DYE-SENSITIZED SOLAR CELLS PROPERTIES FROM NATURAL DYE AS LIGHT-REAPING MATERIALS EXTRACTED FROM GAYO ARABICA COFFEE HUSKS

Hasby^{1,*}, Nurhafidhah², Gawang Pamungkas³, and Said Ali Akbar⁴

^{1,2}Department of Chemical Education, Samudra University, 24415, Aceh, Indonesia,

³PT. Polychem Indonesia, Tbk, 42455, Banten, Indonesia

⁴Department of Chemical Education, Serambi Mekkah University, 23245, Aceh, Indonesia,

*E-mail: hasby@unsam.ac.id

ABSTRACT

The waste of coffee husks was extracted by maceration method using HCl in methanol. This process produced an extract of coffee husks of 1.176 mg/uL. The UV-Vis spectrum of the extract shows the major absorption peak at $\lambda_{\text{max}} = 529$ nm which is determined by the electronic transition from flavilium as a characteristic of anthocyanin compounds. Analysis of the IR spectrum shows that the O-H group at wave number 3328 cm^{-1} , strain C-H at wave number 2925 cm^{-1} , the C-C strain found in the aromatic ring at wave number 1422 cm^{-1} and the C-O group at wave number 1024 cm^{-1} . Based on computational studies through the DFT/B3LYP/6-31G approach to the anthocyanin compound, the difference between HOMO and LUMO (energy gap) obtained for C3G and C3R is 3.37919316 eV and 0.28792381 eV, respectively. Therefore, the anthocyanin compounds in Gayo Arabica Coffee husks extract have potential as candidate photosensitizers in DSSC.

Keywords: Waste of Coffee Husks, Computational Studies, Energy Gap, DSSC.

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INTRODUCTION

The energy crisis is a common problem in every country in the world. Fossil fuels are still widely used because their prices are relatively affordable, easy to use and always available. However, fossil fuels gradually decrease, so that alternative energy sources that are environmentally friendly and inexpensive can be used.¹ One of them is the utilization of solar energy which is converted into electrical energy through the use of solar cell applications. Solar cells are power plants that are able to convert sunlight into electric current. Solar energy is the most promising source of energy because it is very large and sustainable. In 1991, Greatzel developed a type of solar cell known as the Dye Sensitizer Solar Cell (DSSC). DSSC uses natural dyes to improve the photosensitizer properties so as to increase the efficiency of the electricity produced.²

Natural dye is a color pigment that is widespread in plants which is an anthocyanin compound.³ Anthocyanin compounds in addition to giving color to plants can also absorb light at visible wavelengths so that they can absorb photons in DSSC.^{4,5} The use of natural dyes is an appropriate alternative, because of its abundant availability, easy to use, inexpensive, and environmentally friendly.⁶⁻⁸ The results of research on plants that have been studied can be used as natural dyes that have the potential as photosensitizer substances in DSSC, namely dragon fruit, hibiscus flower, purple cabbage, blueberry, turmeric⁹, green algae, *Spinach oleracea*, arugula, parsley⁷, *Amaranthus caudatus*, *Bougainvillea spectabilis*, *Delonix regia*, *Nerium oleander*, *Spathodea companionulata* can be used as natural dyes for DSSC applications¹⁰, *Caesalpinia pulcherrima*¹¹, jengkol husks⁵, black tea waste¹², red cabbage¹³, *Melastoma malabathricum* leaves, *Codiaeum variegatum* leaves.¹⁴

Coffee husks extract is a natural dye that also has potential as active material in DSSC. Coffee is one of the biggest agricultural commodities in Aceh province. Aceh Province is also the largest producer of

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Arabica Coffee in Indonesia. Arabica Coffee production centers in Aceh Province are located in three districts namely Central Aceh Regency, Bener Meriah Regency, and Gayo Lues Regency. Every year Arabica coffee in Central Aceh Regency reaches 26.851 tons or contributes 60.44% of the total Arabica coffee production in Aceh Province. Meanwhile, Arabica coffee (Fig.-1a) production from Bener Meriah Regency and Gayo Lues Regency was 16.5099 tons and 1.063 tons respectively¹⁵. Since coffee has been produced, the waste produced has reached up to 35%¹⁶. So far, the utilization of coffee fruit husks waste is only limited as a natural fertilizer. Therefore, processing technology is needed so that the coffee husks waste becomes more valuable and appropriate. One way is to use coffee fruit husks as a source of natural dye. This can be done because of the presence of anthocyanin (Fig.-1b) which is one of the secondary metabolite content in the husks of the coffee fruit. The assessment of coffee husks waste as a natural dye is indeed very necessary in addition to utilizing agricultural waste as well as its abundant availability in Central Aceh District, Bener Meriah and Gayo Lues, Aceh.

