People's Democratic Republic of Algeria
Ministry of Higher Education and Scientific Research

University Amar Thelidji- Laghouat

FACULTY: TECHNOLOGY

DEPARTMENT: PROCESS ENGINEERING

MASTER'S DEGREE THESIS

Presented by: TERBAH Meriem Nesrine

KROBBA Assia

FILED: Sciences and Technologies

SECTOR: Process Engineering

OPTION: Chemical Engineering

Title

Biomass-derived active carbon (AC) modified ZnO photocatalyst for efficient photocatalytic degradation of Methylene Blue Dye under visible light

Supervisory and examining committee:

First and last name	Grade	quality
MECHRAOUI Omer	MCA	Chair of defense
MAHJOUBI Hadj Aissa	MCB	Examiner
BRAHIMI Djamila	MCB	Supervisor

Promotion: JUNE 2024

Acknowledgment

First and foremost, we would like to sincerely and deeply thank God

*'**Allah'** who has given us life and health.*

The work presented in this thesis was carried out in the Process Engineering Laboratory and the Process Engineering Department of the University of Laghouat Amar Thelidji.

Secondly, we would like to thank our supervisor, Dr. Brahimi Djamila, who supervised and accompanied us daily in the preparation of this work with the greatest diligence and wonderful human qualities, which was a major factor in the completion of this work, both scientifically and morally.

We would also like to thank all the members of the jury:

***Mr. Mechraoui Omer**, Chairman, and **Mr. Mahjoubi Hadj Aissa**, Examiner, for accepting and judging this modest work.*

*We would also like to thank the head of the department, **Mr. Benalia Mokhtar**, and his deputy, **Mr Tounsi Aissa**, as well as all the teachers in the Process Engineering department.*

*Thanks to all the engineers and technicians of the Process Engineering Laboratory at the University of Laghouat, especially engineer **Madjida** and technician **Fathia**.*

Thank you to all the teachers in the Process Engineering department with whom we worked every day during our years of study.

Finally, a big thank you to all my colleagues and to all the people who share our lives and who have contributed greatly to the completion of this work in perfect conditions.

Dedications

To my greatest supporters and sources of inspiration, I dedicate this work with infinite love and gratitude.

To my heart, dear father ***Ben Harzallah***

No words can express my respect and love, to my King Father who taught me the importance of hard work, perseverance, and honesty, I am grateful for your wise counsel and unfailing support. You inspired me to aim higher and pursue my dreams. I am infinitely grateful for your unwavering support, your confidence in me, and your love. I am so lucky to be your daughter. I'd like to thank you for your love, your presence, and the sacrifice you made for my education. Thank you for always being there to make me smile. Without you, I wouldn't be the strong and courageous person I am today. I love you with all my heart.

In my eyes, dear mother ***Asma***

To my Queen Mother, who has always been my port of call and compass, thank you for your unconditional love, devotion, and unwavering support. You have been the light that has illuminated my path in dark moments and you have always believed in me, even when I doubted. Every day you give me a sincere, deep, and incomparable love. Today, I pay tribute to your beautiful heart, mind, and woman qualities. I'm proud to have a mother like you. Thank you for all the love you've given me, I love you with all my heart.

To my brother ***Mohamed Lamine****, my second father, I am so lucky to be your sister. Thank you for your constant support and your presence by my side.*

To my beloved sisters ***Bouchra, Roukia,*** *and* ***Mesouda****, who are also my best friends, thank you for your constant support, infectious humor, and comforting presence.*

To my nieces and nephews ***Ahmed****,* ***Louai****,* ***Hadil, Malik****,* ***Jawad,*** *and* ***Harzallah*** *who o Bijoux filled my life with so much happiness and joy.*

Thank you for my family ***Kroubba*** *and* ***Chourana***

Thank you to the most beautiful and special person in my life for being with me for the last five years. Thank you for your constant support and your presence by my side. You are always unique and special to me.

To my very dear friends ***Fatima a Zahra****,* ***Ibtissam****,* ***Nouna****,* ***Doudi****,* ***Taha,*** *and my cousin* ***Wafa*** *who have been my pillars in difficult times and my party partners in moments of joy, thank you for your sincere friendship, your unfailing support, and your unconditional love.*

Finally, thank you to my partner ***Meriem*** *and their family, who has become a dear friend and talented collaborator, thank you for our fruitful collaboration and friendship.*

Assia

Dedications

To my father, ***Benaamar***

To the man who made me a woman, my source of life, love, and affection.

To my support, who was always by my side to support and encourage me.

To my prince father.

*To my mother****, Kltoum***

For her unconditional love, tireless support, and countless sacrifices. Mum, your faith in me has given me the courage and determination to be the backbone of our family and your devotion has always motivated me to give my best.

To my grandmother

To my grandfather

To my dear sister, ***Aya***

For their constant presence, unwavering support, and brotherly love.

To my dear brothers, ***Maamar*** *and* ***Mohamed***

To my dear friends, ***Ibtissam*** *and* ***Fatima***

For your precious friendship, your encouragement, and your unfailing support. You've been there for me.

To my partner ***Assia*** *and their family, I was happy to have accompanied you throughout my university years and my life and for your participation in this work.*

To all those who have supported me from near and far, this thesis is the fruit of your love, support, and encouragement. It is with immense gratitude and deep appreciation that I dedicate this work to you. Thank you for being an essential part of this journey, and for enabling me to successfully complete this project.

In the end to all my brothers and sisters in Gaza and Palestine, the victory is coming we are praying for you, Gaza will always be an example that no matter what life in this cruel world drops on you never stop fighting for your cause. Long life Palestine Free Palestine

Meriem

List of Figures

Chapter I: Literature Review

Chapter II: Experiment Setup and Conditions

Chapter III: Results and Discussions

List of tables:

List of Abbreviations & symbols:

AC: Activated carbon.

AOPs: Advanced Oxidation Processes.

C_e: Concentration of the solution at equilibrium (mg/L).

C_0: Initial concentration of the solution (mg/L).

COD: Chemical Oxygen Demand.

DS: Date Seeds.

HCl: Hydrochloric Acid.

H_2O: Distilled Water.

KOH: Potassium Hydroxide.

K (g/mg.min): The intra-particle diffusion rate constant

m: The mass of the photocatalyst (g).

MB: Methylene blue.

NaOH: Hydroxide Sodium hydroxide.

pH: Hydrogen potential.

Q_e: Quantity of the BM photodegrades at equilibrium (mg/g).

R (%): The photocatalytic degradation rate.

R^2: Square correlation coefficient.

ROS: Reactive Oxygen Species.

T: Temperature (k), (°C).

UWW: Urbar Waste Water.

UV-Vis: Ultraviolet-Visible.

V: Volume of solution size (L).

ZnO: Zinc Oxide.

$Zn(NO_3)_2$: Zinc Nitrate Hexahydrate.

Table of Contents

Chapter II:Experiment Setup and Conditions

Chapter III: Results and Discussions

General Introduction

Introduction

Water pollution by synthetic dyes is a major environmental problem affecting many aquatic ecosystems. Degrading these contaminants using effective methods is crucial to protecting the environment. Conventional wastewater treatment methods, such as flocculation and filtration, often prove ineffective for completely degrading synthetic dyes. Recently, photocatalytic degradation has emerged as a promising method for treating wastewater contaminated with organic and inorganic pollutants. This process makes it possible to eliminate persistent contaminants from water, such as dyes and pesticides. The degradation of organic dyes present in industrial effluents is a major environmental challenge. Methylene blue (MB), widely used in various industries, is known to be toxic and persistent in the environment. Consequently, developing effective methods for removing MB from aqueous effluents is essential to reduce its environmental impact. This issue has attracted the attention of many researchers in recent years [1-2]. Many of these studies have used aqueous suspensions of semiconductors illuminated by light to photodegrade the pollutants. Zinc oxide (ZnO) is a material widely used as an efficient, inexpensive, and non-toxic semiconducting photocatalyst for degrading a wide range of organic chemicals [3-4]. The performance of a semiconducting photocatalyst (i.e. ZnO) is closely related to its electronic structure [5-6]. It has been established that the photocatalytic degradation of an organic molecule or ion in solution is initiated by photogenerated holes (h^+) in the valence band (VB) and electrons (e^-) in the conduction band (CB) of the semiconducting photocatalyst. The h^+ generated has a high oxidation potential, allowing direct oxidation of the organic molecule/ion to reactive intermediates. In addition, hydroxyl radicals are reactive species that can contribute to the degradation of the organic substrate. Hydroxyl radicals can be generated either by the reaction of h^+ with water and OH anions or by the reaction of dissolved O_2 and e- [4, 7, 8]. The generation of h^+ and e^- on a photocatalyst and the possible reactions of h^+ and e- in an aqueous solution. To overcome this limitation, various strategies have been proposed, including the use of ZnO composites with the incorporation of activated carbon (AC) to improve efficiency.

The main goal of this study is to synthesize a composite photocatalyst based on ZnO and AC. Three different weight ratios were used in this matrix of the composite photocatalysts. The performance of the synthesized ZnO-AC photocatalyst was evaluated in the photodegradation of BM dye under visible light. Specific objectives include:

- Determining the optimum ratio of ZnO and AC for a complete and fast BM photodegradation.
- Studying the effect of various parameters such as catalyst dose, initial BM dye concentration, solution pH, irradiation time, and light source.
- Analysis of the kinetic mechanisms of BM dye degradation over the synthesized photocatalyst.

This dissertation is structured as follows:

- The first chapter presents a review of the literature on heterogeneous photocatalysis and ZnO-AC composites.
- The second chapter describes the experimental part and methods used for the synthesis of the ZnO-AC composite.
- The third chapter discusses the experimental results obtained and analyses the effectiveness of the composite in the degradation of BM dye.
- Finally, a general conclusion is drawn, setting out all the experimental results obtained and the prospects envisaged for the continuation of this study.

Chapter I:

Literature Review

I.1. Water pollution

Pollution can be defined in several ways. Water pollution occurs when energy and other materials are released, degrading water quality for other users. Water pollution includes all residual materials that cannot be naturally ventilated by water. In other words, anything added to water, beyond its capacity to break it down, is pollution. Pollution, in certain circumstances, can be caused by nature itself, as when water flows through highly acidic soils. But in most cases, human actions are responsible for the pollutants that enter the water [9].

Household pollutants are the products we use every day, such as cleaning products, cosmetics, pharmaceuticals, and industrial dyes.

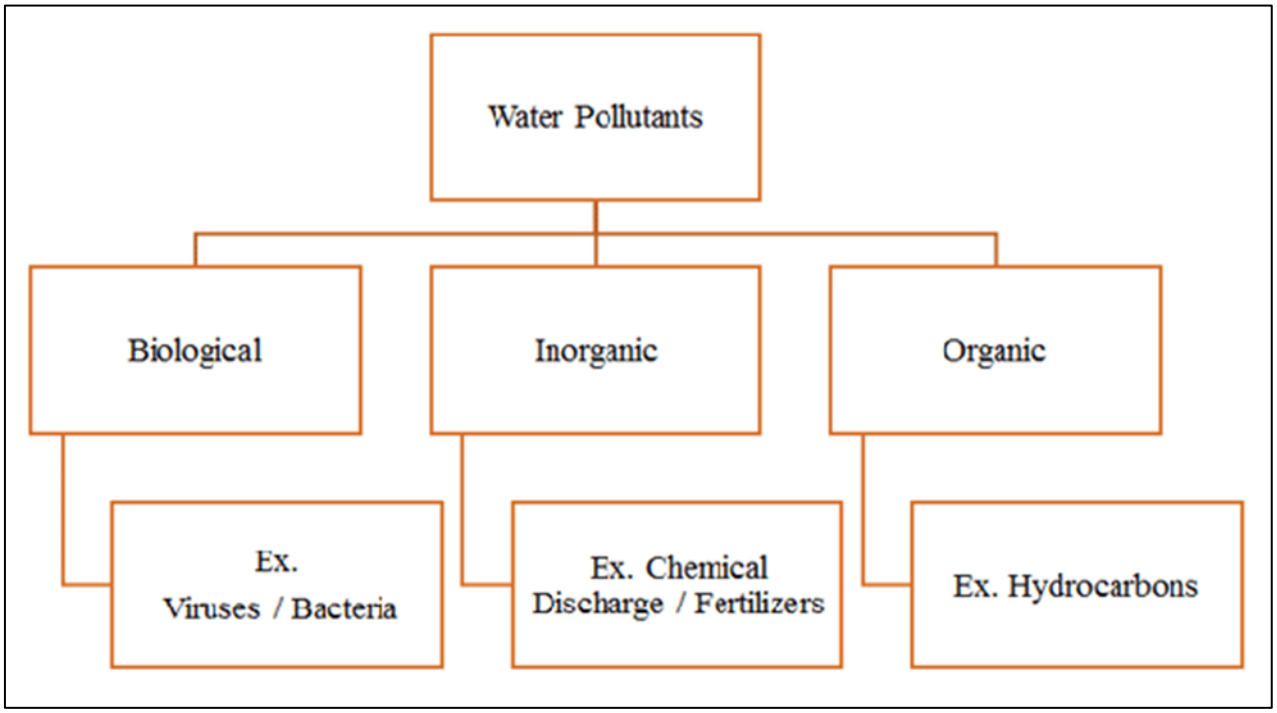

Figure.I.1. The schematic diagram illustrates the different types of water pollutants.

