J. Nanomed. Nanotechnol. 6, 260. Available from: http://dx.doi.org/10.4172/2157-7439.1000260.

[71] Medina-Ramı´rez, I., Herna´ndez-Ramı´rez, A., Maya-Trevin˜o, M.L., 2014. Synthesis methods for photocatalytic materials. Photocatal. Semiconductors 69-102.

[72] Borse, P.H., Kim, J.Y., Lee, J.S., Lim, K.T., Jeong, E.D., Bae, J.S., et al., 2012. Ti-dopant-enhanced photocatalytic activity of a $CaFe_2O_4/MgFe_2O_4$ bulk heterojunction under visible-light irradiation. J. Korean Phys. Soc. 61 (1), 73-79.

[73] Cassano AE, Alfano OM. Reaction engineering of suspended solid heterogeneous photocatalytic reactors. Catal Today 2000; 58: 167- 97.

[74] Photoreactors for Wastewater Treatment: A Review Ewa Kowalska* and Sven Rau Friedrich-Alexander University of Erlangen-Nuremberg, Institute of Inorganic Chemistry, 91058 Erlangen, Germany)2010

[75] Vinu R, Madras G (2011) Photocatalytic degradation of water pollutants using Nano- TiO_2. In: Zang L (ed) Energy efficiency and renewable energy through nanotechnology. Springer, London, pp 625–677

[76] Ahmed S (2011) Impact of operating conditions and recent developments in heterogeneous photocatalytic water purification process. Crit Rev Environ Sci Technol 42(6):601–675

[77] Boarini P, Carassiti V, Maldotti A et al (1998) Photocatalytic oxygenation of cyclohexane on titanium dioxide suspensions: effect of the solvent and of oxygen. Langmuir 14(8):2080–2085

[78] M. D. McCluskey and S. J. Jokela Department of Physics and Astronomy, Washington State University, Pullman, Washington 99164-2814, USA 2 Institute for Shock Physics, Washington State University, Pullman, Washington 99164-2816, USA

[79] C. Richard, F. Bosquet, J.F. Pilichowski, Photocatalytic transformation of aromatic compounds in aqueous zinc oxide suspensions: effect of substrate concentration on the distribution of products, J. Photochem. Photobiol. A: Chem. 108 (1997) 45.

[80] M.C. Yeber, J. Rodrıguez, J. Freer, N. Durian, H.D. Mansilla, Photocatalytic degradation of cellulose bleaching effluent by supported TiO_2 and ZnO, Chemosphere 41 (2000) 1193.

[81] V. Dijken, A.H. Janssen, M.H.P. Smitsmans, D. Vanmaekelbergh, K. Meijerink, Size-Selective Photoetching of Nanocrystalline Semiconductor Particles, Chem. Mater. 10 (1998) 3513.

[82] S. Neppolian, B. Sakthivel, M. Arabindoo, V. Palanichamy, J. Murugesan, Degradation of textile dye by solar light using TiO_2 and ZnO photocatalysts, Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 34 (9) (1999) 1829.

[83] K. Gouvea, F. Wypych, S.G. Moraes, N. Duran, N. Nagata, P. Peralta Zamora, Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, Chemosphere 40 (2000) 433.-13 S.

[84] Hadis Morkoç, Ümit Özgür. Zinc Oxide: Fundamentals, Materials and Device Technology. January 2009. ISBN: 978-3-527-40813-9

[85] Carolina Belver, Jorge Bedia, Almudena Gómez-Avilés, Manuel Peñas-Garzón, Juan J. Rodriguez. Chapter 22 - Semiconductor Photocatalysis for Water Purification.

Nanoscale Materials in Water Purification. Micro and Nano Technologies 2019, Pages 581-651 https://doi.org/10.1016/B978-0-12-813926-4.00028-8

[86] Gupta, S.M., Tripathi, M. A review of TiO_2 nanoparticles. *Chin. Sci. Bull.* **56,** 1639 (2011). https://doi.org/10.1007/s11434-011-4476-1

[87] M. Yu, Y. Ma, J. Liu, X. Li, S. Li, S. Liu, Sub-coherent growth of ZnO nanorod arrays on three-dimensional graphene framework as one-bulk high-performance photocatalyst, Appl. Surf. Sci. 390 (2016) 266-272

[88] S. Bera, M. Pal, A. Naskar, S. Jana, Hierarchically structured ZnO-graphene hollow microspheres towards effective reusable adsorbent for organic pollutant via photodegradation process, J. Alloys Compd. 669 (2016) 177e186.

[89] Kezhen Qi a, b, Bei Cheng a , Jiaguo Yu a, d, , Wingkei Ho c, Review on the improvement of the photocatalytic and antibacterial activities of ZnO . Journal of Alloys and Compounds Volume 727, 15 December 2017, Pages 792-820.

https://doi.org/10.1016/j.jallcom.2017.08.142

[90] K. Aponiene, Z. Luksiene, Effective combination of LED-based visible light, photosensitizer and photocatalyst to combat Gram (-) bacteria, J. Photochem. Photobiol. B 142 (2015) 257-263.

[91] C. Han, M.-Q. Yang, B. Weng, Y.-J. Xu, Improving the photocatalytic activity and anti-photocorrosion of semiconductor ZnO by coupling with versatile carbon, Phys. Chem. Chem. Phys. 16 (2014) 16891-16903

[92] G.P. Awasthi, S.P. Adhikari, S. Ko, H.J. Kim, C.H. Park, C.S. Kim, Facile synthesis of ZnO flowers modified graphene like MoS2 sheets for enhanced visiblelight-driven photocatalytic activity and antibacterial properties, J. Alloys Compd. 682 (2016) 208-215.

