



The effective behavior of ZnO and CuO during the solar desalination of brackish water in southern Algeria

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ABSTRACT

In order to remedy the shortage of drinking water in southern Algeria where solar irradiance and brackish water are abundant, three solar stills are installed in aim to improve their performance by applying the technique of photo-catalysis, since this application in solar heat transfer processes particularly in the solar distillation of brackish water is promising mostly the use of pure and/or mixed metal oxides which has led to encouraging results in the process engineering laboratory of Ouargla University; so, what is the new in this paper? Here, two metal oxides: ZnO and CuO are added separately with varying masses in order to compare their yields with that of the conventional unit where: 20, 40, and 60 g of each metal oxide are added separately to each unit containing the same constant volume of 3.6 L of brackish water; this showed that the two metal oxides are more effective at their low concentrations. Moreover, adding 20 g of ZnO and 20 g of CuO separately in two different units improves the daily production by 79.39% and 74.76%, respectively, compared to the reference case; additionally, photo-catalyzed units produced a high quality distillate.

Keywords: Metal oxide; Solar still; Photo-catalysis; Copper oxide; Zinc oxide; Southern Algeria

1. Introduction

Fresh water is necessary for life on the globe [1]. In many parts of the world, obtaining safe drinking water remains a serious problem and an obsession for many people [2]. The proportion of fresh water in nature is very low compared to the salty water which is not advised for direct use because it causes human infections or even death, especially children [3]. The remarkably population's growth in recent decades, increases dramatically the pressure on water's sources and therefore, makes the problem more aggravated [4,5]. The exploitation of salty water through the

process of desalination to be drinkable is a good solution; so, the removal of salts by different ways and methods such as solar distillation techniques must be widely used [6,7].

Conventional distillation plants consume large amounts of energy resulting from fossil fuels. This method has negative consequences on the environment because of the issuance of greenhouse gases, not to mention the adverse effects on the economic side; thus, there are reasons to look for more alternative methods such as renewable energies' process [8,9]. The solar distillation process is promising since it uses clean energy that protects the environment avoiding the use of fossil fuels. The combination of solar

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energy and solar stills is possible to produce distilled water costly with simple devices. These units are easy to manufacture, maintain, and their set up is recommended in arid and sunny regions rich in brackish underground water where fresh water is unavailable [10,11].

Algeria has a strategic location that makes it an excellent place for solar energy applications such as the solar distillation. Located in southern Algeria, Ouargla's height is 141 m above the sea level and the solar radiation on its horizontal surface reaches about 3,500 h/y, equivalent to about 2,650 kWh/(m² y) [12]. More than 75% of Algeria's water resources are groundwater located in the south estimated to 60 billion m³. This huge amount of water is useful and difficult to regenerate. The annual exploitation reaches 5 billion m³ despite its variable salinity of up to 8 g/L in some sources and this is well beyond the allowed 550 ppm salt levels for human consumption. So, the lack of fresh water in this region causes an alarming shortage [13,14].

This high solar intensity and significant amount of underground water can be exploited to convert brackish water into fresh water by the use of solar desalination. This technique can make a considerable contribution to secure some potable water, especially for the small remote agglomerations [14]. Many attempts have been made to enhance the performance of conventional solar stills by using different methods. Improving the process of heat and mass transfer by using additives such as absorbing materials and storage materials is a technique applied to create heat generating for enhancement of overall yield of conventional type solar stills. Abdallah et al. [15] studied the effects of metallic wiry sponges coated and uncoated and special black rocks on the yield of single slope solar still. Both absorbing materials improved the still thermal performance, they concluded that the black rocks absorb, store, and liberate heat more than sponges coated and uncoated and can enhance the daily efficiency by of 60%.

Also, Ali Ouar et al. [13] investigated the effects of using different absorbent materials in single slope solar still and thus, increase the output of distilled water. Their experimental results show that bitumen, charcoal, and black ink improves the productivity of the solar stills by of 25.35%, 18.42%, and 6.87%, respectively. The best absorbing material used was the bitumen in terms of water productivity; furthermore, the water produced by the charcoal unit was the best in term of quality because of its adsorbent and water's purifying role. The heat storage medium is a technique used to maintain the operating temperature of the absorber sufficiently high to produce distillate when the deficiency of sunshine, overnight, or when the solar irradiance is low.

Some investigators used different substances for energy storage in solar distillation systems. For example, Suneesh et al. [16] examined the use of absorber cement block within a "V" type basin solar still as a heat storage material in aim to improve the yield. This attempt enhanced the solar still efficiency by 4% compared to the conventional case. Sellami et al. [17] have used blackened layers of a sponge polyurethane-type glued in the basin as a means of energy storage; their experiments studied the influence of the sponge thickness on the daily outputs of the single-slope solar still. They found that the yield increased by as much as 57.77% and 23.03% for sponge layers' thicknesses of 0.5

and 1.0 cm, respectively. However, the daily output has been negatively observed with the sponge layer of 1.5 cm thickness by 29.95% compared with the conventional unit. They noted that the sponge plays an important role since that it increases the exchange surface and lowers solar rays' reflection.