1.1. Origin of water pollution

The origins of water pollution are varied and closely linked to human activities: natural, agricultural, and industrial. The main manifestations of this pollution are chemical or biological in nature and can be pathogenic for humans. There are four categories: domestic, urban, agricultural, and industrial pollution [10].

- **Urban pollution:**

Urban wastewater (UWW) includes household wastewater, black water, and runoff. The composition and characteristics of urban wastewater vary little from those of wastewater [11].

- **Agricultural pollution:**

Agricultural pollution has intensified in recent years. It mainly concerns the spreading of chemical fertilizers (nitrates, phosphates), herbicides, insecticides, and other phytosanitary products, as well as excess animal manure from livestock effluents, which enrich waterways with various nitrogen products. These products can affect the receiving environment either directly, through the harmfulness of the products (herbicides, insecticides) or indirectly, through the contribution of nutrient salts that promote the proliferation of algae and lower oxygen levels, which can lead to eutrophication [12].

- **Industrial pollution:**

Industries receive a large quantity of water, which is necessary to ensure their proper functioning and a large quantity is discharged into the environment. This wastewater contains pollutants that vary according to its origin. The textile industry in particular uses a large volume of water, and many dyes are discharged into the environment. Water pollution by these dyes is one of the most common forms of pollution and remains a major challenge, especially in developing countries which do not yet have all the opportunities to integrate sustainable development concepts [13].

I.1.2. Conventional water treatment processes

The diversity of organic pollutants present in water, and their degree of toxicity, have led to the development of several elimination techniques to respond to each type of pollutant. These different treatment methods can be classified according to several criteria: the type of effluent to be treated, the volume, the cost, and the effectiveness of the desired treatment. The methods used fall into 3 main categories: biological, physical, and chemical processes [14].

I.1.2.1. Biological processes

Biological treatment is the decomposition of organic substances dissolved in water by microorganisms. There are two main categories of treatment: aerobic and anaerobic [14].

- **Aerobic treatment:**

Aerobic treatment is a method of oxidizing and degrading organic matter dissolved in water using aerobic bacteria. Organic substances are oxidized and broken down by enzymatic reactions set in motion by the microorganisms in the presence of oxygen to produce energy. They use a portion of this energy as well as a portion of the organic matter to multiply [14].

- **Anaerobic treatment:**

This type of treatment is also known as anaerobic digestion or methane fermentation. In this case, anaerobic bacteria are used to break down organic substances. Remediation is achieved by introducing the effluent to be treated into a tank containing the microorganisms, which are under anaerobic conditions (absence of oxygen). This type of process is used to treat effluent or wastewater with a high organic content.

These processes are not always applicable to industrial effluents, due to the high concentrations of pollutants, toxicity, or very low biodegradability [14].

I.1.3. Textile Dye Industry Pollution

Our world is awash with color, whether in our clothes, our food, our cosmetics, or our pharmaceutical products. Increasingly, these colors come from synthetic dyes, which are valued for their ease and speed of production, as well as for their wide range of shades compared with natural alternatives [15].

The clothes we wear are made from textile fibers dyed with various dyes, which are essentially chemical molecules that give them their distinctive color. However, we often forget the significant environmental and health risks associated with the production of these dyes [15].

I.2. Wastewater Treatment

The world thrives on color evident in everything from clothes, food, cosmetics, pharmaceuticals, and so on. These dyes are increasingly synthetic dyes, due to their ease and speed of production and their wide variety of colors when compared to natural dyes [16].

The clothes people are made from textile fibers colored with different dyes, which are nothing more than chemical molecules giving them their final color. Little do know that the manufacture of these same garments is generating ever-greater and more dangerous pollution for human beings, causing serious environmental disruption and damage to our health [16].

I.2.1. Adsorption

Adsorption is a widely employed method for removing organic and inorganic pollutants from both liquid and gaseous effluents. To elucidate the mechanisms governing these phenomena, various theoretical models have been developed. This process involves the transfer of pollutants from the fluid phase to the solid's surface. Activated carbon stands out as one of the most effective adsorbents, but its high cost restricts its widespread application in dye removal [16].

I.2.1.1. Dye adsorption mechanism

Adsorption is a widely applicable process for dye removal and wastewater treatment. Adsorption separation relies on the selective (thermodynamic and/or kinetic) adsorption of pollutants (adsorbates) onto an adsorbent, driven by specific interactions between the material's surface and the adsorbed species [16]. This process involves a simple mass transfer from the liquid phase to the solid surface and occurs in several steps:

- **External Diffusion:** This stage involves the transfer of the solute (dye) from the solution to the external surface of the adsorbent grains. The rate of external mass transfer depends on the hydrodynamic conditions of fluid flow through the adsorbent bed.
- **Internal Diffusion:** Fluid particles penetrate the pores of the adsorbent. This process is governed by the concentration gradient of the solute.
- **Surface Diffusion to Active Sites:** This final step involves the attachment of dye molecules to the surface of the pores [16].

I.2.1.2. Types of adsorptions

- **Chemical Adsorption (or Chemisorption):**

Chemisorption is an adsorption phenomenon involving one or more covalent or ionic chemical bonds between the adsorbate and the adsorbent. Chemisorption is generally irreversible, leading to a modification of the adsorbed molecules. These molecules cannot accumulate beyond a monolayer. Through this type of adsorption, molecules are directly bonded to the solid. The relatively high heat of adsorption is typically between 20 and 200 kcal/mol [16].

- **Physical Adsorption (or Physisorption):**

Physical adsorption occurs at low temperatures. Molecules are adsorbed in multiple layers (multilayers) with adsorption heats often below 20 kcal/mol. The interactions between the solute molecules (adsorbate) and the solid surface (adsorbent) are facilitated by electrostatic forces such as dipoles, hydrogen bonding, or Van der Waals forces (physical bonding is weaker). Physisorption is rapid and reversible [16].

I.2.2. Photocatalysis

Photocatalysis is part of advanced oxidation processes and is a highly effective method for eliminating organic compounds, including phenols and dyes. In particular, photocatalytic treatment using solar radiation is considered a preferred technology [17], because it is a simple and cost-effective process that utilizes renewable energy. These various characteristics have sparked great interest among researchers in understanding, optimizing, and industrially applying this process.

Photocatalysis was initially developed for water treatment, where numerous studies have demonstrated the method's effectiveness on diverse families of organic compounds such as saturated or unsaturated hydrocarbons, oxygenated compounds, pesticides, and dyes [17].

I.2.2.1. Heterogeneous Photocatalysis

This technique has been one of the processes studied over the past twenty years. Its large-scale application has continued to develop. As we will see shortly, the entity that absorbs the light is a semiconductor characterized by a relatively small band gap. Several photocatalysts have been tested: TiO_2, ZnO, CeO_2, $BaTiO_3$, CdS, ZnS, etc. [18]. TiO_2 is by far the most studied because it exhibits photochemical stability and photocatalytic activity across a wide pH range. It has enabled the degradation of a variety of molecules, including dyes. This photo-active solid is used either in powder form or as a thin film deposited on different materials [19].

I.2.2.2. Principle of photocatalysis

Photocatalysis is one of the Advanced Oxidation Processes (AOPs) that can be carried out at ambient pressure and temperature without the addition of chemical oxidants. It represents a promising alternative for treating organic pollutants in water. The principle of photocatalytic degradation is based on the natural phenomenon of photolysis that occurs in the environment when the necessary conditions for photochemical reactions are met. Absorption of radiation of an appropriate wavelength transitions molecule to an excited state, and this excess energy can be dissipated through chemical modifications: direct modification leading to the formation of a new stable constituent and/or production of a reactive intermediate, such as a radical capable of

initiating a chain reaction. The use of a catalyst promotes the formation of free radicals and ensures a significant increase in degradation rate.

From an engineering perspective, heterogeneous photocatalysis involves circulating the pollutant-laden effluent in a reactor containing a catalyst (usually titanium dioxide). The reactor is exposed to ultraviolet radiation generated naturally via sunlight or artificially using a UV lamp with a wavelength range containing sufficient energy content to irradiate the semiconductor and thus ensure the production of highly oxidizing OH-free radicals through it [20].

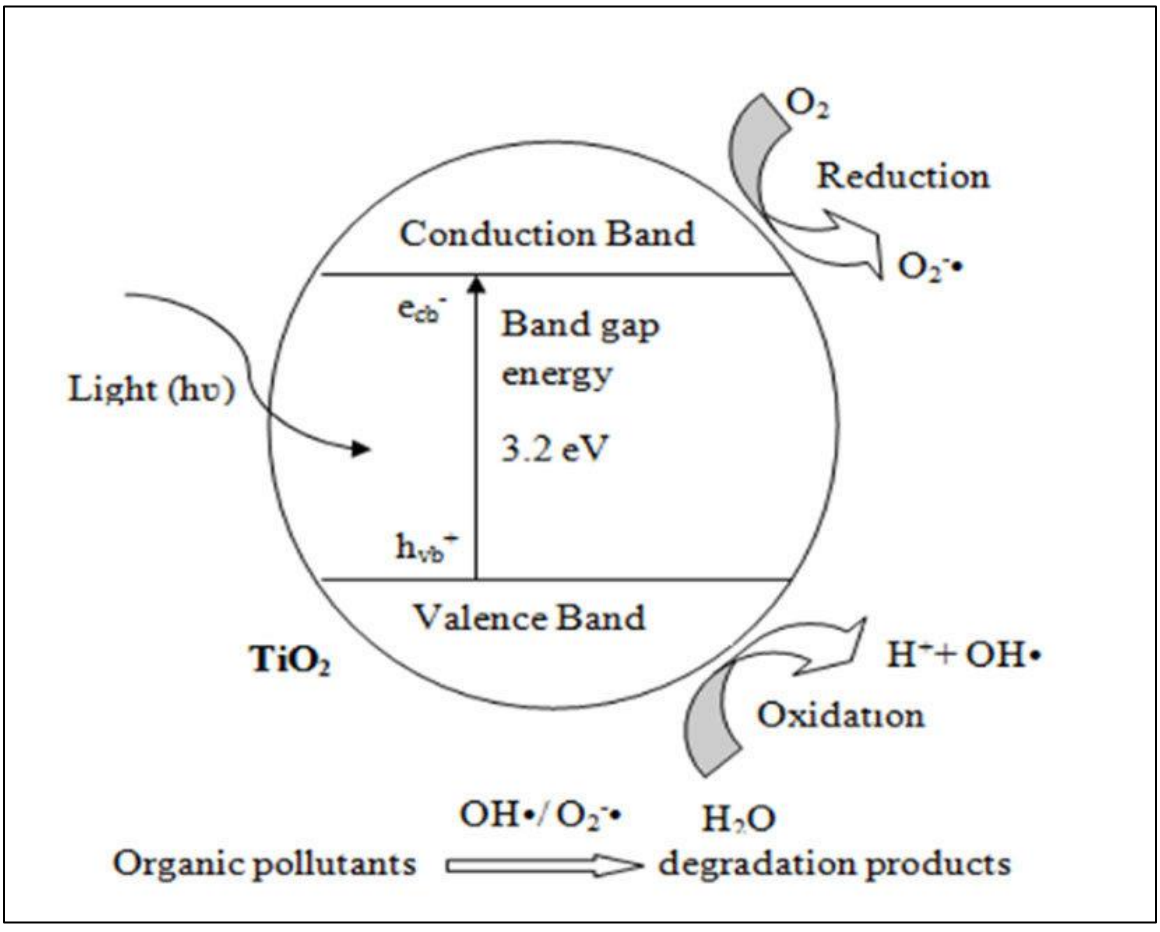

Figure. I.2 Principle of heterogeneous photocatalysis.

I.2.2.3. Parameters affecting the photocatalytic process

Many factors influence the rate of photocatalytic reaction; a distinction can be made between operational parameters and those related to the characteristics of the photocatalyst. Operational or extrinsic parameters are external factors such as operating conditions, including solution pH, initial concentration of the organic compound, light intensity, catalyst dosage, temperature, flow rate, oxygen flow rate, and presence of ions in solution. Parameters related to the properties of the photocatalyst or intrinsic parameters are those linked to the photocatalyst itself (specific surface area, band gap, crystallite size, and pzc pH) [20].

I.2.2.4. Zinc oxide

Several semiconductors have been used for the photocatalytic degradation of environmentally benign organic compounds [21-22]. Among them, the most widely studied is titanium dioxide TiO_2. On the other hand, recently, zinc oxide ZnO, similar to TiO_2, has attracted attention for its photocatalytic applications due to its high photosensitivity, thermal stability, and low cost [23-24]. Therefore, ZnO has been suggested as an alternative to TiO_2 photocatalysts due to its similar electronic properties [25]. It is a material that possesses interesting optoelectronic properties.

The 2p states of oxygen form the valence band, and the 4s states of zinc constitute the conduction band. These structures show that ZnO is a direct bandgap semiconductor (which can emit light). Its fundamental bandgap width Eb is approximately 3.33 eV at room temperature [26].

ZnO has been tested in the decomposition of various dye solutions as well as many other environmental pollutants. In many cases, ZnO has been reported to be more effective than TiO_2 [27-28].

The greatest advantage of ZnO compared to TiO_2 is that it absorbs over a wider region of the UV spectrum, enhancing photocatalytic efficiency. TiO_2 and ZnO are two of the most promising photocatalysts. However, their wide bandgap limits their photocatalytic activity in the UV wavelength region, which contributes to only 3% of the total solar spectrum. Consequently, improving the photocatalytic activity of TiO_2 and ZnO has been studied by many researchers. The

main objective of doping is to decrease the energy level of the bandgap, enabling the absorption of visible light [29].

