Abstract—This study presents the results of light and temperature impact assessment on the efficiency and stability of natural dye-sensitized solar cells (DSSCs). It investigates also the impact of light and temperature on the absorbance, changes in functional groups, and the energy levels of the curcumin natural dye. The natural dyes and DSSCs were irradiated and heated at a temperature of 50°C for 0, 100, and 200 hours and examined by the ultraviolet-visible (UV-Vis) spectrophotometry, the Fourier transform infra-red (FT-IR) spectroscopy, and cyclic voltammetry test. The results show that the light and heat treatment at 50°C for 100 and 200 hours cause the decreasing voltage, current, and efficiency of DSSCs more than 89%. Interestingly, the DSSC with curcumin-dye subjected to heat and light treatment did not have a significant decrease in the value of fill factor (FF). It shows that the quality of the junctions in the DSSCs is good and the physical structure of DSSCs is stable. It can be stated that the performance of DSSCs decreases when subjected a light and heat treatment is due to the changes of HOMO and LUMO levels of curcumin dyes.

Keywords—curcumin, efficiency, natural dye, natural dye-sensitive solar cells, stability.

1. INTRODUCTION

Natural dyes as sensitizing agent in dye-sensitized solar cells (DSSCs) are very promising because they are widely available, renewable, and inexpensive. Natural dyes of rosella-flower, blue pea-flower, papaya-leaf, red Sicilian-orange fruit, bramble, and curcumin have been used for DSSCs and generate electric energy with efficiencies of 0.37% [1], 0.05% [1], 0.09-0.28% [2],[ 3], 0.66% [4], 0.71% [5], and 0.36% [6], respectively. However, the efficiency of DSSCs based on natural dyes including curcumin-dyes is still low compared with DSSCs based on synthetic dyes. Curcumin {1,7-bis (4-hydroxy-3-methoxyphenyl)-1, 6-heptadiene-3, 5-dione} is a yellow dye found in plants such as ginger and turmeric rhizome with a functional group shown in Figure 1. It absorbs visible light at a range of wavelength 420-580 nm [7]. Similar nature of the other natural dyes, curcumin-dyes are also degraded by light, oxidizing agents, and acidity. Moreover, curcumin is also unstable and can undergo hydrolysis degradation very quickly in an alkaline medium with a half-life of 1.45 hours [8]. In contrast, adding acetic acid into curcumin-dye solutions can increase the stability and the efficiency of DSSCs. Furthermore, curcumin-dyes which have functional groups such as phenolic, carbon-carbon double bonds, hydroxyl, and methoxy and are stable within a range of temperature are attracting to be developed and investigated for DSSCs application.

Fig 1. Curcumin group [7].

The stability of natural dye-sensitized solar cells that use anthocyanin [9], [10], [11] and chlorophyll [12], [2] as sensitizer agent has been investigated. The stability of curcumin-dyes regarding to an anti-oxidant agent in pharmacy field has also been reported [11]. Curcumin-dyes were also investigated in relation to the effect of metal-complex modification [13], solvent [14], encapsulation [8], and acidity [15] on the efficiency of DSSCs. The stability of curcumin dyes from light is a big issue because of the existing of an active methylene group (-CH₂-) between two ketone groups in curcumin dyes. Light also causes a photochemical degradation. Unfortunately, studies to investigate the stability and efficiency of DSSCs with natural dyes, especially curcumin-dyes in relation to the effect of light and temperature are limited. Moreover, the investigation on the stability and efficiency of DSSCs when using curcumin natural dyes is new and we discussed it from the experience of absorbance level, FTIR, and energy level of dyes which are rarely discussed previously.

Therefore, we report the impact of light and temperature on the absorbance, changes in functional groups, and the energy levels of the curcumin natural dye. The specific objective was to analyze the impact of light and temperature on the efficiency and stability of natural dye-sensitized solar cells (DSSCs).
2. MATERIALS AND METHOD

The DSSCs sensitized by curcumin dyes have been developed. The DSSCs were constructed from fluorine-doped tin oxide (FTO), counter electrode, photo-anode layer, electrolyte salt, N719 dyes, and curcumin dyes. The materials used for synthesizing the FTO glass were tin(II)chloride (SnCl₂·2H₂O, Merck, Germany), ammonium fluoride (NH₄F, Merck, Germany), and ethanol (96%, Merck, Germany). The materials mixed and deposited onto glass by a spray pyrolysis method [16]. The produced FTOs have the sheet resistance of 20 Ω/cm² and the transmittance of 75%.

