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IMPROVING STABILITY OF CHLOROPHYLL AS NATURAL DYE FOR DYE-SENSITIZED SOLAR CELLS

Zainal Arifin[a,b*], Sudjito Soeparman[a], Denny Widhiyanuriyawan[a], Suyitno[b], Argatya Tara Setyaji[b]

[a]Department of Mechanical Engineering, Brawijaya University, Malang, Indonesia
[b]Department of Mechanical Engineering, Sebelas Maret University, Surakarta, Indonesia

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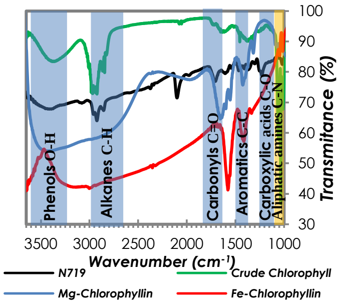
*Corresponding author
zainal_a@uns.ac.id

Graphical abstract



Abstract

Natural dyes have attracted much researcher's attention due to their low-cost production, simple synthesis processes and high natural abundance. However the dye-sensitized solar cells (DSSCs) based natural dyes have higher tendency to degradation. This article reports on the enhancement of performance and stability of dye-sensitized solar cells (DSSCs) using natural dyes. The natural dyes were extracted from papaya leaves by ethanol solvent at a temperature of 50 °C. Then the extracted dyes were isolated and modified into Mg-chlorophyll using column chromatography. Mg-chlorophyll was then synthesized into Fe-chlorophyll to improve stability. The natural dyes were characterized using ultraviolet-visible spectrometry, Fourier transform infrared spectroscopy, and cyclic voltammetry. The performance of DSSCs was tested using a solar simulator. The results showed the open-circuit voltage, the short-circuit current density, and the efficiency of the extracted papaya leaves-based DSSCs to be 325 mV, 0.36 mA/cm2, and 0.07%, respectively. Furthermore, the DSSCs with purified chlorophyll provide high open-circuit voltage of 425 mV and short-circuit current density of 0.45 mA/cm^2. The use of Fe-chlorophyll for sensitizing the DSSCs increases the efficiency up to 2.5 times and the stability up to two times. The DSSCs with Fe-chlorophyll dyes provide open-circuit voltage, short-circuit current density, and efficiency of 500 mV, 0.62 mA/cm2, and 0.16%, respectively. Further studies to improve the current density and stability of natural dye-based DSSCs along with an improvement in the anchor between dyes and semiconducting layers are required.

Keywords: Efficiency, stability, dye-sensitized solar cell, natural dye, papaya leaves, Fe-Chlorophyll

1.0 INTRODUCTION

The demand for dye-sensitized solar cells (DSSCs) used in solar energy harvesters has been increasing because of their improved efficiency and the convenient fabrication process. The dyes used in DSSCs have been known to determine the performance of DSSCs because they absorb sunlight in a wide wavelength range [1]. Moreover, the dyes need to be able to form a bond with active semiconductors such as TiO_2 and ZnO in the DSSCs [2]. For this, the dyes need to contain an active group of chain of OH, C=O and -COOH as a molecular bridge between them and the semiconductor material [3]. The dyes also need to have both a short-chain molecular configuration to enable electron transfer from them to the semiconductors and high chemical stability [4].

Nowadays, the natural dye that is often used as a DSSC sensitizer is chlorophyll [5]. It absorbs extensively in the red and blue portions of the visible light spectrum [6] through a porphyrin-based structure and magnesium ions [7]. Free chlorophyll ions are unstable in nature and easy to react with acids. In the reaction, the Mg^{2+} contained in a chlorophyll molecule is substituted by hydrogen ions [8]. Zinc salt has been used to stabilize the chlorophyll ions. This is since zinc ions form a complex bond with pheophytin that helps stabilize the green color, as was investigated in [9, 10]. The stability of a natural dye is determined by the molecular group it is made of. The stability and efficiency of a dye can be improved by changes the central atomic and group structure substitutions [11]. The latter is affected by the acidity of the environment [12, 13], the oxidation reaction that in turn is affected by sunlight exposure, the amount of oxygen in the ambient air, the acidity of the solvent, and the temperature and proportion of the dye and the solvent.