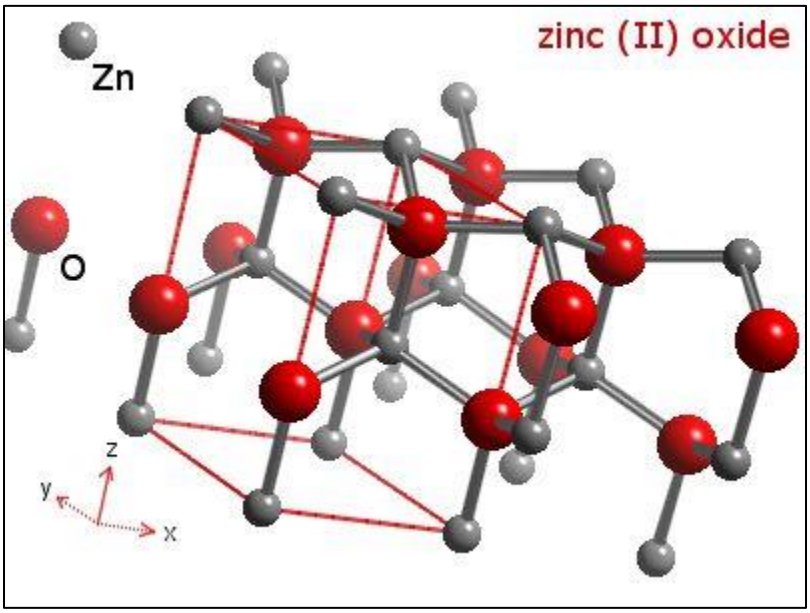

Figure. I.3. Zinc oxide.

I.2.3. Coupling adsorption and photocatalysis

After almost 40 years of research and study into photocatalysis, its practical application is still limited, mainly due to its slow kinetics and the challenges associated with reactor design. A possible solution to these problems could be to couple photocatalysis with a second technology such as adsorption.

Both adsorption and photocatalytic degradation allow the removal of organic pollutants from water. These processes have emerged as cost-effective eco-energy technologies and have received considerable attention for wastewater treatment [30].

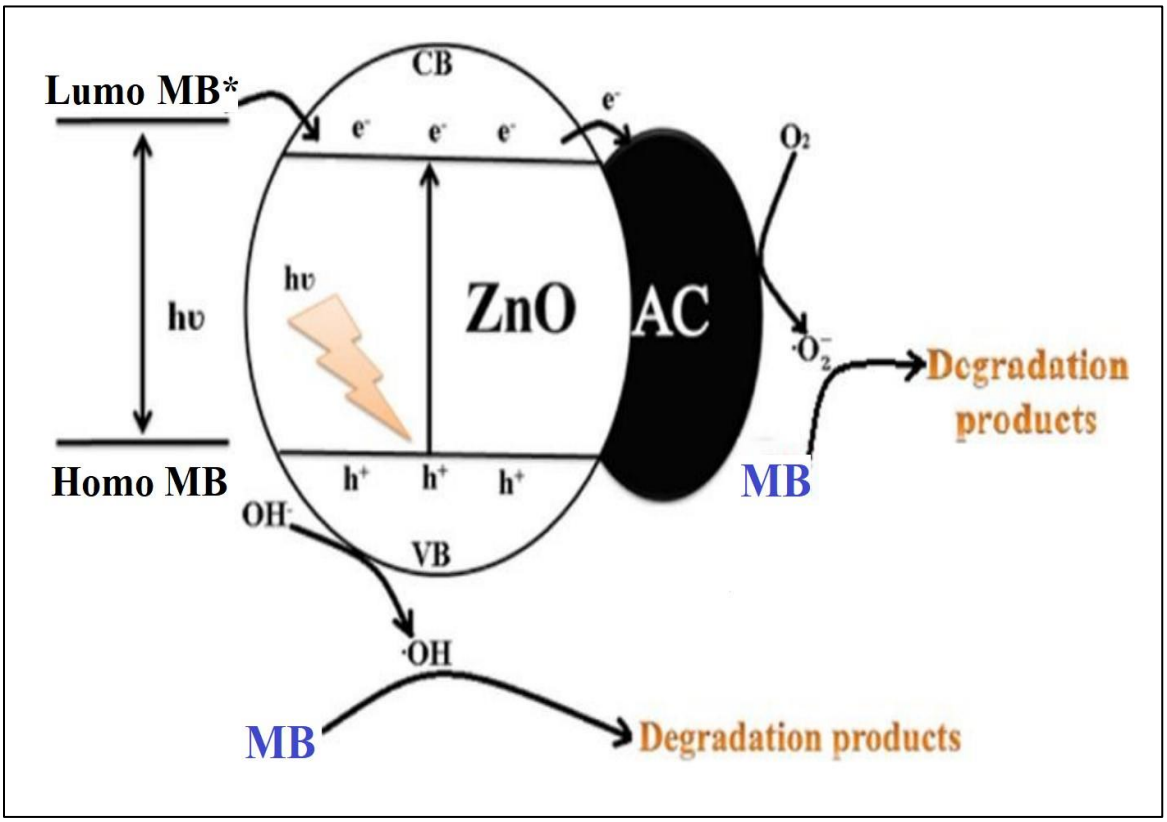

Figure I.4. Coupling adsorption and photocatalysis.

Chapter II

Experiment setup and conditions

II.1. Introduction

This chapter presents a description of the steps involved in the synthesis of ZnO-AC photocatalyst, where alimentary waste DS was used as a raw material. As well as all the equipment needed for that. In addition to the experimental protocols used to test its efficiency in the photodegradation of MB dye under different experimental conditions.

II.2. Materials and products

In this study, date seeds were used as a feedstock to prepare activated carbon, which was used as a support to the synthesized photocatalyst. All chemicals used in the investigation such as Distilled water (H_2O), Potassium hydroxide 85 % (KOH), Methylene blue ($C_{16}H_8C_1N_3S$), Hydroxide Sodium hydroxide (NaOH), Zinc nitrate hexahydrate $Zn(NO_3)_2$ and Hydrochloric acid 37 % (HCl) were of analytical grade.

II.3. Preparation of photocatalysts

A two-step process was used to prepare the photocatalyst, firstly preparation of activated carbon, and secondly, doping of activated carbon with photocatalysts.

II.3.1. Preparation of activated carbon (AC)

The DS have been pre-treated before use by washing and drying them to remove all Impurities then proceed to crushing them to small particle sizes. The work process is summarized in **Figure.II.3.1**.

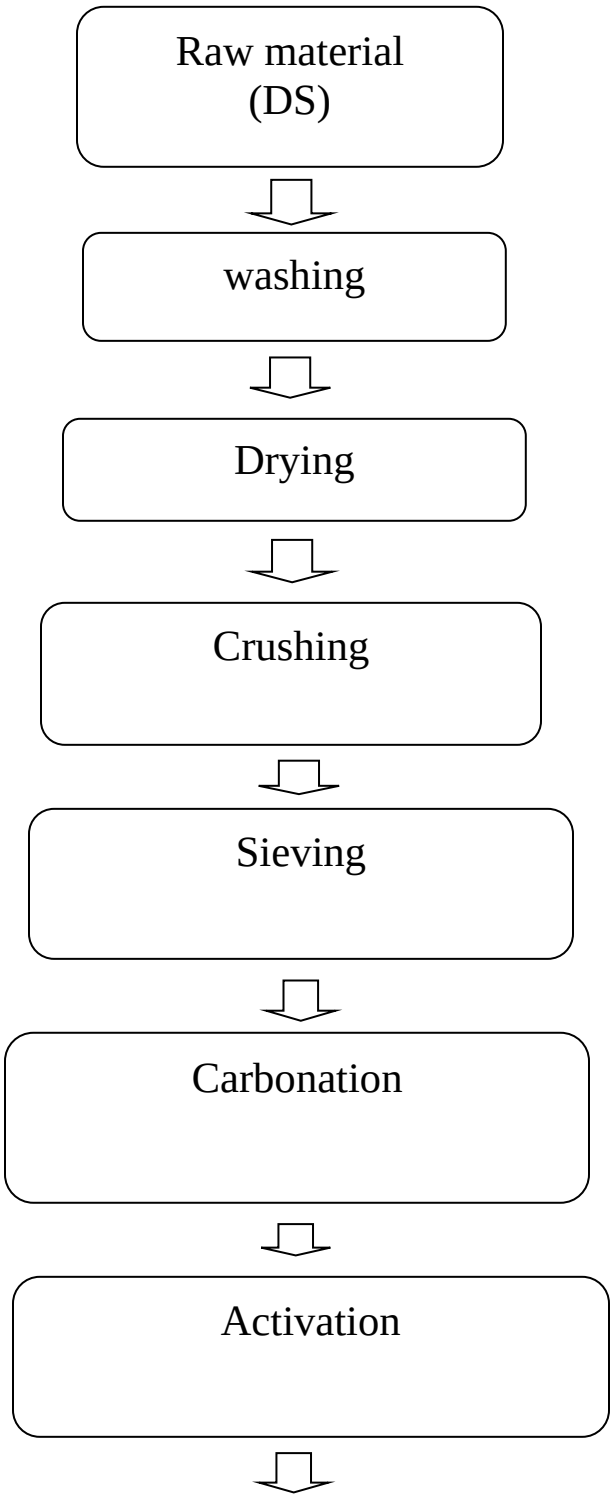

Figure.II.1. Workflow of the preparation of activated carbon AC.

Ⅱ.3.1.1. Washing

In order to remove all impurities stuck on the surface of the DS, the DS were washed before they were used. It should be noted that this process increases the water content in the feedstock and therefore the drying process is a necessity, as **Figure.II.1** shows.

Figure.II.2. Date seeds after washing.

II.3.1.2. Drying

It is important to thoroughly dry DS before using them to make activated carbon. The drying process was carried out by laying DS inside the oven, as shown in **Figure.II.2** for a long period, to ensure that it was completely dried. The experiment period of 12 hours was enough for a temperature of 100 °C.

Figure.II.3. The drying oven.

II.3.1.3. Crushing

This step aims to reduce the size of the particles to form into grains. The crushing was done manually using a manual grinder **(Figure.II.4)**, **Figure.II.4** (b) shows the (Ds) after crushing them.

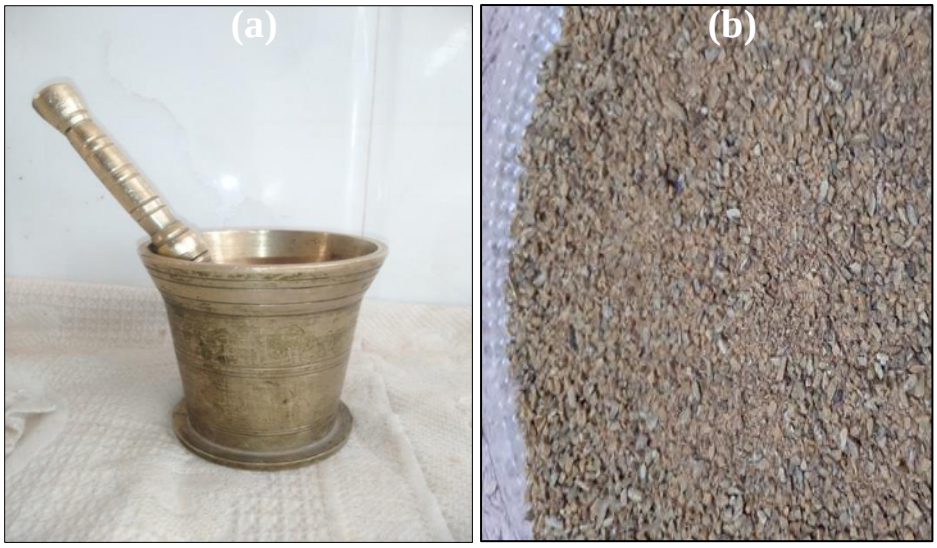

Figure. II.4. Crushing of DS (a) Manual grinder, (b) crushed DS.

II.3.1.4. Carbonation

A quantity of the biomaterial was carbonized in a furnace muffle **(Figure.II.5)** at a temperature of 500 ° C for 2 hours. **Figure.II.5** (b) shows the obtained carbon.

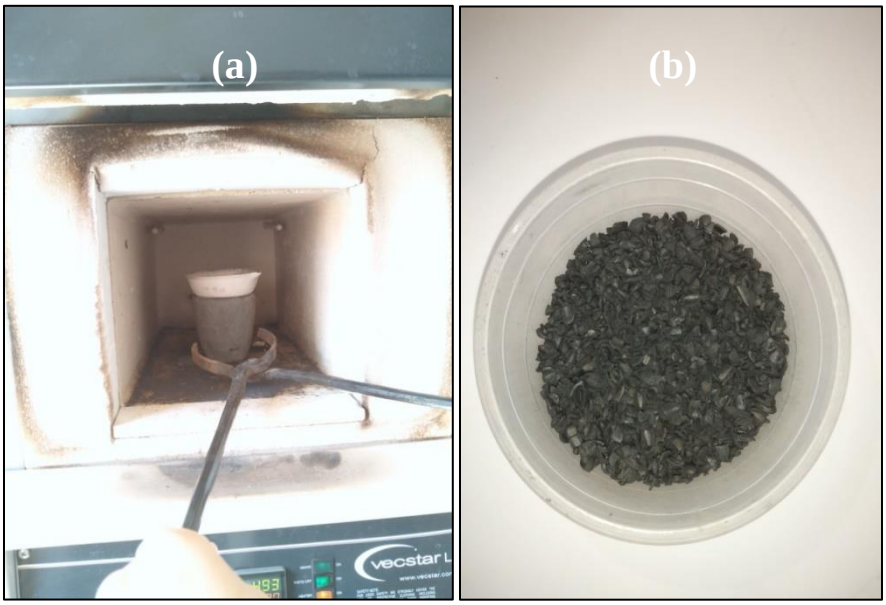

Figure. II.5. Carbonation of DS (a) Furnace, (b) Obtained carbon.