(a)

(b)

Fig.-1: (a) Fruits of Gayo Arabica Coffee (*Coffea arabica*) and (b) Structure of Anthocyanin in Coffee, Where R= Glucose or R= Rutinose.¹⁷

Chemically, a study of the photosensitizer properties of a compound can be seen from the absorption of color in organic compounds that are influenced by functional groups contained in these compounds. These functional groups, called chromophores, were discovered by Regan and Grätzel in 1991. Most of the experiments to obtain this data using sophisticated instruments of analysis and spectroscopy. This is, of course, a very expensive cost, long time and excess energy. As the branch of computational chemistry develops, this method can be used for early-stage studies in studying the process of electronic transition or electronic excitation of a molecule that produces photochemical reactions induced by absorption of ultraviolet (UV) or visible light (Vis) light. Therefore the analysis is needed to examine the photosensitizer (light-reaping materials) of anthocyanin compounds from Gayo Arabica Coffee husks through qualitative experiments and computational studies.

EXPERIMENTAL

Material

The raw materials used are fresh Gayo Arabica Coffee (*Coffea arabica*) husks, aqua dest (H_2O), methanol (CH_3OH) and hydrochloric acid (HCl).

Dye Preparation

The husks of fresh coffee are mashed and macerated using 0.01 M HCl in methanol at a ratio of 1: 2 for 18 hours at temperature ($4^{\circ}C$). Furthermore, the sample has been extracted and filtered. Then the extract of methanol was evaporated using a rotary evaporator (BUCHI Rotavor R-125) at $40^{\circ}C$. The extract was stored at $-20^{\circ}C$ before characterization.

Characterization

The absorbance of Gayo Arabica Coffee husks extract was measured using a UV-1800 spectrophotometer (Serial No. A 114550, Shimadzu Corp.). Methanol is used to calibrate instruments. Next, 0.1 mL sample was diluted with 10 mL methanol and 1 mL sample was measured and placed in a cell. The absorbance of

the extract was determined in the area seen at 300-800 nm. Furthermore, IR research on Gayo Arabica Coffee husks extract was measured using IRPrestige-21 (Serial No. A210050, Shimadzu Corp.).

Computational Modeling and Calculation

The anthocyanin structure used to computational calculations is analogous to the results of previous studies.¹⁷ Photosensitizer properties can be seen from the value of the energy gap of the Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular Orbital (HOMO-LUMO). Computational methods used in this study are Density Functional Theory (DFT), Beckee-3-Lee-Yang-Parr (B3LYP) functional and 6-31G level of theory.¹⁸ Basis sets were used for optimizing the dyes that were performed using NWChem software. Through computational methods, electronic spectra calculations were performed on energy transition values between orbitals experienced by electrons in a compound. Besides that, the energy gap of the HOMO-LUMO of anthocyanin compound can also be calculated. Finally, the photosensitizer properties of these compounds can be studied and understood theoretically (computational studies).

RESULTS AND DISCUSSION

Characterization

A total of 600 grams of fresh coffee husks peeled, washed with clean water. Then in a fresh state immediately extracted using a mixture of 100 ml of 0.01 M HCl solution and 200 mL methanol. The use of acid in the extraction process of coffee fruit husks aims to damage tissue cells in the husks of the coffee fruit so that the anthocyanin in the coffee husks is extracted optimally. Strong acid solvents are used to increase the amount of anthocyanin extracted so that the maximum absorbance spectrum was obtained. The concentration of viscous extract obtained was 1.176 mg / uL.

Fig.-2: (a) Thick extract of Gayo Arabica Coffee Husk (b) The UV-Vis Spectrum of Gayo Arabica Coffee Husks Extract in HCl / methanol

To characterize whether coffee husks extract contains anthocyanin Uv-Vis spectrophotometer is used to measure its absorbance. Anthocyanin shows the maximum absorption band in the range of 450-580 nm. Peak locations in the wavelength range between 450 nm and 580 nm indicate the presence of anthocyanin. These results provide evidence that the anthocyanin properties of pigments are produced in coffee fruit husks waste.

The UV-Vis absorption spectrum is a very strong and wide absorption band. Based on Fig.-2, The UV-Vis spectrum of anthocyanin on coffee husks were detected at $\lambda_{\text{max}} = 529 \text{ nm}$ with an intensity of 0.924 a.u. The sharp peak shows the transition $\pi \rightarrow \pi^*$ for Gayo Arabica Coffee husks extract¹⁹. These peaks indicate the increasing number of anthocyanin pigments in the form of colored cations of flavilium or oxonium and the measurement of absorbance will show the greater amount of anthocyanin¹¹. In this case, the presence of a hydroxyl group at the B ring position in cyanidine can also increase the absorption intensity of UV-vis. UV-Vis spectrum analysis shows that the extract not only absorbs ultraviolet light but also visible light. This shows that Gayo Arabica Coffee husks extract has characteristics as photosensitizer on DSSC.

