THE UV-VIS STUDY ON ANTHOCYANIN PIGMENTS ACTIVITIES EXTRACTED FROM GAYO ARABIKA COFFEE HUSKS

Hasby*, Nurhafidhah, Said Ali Akbar*****
**Department of Chemical Education, University of Samudra, Langsa, Indonesia, hasby@unsam.ac.id*
***Department of Chemical Education, University of Samudra, Langsa,, Indonesia nurhafidhah@unsam.ac.id*
****Department of Chemical Education, Universitas Serambi Mekkah, Banda Aceh, Indonesia, said.aliakbar@serambimekkah.ac.id*
Email korespondensi: hasby@unsam.ac.id

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Abstract: The anthocyanin activity of Gayo Arabica coffee husk in variations in acid solution, temperature, and pH has been assessed through UV-Vis studies. It is important to optimize these factors to increase the long-term stability of anthocyanins for use in various fields. Gayo Arabica coffee husks was extracted through maceration method with methanol. This process obtained a coffee husks extract of 1.176 mg/μL. The UV-Vis spectrum of the extract displayed the major absorption peak at λ_{max}= 529 nm in hydrochloric acid (HCl), this assigned by the electronic transition from flavylium as the particular characteristic of anthocyanin compounds. The anthocyanin from the extract was stable at temperatures of 35ºC and 50ºC, to have a major absorption peak at λ_{max}= 529 nm. Therefore, it could probably be said that the lower the temperature, the higher the absorbance value of anthocyanin. Then, husks extract was getting red at pH 1 and 3; almost colorless at pH 5, 8 and 10; and yellow at pH 12. The more acidic conditions causes more anthocyanin pigments to be observed in the form of flavylium or oxonium cations color. Finally, Gayo arabica coffee husks extract can absorb both ultraviolet (UV) and visible light (visible).
Keywords: anthocyanin, coffee husks, Uv-vis study

Introduction

Arabica coffee *(Coffea arabica)* is one of the important agricultural commodities in Indonesia. In Aceh, Arabica coffee is found in the Gayo highlands, namely in Central Aceh and Bener Meriah districts, known internationally as Gayo Arabica Coffee. In 2017, the area of coffee plantations in Aceh reached 121.226 ha with 46.828 tons of coffee fruit production, comprising 85% of Arabica coffee, and the rest is Robusta coffee (Sekretariat Ditjen Perkebunan Kementerian Pertanian Indonesia, 2017). Arabica coffee is the one of coffee that has the best quality among others, so that the processing process uses a wet method to produce coffee beans with good quality and high selling value. The increasing production of coffee fruit lead to the increase of waste product (Trinafianita & Widyaningsih, 2018). Coffee husks consist of outer skin, pulp and parchment, possibly the main residue of coffee handling and processing. For

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every ton of coffee beans produced, around 1 ton of husk is produced during dry processing, while for wet and semi-wet processing this residue amounts to more than 2 tons (Saenger *et al*, 2001). There are no beneficial uses for this type of residue and disposal is a major problem. In the wet process, coffee husks are removed before drying, while still fresh, and the color is quickly degraded by the action of enzymes (peroxidase and polyphenoloxidase) released by damaged outer skin cells and pulp during the dehulling process, or by other oxidizing agents, such as oxygen. So, a large amount of natural coloring is wasted in this process (Prata & Oliveira, 2007). Meanwhile, Aceh can produce 16,466.4 tons/year of the coffee pulp (coffee husks) (Yufniati, 2015). Investigation results show that fresh coffee husks is very potential as a source of anthocyanin which can be applied as a natural dye (Oliveira & Adriana, 2015).

Anthocyanins contained in fruits and flowers are natural pigments that are usually purple, blue, red, and slightly black, and are soluble in water (Ibrahim *et al*, 2011). Anthocyanins are known as flavonoids that are evenly distributed in plants. Anthocyanins can be found in all parts of plant tissue including stems, roots, leaves, flowers and fruits. Color pigments from anthocyanin are cheaper, abundant, easily extracted, safer and environmentally friendly (Abugri *et al*, 2012).

Anthocyanins consist of two aromatic rings connected by three carbons in oxygenated heterocyclic. Anthocyanin pigments consist of flavylium rings, sugars, and acyl groups. The types of anthocyanins are petunidin, delphinidin, pelargonidin, peonidin, cyanidin and malvidin (Bueno *et al*, 2012). The most widely found anthocyanin in fruits is glycosylation in the 3-OH (3-O-monoglycoside) position. Pure anthocyanins in coffee huskss are identified as cyanindin-3-routineoside and cyanidin-3-glucoside. The red color of coffee skin is associated with the presence of cyanidin-3-routineoside (Murthy *et al*, 2012; Murthy & Naidu, 2012). Anthocyanins found in jamblang (*Syzygium cumini* L.) are delpinidin 3,5-diglucoside, petunidin 3,5-diglucoside and malvidin 3,5-diglucoside (Faria *et al*, 2011). Anthocyanins in eggplant skin (Solanum *melongena*) are identified as nasunin, delpinidin-3-(pcoumaroylrutinosida)-5-glucoside (Nayanathara *et al*, 2016).

