Seawater desalination using distillation method based on convex lens and Ag doped ZnO thin film to improve freshwater productivity and quality

R A Nugroho1, H Ma’rufah1, I M Khusna1, Y Wahyono1 and H Sutanto1
1 Physics Departement, Diponegoro University

Abstract. Water is the most important need to support human life. Potentially, seawater is an alternative solution to solve water crisis problem especially in coastal areas. However, seawater have 3.5% salinity level. Water with high salinity is certainly not consumable. One effort that can be done to overcome the clean water crisis in the coastal areas is through desalination of seawater to produce water with low salinity. Some of the desalination methods that ever existed were MSF (Multi Stage Flash Distillation) and Reverse Osmosis. But both of these methods have high investment cost. Therefore, a cheaper and easier method to apply such as distillation is required. Distillation is done by drying the seawater under the sun which triggers the evaporation of water that evaporates and condenses to obtain freshwater. In this research, distillation system is combined with convex lens and Ag doped ZnO thin film. The convex lens is a lens that can focus heat and sunlight after passing through the lens. The use of the convex lens in the distillation system can speed up the evaporation process of seawater. The distillation system is made of glass and aluminum. Ag doped ZnO thin film was synthesized from AgNO3 and ZnCH3COOH by sol-gel method. Based on photocatalyst activity, when the Ag doped ZnO thin film is exposed with visible light, it will form a superoxide compound that can degrade pollutant such as heavy metals, eliminating harmful microbes and bacteria. This material also has a hydrophilicity that makes the water absorbed by the material coated with the thin film. With this characteristic, it can make the water more easily move on the glass due to the influence of gravity. Tests carried out include characterization of a thin layer of Ag doped ZnO, evaporation rate and water quality. From this technology, it can increase the production of freshwater and quality from the seawater desalination process with distillation method.

1. Introduction
Water is an essential matter that is much needed for the sustainability of living organisms. But, the provision of freshwater is becoming an increasingly important issue along with the increase of population, especially in coastal areas. The problem is particularly significant in developing countries and in arid areas where water sources are scarce. The 97% of water on the Earth is salt water, leaving only 3% as fresh water of which slightly over two thirds is frozen in glaciers and polar ice caps [1]. The remaining unfrozen fresh water is mainly found as groundwater, with only a small fraction present above ground or in the air.

Potentially, seawater is an alternative solution to solve water crisis problem especially in coastal areas. However, seawater have high salinity level that make the water cannot be directly used without any processing first. In addition, freshwater content is also declining due to sustainable development without regard to the environment so as to minimize the area of infiltration of rainwater. The
freshwater content in the soil is dwindling as it is taken continuously so that more seawater is absorbed into the soil replacing the freshwater position [2].

The average seawater in the world's oceans has a salinity of 3.5%, which means that for every liter of seawater there are 35 grams of salt dissolved in it. The main salt content found in seawater include chloride (55%), sodium (31%), sulfate (8%), magnesium (4%), calcium (1%), potassium (1%), and the rest (less than 1%) consisting of bicarbonate, bromide, borax acid, strontium, and fluoride. The presence of these salts affects the physical properties of seawater such as density, compressibility, and freezing. Water with salinity is certainly not consumable.

Seawater with a high salinity level can actually be used as one solution to meet the needs of clean water by separating the content of mineral salts dissolved with water through desalination. Desalination technologies have been used rapidly over the past few decades throughout the globe to produce clean drinking water from seawater to improve the quality of already existing supplies of freshwater for human consumption. Several methods of water desalination ever existed were MSF (Multi Stage Flash Distillation) and Reverse Osmosis. But the disadvantage of these two methods is to have a high investment cost [3]. Therefore, the cheaper and easier method such as distillation is required.

One of the desalination methods available is distillation. Distillation is done by drying the seawater under the sun which triggers the evaporation of water that evaporates and followed by condensation to obtain freshwater. However, the conventional distillation method takes a considerable amount of time and much water falls back into the evaporative container during the condensation process [4].

