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Photocatalysts behavior during hydrogen generation by water electrolysis under solar rays

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ABSTRACT

The fuel extracted from fossil reserves is very polluting for the environment despite its reasonable cost price; hereof, hydrogen produced by the electrolysis of water appears to be the cleanest fuel of the future. Despite the world's water reserves, the yield of hydrogen production by electrolysis remains unsatisfied; hence, its cost price still remains high. The main goal of this work is to increase the efficiency of hydrogen generation by the photocatalytic effect of three different semiconductors: (lead oxide, copper oxide, and manganese oxide) introduced separately in three transparent electrolyzers exposed to sunlight contain local water and the same amount of electrolyte (KOH) and activate under the same climatic and electrical conditions during 8 h/d. The results show that manganese oxide is the best photocatalyst compared to copper oxide and lead oxide which sometimes behave as photo-inhibitors; so, the rate of hydrogen generation increases with the increase of manganese oxide concentration; from where, 25 g/L of manganese oxide in the electrolyzer basin with 30 g/L of KOH as an electrolyte, leads to the production of 3,750 mL of hydrogen; increasing, therefore, the production by 30%. Finally, following the increase in solar intensity, the electrolysis of water in summer is more profitable than in winter.

Keywords: Hydrogen; Solar rays; Photocatalysts; Electrolyser; Water; Ouargla

1. Introduction

The search for alternative sources of energy due to the growth of the world's population and the preservation of the environment from industrial waste is one of the most important challenges in recent years [1] because most industrial systems depend on the consumption of fossil fuels. Fossil fuels (natural gas, petroleum, coal) create many problems such as global warming caused by carbon dioxide emissions [2]; as well as the sources of these non-renewable and limited energies, leading to global economic crises [3].

Hydrogen is an ideal alternative source of energy in terms of not only its application and its environmental impact, but also its high energy potential [4].

There has been growing interest in the development of new methods of H_2 generation based on the electrolysis of water. This technique is considered a promising technology because of its simplicity, low maintenance, and also because it respects the conditions of environmental protection [5]. Despite its importance, improving the low production rate remains the main objective of all research in this area.

To improve the productivity of hydrogen, Sakr et al. [6] carried out an experimental study to separate the electrodes

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by comparing the effect of the acrylic separator and the polymer membrane on the generation rate. They found that increasing hydrogen production is inversely proportional to the distance between the electrodes; furthermore, the use of the polymeric membrane increases the output's efficiency more than the acrylic separator.

In another experiment, and in order to select the best alloy for the production of hydrogen, Chakik et al. [7] used the electrolysis of alkaline water with several bi-alloy tests: mainly based on an alloy of zinc as the cathode material. They found that the better yield of hydrogen productivity was due to the use of mass percentage: (Zn 95% Cr 5%) and (Zn 90% Cr 10%) with a remarkable increase in daily production.

Several methods have been used to improve hydrogen production based on electrolysis of water by maintaining the same conception with different operating principles [8]. Water electrolysis is done by various technologies including alkaline water electrolysis, polymer exchange membranes (PEM), and high-temperature electrolysis for solid oxides [9].

These three techniques have the same design, with an operating temperature of about 60°C and 90°C for alkaline water electrolysis and PEM water electrolysis; while solid oxide may reach 900°C. Alkaline water electrolysis is the most widely used because of its simplicity and low cost compared to previous methods. Cell corrosion, maintenance and cost are the main disadvantages that make PEM electrolysis usage limited. In addition, the use of solid oxide method requires considerable heat energy which makes it difficult to apply in practical operation [6].

On the other hand, some researchers were interested in improving the performance of water electrolysis and production efficiency by using renewable energies as an alimentation power source [10]. In this context, Sellami et al. [11] conducted an experimental study of hydrogen production using solar panels as a source to observe the effect of electrolyte on the rate of hydrogen production based on its nature and compare the yields obtained in summer and winter. They have shown that under the same conditions applied to the cell, the electrolyte (3 M KOH) is more effective than sodium hydroxide (3M NaOH) with a production of 5,122 and 3,279 cm^3 of hydrogen and found that generally, the production of hydrogen in summer is better compared to the period of winter.

