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Theme

Biomass-derived active carbon (AC) modified NiOphoto-catalyst for efficient photo-catalytic water splitting and degradation of Methylene Blue Dye under visible light

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Dedication

وَآخِرُ دَعْوَاهُمْ أَنِ الْحَمْدُ لِلَّهِ رَبِّ الْعَالَمِين

الحمد لله عند البدء وعند الختام، فما تناهى دربٌ، ولا خُتم جهد، ولا تم سعي إلا بفضله.

إلى أسمى آيات العطاء البشريّ، أمي وأبي الغاليين، أهدي ثمرة جهدي المتمثلة في هذه المذكرة المتواضعة، عسى أن أكون مصدر فخر لكما.

إلى من وضع المولى - سبحانه وتعالى - الجنة تحت قدميها، ووقَّرها في كتابه العزيز...

(أمي الحبيبة).

إلى من أسير على خطاه دائما وأبدا ,إلى من أعتمد عليه في كل كبيرة وصغيرة فلم يبخل عليَّ طيلة حياته...

(أبي المُوقَّر).

إلى رفقاء الدرب الرائعين...

(إخوتي).

إلى من رافقوني في رحلة الجامعة ...

(أصدقائي).

إلى جميع أساتذتي الكرام؛ ممن لم يتوانوا في مد يد العون لي ...

Khadra

Dedication

{وَآخِرُ دَعْوَاهُمْ أَنِ الْحَمْدُ لِلَّهِ رَبِّ الْعَالَمِينَ}

الى المعلم الاول الذي انار بضياء هداه بصائرنا واخرجنا من ظلمات الجهل الى نور العلم وارشدنا لطريق العلم و بشر السائرين على هذا الطريق بالجنة فقال (ومن سلك طريقا يلتزم فيه علما سهل الله له به طريقه الى الجنة)

(سيدنا محمد صلى الله عليه و سلم)

من قال انا لها "نالها" و انا لها ابت رغما عنها اتيت بها لم تكن الرحلة قصيرة ولا الطريق محفوفا بالتسهيلات لكنني فعلتها فالحمدلله الذي يسر البدايات وبلغنا النهايات

اهدي هذا النجاح لنفسي الطموحة اولا ,الى نفسي القوية التي تحملت كل العثرات واكملت رغم الصعوبات ,ابتدت بطموح وانتهت بنجاح , ثم الى كل من سعى معي في اتمام مسيرتي الجامعية

الى من احمل اسمه بكل عز وافتخار لمن مهد لنا الطريق ببذل وتعبه والى المراة التي صنعت مني فتاة طموحة تعشق التحديات والصعوبات قدوتي الاولى الى من غمرونا بالمحبة وتحملو معنا عناء الطريق الى من عاهدتهم بهذا النجاح ها انا اتممت وعدي واهديه لكم (امي و ابي)

الكتف الذي لا يميل والظل الذي احتمي به الى القلوب النابضة بصدق الحب و المشاعر الى الاعمدة الثابتة في الحياة الى اخوتي واخواتي الى من شاركني تعبي وسهر من اجلي "اخي محمد"

الى رمز الوفاء الى رفيقي واليد الطاهرة التي ازالت من طريقي اشواك الفشل الى من ساندني عند ضعفي الى من امن بي وبقدراتي " ابراهيم "

الى من راهنوا على نجاحي ويذكروني بمدى قوتي و استطاعتي ....لرفاق السنين

الى اساتذتي الكرام كل باسمه وكل بمقامه شكرا على كل المجهودات المبذولة

لم تكن رحلة قصيرة ولم تكن الامور ميسرة ,ولكن بعون الله فعلتها

اهديكم جميعا هذا العمل المتواضع وثمرة جهدي ,والله ولي التوفيق

Fatiha

List of abbreviations and symbols

AC : Activated Carbone .

C_0: Initial concentration of the solution.

C_t: Concentration of the solution attime .

H_2: Hydrogen .

MB : Methylene bleu .

NaOH : Sodium hydroxide.

NiO : Nickel oxide .

O_2 : Oxygen .

OS : Olives seeds .

PC : Photo-catalyst .

PD: Photo-degradation.

R: Pd rates.

WS : Water splitting .

λ_{max} : Wavelength max.

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General introduction

Introduction

Globally, direct combustion of fuels for transportation and heating accounts for more than half of greenhouse gas emissions, a significant fraction of air pollutant emissions, and about two-thirds of primary energy use[1]. Even with continuing incremental progress in energy technologies, most energy forecasts project that primary energy use and emissions of greenhouse gases and air pollutants from the use of fuels will grow over the next century because of increasing demand, especially in developing countries. Energy-supply security is a serious concern, particularly for transportation fuels [1].

A variety of alternative fuels have been proposed that could help address future environmental and energy-supply challenges. These fuels include reformulated gasoline or diesel, methanol, ethanol, synthetic liquids such as di-methyl-ether made from natural gas or coal, compressed natural gas, and hydrogen [1].

Providing an abundant, clean, and secure renewable energy source is one of the key technological challenges facing mankind. Resurgence in the chemistry and biochemistry of hydrogen, the world's simplest closed-shell molecule, has been spurred by recent scientific and technological interest in hydrogen as an energy carrier and potential transportation fuel. Our current energy infrastructure is dominated by fossil fuel use, which leads to greenhouse gas emissions[2]. Green hydrogen is potentially an ideal energy carrier, as it is nonpolluting and gives up both its electrons upon oxidation to form only water. Although it is the most abundant element in the universe, elemental hydrogen is not present in great quantities on earth. A number of key challenges must be overcome for hydrogen to be used broadly in a sustainable future energy infrastructure to solve the globe's energy problems. To accrue the full environmental benefit of hydrogen as an energy carrier, low-carbon intensive, low polluting, and lower cost processes for producing hydrogen from renewable energy sources need to be developed [2].

Water, of course, contains a virtually endless supply of hydrogen, but considerable energy is required to break its chemical bonds through electrolysis or other technologies [3]. Including water splitting photo-catalysis technology.

This study focuses on the synthesis of an innovative photo-catalyst specifically designed to produce hydrogen from wastewater using sunlight as an energy source.

Introduction

In this studyNiO-ACbased photo-catalysts was synthesized, and four different weight ratios were used for this doping. An evaluation of the synthesized NiO-AC photo-catalyst was conducted in the process of waste-water splitting into hydrogen and oxygen gas.

A number of experimental series were conducted under various conditions, in order to optimize this wastewater splitting process using the synthesized NiO-AC as photo-catalyst.

This work has been divided into three chapters:

Chapter I presents an overview of the process of hydrogen production by photo-catalysis

Chapter II presents the experimental protocols used to synthesize the NiO-AC photo-catalyst, and shows the experimental setup used to test its efficiency in the waste-water splitting process over the synthesized NiO-AC photo-catalyst under different experimental conditions

Chapter III presents the main obtained results from the experimental studies of water splitting over the synthesized photo-catalyst NiO-AC under different experimental condition

Chapter I: Literature Survey

I.1.Hydrogen

Hydrogen is a colorless, odourless, highly flammable gas at normal temperature and pressure. A proton and an electron make up the nucleus. In various fields of science, hydrogen is often used as a reference because of its atomic simplicity. Hydrogen has many applications. It is used as fuel in fuel cells, which convert hydrogen into electricity by combining hydrogen and oxygen from the air. This technology is considered a clean alternative to fossil fuels because it does not produce air pollution. It can also be used as a raw material in the chemical industry for the production of ammonia, methanol, and other chemical compounds, It is also used in the aerospace sector for rocket propulsion and other industrial applications. The use of hydrogen as a clean and renewable energy source is increasingly being studied and developed as part of the energy transition to reduce greenhouse gas emissions and mitigate environmental impact [4].

I.2.Uses of hydrogen

Hydrogen is a very important molecule with an enormous breadth and extent of application and use. It is currently being used in many industries of which [5]:

-Using hydrogen and oxygen, fuel cells generate electricity and water without polluting the environment. They are used in various fields , such as hydrogen vehicles, cogeneration systems for stationary applications and applications [6].

- hydrogen can be used to store and manage intermittent renewable energies for long periods of time. In times of surplus electricity, it can be produced and later used to produce electricity when demand is high[7].

-Hydrogen is used in the chemical industry to produce ammonia, methanol, petrochemicals, and other chemicals. It is also used as a protective gas and fuel in industrial processes [8].

- Fuel cells or modified internal combustion engines can be used as hydrogen fuel in hydrogen vehicles. This technology provides an alternative to conventional combustion vehicles , with the advantage of reducing greenhouse gas emissions[9].

- Hydrogen can be used for residential and commercial heating as well as for the simultaneous production of electricity and heat. Such systems allow efficient use of energy and can contribute to the decarburization of the heating and energy sectors[10].

-As an alternative to fossil fuel-based aviation, hydrogen is also being studied for use in the aviation sector. Research and development projects are underway to explore the use of hydrogen as an aircraft fuel[11].As the **Figure.I.1**shows.

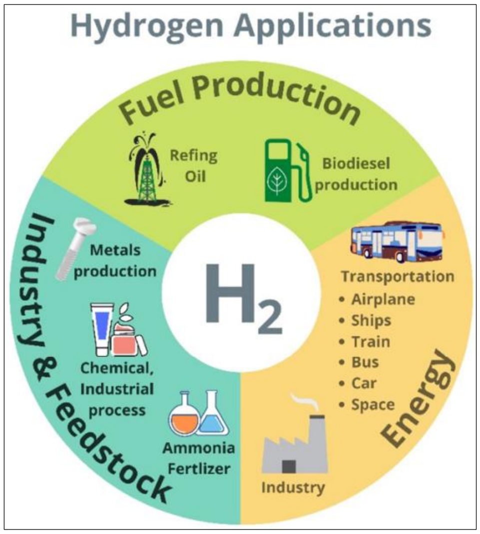

Figure.I.1. Uses of hydrogen

I.3.Hydrogen as future fuel

Hydrogen is the ultimate clean fuel. Whether it is burned or chemically recombined with oxygen in fuel cells, the reaction produces only water and heat. But although it is the most abundant element, convenient sources of pure hydrogen gas are meager.Water of course, contains a virtually endless supply of hydrogen, but considerable energy is required to break its chemical bonds through electrolysis or other technologies. Most of the hydrogen produced today is extracted from natural gas [12].**Figure.I.2**shows the difference between the energy produced from hydrogen and gasoline fuel.