Increasing the temperature difference between the water-glass cover is the main focus when trying to improve the rate of condensation, and consequently, the productivity of the evaporation is increased. This can be done by either decreasing the glass cover temperature or increasing the water temperature. The continuous supply of water film is fed over the glass cover in order to reduce the glass temperature. But this method requires raising the water container to the level of the highest part of the distillation system or using water pump continuously. Therefore, the use of convex lens on the glass cover in the distillation system is a right solution. A convex lens is a lens that can focus heat and sunlight after passing through the lens. Exploiting the nature of this convex lens placed in the distillation system can speed up the increase of water temperature and water evaporation.

The removal of organic pollutants from seawater is an important purpose of environmental protection especially for freshwater production. Water has been disinfected by many methods such as physical and chemical (boiling, UV treatment, filtration, chlorination, iodine treatment, etc.). However, chemical reagents cost may render such options unavailable to low income families. Physical treatment requires materials that may not be easily acquired or purchased [5]. One alternative method that has been proposed is photocatalysis under sunlight, a process that is simple and easily utilized [6].

ZnO based photocatalyst has attracted much attention due to its application in decolorization of hazardous pollutants such as dyes, chemicals, and toxic gases. Since UV light accounts for only 3-5% of the sunlight, the wide bandgap character of pure ZnO photocatalyst limits the utilization of complete solar energy [6]. Visible-light-driven photocatalyst has attracted much attention recently. Metal-doped ZnO photocatalyst exhibited improved photocatalytic property, such as Ag modified ZnO nanostructures. Silver can interact with visible-light by means of the resonance of the free electrons within the particles. The Ag can act as acceptors in ZnO and may change Zn ions. Moreover, the addition of Ag ions can also reduce the energy gap in semiconductor so it can increase the absorption of light wavelength [8].

The goal of this study is to develop a optimize the freshwater productivity by distillation method using convex lens and Ag doped ZnO thin film as photocatalyst with good visible-light driven activity and effectively solve desalination by distillation method problem. The use of convex lenses and Ag doped ZnO thin film can increase the speed of seawater evaporation and improve freshwater...
productivity and quality. Light driven activity and effectively solve desalination by distillation method problem. The use of convex lenses and Ag doped ZnO thin film can increase the speed of seawater evaporation and improve freshwater productivity and quality.

2. Materials and Methods

2.1. Materials

All chemicals were reagent grade and were used without further purification. Zinc acetate dehydrate (Zn(COOCH₃)₂H₂O as precursor of ZnO, Isopropanol ((CH₃)₂CHOH), and monoethanolamine (C₂H₇NO) as a solvent and stabilizer.

2.2. Fabrication of Ag doped ZnO thin films

The sol-gel method was used to prepare ZnO and Ag-doped ZnO thin films. Zinc acetate dihydrate, Zn(COOCH₃)₂H₂O, was dissolved in 2-propanol (CH₃CH(OH)CH₃) at room temperature to obtain 0.3 M solution. Then, monoethanolamine (MEA) was added dropped-wise into the solution while stirring for 30 min at room temperature to obtain a clear solution of ZnO. In case of AG doped ZnO thin films, AgNO₃ solution was mixed with the clear solution of zinc acetate dihydrate in order to yield 4% Ag/Zn weight ratios.

Before deposition, glass substrates were cleaned by the Radio Corporation of America (RCA) method. In this method, glass substrates were cleaned by acetone and methanol for 10 min. An ultrasonic cleaner was used to wash dust and oil out. Then, we immersed the glass slide into the double-distilled water for 8 min and dried the substrates off using a compressor gun. The obtained solutions were sprayed onto glass substrates for 1 hour at 450 °C. Furthermore, the films were annealed at 450 °C for 1 hour.

![Schematic of fabrication Ag doped ZnO thin film](image)

**Figure 1.** Schematic of fabrication Ag doped ZnO thin film.

2.3. Distillation Process

The experimental setup consist of mainly two part [1] ; (i) solar still and (ii) condensation roof. Convex lenses are patched on outside part of the condensation roof and the Ag doped ZnO thin films on inside part. The distillation process was carried out on a lab scale. 30 ml seawater was inserted into
a beaker glass and then covered on top with a glass coated with Ag doped ZnO thin film and a convex lens. The distillation data was taken at 10.00 AM.