Among the accelerators of the solar desalination process, we cite nano-fluids technologies which are the dispersions of metallic or non-metallic nano-particles of nano-metric size in a base fluid. Their presence in the liquid increases the thermal conductivity of the mixture and improves the process' performance [18,19]. The use of nano-particles in conventional solar stills increases the temperature of the salt water, and hence increases the heat transfer coefficients and therefore, the rate of evaporation; resulting in an increase of the productivity [20]. Madhu et al. [21] proved that the use of Al₂O₃ nano-particles with 0.2% concentration increases the water temperature by 7% and the productivity by 50% compared to conventional solar still. Ehab et al. [22] have used MnO₂ nano-particles and sponge as porous materials; they observed that the addition of MnO₂ nano-particles led to 68% of production's enhancement compared to the baseline case.

Comparison study is carried out by Omara et al. [23] between nano-particles of alumina and copper oxide comprising with external condenser and internal reflectors integrated with a corrugated wick solar still. Their results show that using CuO and Al₂O₃ nano-particles improves the productivity by around 105.1% and 74.88%, respectively.

Kabeel et al. [24] conducted an experimental investigation in order to increase the performance of single slope solar still by coating the absorber basin with a mixed of cuprous oxides nano material's and black paint; the two mixtures prepared with 100 and 400 g of CuO nano-particles at a fixed mass of 1 kg of black paint, that is, 10% and 40% as a weight fraction concentration; their experimental results illustrate that the productivity enhances by 25% with a mass concentration of 40% compared to a witness unit. This was explained by the increase occurred in the heat transfer coefficients between the absorber basin mixed of cuprous oxides nano-material's and saltwater within the solar still.

Photo-catalysis is a felicitous process with high significant interest for a wide range of applications concerning the environment and renewable (green) energy. In recent years, several scientific papers on semiconductors metal oxides, which are known by photo-catalysts and its applications, have been published. Mostly in the field of degradation of pollutants, process of water remediation, purification, and distillation [25,26]. Photo-catalysis is basically a natural phenomenon, combined with the use of solar energy; the solar desalination process is in perfect agreement with the principle of sustainable development [27].

Semiconductor-based photo-catalysts have a band of energy between its conduction and valence band. The photo-catalytic process is based on the excitation of a semiconductor by photons, whose energy is at least equal to that of the band gap; the electrons of the valence band pass to the band of conduction, leaving a positive charge or hole in the valence band. These pairs (electron/hole) can recombine by releasing heat. In the presence of water or air, the holes react with electron donors to produce oxidizing

species such as hydroxyl radicals. In the presence of organic and some inorganic compounds, the latter can give an electron to a hole and oxidize in the primary form of a radical cation [28].

Many investigations concerning photo-catalysis applications in solar desalination systems have reported since its utilization has a remarkable improvement on the overall efficiency. Within this axis, Sindal et al. [29–31] studied the influence of CdS, ZnO, and CuO as photo-catalysts on the performance of the still; they concluded that the metal oxides used, give encouraging results not only by improving the yield, but also in the quality of the distillate obtained due to the photo-catalytic and adsorption properties.

Sellami et al. [32] conducted an experimental investigation concerning improvement of solar still performance; this attempt consists of observing the effect of sand diameter's variation at a fixed mass on the still's yield; after this, they fixed the same diameter and change the sand mass in the second experiment. The results showed that for a fixed mass of sand, the improvement in the efficiency is inversely proportional to the diameter. The productivity in the distilled water for a fixed particle diameter improves with the increase of the sand's surface density (kg/m^2). They noted that the increase in production is due to the photo-catalytic property of sand because it contains a high percentage of silicon oxide (SiO_2) and other semiconductors.

Sellami et al. [28] used different layers of mixtures of equal masses of cement and alluvial sand in order to observe the photo-catalytic effect and heat storage medium in the improvement of absorber performance and therefore, the productivity of solar still. It is reported that the absorber coating with $1.811 \text{ (kg of mixing layer}/\text{m}^2 \text{ of absorber area)}$ improves the yield by 39.70% relative to the reference unit (witness) with high distillate quality; this is due to the adsorbent and photo-catalyst behavior of the mixture.

In the same context, to observe more the effect of photo-catalysts present in the cement on the quantity and the quality of distillate, Sellami et al. [33] realized another comparative study between two forms of cement adhesive layer and powder. They found that the rate of distillate improves by 51.14% compared to the conventional device, in the case of adding 150 g of cement powder; but the use of layered cement is more effective when the aim is to improve the quality of distillate.