In the same context, Chennouf et al. [12] conducted an experimental work on hydrogen production using the PV-electrolyzer system and tested different concentrations of NaOH and concluded that the increase in NaOH tension and concentration causes an increase in hydrogen production.

Relying on renewable energies (wind, hydraulic, geothermal, and solar energy) is not new. They have been exploited in several researches [13]; however, their biggest drawback is that these energies are not available in all regions because they relate to climatic conditions that characterize each country depending on its geographical position [14].

Algeria is among the countries rich in renewable energy sources (wind, hydraulic, geothermal and solar energy) [15]. Ouargla city (Southern Algeria) is located between the longitude 5.40 east, latitude 31.95 north and height 141 m above the sea level. It is also characterized by a period of solar radiation of about 3,500 h/y, and delivering about 2,650 kWh/y/m^2 of solar radiation on the horizontal surface. These advantages can be exploited for hydrogen production and other solar energy devices [11].

It is time to operate with other new applications to increase the efficiency of the water decomposition and improve hydrogen production through modern methods that rely on the conversion of electrical energy and solar radiation energy into chemical energy by adding some photocatalysts materials inside the electrolyzer basin [16].

The use of semi-conductors materials that play the role of photocatalysts (metal oxides: TiO_2, MnO_2, CuO or metal sulfides: ZnS, CuS, CdS) [17], is one of the most promising applications these recent years. When the energy of the incident light is sufficient to excite the electrons from the valance band (VB) to the conduction band (CB) of the semiconductor, the latter absorbs the light to generate electrons and holes. Photo generated electrons and holes are transferred to surface reaction sites and are used for oxidation-reduction reactions: evolution reaction of H_2 in (CB) with electrons by reducing protons, the evolution of oxygen (O_2) in the (VB) with holes oxidizing the water [18]. To obtain water decomposition using a photocatalyst, the (CB) level must be more negative than the reduction potential of H^+/H_2 (0 V vs. NHE) and the (VB) level must be more positive than the oxidation potential of O_2/H_2O (1.23 V vs. NHE) [19].

The use of photocatalyst is a great environmental application with high potential in the future, used in many operations, water purification [20], adsorption of pollutants [21] and water desalination using solar distillation [22].

There are many factors that affect the behavior of the photocatalyst to increase or limit its activity during the water electrolysis process to produce hydrogen, related to operating conditions such as medium pH, operating temperature, and sufficient light intensity [23].

The efficiency of water splitting using photocatalyst can be improved by increasing the light intensity with energies above the activation threshold, [24] Baniasadi et al. [25] recorded that hydrogen production using ZnS as a photocatalyst showed 20% efficacy by increasing the light intensity from 900 to 1,000 W/m^2.

The temperature plays a role in improving the desorption of the products from the catalyst surface in order to increase photocatalytic activity. Reducing the temperature has a negative effect by slowing the rate of H_2 production because the products' desorption limits the reaction because it slows the absorption of the reactants. The high temperature allows higher electron transfers in the valance band at higher energy levels. Thus, it facilitates the formation of electrons-holes that could be used in oxidation and reduction reactions [26].

Boudjemaa et al. [27] showed that increasing the temperature from 30, 40 to 50 gave 59, 92, and 370 mol of H_2 respectively.

It can be considered that hydrogen production from water electrolysis depends on the proton concentration, which is the pH of the solution, because the proton reduction by the photo-generated electron is generated during the decomposition of water, and the bandgap energy shift depends on the change of pH [26].

Generally, on the basis of the foregoing research, the reaction used photocatalysts in the base system gives more advantages to improve the release of H_2 [28].

