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Research Paper

Effect of Photosynthetic Pigment Composition of Tropical Marine Microalgae from Ambon Bay *Navicula* sp. TAD on Dye-Sensitized Solar Cell Efficiency

Ivonne Telussa[1*], Eirene G. Fransina[1], Eka Rahmat Mahayani Anthonio Putera Lilipaly[2], Alfa Musa Imanuel Efruan[3]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Science, Pattimura University, Jl. Ir. M. Putuhena, Ambon, 97233, Indonesia*
[2]*Department of Mechanical Engineering, Ambon State Polytechnic, Ir. M. Putuhena, Ambon 97233, Indonesia*
[3]*Biochemistry Laboratory, Department of Chemistry, Faculty of Mathematics and Natural Science, Pattimura University, Jl. Ir. M. Putuhena, Ambon, 97233, Indonesia*
*__Corresponding author__: ivontelussa@gmail.com

Abstract
Solar cells using dyes as sensitizers continue to expand. The synthetic dye used as a sensitizing material for solar cells has high production costs, difficult to find, and can cause environmental pollution. Photosynthetic pigments as sensitizers are considered to be the solution to this matter. In this research, we investigated the effect of photosynthetic pigments from the *Navicula* sp. TAD as a dye-sensitized material on the efficiency of Dye-Sensitized Solar Cell. To obtain high biomass, the *Navicula* sp. TAD was cultivated in a modified medium. Pigment extract from dry biomass using acetone, then continued with purification of the pigment using column chromatography techniques. Characterization of pigment by scanning the absorption pattern of visible rays, the fabrication of solar cells with TiO_2 paste, and the photographic test of the solar cells filled with solar simulators. *Navicula* sp. TAD has photosynthetic pigments consisting of chlorophyll and carotenoid with 8.570 gmL^{-1} and 2.581 gmL^{-1}, respectively. Solar cells using pigment crude extract, chlorophyll, and xanthophyll which TiO_2 absorbs as electrodes, have efficiency values of 6.150×10^{-4}, 3.482×10^{-3}, and 4.117×10^{-3}%, respectively.

Keywords
Chlorophyll, Carotenoid, Dye-Sensitized Solar Cell, *Navicula* sp. TAD, Photosynthetic Pigment, Xanthophyll

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1. INTRODUCTION

The availability of energy sources from fossil fuels has been declining through the years, and it is imperative to consider an alternative energy source. One of the abundant and environmentally friendly alternative energy sources is the sun. Solar cells or photovoltaic cells utilize energy from sunlight and directly convert light to electrical energy. Photovoltaic cells will absorb sunlight and form electron-hole pairs that can generate electricity. Solar cells that are widely used today are silicon-based solar cells. Although silicon materials now dominate solar cells, the problem of high production costs is an obstacle. In addition, the drawback of silicon-based solar cells is the use of hazardous chemicals in the fabrication process.

Along with the development of nanotechnology, silicon-based solar cells are gradually being replaced by the latest generation of solar cells, namely solar cells with light-sensitive dyes or Dye-sensitized Solar Cells (DSSC). The advantage of DSSC is that it does not require high-purity materials, so the production costs are relatively low. In contrast to conventional solar cells, where all processes involve the silicon material, in DSSC, light absorption and electric charge separation occur in separate processes. The dye molecules absorb the light, and the charge separation by the nanocrystal inorganic semiconductor, which has a large band gap. One often used semiconductor is titanium dioxide (TiO_2) (Chapin et al., 1954; Huang et al., 2015; Jeffryes et al., 2008; Wang et al., 2004; Jin et al., 2010). TiO_2 is a relatively inexpensive, widely available, inert, non-toxic, and biocompatible material. Another important component in DSSC is the dye sensitizer. In general, dye-sensitizers used in DSSC are pigments. Using pigments as sensitizing materials for solar cells continues to develop with natural pigments. Sources of natural pigments from fruits and vegetables are used as an alternative because they are easier to obtain, more economical, and environmentally friendly (Chang et al., 2013; Shanmugam et al., 2013; Stramski et al. (2002); Polo and Iha, 2006; Gómez-Ortíz et al., 2010). However, using vegetables and fruits as a source of these pigments will compete with their function as food ingredients. In addition, the relatively long cultivation time is also a drawback of using higher plants as a producer of sensitizers. Based on this fact, efforts to find new sources of natural pigments continue to be made.