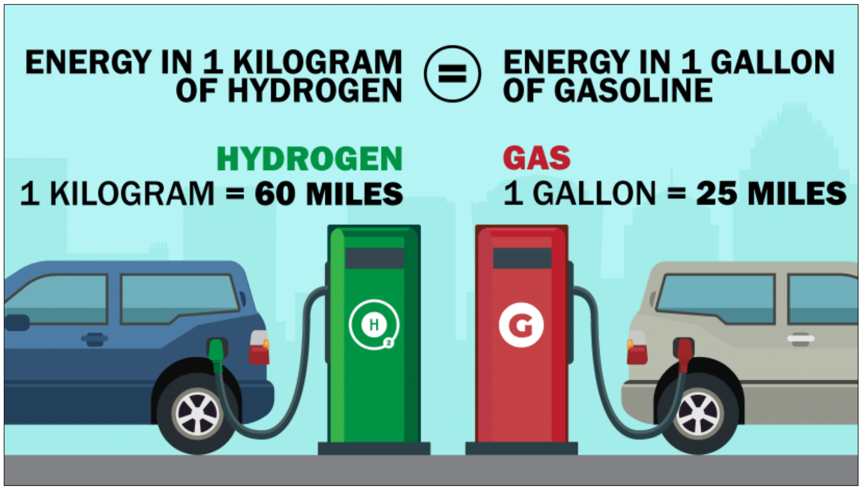

Figure.I.2.The difference between the energy produced from hydrogen and gasoline fuel.

I.4. Hydrogen production methods

Hydrogen is a promising renewable fuel for domestic transportation and applications. Thus, in the near and long term, the demand for hydrogen is expected to increase significantly. The production of hydrogen, as well as any other synthetic fuel, will inevitably cost more energy than pumping oil or using other fossil fuels. In this work, alternative technological methods that can be used to produce this fuel are reviewed. Hydrogen can be generated in several ways, such as electrochemical processes, thermo chemical processes, photochemical processes, photo catalytic processes, or photo electrochemical processes. The thermal production process, which uses steam to produce hydrogen from natural gas or other light hydrocarbons, is the most common. Steam reforming of natural gas is currently the least expensive way to produce hydrogen and is used for about half of the world's hydrogen production. Almost 95% of the hydrogen produced today comes from carbon raw materials, primarily of fossil origin[13].

I.4.1.Steam reforming

The production of hydrogen from ethanol steam reforming will not only be environmentally friendly, but will also open up new opportunities to take advantage of renewable resources that are available globally. Various catalysts have been used to Steam-reform ethanol. Depending on the type of catalysts, reaction conditions, method of Catalyst preparation, ethanol conversion and hydrogen production vary significantly. It has been noted that Co/ZnO, ZnO, Rh/Al_2O_3, $Rh/CeO_2$and nI/La_2O_3 $-Al_2O_3$ are the best in terms of steam reforming of ethanol [14].The reform process consists in two reactors (reform reactor and shift reactor). In the reform reactor occur the catalytic reforming reactions of hydrocarbons, like methane, naphtha or ethanol with water (pre-vaporized by a steam generator). The products of these reactions are H_2 (main objective of the reform) and CO. In the shift reactor all CO produced in the reform reactor, react with water steam. The products of this reaction are H_2 and CO_2. So, in the end of the reform process, the main products are hydrogen (H_2) and carbon dioxide (CO_2)[15] .can be seen in the **Figure.I.3 .**

$CH_4 + H_2O \longrightarrow CO + 3H_2$……………………………………………………………**(I.1)**

$CO + H_2O \longrightarrow CO_2 + H_2$…………………………………………………………**(I.2)**

$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$………………………………………………………**(I.3)**

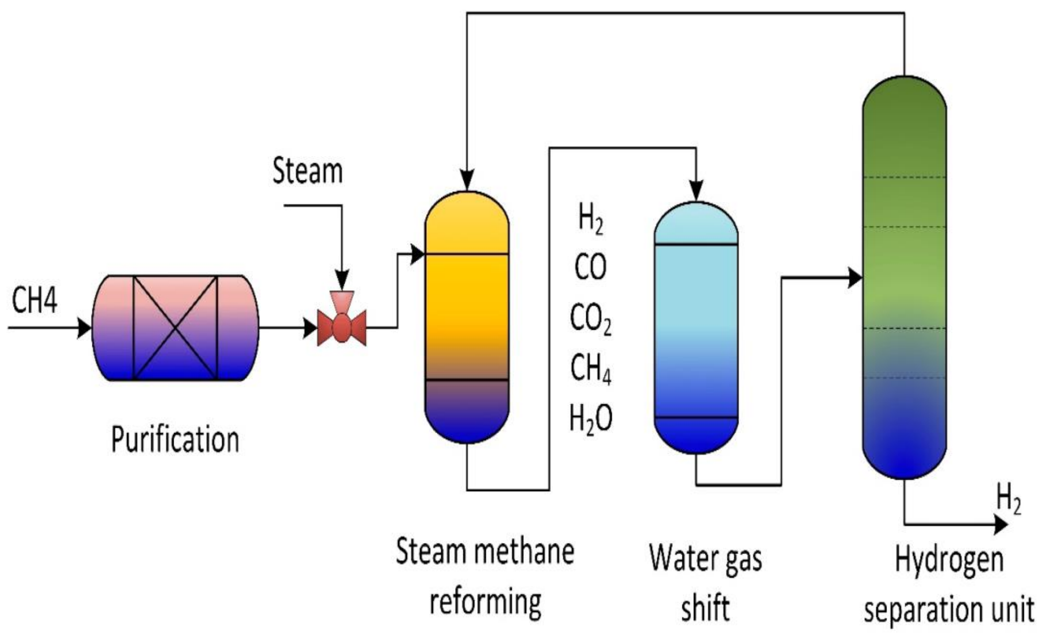

Figure.I.3. Steam reforming scheme

I.4.2.Electrolysis

This method refers to the oldest method of producing hydrogen, dating back to the 19thcentury ; it generally refers to a DC electrical power source connected to two electrodes, which are then placed in water. The flow of an electric current splits water molecules into its constituents, making hydrogen appear at the cathode side and oxygen appear at the anode side. The efficiency of electrolysis is increased through the addition of an electrolyte to the solution (such as a salt, an acid, or a base) and the use of electro catalysts, which raise the reaction's rate too [16] .As can be seen in **Figure.I.4**.

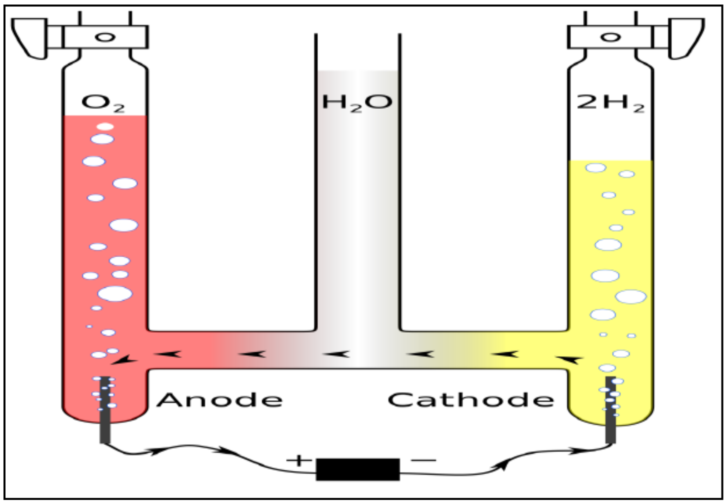

Figure.I.4. Electrolysis scheme

I.4.3.Thermo chemical production

Thermo chemical water decomposition is one of the promising methods of hydrogen production in large scales. In this method, water is dissociated into hydrogen and oxygen through intermediate chemical reactions. Depending on the characteristics of the thermo chemical cycle, the process can utilize both thermal and electrical energy to drive the water decomposition process. Thermo chemical water decomposition is a vast area including various types of cycles characterized by the number of reactions taking place in the overall cycle. Instead of single-step thermal process demanding high reaction temperatures for complete water decomposition (around 4000 °C), employing multi-step cycle can effectively lower the maximum required temperature for the cycle while extending the application and feasibility of thermo chemical hydrogen production [17].The **Figure.I.5** illustrates a schematic of the thermo chemical cycle.

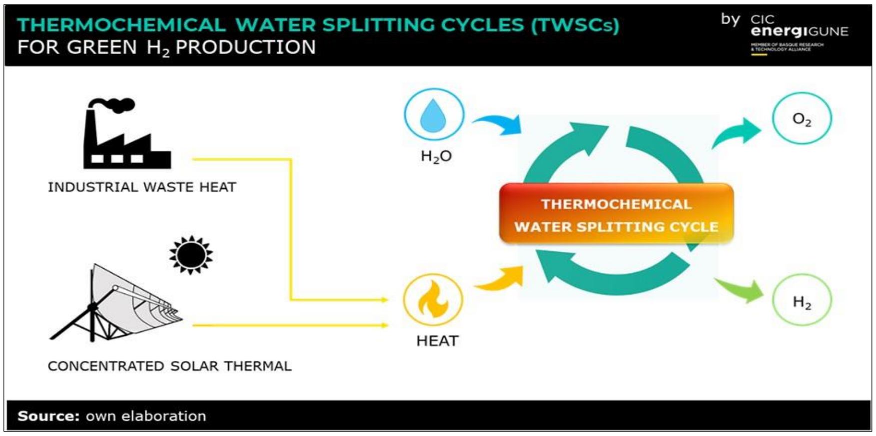

Figure.I.5. Thermo chemical production scheme

I.4.4.Reforming of biomass andwaste

The hydrogen production from biomass (dedicated biomass as a resource, including woods and their by-products) and organic solid wastes (organic fractions of MSW, industrial waste, and agricultural waste), especially related to technological options and advancements, and challenges. The review mainly focuses on feasible thermo chemical and biological routes. Section Green hydrogen from biomass and organic solid waste describes the potential of available biomass and organic solid waste and the trends in hydrogen transition and adoption, especially its correlation with biomass and waste-based hydrogen production[18]. **Figure.I.6** shows a schematic of the reforming of biomass and waste.