In this paper, we present a method for improving the stability and performance of DSCCs using chlorophyll-based natural dyes. The stability of natural dyes is improved by changing crude chlorophyll-to-chlorophyll central group. The crude chlorophyll separated from the extract of papaya leaves is converted to Mg-chlorophyll and then modified to Fe-chlorophyll. An analysis of the stability and performance of the chlorophyll-based dye is performed by comparing the stability and performance of the Ruthenium complexes (N719) dye and the DSSCs.

2.0 METHODDOLOGY

We used papaya leaves, alcohol 96%, silica gel, petroleum ether, diethyl ether, 2-propanol, glacial acetic acid, and sodium acetate $FeCl_2$ to extract the natural dye from chlorophyll. The materials were then carefully processed to obtain crude chlorophyll, Mg-chlorophyll, and Fe-chlorophyll.

2.1 Crude-Chlorophyll Synthesis

The papaya leaves were dried at a temperature of 50-60 °C [14] to remove the water content and then extracted with 96% alcohol at 60 °C with the solvent dissolved at a ratio (F/S) of 1:10. The separation of the crude chlorophyll filtrate was performed using Buchner funnel with single No.1 Whatman filter paper. The resulting substance was then evaporated until solid, crude chlorophyll was obtained.

2.2 Synthesis of Mg-Chlorophyll

The separation of solid, crude chlorophyll and Mg-chlorophyll was performed by mixing silica gel and petroleum ether in the chromatography column. The separation of elements (elution) of chlorophyll was performed by adding petroleum ether until a yellow color appears in the column. The elution process was followed by replacing the eluent with a solution of 10% diethyl ether in petroleum ether until green (chlorophyll), yellow (β-carotene), and orange (phycoerhytrin) colors appear. The next step involves replacing the eluent with a solution of 2-propanol 0.5% in petroleum ether until color separation was observed. Further, NaOH was added to the chlorophyll solution resulting from the chromatography process to obtain a pH value of 8.5, followed by which, the solution was heated to boiling while stirring and then extracted with distilled water. Chlorophyll dissolved in distilled water (Mg-Chlorophyllin) was thus obtained (the first material). The next step was the separation of the extract solvent dye and distilled water using a rotary evaporator in order to obtain Mg-chlorophyll (solid natural dyes; the second material).

2.3 Synthesis of Fe-Chlorophyll

A glacial acetic acid solution was added to the solution of Mg-chlorophyll until a pH value of 3 was achieved. The solvent was then heated to a temperature of 60-80 °C for 30 min until its color turned brown. This stage marks the separation of Mg2+ ions and it indicates that pheophytin is formed (Figure 1).

Solutions of 1.3 M $FeCl_2$ and 0.25 M sodium acetate in AcOH were prepared. Solvents of 6.4 g $FeCl_2$ in 25 ml AcOH and 0.5 g of sodium acetate in 25 ml of AcOH were used to modify pheophytin. The solvent of $FeCl_2$ and sodium acetate solution with a ratio of 5 times the weight of pheophytin (Mg loss Chlorophyll) were added to pheophytin obtained from previously mentioned synthesis process. The mixture was then heated to a temperature of 60-80 °C for 30 min until its color changes; Fe-chlorophyll was thus obtained [15].

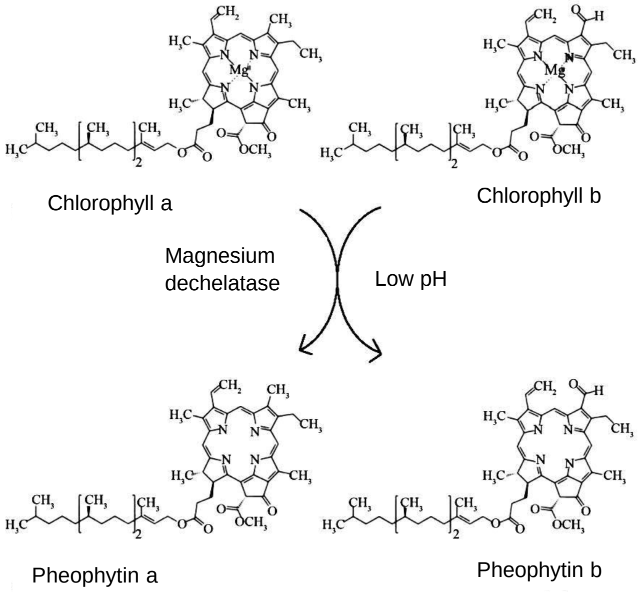


Figure 1 Pheophytin formation [15]

Further, NaOH was added to the Fe-chlorophyll solution to obtain a pH of 8.5. The solution was boiled while being stirred and then extracted with distilled water. Fe-chlorophyll soluble in distilled water was thus obtained through this process. The extract was separated using distilled water by a rotary evaporator; a solid natural dyes (the third material) was obtained after this step.