Microalgae are generally microscopic plants (diameter between 3-30 m) included in the algae class and live as colonies or single cells in all freshwater and marine waters. Microalgae are known to have potential as alternative sources of natural photosynthetic pigments. Likewise, microalgae have advantages over other plants, that is they have a short life span and do not require a large area of land for cultivation (Barsanti and Gualtieri, 2005). Marine waters where microalgae live are very dynamic because oceanographic and meteorological conditions largely determine the quantity of microalgae in water. Microalgae communities commonly found in Maluku sea waters consist of the classes *Bacillariophyceae*, *Dinophyceae*, *Chrystophyceae*, and *Cyanophyceae*. Based on the research, the number of species from the class Bacillariophyceae (diatoms) in Maluku waters is very high compared to the others. Diatom species from the deep waters of Ambon Bay are endemic to Maluku's seawater, making them easier to obtain and develop in Indonesia (Telussa et al., 2022).

Marine microalgae, *Navicula* sp, have a wide variety of photosynthetic pigments (Telussa et al., 2019; Kuczynska et al., 2015). *Navicula* sp. are diatoms that live attached to form colonies, are shaped like boats, have silica walls, and are yellow-brown. The yellow-brown color in *Navicula* sp. indicates high carotenoid pigment content dominance. This pigment protects cells from environmental stress conditions, especially high light intensity (Telussa et al., 2019; Zhang et al., 2014). Furthermore, chlorophyll a and c pigments were also synthesized in the cells of *Navicula* sp., which plays an important role in capturing light in photosynthesis. Therefore, the cells of *Navicula* sp. are very interesting to be explored as a source of photosynthetic pigments. Thus, the manufacture of solar cells based on photosynthetic pigments from *Navicula* sp. taken from deep Ambon Bay became a model organism to be explored as a pigment producer, which has never been done before. Various studies on using photosynthetic pigments as dye-sensitizers from various types of microalgae have been carried out, including using photosynthetic pigments from *Chlorella* sp., which produced a maximum efficiency value of 0.022% (Nurachman et al., 2015). Using photosynthetic pigments from *Scenedesmus obliquus* as a dye-sensitizer has also been carried out and resulted in an efficiency of 0.064% under direct (Orona-Navar et al., 2020). Therefore, in this study, the diatom microalgae *Navicula* sp. TAD taken from the deep Ambon Bay was used to be explored as a producer of photosynthetic pigment as a dye-sensitizer in the manufacture of solar cells.

2. EXPERIMENTAL SECTION

2.1 Materials

Navicula sp. TAD was obtained from the Culture Collection of Algae at Biochemistry Laboratory of Departement Chemistry, Faculty of Mathematics and Natural Science, Pattimura University. All the chemicals used in this research are pro-analysis grade (Merck, Germany): Ethanol, ethyl acetate, n-hexane acetone, silica gel, and TiO_2 power. The equipment used includes glassware, Indium tin oxide (ITO)-glass slide, analytical balance (Ohaus Adventurer^{TM} Pro), hot plate (Cimarec 2), autoclave (TOMY ES-215), refractometer, and 100-1000 μL, hemocytometer, centrifuge (Thermo Scientific S16), water bath, light microscope (Nikon YS-100), solar simulator (artificial light sources GUNT HL 313.01), Rotary Vaccum Evaporator, UV-Vis spectrophotometer (Shimadzu UV-2450).

2.2 Methods

2.2.1 Cultivation of *Navicula* sp. TAD

Cell *Navicula* sp. TAD was grown in a modified medium (Telussa et al., 2019). Cultivation was carried out with an initial cell density of 5×10^5 cells mL^{-1} in a simple photobioreactor at room temperature under a light intensity of 67.5 mmol m^{-2}s^{-1} with photoperiod 12:12 hours (dark: light), salinity 28 ppt, pH 8.2–8.5 and aerated with free air bubbles. The simple photobioreactor used in this study was made of a transparent glass bottle with a height of 25 cm, an external diameter of 9 cm, and a working volume of 900 mL. Cell growth in culture was measured by counting the number of cells (in units of cells mL^{-1}) using a *Neubauer Haemocytometer* under a light microscope. Cell *Navicula* sp. TAD that has been cultivated was harvested using sedimentation and filtration techniques using Masini cotton cloth. Wet biomass *Navicula* sp. TAD was weighed using an analytical balance to get the wet biomass weight. Furthermore, the wet biomass was dried using a freeze dryer for 24 hours and weighed to obtain the dry biomass weight.