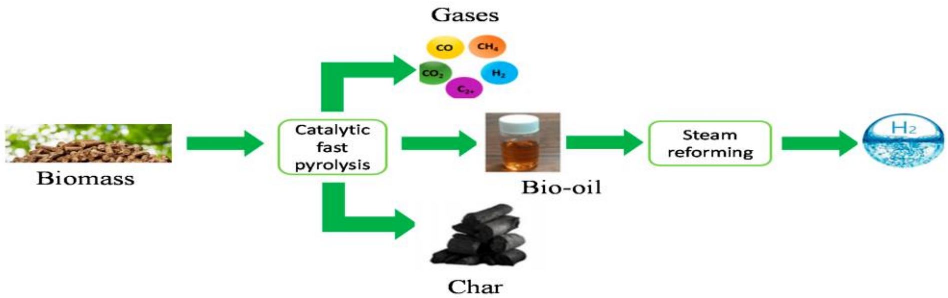

Figure.I.6. Reforming of biomass and wastescheme

I.4.5. Photolysis

Water can in principle release hydrogen, which occurs when water molecules absorb energy at a rate of 285.57 kJ/mol of water from ultraviolet radiation . The disintegration of H-X Bonds by photons is known as photolysis, which occurs at about 190 Nm . This process and thermal decomposition need chemical catalysts such as XrO_2, tin oxide (SnO), zinc oxide(ZnO) and other semiconductor sulfur oxides[19] .The **Figure.I.7**shows the basic principle of the photolysis.

$Mox^{z+} + H_2O \rightarrow Mox^{(Z+1)} + H + OH^-$ ………………………………………....**(I.4)**

$2H \rightarrow H_2$ ……………………………………………………………..**(I.5)**

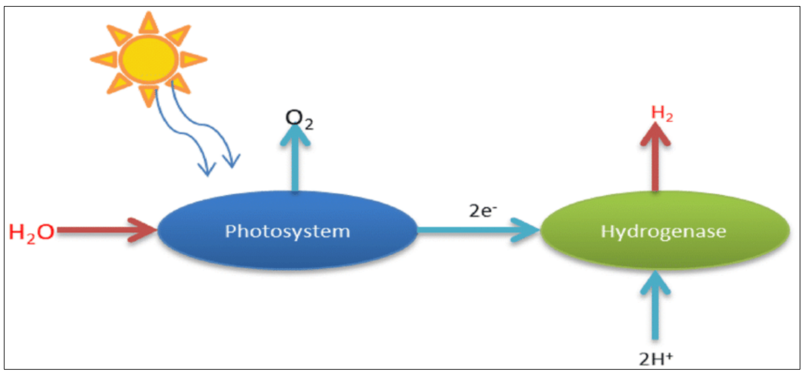

Figure.I.7. Photolysisscheme

I.5.Photo-catalysis (water splitting)

To achieve water splitting in general and investigate the structure-property relationships of photo-catalysts, two water splitting half-reactions have been extensively studied. These reactions are hydrogen-oxygen evolution reactions usually involving the use of sacrificial reagents to improve the production of hydrogen and oxygen. Although the catalyst can catalyze both reactions with the help of sacrificial electron donors and acceptors, this may not work for water splitting in general. For clarification, the splitting of water discussed in this review refers to the splitting of water directly into hydrogen and oxygen in a 2:1 ratio using a suitable photo-catalyst[20]. Several research and review articles have proposed the mechanisms of photo-catalytic water splitting . The reaction first begins by absorbing a photon, which generates many pairs of electron holes with sufficient potential. These charge carriers then migrate to the surface of the catalysts and interact with the active sites on the surface. Finally, the photo-generated electrons reduce the water to form hydrogen, and the holes oxidize the water molecules to give oxygen[20]. As illustrated in **Figure.I.8**.

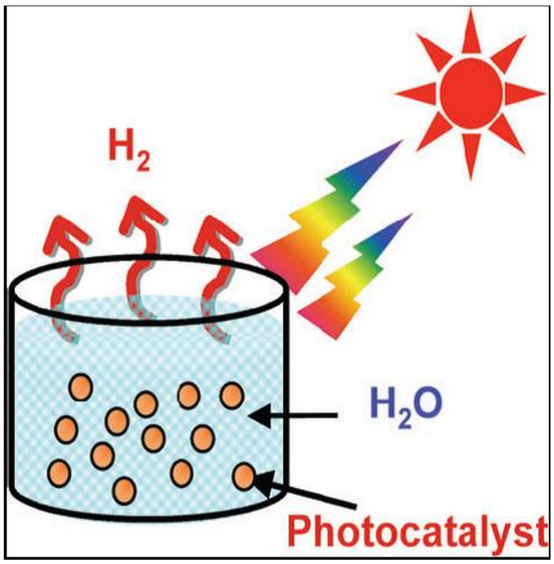

Figure.I.8. Photo-catalysis scheme

I.6.Photo-catalyst

The term photo-catalyst is a combination of two words: photo related to photon andcatalyst,which is a substance altering the reaction rate in its presence. Therefore, photo-catalysts arematerials that change the rate of a chemical reaction on exposure to light**(Figure.I.9).** This phenomenon is known as photo-catalysis. Photo-catalysis includes reactions that take place by utilizing light and semiconductor. The substrate that absorbs light and acts as a catalyst for chemical reactions isknown as a photo-catalyst. All the photo-catalysts are basically semiconductors. Photo-catalysis is a phenomenon, in which an electron-hole pair is generated on exposure of a semiconducting material to light[21].

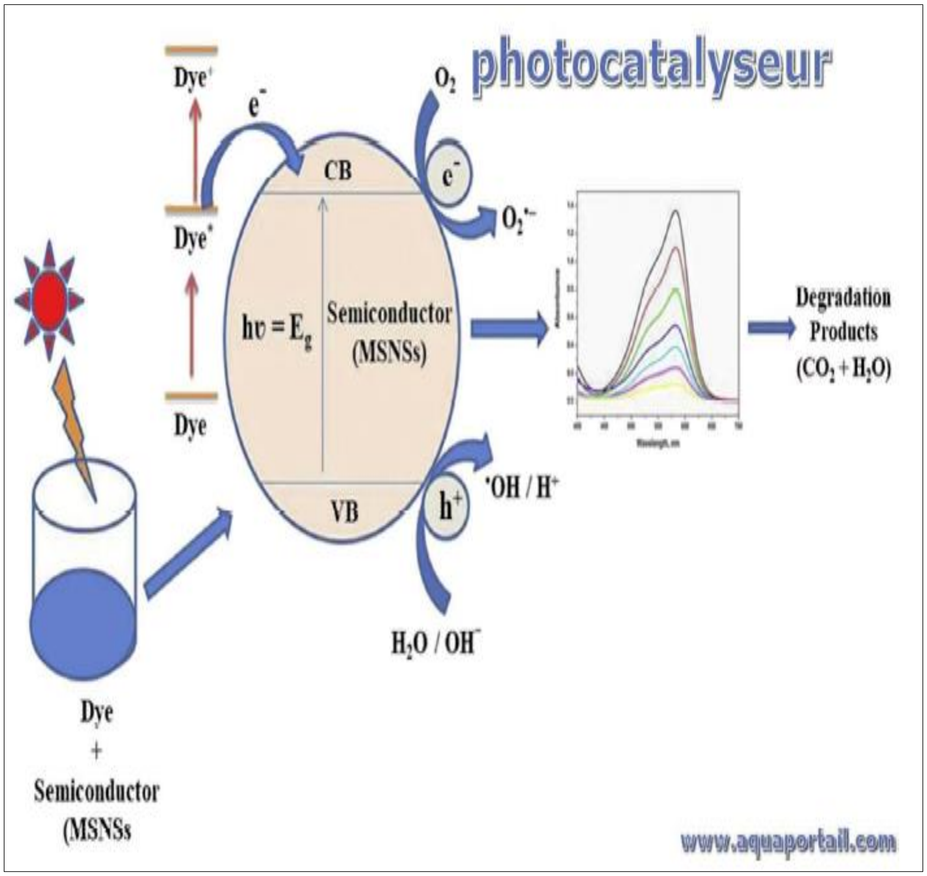

Figure.I.9. Principle of photo-catalyst

Chapter II: Experimental setup and Conditions

II.1. Introduction

This chapter presents a description of the steps involved in the synthesis of NiO-AC, where alimentary waste OS 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.

And finally, the experimental setup for testing the ability of the synthesized NiO-AC photo-catalyst in wastewater splitting to hydrogen and oxygen, and treated water.

Ⅱ.2. Material

In this study, olive seeds (OS)were used as a feedstock to prepare activated carbon (AC), which was used as a support to the synthesized photo-catalyst. All chemicals used in the investigation such as KOH, Nickel acetate ,Methylene Blue, NaOH and HCl were of analytical grade.

II.2.1. Olive seeds

The Algerian production of olives exceeds 12 million hectares and provides an average of 62million tons of olive yearly [22] . With these numbers, it was suited to use OS in this work as a feedstock. the OS used are obtained from a local area of Ksar-EL Hirane - Laghouat.

II.3.Preparation of photo-catalysts

A two-step process was used to prepare the photo-catalyst, firstly preparation of activated carbon, and secondly, doping of activated carbon with photo-catalysts

II.3.1. Preparation of activated carbon (AC)

The OS have been pre-treated before use by washing and dryingthem to removeall impurities then proceed to crushing them to small particle sizes.The work process is summarized in **Figure.II.1.**

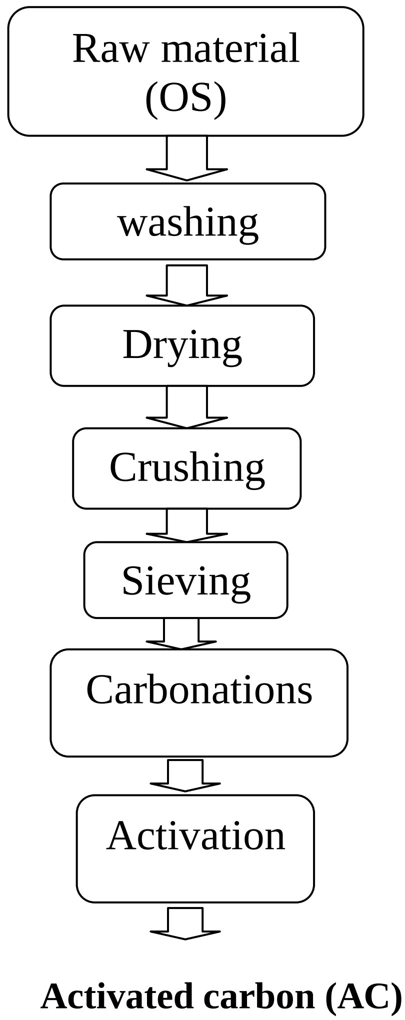

Figure.II.1.Workflow of the preparation of activated carbon (AC)

II.3.1.1. Washing

In order to remove all impurities stuck on the surface of the olive seeds, the olive seeds were washed before they were used. It should be noted that this process increases the water content in the feedstock and there fore the drying process is a necessity, as the **Figure.II.2** shows.

