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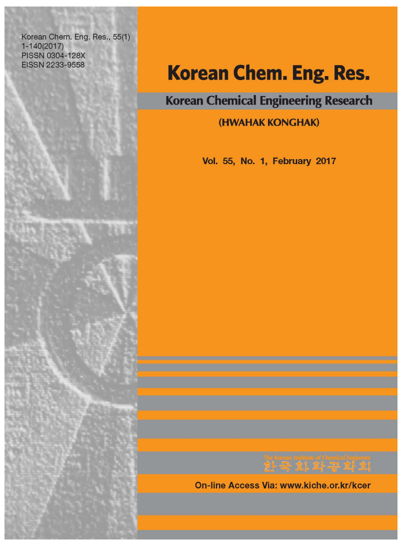

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Korean Chemical Engineering Research (Korean Chem. Eng. Res.), which is published bimonthly, is an official publication of the Korean Institute of Chemical Engineers. It publishes papers in the fields of chemical engineering ranging from fundamentals to applications. The journal aims at the publication of original and significant results which are lasting in chemical engineering. The scope of the journal is including biochemical process and technology, material synthesis and development, separation, thermodynamics, catalysis, reaction and reactor development, process analysis, powder technology, fluid dynamics, energy and environmental technologies.

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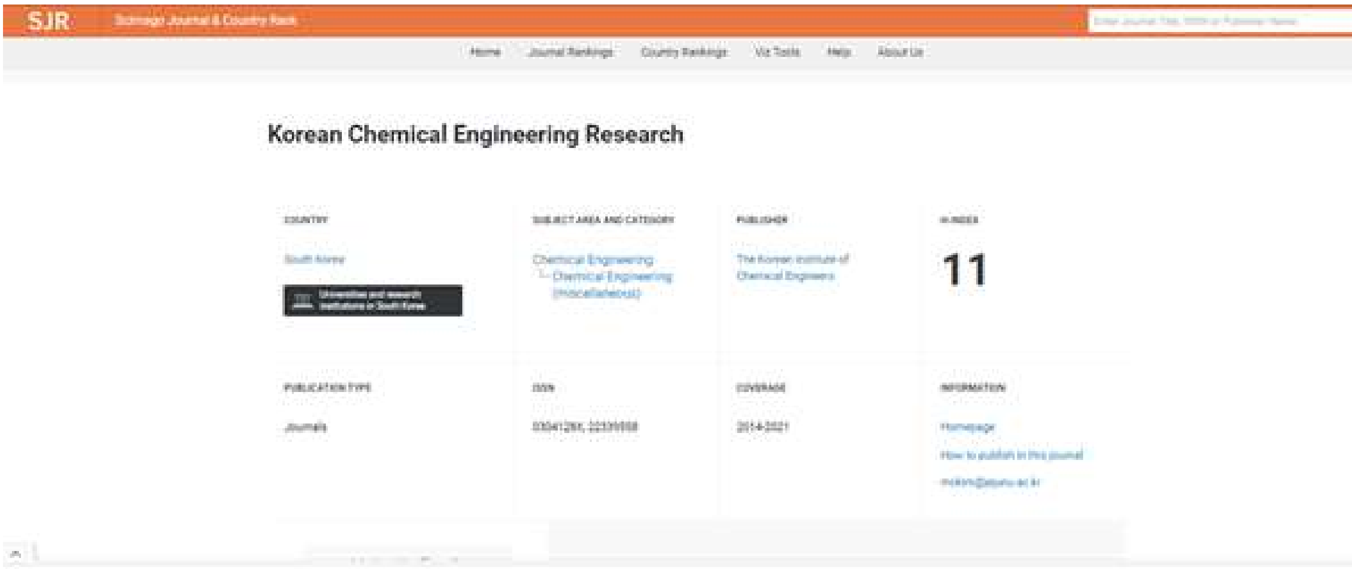