2.2.2 Photosynthetic Pigment Purification

A total of 5 grams of dry biomass was macerated in an ice bath with acetone as a solvent, for 2 hours. Then it was centrifuged at 5000 rpm for 10 minutes, and the supernatant was taken. The supernatant is a crude extract of the pigment to be purified. Purification was carried out by column chromatography using silica gel 60 G with n-hexane: acetone: ethyl acetate as the eluent (7:1:2, v/v). 2 mL of crude pigment extract was put into a column containing silica gel 60 G, which had been prepared with n-hexane: acetone: ethyl acetate. The separation was carried out at a flow rate of 1 mL/min. The carotenoid and chlorophyll fractions were accommodated for identification and characterization (Telussa et al., 2019).

Pigment crude extract, carotenoid fraction (β-carotene; xanthophyll), and chlorophyll fraction were characterized qualitatively by spectrophotometry. The pigment crude extract, chlorophyll, and carotenoids were measured at 300 - 800 nm. Quantitative analysis of pigment by spectroscopy has been described previously (Telussa et al., 2019). To determine the pigment content in the diatom *Navicula* sp. TAD was determined based on the wavelength absorbed by the carotenoid and chlorophyll pigments. The absorbance of the filtrate was measured at wavelengths 470, 652, and 665 nm. Determination of pigment content was determined using the equation of Lichtenthaler (1987).

Pigment identification was carried out using thin-layer chromatography (TLC) with n-hexane: ethyl acetate: acetone (7:1:2 v/v) as the mobile phase and silica gel as a stationary

phase. The dry pigment extract was dissolved in 2 mL of acetone diethyl ether, then spotted on a TLC plate coated with silica gel, and then put in a jar containing the mobile phase. The color of each pigment on the TLC plate was observed, and its Rf value was calculated (Telussa et al., 2019).

2.2.3 Preparation of Photosynthetic Pigment Adsorbed on TiO_2 Electrode

The solar cells fabricated in this study used crude extracts of pigment, chlorophyll, and xanthophyll. The substrate used to manufacture this solar cell is ITO transparent conductive glass with a size of 1.25×1.25 cm. Before use, ITO glass was cleaned with a special glass cleaner and washed with acetone, aquabidest, and ethanol, respectively. After cleaning, the ITO glass was sonicated for 20 minutes and then rinsed thoroughly. The ITO glass was dried in an oven at 60°C, and then ready to use (Chiba et al., 2006). TiO_2 paste was prepared by dispersing 0.5 g of TiO_2 powder in 10 mL 96% ethanol at 100°C for 30 minutes. The nanocrystalline TiO_2 film was produced by annealing the TiO_2 film onto an ITO glass slide at 300°C for 10 min. To introduce photosynthetic pigments, ITO glass slides with nanocrystalline TiO_2 film were immersed in photosynthetic pigments for 1 h, after which the slides were dried at room temperature.

2.2.4 Photoelectric Characterization of DSSC

The solar cell was then measured for its ability to capture light and convert it into an electric current. The light used is sourced from the solar simulator Sol 3A (AM 1.5) with a power of 1000 mW cm^{-2}, an intensity of 1 Sun (94000 lux = 1269 mol $^{-2}s^{-1}$), and the distance between the light source and the solar cell is 1 m. The electricity generated by the solar cells is measured using a digital multimeter (Keithley-2400) at a certain voltage. The distance between the light source and the cell is 1 m. The photoelectric conversion efficiency is determined as Equation (1) shows:

$$\eta(\%) = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \quad (1)$$

Where J_{sc} is the short-circuit photocurrent density (mA cm^{-2}), V_{oc} is the open-circuit voltage (V), P_{in} is the intensity of the incident light (W cm^{-2}), and FF is the fill factor calculated as follows in Equation (2):

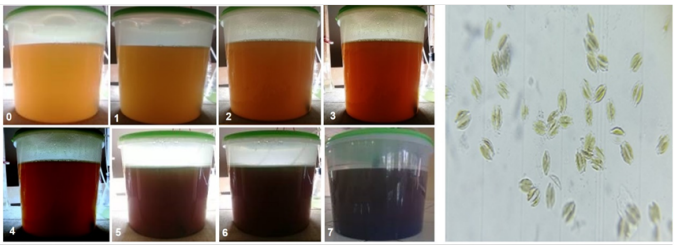
$$FF(\%) = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (2)$$

J_{max} and V_{max} were extracted from the maximum current and voltage of the $J-V$ curve data.