Figure.II.2. Olive seeds after washing

II.3.1.2. Drying

It is important to thoroughly dry OS before using them to make AC. The drying process was carried out by laying OS 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 temperature100 °C[23].

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 olive seeds (a) Manual grinder, (b) crushed olive 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[23].**Figure.II.5(b)** shows the obtained carbon.

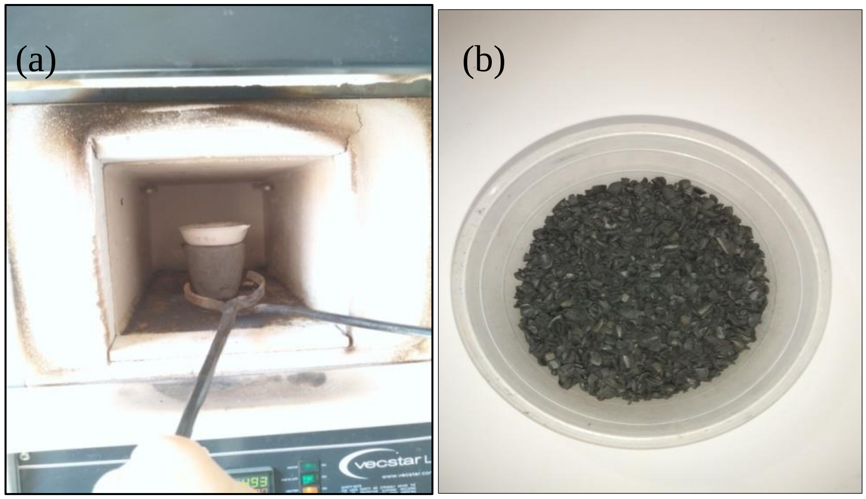

Figure.II.5. Carbonation of olive seeds (a) Furnace muffle, (b) Obtained carbon

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[23], with the presence of nitrogen gas at a flow rate of 0.8 ml/h,as shown in the **Figure.II.6**.

Theobtained AC was washed, and its pH was monitored until obtaining a neutral value with a portable pH meter.

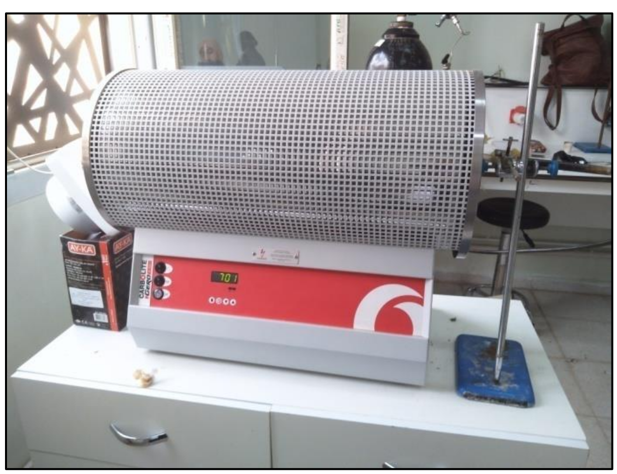

Figure.II.6. Tubular furnace used in the bio-char activation process

II.3.2. Synthesis of NiO-supported activated carbon (AC) composite

The method of preparing nickel oxide NiO photo-catalyst supported by activated carbon (AC) is based on the precipitation method. In the first step, solution A was prepared in a beaker by dissolving a mass (w_1) of Nickel acetate $Ni(CH_3CO_2)_2$ in 50 ml of distilled water under continuous stirring for 30 minutes, and another solution B was prepared by dissolving a mass (w_2) of AC in 50 ml. of distilled water with continuous stirring for 30 minutes, then pouring solution A into B with continuous stirring for an hour at a temperature not exceeding 180 °C until all the watere vaporates, then dry the mixture in an oven at a temperature of 120 °C for a period of 1 to 5 hours to produce the NiO-AC PC.

AC is one of the most important candidates for the manufacture of high-performance NiO-AC nanospheres due to its large surface area, high conductivity, and high durability[24-25] .Moreover, due to its environmental friendship, abundance, rapid renewal, and low cost, the biomass-derived AC has attracted wide attention from the next-generation energy technology community [24-25].

In this study, four different photo-catalysts were prepared with different weight ratios of nickel oxide (NiO)/activated carbon (AC), in order to study the weight ratio on the performance of the photo-catalyst, as summarized in **Table.II.1**.

Table.II.1.Four different photo catalysts were synthesized in this study.

Representation of photo-catalyst	Weight of NiO (w_1) (g)	Weight of AC (w_2) (g)	Weight ratio $\frac{NiO}{AC}$(-)
2/8NiO-AC	2	8	0.25
3/7 NiO-AC	3	7	0.43
4/6 NiO-AC	4	6	0.67
5/5 NiO-AC	5	5	1

II.3.2.1. Calcination

Calcinations is the last stage in the preparation of the photo-catalyst, the NiO/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 nano composite [23].The general protocol followed in this study is described in **Figure.II.7**.

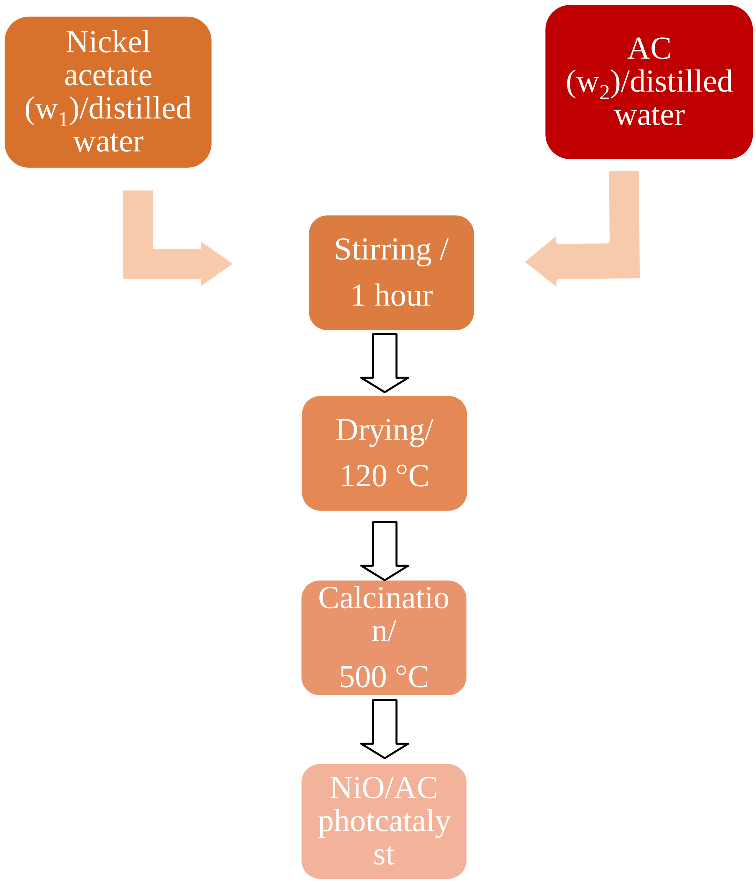

Figure.II.7. Method for preparing the NiO/ACphotocatalyst.

II.4.Photo-catalytic activity experiments

An experiment was conducted with 1g of NiO/AC added to 1200 ml of water (messed water) to examine how the photo-catalyst enhanced the water-splitting process in the electrolyse as shown in the **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 1000 W. The flow rates of produced gases including oxygen and hydrogen produced through the water splitting process are measured during the test.

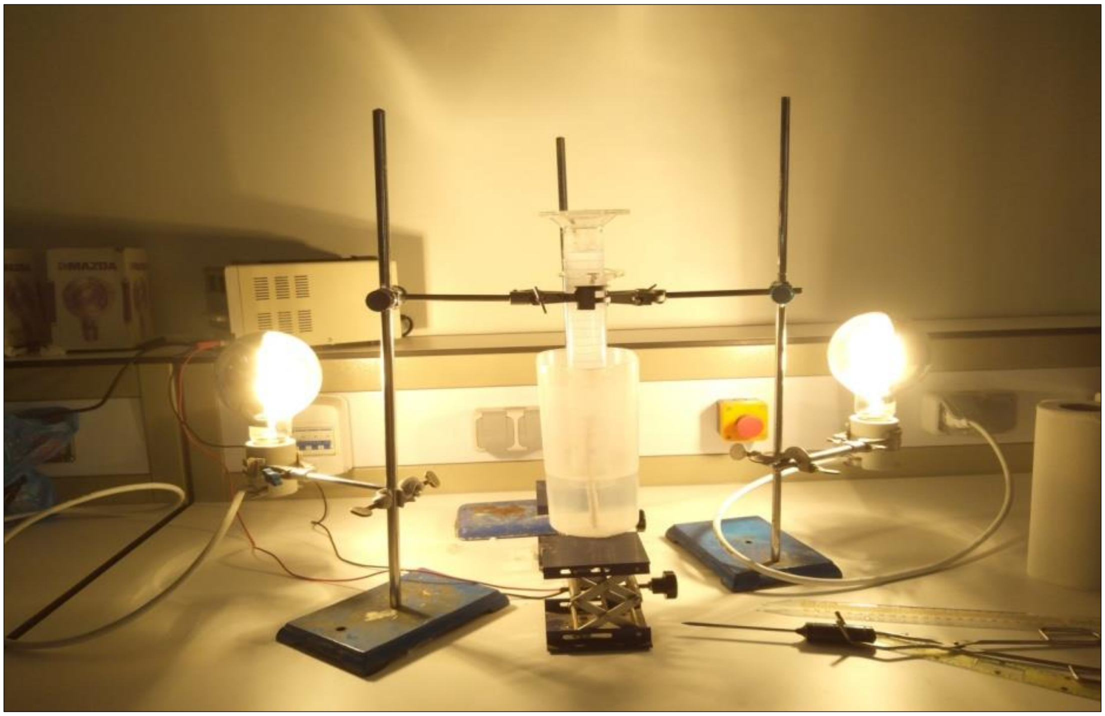

Figure.II.8. Experimental set-up for electrolysis test

II.4.1. Measurement of the flow rate of produced gases

The flow rates of hydrogen and oxygen or the volume of the produced gases are measured every 10 minutes during the water-splitting process, two graduated cylinders filled with the same solution used in the electrolyse, and placed inversely above the anode and the cathode to measure the volume of produced oxygen and hydrogen respectively. Temperature was also measured by using a thermometer **Figure.II.9**.