According to previous research and findings, the importance of this experimental work lies in studying the behavior of metal oxides (semiconductors) called photo-catalysts which have a strong effect on the heat transfer process in solar desalination.

In the present work, we'll study the effect of using zinc oxide and copper oxide separately with different concentrations on the performance of single-slope solar still.

2. Experimental setup

2.1. Construction of solar stills

Three prototypes of identical solar stills designed, manufactured, and tested; one was used as a witness unit, while the parameters under study were applied to the others.

Fig. 1 shows a photo of the three single slope solar stills used in these experiments. Each solar still is made of



Fig. 1. Photo of experimental setup.

2 cm thick wood. Its basin is a plate ($60 \text{ cm} \times 40 \text{ cm} \times 5 \text{ cm}$) made with galvanized iron 0.2 cm thick. The absorbers of the three units have been blackened with a matt paint over their entire surface to ensure maximum absorption of solar irradiance and prevent any likely corrosion. The base of each assembly was further reinforced and insulated with 4 cm thick polystyrene to prevent heat loss toward the environment. The 0.3 cm thick removable glass cover of the stills has been tilted 30° with the horizontal to facilitate the flow of distilled water.

To prevent any vapor leakage, the glass cover has been sealed with silicone. Underground brackish water was supplied to each still from a reservoir via an adjustable float to maintain the desired brackish water level in the still. In our case, and according to our previous studies, the brackish water level in the basin is fixed at 1.5 cm.

The distillate leaves the lower side of the glass to be directed out of the enclosure and collected by graduated cylinders through plastic tubes.

2.2. Measuring tools

Several instruments are used in this experimental study to measure physical parameters of brackish and distilled water and meteorological parameters.

- Solar-meter to measure the solar irradiance (W/m^2).
- Thermocouples (K type) for measuring temperatures of different still parts ($^\circ\text{C}$).
- Thermometer for measuring input brackish water's temperature ($^\circ\text{C}$).
- Hygrometer for measuring the relative humidity (%), and the ambient temperature ($^\circ\text{C}$).
- Hot wire anemometer for measuring the wind speed (m/s).
- Analytical balance for weighing metal oxides mass (g).
- Graduates tubes for measuring the distilled water volume (mL).
- Multi-parameter (Hanna – HI9829, HANNA Instruments France Parc d'Activit es des Tanneries 1 rue du Tanin) for measuring water's pH, electric conductivity ($\mu\text{s}/\text{cm}$), salinity (%), and TDS (total dissolved solids) (mg/L).

The accuracy, range, and errors of the measuring tools are presented in Table 1.

2.3. Experimental procedure

All units (stills) were installed and examined in the Process Engineering Laboratory (PEL) at Ouargla University, south of Algeria, with long axes of the stills facing south-north direction in order to take in high solar radiation.

Each experiment started at 08 h:00 and terminated at 17 h:00 local time. During operations, the measurement of the followed parameters was made regularly:

- The temperature of inner surface of the glass cover;
- The temperature of the water (brackish water) inside the still;
- The temperature of the basin;
- Input brackish water’s temperature;
- The ambient temperature;
- Solar irradiance;
- Wind speed;
- Distilled water’s volume.

The main objective of this work is to study the effect and the behavior of the two metal oxides: copper oxide and zinc oxide on the still’s yield. The metal oxides (CuO and ZnO) were added separately with 20, 40, and 60 g into the single slope solar still’s absorber while the third unit remains as witness. The choice of these two oxides is that their molecular weights are closer which makes their concentrations very close and this facilitate the task of weighing and adding the same quantity if necessary in each unit.

Molecular weight for CuO and ZnO are, respectively, 79.55 and 81.38 g/mol. The water level in the basin is fixed at 1.5 cm, so the amount of brackish water within absorber is 3.6 L; their molar concentrations are respectively: 6.97×10^{-2} and 6.83×10^{-2} mol/L in the case of 20 g for example.

3. Results and discussions

Generally, the solar irradiance and the ambient temperature reflect the quality of a climate in any region. The increase in solar intensity is generally accompanied by an increase in ambient temperature. The maximum values of these two climatic variables are noticed during half of a sunny day for the hot season despite the fact that the wind and passing clouds sometimes contribute to the reduction of the ambient temperature. The shape of the ambient

temperature and solar irradiance curves is similar to a Gaussian curve.

For a chosen day (December 11th 2019), the maximum of solar irradiance recorded is 1,015 W/m² while the maximum value of the ambient temperature is 23.2°C. The mean values of the solar irradiance and ambient temperature are, respectively: 850.6 W/m² and 18.37°C (Fig. 2).