The counter electrode was fabricated by sputtering the platinum on to FTO glass. The target and the FTO substrate is 404 Volts with a current of 125 mA. High voltage differences under low pressure vacuum chamber. The potential difference between the platinum surface. The atoms lead to FTO substrate having a potential difference opposite to platinum. Therefore, the platinum atoms stuck on to the surface of the FTO substrate. The substrate was rotated at a rotational speed of 5 rpm to produce a uniform deposition. Sputtering process was done for 20 minutes.

Meanwhile, the materials used to manufacture the photo-anode layer were TiO₂ (nanopowder, 21 nm, Sigma-Aldrich) and ethyl alcohol (96%, Merck, Germany). The photo-anode semiconductor layer was made of TiO₂ (Nano powder, 21 nm Sigma-Aldrich) with a screen printing method. TiO₂ of 0.5 g and ethanol of 0.4 ml were mixed, stirred, and formed to a paste solution. The thickness of the photo-anode semiconductor layer on the FTO glass is 20 μm. Furthermore, the TiO₂ layer was attached onto the FTO. The sintering process was then conducted at a temperature of 450°C for 2 hours to enable the interlock bonding between the FTO and TiO₂ semiconductors. The photo-anode layer attached on the FTO glass with an active area of 1 cm x 1 cm was soaked in the curcumin-dye solution for 24 hours at room temperature.

The materials used for the electrolyte salt were sodium iodide (NaI, 99.95% pure, Merck), iodide (I₂, 99.95% pure, Merck), and tungstophosphoric acid hydrate (H₃OPO₄PW₁₂·xH₂O, Merck). Electrolytes used in this study is composed of NaI of 3.3 g, I₂ of 523.875 mg, HPA of 5.481 mg, and acetonitrile of 30 ml. NaI was dissolved into acetonitrile and stirred for 15 minutes. Afterwards, I₂ was added into the solution, stirred for 15 minutes, followed by adding HPA, and stirred again for 4 hours.

2.1 Curcumin

The curcumin was extracted from turmeric roots with ethanol (96%, Merck, Germany) as a solvent. The turmeric powder and ethanol with a ratio of 1:7 were extracted using maceration method for 7 hours at a temperature of 70°C followed by thickening in a rotary vacuum evaporator. The result of extraction process is curcumin extract.

Next process is to isolate curcumin compound by using a column chromatography filled with silica gel as explained in the previous procedures [17]. The mixture of chloroform and ethanol at a ratio of 95:5 was dripped in the chromatography column followed by a separation based on polarity level indicated by the color difference. The extracted curcumin exhibits a reddish yellow color. The curcumin was then separated from its solvent by using a rotary vacuum evaporator. The curcumin dye for DSSCs has a concentration of 8 g/100 ml. The characterization of dyes was performed by UV-1800 UV-Vis Rayleigh, FTIR IR Prestige-21 Shimadzu, and cyclic voltammetry μAUTOLAB TYPE II Ω Metrohm.

2.2 Assembly of DSSCs

The FTO glass coated with a photo-anode semiconductor layer that has been soaked into the curcumin-dye solution was then assembled with a counter electrode. FTO glass and counter electrode were separated by a 35 μm seal. The electrolytes were injected into DSSCs through the hole made in counter electrode glass.

2.3 Performance Tests to Investigate the Efficiency and Stability of DSSCs

The assembled DSSCs were examined their performance by using a solar simulator of a light 1000 W/m² irradiance. For testing the stability and performance, five DSSCs and curcumin-dyes were subjected to a light and heat treatment at temperature of 50°C for 100 hours and 200 hours. Each 100 hours, the current and voltage of the DSSCs were measured by using a digital sourcemeter (Keithley 2602A). The current and voltage were calculated from the average of five DSSCs.

2.4 UV-Vis Spectrophotometry, FT-IR Spectroscopy, and Cyclic Voltammetry Test

UV-Vis spectrophotometry, FT-IR spectroscopy, and cyclic voltammetry test were performed to measure the absorbance, functional groups, and energy level for every 100 hours treatment of curcumin-dyes, respectively.