Before being used in DSSCs, the natural dyes from the papaya leaves extract, i.e. crude chlorophyll, Mg-chlorophyll, and Fe-chlorophyll were dissolved in 96% ethanol at a concentration of 8g/100ml.

2.4 Characterization

The dyes were tested using ultra violet-visible (UV-Vis), Fourier transform spectrophotometer infrared (FTIR) and cyclic voltammetry (CV) tests. The equipment used for the three tests were UV-Vis Spectrometer Lambda 25, Perkin Elmer; IR Prestige-21 SHIMADZU; and µ AUTOLAB II Ω Metrohm, respectively. The stability test for DSSCs was performed using the DSSCs cooked in an oven for 0 h, 100 h, and 200 h at temperature of 50 °C ± 2 °C. The I-V characteristic curves of DSSCs were obtained by using Keithley 2602A digital multimeter and light fixtures OSRAM 300 W/230V SK IT at an intensity of 1000 W/m2.

3.0 RESULTS AND DISCUSSION

Synthesis of crude chlorophyll, Mg-chlorophyll and Fe-Chlorophyll from papaya leaves were successfully performed. The substances, before being used as a dye in DSSC solar cells, were subject to an absorbance test using UV-Vis. The results of the UV-Vis test show a wavelength shift from crude chlorophyll to Mg-chlorophyll and from Mg-chlorophyll to Fe-chlorophyll, as shown in Figure 2. The values of the shift in terms of maximum wavelength (nm) are listed in Table 1. The results indicate that modifying the central atomic structure changes the level of shift absorbance energy. This confirms the results of the research conducted by [16] and [17]. As a consequence of this energy level shift, the absorption wavelength region of sunlight also shifts.

The absorbance level of dye determines the value of short-circuit current density (Jsc). Figure 3 shows the absorbance level of the N719 dye, crude chlorophyll, Mg-chlorophyll, and Fe-chlorophyll. Although the absorbance value of N719 is the lowest, it cannot be concluded that the absorbance value is the most important factor that determines the value of Jsc. Another factor that affects the value of Jsc of a solar cell is the contact between the components in a DSSC [18, 19].

Table 1 Wavelengths of chlorophyll, Mg-chlorophyll, and Fe-chlorophyll

No	Dye	Maximum Wavelength (nm)	
		Soret Band	**Q Band**
1	Crude chlorophyll	421	664
2	Mg-chlorophyll	412	666
3	Fe-chlorophyll	384	622

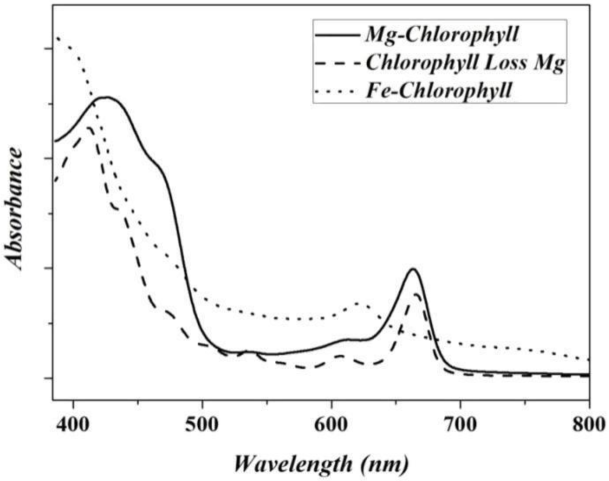


Figure 2 Absorbance curves for the UV-Vis solution of Mg-Chlorophyll, Mg loss chlorophyll (Crude chlorophyll), and Fe-Chlorophyll