Figure.II.9. The measurements of the produced gases during the water-splitting process

Ⅱ.4.2. Determination of(λ_{max}) and calibration curve

In addition, the performance of the NiO-AC photo-catalyst was also tested in the splitting of colored water process and the dye photo-degradation simultaneously. 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 [26].

A 1200 ml solution of 20 ppm of MB dye was prepared, 1 g of NiO-AC photo-catalyst, and 2 g of NaOH were added, and then the mixture was poured into the electrolyse. Every 10 minutes, 10 ml of the solution was drawn to measure its absorbance using a UV-Vis spectrophotometer (SHIMADZU 1280) As the **Figure. Ⅱ.10**. shows

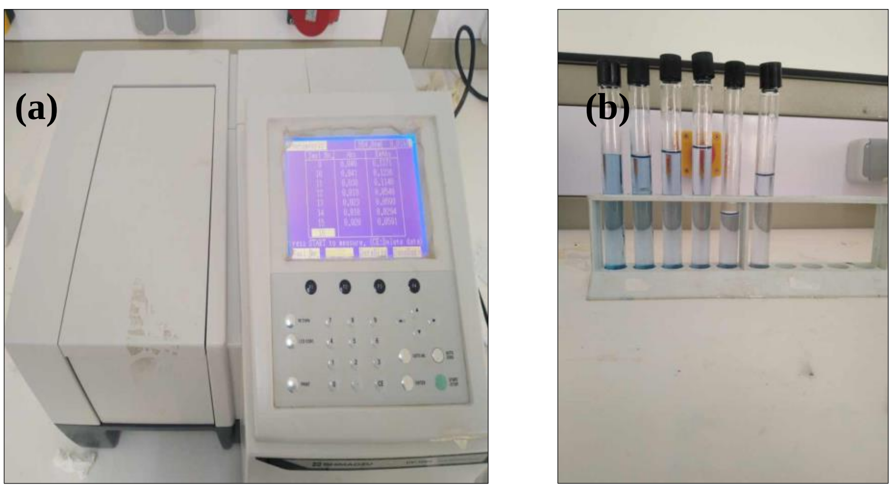

Figure. Ⅱ.10.(a)UV-Vis spectrophotometer (SHIMADZU UV 1280),(b) Degradation of the MB dye of solution

Ⅱ.4.2.1. Calibration curve for Methylene Blue (MB)

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

The amount of BM photo-degraded over NiO-AC photo-catalyst is calculated by the following relation:

$$R=(C_0-C_t)/C_0*100 \qquad (Ⅱ.1)$$

Where:

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

C_t: Concentration of the solution attime t (mg/L)

R:Pd rates (%)

II.5. Parameters affecting photo-catalytic activity

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

In addition, the performance of the NiO- AC photo-catalyst 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 photo-catalytic activity.

	Mass of NaOH (g)	Catalyst type	Time (min)	Light source (W)	Volume of water (ml)	Temperature (^0C)	Initial concentration of MB dye (ppm)	Mass of catalyst (g)
Serie (1)	1 2 3	/ / /	40 180 40	1000	1200	23-60	/ / /	/ / /
Serie (2)	2	5/5 NiO-AC 4/6 NiO-AC 3/7 NiO-AC 2/8 NiO-AC	180 180 180 180	1000	1200	22-60	/ / / /	1 1 1 1
Serie (3)	2	4/6 NiO-AC 3/7 NiO-AC 2/8 NiO-AC	80 80 80	1000	1200	20-60	20	1 1 1

Chapter Ⅲ: Results and discussion

III.1.Electrolytic activity

It has been studied hydrogen and oxygen production by the water splitting process and the performance of NaOH mass (1,2,3g) on H_2 and O_2 productivity under the influence of light rays (1000W), electric current.

III.1.1. Effect of NaOH mass

Figure.III.1shows 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's efficiency increases, leading to higher hydrogen and oxygen productivity.

The electrolysis of water with the addition of 1 g of NaOH produced (115 ml) of hydrogen and (0.09ml) of oxygen. The water-splitting process with 3 g of NaOH reached the highest production of hydrogen(329 ml) and oxygen(30 ml).However, all three experiments were conducted at the same temperature interval, as shown in **Figure.III.1.(a).**

The 3 g NaOH mass is the best in terms of production and efficiency, the increase in hydrogen production due to the increased availability of electrons involved in the electrolysis process. When the electric current is applied to the solution containing sodium hydroxide, the mass of NaOH increases the availability of electrons and contributes to the reactions of the analysis and the production of hydrogen gas [27].

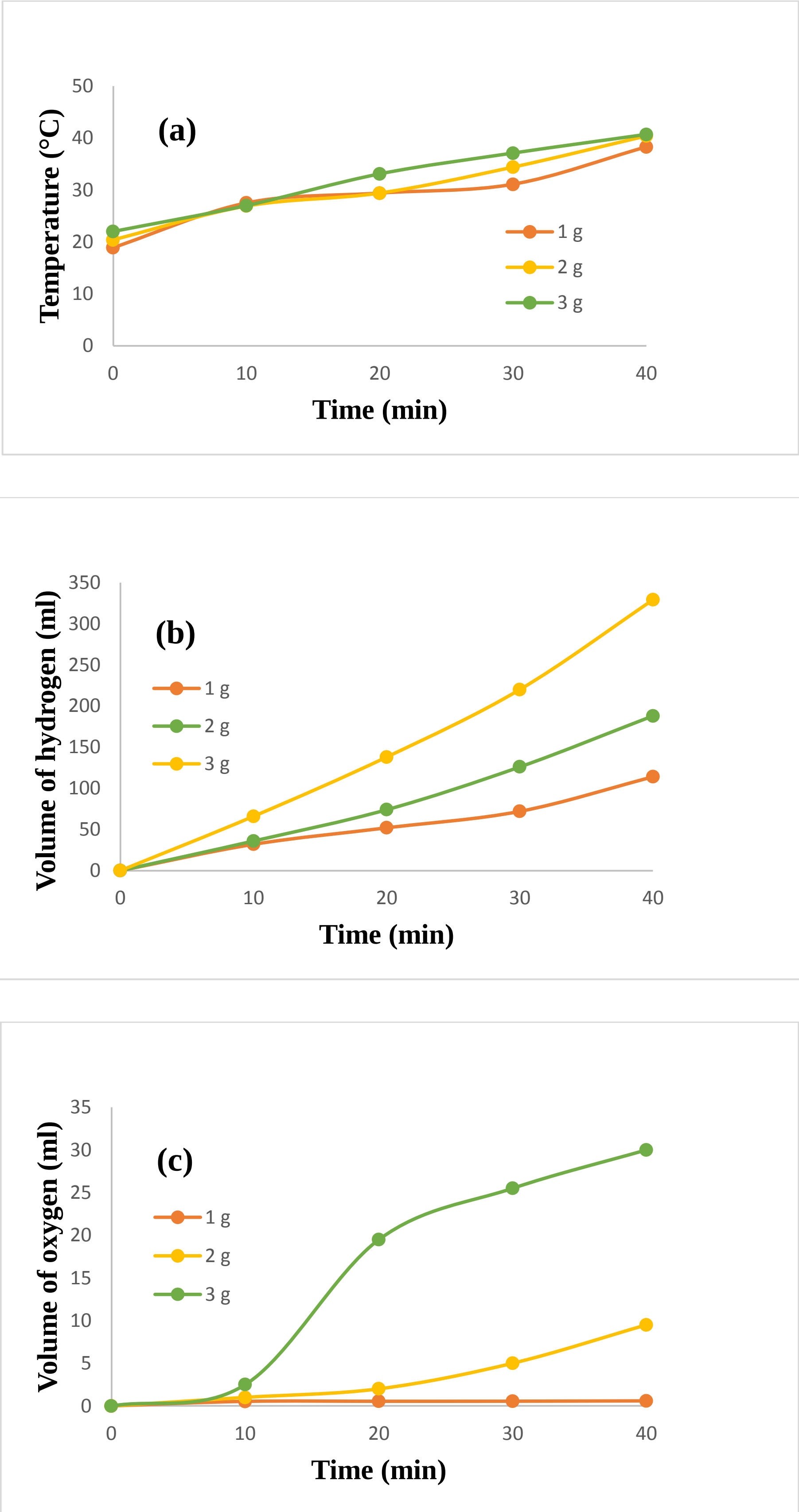

Figure.III.1. Effect of NaOH mass on electrolyticactivity, variation of (a- Temperature, b- Volume of hydrogen produced, and c- Volume of oxygen)

III.2. Photo-catalyticactivity

The performance of photo-catalytic water splitting was studied and compared with electrolyte in terms of hydrogen and oxygen production.

III.2.1. Photo-catalytic water splitting

Figure.III.2shows the performance of 1 g of the 5/5 NiO-AC photo-catalyst in the water splitting process, it is observed that the effect of the photo-catalyst on the water splitting is divided into two phases, in the first phase (0-90 min) the productivity of hydrogen and oxygen was identical, this indicates that the process of splitting water through an electrolyte is identical to the process of splitting water through a photo-catalyst, which means that the effect of the 5/5 NiO-AC photo-catalyst is neglected. In the second phases(150-180 min) increase in productivity of hydrogen and oxygen,which means that the effect of 5/5 NiO-AC photo-catalyst is a noticed on the efficiency of the WS process.