The color and stability of the anthocyanin pigments depend on the overall molecular structure. Anthocyanin A and B structure substitution will affect the color. In the condition of anthocyanin acid color is determined by the number of substitutions in the B ring. The more OH substitution can cause the color getting more blue, while methoxylation will cause the color getting red (Hsiao & Hsieh, 2018). The stability of anthocyanin is influenced by several factors including pH, temperature, light, and oxygen (Sui *et al*, 2014; Iren *et al*, 2017; Prabavathy *et al*, 2017). Anthocyanins are very sensitive to acidity (pH) and heat (Aal *et al*, 2018; Hsiao & Hsieh, 2018; Uranga *et al*, 2018). The pH factor apparently affects not only the color of anthocyanin but also its stability. Anthocyanins are more stable in acidic solutions than in basic solutions (Moloney *et al*, 2018). Temperature

affects the stability of anthocyanin. Hot temperatures can damage to the structure of anthocyanin, therefore food processing must be carried out at a temperature of 50-60^{o}C which is a stable temperature in the heating process (Novelina *et al*, 2016). The purpose of this study was to study the anthocyanin activity of Gayo Arabica coffee husks in variations in acid solution, temperature, and pH. It is important to optimize these factors to increase the long-term stability of anthocyanins for use in various fields.

Material And Methods

Material

Fresh Gayo Arabica coffee (*Coffea arabica*) husks, methanol (CH_3OH 96%), aquadest (H_2O), hydrochloric acid (HCl) 0.01 M, nitric acid (HNO_3) 0.01 M, sulfuric acid (H_2SO_4) 0.01 M and citric acid ($C_6H_8O_7$) 0.01 M.

Anthocyanin Extraction of Gayo Arabica Coffee Husks

Acid Variations

The husks of fresh coffee was separated from the seeds and washed, then macerated using HCl 0.01 M in methanol in a ratio of 1: 2 for 18 hours at 4^{o}C (for the further extraction, HCl was replaced by HNO_3, H_2SO_4 and $C_6H_8O_7$). The extract is filtered using filter paper. The methanolic extract was then evaporated using a rotary evaporator (BUCHI Rotavapor R-215) at 40^{o}C. Then the solvent-free extract was stored at -20^{o}C prior to characterization.

Temperature Variations

An anthocyanin study of temperature variants was carried out on the extract of fresh coffee husks (0.01 M HCl in methanol, 1: 2 ratio) for 18 hours at -20^{o}C. Furthermore, coffee husks extract was carry out at a temperature of 35^{o}C, 50^{o}C and 70^{o}C.

pH Variations

A buffer solution of pH 1, 3, 5, 8, 10, 12 was prepared to measure the warm intensity of the extract. pH variants were carried out on fresh coffee fruit peel extract (0.01 M HCl in methanol, 1: 2 ratio) for 18 hours at -20^{o}C.

Characterization

UV-1800 spectrophotometer (Serial No. A114550, Shimadzu Corp.) was used to measure samples, methanol 96% was used to calibrate instruments. Subsequently, 0.1 mL of each sample was diluted with 10 mL of methanol 96% and 1 mL of sample was measured and placed in a cell. The absorbance of the extract was determined in the visible area at 300-800 nm.

Discussion

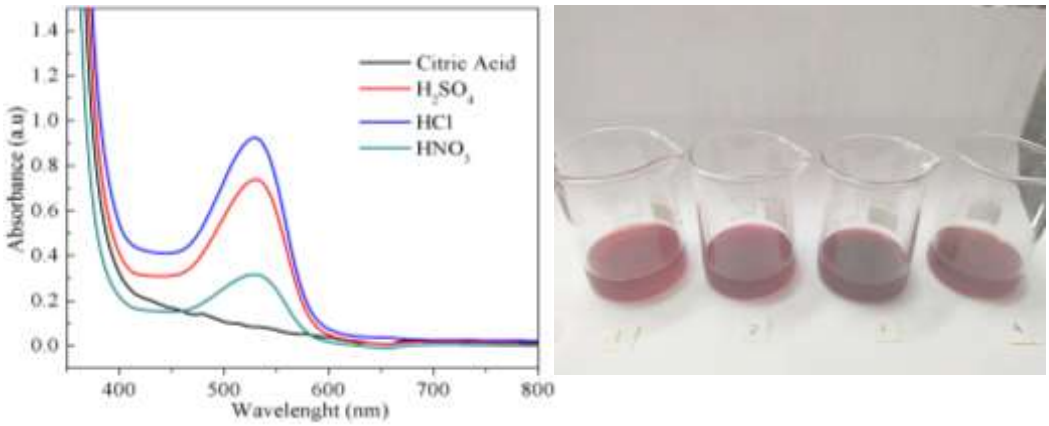
Anthocyanin Extraction of Gayo Arabica Coffee Husks