[93] M. Humayun, F. Raziq, A. Khan & W. Luo (2018) Modification strategies of TiO_2 for potential applications in photocatalysis: a critical review, Green Chemistry Letters and Reviews, 11:2, 86-102, DOI: 10.1080/17518253.2018.1440324

[94] Rakshit Ameta , Meenakshi S. Solanki , Surbhi Benjamin and Suresh C. Ameta . Emerging Green Chemical Technology. Advanced oxidation Processes for Wastewater Treatment (2018) ISBN: 978-0-12-810499-6.

[95] Ferrer C., Gomez M. J., Garcia-Reyes J. F., Ferrer I., Thurman E. M, Fernandez-Alba A. R., J. Chromatogr. A; Determination of pesticide residues in olives and olive oil by matrix solid-phase dispersion followed by gas chromatography/mass spectrometry and liquid chromatography/tandem mass spectrometry; Journal of Chromatography A; Volume 1069, Issue 2, (2005), Pages 183-194.

[96] Rastrelli L., Totaro K., De Simone F; Determination of organophosphorus pesticide residues in Cilento (Campania, Italy) virgin olive oil by capillary gas chromatography; Food Chemistry; Volume 79, Issue 3, (2002), Pages 303-305.

[97] Babina K., Dollard M., Pilotto L., Edwards J.W; Environmental exposure to organophosphorus and pyrethroid pesticides in South Australian preschool children: A cross sectional study; Environment International; Volume 48, 1 (2012), Pages 109-120.

[98] Lozowicka B., Mojsak P., Jankowska M., Kaczynski P., Hrynko I., Rutkowska E., Szabunko J. Borusiewicz, A., Toxicological studies for adults and children of insecticide residues with common mode of action (MoA) in pome, stone, berries and other small fruit, Sci. Total Environ.t 566–567 (2016) 144.

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

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

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

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

[103] Soro Donafologo Baba, Photodégradation en milieu aqueux de trois pesticides : thiabendazole, diméthoate et diazinon, THESE Pour l'obtention du grade de : Docteur en Sciences et Gestion de l'Environnement de l'Université d'Abobo-Adjamé, Novembre 2012.

[104] Iwan Sugihartono, Atika Retnoningtyas, Cecep Rustana, Umiatin, Nurfina Yudasari, Isnaeni, Cuk Imawan, and Fera Kurniadewi. The influence of calcination temperature on optical properties of ZnO nanoparticles. AIP Conference Proceedings **2169**, 060010 (2019);

https://doi.org/10.1063/1.5132688

[105] A.M.Ismail, A.A.Menazea, Hoda A.Kabary, A.E.El-Sherbiny, A.Samy . The influence of calcination temperature on structural and antimicrobial characteristics of zinc oxide nanoparticles synthesized by Sol–Gel method. Journal of Molecular Structure; Volume 1196, 15 November 2019, Pages 332-337.

https://doi.org/10.1016/j.molstruc.2019.06.084

دراسة مقارنة للتحفيز الضوئي للمبيدات باستخدام أنواع مختلفة من المحفزات

الملخص:

أصبحت القضايا البيئية المتعلقة بالتلوث الكيميائي والبيولوجي للمياه مصدر قلق كبير للمجتمع والحكومة والصناعة في الثلاثين عامًا الماضية. ينتج عن غالبية الأنشطة المنزلية والصناعية مياه صرف تحتوي على ملوثات ضارة. بشكل خاص الملوثات العضوية، ولا سيما المبيدات المستعملة في الزراعة لتحسين غلة المحاصيل. تشكل هذه الممارسات تهديدًا مباشرًا للبيئة والكائنات الحية وصحة الإنسان على وجه الخصوص. لذلك، تم تطوير تقنيات لإزالة بقايا هذه المبيدات للحد من تأثيرها.

في هذا السياق، تم إجراء دراسة على عملية التحفيز الضوئي للمبيدات باستخدام محفزين مختلفين (TiO_2 ، ZnO) لجزيء نموذجي (ثيابانداز ول مع ديميثوات). تم قياس اختفاء الجزيء العضوي (ZnO: 60%, TiO_2: 30%) وتقييم درجة تمعدن المحلول من خلال قياس المعلمات العالمية مثل مؤشر البرمنجنات (ZnO: 70%). تم إجراء هذه الدراسة حول محاليل تجارية كما تم دراسة العوامل الأخرى التي تؤثر على التحلل مثل مستوى الأس الهيدروجيني (معتدل pH=7.5) وتركيز المحفزات (ZnO: 5g/L, TiO_2:0.2g/L) ودرجة حرارة التكليس (ZnO: 400-500°C, TiO_2: 600°C).

الكلمات المفتاحية: التحفيز الضوئي، معالجة المياه، جذور الهيدروكسيل، المبيدات.

Abstract:

Environmental issues with the chemical and biological contamination of water have become a major concern for society, government, and the industry in the last 30 years. The majority of domestic and industrial activities result in wastewater that contains harmful pollutants. Especially 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 to human health. Therefore, techniques to remove pesticide residues have been developed to reduce the contaminated areas and matrix.

In this context, a study is carried out on pesticides photocatalysis process using two different catalysts (TiO_2, ZnO) of a model molecule (Thiabendazole with Dimethoate). The disappearance of the organic molecule is measured (60% for ZnO against 30% for TiO_2) and the degree of mineralization of the solution is evaluated by the measurement of global parameters such as the permanganate index (70% for ZnO). This study is carried out with commercial solutions also, other parameters that influence the degradation were studied, the neutral pH is by far the best condition, concentration of the catalysts (5g/L for ZnO and 0.2g/L for TiO_2) and the calcination temperature (400 and 500°C for ZnO, 600°C for TiO_2).

Keywords: Photocatalysis, water treatment, hydroxyl radicals, pesticide.