Previous studies have proven that theNiO photo-catalysis a good candidate in WS process[28-30].

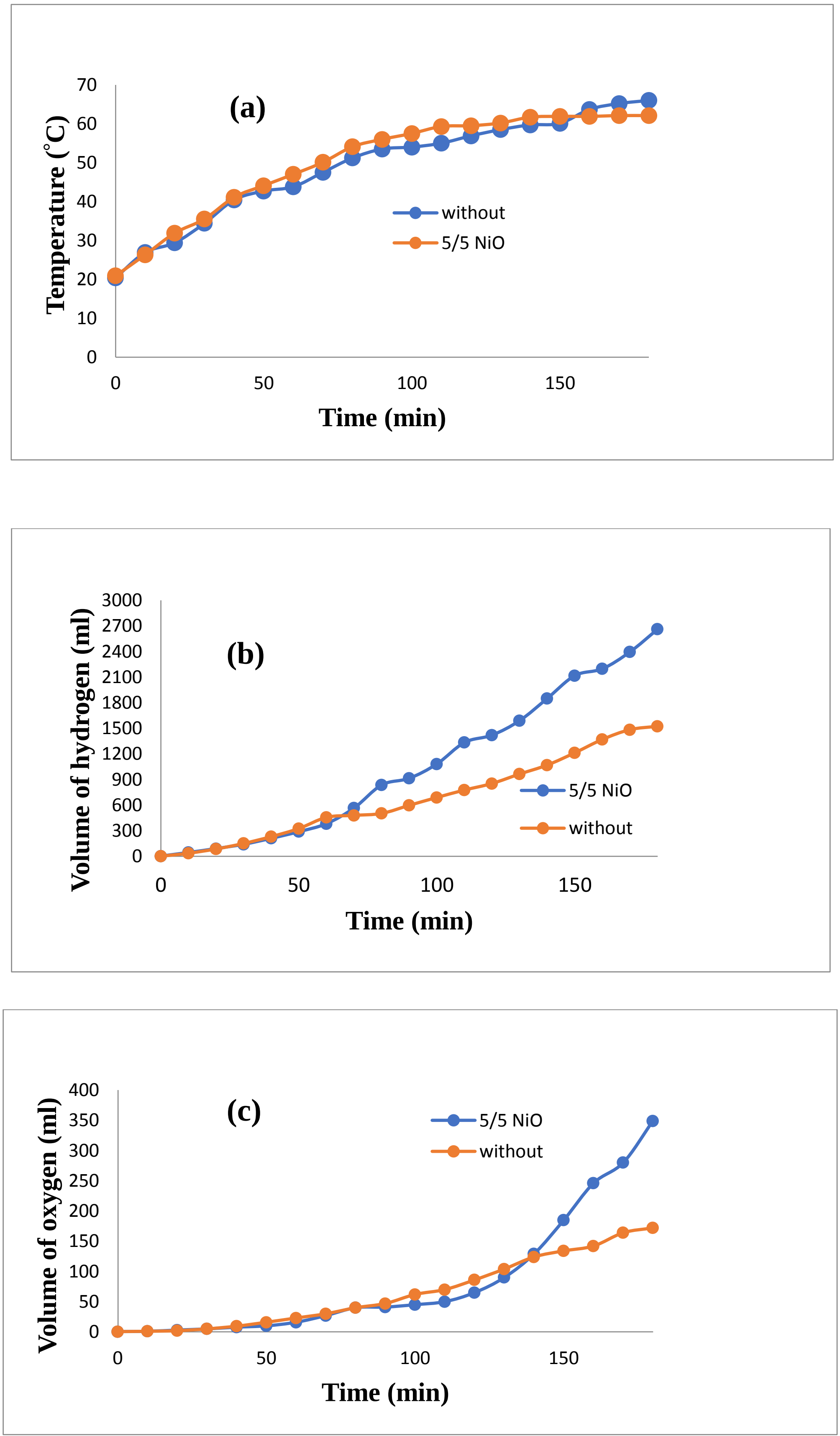

Figure.III.2. Photo-catalytic activity of 5/5NiO-AC,variation of (a-Temperature, b- Volume of hydrogen produced, and c- Volume of oxygen)

III.2.1.1.Effect of the weight ratio of NiO-activated carbon(AC)

Figure.III.3represents the effect of the weight ratio of NiO-AC on the efficiency of the W.S 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 NiO-AC decreasesfrom 5/5 to 3/7, this means that the increase in AC has a positive impact on hydrogen production. And after that decreases from 3/7 to 2/8 the volume of hydrogen produced decreases .Meaning AC has a positive effect on the performance of the NiO due to the increase of specific surface of the photo-catalyst.

The previous study proved that the addition of significant amounts of activated carbon to NiOgives good decomposition results, this may be explain by the efficiency of the semiconductor system is improved by increase its surface area and make appropriate adjustments to it surface sites[31-32].

The aggregated structure of the NiO-AC PC composites could improve its performances because of the increases in both the electrochemically active area and the electrical conductivity due to the incorporation of AC [33].

The decrease in the productivity from 3/7 to 2/8, can be explained as follows:

Insufficient catalyst weight ratio limits the number of active sites off available for photo-catalytic reactions, and an excessive amount of alternating current may overwhelm the active sites of NiO or prevent light absorption, reducing the efficiency of the PC,thereby reducing of hydrogen production rate. Excessive activated carbon weight ratio causes aggregation of the catalyst, reducing the surface area available for photo-catalytic reactions [34].

The optimal ratio is considered to be 4/6 NiO-AC for the WS process.

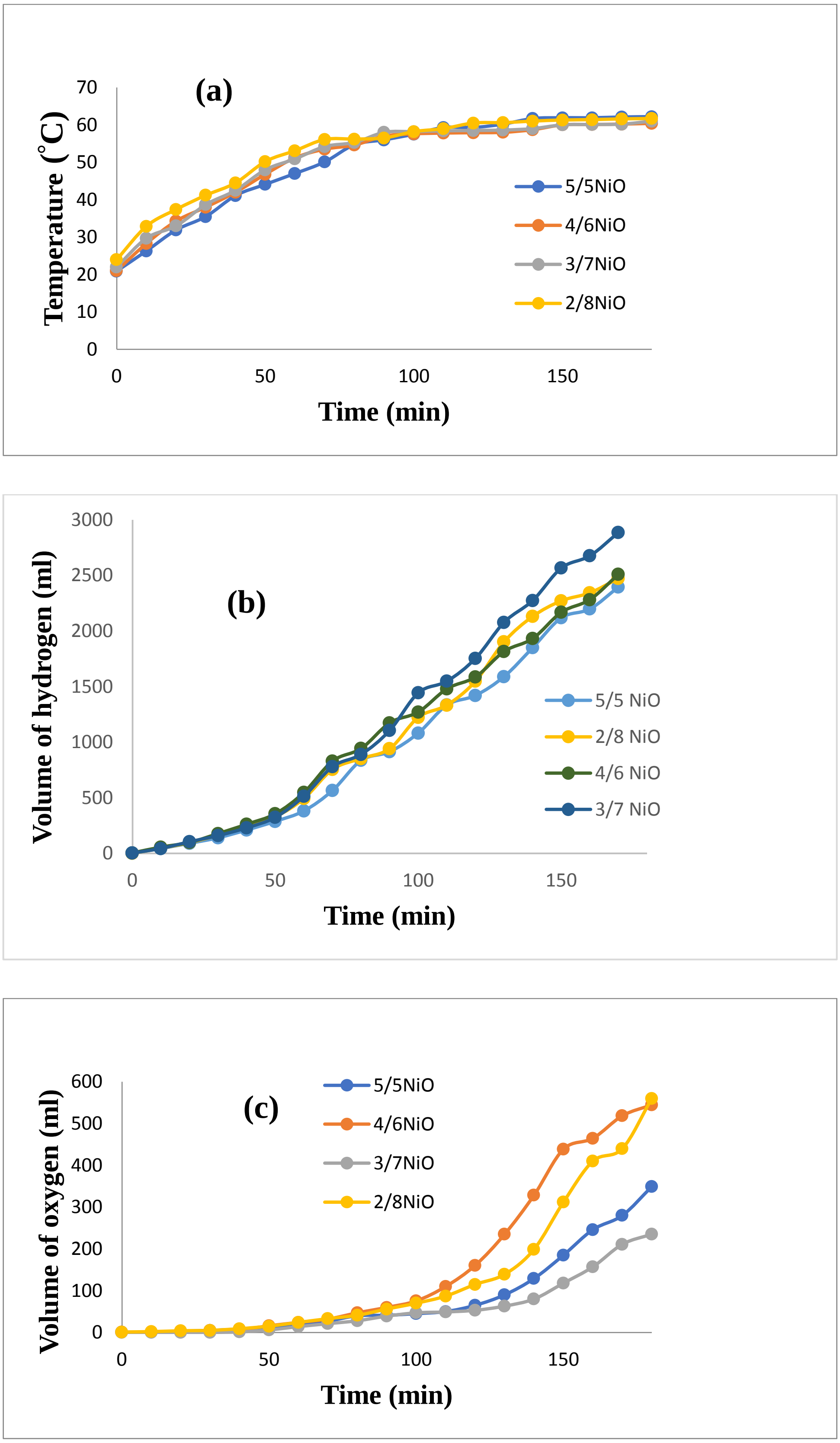

Figure.III.3. Effect of the weight ratio of NiO and activated carbon(AC) on photo-catalytic activity of NiO-AC variation of (a- Temperature, b- Volume of hydrogen produced, and c- Volume of oxygen)

III.2.2. Photo-catalyticcoupled-dyedegradation, and water splitting

To investigate the performance of the photo-catalyst in water splitting and Methylene Blue (MB) dye degradation simultaneously, Methylene Blue (MB) dye was added to the solution.

