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

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DOMAINE: Sciences and Technologies

SPECIALTY: Petrochemical Industries

OPTION: Petrochemical engineering

Theme

Preparation of zinc oxide (ZnO)-doped activated carbon (AC) based photocatalytic material, and its application in photocatalytic waste water splitting process

Supervisory and examining committee:

First and last name	Grade	Quality
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Promotion: JUNE 2024

Acknowledgment

First, we would like to express our sincere thanks and gratitude to my supervisor Dr. Djamila BRAHIMI for her continuous support during this work, her help, patience, guidance, and constructive criticism, and been the best supervisor in our years of studying.

I sincerely thank the committee members Dr. BOURZEG Mohammed Taher and Dr. ABDELMOUIZ Ahmed for agreeing to examine our work.

The gratitude is extended to Dr. Mokhtar BENALIA, head of the Department of Process Engineering, for his efforts to provide us with the materials needed for this work.

Our thanks also go to the workers at the process-engineering laboratory for their consent and continuous help throughout this work. Throughout this work, we met many people who helped us in many forms and ways. We express our deepest gratitude to all the professors and students who helped us here at the University of Ammar Thlidji-Laghouat.

Dedication

I dedicate this work first to my dear parents the guide of my life Dad and my sweet and beloved Mom the queen who sacrificed for me for all their support and unconditional love and for all that, they did for me throughout my years at the university thanks mom and dad love you**.**

To my brothers and sister Sarah Mohamed Abderahim and the rest of my family the Remilat and Mahi proud of being one of you guys.

To a special person thanks for being in these 5 years and always alongside me in the bad days and the good ones you will always be special to me the exceptional one.

To all the brothers i had in university and honored to know them thanks for the best experience i could imagine for countless fights on controversial discussions even though i was always right especially on football subjects (Hala Madrid) glad and happy to know you, brothers.

It was a wonderful journey with a lot of experience in university and life these 5 years were the beginning for me to discover the world and understand it i want to say thanks for everything.

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

To my dear brother Tahar Yahyoui, the first part of the plan is done are you ready for the next chapter?

Oussama

Dedication

To my dearest loved ones,

On this day, which marks the end of an important chapter in my academic life and the beginning of a new journey, I want to express my deepest thanks and gratitude to all of you. To my caring mother and father, to those who are unmatched by anyone in the universe, to those whom God has commanded us to be kind to, to those who have given so much and given what cannot be returned, may God grant you continued health and wellness. You have been my shining candle amid difficult circumstances and great achievements. Each letter of these words is not enough to express the extent of my love and gratitude to you. You have my sincere love, respect, and majesty.

To my dear brothers and sisters, each of you played your role in building my character and supporting me during these precious years. You were the compass that directed me toward success and excellence.

I owe you so much to everyone who has supported me and stood by me on this journey, whether they are friends, colleagues, or teachers. Your wise words and continued support gave me the strength to move forward on this path. In addition, to everyone who helped me from far or near and helped me complete this study

We also do not forget our brothers in Palestine, in Gaza. We ask God to grant them victory, steadfastness, and empowerment. God to grant them victory, steadfastness, and empowerment.

To my brother and colleague in this work, Oussama Remilat. Yeah I am ready

Tahar

List of abbreviations and symbols

AC: Active **C**arbon

BG: Band **G**ap

CB: Conductor **B**and

DS: Date **S**eeds

LPG: Liquefied **P**etroleum **G**as

MB: Methylene **B**lue

NA: Number of **A**vogadro

PEC: Photo **E**lectrochemical **C**ell

QY (%): Quantum **Y**ield

R (%): Rate of MB dye degradation

ROS: Reactive **O**xygen **S**pecies

SMR: Steam **M**ethane **R**eformer

TWSC: Thermochemical **W**ater **S**plitting **C**ycles

UV: Ultra **V**iolet

UVA: Ultra **V**iolet **A**

UVB: Ultra **V**iolet **B**

VB: Valence **B**and

ΔG°: Standard Gibbs free energy of formation

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General Introduction

Introduction:

Energy and environment are two key issues in modern society, which are necessities for the economic and social sustainable development of the world. Where the energy economy relies heavily on conventional energy sources such as coal, petroleum oil, and natural gas, which are not renewable and environmentally benign to deal with this problem, there has been a global drive seeking renewable and clean alternatives to fossil fuels [1].

The optimal approach for hydrogen generation involves utilizing alternative energy sources such as hydroelectric power, wind power, low-energy nuclear reactions, and solar-driven water-splitting methods. Among these alternatives, solar-driven technology appears to be the most promising because it imposes fewer constraints compared to wind and hydroelectric power [1].

Indeed, systems such as hydrogen production from water splitting by electrolysis, have drawn a great deal of attention in recent decades as a promising substitute for fossil fuels, hydrogen has emerged as a clean and renewable energy. A key challenge is the efficient production of hydrogen to meet the commercial-scale demand for hydrogen. Solar-driven hydrogen production encompasses three main methods: thermochemical water splitting, photobiological water splitting, and photocatalytic or photoelectrochemical water splitting. One promising method to enhance this process to achieve efficient hydrogen production in terms of energy conversion and storage is photocatalysis. This technique uses light-absorbing materials to drive chemical reactions. In the context of green hydrogen production, photocatalysts can efficiently split water molecules into hydrogen and oxygen when exposed to sunlight or artificial light sources. This approach offers several advantages, including higher efficiency, lower cost, and reduced environmental impact compared to traditional electrolysis methods. However, challenges such as catalyst stability, efficiency under different light conditions, and scalability need to be addressed for widespread adoption. Despite these challenges, the development of photocatalytic systems for green hydrogen production holds promise for a more sustainable energy future [2].

The photocatalysis of zinc oxide (ZnO) supported by activated carbon for hydrogen production through water electrolysis involves a process where ZnO acts as a photocatalyst to facilitate hydrogen generation from water under light irradiation. ZnO is an inexpensive, abundant, and stable semiconductor that can efficiently absorb UV light to generate electron-hole pairs for redox reactions. However, ZnO suffers from high electron-hole recombination rates and poor adsorption capacity, limiting its photocatalytic performance [3]. So, this method aims to harness the abundant, inexpensive, and stable properties of ZnO while addressing its limitations such as low photon-to-electron conversion efficiency and high electron-hole recombination rate.

This study aims to synthesize a photocatalyst based on zinc oxide (ZnO) doped with activated carbon (AC), which is made from date seed waste.

Three different weight ratios of ZnO/AC were used for this doping their performances were evaluated in the water-splitting process into hydrogen and oxygen to answer these questions:

- Would the activated carbon enhance the performance of the photocatalyst?
- Would the weight ratio affect the efficiency of the water-splitting process?
- Could it be a good candidate for the water-splitting process?

This work was divided into three chapters:

Chapter I presents generalities and definitions related to the water-splitting process over photocatalysts based on ZnO -AC.

Chapter II presents a description of the steps involved in the synthesis of ZnO-AC photocatlyst, and the experimental protocols used to test its efficiency in the water-splitting process into hydrogen and oxygen.

Chapter III presents the main obtained results from the experimental water splitting over the synthesized photocatalyst ZnO-AC under different experimental conditions.

Chapter I: Generalities And Definitions

I.1.Hydrogene as future fuel:

Various alternative fuels are competing to be tomorrow's vehicle fuel. By definition, alternative fuels are non-hydrocarbon-based fuels. They rely on the production of different feedstocks and different energy sources [4]. Among these alternative fuels, there are hydrogen, natural gas, methanol, ethanol, LGP, biodiesel, and electricity both plug-in and fuel cell [5]. The hydrogen give the highest lower heating value as represented in **Table I.1**

Though a common element in the universe, hydrogen can be found on earth only mainly in combination with other elements such as oxygen in water and carbon in hydrocarbons. Then, hydrogen must be produced. The production methods rely on the nature of the feedstock, the process involved and the energy used for the process. There are various processes, feedstocks, and energy sources. The number of production techniques is significantly important [6].

Table I.1: energy content of different fuels [7]:

Fuel	Density (g/l)	Lower heating value (MJ/Kg)	Carbon Percentage %
Crude Oil	845	42.8	85.0
Natural gas	0.654	50.1	5.0
Conventional Gasoline	737	43.7	85.5
Conventional diesel	856	41.8	87.0
Hydrogen	0.0818	142.0	0

I.1.1. Advantages and disadvantages of hydrogen:

Hydrogen offers both advantages and challenges as an energy carrier. Its clean nature and versatility make it a promising solution, but energy-intensive production, storage complexities, and infrastructure needs currently limit its widespread use [8]. Where the advantages and disadvantages of hydrogen as fuel shown in **Table I.2**

Table I.2: Use of hydrogen as a transportation fuel [9]:

Use of Hydrogen as a Transportation Fuel	
Advantages	**Disadvantages**
High energy yield (122 kJ/g)	Low-density (large storage areas)
Most abundant element	Not found free in nature
Produced from many primary energy sources	Low ignition energy (similar to gasoline)
Wide flammability range (hydrogen engines operated on lean mixtures)	Currently expensive
High diffusivity	
Water vapor is a major oxidation product	
Most versatile fuel	

I.2. Hydrogen production method:

Hydrogen can be produced by several methods using chemical, electrochemical, catalytic, thermal or biological reactions; however, most of these reactions raise severe safety and environmental issues, while the availability of raw materials is a critical problem. The emergence of the hydrogen economy will depend upon the development of safe, efficient, widely available and environmentally responsible means for generating hydrogen. Since fossil fuel sources are currently abundant, almost all hydrogen is produced from these sources. However, the aim of any realistic sustained energy system based on hydrogen necessitates the fabrication of hydrogen from renewable sources In this regard hydrogen from water and sunlight is the ultimate choice [10]. Most of them involve splitting water into its two components of hydrogen and oxygen, as water makes

up 70% of the earth's surface. Some of these methods are described below, but not all the methods are appropriate for a hydrogen economy or are environmentally safe [11].

I.2.1. Stream reforming:

Steam Methane Reforming (SMR) was developed in 1930 and became one of the most important processes for hydrogen production. The principle reaction of SMR is presented by the following equations [12]:

$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$ $\Delta H_{SR} = 206.2$ kJ/mol……. **(**I.1)

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H_{SR} = -\ 41.2$ kJ/mol……(I.2)

$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4\ H_2$ $\Delta H_{SR} = 165$ kJ/mol……..……..(I.3)

This process is reversible and endothermic, so it is carried out at 700 -900 °C and $15 – 30 \times 10^5$ Pa with nickel supported on alumina as a catalyst.

Despite the importance of this method, it faces some problems and limitations:

a) Hydrogen production is limited to the equilibrium conversion of methane owing to the reversibility of the reaction [12].

b) It has CO_2 production as a by-product, which affects climate change.

c) There is catalyst deactivation due to carbon formation; therefore, there is a limit to the catalyst's lifetime, and finally.

d) This process relies on using a fossil fuel (methane).

The process of the (SMR) is diagrammed in the (**Figure I.1.)**

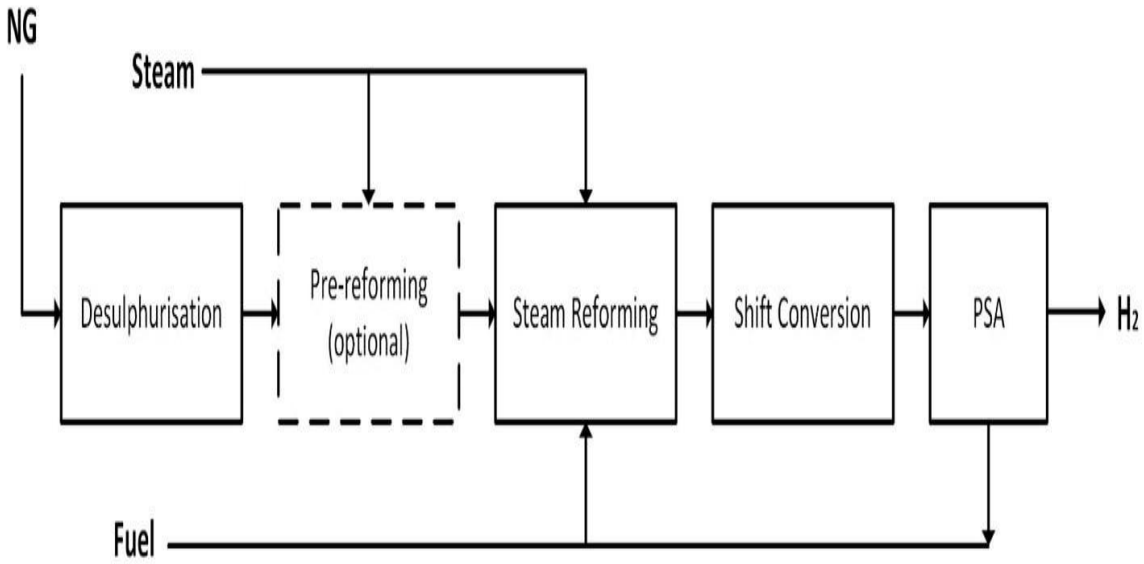


Figure I.1. Common process flow for a Steam Reforming plant. Adapted from "Hydrocarbon Processing: Gas Processing Handbook (2012)

I.2.2. Electrolysis:

Electrolysis is a promising option for carbon-free hydrogen production from renewable and nuclear resources. Electrolysis is the process of using electricity to split water into hydrogen and oxygen. This reaction takes place in a unit called an electrolyze.