This article presents an experimental study concerning some factors and operating conditions affecting hydrogen production via water electrolysis using different metal oxides as photocatalysts. The work consists of observing the effect of three photocatalysts (CuO, PbO_2, and MnO_2) as well as the influence of climatic conditions (summer and winter) on the water electrolysis process, in addition to the effect of the variation of the concentration of the electrolyte and the concentration of the best photocatalyst on the efficiency of hydrogen production.

2. Material and methods

Fig. 1 shows the experimental schematic sketch of hydrogen production in this study. The experimental prototype consists of four identical transparent electrolyzers E_1, E_2, E_3, and E_4 manufactured with a glass basin of (23.5 cm × 23.5 cm × 13 cm) of volume. In each electrolyzer basin, two copper electrodes were fixed by wooden support, powered by a DC generator. Two glass test-tubes covering electrodes were placed for capturing hydrogen produced during the experiment. The electrolyzer (E_1) used as a witness and the others are the object of our study. Experiments were carried out under atmospheric pressure, ambient temperature and solar radiation measured every hour (from 8:00 to 17:00 local time). The same operating conditions were applied to all electrolyzers (1.5 A amperage and 15 V voltage) during the experiments.

2.1. First-test: (effect of photocatalyst nature)

In this experiment, the concentration of electrolyte (KOH) is fixed at 30 and 10 g/L of CuO, PbO_2 and MnO_2 are added separately to the basin of electrolyzers E_2, E_3, and E_4, respectively.

During the experiments, the following parameters are observed and checked: the temperature of the electrolyte and the volume of hydrogen generated.

2.2. Second-test: (influence of electrolyte concentration)

Our study in this experiment consists of fixing the concentration of the best photocatalyst at 10 g/L and varying the electrolyte concentration (KOH) between 10 g/L and 50 g/L by adding a regular amount of 10 g/L each time, in order to know the effect of electrolyte concentration on the photocatalyst activity and the rate of hydrogen production.

2.3. Third-test: (influence of photocatalyst concentration)

In order to study the influence of the photocatalyst's concentration, 30 g/L of KOH are used as a fixed electrolyte concentration with varying concentrations of the better photocatalyst in the range of 10–25 g/L by the addition of 5 g/L each time.

Finally, we made a comparative study concerning the effect of the climatic conditions of summer and winter on the activity of 10 g/L of the best photocatalyst under 30 g/L of KOH on the production of hydrogen.

3. Results and discussion

Fig. 2 shows the curves of solar irradiance and ambient temperature vs. local time recorded for a chosen day in summer and winter seasons at Ouargla City. The Saharan environment existing in the Ouargla region is dusty; in winter, rain and humidity reduce the rate of dust in the ambient air, from which the lighting is important despite the fact that solar irradiation remains less important than summer. The sunshine in summer remains higher; it can exceed an average of 1,000 W/m^2 while it remains around 900 W/m^2 [15,22].

The ambient temperature also follows the same behavior as solar irradiation, only sometimes we encounter exceptional days that are thought to be foreign for the season. At the start of the day, the temperature starts to rise depending on the solar intensity until the middle of the day when it reaches its maximum and then starts to drop in the evening. The shape of the ambient temperature and solar intensity curves is generally Gaussian [11].

Fig. 3 shows the comparative experiment between the behaviors of the three metal oxides: MnO_2, PbO_2 and CuO in the presence of solar rays at the same weight concentrations (10 g/L) and the same electrolyte concentration (30 g/L of KOH) with the possibility of an improvement in Hydrogen production compared to the witness unit.