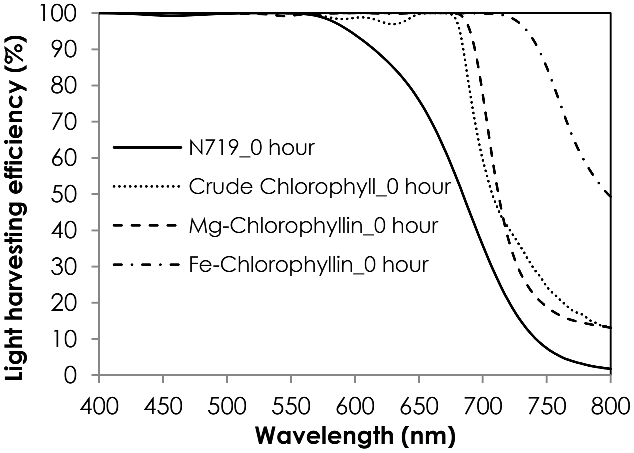


Figure 3 Light harvesting efficiency of N719 dye, papaya leaf extract, Mg-chlorophyll, and Fe- chlorophyll

3.1 Cyclic Voltammetry

Cyclic voltammetry was analyzed to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of dye solutions. The results of the cyclic voltammetry test are shown in Table 2.

Table 3 shows the values of n for N719 and papaya leaf dyes that are approximately 0.62 and 0.65, respectively. This indicates that redox reaction in both dyes is not reversible. The addition of the chlorophyll group converted to Mg-chlorophyll and Fe-chlorophyll increases n to 1.17 and 0.79, respectively, indicating that the redox reaction in Mg-chlorophyll and Fe-chlorophyll dyes is reversible. As a result, electrons in the Mg-chlorophyll and Fe-chlorophyll dyes (HOMO) are more easily regenerated by the electrolyte.

Table 2 Test results of cyclic voltammetry for various dyes

${}^{a}E_{HOMO} = -e[E_{ox} + 4.4]$.

${}^{b}E_{LUMO} = -e[E_{red} + 4.4]$.

No	Dye	E_{ox} (V)	$E_{HOMO}{}^{a}$ (eV)	E_{red} (V)	$E_{LUMO}{}^{b}$ (eV)	$E_{Band\ Gap}$ (eV)
1	N719	0,78	-5,18	1,33	-3,08	2,10
2	Crude chlorophyll	0,68	-5,08	-1,63	2,78	2,30
3	Mg-Chlorophyllin	0,95	-5,35	-1,18	3,22	2,13
4	Fe-Chlorophyllin	1.17	-5,57	-1,24	-3,16	2,41

The value of J_{sc} is strongly influenced by the level of the LUMO energy because it can affect the injection of electrons into the conductive band (CB) of TiO_2 [11]. Our study shows that even if the dye of papaya leaf extract that has been modified to Fe-chlorophyll has a higher LUMO than N719 dye, the value of J_{sc} of the solar cells with N719 dye is still 5.5 times higher than that of Fe-chlorophyll dye. This suggests that, in addition to the HOMO-LUMO energy level and energy band gap of the semiconductor and electrolyte, other factors affect the value of J_{sc} generated by solar cells.

Table 3 Values of I_{pc} and I_{pa} of various dyes tested by cyclic voltammetry

No	Dye	I_{pc} (A)	I_{pa} (A)	n = I_{pc}/I_{pa}
1	N719	-3,03E-04	-3,03E-04	0.62
2	Crude chlorophyll	1,80E-03	-2,76E-03	0.65
3	Mg-Chlorophyllin	-7,92E-03	-7,92E-03	1.17
4	Fe-Chlorophyllin	1,73E-03	-2,18E-03	0.79

3.2 FTIR

FTIR test results show that N719 and papaya leaf dyes both have chain groups of C = O and OH (Figure 4). However the amount of C = O and OH groups in the papaya leaf dye are lower than those in the N719 dye. The -COOH group in the N719 dye constructs a bond with a hydroxyl of TiO_2 particles, producing esters and enhancing the effects of coupling of electrons in the CB of TiO_2 that allows fast and efficient electron transfer [1]. The existence of a large CN group is a remarkable difference between the N719 dye and the papaya leaf dye with unmodified molecular groups. The CN group in the papaya leaf dye is impurities and cannot construct a bond with the semiconductor. Consequently, Jsc of the solar cells with the papaya leaf dye is lower than that with the N719 dye.