![Distillation Process Diagram](image)

**Figure 2.** Schematic diagram of distillation process.

### 2.4. Optical Characterizations of Prepared Thin Films

The X-Ray Diffraction (XRD) analysis of the samples was performed at room temperature by diffractometer (Philips diffract meter (40 kV, 30 mA) with nickel filter and copper radiation. The Optical absorbance of the thin films was performed by UV-Vis spectrophotometer (JASCO V500, Japan).

The SEM (Scanning Electron Microscopy) analysis of the thin film was performed by JSM 6510. The digital microscope was used to analyze the hydrophilicity of the thin film. To find out the hydrophilicity properties of the synthesized thin film, it was measured the contact angle between the surface of the thin film and the water molecules dripped on the surface of the thin film.

### 3. Result and Discussion

#### 3.1. UV-Visible Spectrophotometer Analysis

UV-Visible light absorbance spectra provide useful information about the band gap of semiconductors. The recorded absorbance spectra of ZnO and Ag doped ZnO thin films deposited on glass substrate in range 200-800 nm are shown in Figure 3. ZnO exhibited a UV absorption band at 310 nm. The presence of Ag dopant on the photocatalyst can influence the optical properties of the ZnO and shift the absorption peak towards the visible light range of the spectrum. The absorption edge of ZnO was drastically extended to the visible light region due to the surface plasmon resonance absorption of Ag nanoparticles. A new absorption peak at around 370 nm is clearly observed, which should be ascribed to characteristic of Ag nanoparticles absorption [9]. This shift shows electron movement from metallic Ag levels to ZnO nanoparticles and influences the formation of silver with unit valance.
3.2. X-Ray Diffractogram (XRD) Analysis
The XRD pattern of prepared thin films fabricated by sol-gel method on glass substrates is shown in Fig. 1. All the peaks of the ZnO thin films were confirmed using JCPDS 36-1451. The thin films show evidence of polycrystalline structure, which is a hexagonal wurtzite structure. For the sample, (002) and (220) diffraction peaks are observed. The (002) orientation is the main peak in the spectra. This indicated that the films had a strong preferred orientation toward c-axis. Ag is attributed to the increase of ZnO c-axis lattice constant caused by substitution of Zn^{2+} ions by Ag^{+} ions [10].

3.3. SEM (Scanning Electron Microscopy) Analysis
SEM images of ZnO and Ag-doped ZnO thin films were shown in Fig. 4 with magnification 10000 X. There is a significant change in the surface morphology of Ag-doped ZnO thin film. It can be seen that ZnO thin film has a rod-like morphology and Ag-doped ZnO has a porous surface which is important for the photocatalytic application. The Ag content strongly affects the ZnO surface, and the same
result was obtained by Habibi et al. [12] which used the sol-gel and photochemical method to obtain the films.

![SEM image of ZnO (a) and Ag doped ZnO (b)](image)

**Figure 5.** SEM image of ZnO (a) and Ag doped ZnO (b)

### 3.4. Hydrophilicity of thin film analysis

![Hydrophilicity of glass surface (a) ZnO thin film (b) and Ag doped ZnO thin film (c)](image)

**Figure 6.** Hydrophilicity of glass surface (a) ZnO thin film (b) and Ag doped ZnO thin film (c)

Figure 6 shows that coating the ZnO thin film on a surface of the glass will decrease the contact angle between the surface of glass and water molecules, that is 56,629° from 61,70°. Then, doping of Ag on ZnO will decrease the contact angle become 52,196° and increase the hydrophilicity of thin film.

The mechanism of hydrophilicity of thin film is via irradiation by the visible light with photon energy, higher than or equal with the bandgap energy of the semiconductor, the electrons (e−) in the valence band are excited to the conduction band. The same number of the holes (h+) are simultaneously generated in the valence band [10].

\[ \text{ZnO} + \text{hv} \rightarrow 2\text{h}^+ + 2\text{e}^- \text{CB} \]  

Some of the holes react with lattice oxygen (O2−) to form surface oxygen vacancies O2− (surface trapped hole), while some of the electrons react with lattice metal ions (Zn2+) to form Zn+ defective sites (surface trapped electrons).

\[ \text{e}^- + \text{Zn}^{2+} \rightarrow \text{Zn}^+ \text{ (surface trapped electrons)} \]  
\[ \text{O}^{2-} + \text{h}^+ \rightarrow \text{O}^- \text{ (surface trapped hole)} \]  
\[ \text{h}^+ + \text{O}^- \rightarrow 1/2\text{O}_2 + \text{V}_o \text{ (oxygen vacancy)} \]