Electrolyzes consist of an anode and a cathode separated by an electrolyte. Different electrolyzes function in different ways, mainly due to the different types of electrolyte material involved and the ionic species it conducts [13].

Electrolysis consists of an oxidation process at the anode to produce oxygen, and a reduction process at the cathode to produce hydrogen, as observed in the following equations:

Cathode (Reduction): $2\ H_2O\ (I) + 2e^- \text{--------►}\ H_2\ (g) + 2\ OH^-\ (aq)$…….…… (I.4)

Anode (Oxidation): $4\ OH^-(aq)\ \text{--------►} O_2\ (g) + 2\ H_2O\ (I) + 4e^-$…… (I.5)

Overall: $2H_2O\ (I)\ \text{-------►}\ 2H_2\ (g) + O_2\ (g)$ ……..(I.6)

This process is slow if the above reaction occurs in pure water, so an electrolyte (such as potassium chloride) must be added. Hydrogen produced by electrolysis accounts for about 4% of production worldwide. Most of it is produced as a by-product of chlorine production. The efficiency of the electrolysis of water is about 50-80% to convert the electrical energy to hydrogen's chemical energy [11].

I.2.3. Thermochemical Production:

The thermochemical production of hydrogen, also known as a thermochemical water cycle, involves using high-temperature heat to drive a series of chemical reactions that produce hydrogen and oxygen from water. This process is a promising technology for green hydrogen production, especially when coupled with concentrated solar energy or waste heat from advanced nuclear reactors. Thermochemical water splitting cycles, (TWSCs), offer advantages such as decentralized hydrogen production, reduced risk of accidents, and eliminating high-temperature gas separation needs. These cycles are catalyst-free and do not rely on expensive elements, making them a natural alternative to water electrolysis for large-scale hydrogen production [14].

I.2.4. Reforming of biomass and waste:

Hydrogen can be produced from biomass and wastes as new renewable energy sources. The gasification of biomass is efficient, environmentally friendly, and has operational advantages. This process is classified according to the type of gasifying agent: air, steam, steam oxygen, air-steam, oxygen-enriched air, and so on [15, 16]. There have been extensive studies regarding hydrogen production from waste materials and wastewater from industrial processes. The problems arising from this method are the low hydrogen production rate and yield [17, 18].

I.2.5. Photolysis:

Two decades ago, great interest was shown in the photochemical reduction of water to generate hydrogen. Photolysis of water, photodecomposition, involves splitting water into hydrogen and oxygen using the photons. In other words, it is the conversion of photon energy to chemical energy, which is stored as hydrogen fuel [11]. This process is presented in equation (I.7):

H_2O (I) + H_2O ---------- ► H_2 (g) + 1/2 O_2 (g)…….….(I.7)

This reaction occurs when the potential difference is equal to or greater than 1.23 eV, the electromotive force, which is also derived from the following relation (I.1): [19]

$E = \Delta G° (H_2O) /2NA$……..(I.1)

Where: E: is the electromotive force in (eV).

(ΔG°): is the standard Gibbs free energy is 237.2 KJ/mol (2.46 eV) at 25 °C and

(NA): is Avogadro's number (6.022×10^{23}).

The potential applications of photolysis include using transparent plastic tubes filled with a water-catalyst solution exposed to sunlight, which could make hydrogen production up to four times cheaper than traditional electrolysis methods. This innovative approach holds promise for sustainable and efficient hydrogen generation, contributing to the advancement of green energy technologies [19].

I.3. Photoelectrolysis:

Hydrogen can be produced using solar energy as the driving force by the photoelectrolysis of water. In the process, solar photons are absorbed directly into an absorber material. Without complete conversion to heat. The absorber can either convert part of the photon energy to electricity (as in a photovoltaic cell) or use it in the decomposition of water to hydrogen and oxygen, that is the solar photoelectrolysis of water (**Figure I.2)** Fujishima and Honda (1972) where the first to report the generation of hydrogen and oxygen in a photoelectrochemical cell (PEC) using a TiO_2 photo anode illuminated with near light. Since then, scientists have extensively studied water splitting to search for semiconductor photo electrodes and photocatalysts [20].

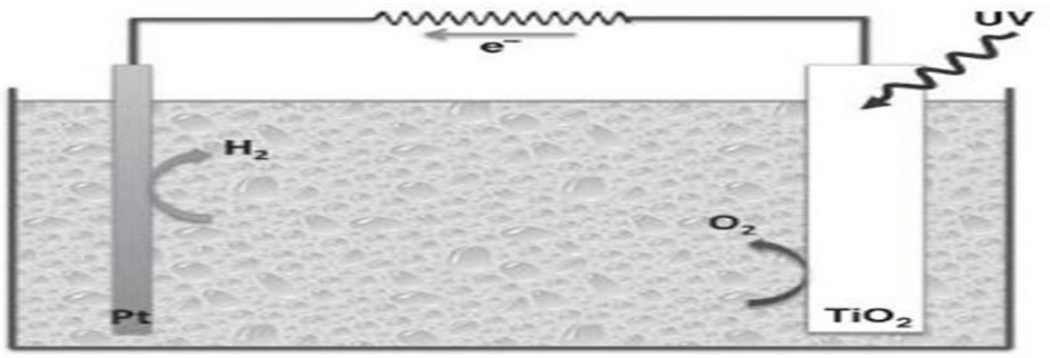


Figure I.2. Honda/ Fujishima effect of water splitting using a TiO_2 photoelectrode.

Photocatalysts used in water splitting have several basic requirements for the bandgap and band levels, Photocatalysts need to meet the special band requirements and typically have dopants and/or co-catalysts added to optimize their performance[21].

Electrons and holes are generated and separated into different, the electrons generated at the anode pass to a Pt cathode, and the photogenerated electrons reduce water to form H_2 on a Pt counter electrode, while holes oxidize water to form an O_2 electrode.

In general, photochemical systems for hydrogen generation can be classified into the following categories [21].

1) Photochemical systems that solution-based molecules absorb sunlight.

2) Semiconductor systems, that is sunlight is absorbed by either a suspended semiconductor, a particle in a liquid, or as a semiconductor surface in a photovoltaic or an electrochemical cell.

3) Photobiological systems, that is sunlight is absorbed by a chloroplast or algae in a configuration coupled to a hydrogen-generating enzyme.

4) Hybrid systems.

For efficient water splitting, photocatalysts must possess a few key elements. One key element is that H_2 and O_2 evolution should occur in a stoichiometric 2:1 ratio. The prime measure of photocatalyst effectiveness is quantum yield (QY), which is:

$$QY(\%) = Nre/Nip \times 100 \quad \text{(I.2)}$$

Where: QY (%): is the quantum yield in (%)

Nre: is the number of reacted electrons

Nip: is the number of incident photons

This quantity is used to determine how effective a photocatalyst is, however, it can be complex, depending on the experimental reaction conditions [22].

In general, the efficient photocatalyst would have a high quantum yield and give a high rate of gas evolution.

The other important element for an efficient photocatalyst is the spectral range of sunlight absorbed. As light has higher photon energy, photocatalysts will perform better per photon than visible light-based photocatalysts, but less light reaches the earth's surface than visible light from the sun. Thus, even a less efficient photocatalyst that absorbs visible light can be more useful than a more efficient photocatalyst absorbing solely light [22].

I.4. Photocatalyst:

A photocatalyst is a material that accelerates the rate of a photochemical reaction without being consumed or altered. In hydrogen production by photocatalytic water splitting, a photocatalyst is a semiconductor material that can absorb light energy to generate electron-hole pairs, which then participate in redox reactions to split water molecules into hydrogen and oxygen [23].

Enormous numbers of photochemical, chemical, and electrochemical processes occur on the surface of photocatalysts. The efficiency and rates of these reactions depend on several factors, some of which are related to the type of photocatalyst, and the behavior of photocatalysts influenced by the band gap of the semiconductor.

Semiconductors have been studied intensively and used widely in all the applications of photocatalysis [23].

The term 'band gap' refers to the energy difference between the top of the valence band and the bottom of the conduction band. Electrons can jump from a valence band to a conduction band, if a minimum amount of energy for the transition is provided, for a specific photocatalyst material, by absorbing a photon (light).

In general, the band gap is a major factor determining the electrical conductivity of a solid (**Figure I.3).** A semiconductor is a material with a small enough band gap that allows thermal excitation of electrons into its conduction band at temperatures below its melting point [11].

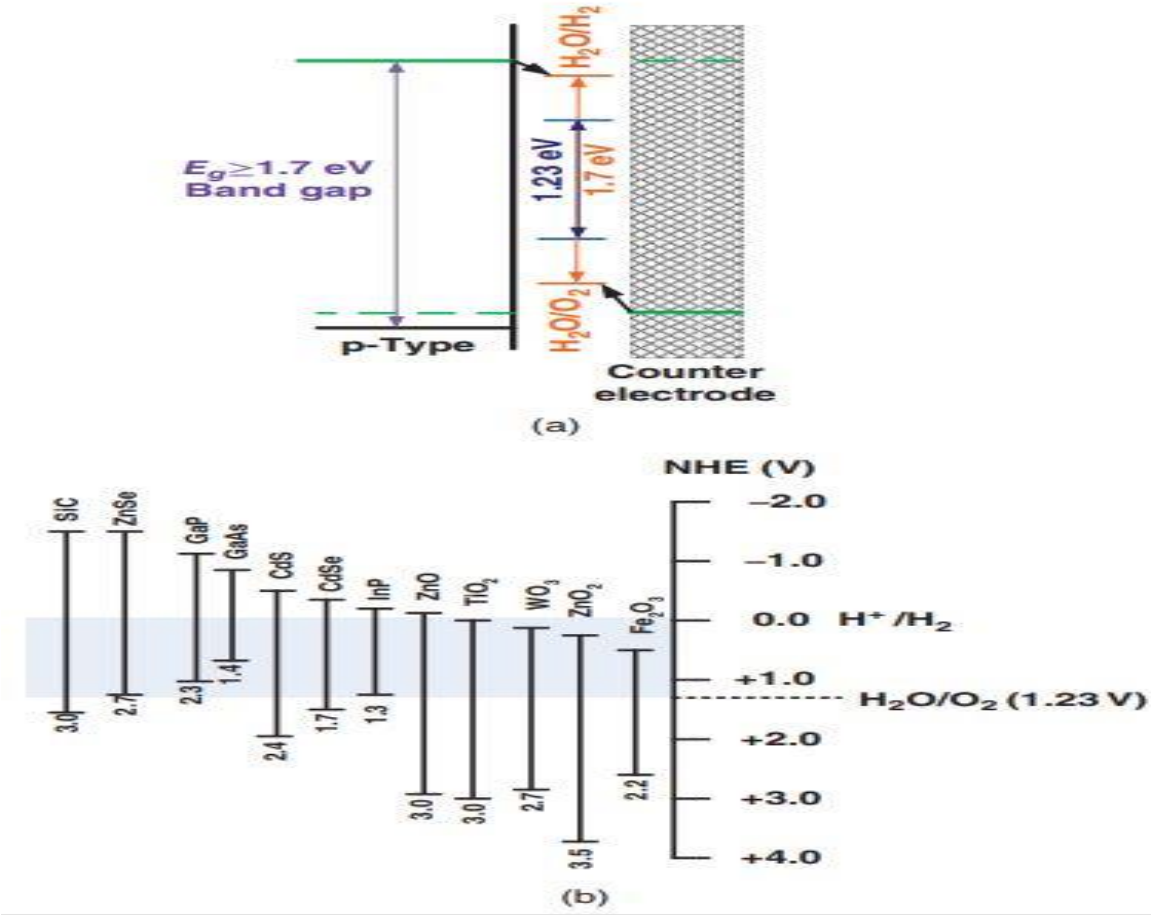


Figure I.3. Bandwidth and band edge criteria for photocatalytic production of hydrogen. (b) Position of valence and conduction band edges for a range of semiconductors (pH =1).