Figs. 3a–c show the different temperature of the three units under study: (unit with 60 g of CuO, that of 60 g of ZnO, and the witness); additionally, the ambient temperature (T_{am}) and that of the inlet of brackish water (T_{iw}) are also drawn. The temperature of the brackish water in the tank or otherwise that of the water inlet remains slightly high that the ambient temperature because the plastic (tank matter) isolates the water within from ambient conditions (cold air). The main difference between them remains around 2.82°C only.

Mean values of climatic parameters of the chosen day (December 13th 2019) are: 18.08°C for ambient temperature, 870.1 W/m² for solar irradiance and 2.15 m/s for the wind velocity.

Inside units, temperatures are relatively high because of the green house effect.

When the heat transfer by convection between the brackish water and the absorber is high, the temperature difference between brackish water and that of absorber-plate is close to one degree; this phenomenon is observed in the presence of metal oxides; contrariwise, the difference exceeds 1° in the witness still; then, it can be deduced that the added metal oxides have played the role of photo-catalysts since they enhance the convection transfer coefficient.

The maximum of absorber’s temperature (T_{ba}) recorded for the two units with metal oxides are close to 55°C compared to 53°C recorded with the baseline case.

Sometimes, we note that there are small anomalies observed between temperatures within the basin, this is mainly due to the non-agitation of the brackish water in the absorber (backwater) which in turn leads to their non-homogenization.

The mean temperature of the glass-cover (T_{gc}) recorded for the unit with 60 g of CuO, the unit with 60 g of ZnO

Table 1 Accuracy, measurement range and error limit for different measurement tools

Instrument	Accuracy	Range	Error %
Anemometer	+0.1 m/s	0–40 m/s	1.5%
Thermometer	+0.01°C	0°C–300°C	1%
Thermocouple	+0.1°C	0°C–100°C	1%
Solar meter	+1 W/m ²	0–1,500 W/m ²	<3% ± 1
Graduate tube	+10 mL	0–1,000 mL	1%

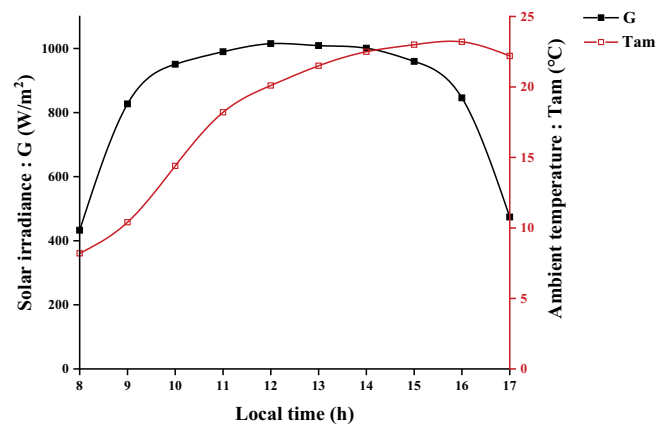


Fig. 2. Solar irradiance and ambient temperature recorded for December 11th 2019.