3. RESULT AND DISCUSSSION

3.1 Cultivation of *Navicula* sp. TAD

Navicula sp. TAD was grown in a modified medium to obtain many cells. A modified medium is a simple medium containing a mixture of nitrate, silicate, iron, and phosphate. Using 5×105 cells, mL^{-1} at a light intensity of 67.5 mmol m^{-2} s^{-1}, photoperiod 12:12, cells were grown for seven days. Figure 1(a) shows the change in culture color and different cell densities during growth. Changes in the color of the culture for seven days indicated a change in cell density on the growth of *Navicula* sp. TAD, where a darker culture color indicates a higher cell count and higher biomass productivity. Cell morphology was observed using a light microscope. The light microscope image shows the cell morphology of *Navicula* sp. TAD is oval (like the letter D) and yellow (Figure 1b).



(a) (b)

Figure 1. Culture of *Navicula* sp TAD (a) Cultivation for Seven Days, (b) Observation of Cells Under a Light Microscope

*Navicula*a sp. TAD was harvested on the 7^{th} day with a dark culture color indicating a large number of cells. Harvesting is done by sedimentation and filtration techniques. In the sedimentation technique, the deposition process is faster if the difference in specific gravity and particle size or material is larger. In comparison, the deposition process is slower if the difference in specific gravity and particle size is small (Santoso et al., 2017). Cell *Navicula* sp. TAD has a large weight and cell size, so the time required for the sedimentation process is not too long, which is about ±30 minutes. Furthermore, the process of separating the biomass from the culture is carried out by filtering. *Navicula* sp. TAD filtration is easier to do because the cells have a relatively large size. The wet biomass weight obtained was 65.217 g with the obtained biomass productivity of 0.932 $gL^{-1}d^{-1}$ and dry biomass of 6.317 g with the obtained biomass productivity of 0.090 $gL^{-1}d^{-1}$.

3.2 Isolation and Identification of Photosynthetic Pigments in *Navicula* sp. TAD

Crude extract of photosynthetic pigment *Navicula* sp. TAD was identified using thin-layer chromatography (TLC) and UV-Vis spectrophotometer. Figure 2a shows 9 spots on the crude extract pigment chromatogram. Rf value of 0.05 belongs to the chlorophyll group (chlorophyll c), Rf 0.11, 0.25, 0.33 belongs to the carotenoid (xanthophyll) group, Rf 0.36, 0.39, 0.43 belongs to the chlorophyll group (chlorophyll a), Rf of 0.57 is pheophytin, and Rf 0.98 belongs to the carotene group (β-carotene). Meanwhile, the crude extract spectrum of the photosynthetic pigment *Navicula* sp. TAD was identified in the wavelength range of 350-700 nm (Figure 2b). Chlorophyll

absorbs blue-violet light in the 350–450 nm wavelength range (soret band) and red light in the 550–700 nm wavelength range (Q band). Specifically, chlorophyll absorbs light at wavelengths 380, 410, and 430 nm (Soret band) and wavelengths 533, 579, 616, and 662 nm (Q band), while carotenoids absorb light in the wavelength range of 400–500 nm. The absorption peaks of β-carotene were observed at wavelengths 450 and 474 nm, while the absorption peaks of fucoxanthin were at 447 and 479 nm. Spectroscopic characteristics of chlorophyll a, β-carotene, and fucoxanthin were used to quantitatively determine the photosynthetic pigment's content.