Water and Oxygen may compete to dissociatively adsorb on these defective sites. The surface trapped electrons (Zn+) tend to react with oxygen molecules adsorbed on the surface.

\[ \text{Zn} + \text{O}_2 \rightarrow \text{Zn}^{2+} + \text{O}^- \]

At the same time, the water molecules may coordinate into the oxygen vacancy sites, which cause the dissociative adsorption of the water molecules on the surface. Hence, the surface becomes more hydrophilic because water can easily fill in the existing void and produce adsorbed OH groups. In the style of Van der Waals and hydrogen bonds, the OH groups can bind to water on the surface [14]. The effect of Ag on hydrophilicity show that the Ag can reduce the water contact angle of this thin film. The doping of Ag on ZnO particles effectively increase the photon energy absorbed in the
photocatalytic process under the sun. Owing to the surface plasmon resonance effect, the presence of sAg may induce the absorption in the visible light region [15] which was proved by UV-Visible absorption spectrum of Ag doped ZnO on Figure 3. As a consequence, the absorption in the visible light region should increase the visible light response of Ag doped ZnO. Moreover, silver metal deposited on the surface of ZnO can induce the Schottky barrier at the interface between silver Ag and ZnO. It prevents photogenerated electrons to migrate to the surface by promoting the charge separation and the photocatalysis of semiconductor [16].

3.5. The Effect of convex lenses on Distillation Process
Table 1 shows that the use of convex lens can heat glass which is indicated by the temperature change of 10°C for 10 minutes. However, on its application to the distillation of seawater, there is no temperature change for 3 minutes in water.

Table 1. Effect of convex lens on temperature change of glass and water during the distillation process.

| No | Tested characteristic                                      | Before Distillation | After Distillation | Time   |
|----|------------------------------------------------------------|---------------------|--------------------|--------|
| 1  | The temperature of Glass filled no water with the convex lens (°C) | 36                  | 36                 | 10 minutes |
| 2  | The temperature of Glass filled no water without convex lens (°C) | 36                  | 46                 | 10 minutes |
| 3  | The temperature of Water in Glass with the convex lens (°C)   | 70                  | 70                 | 3 minutes  |
| 4  | The temperature of Water in Glass without convex lens (°C)   | 70                  | 70                 | 3 minutes  |

The convex lens concretize the solar radiation at their focus on the surface of radiating water. It will increase the water temperature and decrease the glass cover temperature. Thus the temperature difference between the water and glass increase. The temperature difference between the water-glass cover will improve the rate of condensation and consequently the productivity of freshwater is increased [17]. However, there is a discrepancy between the data obtained and the theory. There is no change in water temperature after desalination process using convex lens. This is due to less warming time. Short heating time causes the heat received to be mainly still distributed in beaker glass. Glass material has small conductivity, that is 1.1 W/(m.K). It means that the glass material is not good enough in conducting heat which causes the amount of heat received to be impossible for heat transfer due to short heating time [18].

3.6. Water Quality Analysis
Photocatalytic activity on distillation process shown on table 2. The data show that there are quality improvement on the distilled water with photocatalytic activity. The photocatalytic process occurs when the Ag doped ZnO material is irradiated by light that its energy is greater than the gap energy of ZnO.
### Tabel 2. Result of the distillation process.

| No | Tested characteristic | Unit   | Standard Quality | Control Water | Distilled Water | Distilled water with photocatalytic treatment | Efficiency (%) |
|----|-----------------------|--------|------------------|---------------|-----------------|-----------------------------------------------|----------------|
| 1  | Total Dissolved Solids| mg/L   | 500              | 5800          | 388             | 201                                           | 96.53          |
| 2  | pH                    | -      | 6.5 – 8.5        | 4.9           | 6.8             | 6.9                                           | 40.8           |
| 3  | Electric Conductivity  | mS     | -                | 18.5          | 0.3             | 0.3                                           | 98.37          |
| 4  | Salinity              | ppm    | 600              | 26.4 x 10^6   | 519             | 534                                           | 99.99997       |
| 5  | Total Coli            | ppm    | 0                | 58000         | 6400            | 1400                                          | 97.58          |
| 6  | Pb                    | ppm    | 0.05             | 0.399         | 0.072           | 0.070                                         | 81.95          |
| 7  | Cu                    | ppm    | 1.0              | 0.03          | 0               | 0                                             | 100            |
| 8  | Cd                    | ppm    | 0.005            | 0.121         | 0.053           | 0.048                                         | 60.33          |