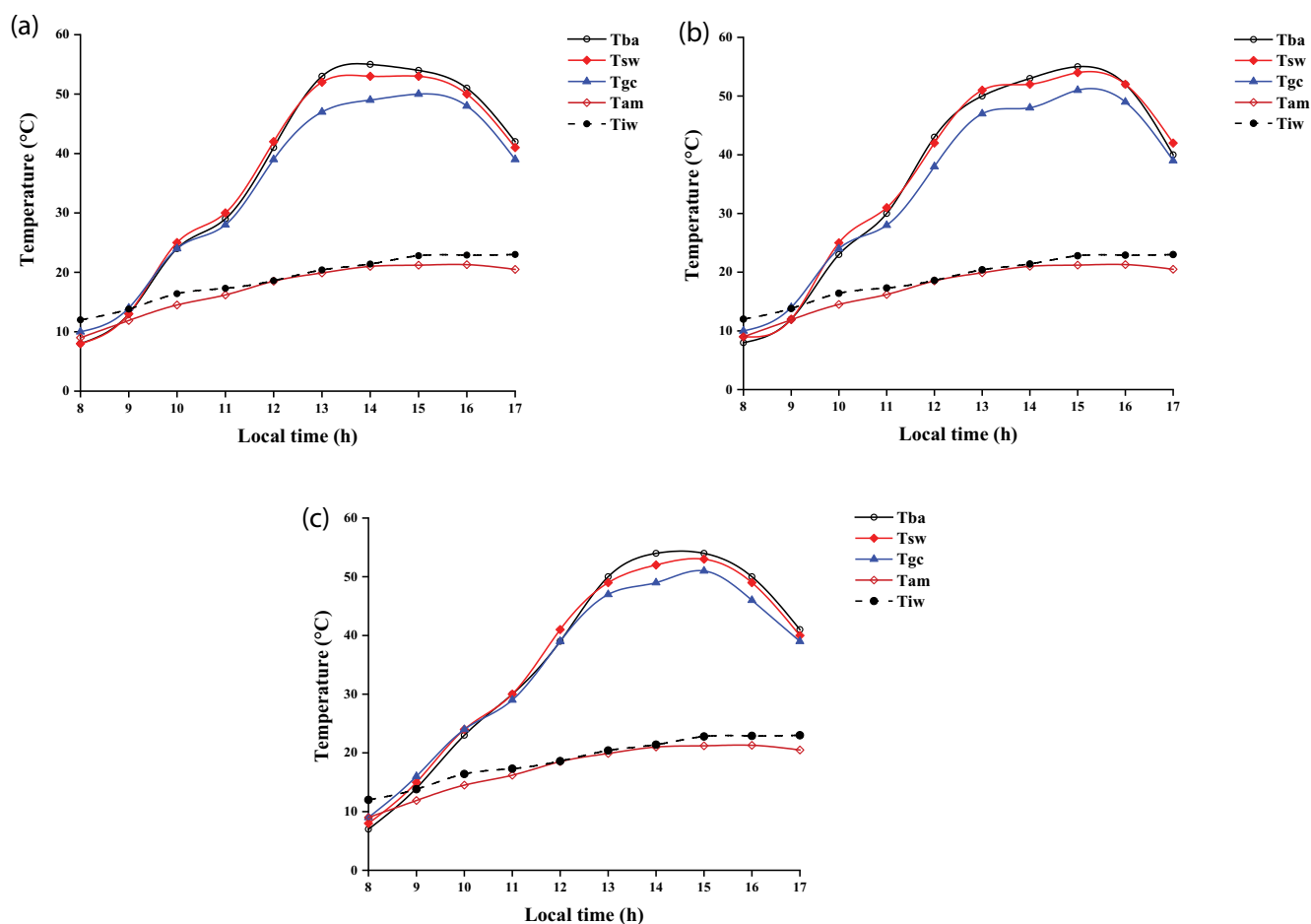


Fig. 3. Different temperatures of the still with 60 g of (a) ZnO (December 13th 2019) vs. local time, (b) CuO (December 13th 2019) vs. local time, and (c) witness (December 13th 2019) vs. local time.

and the witness are, respectively 35.0°C, 34.8°C, and 34.0°C. These temperatures reflect the amount of the condensation's heat of vapor which leads to the increase of its inner surface's temperature.

In this cold season (winter) the maximum of all units' temperature are recorded between 13 h:00 and 16 h:00 when the solar irradiance is high.

At the beginning of experiments (08 h:00), the temperature of all units are below 10°C; contrariwise the temperature of brackish water in the tank is 10.9°C because of the difference between the heat capacity of the tank and that of the still's absorber.

Figs. 4a–c show the hourly yield of the three units in the three cases: 20, 40, and 60 g of CuO and ZnO vs. local time.

Fig. 4a displays the hourly production of the three units in the case of adding 20 g of each metal oxide. The appearance of the distillate drops begins around 09 h:30 because the cold climate causes the decrease of water evaporation. Between 14 h:00 and 16 h:00, the hourly production of the still provided by ZnO is better than that of the still provided by CuO; in addition, all units produce more than 300 mL/(h m²); we must point out that in this period, the solar irradiance is high.

Maximum productions' values recorded for the three units are: 329.16, 320.81, and 166.66 mL/(h m²) for the units: ZnO, CuO, and the witness, respectively.

Fig. 4b shows the hourly production of the three units in the case of adding 40 g of each metal oxide. The same previous remarks can be reported but here in this case, the curve shows that the unit provided by CuO is the best.

In the second case, maximum productions' values recorded for the three units are: 283.33, 300.00, and 216.66 mL/(h m²) for the units: ZnO, CuO, and the witness, respectively.

Fig. 4c displays the hourly yield of the three units in the case of adding 60 g of each metal oxide. The same previous remarks can be reported but here in this final case, as the second case, the curve shows that the unit provided by CuO is also the best.

In this case, maximum values recorded for the three units are: 300.01, 308.33, and 266.66 mL/(h m²) for the units: ZnO, CuO, and the witness, respectively.

So, according to (Figs. 4a–c), in low amounts (20 g), the ZnO is better in term of photo-catalysis than CuO; but for the amounts: (40 and 60 g), the CuO becomes the best.