By exposing the transparent electrolyzers in working order to solar radiation, it is noted that the flow of hydrogen collected is greater in the electrolyzer containing MnO_2

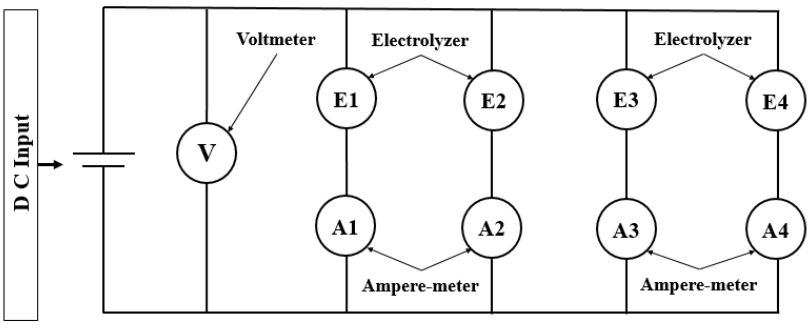

Fig. 1. Experimental schematic sketch of hydrogen production.

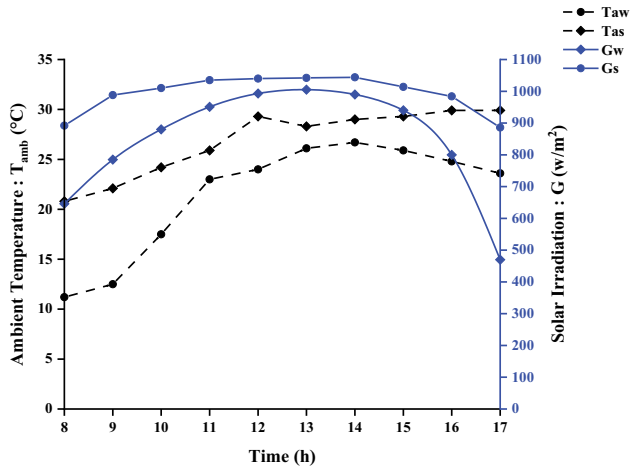

Fig. 2. Typical measured of ambient temperature and solar irradiance of winter and summer seasons vs. local time.

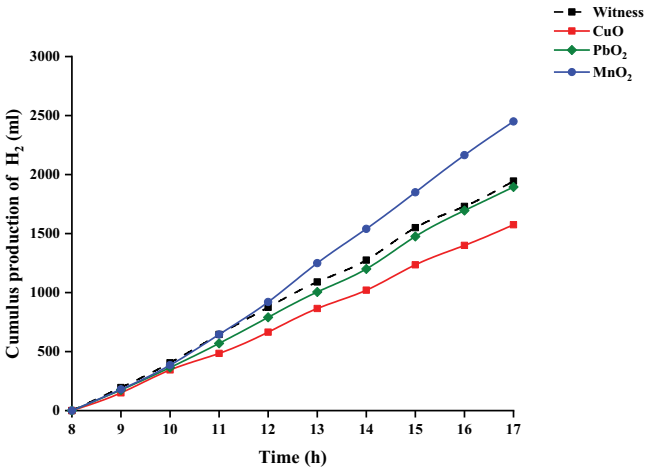

Fig. 3. Hourly cumulus of hydrogen volume with different nature of photo-catalyst vs. local time.

than that of the witness or those containing PbO_2 and CuO. It can be deduced that the metal oxide MnO_2 plays the role of a photocatalyst; on the other hand, the PbO_2 and the CuO are either neutral with respect to the photocatalyst or are less photocatalytic than MnO_2 or maybe behave as photo-inhibitors in KOH medium.

Fig. 4 clarifies the gain in hydrogen production obtained by using the 3 metal oxides separately at the same concentration of 10 g/L vs. KOH concentration. It's clear that the enhancement rate of hydrogen production for MnO_2 is generally better than those of the two other metal oxides. The best result of 30% of enhancement rate is obtained for 10 g/L of MnO_2 under 30 g/L of KOH.

Negatives values obtained for the enhancement rate are explained by the fact that certain metal oxides sometimes play the role of photo-inhibitors according to the concentration of the environment in which they are found. In the presence of KOH as an electrolyte, the metal oxide CuO behaves completely as a photo-inhibitor; but PbO_2 has a wobbly behavior.