According to band theory, the valence electrons occupy several levels, which are grouped as bands. The highest occupied band called the valence band (VB) is fully occupied in a semiconductor. The next band called the conduction band (CB) is empty and exists only if some electrons are excited to this band, whereby its energy level becomes higher than that of the VB. These bands are separated by a forbidden region, which can contain no electron states; it extends from the top of the VB to the bottom of CB and is known as the band gap. The size of this region affects the properties of semiconductors. This kind of photocatalyst is strongly affected by temperature, as is its conductivity. Increasing the temperature leads to an increase in the energy of the electrons. The conductivity depends on the number of electrons that have been promoted across the band gap. This, the conductivity increases in proportion to the increase in temperature [24].

In the process of photoelectrolysis, a photoactive material forms a junction when in contact with a liquid (or a solid) electrolyte, and at the junction photon absorption creates a local electron−hole pair that generates sufficient voltage to electrochemically split a neighboring water molecule [22].

The technical challenges in robust semiconductor materials development for direct photoelectrochemical decomposition of water include the condition that the band edges of the semiconductor must overlap those of the hydrogen and oxygen redox reactions.

In addition, charge transfer from the surface of the semiconductor must be fast enough to prevent corrosion and to achieve low overvoltage to reduce energy losses and the semiconductor system must be stable in aqueous electrolytes [22].

This Improving, photocatalytic activity by modification has become a rule of great importance in the scientific community in recent years.

Photocatalyst materials are generally semiconductor materials doped with another element, and examples include oxynitrides, (TaON), (Ta_3N_5), and ($LaTiO_2N$), nickel-doped indium-tantalum-oxide catalysts, and CdS/ZnS systems. Titanium dioxide (TiO_2), zinc oxide (ZnO), and bismuth vanadate ($BiVO_4$). Water splitting occurs when the

catalyst is irradiated with light in the presence of an electron donor and acceptor, oxidizing (OH^-)

ions to produce (O_2) and reducing (H^+) ions to (H_2). The semiconductor-based oxidation and reduction reactions can be promoted by using catalysts in the structure [24].

I.4.1. Zinc oxide (ZnO) supported on activated carbon (AC):

Zinc oxide (ZnO) is a versatile inorganic material with a wide range of applications due to its unique properties. It is classified as an II-VI semiconductor, characterized by a direct wide band gap of 3.3 eV in the near-UV spectrum and high excitonic binding energy at room temperature. ZnO exhibits optical, chemical sensing, semiconducting, electric conductivity, and piezoelectric properties, making it valuable in various fields [25].

ZnO nanoparticles have been studied for their antibacterial, antifungal, catalytic, and photochemical activities. They possess high optical absorption in the UVA and UVB regions [26].

The wide band gap of ZnO significantly influences its properties, such as electrical conductivity and optical absorption. When doped with other metals, ZnO can exhibit enhanced conductivity. The material's strong ionic bonding in the Zn

O structure contributes to its durability, selectivity, and heat resistance, surpassing many organic and inorganic materials [27].

Zinc oxide (ZnO) supported on activated carbon (AC) is a promising photocatalyst with enhanced performance compared to pristine ZnO. The ZnO/AC composite is typically synthesized using a hydrothermal process, where ZnO nanorods are decorated onto the surface of porous AC [28].

I.4.2. Mechanism of photocatalyst ZnO supported by activated carbon:

ZnO, a semiconductor, absorbs visible light due to its wide bandgap (about 3.37 eV). When ZnO absorbs photons with energy equal to or greater than its bandgap, electrons (e^-) in the valence band are excited to the conduction band, leaving behind holes (h^+) in the valence band [29].

- The basic reaction can be summarized as:

$ZnO + hv \longrightarrow e^- + h^+$ ……(I.8)

Effective photocatalysis requires the separation of the photo-generated electrons and holes to prevent recombination. Activated carbon (AC) is plays a crucial role here. because he has a large surface area and excellent electron conductivity. When ZnO is supported on AC, the AC can trap and transport electrons efficiently, reducing the rate of electron-hole recombination [29].

The photo-generated electrons and holes migrate to the surface of the photocatalyst where they participate in redox reactions [30].

The electrons (e^-) reduce protons (H^+) in water to produce hydrogen gas (H_2):

$2H^+ + 2e^- \longrightarrow H_2$ ……(I.9)

The holes (h^+) oxidize water (H_2O) to produce oxygen gas (O_2) and protons (H^+):

$2H_2O + 4H^+ \longrightarrow O_2 + 4H^+$ ……(I.10)

The combination of ZnO and AC creates a synergistic effect. ZnO is the active photocatalyst, while AC enhances charge separation and provides more active sites for reactions due to its high surface area [30].

In an aqueous solution, the overall reaction for water splitting into hydrogen and oxygen can be summarized as

$2H_2O \longrightarrow 2H_2 + O_2$ ……...(I.11)

This mechanism is explained in **Figure I.4.**

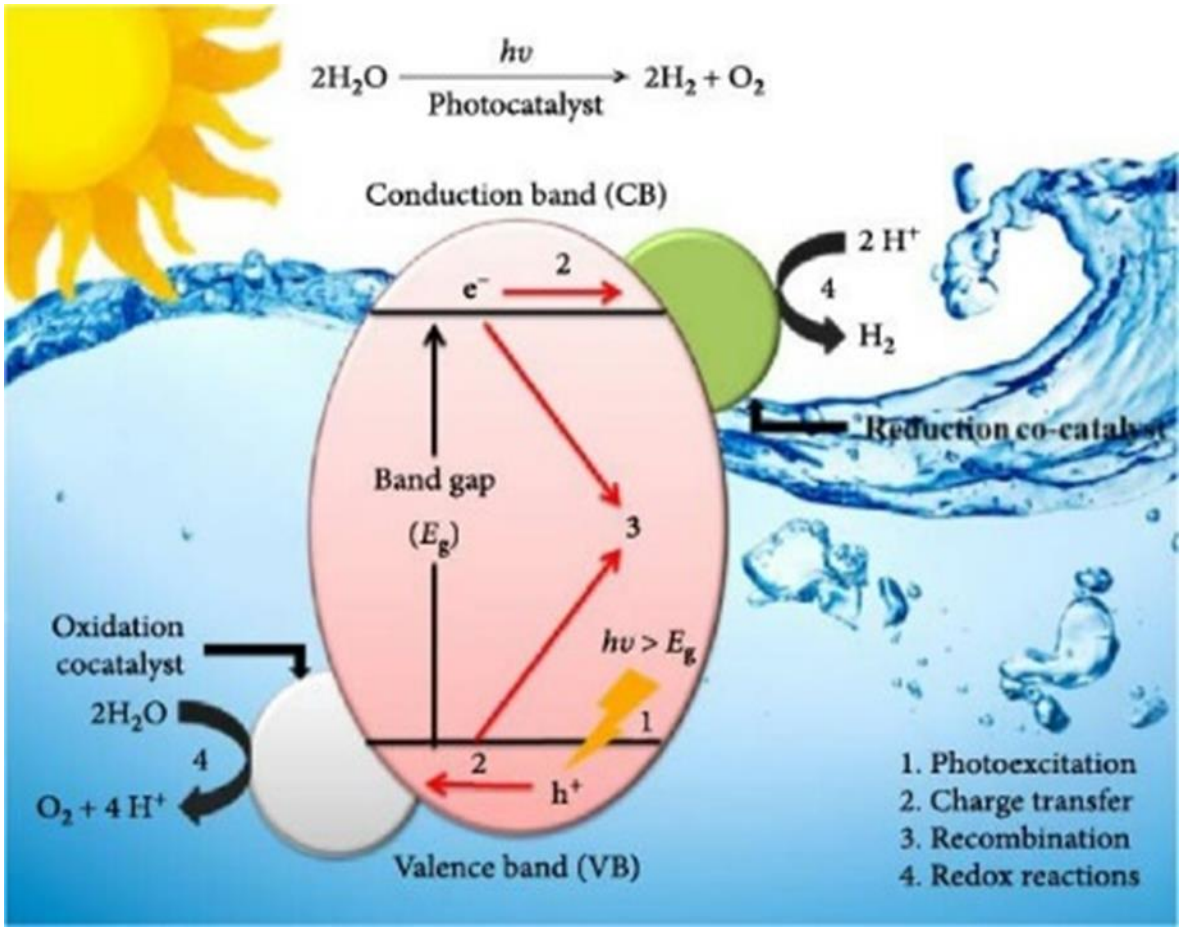


Figure I.4. Mechanism-of-the-photocatalytic-water-splitting

Chapter II: Experimental Setup and Conditions

II.1. Introduction:

This chapter presents a description of the steps involved in the synthesis of ZnO/AC, 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 pure water splitting to hydrogen and oxygen.

Finally, the experimental setup for testing the ability of the synthesized ZnO/AC photo catalyst in wastewater splitting to hydrogen and oxygen, and treated water.

II.2. Materials and products:

In this study, date seeds (DS) were used as a feedstock to prepare (AC), which was used to support the synthesized photocatalyst. All chemicals and materials used in the investigation such as acid 37% (HCl), potassium hydroxide 85% (KOH), and methylene blue (MB) alongside NaOH and main subject zinc nitrate hydroxide $Zn(NO_3)_{2.}$

For the materials, a tubular furnace, UV-Vis spectrophotometer, and, a generator ensure uninterrupted power.

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 date seeds (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.1.**

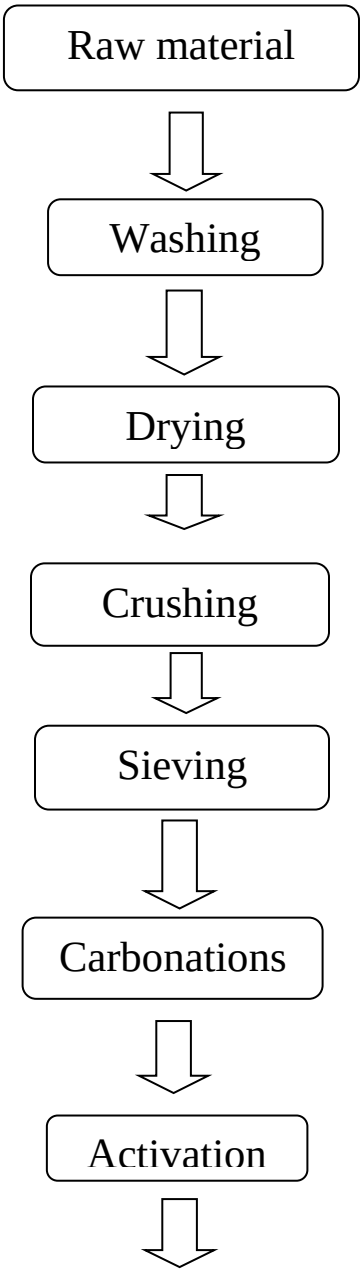


Figure II.1. Workflow of the preparation of activated carbon (AC)

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 the **(Figure Ⅱ.2)**shows.

Figure Ⅱ.2. Date seeds after washing.

II.3.1.2 Drying:

It is important to thoroughly dry date seeds before using them to make activated carbon. The drying process was carried out by laying Date seeds inside the oven, as shown in (**Figure Ⅱ.3)** for a long period, to ensure that it was completely dried. The experiment period of 14 hours was enough for a temperature 100 °C [31].

Figure II.3. 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 seeds after crushing them.

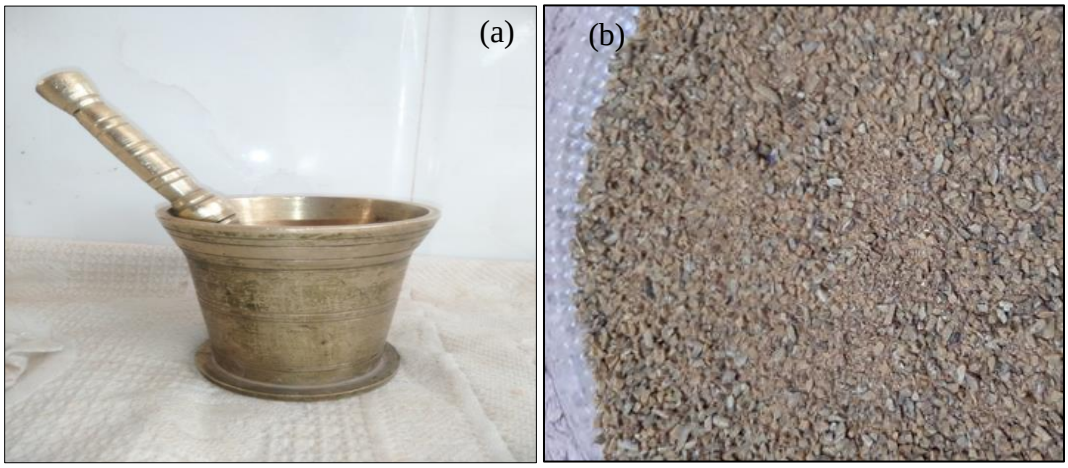


Figure II.4. Crushing of date seeds (a) Manual grinder, (b) crushed date seeds.