From the literature, CuO has a weakly basic behavior, but ZnO has an amphoteric behavior (neutral); so, in high

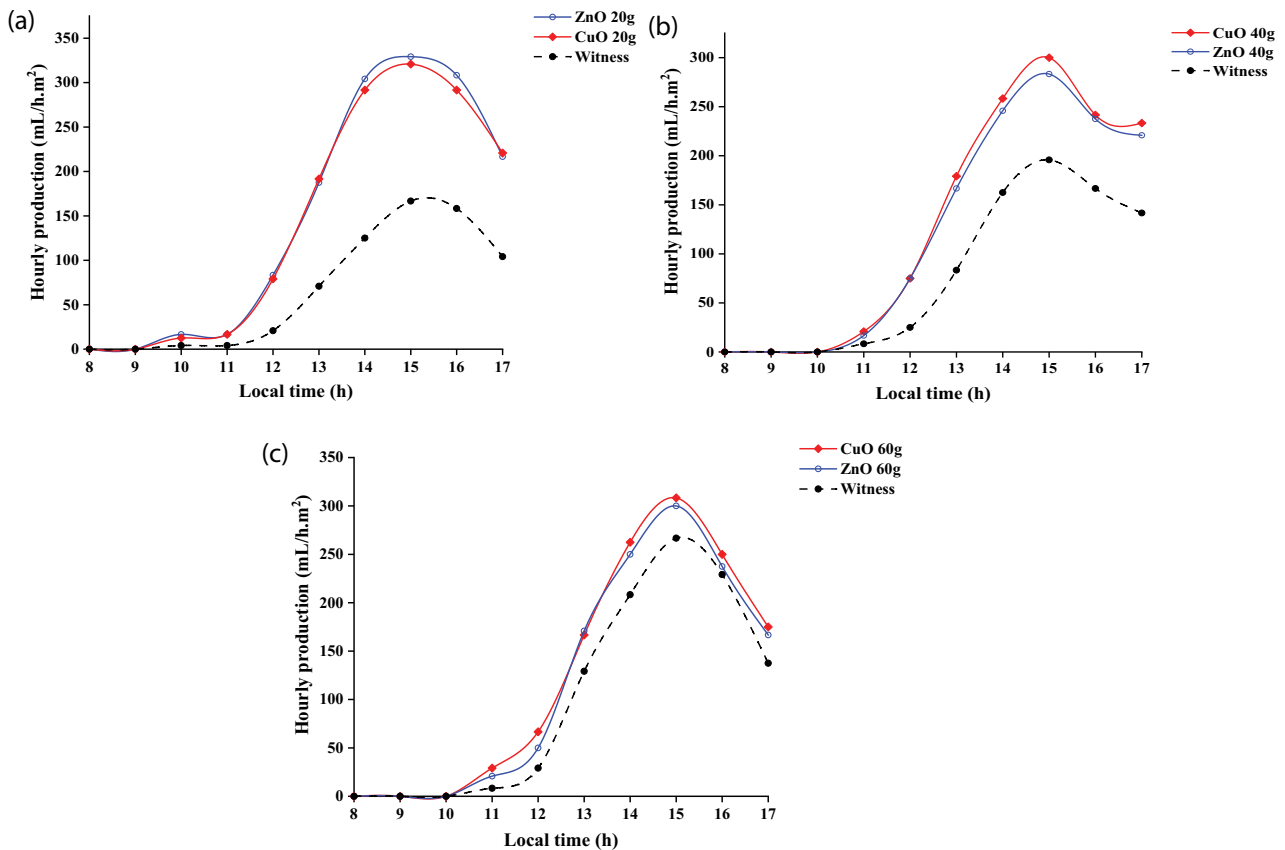


Fig. 4. Hourly production for different units with (a) 20 g ZnO, 20 g CuO and the witness vs. local time, (b) 40 g ZnO, 40 g CuO and the witness vs. local time, and (c) 60 g ZnO, 60 g CuO and the witness vs. local time.

concentrations of CuO (40 and 60 g), the aqueous medium is basic and it is possible that the photo-catalytic effect is better in basic medium.

Generally, the hourly production does not give a correct idea about the real daily yield; only the hourly cumulus of each unit can clarify this ambiguity.

Figs. 5a–c show the hourly cumulus (daily yield) of the three units in three cases: 20, 40, and 60 g of CuO and ZnO vs. local time. We point out that the mean value of the witness' yield which is: 815.41 mL/(h m²) is taken to calculate the enhancement of units' yield.

In the first case (Fig. 5a) when the two units are provided separately by 20 g of CuO and ZnO, it's clear that ZnO is slightly more effective than CuO. The yield recorded at the end of experiences is: 1,462.5 and 1,425 mL/m² for ZnO and CuO, respectively, compared with 815.41 mL/m² in the baseline case.

Fig. 5b presents the second case of 40 g of each metal oxide. Here, the phenomenon is reversed and the CuO becomes more effective than ZnO. The yield recorded in this case is lower than that of the first case; 1,308 and 1,245.8 mL/m² of distillate are produced by the units provided by CuO and by ZnO, respectively.