3.3 Performance of DSSCs

The performance of solar cells is analyzed on the basis of current (I) and voltage (V) generated by the solar cells with an irradiation of 1000 W/m^2. The J_{sc} value is the value of current exit (I) divided by the active area of the solar cell. Table 4 shows the performance of solar cells estimated directly after assembly (0 h).

V_{oc} and J_{sc} values of the N719 dye is higher than those of the papaya leaf dyes and Mg-chlorophyll. However, the use of Fe-chlorophyll dye enables the solar cell to produce the highest value of V_{oc} among other test samples. This is determined by low or high values of HOMO and LUMO of each type of dye.

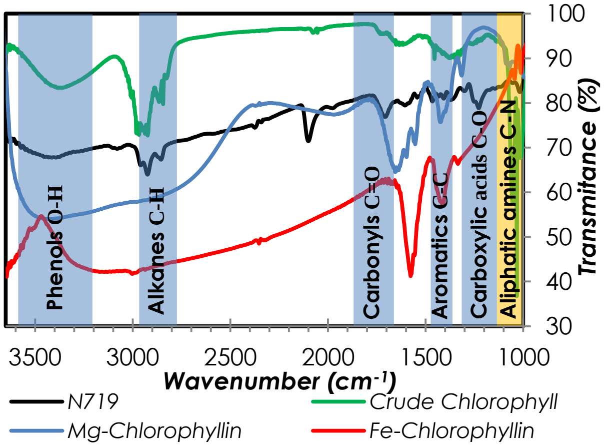


Figure 4 FTIR test of N719, crude chlorophyll, Mg-Chlorophyll, and Fe-Chlorophyll

Table 4 Performance of solar cells with natural dyes and N719 estimated directly after assembly (0 h)

No	Dye types	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)
1	N719	475	3.40	54	0.87
2	Crude chlorophyll	325	0.36	56	0.07
3	Mg-Chlorophyllin	425	0.45	38	0.07
4	Fe-Chlorophyllin	500	0.62	52	0.16

3.4 Stability of DSSCs

Stability of the solar cells was tested at temperature of 50 °C for 100 h and 200 h on the DSSCs. The performance of the solar cells is shown in Table 5. A clear major decline in DSSC performance is indicated by the significant drop in current after 200 h.

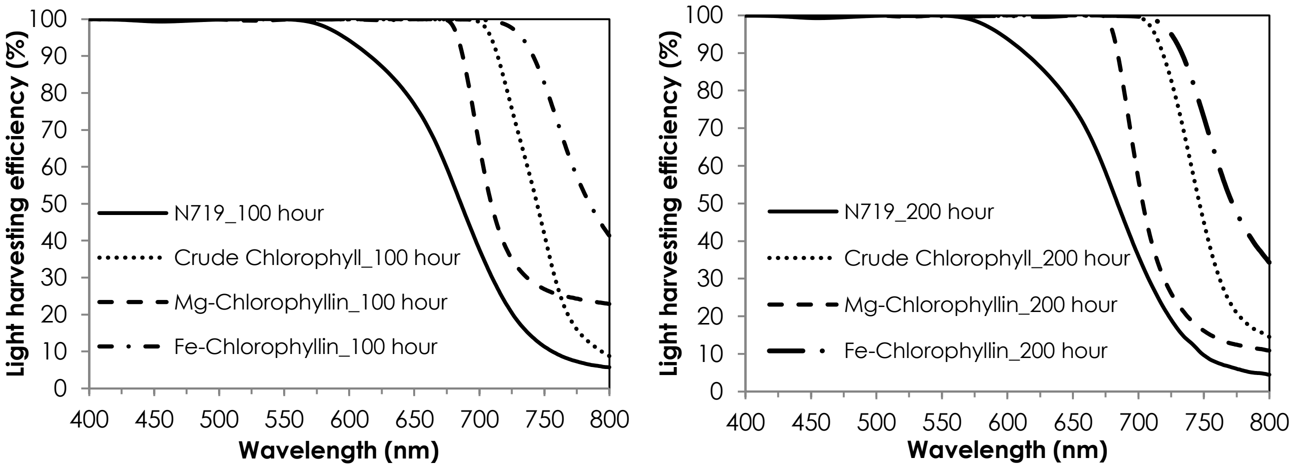
Table 6 shows that voltage and current generated by the papaya leaf dye-solar cell decrease by more than 71.4% from 100 h to 200 h, whereas the efficiency of N719 dye solar cells decreases to 35.6%, mainly because of the decrease in the value of J_{sc}.