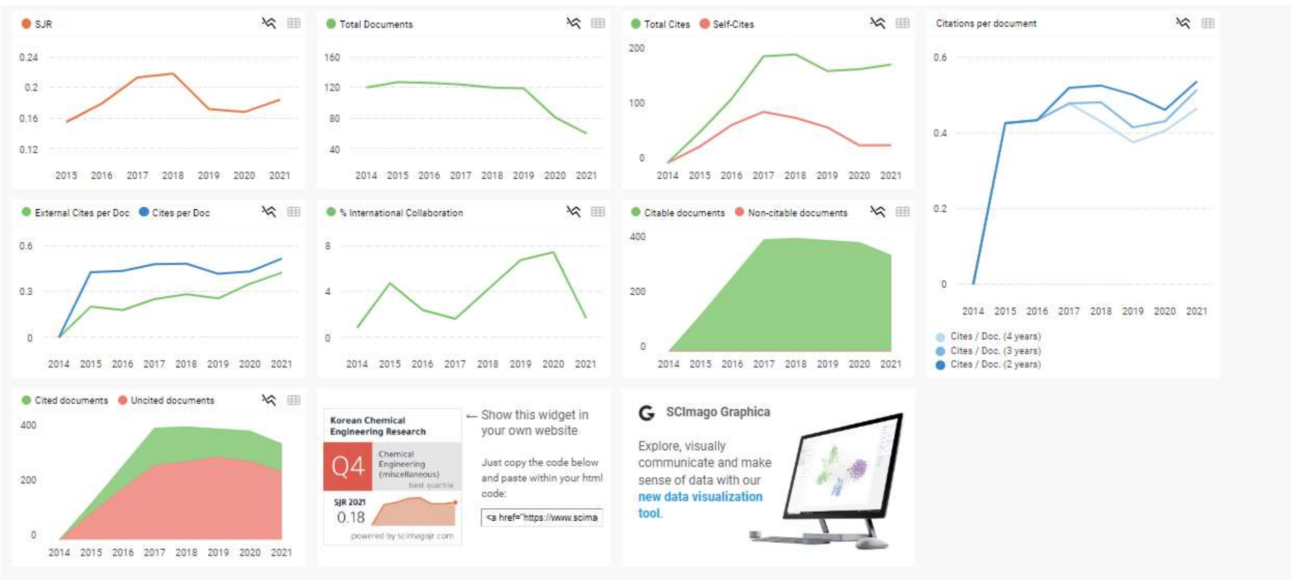

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Synthesis of Complex Compounds Ni(II)-Chlorophyll as Dye Sensitizer in Dye Sensitizer Solar Cell (DSSC)

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Abstract – Increasing global energy demand has resulted in an energy crisis. The dye sensitizer solar cell (DSSC) is an alternative source because of its ability to convert the sun's energy into electrical energy. Our aim was to determine the effect of synthesized Ni(II)-Chlorophyll for enhancing the efficiency of solar cells based DSSC. Complex compound Ni(II)-Chlorophyll was successfully synthesized as a dye sensitizer of $Ni(NO_3)_2.6H_2O$ and chlorophyll ligand with saponification method. Characterization results with spectrophotometer UV-Vis showed that the complex compounds of Ni(II)-Chlorophyll have a maximum wavelength of 295.00 nm, 451.00 and 665.00 nm. The bond between the ligand and metal appears in the vibration Ni-O at wave number 455.2 cm^{-1}. Complex compoun Ni(II)-Chlorophyll has a magnetic moment 7.10 Bohr Magneton (BM). The performance of complex compound Ni(II)-Chlorophyll as a dye sensitizer shows the value of short-circuit current (Jsc) at 3.00 mA/cm^2, open circuit voltage (Voc) at 0.15 V and the efficiency (η) 0.20%.

Key words: Ni(II)-Chlorophyll, Dye sensitizer, DSSC, Efficiency

1. Introduction

The energy crisis has become a major problem for every country in the world, especially for fossil fuel sources [1]. Global energy demand is increasing, but the fossil fuels amount decreases every time, this make researchers more active in studying and finding new alternative energy sources [2]. Some alternative energy has developed as a solution to the depletion of fossil fuel supply, such the development of hydropower, wind power, solar power, nuclear power and biomass energy [3]. One of the few solutions offered is the development of solar cell technology because solar energy is one of the abundant energy, especially in tropical countries like Indonesia [1].

Dye sensitizer solar cell (DSSC) is one of the most promising alternative energy sources, because it has a high efficiency in converting sunlight, the production process is simple, low-cost production is needed as well as nontoxicity [4]. DSSC consists of a layer of dye, a conductive glass, the working electrode, electrolyte and reference electrode [5]. Dye layer is the main component of the DSSC that serves to absorb sunlight so that the process of converting sunlight into electricity energy goes well [1].

In this study, the dye was synthesized from the complex compound Ni(II)-Chlorophyll, where the complex compound was derived from Ni^{2+} metals and chlorophyll as ligands with saponification method. Therefore, our objective was to determine the effect of synthesized Ni(II)-Chlorophyll for enhancing the efficiency of solar cells based DSSC.

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2. Experimental

2-1. Tools and materials

The tools used in this study included glassware, which is commonly used in laboratories, glass plates (2.5 cm × 2.5 cm × 0.01 cm), light meter, multimeter, potentiometer 100 KΩ, the scales of analysis METLER AE 200, graphite pencil, hotplate, stirrer, thermometer, pipette, furnace, stir bar, and oven. The characterization tools which used in this study were a Shimadzu spectrophotometer UV-Vis 1800, Shimadzu FTIR spectrophotometer, MSB Sherwood Scientific, Conductometer Eutech CON 510 and XRD Instrument X'Pert PRO.

The chemicals used were chlorophyll powder CMP, titanium dioxide Degussa P 25, sodium hydroxide (NaOH, 99%), methanol (CH_3OH, 99%), ethanol (C_2H_5OH, 99%), hydrochloric acid (HCl, 37%), nickel nitrate ($Ni(NO_3).6H_2O$), aquabidest, electrolyte solution of I_2 in KI. All the ingredients in the above were pro-quality analysis (p.a) unless otherwise stated.

2-2. Making the Chlorophyll solution

This experiment using CMP brands as the chlorophyll powder. One gram of chlorophyll was dissolved in 10 ml aquabidest in 10 ml flask. Furthermore, the solution was homogenized in the flask.

2-3. Chlorophyll saponification reaction

The saponification reaction involved dissolving 2 g of NaOH in 50 mL aquabidest, then adding 2 mL solution of NaOH in ethanol to form ethanol-NaOH with a total volume of 10 mL. Subsequently, 5 mL of chlorophyll was added to the solution and homogenized for 2 hours in a water bath at a constant temperature. The top layer was taken and dissolved in 50 ml aquabidest, then examined using a spectrophotometer Shimadzu UV-Vis 1800 at 639.00 nm [6].