The process of characterizing anthocyanin functional groups from Gayo Arabica Coffee (*Coffea arabica*) was identified by FTIR spectrophotometer. Measurements were made in the range of wavenumbers from 4000 to 900 cm^{-1} , as shown in the Fig-3.

Fig.-3: Characterization of FTIR Spectrum of Coffee Husks Extract in HCl / Methanol

Figure 3. Shows that there are four specific functional groups detected, namely the O-H group at wave number 3328 cm^{-1} , strain C-H at wave number 2925 cm^{-1} , the C-C strain found in the aromatic ring at wave number 1422 cm^{-1} and the C-O group at wave number 1024 cm^{-1} . Analysis of the IR spectrum confirms that the structure of anthocyanin consistently contains a benzene skeleton, a conjugated double bond, a C-H carbonyl group and an OH bond.²⁰

Computational Modeling and Calculation

The modeling of anthocyanin molecular structure in this study was adopted from the results of the study¹⁷. The results of the calculation of the gap energy (HOMO-LUMO) obtained in this study were compared with the results of laboratory test experiments in the form of maximum wavelength values, using equation (1).

Molecular Optimization and energy gap of HOMO-LUMO

The energy gap of (HOMO-LUMO) will describe the ease of a molecular system to experience excitation to a higher electronic state. The lower energy gap of HOMO-LUMO will illustrate that a molecular system is relatively more easily subjected to electronic excitation to a higher electronic state.

Fig.-4: Optimization of DFT Cyanidin-3-Glucoside (C3G) and Cyanidin-3-Rutinoside (C3R)

The energy gap of anthocyanin compounds found in coffee husk was 3.37919316 eV for C3G and 0.28792381 eV for C3R. This shows that the energy gap of the C3R molecule is smaller than the C3G molecular energy gap. The bandgap (energy gap), the difference between HOMO and LUMO, is an indication of the capability of electronic transitions from occupied orbitals (HOMO) to unoccupied (LUMO) ones. The energy gap is a parameter to determine the molecular electrical transport property because it is a measure of electron conductivity. Lower value in the energy gap explains the eventual charge transfer interactions taking place within the molecule²¹. The lower value the energy gap, the easier the occurrence of electron excitation so that it has photosensitivity which tends to be stronger and vice versa²².

To calculate the total energy (energy gap) of the results of experiments on crude extracts of Gayo Arabica Coffee husks containing C3G and C3R, the following formula is used:

$$E = \frac{h C}{\lambda_{\max}} \quad (1)$$

Where E is the minimum energy to the excited electron, h is the Planck constant ($6.62607004 \times 10^{-34}$ J.s), C is the speed of light (3×10^8 m/s) and $\lambda_{\max}$ is the maximum wavelength of experimental results obtained from UV-vis measurements (529 nm). The total experimental energy obtained for the energy gap of anthocyanin compounds found in coffee husk was 2.3456423 eV. The results of computational and experimental calculations show that the energy gap obtained is different. The reason is the impurities in the extract on arabica coffee husks, because of the extraction method is not used to get "pure compound".

Table-1: Energy of HOMO, LUMO, and Band Gap of Cyanidine-3-Glucoside and Cyanidine-3-Rutinoside

	Cyanidine-3-Glucoside (C3G)	Cyanidine-3- Rutinoside (C3R)	Experiment
Homo (eV)	-8.86212679	-4.91614740	
Lumo (eV)	-5.48293363	-4.62822359	
Energy gap (eV)	3.37919316	0.28792381	2.3456423

Based on its molecular structure, C3G and C3R have differences in the number of hydroxy and methoxy groups of the 2-phenylbenzopyrylium group (cation flavylum). This is the reason for the absorption of color in cyanidin-3-rutinoside (C3R) compounds by these functional groups, resulting in differences in the energy gap in the two compounds. Substituents that tend to be as pullers or as electron boosters will cause changes to the energy gap. Another reason to strengthen it by stating that the red color on the coffee husks is characteristic of the presence of the compound C3R.¹⁷

CONCLUSION

The experimental results of UV-Vis measurements of coffee husks extract showed the main absorption peak at $\lambda_{\max}$ = 529 nm which was determined by the electronic transition from flavilium as a characteristic of anthocyanin compounds. Analysis of the IR spectrum shows that the anthocyanin structure consistently contains a benzene skeleton, a double bond conjugated to a carbonyl group C-H bond and an O-H bond. The energy gap that calculated by the computational method was 3.37919316 eV and 0.28792381 eV for C3G and C3R, respectively. The result shows that the anthocyanin compounds found in coffee fruit husks extract is potential as a natural dye on the DSSC application.

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