Table 5 Performance of solar cells with natural dyes and N719 dye after treatment for 100 h and 200 h

No.	Dye types	V_{oc} (mV)		J_{sc} (mA/cm^2)		η (%)	
		100 h	200 h	100 h	200 h	100 h	200 h
1	N719	470	423	1.58	1.23	0.56	0.40
2	Crude chlorophyll	132	82	0.14	0.04	0.02	0.001
3	Mg-Chlorophyllin	290	253	0.17	0.07	0.02	0.01
4	Fe-Chlorophyllin	410	357	0.46	0.31	0.09	0.06

Table 6 Percentage of reduction in solar cell performance after treatment for 100 h and 200 h.

No.	Dye type	Decrease of V_{oc}		Decrease of J_{sc}		Decrease of efficiency	
		100 h	200 h	100 h	200 h	100 h	200 h
1	N719	1.1 %	10.9 %	53.5 %	63.8 %	35.6 %	54.0 %
2	Crude chlorophyll	59.4 %	74.8 %	61.1 %	88.9 %	71.4 %	98.6 %
3	Mg-Chlorophyllin	31.8 %	40.47 %	62.2 %	84.4 %	77.1 %	85.7 %
4	Fe-Chlorophyllin	18.8 %	29.3 %	24.5 %	50.0 %	43.8 %	62.5 %



(a) (b)

Figure 5 Light harvesting efficiency of N719, papaya leaf extract, Mg-chlorophyll, and Fe-chlorophyll after treatment for (a) 100 h and (b) 200 h

The performance of the solar cells with N719 dye decreases to 54% and that with papaya leaf dyes decrease drastically by more than 98% after treatment for 200 h. From Table 6, it can be concluded that solar cell with Fe-chlorophyll dye is the most durable of the solar cells with natural dyes.

Figure 5 shows curves of light harvesting efficiency (LHE) for DSSC with various dyes. The LHE of dyes subjected to temperature treatment for 100 h and 200 h did not change significantly, except for Mg-chlorophyll. However FTIR analysis shows that a significant degradation of -OH and C=O groups of the papaya leaf dye occurred because of the weak contact between the dye and semiconductor, inhibiting electron transfer (Figure 6).

The treatment also leads to changes in the energy level of LUMO and HOMO of both N719 and papaya leaf dyes, as shown in Table 7. The potential difference between the LUMO and electrolyte decreases because LUMO and HOMO energy levels decrease; consequently, V_{OC} also decreases.

Table 8 shows that the value of n of N719 dye did not significantly change after the treatment (approximately 0.62–0.65). Similarly, in the CV-test results for the papaya leaf and Mg-chlorophyll dyes, the value of n is similar. In the Fe-chlorophyll dye, the value of n decreases from 0.83 to 0.62, and the rate of electron transfer decreases, eventually leading to decreased J_{SC}. The performance of solar cell decreases because electrons in the dye (HOMO) start to resist regeneration.