2.5 Fill Factor and Efficiency of DSSCs

The open-circuit voltage (V_OC), short-circuit photocurrent density (J_SC), fill factor (FF), and efficiency (η) were calculated from the current-voltage curve of the DSSCs. The point of maximum power (P_MPP) is the maximum value of the product of the current and voltage. Therefore, FF was calculated as follows [18]

\[ FF = \frac{V_{MPP} \times J_{MPP}}{V_{OC} \times J_{SC}} \]  

The efficiency of solar cells to convert solar energy into electrical energy is defined as the ratio of maximum power (P_MPP) generated from DSSC to power emitted from solar simulator in the active region of a DSSC [19].
The power emitted by light was the product of the intensity of incident light \( G \) at 1000 W/m² and the active area of DSSC [20]. The efficiency of DSSCs was calculated by the following equation:

\[
\eta = \frac{P_{\text{MPP}}}{P_{\text{light}}} = \frac{I_{SC} \times V_{OC} \times FF}{G \times A}
\]

(2)

3. RESULTS AND DISCUSSION

3.1. UV-Vis and FTIR Spectra of Curcumin-Dye

Figure 2 shows the absorption spectra of curcumin-dye resulted of UV-Vis spectrophotometry test. It can be seen that absorbance peaks occurs in the range of wavelength of 400-520 nm. The wide range absorption spectra at 400-520 nm indicate the possibility of the presence of more than one isomeric form at the ground state of curcumin-dyes [21]; [22].

Figure 2 shows also the light and heat subjected to the DSSCs can shift the absorption peak into bathochromic as the light exposure time and heat treatment time increase. Absorption peak occurs at a wavelength of 540 nm after 200 hours of heat and light exposure treatment. The shift of absorption band was known to be caused by the changing of auxochrome rather than by solvent. Particularly the treatment leads the absorbance band shifts to bathochromic and the absorbance peak increases indicates the growth of new auxochrome. This is indicated by the color of dye changes into brownish.

Fig. 2. Absorption spectra of curcumin-dyes exposure to light and heat for 0, 100, and 200 hours.

Fig. 3. FT-IR spectra of curcumin-dyes subjected to lights and heats for 0, 100, and 200 hours.
Figure 3 shows the FTIR spectra of curcumin-dye subjected to lights and heats at a temperature of 50°C for 0, 100, and 200 hours. The wide range absorption at a wavenumber of 3250-3700 cm⁻¹ corresponds to the O-H stretching vibration of ethanol and curcumin-dyes. The peak at a wavenumber of 2800-3250 cm⁻¹ corresponds to C-H stretching vibration of curcumin-dyes. The remarkable peaks in the FTIR spectra of curcumin-dyes also occur at a wavenumber of 1000-1300 cm⁻¹, 1300-1550 cm⁻¹, and 1600-1750 cm⁻¹ which correspond to C-O stretch, C=C aromatic, and C=O stretch vibration, respectively. They indicate the functional groups in the curcumin-dyes.

Moreover, the presence of hydroxyl (-OH) and carbonyl (-C=O) functional groups in curcumin proved the interaction between TiO₂ and curcumin dyes which capable of chelating with Ti(IV) sites on the TiO₂ surface [23]. As shown in Figure 4, the anchoring group between TiO₂ and either N719 dye or curcumin dye is mainly Ti-O-Ti. The stretching bond corresponding to skeletal Ti-O-Ti is clearly represented in Figure 4 in the region of 500-800 cm⁻¹. Moreover, the band at 2950-3350 cm⁻¹ is more prominent in TiO₂ immersed in curcumin dyes than that of TiO₂ immersed in N719 dyes, indicating that there were more hydroxyl functional groups in the TiO₂ immersed in curcumin dyes. Notably, hydroxyl functional groups lead to generation of -OH radicals. The more the -OH groups, the higher the photoelectric conversion efficiency of the DSSCs but the stability was getting worse soon.

The C-O and O-H existing in the curcumin dyes serve as good anchoring groups to the TiO₂ semiconductors as well as to construct a chelating bond as shown in Figure 5. Good anchors provide fast and efficient electrons injection from LUMO level of dyes to TiO₂ semiconductors energy level.