II.3.1.5. Activation

An activation method combining chemical and thermal processes was used to activate the obtained carbon, by mixing KOH with carbon, the ratio is 4:1 (four grams of KOH for every one gram of carbon), the mixture was then introduced to a tubular furnace at a temperature of 700 °C for an hour, with the presence of nitrogen gas at a flow rate of ml/h, as shown in the **Figure.II.6.** The obtained activated carbon was washed, and its pH was monitored until obtaining a neutral value with a portable pH meter [31].

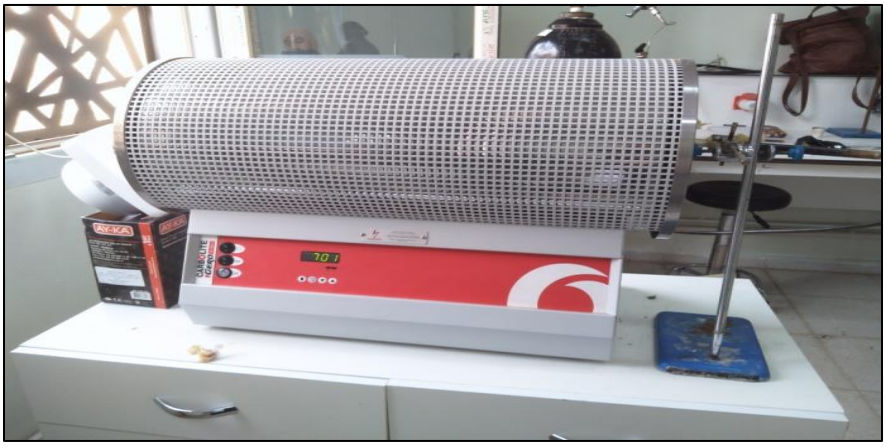

Figure. II.6. Tubular furnace used in the biochar activation process.

II.3.2. Synthesis of ZnO-supported activated carbon AC composite

The method for preparing a photocatalyst zinc oxide ZnO supported on activated carbon AC is based on the impregnation method. AC is one of the most important candidates for the manufacture of high-performance ZnO-AC nanospheres due to its large surface area, high conductivity, and high durability [32-33]. Moreover, due to its environmental friendship, abundance, rapid renewal, and low cost, biomass-derived AC has attracted wide attention from the next-generation energy technology community [33-34]. In the first step, solution A was prepared in a beaker by dissolving mass (m_1) of zinc nitrate ($Zn(NO_3)_2$ in 50 ml of distilled water under constant stirring for 30 min, and another solution B was prepared by dissolving mass (m_2) of AC in 50 ml of distilled water with constant stirring for 30 min, then pouring solution A into B with constant stirring for 1 hour at a temperature not exceeding 180 °C until all the water has evaporated, then drying the mixture in an oven at a temperature of 120 °C for 1h to produce the ZnO-AC nanocomposite. Three different photocatalysts with different weight ratios of Zinc oxide ZnO/ Activated carbon AC were prepared in this study, to investigate the weight ratio on the performance of the photocatalyst as summarized in **Table.II.1**.

Table.II.1. Three different photocatalysts were synthesized in this study.

Representation of photocatalyst	Weight of zinc nitrate $Zn(NO_3)_2$ (g) (m_1)	Weight of AC (g) (m_2)	Weight ratio (-)
3/7 ZnO-AC	3	7	0.43
4/6 ZnO-AC	4	6	0.67
5/5 ZnO-AC	5	5	1

II.3.2.1. Calcination

Calcination is the last stage in the preparation of the photo-catalyst, the ZnO/AC powder prepared from the synthesis is poured into a ceramic crucible and placed in the muffle furnace **(Figure.II.5)** at a temperature of 500 °C for 3 hours to prepare the photocatalyst. The general protocol used is described in **Figure.II.3.2** [31].

$$2Zn(NO_3)_2 \rightarrow 2ZnO + 4NO_2 + O_2$$

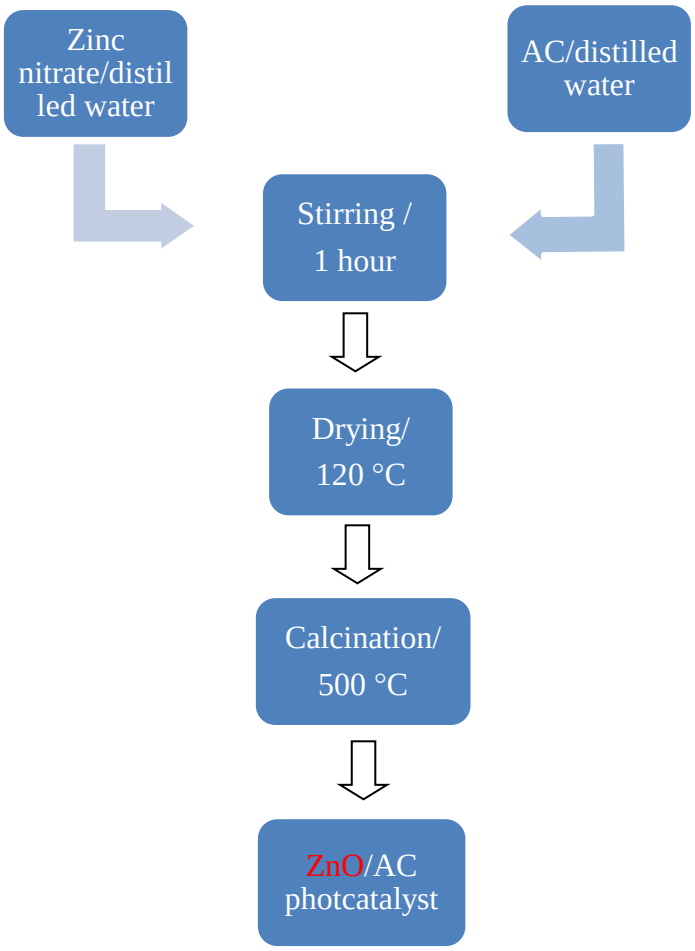

Figure.II.7. Method for preparing the ZnO/AC photocatalyst.

II.4. Photocatalyst activity experiments

To understand the performance of the synthesized photocatalyst, several series of experiments were conducted. 50 ml of a solution with an initial concentration of methylene blue MB of 20 ppm was mixed with 0.02 g of ZnO-AC photocatalyst, the mixture was stirred at 500 rpm for 1 hour. An exposure to 1000 W of light was employed to enhance the photodegradation of MB over ZnO photocatalyst, as shown in **Figure.II.8**.

In order to determine how much MB was degraded over the ZnO-AC photocatalyst, the solution was centrifuged, and its absorbance was measured using a UV-Vis Spectrophotometer (SHIMADZU UV-1280).

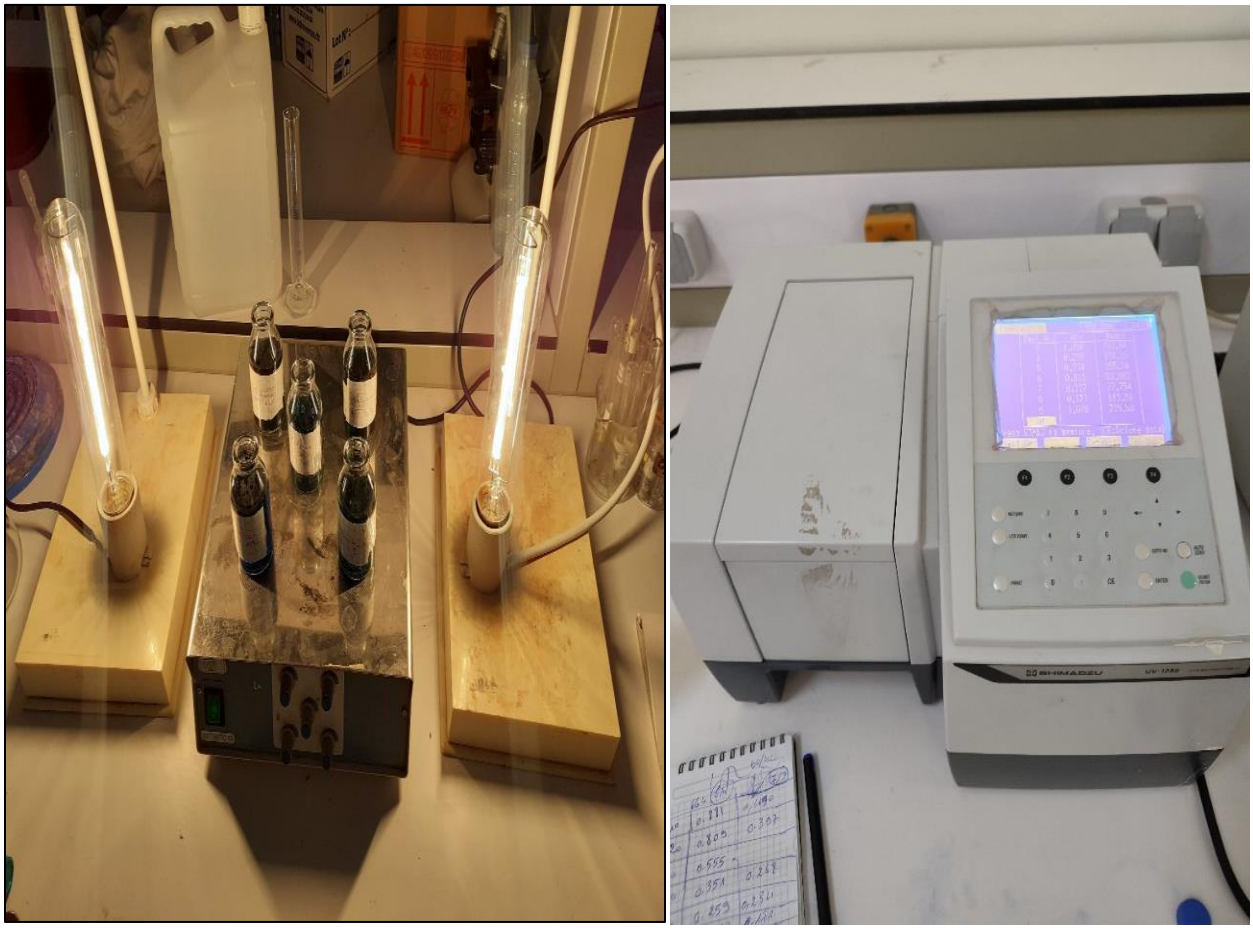

Figure.II.8. Experimental set-up for photodegradation of MB over ZnO-AC photocatalyst test and UV-Vis Spectrophotometer.

II.4.2. Determination of (λ_{max}) and calibration curve

Methylene blue MB dye was chosen in this study due to its known strong adsorption on materials. Solids, and their recognized usefulness in describing adsorptive materials, often serve as a model for the removal of organic pollutants and colored particles from aqueous solutions [1]. The maximum absorption wavelength (λ_{max}) was determined by plotting the absorption spectrum of a sample of a solution of known dye concentration, after a wave sweep in the visible range of 400-800 nm. Having determined the maximum absorption wavelength for methylene blue, a standard dye solution was prepared from the dye stock solution (20 ppm) to measure absorbance and plot the appropriate calibration curve.

II.4.2.1. Calibration curve for methylene blue (MB)

A calibration curve is generated by preparing several diluted solutions with different concentrations of MB dye. Absorbance is measured at the maximum wavelength of (λ_{max}).

The amount of the photodegraded MB dye over the ZnO-AC photocatalyst is calculated through the following relationship:

$$Q_e=\frac{(C0-Ce)\,V}{m} \quad \text{.....(II.1)}$$

Where:

C_0: initial concentration of the solution (mg/L).

C_e: concentration of the solution at equilibrium (mg/L).

Q_e: quantity of the BM photodegrades in equilibrium (mg/g).

m: the mass of the photocatalyst (g).

V: volume of solution size (L).

The photodegradation rate of the photodegraded MB dye over the ZnO-AC photocatalyst is calculated through the following relationship:

Where: $\mathbf{R} = \frac{C0 - Ct}{C0} \times 100$ **……..(II.2)**

R =the photodegradation rate (%).

$\mathbf{C_0}$= initial concentration of the solution (mg/L).

$\mathbf{C_t}$= concentration of the solution at time t (mg/L).