2-4. Determination of Optimum Conditions from Saponification Reaction of Chlorophyll

This process was used to obtain the optimum condition chlorophyll saponification reaction, which was performed with some variations: First, variations in the concentration of NaOH at concentration of 0.1 M; 0.5 M; 1 M, and temperature variations at 25 ^oC; 50 ^oC; 70 ^oC. Each experiment was carried out three times [6].

2-5. Synthesis Compounds Complex Ni-Chlorophyll

5 mL optimization results on the procedure 2.4 were by taking the top layer and added by HCl 37% ± 1~2 drops until the solution was at pH 2-3. Then adding 5 ml of $Ni(NO_3)_2.6H_2O$ 10% which was homogenized and heated at 60~70 ^oC for 1 hour, the precipitate oven at a temperature of ± 80 ^oC for 24 hours [6].

2-6. Preparation Dye Sensitizer Solar Cell (DSSC)

2-6-1. Coating TiO_2 film on glass plates by doctor blade method

The 0.1 g of TiO_2 Degussa P 25 compound was suspended in 100 mL of methanol 98% [7]. Suspension of TiO_2 was coated on a glass plate 2.5 cm × 2.5 cm × 0,01 cm using the rod by sliding it on the surface of the glass to flatten the TiO_2 suspension that had dripped until it reached a certain thickness. TiO_2 coated glass was cooled at room temperature for 45 minutes and then heated at 450 ^oC for 30 minutes, then cooled to 70 ^oC [8].

2-6-2. Making of electrolytes

The electrolyte solution was made by comparison of alkali iodide salt concentration of 0.5 M and 0.05 M I_2. The 0.4980 g KI was dissolved in 6 mL acetonitrile in a glass beaker. In another beaker was put as much as 0.0760 g I_2 and 6 mL asetonitrile, then stirred until homogeneous. The solution in the second beaker was mixed and stirred [9].

2-6-3. Making of working electrode for DSSC

Glass plate that had been coated TiO_2 suspension was immersed in a complex compound Ni(II) -chlorophyll on a petri dish for 24 hours. For use in the long term, after coating, glass plates were stored in dark glass bottles, and an effort was made to avoid from scratches so as not to damage the layer of TiO_2 [8].

2-6-4. Making of reference electrode for DSSC

The glass plate which was ready to use was coated with a graphite pencil at the surface, which was created as a pencil tip chisel eye so that the coating on the glass plate spread well. Then, the glass plate was heated at 450 ^oC for 30 minutes [8].

2-6-5. DSSC assembly

The working electrode that had been made was placed on the table where the layers were coated with complex compound Ni(II)-Chlorophyll at the top. Then, the working electrode with reference electrode was attached to the position facing each other. Among the two electrodes coated with the electrolyte solution I_2 in KI. Furthermore, the two electrodes were pressed to each other, then clamped at the edges with clamp clips to form a series of solar cells [8].

2-6-6. Current and voltage measurement DSSC with solar light irradiation

DSSC cell that had been made was with multimeter cable on both sides of the glass plate, where reference electrodes were connected to the positive pole, and the working electrode was connected to the negative pole. Furthermore, the circuit was exposed to the sun directly with the working electrode located at the top, then the maximum current and voltage was measured for 14 days [10].

2-6-7. Current and voltage characterization of DSSC using a potentiometer

Current and voltage I-V can be characterized by making a series circuit by connecting the multimeter, DSSC cells, and potentiometers, which are minimized and maximized.

3. Results and Discussion

3-1. Characterization of Compound Complex Ni(II)-Chlorophyll

Synthesized complex compounds were characterized to determine their characteristics. The characterization used UV-Vis spectrophotometer, FTIR spectrophotometer, MSB and conductometer.

3-1-1. Characterization of compound complex Ni(II)-Chlorophyll using UV-VIS spectrophotometer

Characterization by UV-Vis spectrophotometer was conducted to determine the maximum absorption wavelength in the wavelength range 200~800 nm. The characterization results with UV-Vis spectrophotometer are shown in Table 1.

Table 1 shows that the maximum wavelength of complex compounds Ni(II)- chlorophyll and chlorophyll has a different maximum wavelength. The maximum wavelength of chlorophyll is 404.00 nm and 630.00 nm, while the maximum wavelength of complex compound Ni(II)-chlorophyll is 295.00 nm, 451.50 nm and 665.00 nm. From the different wavelengths we can see that complex compound Ni(II)-chlorophyll was successfully synthesized. Complex compound Ni(II)-chlorophyll wavelength appears in the UV and visible at 295.00 nm and 736.00. The wavelengths appear in the UV due to the phenomenon of charge transfer in the form metal to ligand charge transfer (MLCT), which phenomenon occurs because the metal Ni(II) has

Table 1. Results of characterization of complex compounds of Ni(II)-Chlorophyll, chlorophyll and $Ni(NO_3)\cdot 6H_2O$

Compound	Maximum Wavelength (nm)			
Ni(II)-chlorophyll	295.00	-	451.50	665.00
Chlorophyll	-	404.00	-	630.00

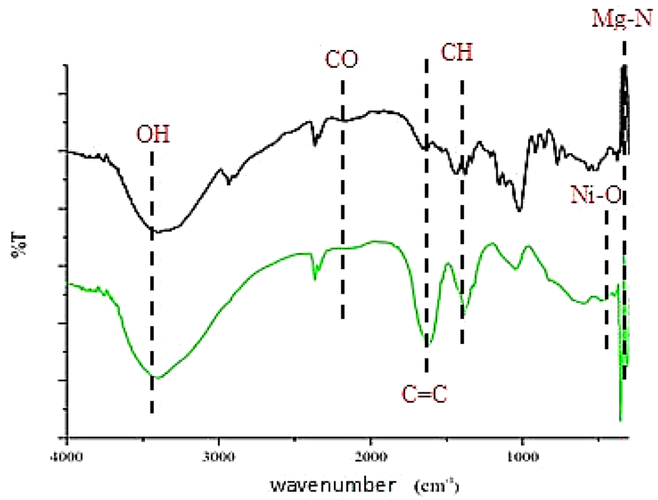

Fig. 1. The FTIR spectra of chlorophyll ligands and complex compounds Ni(II)-Chlorophyll.