III.2.2.1. Photo-degradation of Methylene Blue (MB) dye on 4/6 NiO-AC

The obtained results are represented in **Figure.III.4,**it is noted that as time passes the photo-degradation rate of MB dye rate over 4/6 NiO-AC increases until reaching a complete photo-degradation rate of MB dye (100 %), the photo-degradation is a very fast to degrade 1200 ml solution of 20 ppm of MB dye in 20 min.Results reveal that the NiO-AC act as an excellent in photo-catalyst degradation of MB dye

The previous results revealed that the NiO-AC are potential photo-catalyst in degradation of MB dye [35].

NiOPC were synthesized by a chemical precipitation method using nickel acetate as precursors and Sodium hydroxide as precipitating agent. The NiOPC have been successfully used as a photo-catalyst for degradation of Methylene Blue dye from the aqueous medium. The photo-catalytic degradation study results revealed that the NiOPC are potential photo-catalyst in degradation of Methylene Blue[36].

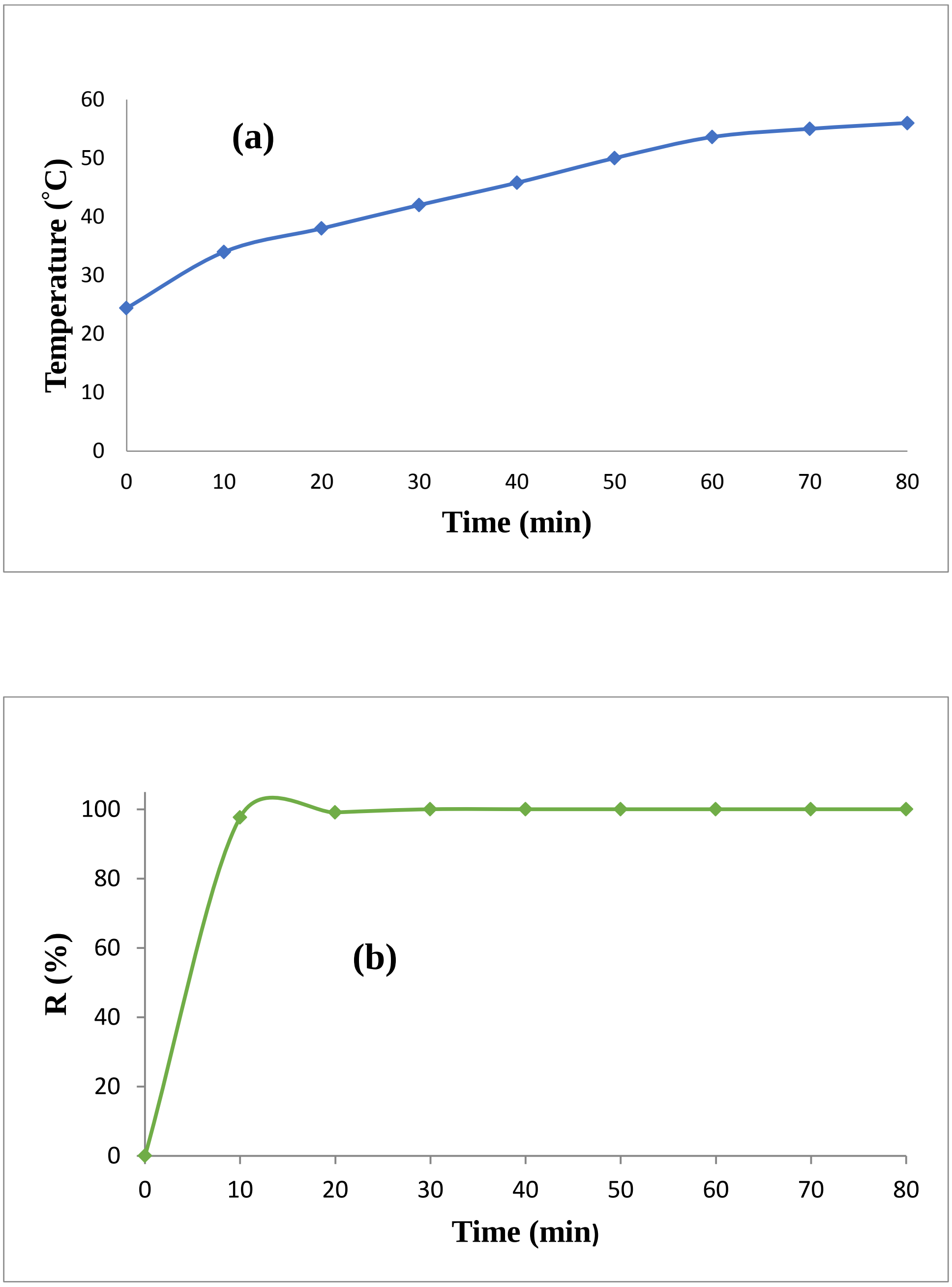

Figure.III.4. Photo-degradation of Methylene Blue (MB) dye on 4/6 NiO-AC, variation of (a-Temperature, b-Dye removal)

III.2.2.2. Photo-catalytic water splitting on 4/6 NiO-AC:

A comparison was conducted between the performance of the photo-catalyst 4/6NiO-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 NiO-AC photo-catalyst.It is noted from**Figure.III.5(a,b)** a decrease in the volume of hydrogen and oxygen production in water-splitting with MB dyecompared to its productivity without MB dye,which means that the addition of MB dye has a negative effect on the performance of the photo-catalyst of 4/6 NiO-AC, this is maydue to the double function of the photo-catalyst 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 photo-catalyst has dual functions degrading Methylene Blue and splitting water. This dual functionality means that some of the photo-catalyst'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 [37].

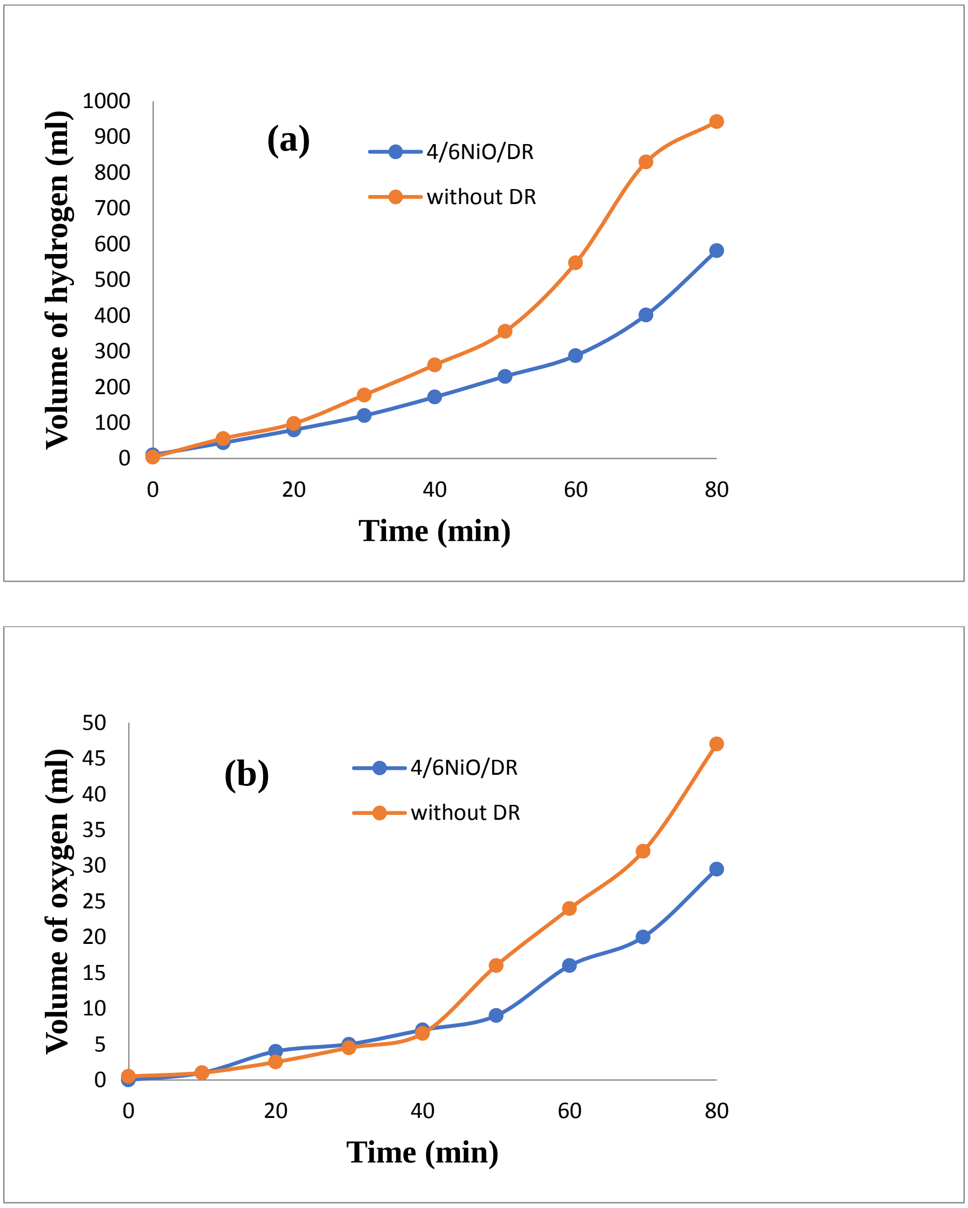

Figure.III.5. Photo-catalytic activity of 4/6 NiO-AC, variation of (a- Volume of hydrogen produced, and b- Volume of oxygen)

III.3. Comparison of photo-catalytic performance over different weight ratiosNiO-AC

A comparison was conducted between the performance of the photo-catalyst 4/6,3/7, and 2/8 NiO-AC in water-splitting with MB dye .The obtained results are represented in **Figure.III.6.**As seen from**Figure.III.6.(a)** shows the PD rate of MB dye as function of time,it is noted that as time passes in general photo-degradation rate of MB dye increases until reaching a complete photo-degradation rate of MB dye (100 %), it is also very important to note that the PC 4/6 NiO-AC shows an excellent performance in degradation of MB dye followed by the PC 2/8 NiO-AC ,at the buttom 3/7 NiO-AC .

The productivity of hydrogen and oxygen through the wastewater splitting over NiO-AC was also presented in **Figure.III.6(b,c)**, it noted that 2/8 NiO-AC offers the highest volume of H_2 and O_2 it could be considered the optimal ratio.