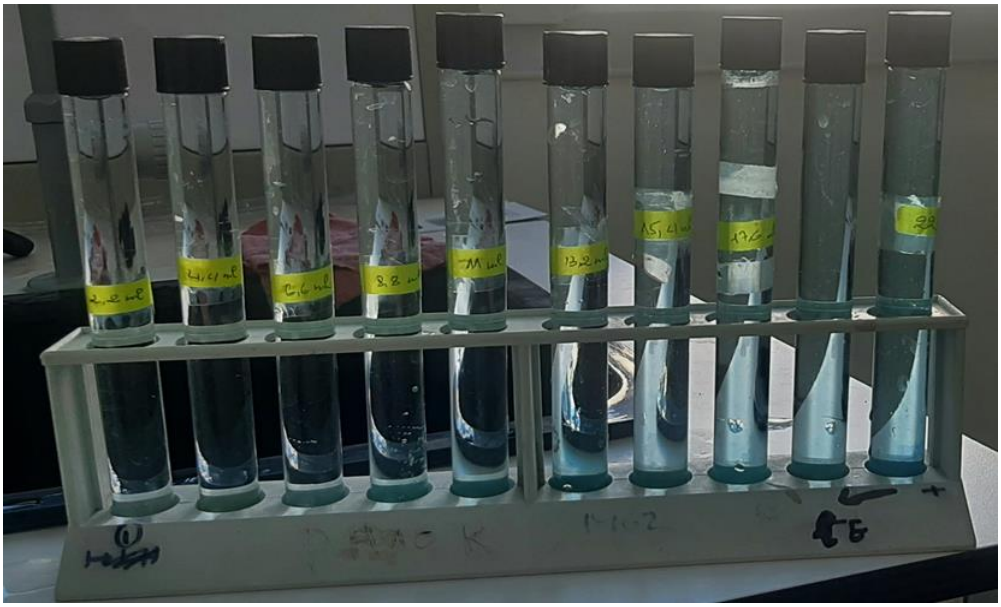

Figure. II.9. The diluted solutions of MB.

II.5. Parameters affecting the photocatalytic activity

To deeply understand the performance of the photodegradation of MB dye over ZnO-AC photocatalyst, the effect of several parameters was investigated in this study, such as time, light source, volume, weight ratio of ZnO/AC, Temperature, Initial concentration of MB dye, and mass of catalyst. **Table.II.2.** summarize the parameters investigated in this study.

Table.II.2. Parameters affecting photocatalytic activity.

	Catalyst type	Time (min)	Light source (W)	volume of water (ml)	Temperature (°C)	Initial concentration of MB dye (ppm)	Mass of Catalyst (g)	pH
Serie (1)	5/5 ZnO-AC 4/6 ZnO-AC 3/7 ZnO-AC	40 40 40	1000	50	23	20	0.2	7
Serie (2)	3/7 ZnO-AC	60	1000	50	23	20	0.005 0.01 0.015 0.02 0.025 0.03	7
Serie (3)	3/7 ZnO-AC	60	1000	50	23	5 10 15 20 30 40	0.02	7
Serie (4)	3/7 ZnO-AC	5 10 15 20 25 30 40 50 60	1000	50	23	20	0.02	7
Serie (5)	3/7 ZnO-AC	5 10 15 20 25 30 40 50 60	Drak	50	23	20	0.02	7
Serie (6)	3/7 ZnO-AC	60	1000	50	23	20	0.02	1 3 5 8 10 12 14

Chapter III:

Results and Discussions

III.1. Photocatalytic Degradation of Methylene Blue over ZnO-AC

The photocatalytic degradation of methylene blue MB, a well-known organic azo dye, was performed using a ZnO-AC photocatalyst. MB was used as a pollutant simulator in the textile industry and is known as a toxic material with a complex structure. Therefore, the identification of decomposition products and degradation pathways is crucial. To obtain relevant information on the photocatalytic degradation MB over ZnO-AC photocatalyst.

III.1.1. Photocatalytic degradation of methylene blue (MB) over ZnO and AC with different weight ratios

Figure.III.1. represent photocatalytic degradation of MB over ZnO-AC composites with different weight ratios. it was observed from the results there is an inverse relationship between the photocatalytic degradation rate of MB over ZnO-AC and the weight ratio of the ZnO/AC in the photocatalyst, where the photocatalytic degradation rate increases with decreasing weight ratio. The data suggests that the 3/7 ZnO-AC composite has the highest photocatalytic degradation efficiency, reaching nearly 100% degradation. While there is a slight decrease in performance for the 4/6 ZnO-AC composite, it still achieves a high degradation rate of around 99,38 %. The 5/5 ZnO-AC composite shows the lowest degradation efficiency at around 39,29% generally, Figure.III.1 indicates that incorporating activated carbon (AC) into zinc oxide (ZnO) enhances the photocatalytic degradation of (MB). The insufficient weight ratio of the catalyst limited the number of active sites available for photocatalytic reactions, and an excessive amount of AC might overshadow the active sites of ZnO or block the light absorption, reducing the efficiency of the photocatalyst which reduced the photodegradation rate of MB dye. An excessive activated carbon weight ratio leads to aggregation of the catalyst, reducing the surface area available for photocatalytic reactions. Moreover, hinders the absorption of light [35], and the optimal weight ratio for complete degradation of MB 100 % is 3/7 of ZnO-AC, this catalytic is selected for the rest of this study.

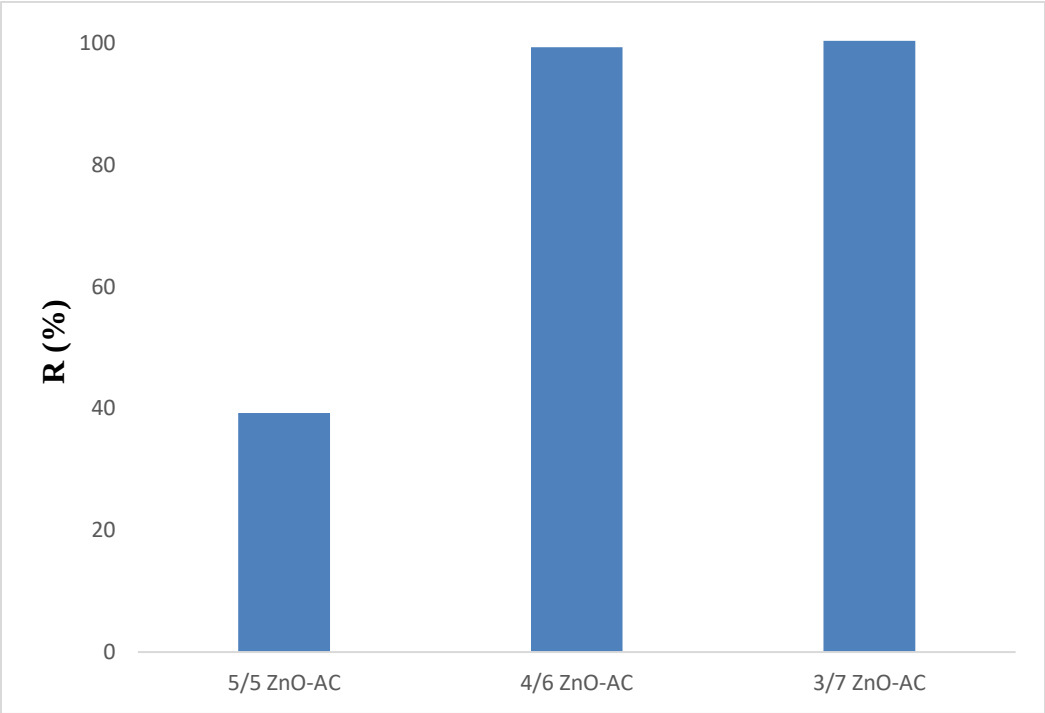

Figure.III.1. Photocatalytic degradation of methylene blue (MB) over (AC) and ZnO-AC composites with different weight ratios of AC.

III.1.2. Effect of catalyst dose

Figure. III.2. represent the **e**ffect of catalyst dose on the photocatalytic degradation of (MB) dye. It is observed that the photocatalytic degradation rate increases with the increase of catalyst dose until reaching 100 % at 0.02 g, However, any further increase in the catalyst dose leads to stabilization of the photodegradation rate at 100 %. The reason generally advanced for this result is that an increase in catalyst loading increases the active sites on the catalyst's surface [36]. Accordingly, the optimal catalyst dose corresponding to 20 ppm is 0.02 g.

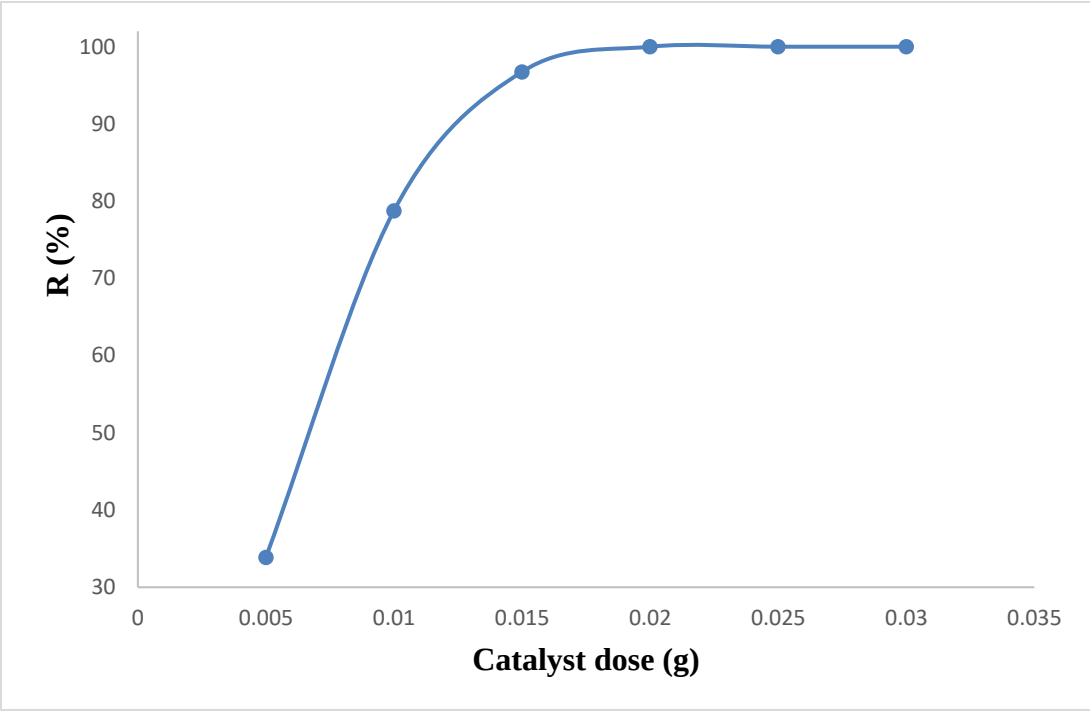

Figure.III.2. Effect of catalyst dose on the photocatalytic degradation of dye.

III.1.3. Effect of initial dye concentrations

Figure.III.3. demonstrates the effect of the initial concentration of the dye (MB) on the efficiency of the 3/7 ZnO/AC catalyst, the results have shown a significant impact of the initial concentration of the MB dye on the photocatalytic degradation. In the first phase, the photodegradation of the dye (MB) remains stable at 100 % with decreased concentration. In contrast, in the second phase, the photocatalytic degradation decreases progressively to 70 %, this is justified as, the photodegradation efficiency relates to the formation of hydroxyl radicals, which are the critical species in the degradation process. Hence an explanation for this behavior is that the higher the initial concentration, the higher the adsorbed organic substances on the surface of the catalyst, and the solution became more intensely colored. Therefore, there are only fewer active sites for adsorption of HO^- so the generation of HO• will be reduced. Furthermore, as the concentration of methylene blue increases with the constant intensity of light and illumination, the path length of photons entering the solution decreases, so only a few photons reach the catalyst surface. As a result, the production of holes or hydroxyl radicals that can attack the pollutants was limited. Therefore, the relative HO• number attaching the compound decreases and thus the

photodegradation efficiency decreases [37, 38]**.** So, the optimal initial dye concentration is 20 ppm at a photodegradation efficiency of 100 %.

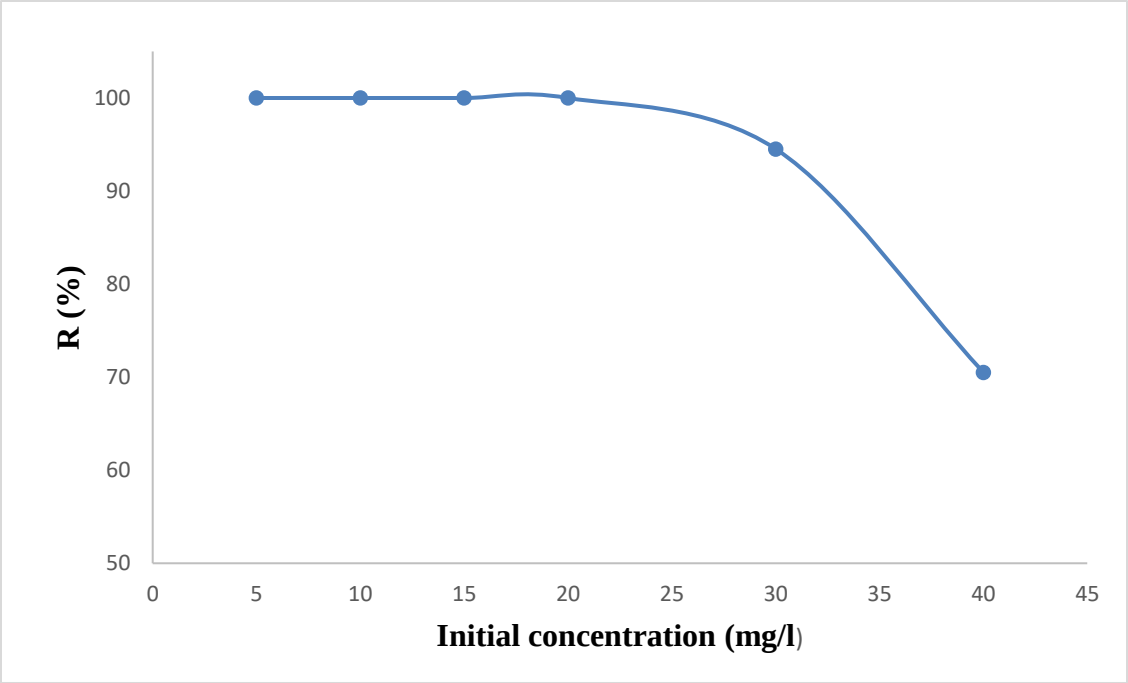

Figure.III.3. Effect of initial concentration on the photocatalytic degradation of dye.