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.

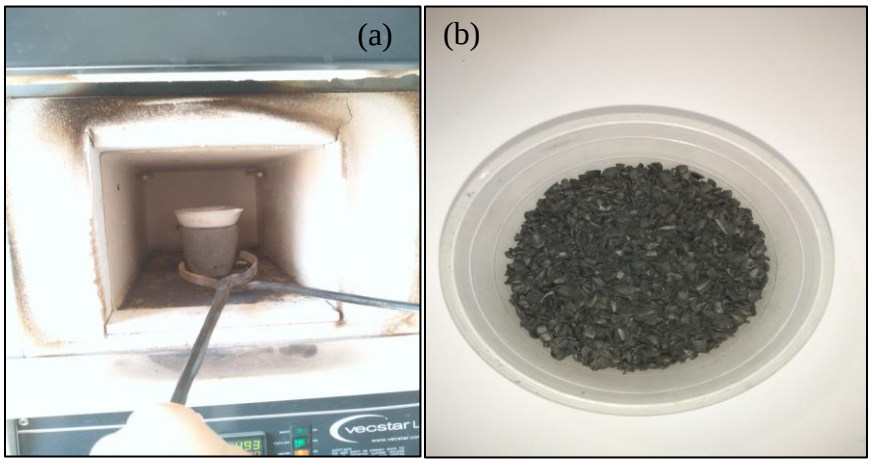


Figure II.5. Carbonation of date seeds (a) Furnace muffle, (b) Obtained carbon.

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.

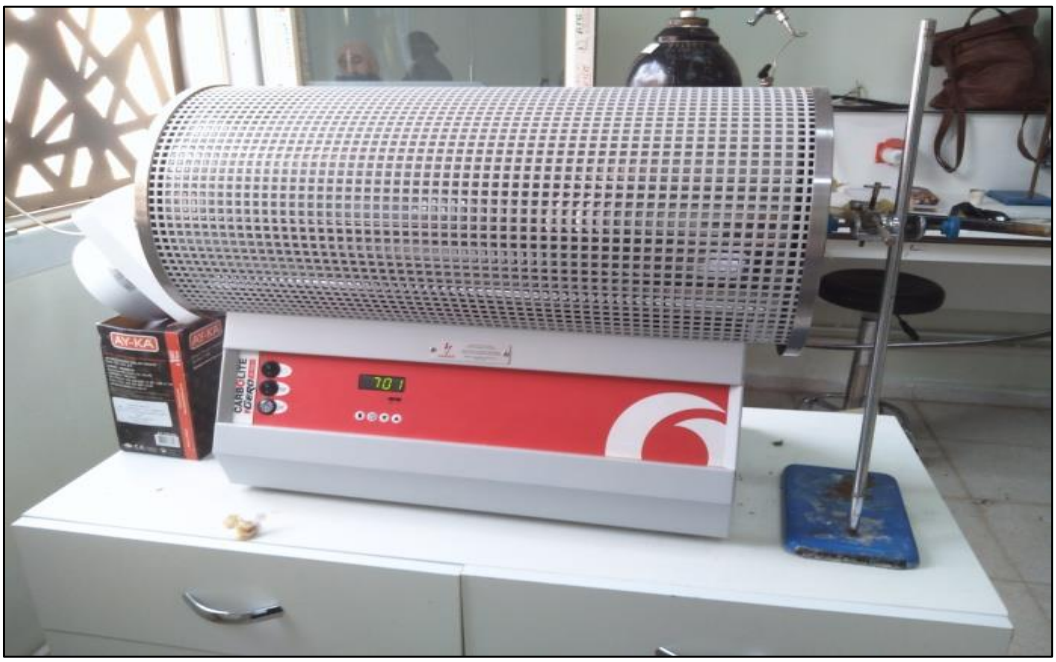


Figure II.6. Tubular furnace used in the bio char activation process

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. In the first step, solution A was prepared in a beaker by dissolving a mass (m_1) of zinc nitrate ($Zn(NO_3)_2$) in 50 ml of distilled water under constant stirring for 30 min. Another solution B was prepared by dissolving a mass (m_2) of AC in 50 ml of distilled water with continuous 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: different photocatalysts ratios in the synthesis.

Representation of photocatalyst	Weight of zinc nitrate $Zn(NO_3)_2$ (g) ($m_{1)}$	Weight of AC (g) (m_2)	Weight ratio $\frac{ZnO}{AC}$ (-)
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 nanocomposite. The general protocol used is described in (**Figure II.7.)**

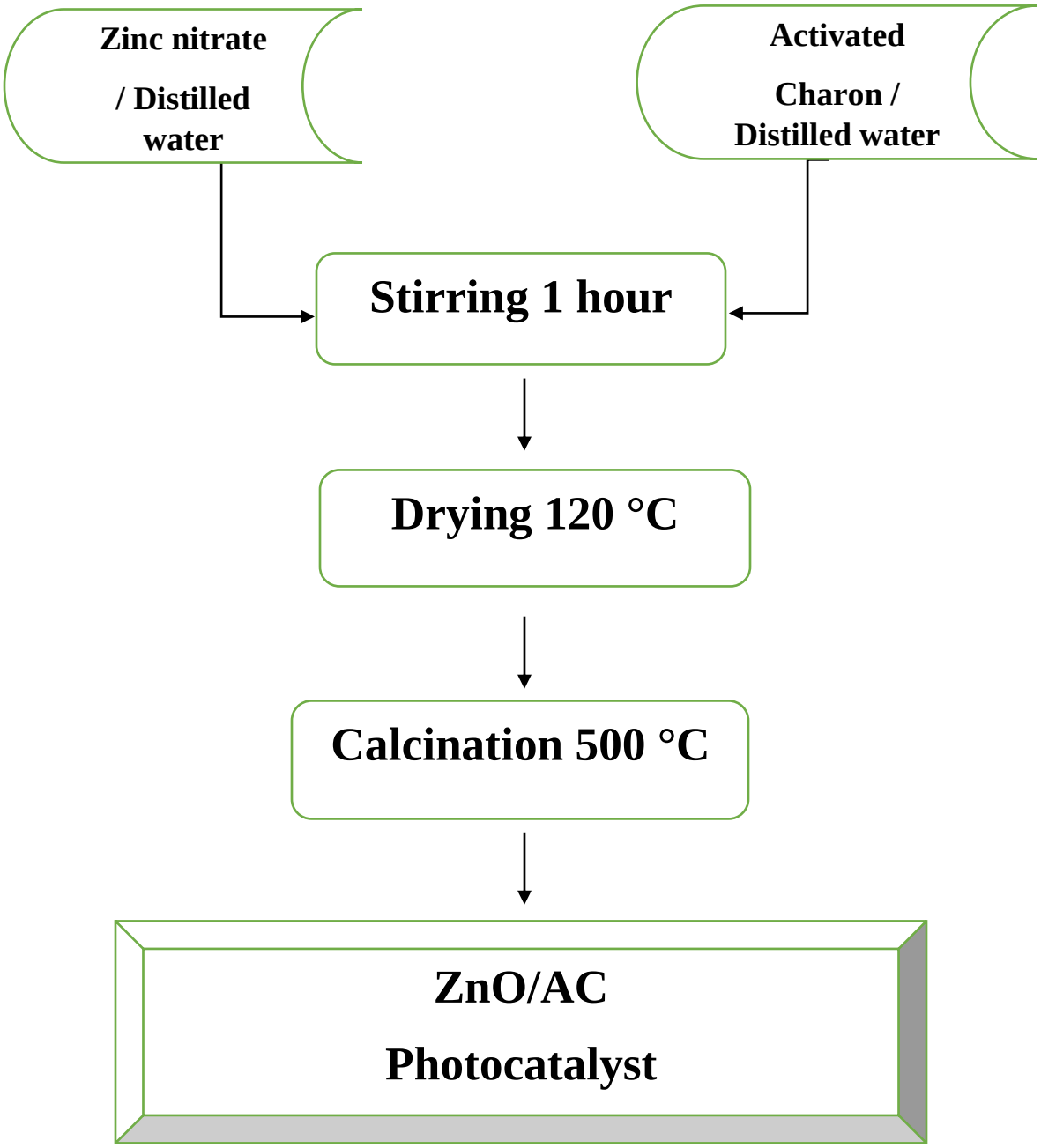


Figure II.7. Method for preparing the ZnO/AC photocatalyst.

II.4. Photocatalyst activity experiments:

II.4.1.Water splitting:

An experiment was conducted with 1 g of ZnO /AC added to 1200 ml of water (messed water) to examine how the photocatalyst enhanced the water-splitting process in the electrolyze as shown in **Figure.II.8**, an electric generator is used to generate an electric current of 24 volts. The experimental set-up for the electrolysis test is exposed to the visible light of 500 W. The flow rates of produced gases including oxygen and hydrogen produced through the water splitting process are measured during the test.

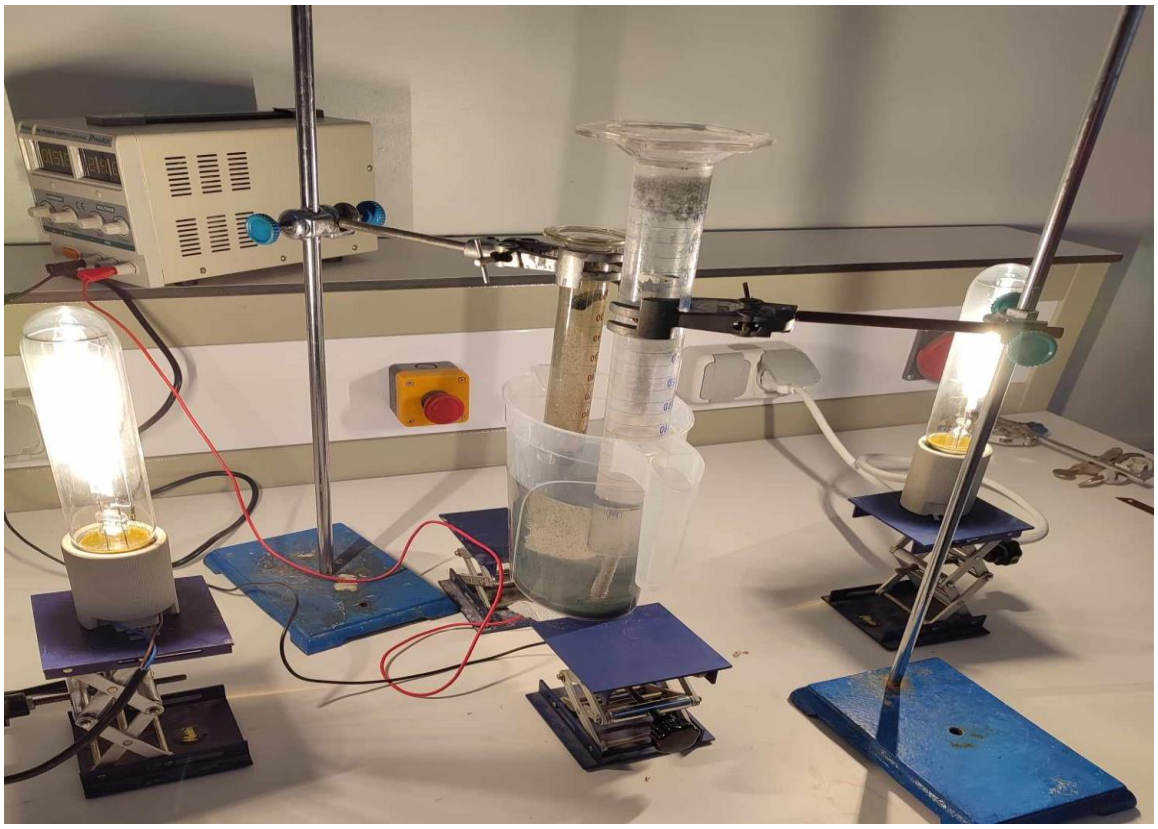


Figure II.8. Water splitting experiment to determine the activity of the photocatalytic

II.4.1.2. MB dye photodegradation:

In addition to the performance of the synthesized photocatalyst ZnO-AC in the water-splitting process, a solution containing 20 ppm blue methylene (MB) was prepared

to test its ability to photodegrade MB dye, at the same time as splitting water into hydrogen and oxygen.