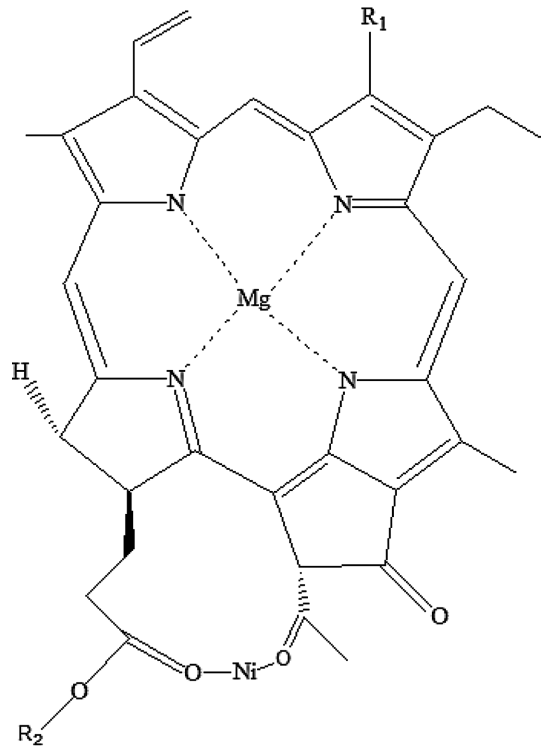

Fig. 2. Prediction of bonding between the metal Ni (II) with ligands chlorophyll.

lower oxidation states [15]. Meanwhile, the wavelength appearing on visible areas is caused by the transition d-d in the complex compound. This transition is changing the distribution of metal-ligand charge, because the electron density shifts from orbital with high metal character to a high ligand orbitals, and these phenomena belong to MLCT [25]. The solvent of this complex compound Ni(II)-Chlorophyll is DMSO (Dimethyl Sufoxide), which has a high polarity so it causes a bathochromic shift in the visible region. MLCT complex compounds are good to be applied as a dye sensitizer because they can absorb more sunlight that can be converted into electrical energy [24].

3-1-2. Characterization of compound complex Ni(II)-Chlorophyll with fourier transform infrared (FTIR) spectrophotometer

The results of the synthesis of complex compound of Ni(II)-Chlorophyll are characterized by a Fourier transform infrared (FTIR) spectrophotometer to determine the functional groups and the bond between the metal ligands. The differences in the results of the FTIR spectra of chlorophyll ligand with complex compound Ni(II)-Chlorophyll indicate that the complex compound has been synthesized successfully. The characterization results of chlorophyll ligand and complex compound Ni (II)-Chlorophyll can be seen in Fig. 1; the information of FTIR spectrum of ligands and complex compound can be seen in Table 2.

Based on the FTIR spectra and descriptions of the table, there is a bond between the metal Ni(II) with ligands chlorophyll that can be seen from the formation of Ni-O bond, so it can be concluded that the complex compound of Ni (II)-chlorophyll has been successfully synthesized. Prediction of bonding between the metal Ni (II) with ligands chlorophyll can be seen in Fig. 2.

3-1-3. Complex compound Ni(II)-Chlorophyll characteriztion using magnetic susceptibility balance (MSB)

This complex compound Ni(II)-Chlorophyll was characterized using magnetic succeptibility balance (MSB) to measure the magnetic moment so we could categorize its magnetic characteristics.

According to Table 3 we can seen the difference in value of the magnetic moment in $Ni(NO_3)_2$ .6H_2O, chlorophyll ligands and complex compounds Ni(II)-Chlorophyll, indicating that the complex

Table 3. Results of the magnetic moment of $Ni(NO_3)_2 \cdot 6H_2O$, chlorophyll ligand and Ni(II)-Chlorophyll

Compound	Magnetic Moment (BM)
$Ni(NO_3)_2 \cdot 6H_20$	2.32
Ligand Chlorophyll	0.81
Ni(II)-Chlorophyll	7.10

Table 2. Data Translation The FTIR spectrum of ligands and complex compounds

Bonds	Ligand wavenumber (cm^{-1})	Complex compound wavenumber (cm^{-1})	Theoretical wavenumber (cm^{-1})	References
Ni-O		455.2	430~480	Adekunle et al., 2014
Mg-N	300.9	308.61	242~310	Mojumdar et al., 1998
OH	3394.72	3402	3362~3421	Ahmed et al., 2014
CO	2167.99	2167.99	2150~2200	Chakarova et al., 2011
CH	1381	1381	1350~1400	Bodirlau et al., 2007
C=C Aromatic	1635	1620	1619~1640	Ahmed et al., 2014