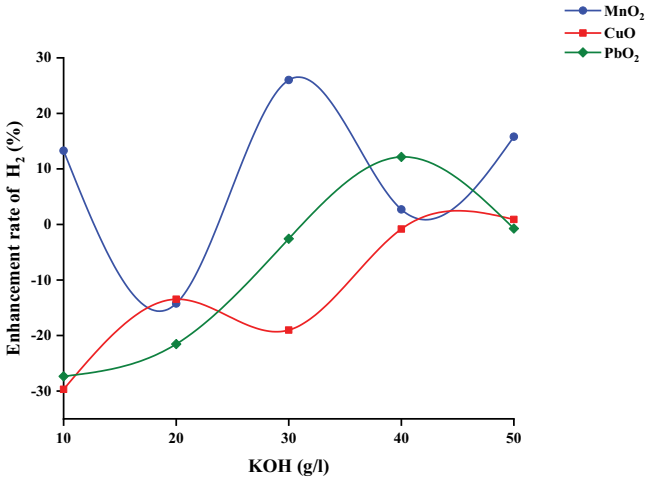

Fig. 4. Enhancement rate of hydrogen generation vs. KOH' concentration.

Fig. 5 shows the enhancement rate of hydrogen generation for MnO_2 within a KOH concentration of 30 g/L. According to Fig. 4 and this figure, we can deduce that MnO_2 behaves as photocatalyst material under high concentrations of KOH. It is clear that the enhancement rate of hydrogen generation generally increases with the increase of the concentration of MnO_2. Unfortunately, because of the lack of chemical products in our laboratory, our experiments are limited to 25 g/L of MnO_2 and 50 g/L oh KOH; so, we meet researchers and investigators to continue this experimental study.

Fig. 6 shows the temperature of the basin during the electrolyzing of water for two different climate conditions with 10 g/L of MnO_2 and 30 g/L of KOH in order to save chemical products.

Generally, the temperature of water increases slightly during electrolysis because of different factors namely: Joule effect (due to solution resistance), parasitic reactions (due to the electrolyte and/or the metal oxide's impurities) … etc.

In winter, electrolyte's temperature begins to rise from 10°C at 08:00 to reach 29°C at the end of the experiment.

In summer, the climate effect is clear; the temperature rises from 20°C at 08:00 to 36°C as a maximum value but it decreases slightly near the end of experiments; so, the mean temperature difference between the two seasons within the electrolyzer is approximately 7°C.

The second-test is to see the effect of electrolyte concentration on the hydrogen generation rate. Fig. 7 shows the results. It is clear from this figure that hydrogen production is directly proportional to the (KOH) concentration. The best results of hydrogen cumulus are obtained for 50 g/L of KOH.

This is explained by the fact that increasing the amount of KOH means that increasing ions within the solution which leads to high electrical conductivity and hence, a high hydrogen production rate [11].

Fig. 8 indicates the effect of the concentration of MnO_2 on hydrogen cumulus vs. local time. It is clear that the hydrogen generation rate is directly proportional to the photocatalyst's concentration. The best value of 3,750 mL

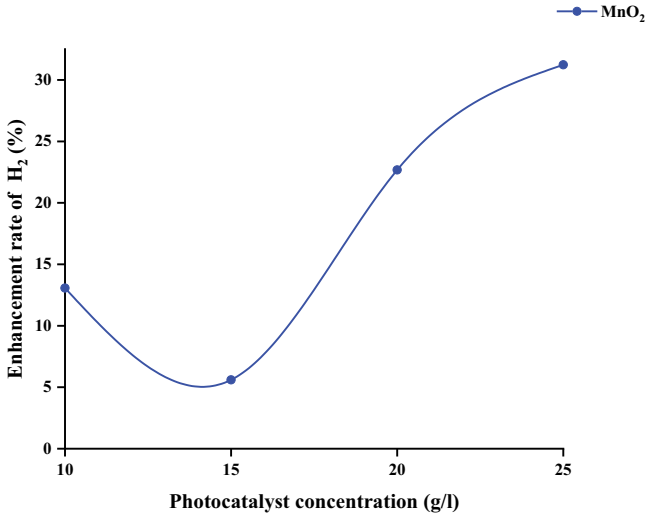

Fig. 5. Enhancement rate of hydrogen generation vs. the concentration of MnO_2 at 30 g/L of KOH.