III.1.4. Effect of illumination time

Figure.III.4. shows photocatalytic degradation of MB dye over 3/7 ZnO-AC as a function of the irradiation time. The effect of irradiation time was investigated by measuring the degradation efficiency at different irradiation times under optimum conditions of photocatalyst dosage (0,02 g), and initial MB concentration (20 ppm). The Figure shows an increase in the photocatalytic degradation rate as a function of illumination time, this observation suggests an optimal duration of irradiation time at 20 min for complete dye removal, with the initial increase indicating the effectiveness of the process and the stabilization. Such data reveals the relatively high activity of the prepared catalysts which enables the complete degradation of the methylene blue in such short illumination time, and the catalyst has active sites for carrying out the reaction [36].

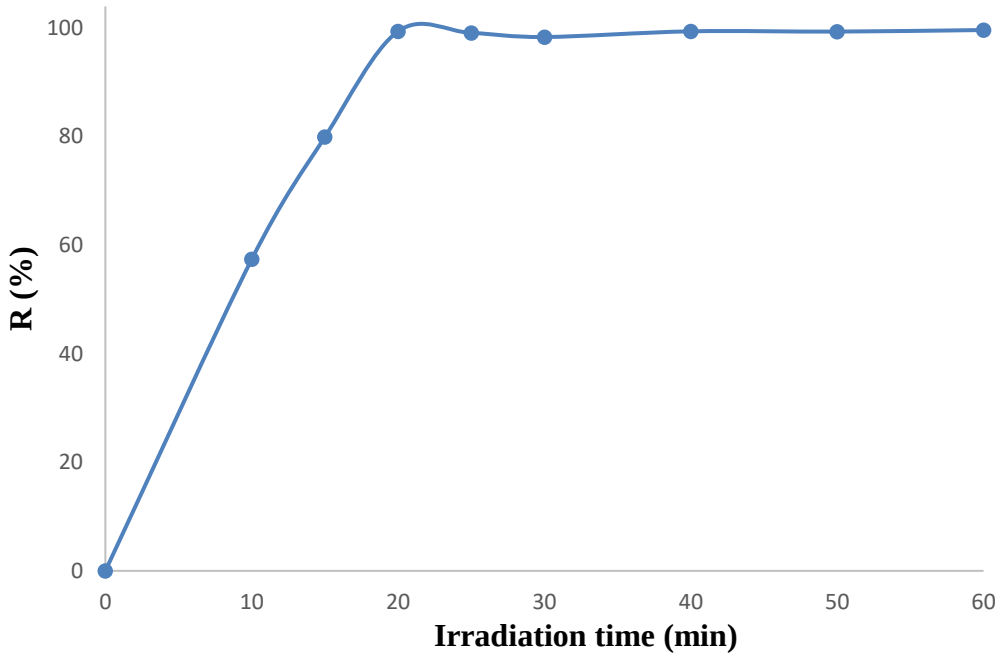

Figure. III.4. Effect of irradiation time on the photocatalytic degradation rate of dye.

III.1.5. Effect of light source

Figure.III.5. illustrates the impact of light sources on the photodegradation of MB over time. Photodegradation occurs when a substance is degraded by light, the figure shows two sets of data, one for darkness and one for light the dark data set shows a gradual decrease in MB concentration over time. This indicates a slower increase in the photocatalytic degradation of MB, suggesting that photodegradation is less efficient in the absence of light. In contrast, the figure for the light condition displays a rapid decrease in MB concentration over time. This indicates an accelerated increase in the percentage removal of MB, suggesting effective photodegradation in the presence of light. The contrasting trends between the dark and light conditions highlight the significant role of light in promoting the photodegradation of MB. This remarkable efficiency is attributed to the photosensitizing property of MB. The increase suggests that light activates the ZnO catalyst, leading to the generation of reactive oxygen species (ROS), particularly hydroxyl radicals (OH•), which are highly effective in breaking down organic pollutants like MB [38]. which means that the efficiency of the photocatalytic process of degradation of MB dye is enhanced under visible light, resulting in faster degradation.

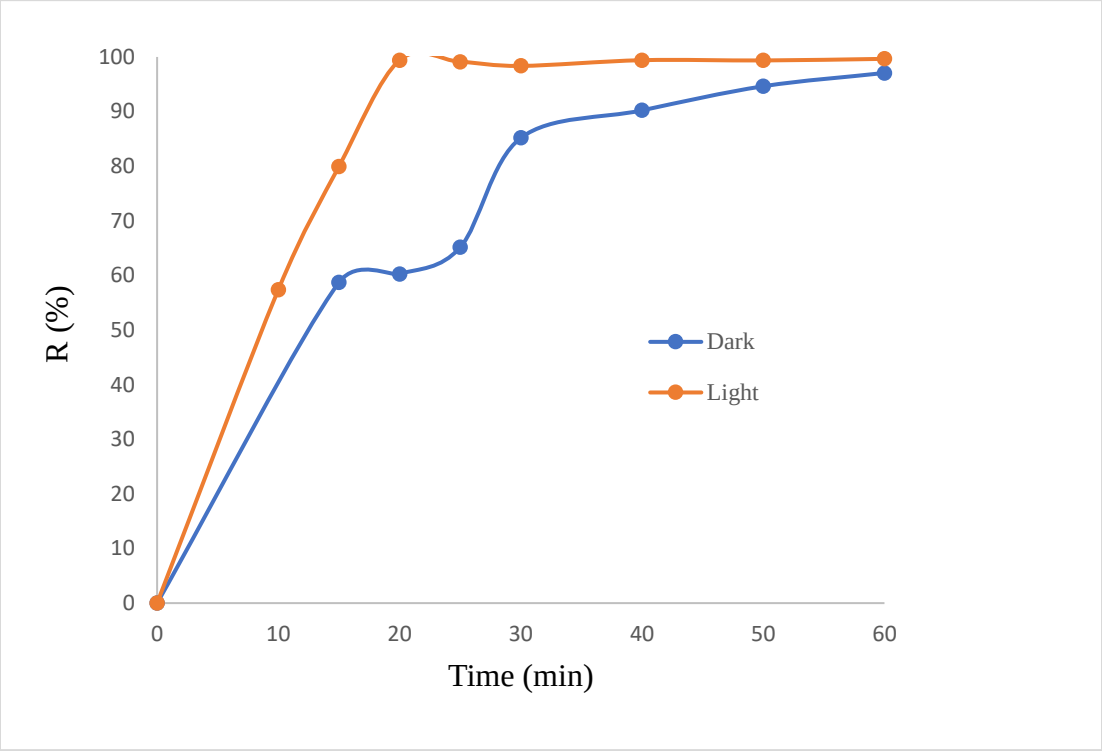

Figure. III.5. Effect of the light source on MB photodegradation.

III.6. Effect of pH solution

Figure III.6 shows the effect of the pH of the solution on the MB dye photodegradation rate, a slight decrease in photodegradation rate was observed (from 99,41 to 96,17 %) with an increase in pH. The ZnO-AC 3/7 photocatalyst, however, has generally good performance across a wide pH range. In acidic pH ranges (1 to 5), the highest photodegradation rate was achieved. This observation can be explained by the fact that at low pH values, the surfaces of the catalysts were highly protonated and became positively charged so that the dye cations were electrostatically attracted more towards the catalyst surface as more oxidizing holes increased and thus decoloration of MB dye was enhanced. At acidic pH, the positive holes are considered the major oxidation species, whereas hydroxyl radicals are considered the predominant species at neutral or alkaline pH [39].

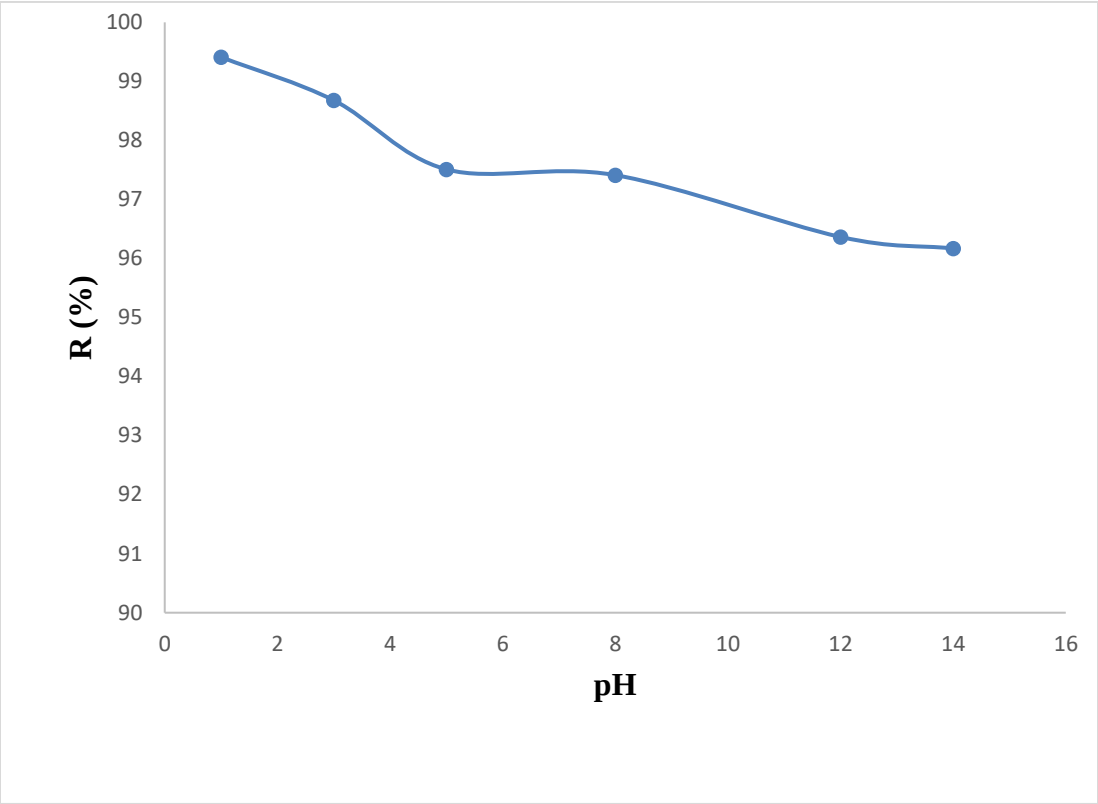

Figure.III.6. Effect of pH solution on MB dye photodegradation.

III.7. Kinetic modeling of photodegradation of MB dye over ZnO-AC

Different kinetic models were used to evaluate the photocatalytic degradation process of MB dye over 3/7 ZnO-AC. The three models used were the pseudo-zero order model, the pseudo-first-order model, and the pseudo-second-order model. These models were used to determine kinetic parameters such as the rate constant and the quantity adsorbed at equilibrium. The results were presented in the form of curves shown in **Figure III.7, Figure III.8,** and **Figure III.9**. By analyzing the linearity of these curves, the values of k and q_i were calculated and presented in **Table III.1**. The linear regression coefficient R^2 was also calculated, which indicates the appropriateness of the model used. A higher value of R^2 indicates a more appropriate model.

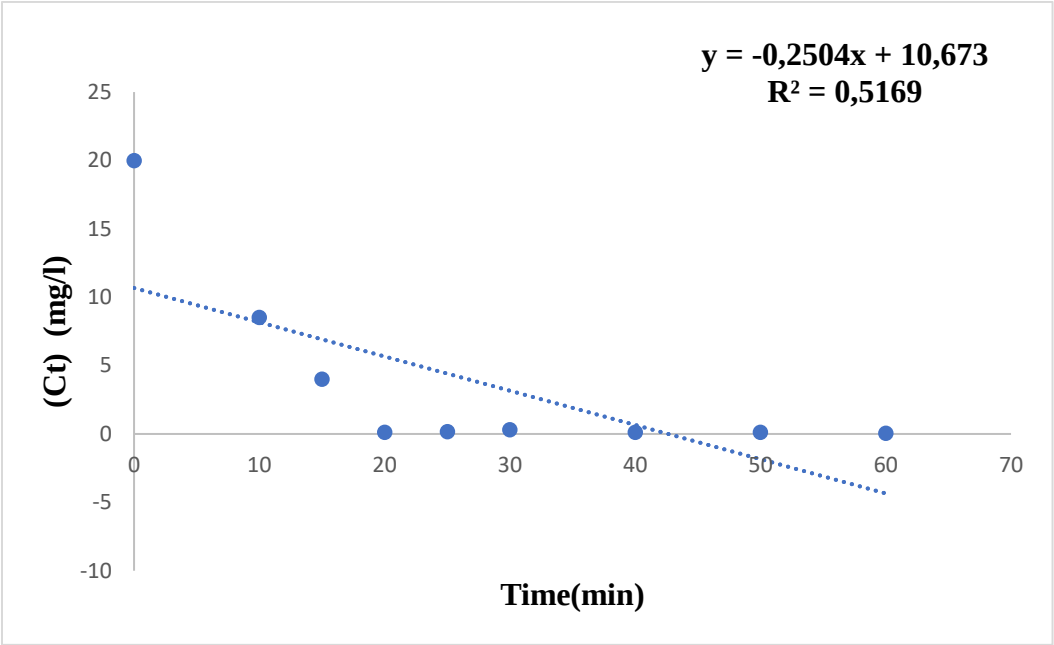

Figure.III.7. Linear representation of the pseudo-zero-order kinetic model for MB photodegradation.