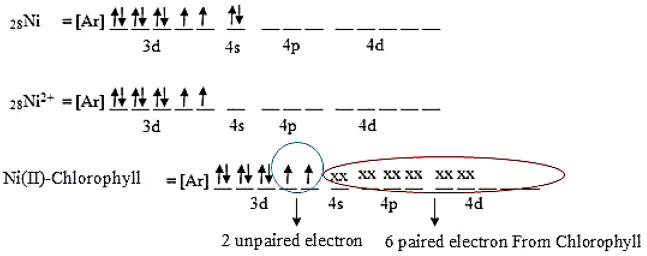

Fig. 3. Prediction of formation of complex compounds of Ni(II)-Chlorophyll.

compound Ni(II)-Chlorophyll has been successfully synthesized. From the table above, it can be seen that the $Ni(NO_3)_2$ $.6H_2O$ and ligand chlorophyll have magnetic properties which can increase the magnetic moment of the complex compound Ni(II)-Chlorophyll. Chlorophyll ligands are weak ligands and not strong enough to push the electrons in the metal d orbitals Ni (II) to pair [11]. In this experiment, chlorophyll ligands donated five pairs of free electron pairs at the metal Ni(II) on orbital s, p and d to form hybridization sp^3d^2 which is the octahedral shaped structure [10]. Prediction of magnetic properties of complex Ni(II)-Chlorophyll by valence bond theory is contained in Fig. 3.

According to Table 3, complex compound Ni(II)-Chlorophyll has a value of 7.10 BM, which indicates there are seven unpaired electrons, but as shown in Fig. 3.4, there are only two unpaired electrons in this case because the chlorophyll ligands bound Ni metal contributing to donating magnetic properties, resulting in a complex compound magnetization value also increasing.

3-1-4. Electrical conductivity characterization of complex compound Ni (II)-chlorophyll by conductometer

Electrical conductivity of complex compounds with conductometer was characterized to determine whether the complex compounds synthesized a molecular or ionic complex compound. The synthesis of complex compound of Ni(II)-Chlorophyll electrical conductivity was measured by comparing the value of the conductance of a solution of complex compounds of Ni(II)-Chlorophyll with solvent, where the solvent of complex compounds of Ni(II)-Chlorophyll is DMSO (dimethyl sulfoxide). If the conductivity value of complex compound Ni(II)-Chlorophyll was higher than DMSO, then this complex compound was included to ionic complex compound, but if the conductivity of DMSO was higher than the complex compound, then this complex compound was a molecular complex compound. Data conductivity values can be seen in Table 4.

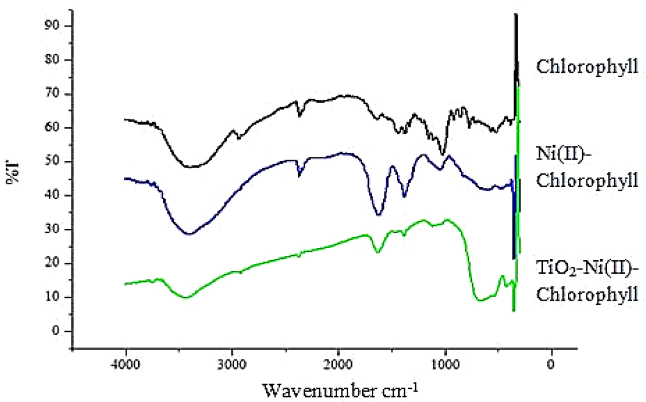

Fig. 4. Spectra of ligand chlorophyll, complex compounds Ni(II)-Chlorophyll and TiO_2 with Ni(II)-Chlorophyll.

Table 4. Data conductivity value of complex compounds and DMSO (dimethyl sulfoxide)

Compound	Conductivity (μs)
DMSO Solvent	0.08
Ni(II)-Chlorophyll in DMSO solvent	1.09

Based on Table 4, the conductivity of complex compound Ni(II)-Chlorophyll was greater when compared with the solvent DMSO, so it can be concluded that the complex compound of Ni(II)-Chlorophyll is an ionic complex compound. The advantage of an ionic compound is that it has a boiling point and a high melting point; in addition, ionic compounds easily decompose into ions, making it easier to conduct electricity.

3-2. Applications of Complex Compound Ni(II)-Chlorophyll as a dye sensitizer in DSSC

3-2-1. Characterization of compound complex bond Ni(II)-Chlorophyll and TiO_2 with FTIR spectrophotometer

This characterization proves the existence of chemical bonds formed between TiO_2 with Ni(II)-Chlorophyll. Ligand functional groups must have a lone pair of electrons that can bind with TiO_2 [13].

From the above spectra, at a wavenumber of 671.23 cm^{-1} bonds are formed Ti-O, indicating that the complex compound Ni(II)-Chlorophyll is bound to Ti. The wavenumber range is in accordance with the literature where Ti bonds with group O ligands will appear in the wavenumber range of 450~1000 cm^{-1} [18]. Prediction of chemical

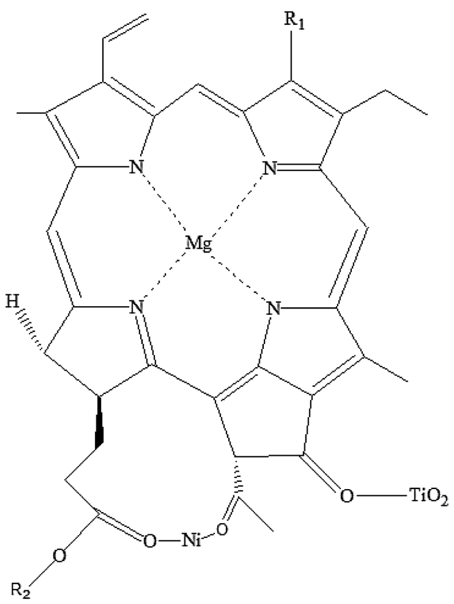

Fig. 5. Prediction of chemical bonds between TiO_2 with Ni(II)-Chlorophyll.

bonds between TiO_2 with complex compounds of Ni(II)-Chlorophyll is shown in Fig. 5.