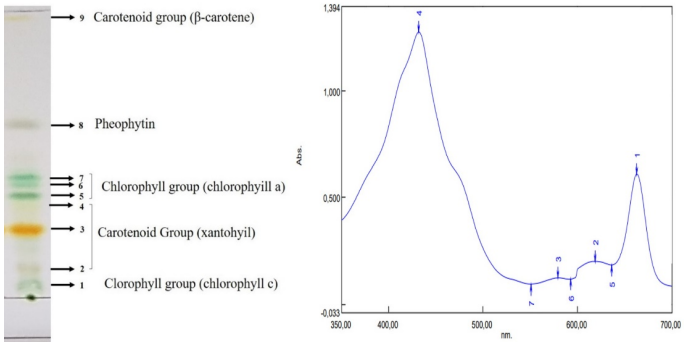


Figure 2. Chromatogram (a) and Spectrum Visible (b) from Crude Extract of Photosynthetic Pigment *Navicula* sp. TAD

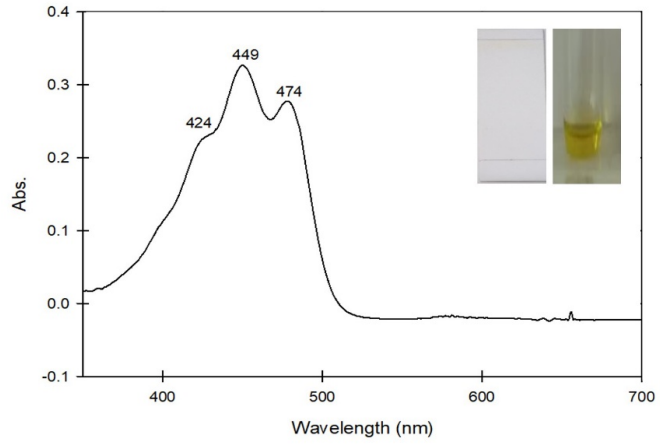


Figure 3. The Absorption Spectrum of the β-carotene Fraction

The photosynthetic pigment content was determined from the 0.05 biomass of *Navicula* sp. TAD and obtained chlorophyll an of 8,570±0.667 gmL^{-1} and carotenoids 2,581±0.289 gmL^{-1}. Furthermore, the photosynthetic pigment extract of *Navicula* sp. TAD was purified using column chromatography with 60 G silica gel as the stationary phase and n-hexane: acetone: ethyl acetate (7:2:1, v/v) as the mobile phase. Purification was carried out at a flow rate of 1 mL/min and obtained 73 fractions (fraction 1-4: carotenoid group (β-carotene), fraction 5-22: chlorophyll group (chlorophyll a), fraction 23-60: carotenoid group (xanthophylls), fraction 61-73: chlorophyll group (chlorophyll c).

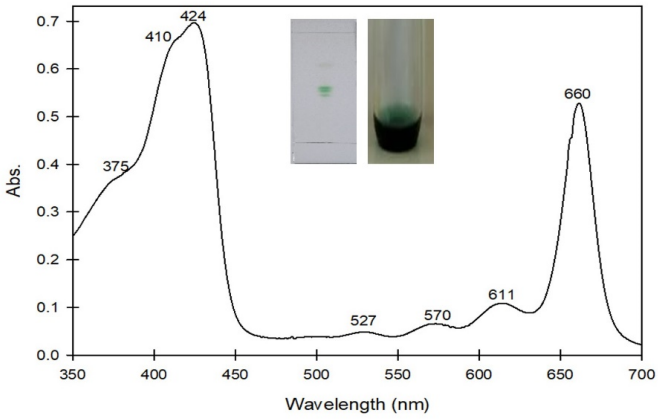


Figure 4. The Absorption Spectrum of the Chlorophyll Fraction

Purification of photosynthetic pigment *Navicula* sp. TAD showed a good separation between chlorophyll (green color) and carotenoids (yellow and orange), which were identified using TLC and UV-Vis spectrophotometer. Identification by UV-Vis spectrophotometer showed the presence of 3 absorption peaks at wavelengths of 424, 449, and 474 nm which are characteristic of β-carotene (Figure 3). Fractions 1-4 are yellow with 1 spot on the chromatogram (insert Figure 3).