However, a new peak at a wavenumber of 1041 cm⁻¹ was detected after treatment for 200 h as shown in the Figure 3 indicated the new group of alkoxy R-O or R-O-R. A new peak at a wavenumber of 2700 cm⁻¹ was also detected. This might be caused by the existence of auxochrome. This lead to curcumin dyes that degrades into furelic acid and vanillin [24]. However, the furelic acid and vanillin are not the main result of curcumin degradation [25] instead of that the curcumin degrades into bicyclopentadione and hexahydrocurcumin by the mechanism of auto-oxidative degradation [25]. It is consistent with the results of FTIR spectra as shown in Figure 3. The figure shows the peak of C=C and C=O stretch at a wavelength of 1430-1600 and 1660-1680 cm⁻¹ become short, while a new peak occurs at a wavelength of 1041 cm⁻¹ indicating the existence of a new group of alkoxy of C-O or C-O-C.

![Fig. 4. FT-IR spectra of TiO₂ immersed in curcumin and N719 dye.](image1)

![Fig. 5. Chelating bound of curcumin dye, N719 dye, and TiO₂.](image2)
3.2 Cyclic Voltammetry Test of Curcumin-Dyes

Figure 6 shows the cyclic voltammetry (CV) curve for curcumin-dyes. The shape of CV curve for curcumin-dyes when subjected to lights and heats for 0, 100, and 200 hours are similar. CV test measures the oxidation and reduction energy level of curcumin-dyes corresponding to HOMO and LUMO. HOMO is the highest occupied molecular orbital, while LUMO is the lowest unoccupied molecular orbital. Electrons from the dyes can be efficiently injected to the TiO$_2$ semiconductors when the LUMO energy of dyes is more negative than the conduction band (CB) of TiO$_2$ [26]; [27]. The electron regeneration is effective when the HOMO energy of dyes is more positive than the potential energy of the redox electrolyte as shown schematically in Figure 7. The HOMO and LUMO energies of dyes were determined from the respective oxidation and reduction potential value compared to ferrocene using a reference electrode of Ag/AgCl. The LUMO, HOMO, and band-gap energy of curcumin-dyes are -3.62 eV, -5.55 eV, and 1.93 eV, respectively.

When subjected to the treatment of light and heat at 50°C for 100 and 200 h exposures, the LUMO decreases and the HOMO of the dyes increases. It causes the ability of the dyes to inject and regenerate electrons decreases. The auto-oxidative degradation process of curcumin dyes introduces the degradation of the C=C and C=O functional groups and the rise of the new functional groups such as C-O or C-O-C. Because the ionic charge of O is higher than that of C, then the LUMO levels of curcumin were relegated to decline.

![Cyclic voltammetry curve for curcumin-dyes subjected to lights and heats for 0, 100, and 200 hours.](image1)

![HOMO-LUMO energy of curcumin-dyes.](image2)
3.3 IPCE Measurements of DSSCs

Figure 8 shows the IPCE curve of DSSCs with curcumin and N719 dye. The action spectra of incident photon-to-current conversion efficiency (IPCE) for DSSCs is given by the following equation

\[
\text{IPCE} \, (\%) = \frac{1240 \times I_{sc}}{\lambda \times P} \times 100
\]  

(3)

where \(I_{sc}\) is the short circuit photocurrent density for monochromatic irradiation (mA/cm²), \(\lambda\) is the wavelength of the monochromatic light (nm), \(P\) is the intensity of the monochromatic light (mW/m²).

Interestingly, the IPCE of DSSC based on N719 dye takes a higher value than 50% at broader wavelengths between 430 and 650 nm. The highest IPCE of N719-based DSSC is 98.2% at a wavelength of 560 nm. In addition, Figure 8 shows a narrow shape with IPCE lower than 20% at wavelengths higher than 700 nm which is similar to the previous study [28]. It is proved that N719 has a low absorption of the red light producing a great loss in the photon spectral region from 700 to 800 nm.

Notably, the IPCE of the DSSC based on N719 dye is apparently superior to that of based on curcumin dye. The DSSC based on curcumin has a lower value of IPCE than 50% at all wavelength spectra between 375 and 800 nm. The highest IPCE of N719-based DSSC is 98.2% at a wavelength of 560 nm. In addition, Figure 8 shows a narrow shape with IPCE lower than 20% at wavelengths higher than 700 nm which is similar to the previous study [28]. It is proved that N719 has a low absorption of the red light producing a great loss in the photon spectral region from 700 to 800 nm.