The flow rates of produced gases including oxygen and hydrogen produced through the water splitting process are measured during the test. Also, MB dye was tested for photodegradation by withdrawing a sample every 10 minutes and analyzing it using a UV-Vis spectrophotometer (SHIMADZU UV -1280)**.**

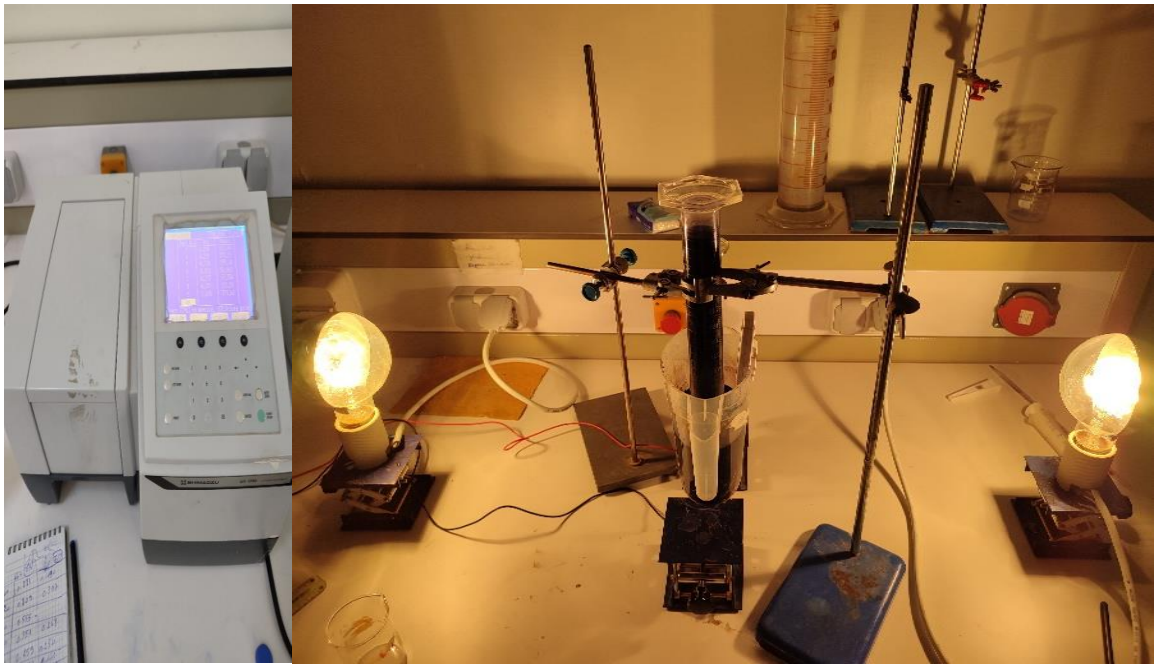


Figure II.9. Coupled water splitting and photocatalytic degradation of MB dye over ZnO-AC photocatalyst

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.

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 BM dye. Absorbance is measured at the maximum wavelength of (λ max).

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

$$\mathbf{R(\%)=(C_0 - C_t) / C_0 \times 100} \quad \textbf{(II.1)}$$

Where:

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

C_t: concentration of the solution at time (t)

R (%): The Photodegradtion rate of the MB over the photocatalyst

II.5. Parameters affecting photocatalytic activity:

To deeply understand the performance of the water-splitting process over ZnO-AC photocatalyst, the effect of several parameters was investigated in this study, such as time, light source, NaOH mass, and the weight ratio of ZnO/AC.

In addition, the performance of the ZnO- AC photocatalyst was also tested in the presence of 20 ppm of methylene blue (MB) dye in the water. **Table II.2.** Summarize the parameters investigated in this study.

Table II.2: Parameters affecting photocatalytic activity.

	Mass of NaoH (g)	**Catalyst type**	**Time (min)**	**Light source (W)**	**Volume of water (ml)**	**Temperature (°C)**	**Initial concentration of MB dye (ppm)**	**Mass of Catalyst(g)**
Serie (1)	1 2 3	- - -	40 40 40	500 500 500	1200	20-40	- - -	- - -
Serie (2)	2 2 2	5/5 ZnO-AC 4/6 ZnO-AC 3/7 ZnO-AC	180 180 180	500 500 500	1200	22-54	- - -	1 1 1
Serie (3)	2 2	5/5 ZnO-AC 5/5 ZnO-AC	180 180	500 1000	1200	24-60	- -	1 1
Serie (4)	2 2	4/6 ZnO-AC 3/7 ZnO-AC	80 80	1000 1000	1200	23-61	20 20	1 1

Chapter III:

Results and Discussion

III.1. Electrolytic activity:

This chapter has studied hydrogen and oxygen production by the water splitting process and the performance of sodium hydroxide mass (1, 2,3g) on H_2 and O_2 productivity under the influence of light rays 1000W, electric current 0.86 A.

III.1.1. Effect of NaOH mass:

Figure.III.1. shows the effect of the sodium hydroxide mass on the efficiency of the water-splitting process and the total productivity of hydrogen and oxygen. The NaOH mass strongly affects the efficiency of the water-splitting process, as the NaOH mass increases the water-splitting efficiency increases, leading to higher hydrogen and oxygen productivity.

The electrolysis of water by adding 1 g of sodium hydroxide produced (114 ml) of hydrogen and (0.59 ml) of oxygen. The highest production of hydrogen and oxygen is made through the process of water splitting into hydrogen and oxygen with 2 g of NaOH is (188 ml) and (9.5 ml). The water-splitting process with 3 g of NaOH reached the highest production of hydrogen and oxygen with (329 ml) and (30 ml). However, all three experiments were conducted at the same temperature interval as shown in Figure.**III.1. (a)**

All experiments were conducted within the same temperature range, ensuring that the observed differences in gas production were primarily due to the varying NaOH mass.

It is noted that the hydrogen gas produced has increment in the addition of the mass of sodium hydroxide solution. This condition shows that the higher the mass of the NaOH electrolyte solution, the formed electrons are denser and more numerous, making it easier to transfer electrons from the solution to the electrode [32].

However, there is a limit to this effect. Beyond a certain concentration, additional NaOH may not significantly increase the conductivity further, as the solution may reach a saturation point where additional NaOH does not dissolve effectively or the system may have other limiting factors such as electrode surface area or power supply limitations [33].

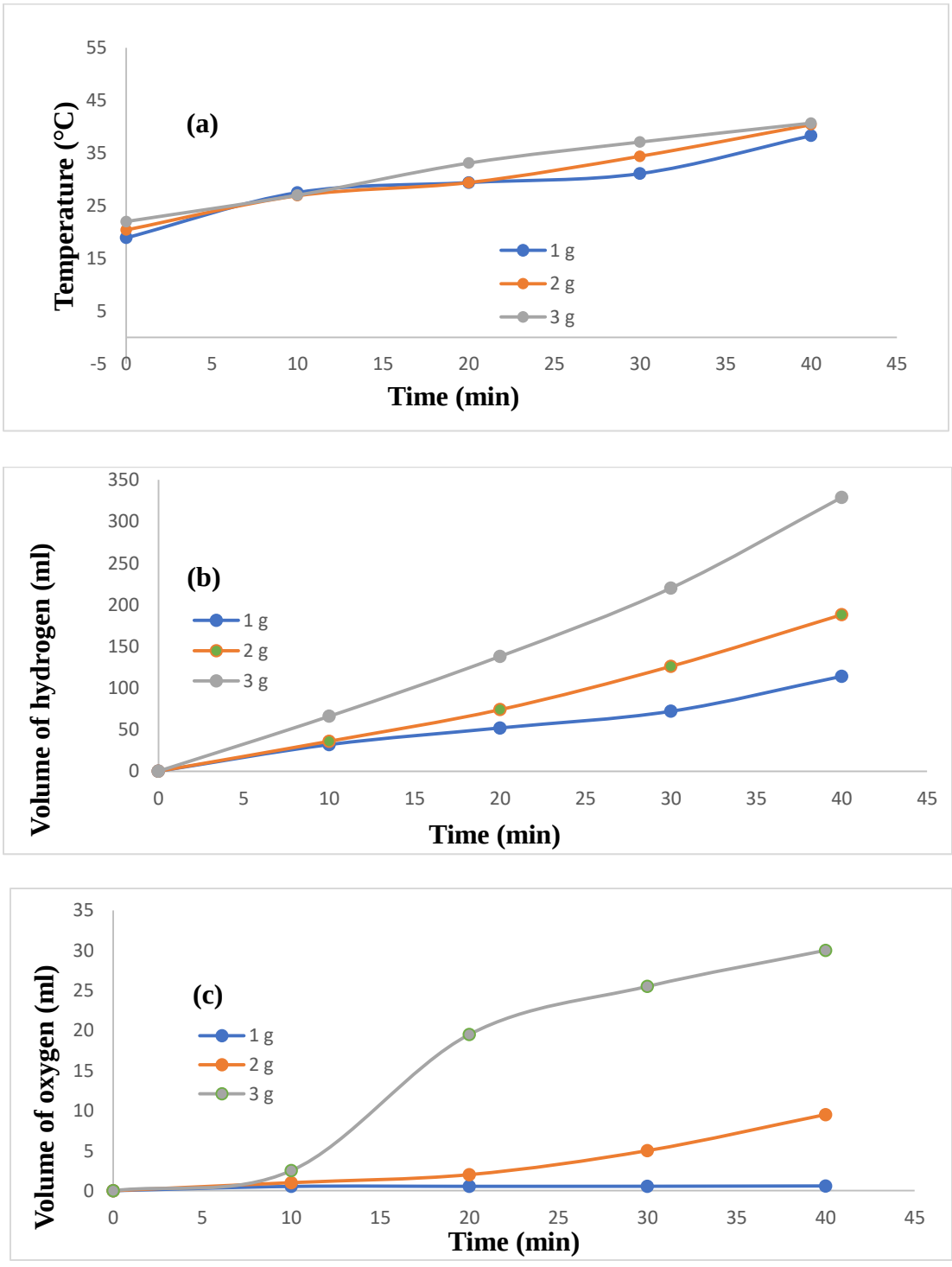


Figure.III.1.Effect of NaOH mass on electrolytic activity, variation of (a Temperature, b-Volume of hydrogen produced, and c- Volume of oxygen)

III.2. Photocatalytic activity:

The performance of the photocatalyst on the water splitting of hydrogen and oxygen production and compared to the electrolyte.

III.2.1. Photocatalytic water splitting:

Figure.III.2. shows the performance of 1 g of the 5/5 ZnO-AC photocatalyst in the water splitting process, It is observed that the effect of the photocatalyst on the water splitting is divided into two phases, in the first phase the productivity of hydrogen and oxygen was identical, this indicates that the process of splitting water through an electrolyte is similar to the process of splitting water through a photocatalyst, which means that the effect of the 5/5 ZnO-AC photocatalyst is neglected. In the second phase, (40-140 min) the productivity of hydrogen and oxygen was different, this indicates that the process of splitting water through an electrolyte is different from the process of splitting water through a photocatalyst, which means that the effect of 5/5 ZnO-AC photocatalyst is remarkable and affects positively on the efficiency of the water splitting process, However, the photocatalyst required time where observed.

NaOH in the electrolyte solution typically serves to increase the ionic conductivity of the solution, facilitating the movement of ions necessary for the water splitting reaction. However, without the photocatalyst, the reaction relies solely on the thermodynamic properties and the electrochemical potential provided by the NaOH [34]. Which seems less effective over a prolonged period compared to the photocatalyst-enhanced reaction.

The photocatalyst requires a certain period to become fully active. During this period, the effect of the photocatalyst is negligible, and the process resembles a typical electrolysis reaction.

Over time, the photocatalyst becomes more effective, likely due to the activation of more photocatalytic sites or the stabilization of reaction intermediates [35].

Photocatalysts, such as 5/5 ZnO-AC, are known to enhance the rate of hydrogen production by absorbing photons and generating excited electrons and holes. These

charge carriers participate in redox reactions, splitting water molecules into hydrogen and oxygen.

The improvement in performance seen in the second stage suggests that the photocatalyst becomes more effective over time, possibly due to reaching a more active state or the accumulation of more reactive intermediates [36].