In the final case (Fig. 5c) when 60 g of each metal oxide are added, the CuO remains the most effective with 1,258 mL/m² of distillate compared with only 1,195 mL/m² produced by the still provided by ZnO.

Finally, from the three figures (Figs. 5a–c) it can be seen that CuO is more effective than ZnO for high masses (40 and 60 g) and the ZnO is the best photo-catalyst for low masse (20 g).

It should also be noted that the production decreases when metal oxides' quantity is increased; therefore, it is economically preferable to work with low quantities of metal oxides to obtain the best yields.

Fig. 6 presents the enhancement rate vs. the amount of ZnO and CuO. The gain in distillate increases with the decrease of the metal oxide's amount; otherwise, it is better to operate at low concentrations to obtain high yields. The best value calculated for the enhancement rate is 79.39% and 74.76% for ZnO and CuO respectively when 20 g of each metal oxide is added. Therefore, from an economic point of view, 20 g of ZnO, that is, 6.83×10^{-2} mol/L or (5.56 g/L) enhances the yield by of 79.39%.

4. Summary

Table 2 summarizes the major results.

5. Water analysis' results

To determine the quality of water before and after distillation, several parameters namely: salinity, pH, TDS, and electrical conductivity are analyzed. Table 3 summarizes the

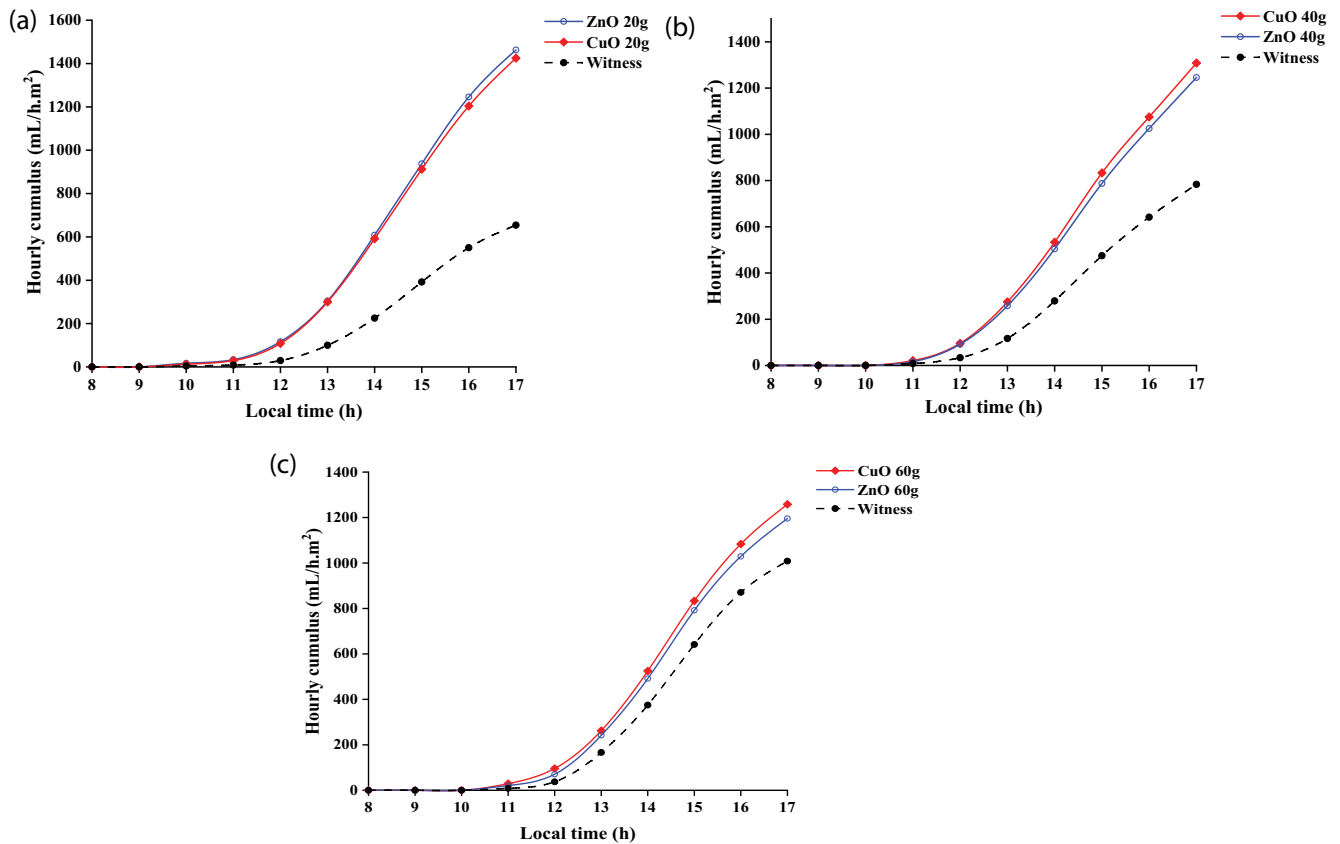


Fig. 5. Hourly cumulus for different units with (a) 20 g ZnO, 20 g CuO and the witness vs. local time, (b) 40 g ZnO, 40 g CuO and the witness vs. local time, (c) 60 g ZnO, 60 g CuO and the witness vs. local time.