3.4 Current-Voltage Measurements of DSSCs

Figure 9 shows the current-voltage curve of DSSCs with curcumin-dyes just after assembled, after treatment for 100 h, and after treatment for 200 h. In our experiment, the open circuit voltage generated from DSSCs with curcumin-dyes is high enough, i.e. 633 mV and slightly higher than either from previous study, i.e. 0.563 V [6] or from DSSC with N719 dye, i.e. 601 mV. The \(V_{oc}\) of DSSCs with curcumin dyes was almost doubled than that of organic DSCs [29] and similar to that of black carrot and bramble [30]. This indicates that the energy level and the LUMO energy level of the electrolyte is enough to generate a high voltage difference. The higher the LUMO, the greater the value of \(V_{oc}\) is generated. Therefore, the light and heat treatment for 100 and 200 h cause the LUMO energy levels decreases because of the DSSCs generating low \(V_{oc}\) and it is not caused by recombination effect. Figure 7 shows that the LUMO energy levels decreases correspond to the DSSCs that generates low \(V_{oc}\).

The short circuit current (\(I_{sc}\)) and the efficiency of DSSCs use curcumin-dyes were 0.577 mA/cm² and 0.185% were obtained in our experiment. This value is low and similar to the previous research that is of 0.36% [6]. Meanwhile, the short circuit current (\(I_{sc}\)) and the efficiency of DSSCs use N719 dye were 1.599 mA/cm² and 0.460%. The efficiency of DSSC with N719 dye was almost 2.5 times bigger than that of with curcumin dye and similar to that of with turmeric dyes [31]. The DSSC with Curcumin dye was little bit lower than that with black carrot and bramble which were 0.33% and 0.69% [5], [30].

Notably also from Table 1 that the substantial decrease of current after light and heat treatment is not affected directly by the changes in absorbance but rather is caused by the ability of the electrons injection into the TiO\(_2\) semiconductor decreases and the electron regeneration from electrolytes indicated by level of LUMO that decreases and level of HOMO that increases. Thus, the light and heat treatment at 50°C for 100 and 200 hours caused the value of voltage, current, and efficiency decrease. After 100 hours of treatment, the efficiency of DSSCs with curcumin-dyes decreases 48%. This was caused by a decrease in electric current (\(I_{sc}\)) and voltage (\(V_{oc}\)). Meanwhile, after treatment of 200 hours, the performance of DSSCs decreases drastically more than 89%. Interestingly, subjecting DSSCs into heat and light treatment did not cause a significant decrease in FF of DSSCs. It shows that the quality of the junctions in the DSSCs is good and the physical structure of DSSCs is stable.

![Fig. 8. IPCE curve of DSSCs with curcumin- and N719-dyes.](image_url)
Fig. 9. I-V curve of DSSCs with curcumin- and N719-dyes.

Table 1. Performance of DSSCs.

<table>
<thead>
<tr>
<th>Treatment (h)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>Fill Factor</th>
<th>$\eta_{DSSC}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curcumin-0</td>
<td>633</td>
<td>0.577</td>
<td>0.507</td>
<td>0.185</td>
</tr>
<tr>
<td>Curcumin-100</td>
<td>527</td>
<td>0.332</td>
<td>0.552</td>
<td>0.097</td>
</tr>
<tr>
<td>Curcumin-200</td>
<td>480</td>
<td>0.079</td>
<td>0.540</td>
<td>0.021</td>
</tr>
<tr>
<td>N719</td>
<td>601</td>
<td>1.599</td>
<td>0.478</td>
<td>0.460</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS
Natural curcumin dyes extracted from turmeric roots have been isolated in our experiment and used successfully as a photosensitizer for DSSCs. Dye-sensitized solar cells with curcumin dyes generates $V_{oc}$, $J_{sc}$, and efficiency of 633 mV, 0.557 mA/cm², and 0.185%, respectively. Our DSSCs have a good quality of junctions and stable physical structure. However, the performance of DSSCs decreases when subjected a light and heat treatment due to the changes of HOMO and LUMO level of curcumin dyes.

ACKNOWLEDGEMENT
The authors would like to thank the Rector of UNS and LPDP which has given funding to this research with a letter agreement No. 623 / UN.27.21 / PP / 2017, 204 / UN27.21 / TU / 2018, and 2620 / UN27.1 / PP / 2017.

REFERENCES