3-2-2. Making of electrolytes

The electrolyte solution was prepared by dissolving 0.4980 g of KI in 6 mL acetonitrile and 0.0760 g of I_2 in 6 mL acetonitrile. After dissolving completely, the solution was mixed and homogenized; the solution obtained a blood red color. For time use, the electrolytic solution was stored in a brown glass bottle.

Fig. 6. The series of DSSC.

3-2-3. DSSC assembly

DSSC was assembled by working electrode and a reference electrode mounted facing each other, is a side with the one containing dye dealing with the side containing carbon. Furthermore, between the two electrodes was spilled two drops of electrolyte solution. DSSC circuit was then clamped with clamp clips and then its efficiency was measured with a multimeter.

3-2-4. Current measurement of DSSC

In this study, the current measurement was done consistently for 14 days at around 10:00 to 13:00 pm on June 7 to 20, 2016. These measurements were performed by using the working electrode TiO_2, TiO_2-chlorophyll, TiO_2 with Ni(II)-Chlorophyll, TiO_2 with a mixture of chlorophyll and $Ni(NO_3)_2{\cdot}6H_2O$. These measurements were performed on each DSSC cell in order to know the current generated during 14 days. In addition, a comparison was made of the current generated in the TiO_2 with Ni(II)-Chlorophyll and TiO_2 with a mix-

Table 5. Flow of the working electrode TiO_2, TiO_2-chlorophyll, TiO_2 with Ni(II)-Chlorophyll and TiO_2 with a mixture of chlorophyll and $Ni(NO_3)_2{\cdot}6H_2O$

Days	Current Isc (mA)				Lux
	TiO_2	TiO_2-Chlorophyll	TiO_2 with Ni(II)-Chlorophyll	TiO_2 mix with Chlorophyll and $Ni(NO_3)_2.6H_2O$	
1	17.70	19.20	20.60	15.80	750.90
2	19.20	20.50	21.20	15.50	756.30
3	17.10	19.70	20.53	15.70	756.25
4	17.60	20.30	21.30	16.20	757.95
5	18.90	19.80	22.00	17.10	736.85
6	17.20	18.90	21.60	14.30	758.20
7	17.90	19.70	20.50	16.30	759.35
8	17.60	19.40	19.80	15.70	756.35
9	17.30	19.00	18.90	16.60	742.45
10	17.60	17.30	18.30	15.60	731.05
11	17.20	18.00	18.50	15.50	722.30
12	16.80	17.00	17.80	14.40	719.65
13	16.10	17.70	17.40	14.20	702.45
14	15.70	15.50	17.10	13.80	698.30

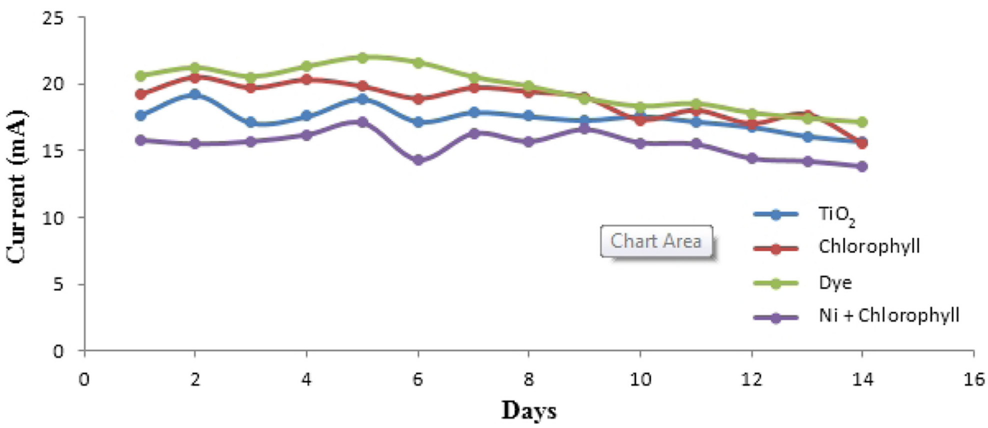

Fig. 7. Current measurement each day.

ture of chlorophyll and $Ni(NO_3)_2 \cdot 6H_2O$ to determine whether the chemical bond between the compound and the ligand complexes affected the resulting current. The measurement results are shown in Table 5 and Fig. 7.

From Fig. 7 the TiO_2 + Ni(II)-Chlorophyll produces a more stable current than the others, but it can be seen that the TiO_2 + Ni(II)-Chlorophyll l generates the most current high compared with only TiO_2, TiO_2 + chlorophyll and TiO_2 + Ni + chlorophyll. This is due to the complex compound Ni(II)-Chlorophyll occurring MLCT, so it can absorb more sunlight [24]. In addition, the complex compound contained a conjugation bond and a lone pair of electrons, making it easy to become excited, gained as a result of current being larger than the other circuits [5]. From day 9 to day 14 all series of DSSC cells decreased flow as the light intensity also decreased; where the intensity of sunlight affected the output current, the greater the intensity of sunlight the output current was getting bigger too, and if the sun intensity decreased smaller, then the output generated current also decreased [2].