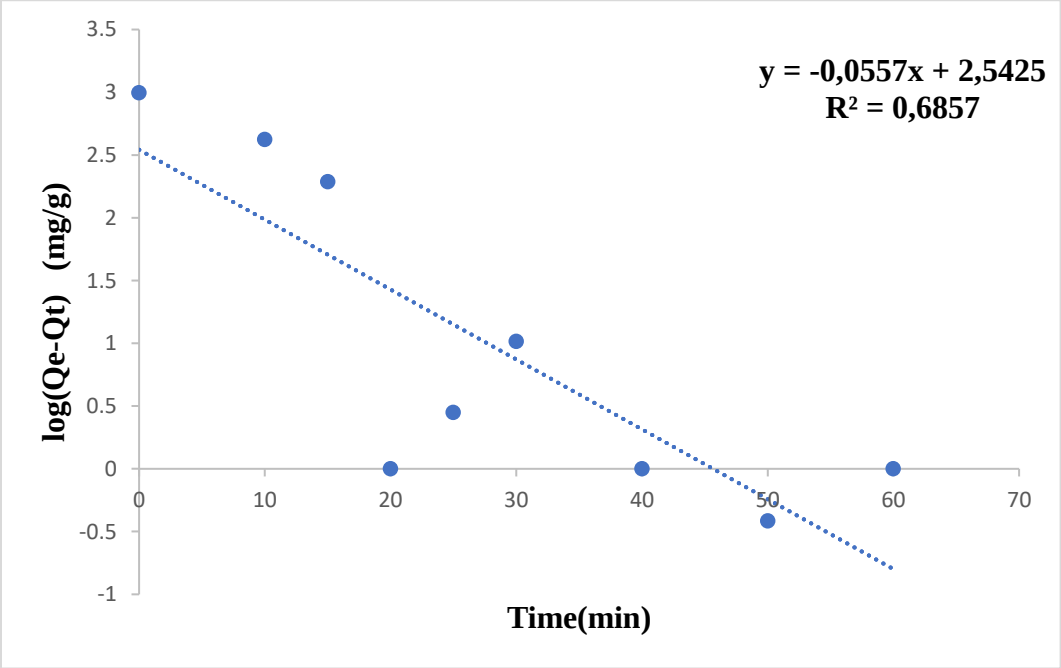

Figure.III.8. Linear representation of the pseudo-first-order kinetic model for MB photodegradation.

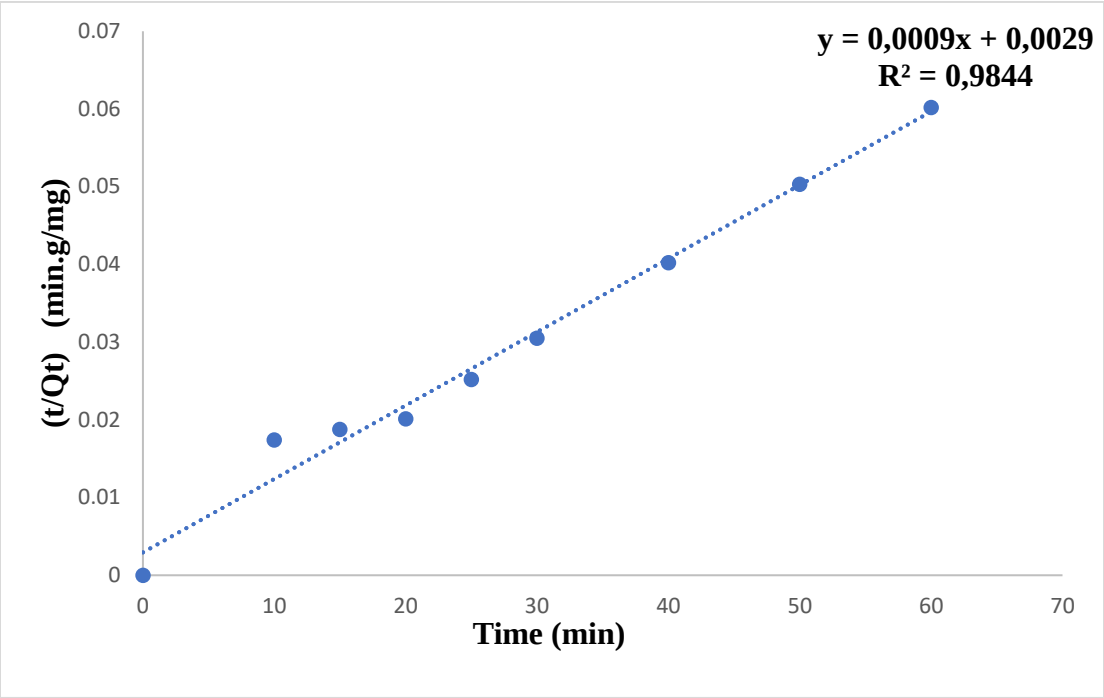

Figure.III.9. Linear representation of the pseudo-second-order kinetic model for MB photodegradation.

From the data presented in **Table.III.1.**, it is observed that the pseudo-second-order model has the highest correlation coefficient R^2 =0.9844, for the concentration used (20 ppm), These results indicate that the pseudo-second-order model is the most appropriate for studying photodegradation kinetics.

Table.III.1. Application results of the pseudo-zero order pseudo-pseudo-first order and pseudo-second-order kinetic model for MB photodegradation.

Kinetic model		**Pseudo zero order**			**Pseudo first order**			**Pseudo-second-order**		
C (ppm)	**Qe exp (mg/g)**	**Qe cal (mg/g)**	**K_0 (min^{-1})**	**R^2**	**Qe cal (mg/g)**	**K_1 (g/mg.min)**	**R^2**	**Qe cal (mg/g)**	**K_2 (g/mg.min)**	**R^2**
20	994	10,673	0,2504	0,5169	348,7386	0,128	0,6857	1111,11	0,000279	0,9844

III.8. Comparison of kinetic model predictions and experimental data of photodegradation of MB dye over 3/7 ZnO-AC

The non-linear forms of pseudo-first order and pseudo-second order kinetic models for the photodegradation of MB dye over 3/7 ZnO-AC are represented in the **Figure.III.10**. By plotting (Qt) the amount of MB dye photodegradation over 3/7 ZnO-AC as a function of time. There are three ascending lines: The dotted line labeled "Exp" represents the experimental data showing a gradual increase in the amount of MB dye remaining over time. The orange line labeled "1st Order" represents a prediction from the first-order kinetic model. It shows a greater increase in the amount of MB dye remaining over time compared with the experimental data. The blue line labeled "2nd Order" represents a prediction of the 2nd order kinetic model. It shows an even greater increase in the amount of MB dye remaining over time compared with the experimental data and the first-order kinetic model prediction. The fact that the experimental data exceed the predictions of the first- and second-order kinetic models suggests that the photodegradation of MB dye over 3/7 ZnO-AC 3/7 follows a stronger reaction rate than predicted by the two models. It is concluded that the pseudo-second-order kinetic model is better suited to the photodegradation of MB dye using the ZnO-AC 3/7 composite, which is consistent with the usual results of photocatalytic degradation studies. This suggests that the process could be more accurately described by mechanisms that take into account the interactions and complexities captured by the pseudo-second-order model.

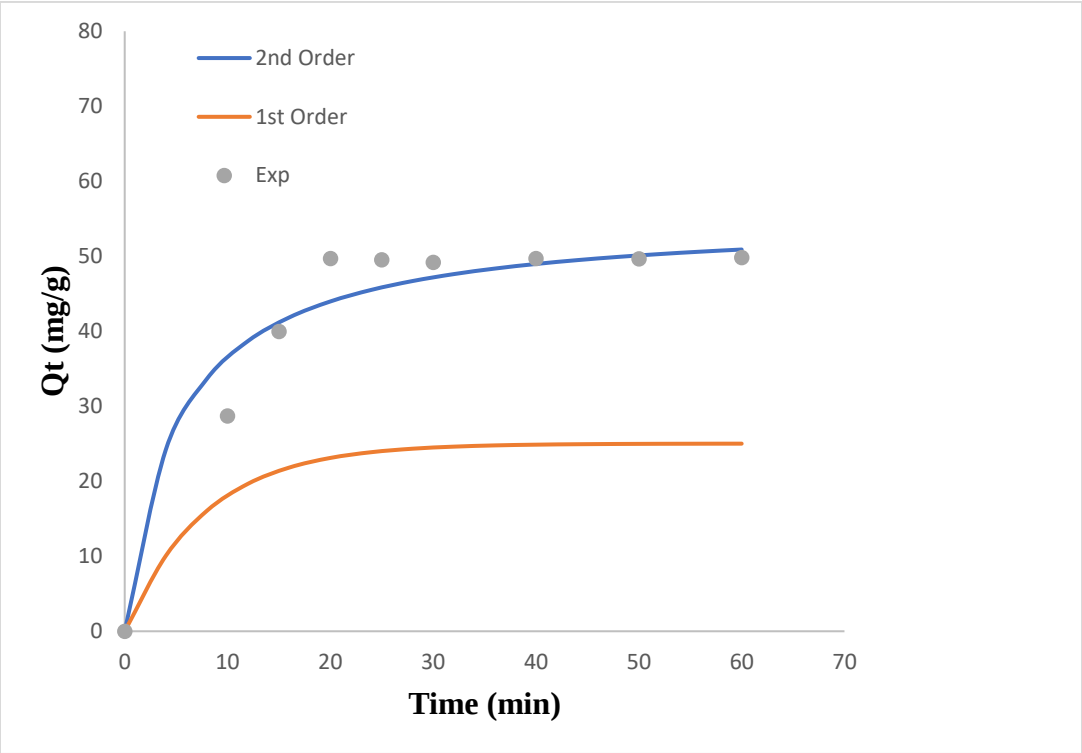

Figure.III. 10. Nonlinear plots of pseudo-first order and pseudo-second order kinetic models for the photodegradation of MB dye. over 3/7 ZnO-AC.

General conclusion

Conclusion

In conclusion, this study succeeded in synthesizing an effective photocatalytic composite based on ZnO and activated carbon AC, demonstrating exceptional performance in the degradation of methylene blue MB under the light source. The optimum ratio of 3/7 (ZnO-CA) was identified as offering the best efficiency, achieving almost complete degradation of BM dye in 20 minutes under optimal conditions: a catalyst dose of 0.02 mg/L, and an initial BM concentration of 20 mg/L.

These results confirm the initial hypothesis that the incorporation of activated carbon significantly improves the photocatalytic properties of ZnO by increasing the specific surface area and facilitating the degradation of the MB dye.

Light source was found to be the most effective in activating the photocatalyst, leading to accelerated and complete degradation of the MB dye. In the absence of light, slow degradation of the MB dye was observed, confirming the essential role of light energy for accelerated and efficient degradation.

Kinetic analyses showed that the degradation of the BM dye followed a pseudo-second-order pattern with a correlation coefficient greater than $R^2 = 0.9844$, suggesting a complex chemical interaction between the BM and the ZnO-AC composite. This finding is important for the future development of predictive models of photocatalytic performance and the optimization of large-scale reaction conditions. These results confirm the potential of the ZnO-AC composite as an environmentally friendly candidate for the treatment of wastewater containing synthetic dyes. Although this study produced promising results, certain limitations must be recognized. The experiments were conducted on a laboratory scale, and it is necessary to test these composites on a larger scale to confirm their effectiveness under real conditions. In addition, the effect of the presence of other contaminants in wastewater on the performance of the ZnO-AC composite has not been studied and deserves future attention.

Future research could focus on the large-scale evaluation of the effectiveness of ZnO-AC composites in wastewater treatment plants. It would also be interesting to study the effect of the presence of multiple contaminants on the photocatalytic performance of the composite. In conclusion, this study has demonstrated that the ZnO-AC composite offers an effective and durable

candidate for the photodegradation of MB dye, making a significant contribution to the development of bio-based photocatalysts and offering promising prospects for their industrial application.

References

References

[1] Xu, C.; Rangaiah, G.P., Zhao, X.S., Ind. Eng. Chem. Res., 2014, 53, 14641-14649.

[2] Liu, B.; Zhao, X.; Terashima, C.; Fujishima, A., Nakata, K., Phys. Chem. Chem. Phys., 2014, 16, 8751-8760.

[3] Fan, H.; Zhao, X.; Yang, J.; Shan, X.; Yang, L.; Zhang, Y.; Li, X., Gao, M., Catal. Commun., 2012, 29, 29-34.