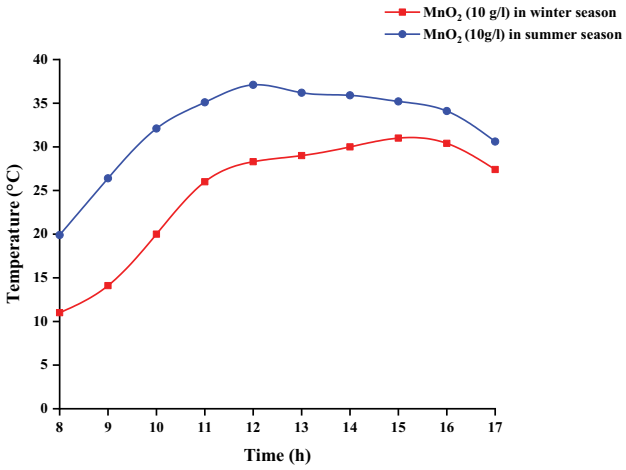

Fig. 6. Electrolyte temperature for MnO_2 in winter and summer seasons vs. local time.

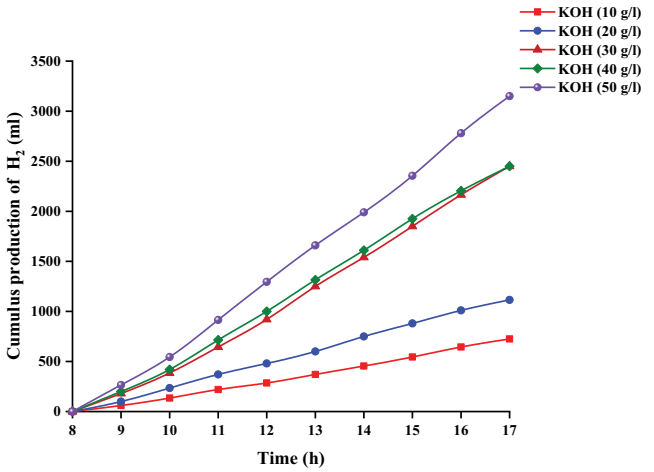

Fig. 7. Hourly cumulus of hydrogen volume of MnO_2 with different KOH' concentrations vs. local time.

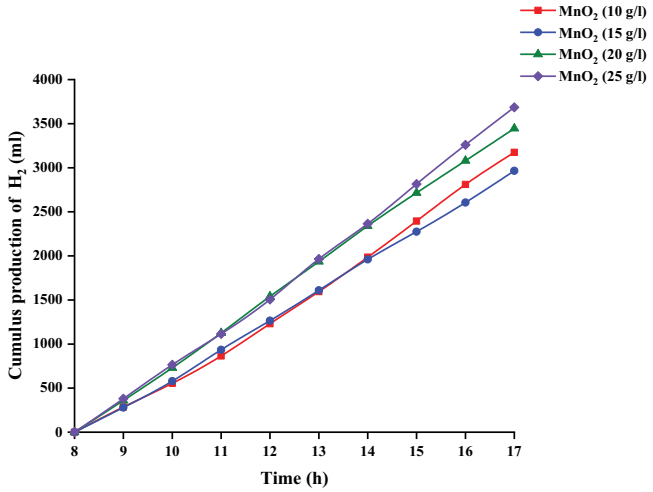

Fig. 8. Hourly cumulus of hydrogen volume with different concentrations of MnO_2 vs. local time.