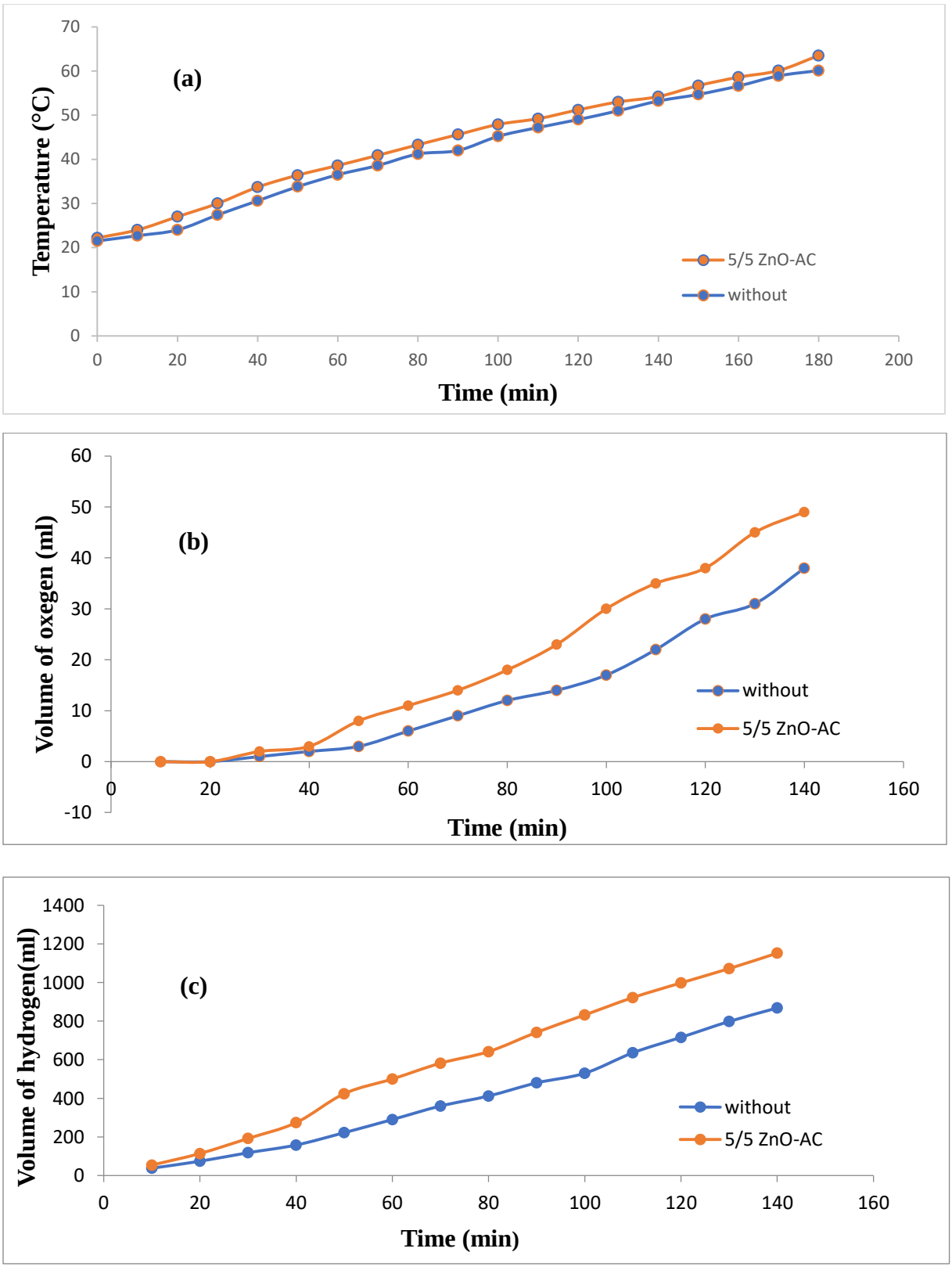


Figure.III.2.Photocatalytic activity of 5/5 ZnO-AC, variation of (a-Temperature, b-Volume of hydrogen produced, and c- Volume of oxygen)

III.2.1.1.Effect of the weight ratio of ZnO and activated carbon (AC):

Figure.III.3 represents the effect of the weight ratio of ZnO/AC on the efficiency of the water-splitting process. It is seen from **Figure.III.3 (b)**, the volume of hydrogen produced from the water-splitting process increases as the weight ratio of ZnO/AC decreases from 5/5 to 4/6, this means that the increase in AC has a positive impact on hydrogen production.

In addition, after that decreases from 4/6 to 3/7 have the opposite effect, as it is noticed that the volume of hydrogen produced decreases.

The optimal ratio is considered to be 4/6 ZnO-AC for the best performance of the water-splitting process.

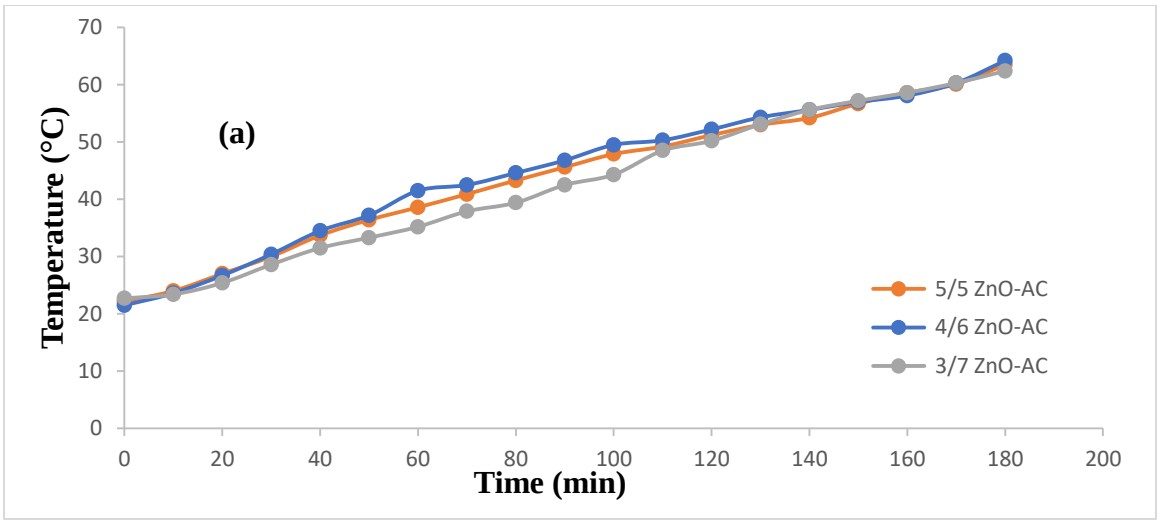
It strikes us a balance where the benefits of AC (increased surface area, improved charge separation) are maximized maximizing the number of active sites, while still maintaining sufficient ZnO content for effective photocatalytic activity. Also, the moderate weight ratio of activated carbon enhanced the performance of ZnO photocatalysts by improving the charge transfer processes [37].

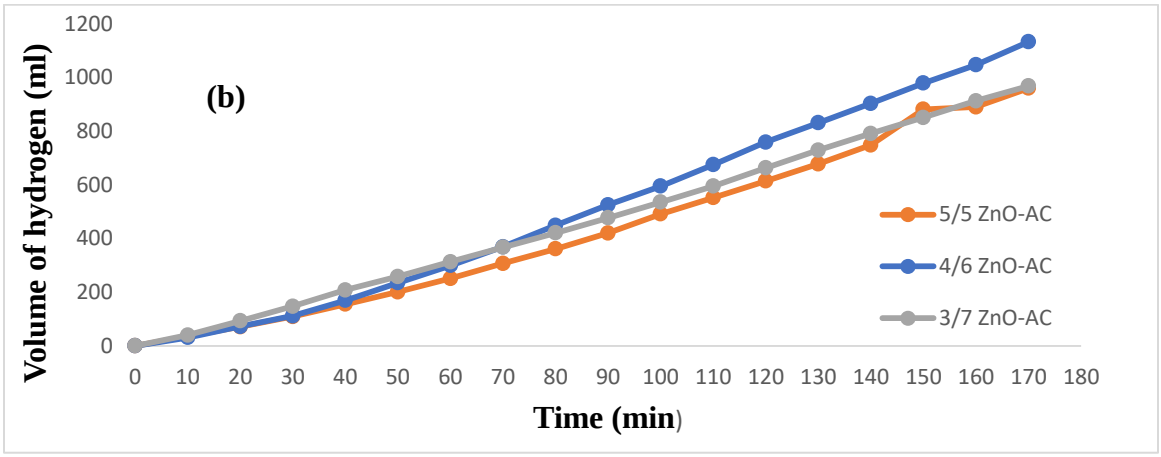
At this ratio, the synergistic effect between ZnO and AC is optimized, leading to the highest hydrogen production in the water-splitting process. This indicates that there is an optimal balance between ZnO and AC, where the beneficial effects of AC are maximized without compromising the photocatalytic properties of ZnO [37].

The volume of hydrogen produced from the dissociation of water decreases in the case of 3/7: the explanation of this is as follows: 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 rate of hydrogen production. 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 [38].

In 5/5, the volume of hydrogen produced decreases and, it can be interpreted as the high catalyst weight ratio reduced the effective surface area because the growth of ZnO on the surface was closing some of the activated carbon's pores. Besides, the specific surface area of the zinc is lower than that of activated carbon. In addition, the low weight ratio of activated carbon does not provide sufficient surface area for the adsorption of reactants or may not effectively promote the separation of photogenerated charge carriers, thus reducing the efficiency of hydrogen production [39].

From this, the conclusion is that the weight ratio of ZnO and activated carbon significantly affects the performance of ZnO photocatalysts in hydrogen production. Increasing the ZnO content enhances the photocatalytic activity for hydrogen generation due to the increase in active sites on the photocatalyst's surface. However, beyond a certain quantity, the hydrogen evolution rate may decrease because of aggregation of the photocatalysts, leading to reduced surface area and light penetration. This decrease in hydrogen evolution rate can be attributed to factors like light scattering and hindered light penetration through ZnO [40]. Therefore, optimizing the weight ratio of ZnO and activated carbon is crucial to maximize the efficiency of ZnO photocatalysts in hydrogen production.





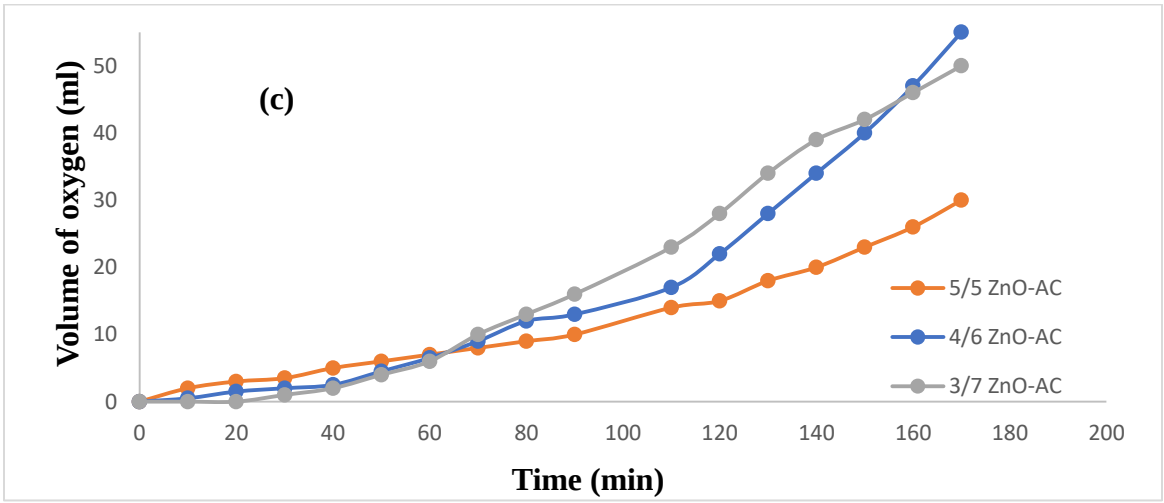


Figure.III.3. Effect of the weight ratio of ZnO and activated carbon (AC) on photocatalytic activity of ZnO-AC variation of (a Temperature, b Volume of hydrogen produced, and c Volume of oxygen)

III.2.1.2 Comparison of photocatalytic performance over different light sources:

The influence of light intensity was examined using two different lamps (500 and 1000 W), the obtained results are presented in **Figure.III.4.** Inform where the 1000 W lamp showed improved photocatalytic activity compared to the 500 W.

The explanation for this as Photocatalytic reactions are initiated by the absorption of photons by photocatalysts. This absorption generates electron-hole pairs that dissociate into photo-excited electrons and holes (electron vacancies) [41].

In addition, ZnO photocatalysts are also considered more sensitive to source light, so the lamp that emits moresource light might perform better [42]; So that high-wattage lamps can generate more energy and more light intensity, and this enhances the efficiency of photocatalytic reactions and reaction kinetics.