Photogeneration of the electron-hole pair between conduction and valence bands is generally responsible for pollutant degradation on distilled water in the photocatalytic decomposition process. The mechanism of pollutant degradation on photocatalytic activity is going by photogenerated $h^+$ in valence band which reacts with either H$_2$O or OH$^-$ to produce HO$^*$ [19]. It can be seen from the following reaction:

\[
h^+ + H_2O \rightarrow OH^* + H^+ \quad (6)
\]

\[
h^+ + OH^- \rightarrow OH^* \quad (7)
\]

Electrons in the conduction band react with absorbed O$_2$ on the Ag doped ZnO thin film surface to generate O$_2^*$ and according to the following steps leads to generate HO radicals [20]:

\[
e^- + O_2 \rightarrow O_2^- \quad (8)
\]

\[
2O_2^- + H^+ \rightarrow HO_2^- + O_2^- \quad (9)
\]

\[
2H_2O_2 \rightarrow H_2O_2 + O_2 \quad (10)
\]

\[
H_2O_2 + O_2^- \rightarrow HO^- + OH^- + O_2 \quad (11)
\]

\[
H_2O_2 + O_2 \rightarrow HO^- + OH^- \quad (12)
\]

By these reactions, either electrons or holes of photogenerated electron-hole pairs can produce hydroxyl and superoxide radicals that can subsequently degrade organic compound. Whether degradation occurs predominantly due to reaction with free-radicals or directly with the holes themselves is controversial, with some groups even proposing a predominant electron-based catalytic pathway on ZnO single-crystal surfaces [21].
Figure 7. Schematic diagram of pollutant degradation reaction mechanism over the surface of Ag doped ZnO nanoparticles

Pollutant degradation activity of Ag doped ZnO thin film is caused by the increase of $O_2^-$, $OH^-$, and $H_2O_2$. ZnO is a p-type semiconductor, which has more hole concentrations than n-type semiconductors, resulting in increased hole density and more radical ($OH^-$) hydroxyl formation. The $OH$ reactivity is higher than that of $O_2^-$, which can be seen from the number of valence electrons, where $OH^-$ lacks one electron while the $O_2^-$ excess of one electron makes the $OH^-$ more likely to achieve equilibrium.

The improved activity of Ag doped ZnO make the charge separation better. The presence of Ag ions was reported to be able to enhance the photocatalytic activity since $O_2^- - Ag^+ - O_2^-$ joints can trap the photoelectrons to form $O_2^- - Ag^- - O_2^-$ joints and then react with surface of absorbed oxygen molecules [22].

The incorporation of metal such as Ag onto the ZnO surface increases the rate of electron transfer to dissolved oxygen [23]. Ag particles act as recombination centers at high silver content and prevent the recombination of photogenerated electron-hole, which is caused by electrostatic attraction of negatively charged silver and positively charged holes [24]. The interaction between Ag and ZnO was proposed, which could regulate the position if Fermi level of Ag and ZnO and result in the formation of a new Fermi level might be tunneled to the conduction band, because the conduction band of ZnO was empty [16].

4. Conclusion
Seawater desalination using distillation method based on convex lens and Ag-doped ZnO thin films has been successfully done. A systematic study on the effect of convex lens and Ag doped ZnO content on the morphological and optical properties of thin films, the hydrophilicity of thin films, the temperature change of seawater during distillation and photocatalytic activity of thin films has been performed. The doped Ag remarkably facilities the electron transfer rate of the Ag doped ZnO and enhanced the optical characteristic of Ag doped ZnO thin film and improve the hydrophilicity, although it slightly diminished the surface roughness of ZnO thin film. Concurrently, the use of convex lens has no effect to water in a short time. However, the experimental result shows that seawater distillation with photocatalyst and convex lenses is better than conventional seawater distillation method.

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