Increasing the NiO content leads to enhanced photo-catalytic activity of hydrogen generation due to the increase of active sites on the surface of the photo-catalyst [38].

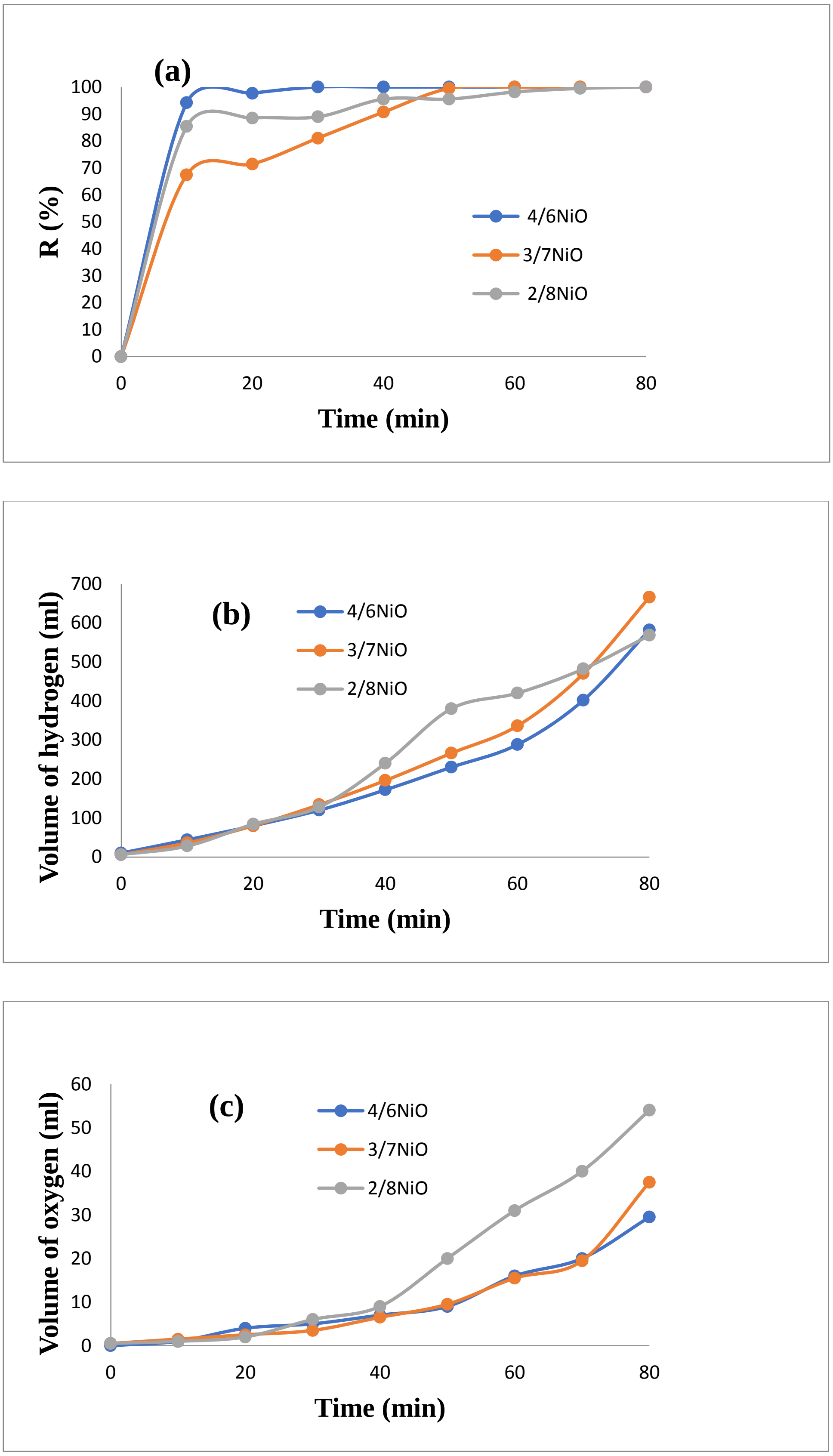

Figure.III.6. Photo-catalytic activity of 4/6, 3/7 and 2/8 NiO-AC, variation of (a-dye removal, and b- Volume ofhydrogenproduced, c-Volume ofoxygenproduced)

General conclusion

Conclusion

Photo-catalysts based on NiO-AC with different weight ratios were synthesized by a chemical precipitation method, using nickel acetate as precursors and activated carbon as a support. The synthesized NiO-AC has been successfully used as a photo-catalyst in pure water splitting into hydrogen and oxygen gases.

The weight ratio of NiO/AC plays a significant role in the efficiency of the water-splittingprocess, it was found that the optimal ratio is considered to be 4/6 NiO-AC.

In addition, NiO-AC showed a good performance in the similated wastewater splitting into hydrogen and oxygen, and in photo-degrading the MB dye.

The results obtained on the performance of the photo-catalyst over a variety of weight ratios have indicated that a weight ratio of 2/8 NiO-AC produces hydrogen and oxygen with high efficiency and quickly degrades MB dye from the solution with the highest success. However, the results suggest that 2/8 NiO-AC could act as a photo-catalyst for similated wastewater splitting by treating similated waste water from one side and producing hydrogen and oxygen from the other.

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عنوان المذكرة: الكربون النشط المشتق من الكتلة الحيوية (AC)المحفز الضوئي (NiO) المعدل لفصل الماء التحفيزي الضوئي الفعال وتحلل صبغة الميثيلين الزرقاء تحت الضوء المرئي.

اللقب: بلعيد **الإسم:** خضرة **المؤطر:** براهيمي جميلة

اللقب: رمضاني **الإسم:** فتيحة

ملخص: تم تصنيع المحفزات الضوئية القائمة على NiO-AC بنسب وزن مختلفة بواسطة طريقة ترسيب كيميائية ، باستخدام أسيتات النيكل كسلائف وكربون نشط كدعم. تم استخدام NiO-AC المصنّع بنجاح كمحفز ضوئي في الماء النقي مقسمًا إلى غازات هيدروجين وأكسجين. تلعب نسبة الوزن لـ NiO / AC دورًا مهمًا في كفاءة عملية تقسيم الماء ، وقد وجد أن النسبة المثلى تعتبر 6/4 .NiO-AC بالإضافة إلى ذلك ، أظهر NiO-AC أداءً جيدًا في تقسيم المياه العادمة إلى هيدروجين وأكسجين ، وفي تحلل صبغة .MB أشارت النتائج التي تم الحصول عليها على أداء المحفز الضوئي على مجموعة متنوعة من نسب الوزن إلى أن نسبة وزن 8/2 NiO-AC تنتج الهيدروجين والأكسجين بكفاءة عالية وتتحلل بسرعة من صبغة MB من المحلول مع أعلى نجاح. ومع ذلك ، تشير النتائج إلى أن 8/2 NiO-AC يمكن أن يعمل كمحفز ضوئي لتقسيم مياه الصرف الصحي عن طريق معالجة مياه الصرف من جانب وإنتاج الهيدروجين والأكسجين من الجانب الآخر.

الكلمات المفتاحية :تقسيمالماء، محفز ضوئي، صبغة أزرق الميثلين ،كربون منشط ، بذور زيتون.

Memory title : Biomass-derived active carbon (AC) modified NiO photo-catalyst for efficient photo-catalytic water splitting and degradation of Methylene Blue Dye under visible light

Name: BELAID **First name:** Khadra **Directed by:** BRAHIMI Djamila

Name: RAMDANI **First name:** Fatiha

Abstract : The goal of this study is to synthesize an effective photo-catalyst based on NiO-AC with a different NiO/AC weight ratio, photo-catalysts synthesized were applied to the water-splitting process to produce hydrogen and oxygen. It also investigated how various operating parameters, such as the weight ratio of NiO/AC, the irradiation time, and the mass of NaOH, affected the water-splitting efficiency over the NiO-AC photo-catalyst. According to the findings, the optimal weight ratio of NiO/AC is 2/8 to achieve the maximum productivity of both oxygen and hydrogen. Furthermore, it demonstrates its excellent performance in the coupled splitting water and MB dye degradation, providing a thorough and incredibly quick photo-degradation coupled with 20 ppm of MB dye. Further more, it demonstrates its excellent performance in the combined splitting water and dye degradation, offering the maximum levels of oxygen and hydrogen productivity while enabling a complete and rapid photo-degradation in the presence of 20 ppm MB dye.

Key words: Water splitting, photo-catalyst, M-ethylene Blue dye, activated carbon, olive seeds.

Titre du mémoire : Le photo-catalyseur NiO modifié dérivé de la biomasse pour un effet photo-catalytique efficace de la séparation et de la dégradation du bleu de méthylène sous la lumière visible

Nom : Belaid **Prénom :**Khadra **Encadreur :** Brahimi Djamila

Nom : Ramdani **Prénom :** Fatiha

Résumé : Les photo-catalyseurs basés sur NiO-AC avec différents rapports de poids ont été synthétisés par une méthode de précipitation chimique, en utilisant du nickel acétate comme précurseurs et du charbon actif comme support. Le NiO-AC synthétisé a été utilisé avec succès comme photo-catalyseur dans la division d'eau pure en gaz d'hydrogène et d'oxygène. Le rapport pondéral de NiO/AC joue un rôle important dans l'efficacité du processus de répartition de l'eau, il a été constaté que le rapport optimal est considéré comme étant de 4/6 NiO-AC. De plus, le NiO-AC a montré une bonne performance dans la division des eaux usées en hydrogène et en oxygène, et dans la photo-dégradation du colorant MB. Les résultats obtenus sur les performances du photo-catalyseur sur une variété de rapports pondéraux on tindiqué qu'un rapport pondéral de 2/8 NiO-AC produit de l'hydrogène et de l'oxygène avec un rendement élevé et dégrade rapide mentle colorant de MB de la solution avec le plus grand succès. Cependant, les résultats suggèrent que 2/8 NiO-AC pourrai agircomme un photo-catalyseur pour la séparation des eaux uées entraitant les eaux usées d'un côté et en produisant de l'hydrogène et de l'oxygène de l'autre.

Mots clés : Fractionnement de l'eau, photo-catalyseur, colorant bleu M-éthylène, charbon actif, graines d'olive