From this, it concluded that it is seen that the photocatalytic efficiency increased with an increase in the light intensity. Moreover, the overall energy input to a photocatalytic process is dependent on light intensity. [43]

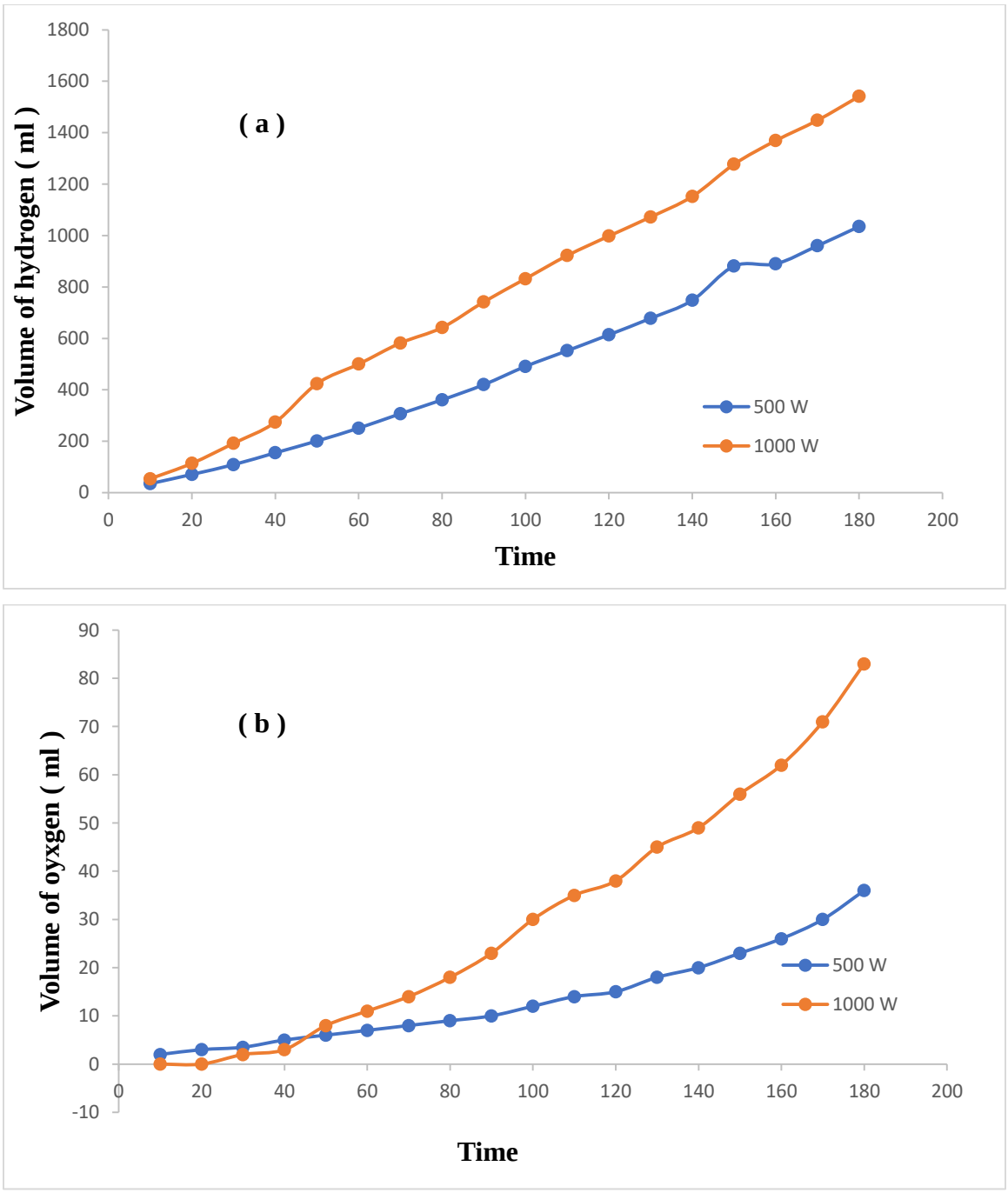


Figure.III.4. Performance over different light sources between the 500 W and the 1000 W lamps variation of (a- Volume of hydrogen produced, and b- Volume of oxygen).

III.2.2. Photocatalyticcoupled-dye degradation, and water splitting:

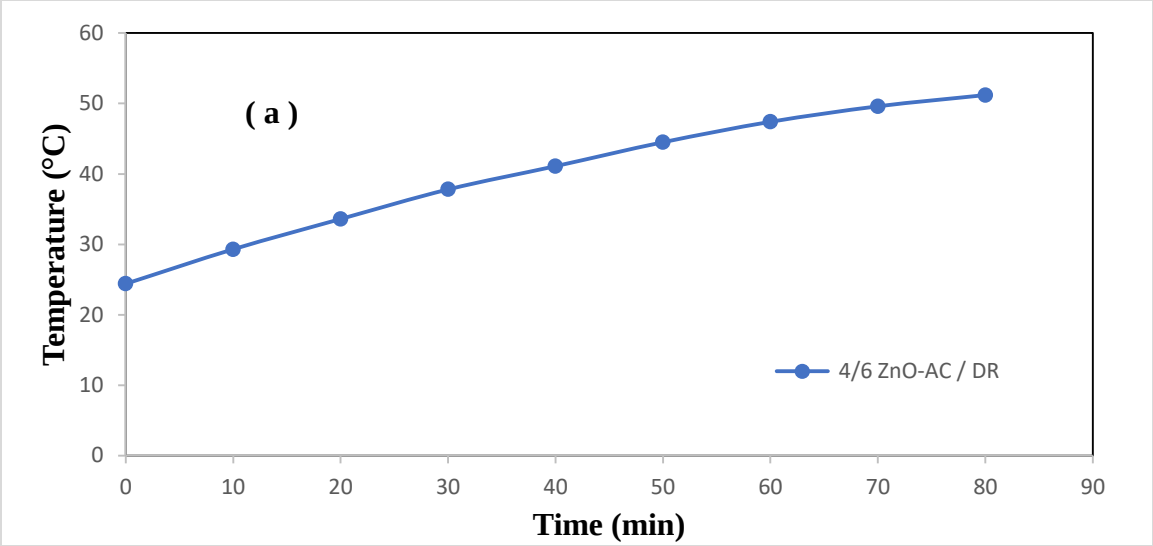
To investigate the performance of the photocatalyst in water splitting and methylene blue (MB) dye degradation simultaneously, methylene blue (MB) dye was added to water.

III.2.2.1. Photodegradation of methylene blue (MB) dye on 4/6 ZnO-AC:

The obtained results are represented in **Figure.III.4**, it is noted that as time passes the photodegradation rate of MB dye over 4/6 ZnO-AC increases until reaching a complete photodegradation rate of MB dye (100 %).

The photocatalyst ZnO-AC degrades methylene blue dye through a photocatalytic process that involves the adsorption of the dye molecules onto the surface of the ZnO-AC material, followed by the degradation of the dye through a series of redox reactions [44]. The absorption of light energy by the ZnO-AC material initiates the process, which excites electrons and creates electron-hole pairs. These electron-hole pairs then participate in redox reactions with the adsorbed dye molecules, leading to their degradation [45].

The degradation mechanism involves the formation of reactive oxygen species (ROS) such as hydroxyl radicals ($OH^{\bullet}$) and superoxide ions ($O^{2-\bullet}$) on the surface of the ZnO-AC material. These highly reactive ROS species can oxidize the dye molecules, breaking them down into smaller, less harmful compounds [46].



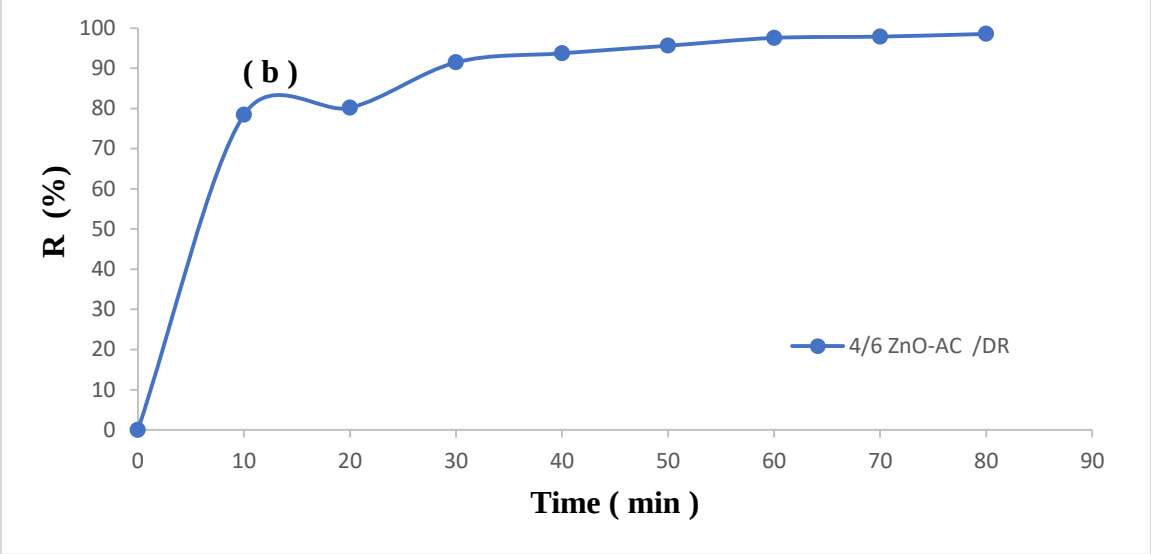


Figure.III.5. Photodegradation of methylene blue (MB) dye on 4/6 ZnO-AC, variation of (a- Temperature, b-Dye removal)

III.2.2.2. Photocatalytic water splitting on 4/6 ZnO-AC:

A comparison was conducted between the performance of the photocatalyst 4/6 ZnO-AC in water splitting with and without MB dye. The obtained results are represented in **Figure.III.5.** As expected, the addition of MB dye has negatively affected the performance of the 4/6 ZnO-AC photocatalyst.

It is noted in **Figure.III.5 (a, b)** a decrease in the volume of hydrogen and oxygen production in water-splitting with dye MB compared to its productivity without dye MB, this may be due to the double function of the photocatalyst in degrading the MB dye and splitting the water simultaneously.

For the decrease of volumes of hydrogen and oxygen produced when methylene blue is present, the explanation is that the photocatalyst has dual functions degrading methylene blue and splitting water. This dual functionality means that some of the photocatalyst's active sites are occupied with degrading the dye, which reduces its availability for the water-splitting reaction. As a result, less hydrogen and oxygen are produced [47].

When the methylene blue dye is absent, there is an increase in the production volumes of both hydrogen and oxygen. The explanation for this is that without the dye, the photocatalyst can focus entirely on the water-splitting reaction. All the active sites of the ZnO-AC photocatalyst are available for this purpose, leading to higher efficiency and, consequently, higher volumes of hydrogen and oxygen production [48].