3-2-5. Voltage measurements of DSSC

In this study, the voltage was measured for 14 days at 10:00 to 13:00 pm on June 7 to 20, 2016. These measurements were performed by using the working electrode TiO_2, TiO_2-chlorophyll, TiO_2 with Ni(II)-Chlorophyll and TiO_2 with a mixture of chlorophyll and $Ni(NO_3)_2 \cdot 6H_2O$. The aim of this measurement was find out how much voltage was generated in each DSSC cell that had been assembled with a variety of different compositions. The resulting voltage was further processed into a graph so that the voltage in each DSSC cell could be seen. The measurement results are shown in Table 6 and Fig. 8.

Fig. 8 shows the current and voltage measurements are not much different, because the cell used for the measurement is the same cell. However, on days 3, 4 and 5 the DSSC cell of the comparative electrode consisting only TiO_2 decreased significantly which indicates instability; it may be due to differences in the level of the conduction band of TiO_2 with electrolite redox couples. In addition, voltage generated by TiO_2 + Ni(II)-Chlorophyll produced the highest scores because the electrons captured by TiO_2 contained more complex compounds than the others [14].

3-2-6-. I-V curve measurement

I-V curve measurements were performed to determine the efficiency of DSSC cells in converting sunlight into electrical energy.

Table 6. Voltage of the working electrode TiO_2, TiO_2-chlorophyll, TiO_2 with Ni(II)-Chlorophyll and TiO_2 with a mixture of chlorophyll and $Ni(NO_3)_2 \cdot 6H_2O$

Days	Voltage (V)				Lux
	TiO_2	TiO_2-Chlorophyll	TiO_2 with Ni(II)-Chlorophyll	TiO_2 mix with chlorophyll and $Ni(NO_3)_2 \cdot 6H_2O$	
1	1.12	1.23	1.34	1.21	750.90
2	1.12	1.21	1.42	1.41	756.30
3	0.50	1.30	1.57	1.39	756.25
4	0.50	1.14	1.51	1.32	757.95
5	0.46	1.50	1.56	1.53	736.85
6	1.32	1.43	1.53	1.32	758.20
7	1.35	1.54	1.60	1.32	759.35
8	1.30	1.50	1.56	1.49	756.35
9	1.32	1.43	1.58	1.52	742.45
10	1.47	1.30	1.51	1.47	731.05
11	1.36	1.32	1.53	1.40	722.30
12	1.44	1.31	1.47	1.50	719.65
13	1.36	1.43	1.43	1.40	702.45
14	1.38	1.36	1.40	1.31	698.30

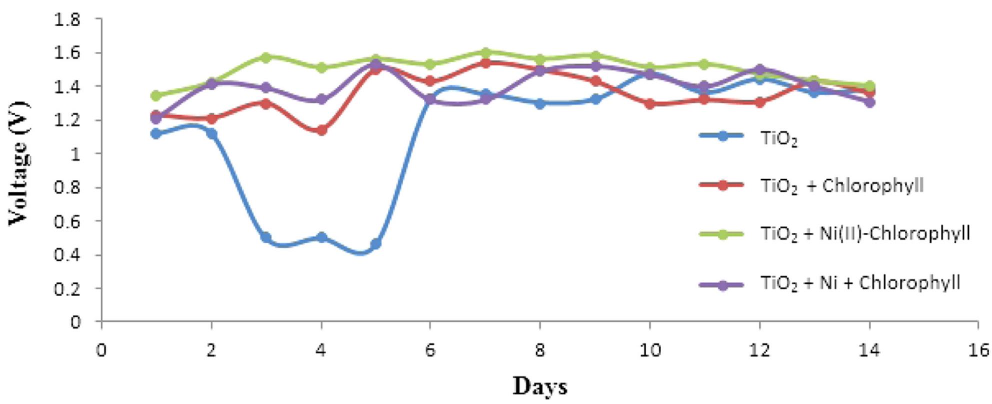

Fig. 8. Graph Voltage Measurement of DSSC.

Table 7. Data from current measurement voltage (I-V)

Compound	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
Ni(II)-Chlorophyll	3.00	0.15	0.23	0.20
TiO_2	1.25	0.19	0.13	0.06
Chlorophyll	3.25	0.09	0.22	0.12
Mixing $Ni(NO_3)_2 \cdot 6H_2O$ with chlorophyll	1.50	0.07	0.21	0.04

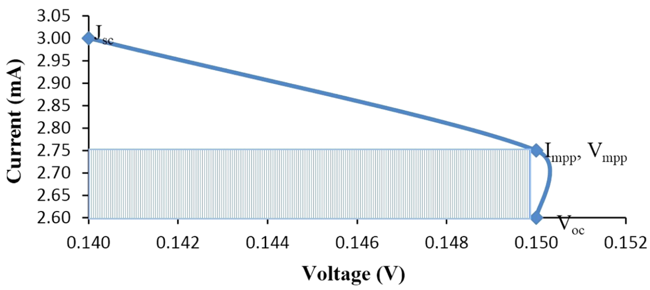

Fig. 9. I-V curve compounds Complex Ni(II)-Chlorophyll.