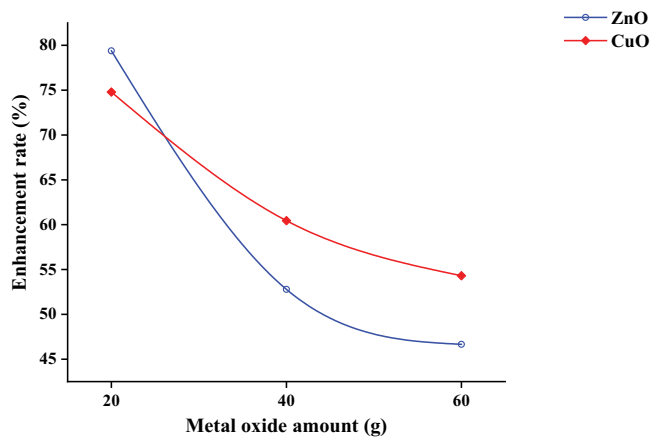


Fig. 6. Enhancement rate (%) for the two units vs. the metal oxide's amount.

Table 3
Results of water analysis

Water quality	Salinity (%)	Conductivity (µs/cm)	TDS (mg/L)	pH
Brackish water	02.1	2,895	1,943	8.10
Witness	00.03	02.33	6.00	7.01
(CuO and ZnO) units	00.02	02.12	4.19	6.98

values of these analyzes. The results show that adding photo-catalysts improves the quality of the distillate because of the second adsorbent behavior of these metal oxides. The quality of water produced by units provided by CuO and/or ZnO is purer than that produced by the conventional unit.

Table 2
Summary of major results

Mass (g)	20		40		60		Witness
Photo-catalyst	CuO	ZnO	CuO	ZnO	CuO	ZnO	0
Yield (mL/m ² d)	1,425	1,462.5	1,308	1,245.8	1,258	1,195	815.41
Enhancement (%)	74.76	79.36	60.41	52.78	54.28	46.55	0%

Table 4
Comparison of results

Authors name	Location	Experimental method	Enhancement rate (%)
El Hadi Attia et al. [34]	El Oued, Algeria	CuO Nanoparticule	26.34%
Sathyamurthy et al. [35]	Chennai, India	SiO ₂ Nanoparticule	34.3%
Sathyamurthy et al. [36]	Chennai, India	TiO ₂ Nanoparticule	40%
		MgO Nanoparticule	60%
Mohamed Thalib et al. [37]	Chennai, India	Paraffin wax and nano-graphene	81%
Present study	Ouargla, Algeria	ZnO metal oxide	79.36%
		CuO metal oxide	74.76%

6. Comparison results

Table 4 presents a comparison of the results obtained with some other recent results carried out by investigators around the world. It is clear that the results obtained are encouraging.

7. Conclusion

As part of the contribution to solve the shortage of fresh water in southern Algeria where the sun reigns throughout the year, three single-slope solar stills are installed at the University of Ouargla. Generally, the yield of conventional units is low; our goal in this investigation is to improve this yield by the photo-catalysis effect.

Two semiconductors of close atomic masses (ZnO and CuO) were added separately with the same concentration in two different units with variable masses in order to compare their behavior and their production with that of the witness unit.

20, 40, and 60 g of each metal oxide are added separately within the absorber of each unit containing a constant volume of 3.6 L of local brackish water and exposed to the sun rays.

The results show that the two metal oxides are more effective as photo-catalysts at their low concentrations.

The addition of 20 g of ZnO and 20 g of CuO separately within the absorber of the two different units, improves the daily yield by about 79.39% and 74.76%, respectively, compared to the baseline case.

After analysis and because of the double roles that play both of CuO and ZnO as photo-catalysts and adsorbent materials, the distillate produced by their units is purer than that produced by the conventional unit in the same atmospheric conditions.

Symbols

G	—	Solar irradiance, W/m ²
T_{am}	—	Ambient temperature, °C
T_{ba}	—	Absorber temperature, °C
T_{iw}	—	Inlet water temperature, °C
T_{sw}	—	Brackish water temperature, °C
T_{gc}	—	Glass-cover temperature, °C

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