Methanol is the most common solvent used to extract anthocyanin because its low boiling point allows rapid concentration of the extracted material. This is a classic method for extracting anthocyanin from plant material. This procedure involves maceration or soaking of plant material in methanol which contains a small amount of mineral acid (eg, HCl). Methanol extraction is a fast, easy, and efficient method for anthocyanin extraction (Luis *et al*, 2001). The use of acid in the coffee husks extraction process aims to damage the tissue cells in the husks of the coffee fruit so that the antioxidants in the coffee husks are optimally extracted (Ariadi, 2015). Extraction was carried out for 18 hours at -20^{o}C. The extract was then filtered successively using Whatman No. filter paper. 4 and a rotary vacuum evaporator is carried out at 40^{o}C. The concentration of viscous extract obtained was 1.176 mg/μL.

Figure 1. Extract of Gayo Arabica Coffee Husks (author's documentation)

Study of Acid Variations

Based on Figure 2 (a). The anthocyanin UV-Vis absorption spectrum in the husks of coffee fruit was recorded between wavelengths (λ) of 529-531 nm with different acid control. The UV-Vis spectrum of the four acidic solutions showed significant absorption peaks and significant intensities at λ_{max} = 529 nm and 0.924 a.u on HCl. The higher the intensity of the transition, the better the color of anthocyanin obtained. The peaks occur because of the electronic transition from stable electrons to the flavylium cation on oxygen atoms (Ryu & Koh, 2018). On the other hand, a slight peak appeared also at λ_{max} = 530 nm and 531, where the values of the transition intensities were 0.317 a.u and 0.738 a.u. The intensity of the transition was quite low, so it can be ascertained that it is an electronic transition between electrons around the B ring of benzene (Abdel-Aty *et al*, 2018; Chen *et al*, 2018).



(a) (b)

Figure 2. (a) UV-Vis spectrum of coffee husks extract using acid|methanol variation, (b) Coffee husks extract using acid | methanol variation (1 = HCl, 2 = HNO_3, 3 = H_2SO_4, 4 = $C_6H_8O_7$)

HCl is a type of strong acid characterized by pH ranging between 1 and 3 while $C_6H_8O_7$ is a weaker with pH ranging between 5, 8 and 10. The results of the UV-Vis study on the use of various acid solutions in extracting anthocyanin compounds from Gayo Arabica coffee husks showed that HCl is a strong acid which is more effective in degrading cell walls so that the extract of anthocyanins produced is more maximal. According to Sampebarra (2018) anthocyanin is a red substance that is stable at low pH and stability will decrease if the pH is raised. The more acidic situation, especially close to pH 1, will cause more and more anthocyanin pigments to be in the form of colored flavylium cation or oxonium and absorbance measurements will show a greater amount of anthocyanin (Moulana *et al*., 2012).

Study of Temperature Variations

Anthocyanin extracts from coffee huskss (1176 mg/µL) were measured at different temperatures, from 35ºC, 50ºC and 70ºC. The UV-Vis spectrum of three anthocyanin solutions showed significant absorption and intensity peaks at λ_{max}= 529 nm with a transition intensity value of 1.547 a.u at 35ºC and at λ_{max}= 529 nm with a transition intensity value of 1.49 a.u at 50ºC. This was because the absorbance of anthocyanin at the maximum wavelength decreases with increasing temperature.

Anthocyanin degradation is affected by temperature. Heating is irreversible in influencing the stability of anthocyanin. The flavylium cation (red) will change form into chalcons (no color) due to temperature increase, but can not be returned. (Sampebarra, 2018). Meanwhile, According to Fatonah (2016) the colder the temperature, the higher the absorbance value of anthocyanin compounds.