[4] Daneshvar, N.; Rasoulifard, M.; Khataee, A., Hosseinzadeh, F., J. Hazard. Mater., 2007, 143, 95-101.

[5] Boppella, R. ; Anjaneyulu, K. ; Basak, P., Manorama, S.V., J. Phys. Chem. C, 2013, 117, 4597-4605.

[6] Alenezi, M.R. ; Alshammari, A.S. ; Jayawardena, K.D.G.I. ; Beliatis, M.J. ; Henley, S.J., Silva, S.R.P., J. Phys. Chem. C, 2013, 117, 17850-17858.

[7] Khodja, A.A.; Sehili, T.; Pilichowski, J.-F., Boule, P., Journal of Photochemistry and Photobiology A: Chemistry, 2001, 141, 231-239.

[8] Kohtani, S.; Kamoi, Y.; Yoshioka, E., Miyabe, H., Catalysis Science & Technology, 2014, 4, 1084-1091.

[9] http://www.cbc.ca/manitoba/features/lakewinnipeg/checkup.html.

[10] Spadaro. J.T, L. Isabelle, Renganathan. V, Hydroxyl radical-mediated degradation of azo dyes: evidence for benzene generation, Environ. Sci. Technol. 28 (1994) 1389-1393.

[11] D. Memento « technique de l'eau, technique et documentation », tome 1, P : 5, 24,25, (1989).

[12] N. Oubagha, « décontamination des eaux contenant les colorants textiles et les adjuvants par des matériaux naturels et synthétiques », thèse de magister, Université Mouloud Mammeri Tizi ouzou, (2011).

[13] A. Houas, H. Lachheb, MG- Esibi, E. Elaloui, C. Guillard, J.M Herrmann, « Photocatalytic degradation pathway of methylene blue in water », Appl.Catal, B: Environ. 31, (2001) 145-157.

References

[14] J. Reungoat, « Etude d'un procédé hybride couplant adsorption sur zéolithes et oxydation par l'ozone. Application au traitement des effluents aqueux industriel », thèse doctorat, Université de Toulouse, (2007).

[15] BEN MENSOUR, H, BOUGHZALA, O, DRIDI, D, BARILLIER, D, CHEKIR, L, MOSRATI, R, les colorants textiles sources de contamination de l'eau : criblage de la toxicité et des méthodes de traitement, revue des sciences de l'eau, 24, 2018.

[16] BEBAMRAOUI, F, ‹‹ élimination des colorants cationiques par des charbons actifs synthétisés à partir des résidus de l'agriculture ››, mémoire de magistère, université Ferhat Abbas Sétif, (2014).

[17] BARKA, N, ‹‹ L'élimination des colorants de synthèse par adsorption sur un phosphate naturel et par dégradation photocatalytique sur TiO2 supporté ››. Thèse de doctorat, Ibn Zohr University Agadir, 2008.

[18] C. Karunakaran, P.J. Anilkumar, « Photoproduction of iodine with nanoparticulate Semiconductors and insulators», Molecular Catal. A: Chem. 265 (2007) 153-158.

[19] F. Sunada, A. Heller, « Effects of Water, Salt Water, and Silicone Overcoating of the TiO2 Photocatalyst on the Rates and Products of Photocatalytic Oxidation of Liquid 3- Octanol and 3-Octanone », Environ. Sci. Technol. 32 (1998) 282-286.

[20] AICHE, Z, « Application de la photocatalyse pour la dégradation d'un polluant récalcitrant dans l'eau en utilisant l'énergie solaire », thèse d'ingéniorat, Université des sciences et de la technologie Houari Boumediene, Algérie, 2014.

[21] BAHNEMANN, D.W, KORMANN, C, Hoffmann, M.R, Preparation and characterization of quantum size zinc oxide: a detailed spectroscopic study, J. Phys. Chem. 91 (1987) 3789–3798.

[22] DI PAOLA, A, GARCIA-LOPEZ, E, MARCI, G, PALMISANO, L, A survey of photocatalytic materials for environmental remediation, J. Hazard. Mater. 211–212 (2012) 3–29.

[23] HOFFMAN, A.J, CARRAWAY, E.R, HOFFMANN, M.R, Photocatalytic production of H2O2 and organic peroxides on quantum-sized semiconductor colloids, Environ. Sci. Technol. 28 (1994) 776–785.

References

[24] ZHANG, Y, RAM, M.K, STEFANAKOS, E.K, GOSWAMI, D.Y, Synthesis characterization, and applications of ZnO nanowires, J. Nanomater. 2012 (2012) 1– 22.

[25] MORALES FLORES, N, PAL, U, GALEAZZI, R, SANDOVAL, A, Effects of morphology, surface area, and defect content on the photocatalytic dye degradation performance of ZnO nanostructures, RSC Adv. 4 (2014) 41099–41110.

[26] http://physique.unice.fr/sem6/2016-2017/PagesWeb/PT/Surfaces/nusemi.html.

[27] DANESHVAR, N, SALARI, D, KHATAEE, A.R, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO2, J. Photochem. Photobiol. A Chem. 162 (2004) 317–322.

[28] GARCIA-LOPEZ, E, MARCI, G, SERPONE, N, HIDAKA, H, Photoassisted oxidation of the recalcitrant cyanuric acid substrate in aqueous ZnO suspensions, J. Phys. Chem. C 111 (2007) 18025–18032.

[29] DELSOUZ KHAKI, MR, SHFEEYAN, MS, ABDUL RAHMAN, A, WAN DAUD, W, applications of doped photocatalysts for organic pollutant degradation, Journal of Environmental Management 198 (2017) 78-94.

[30] SHON, H.K, VIGNESWARAN, S, NGO, H.H, KIM, J.-H, Chemical coupling of photocatalysis with flocculation and adsorption in the removal of organic matter, Water Research 39 (2005) 2549–2558.

[31] From nutshells to energy cells: Pioneering supercapacitor electrodes via innovative argan nutshell-activated carbon synthesis

References

[32] Rufford, T.E.; Hulicova-Jurcakova, D.; Khosla, K.; Zhu, Z.; Lu, G.Q. Microstructure and electrochemical J. Power Sources 2010, 195, 912–918 [CrossRef].

[33] Sekar, S.; Aqueel Ahmed, A.T.; Inamdar, A.I.; Lee, Y.; Im, H.; Kim, D.Y.; Lee, S. Activated carbon-decorated Spherical silicon nanocrystal composites synchronously-derived from rice husks for the anodic source of Lithium-ion battery. Nanomaterials 2019, 9, 1055 [CrossRef].

[34] Book "Introduction to Photocatalysis Fundamentals and Applications", By Tahir Iqbal Awan, Sumera Afsheen, Iqra Maryam.

[35] Wang, Q.P.; Zhang, D.H.; Xue, Z.Y.; Hao, X.T. Violet Luminescence Emitted from ZnO Films Deposited on Si Substrate by RF Magnetron Sputtering. Appl. Surf. Sci. 2002, 201, 123–128.

[36] Z. M. El-Bahy, A. A. Ismail, and R. M. Mohamed, “Enhancement of titania by doping rare-earth for photodegradation of organic dye (Direct Blue),” Journal of Hazardous Materials, vol. 166, no. 1, pp. 138–143, 2009.

[37] K. Byrappa, A. K. Subramani, S. Ananda, K. M. Lokanatha Rai, R. Dinesh, and M. Yoshimura, “Photocatalytic degradation of rhodamine B dye using hydrothermally synthesized ZnO,” Bulletin of Materials Science, vol. 29, no. 5, pp. 433–438, 2006.

[38] Murugan, R., Ganesh, I., & Umarani, C. S. (2017). Photocatalytic degradation of methylene blue using ZnO/rGO nanocomposite under visible light irradiation. Journal of Materials Science: Materials in Electronics, 28(8), 6332-6341.

[39] Khairnar SD, Patil MR, Shrivastava VS (2018) Hydrothermally synthesized nanocrystalline Nb2O5 and its visible-light photocatalytic activity for the degradation of congo red and methylene blue. Iran J Catal 8:143–150.

عنوان المذكرة : محفز ضوئي من الكربون المنشط المشتق من الكتلة الحيوية (AC) المعدل بالزنك (ZnO) من أجل التحلل الضوئي الفعال لصبغة الميثيلين الأزرق تحت الضوء المرئي

اللقب : قربة **الإسم: آسيا** **المؤطر: الدكتورة براهيمي جميلة**

اللقب: تربح **الإسم: مريم نسرين**

ملخص: يتمثل الهدف الرئيسي من هذا البحث في تصنيع مركب التحفيز الضوئي من الزنك والكربون المنشط وتقييم فعاليته في التحلل الضوئي لصبغة MB تحت الضوء المرئي. وتركز هذه الدراسة على التحلل الضوئي لصبغة أزرق الميثيل باستخدام الزنك كمحفز ضوئي مضاف إليه الكربون المنشط (AC)، الذي تم اشتقاقه من نوى التمر. تمت دراسة تأثيرات الظروف التجريبية المختلفة على كفاءة التحلل الضوئي لصبغة MB على ZnO-AC، بما في ذلك مصدر الضوء، وجرعة المحفز، والتركيز الأولي لصبغة MB، ودرجة الحموضة في الوسط، ووقت الإشعاع. أظهرت النتائج أن مركب ZnO-AC بنسبة 7/3 حقق تحلل كامل لصبغة MB في 20 دقيقة، بجرعة محفزة 0.02 ملجم/لتر، وتركيز أولي لصبغة MB قدره 20 ملجم/لتر. أكدت هذه الدراسة أن مصدر الضوء ضروري للتنشيط الفعال لمركب ZnO-AC، مما يؤدي إلى تحلل سريع وكامل لصبغة BM.

تتناسب البيانات التجريبية بشكل جيد مع النموذج الحركي من الدرجة الثانية الزائفة، مع معامل ارتباط أكبر من R^2=0.9844. تشير النتائج إلى أن مركب ZnO-AC 7/3 المركب هو مرشح بيئي واعد لمعالجة مياه الصرف الصحي.

كلمات مفتاحية: محفز ضوئي، نوى التمر، أكسيد الزنك ZnO، معدل التحلل الضوئي، أزرق الميثيلين.

Memory Title: Biomass-derived active carbon (AC) modified ZnO photocatalyst for efficient photocatalytic degradation of Methylene Blue Dye under visible light

Name: krobba **First name: Assia** **Directed by. Dr. Brahimi. Djamila**
Name: Terbah **First name: Meriem Nesrine**

Abstract: The main objective of this research is to synthesize a ZnO-AC photocatalytic composite and evaluate its effectiveness in the photodegradation of MB under visible light. This study focuses on the photodegradation of MB dye using a ZnO as a photocatalyst doped with activated carbon (AC), which was derived from date seeds. The effects of various experimental conditions on the efficiency of the photocatalytic degradation of MB dye over ZnO-AC were studied, including light source, catalyst dose, initial concentration of MB, pH of the medium, and irradiation time. The results showed that the ZnO-AC composite with a ratio of 3/7 achieved complete BM degradation in 20 minutes, with a catalyst dose of 0.02 mg/L, and an initial BM concentration of 20 mg/L. This study confirmed that the light source is essential for efficient activation of the ZnO-AC composite, leading to accelerated and complete degradation of the BM dye.

The experimental data fits well with the pseudo-second-order kinetic model, with a correlation coefficient greater than R^2=0.9844. The results suggest that the 3/7 ZnO-AC composite is a promising ecological candidate for wastewater treatment.

Keywords: Photocatalyst, date seeds, Zinc oxide ZnO, photodegradation rate. Methylene bleu MB.

Titre du mémoire : Photocatalyseur ZnO modifié au charbon actif (AC) dérivé de la biomasse pour une dégradation photocatalytique efficace du colorant bleu de méthylène sous la lumière visible

Nom : krobba **Prénom : Assia** **Encadreur : Dr : Brahimi.Djamila**
Nom : Terbah **Prénom : Meriem Nesrine**

Résumé :

L'objectif principal de cette recherche est de synthétiser un composite photocatalytique ZnO-AC et d'évaluer son efficacité dans la photodégradation du MB sous lumière visible. Cette étude se concentre sur la photodégradation du colorant MB en utilisant un ZnO comme photocatalyseur dopé avec du charbon actif (CA), qui a été dérivé de graines de dattes. Les effets de diverses conditions expérimentales sur l'efficacité de la dégradation photocatalytique du colorant MB sur ZnO-AC ont été étudiés, notamment la source de lumière, la dose de catalyseur, la concentration initiale de MB, le pH du milieu et le temps d'irradiation. Les résultats ont montré que le composite ZnO-AC avec un rapport de 3/7 permettait une dégradation complète du colorant MB en 20 minutes, avec une dose de catalyseur de 0,02 mg/L et une concentration initiale de MB de 20 mg/L. Cette étude a confirmé que la source de lumière est essentielle pour une activation efficace du composite ZnO-AC, conduisant à une dégradation accélérée et complète du colorant BM. Les données expérimentales correspondent bien au modèle cinétique du pseudo-second ordre, avec un coefficient de corrélation supérieur à R^2=0,9844. Les résultats suggèrent que le composite ZnO-AC 3/7 est un candidat écologique prometteur pour le traitement des eaux usées.

Mots clés : Photocatalyseur, graines de dattes, oxyde de zinc ZnO, taux de photodégradation. Méthylène bleu MB.