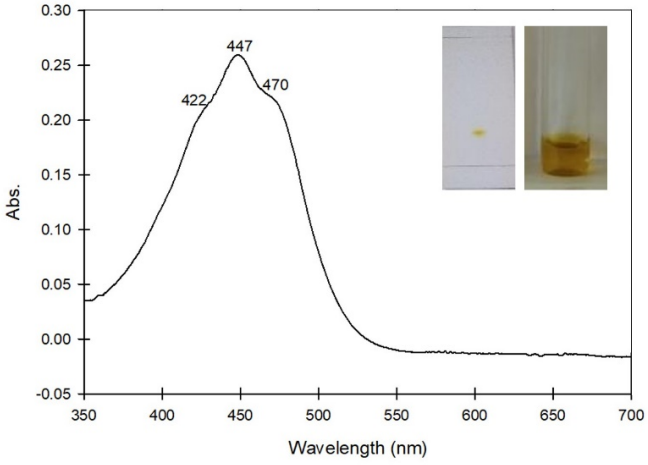


Figure 5. The Absorption Spectrum of the Xanthophyll Fraction

Identification by UV-Vis spectrophotometer showed absorption peaks of chlorophyll a at wavelengths of 375, 410, and 424 nm (soret band) and 527, 570, 611, and 660 nm (Q band). Fractions 5–22 are dark green colored fractions and

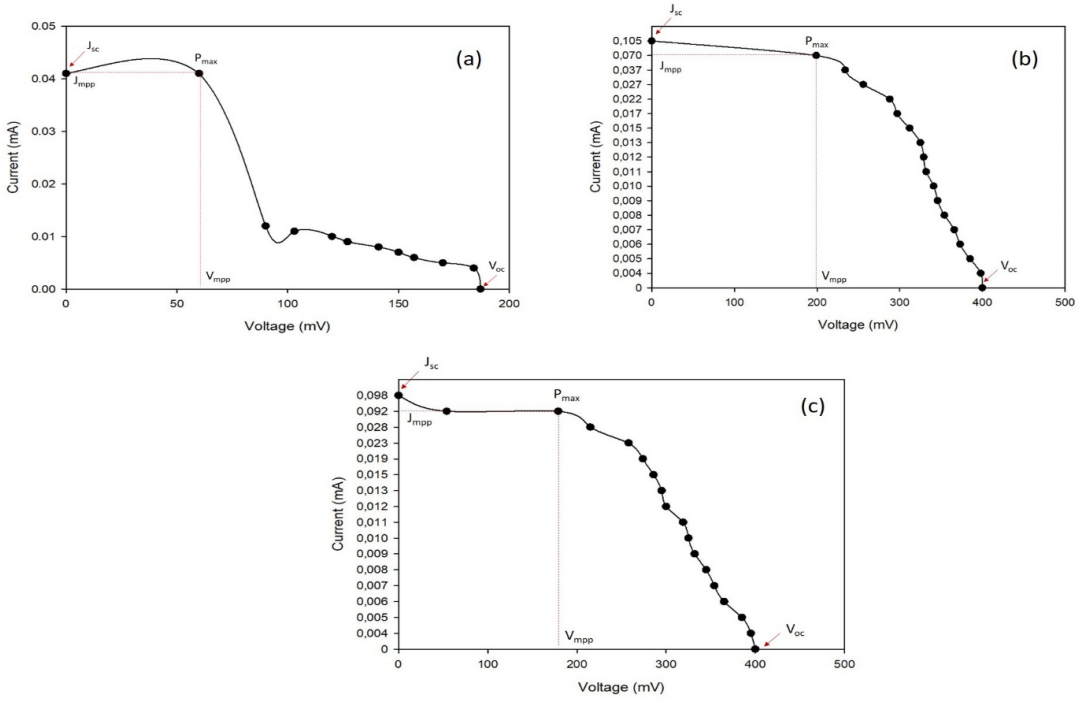


Figure 6. The I-V Curve of the Solar Cell is Sensitive to the Photosynthetic Pigment *Navicula* sp. TAD (a) Crude Extract Pigment, (b) Chlorophyll, (c) Xanthophyll

Table 1. The Photoelectric Characteristics of the Pigment-sensitized Solar cell *Navicula* sp. TAD

Pigment Type	Photoelectric Value			
	V_{oc} (V)	J_{sc} (A)	FF	η (%)
Crude Extract	0.187	4.1×10^{-5}	0.321	6.150×10^{-4}
Chlorophyll	0.4	1.05×10^{-5}	0.332	3.482×10^{-3}
Xanthophyll	0.4	9.8×10^{-5}	0.420	4.117×10^{-3}

the chromatogram has 3 spots (insert Figure 4). Where the absorption peak is the character of the porphyrin group. Ring porphyrin is a molecule with a stable ring shape and allows electrons to move freely. The presence of Mg^{2+} ions in the center of the porphyrin ring persists in its planar configuration. The presence of a phytol group in chlorophyll contributes to the stabilization of the chlorophyll confirmation and the presence of this group is needed to create a good relationship between chlorophyll and apoprotein (Fiedor et al., 2008).