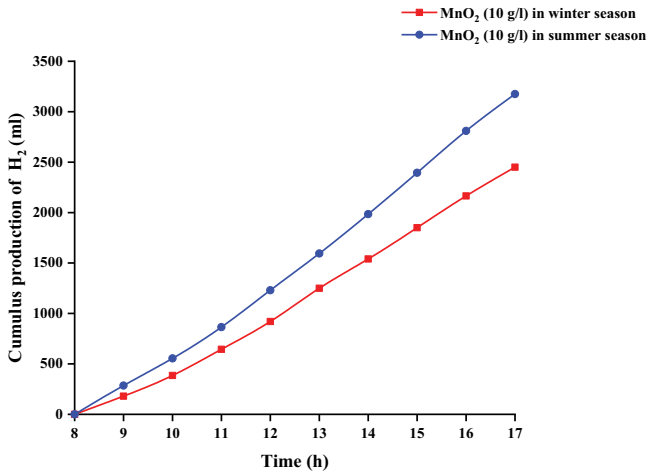

Fig. 9. Hourly cumulus of hydrogen volume for MnO_2 in winter and summer season vs. local time.

of hydrogen volume is obtained for 25 g/L of MnO_2 under experiment conditions of temperature, pressure, and solar rays between 8:00 and 17:00 local time. Unfortunately, because of the lack of chemical products, our results are limited to 25 g/L of MnO_2 and 30 g/L of KOH.

Fig. 9 shows the comparison of the hydrogen generation rate under two climate conditions: winter and summer season in Ouargla city. As shown previously (Fig. 2), either solar irradiance and ambient temperature are higher in the summer season; so, the photocatalyst's role is clearly observed in the summer; hence, we can summarize from Fig. 9 that hydrogen generation rate is better in the summer season.

4. Conclusion

The production of hydrogen with high flow rates and a reasonable price remains a concern for humanity because it is the fuel of the future which must replace fossil fuel.

Obtaining hydrogen by electrolysis of water is simple from a method point of view, but given the low efficiency of this process, the problem remains unsolved.

During electrolysis, several parasitic reactions take place because of salts and impurities which causes increase in the temperature of the medium on the one hand and the loss of electrical energy on the other hand.

To overcome this problem, we must choose a pure electrolyte and non-aggressive water; in addition, we must think about increasing the efficiency of this operation.

One of the solutions proposed is the choice of a photocatalyst which activates the electric transfer phenomenon and consequently improves the hydrogen recovery rate.

Our work carried out in Ouargla University, consists of testing between three different photocatalysts (MnO_2, PbO_2, and CuO) added separately with the same mass concentration in 3 similar and transparent electrolyzers of basic water, operating under the same climatic and electrical conditions and exposed to the sun. Electrolyzers' yields are compared with that of the witness at the same conditions to evaluate the improvement between 08:00 and 17:00 local time.

The experimental results obtained show that:

MnO_2 is the best photocatalyst compared to the two other photocatalysts (PbO_2 and CuO) which sometimes behave as photo-inhibitors.

Hydrogen generation rate increases with the increase of MnO_2 concentration.

25 g/L of MnO_2 within electrolyzer basin at 30 g/L of KOH as an electrolyte leads to the production of 3,750 mL of hydrogen increasing therefore hydrogen generation by 30% compared to the baseline case.

Additionally, following the increase in solar intensity, the electrolysis of water in summer is more profitable than in winter.

Symbols

A	—	Amperemeter
CB	—	Conduction band
DC	—	Direct current
E	—	Electrolyzer
NHE	—	Normal hydrogen electrode
V	—	Voltmeter
VB	—	Valence band
Gs	—	Solar irradiance in the summer season, W/m^2
Gw	—	Solar irradiance in the winter season, W/m^2
Tas	—	Ambient temperature in the summer season, °C
Taw	—	Ambient temperature in the winter season, °C

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