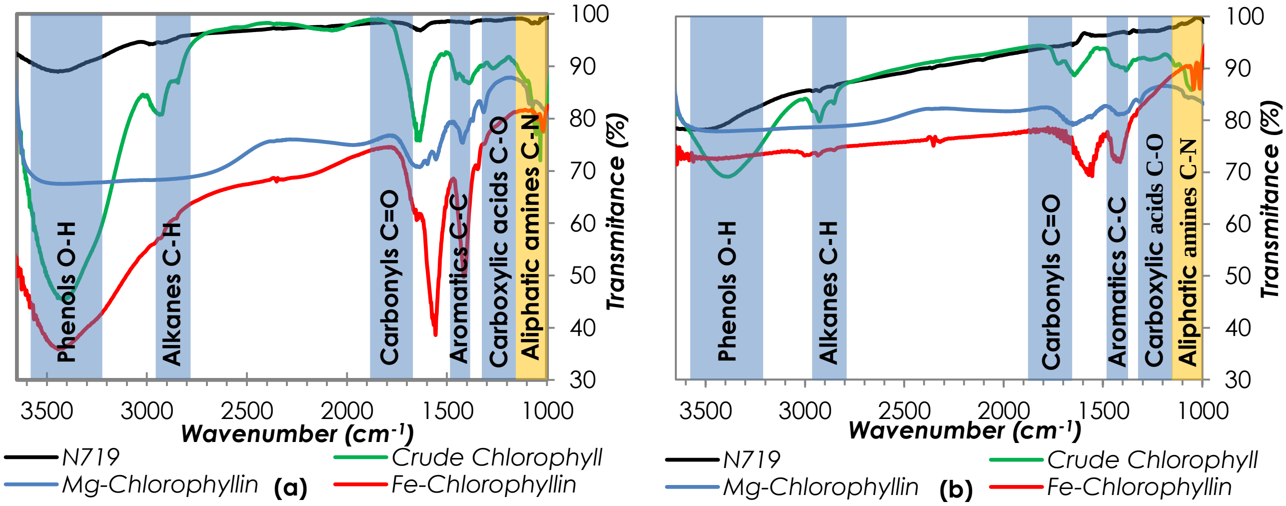


Figure 6 FTIR test of N719, papaya leaf extract, Mg-chlorophyll, and Fe-chlorophyll after treatment for (a) 100 h and (b) 200 h

Table 7 Test results of cyclic voltammetry for various dyes after treatment for 100 h and 200 h

No.	Dye	E^{onset}_{ox} vs Ag/AgCl (V)		HOMO		E^{onset}_{red} vs Ag/AgCl (V)		LUMO		Eg CV	
		100 h	**200 h**	**100 h**	**200 h**	**100 h**	**200 h**	**100 h**	**200 h**	**100 h**	**200 h**
1	N719	0.91	0.86	-5.31	-5.26	-1.12	-1.18	-3.28	-3.22	-2.03	-2.04
2	Crude chlorophyll	1.04	1.13	-5.44	-5.53	-1.58	-1.62	-2.82	-2.78	-2.62	-2.75
3	Mg-Chlorophyllin	0.98	1.00	-5.38	-5.40	-1.17	-1.18	-3.23	-3.22	-2.15	-2.18
4	Fe-Chlorophyllin	1.20	1.08	-5.60	-5.48	-1.29	-1.07	-3.11	-3.33	-2.49	-2.15

Table 8 Values of I_{pc} and I_{pa} of various dyes after treatment for 100 h after cyclic voltammetry test

No.	Dye types	I_{pc} (A)		I_{pa} (A)		$n = I_{pc}/I_{pa}$	
		100 h	**200 h**	**100 h**	**200 h**	**100 h**	**200 h**
1	N719	2,17E-04	2,20E-04	-3,50E-04	-3,40E-04	0.62	0.65
2	Crude chlorophyll	2,62E-03	2,65E-03	-4,80E-03	-4,99E-03	0.55	0.53
3	Mg-Chlorophyllin	7,79E-03	8,43E-03	-6,53E-03	-6,87E-03	1.19	1.23
4	Fe-Chlorophyllin	1,84E-03	4,09E-03	-2,21E-03	-6,56E-03	0.83	0.62

4.0 CONCLUSION

Natural dyes based on papaya leaf extract (Mg-chlorophyll and Fe-chlorophyll) have been successfully produced and used as solar cell DSSC sensitizers. The highest efficiency is achieved for solar cell DSSC with N719 dye sensitizer, at about 0.87%. The substitution of the central atom of chlorophyll of Mg^{2+} into Fe^{2+} is proved to improve efficiency by more than 2.5 and stability by two times, compared to papaya extract dyes. Moreover, DSSC with Fe-chlorophyll dye produces the highest efficiency, compared with other natural dyes. Further studies are required to improve the current density and stability of natural dye-based DSSCs including enhancement of anchor between dyes and semiconducting layers.

Research on the stability of natural dyes, such as manipulating groups in natural dyes using other metals such as Cu or Zn, are therefore suggested.

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