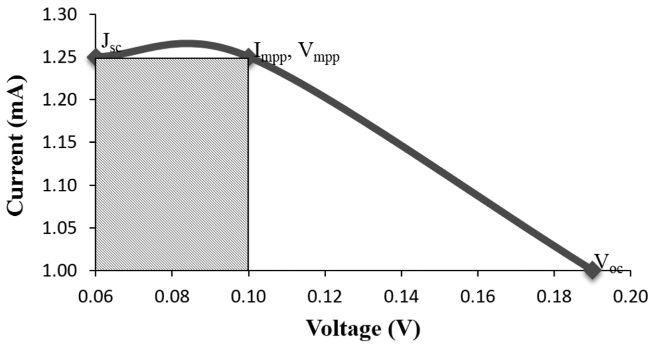

Fig. 10. I-V curve TiO_2.

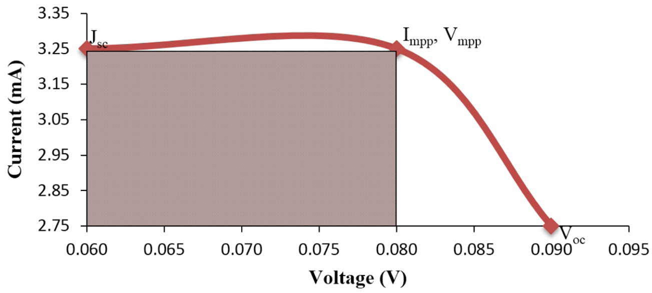

Fig. 11. I-V curve Chlorophyll.

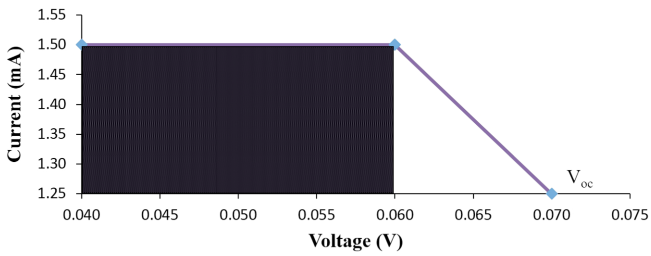

Fig. 12. I-V curve of Ni(II) + Chlorophyll.

DSSC cell will generate power when it is loaded at the same time. The load given in this study is a potentiometer which has a resistivity of 100 KΩ. The results of the current I-V measurements are shown in Table 7.

In this study we measured the I-V curve to the compound complex Ni(II)-Chlorophyll, TiO_2, ligand chlorophyll and mixing $Ni(NO_3)_2 \cdot 6H_2O$ with chlorophyll in order to get the efficiency of each of these compounds.

In Figs. 9, 10, 11 and 12 are the obtained values of short circuit current (Isc) of 12.00 mA; 5.00 mA; 13.00 mA and 6.00 mA. We also obtained the value of current open circuit (Voc) of 0.15 V; 0.19 V; 0.09 V and 0.07 V. Impp and Vmpp values were obtained by multiplying the current and voltage of each point in order to obtain the greatest extent. From the data obtained then can be determined the efficiency of complex compounds Ni(II)-Chlorophyll, TiO_2, ligand chlorophyll and mixing $Ni(NO_3)_2 \cdot 6H_2O$ with chlorophyll, respectively, by 1.81%; 0.55%; 1.14% and 0.04%.

Complex compound Ni(II)-Chlorophyll has the greatest efficiency values when compared with previous studies that use the metal Ni (II). The efficiency of complex compound Ni(II)-Chlorophyll is also greater than the efficiency of chlorophyll conducted in this study; this is due to the complex compound Ni(II)-Chlorophyll MLCT phenomenon that occurred ,so it can absorb more. Thus the sunlight was converted into larger, and the resulting efficiency was greater too if compared with chlorophyll [24]. In addition, the use of chlorophyll ligands, which also have an ability to convert sunlight, become one of the factors that efficiency of the complex compound Ni(II)-Chlorophyll becomes larger too.

Table 8. Table comparing the efficiency of DSSC some metals Ni^{2+} and chlorophyll as a dye sensitizer

Complex compound	Efficiency (%)	References
Chlorophyll (from bayleaf)	0.54%	Syafinar et al., 2015
Chl-e_6	0.73%	Amao et al., 2004
Nickel(II)-porphyrinato	0.05%	
Nickel(II)-polycarbazole backbone dan 8-hydroxyquinolinato	0.45%	Weber et al., 2013
Nickel-dithiolene	0.006~0.084%	
Chlorophyll	0.12%	
Ni(II)-Chlorophyll	0.20%	The results of the current study
Mixing of $Ni(NO_3)_2 \cdot 6H_2O$ with chlorophyll	0.04%	

Comparison of the efficiency of dye Ni(II)-Chlorophyll and chlorophyll with other studies that have been done before from several sources is presented in Table 8. Based on Table 8 the efficiency of complex compound of Ni(II)-Chlorophyll is 0.20%. The value of the efficiency is not higher than studies that have been done before, though complex compounds have the potential to be used as a dye sensitizer for higher efficiency, resulting then in ligand chlorophyll and mixing metals Ni(II) with chlorophyll.

4. Conclusion

Complex compound Ni(II)-Chlorophyll was synthesized from $Ni(NO_3)_2 \cdot 6H_2O$ and chlorophyll ligand by saponification methods. Ni(II)-Chlorophyll performance as a dye sensitizer has produced short-circuit current (Jsc) at 3.00 mA/cm^2, an open circuit voltage (Voc) at 0.15 V and has an efficiency (η) of 0.20%.

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