Fraction 23-60 is dark orange and the chromatogram has 1 spot (insert Figure 5). The scan results, the absorption spectrum pattern of this fraction has a similar spectrum with the fucoxanthin pigment where 3 typical absorption peaks of fucoxanthin are at 422, 447, and 470 nm (Telussa et al., 2019; Wright and Jeffrey, 1987). Fucoxanthin is the main and most abundant pigment in brown microalgae such as diatoms. This pigment plays a role in giving the diatom species the brown color of microalgae.

3.3 Photovoltaic Characteristic of Solar Cells

In this study, the pigments used as sensitizers for solar cells were chlorophyll a, xanthophyll, and pigment crude extract. The paste used as a semiconductor in the photoanode is a paste made using TiO_2 powder added with 96% ethanol. The photoanode coated with TiO_2 is then dripped with pigment, changing its color and indicating that the pigment is adsorbed on the titanium surface. The photoanode part is then coupled with the ITO glass part, which is coated with carbon as the cathode with the electrolyte solvent used KI/I^3. Then the sensitized solar cells were tested for their photoelectric capabilities using a solar simulator.

These solar cells convert sunlight into electrical energy using electrolytes to transfer electrons and create an electric current. This cell system is composed of layers of carbon linked to the chromophore of photosynthetic pigments. Photosynthetic pigments act as absorbers of sunlight energy which will transfer electrons to carbon through electrolytes. Carbon, which is a

good conductor, will then produce an electric current from electrons, which can be used for various human purposes. The results show that the highest efficiency value is obtained using the xanthophyll pigment (Table 1). Figure 6 is a photovoltaic curve generated from solar cells sensitive to the xanthophyll pigment from *Navicula* sp. TAD. This solar cell produces a current value (J_{sc}) of 9.8×10^{-5} A, a reverse voltage value (V_{oc}) of 0.3 V, a fill factor (FF) of 0.420, and efficiency of 4.117×10-3%. The high efficiency of these solar cells cannot be separated from the important role of xanthophylls as light-harvesting molecules, and in maintaining the structure and function of photosystems, they also extinguish exposure to high light intensity (Hynninen et al., 1973; Milenković et al., 2012). During photosynthesis, carotenoids such as carotenes and xanthophylls can harvest the energy of sunlight; they absorb energy to excite the singlet from the ground state to the excited state and then transmit the absorbed energy to the chlorophyll pigment.

In a study conducted by Pangestuti et al. (2008), solar cells were sensitized using anthocyanin from Buni Fruit (*Antidesma bunius* L), resulting in an efficiency of 3.3×10^{-5}% with Jsc 0.179 A, Voc 0.223 V, and FF 0.251. Meanwhile, Nurachman et al. (2015) reported the photosynthetic pigment extract from Chlorella sp. PP1 produces an efficiency of 2.2×10^{-2}% with Jsc 0.012 mA/cm^2, Voc 0.230 V, and FF 0.352. When compared with research by Pangestuti et al., 2008 the efficiency obtained in this study is still quite high. This indicates the use of photosynthetic pigments from marine microalgae *Navicula* sp. TAD strain is better at absorbing photon energy. Thus, it can be used as a sensitizing material for solar cells and is capable of producing an electric current.

4. CONCLUSION

Cultivation *Navicula* sp. TAD biomass productivity obtained was 0.090 gL^{-1}h^{-1} with chlorophyll a and carotenoid content of 8.570 gmL^{-1} and 2.581 gmL^{-1}, respectively. Solar cells using crude pigment extract, chlorophyll, and xanthophyll which TiO_2 absorbs as electrodes, have efficiency values of 6.150×10^{-4}, 3.482×10^{-3}, and 4.117×10^{-3}%, respectively.

5. ACKNOWLEDGMENT

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