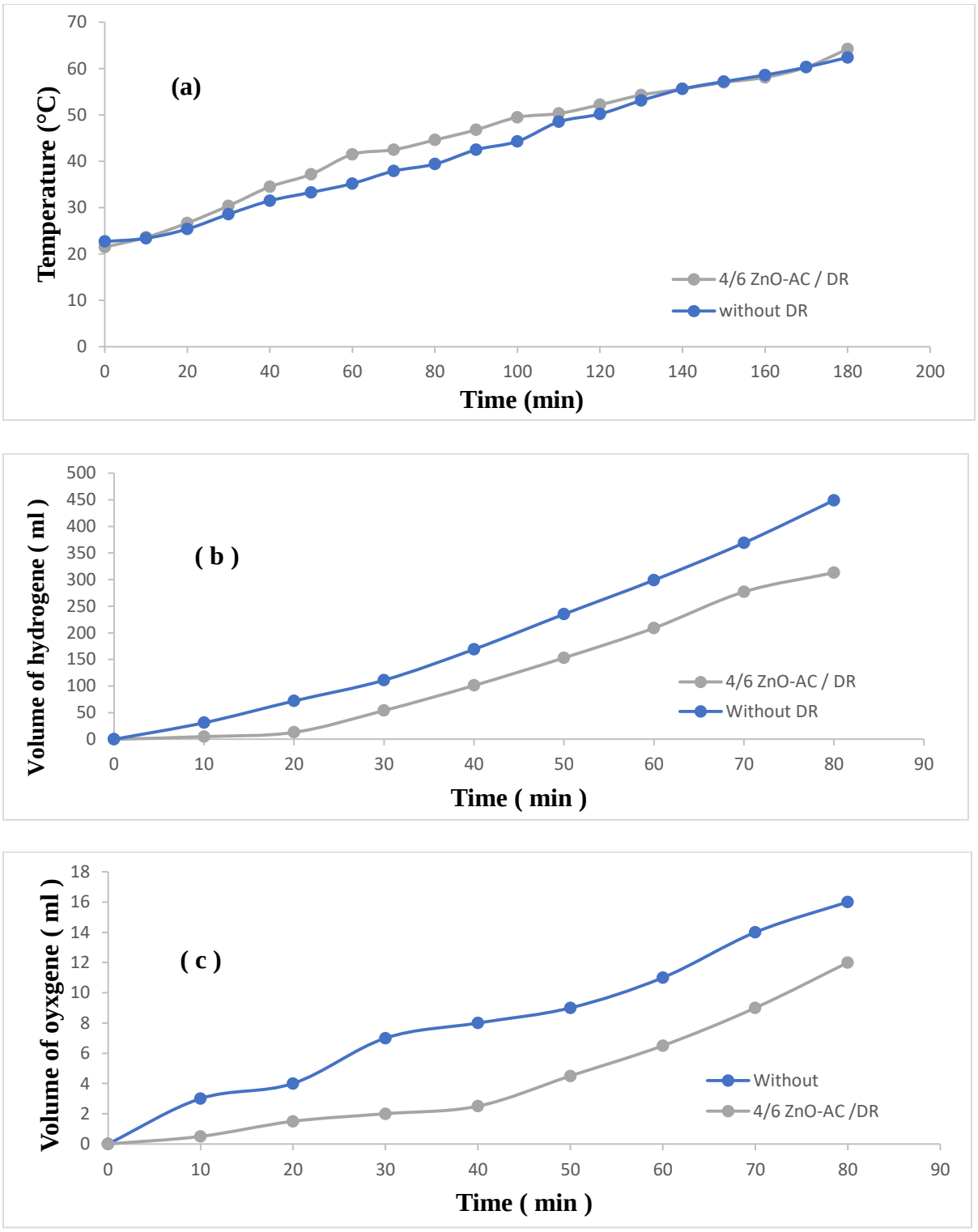


Figure.III.6. Photocatalytic activity of 4/6 ZnO/AC, variation of (a- Temperature, b- Volume of hydrogen produced, and c- Volume of oxygen)

III.3. Comparison of photocatalytic performance over different weight ratios ZnO/AC:

Figure.III.6. A. Represent comparison that conducted between the photocatalyst 4/6 and 3/7 ZnO/AC performance in water splitting with MB dye.as can be seen from the **Figure.III.6 (c)**, in (0-10 min) dye removal increase to 80 and 85 % over 3/7 and 4/6 ZnO-AC respectively, then, it is noted that as time passes the photodegradation of MB dye rates over 4/6 and 3/7 ZnO-AC increases until reaching a complete photodegradation of MB dye (100 %).

The observed differences in photodegradation rates of MB dye using 4/6 and 3/7 ZnO/AC photocatalysts can be explained by the balance between degradation capacity and photocatalytic activity [49].

The photodegradation rate over the 3/7 ZnO-AC was more efficient compared to the 4/6 ZnO-AC. This is likely because the higher AC content in the 3/7 ratio while increasing initial adsorption capacity, may overshadow the photocatalytic activity of ZnO [49]. The 4/6 ZnO-AC ratio, with a higher proportion of ZnO, maintains a better balance, allowing for faster and more efficient photocatalysis.

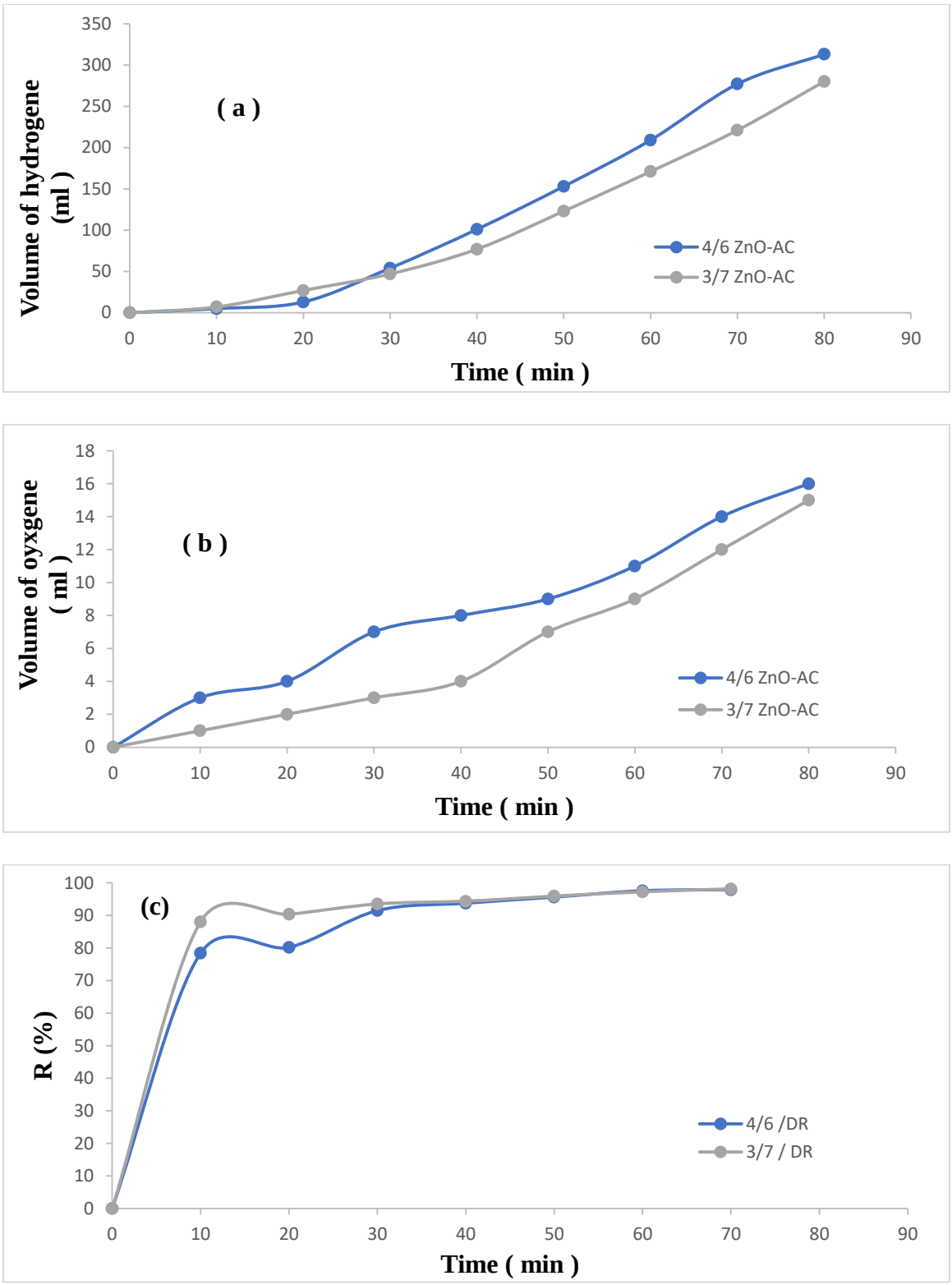


Figure.III.7. Photocatalytic activity of 4/6 and 3/7 ZnO-AC, variation of (a- Volume of hydrogen produced, and b- Volume of oxygen, c- dye removal)

General Conclusion

Conclusion

A photocatalyst based on ZnO doped with activated carbon with different ratios has been successfully synthesized in this work, and its performance was evaluated in the process of water splitting into hydrogen and oxygen gas.

By increasing the mass of NaOH, the water splits more efficiently into hydrogen and oxygen, enhancing the performance of the water-splitting process.

Activated carbon greatly enhanced the effectiveness of the ZnO-AC photocatalyst in splitting water, based on the results obtained.

The optimal ratio is considered to be 4/6 ZnO-AC for the water splitting, leading to the highest hydrogen and oxygen production in the water-splitting process.

Moreover, the photocatalyst ZnO-AC has demonstrated excellent performance in splitting waste water into hydrogen and oxygen in 1200 ml solutions containing 20 ppm of MB dye.

It retains almost the same level of hydrogen and oxygen productivity as pure water, and the photodegradation rate of MB dye reached 100% in a short period, demonstrating its high performance in the coupled water splitting and MB dye degradation processes.

The optimal ratio was found to 4/6 ZnO-AC for the waste-water splitting, leading to the highest hydrogen and oxygen production in the water-splitting process, and simultaneously to complete photodegradation of MB dye.

Based on the results, the synthesized photocatalyst 4/6 ZnO-AC has been shown to be an excellent candidate for the wastewater splitting process.

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عنوان المذكرة: تحضير مادة التحفيز الضوئي المعتمدة على أكسيد الزنك (ZnO) والكربون المنشط (AC)، وتطبيقها في عملية تقسيم مياه الصرف الصحي بالتحفيز الضوئي

اللقب: **رميلات** **الإسم: أسامة** **المؤطر: ج. براهيمي**

اللقب: **يحياوي** **الإسم: طاهر**

ملخص: في هذه الدراسة تم تطعيم أكسيد الزنك (ZnO) بالكربون المنشط المحضر من بذور التمر بطريقة الانحلال الحراري لتصنيع المحفز الضوئي ZnO-AC. تم تقييم أداء المحفز الضوئي المركب في عملية تقسيم مياه الصرف الصحي. وتم التحقق من كفاءة عملية تقسيم المياه على المحفز الضوئي ZnO-AC في ظل معايير تجريبية مختلفة مثل مصدر الضوء، ونسبة الوزن ZnO/AC، ووقت التشعيع. تشير النتائج إلى أن النسبة المثلى للمحفز الضوئي هي ZnO-AC 6/4، حيث أن أفضل مصدر للضوء هو 1000 واط. وأظهرت النتائج التي تم الحصول عليها أن المحفز الضوئي ZnO-AC 6/4 هو مرشح واعد لفصل مياه الصرف الصحي، حيث تكون مياه الصرف الصحي يمكن معالجتها ويتم إنتاج الهيدروجين والأكسجين أيضًا.

الكلمات المفتاحية: المحفز الضوئي ZnO-AC لفصل الماء، بذور التمر، معدل التحلل الضوئي.

Memory title: Preparation of zinc oxide (ZnO)-doped activated carbon (AC) based photocatalytic material, and its application in photocatalytic waste water splitting process

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Abstract: In the present study, zinc oxide (ZnO) was doped with activated carbon prepared from date seeds by pyrolysis to synthesize a photocatalyst ZnO-AC. The performance of the synthesized photocatalyst was evaluated in the waste-water splitting process.The efficiency of the water splitting process over the photocatalyst ZnO-AC was investigated under various experimental parameters such as light source, weight ratio ZnO/AC, and irradiation time. The results indicate that the optimal ratio for the photocatalyst is 4/6 ZnO-AC, as the best light source is 1000 w.Results obtained showed that 4/6 ZnO-AC photocatalyst is a promising candidate for waste-water splitting, where wastewater can be treated and hydrogen and oxygen are also produced.

Keywords: water splitting ZnO-AC photocatalyst, date seeds, photodegradation rate.

Titre du mémoire : Préparation d'un matériau photocatalytique à base de charbon actif (AC) dopé à l'oxyde de zinc (ZnO) et son application dans le processus de séparation photocatalytique des eaux usées

Nom : Remilat **Prénom : Oussama** **Encadreur :** D. Brahimi

Nom : Yahyaoui **Prénom : Tahar**

Résumé : Dans la présente étude, l'oxyde de zinc (ZnO) a été dopé avec du charbon actif préparé à partir de graines de dattes par pyrolyse pour synthétiser un photocatalyseur ZnO-AC. Les performances du photocatalyseur synthétisé ont été évaluées dans le processus de division des eaux usées. L'efficacité du processus de division de l'eau par rapport au photocatalyseur ZnO-AC a été étudiée sous divers paramètres expérimentaux tels que la source de lumière, le rapport pondéral ZnO/AC et le temps d'irradiation. Les résultats indiquent que le rapport optimal pour le photocatalyseur est de 4/6 ZnO-AC, car la meilleure source de lumière est de 1 000 W. Les résultats obtenus ont montré que le photocatalyseur 4/6 ZnO-AC est un candidat prometteur pour la séparation des eaux usées, où les eaux usées peut être traité et de l'hydrogène et de l'oxygène sont également produits.

Mots clés : Photocatalyseur, graines de dattes, oxyde de zinc, élimination des colorants.