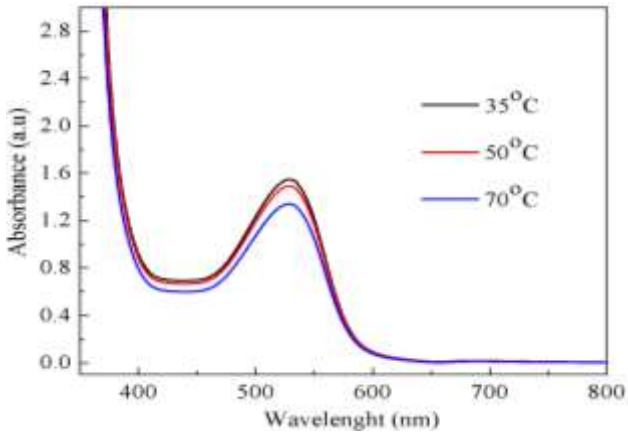
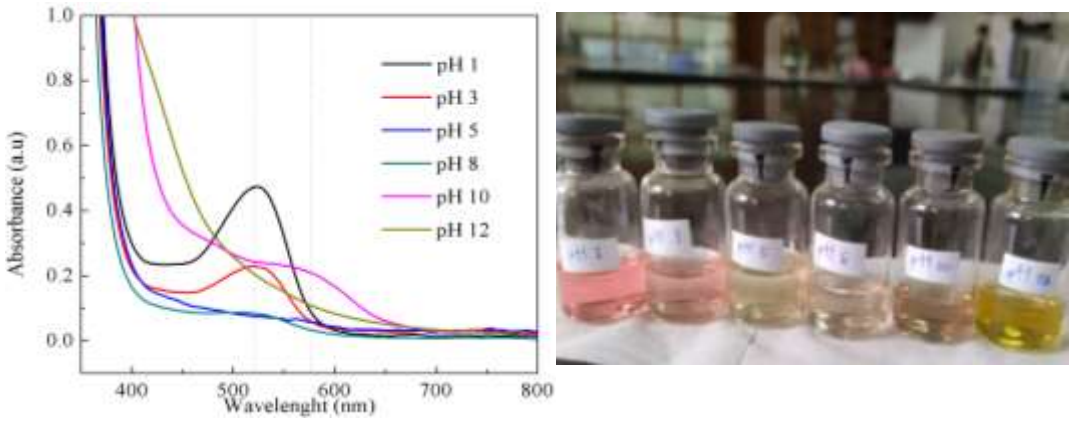


Figure 3. UV-Vis spectrum of coffee husks extract in HCl | methanol at temperature variations

Study of pH Variations

The anthocyanin UV-Vis absorption spectrum in coffee huskss was recorded between wavelengths of 524.5-563.5 nm with different pH controls. Anthocyanin extracts show very different color changes at pH 1 and 3, whereas smaller pH indicates the color is extracted to bright red (Figure 4). The UV-Vis spectrum of these six solutions shows a significant absorption peak at λ_{max}= 524.5 nm with a transition intensity of 0.474 a.u. The peaks occur because of the electronic transition from stable electrons to the flavylium cation on oxygen atoms (Ryu & Koh, 2018). At pH 5, 8, 10 and 12 coffee husks extracts are colorless to yellowish color (Figure 4). Observation through the UV-Vis spectrum, coffee skin extract showed a shift in intensity at λmax = 526.5 and nm λmax = 563.5 nm. This peak has decreased in intensity with the transition intensity of 0.226 a.u to 0.223 a.u.



(a) (b)

Figure 4. (a) UV-Vis spectrum of coffee husks extract in HCl | methanol at various pH and (b) Coffee husks extract in HCl | methanol at various pH

The UV-Vis spectrum shows that the pH value is strongly influenced by the anthocyanin stability of the coffee husks. Anthocyanins from coffee husks are stable in acidic solutions (pH < 3, from colorless/yellow to red), but unstable in

neutral or alkaline solutions (pH > 3, from colored to colorless/yellow). Anthocyanin levels decrease with increasing pH. This is because when in a very acidic pH, anthocyanin is in the most stable and most colorful conditions whereas at a more alkaline pH anthocyanin will be yellow, blue or colorless (Misbachudin, *et al*., 2014). At a high acidity level, approaching pH 1 will cause more and more anthocyanin pigments to be in the form of colored flavylium cation or oxonium. This also causes absorbance measurements to show ever greater amounts of anthocyanin. Therefore, the maximum absorbance value of Gayo Arabica Coffee husks extract is pH 1 (Moulana, *et al*., 2012).

Intensity shifts at λ_{max} = 524.5 nm up to λ_{max}= 563.5 nm can be explained as the loss of the presence of flavylium cation. Based on Figures 2 and 4, the addition of acid dehydrates the OH group in ring C. The loss of this group makes the stability of the resonance of positive ions in the C ring achieved, resulting stable charge state of the atoms in the chain. The addition of bases causes the H atoms in the phenolic group in ring A to be released. Consequently, the charge of anthocyanin at high pH less positive. This process causes the formation of quinones in ring A. The presence of quinones lead to a shift in the electronic transition at λ_{max} = 524.5 nm to λ_{max} = 563.5 nm (Hsiao & Hsieh, 2018).

Conclusions

The UV-Vis spectrum of coffee husks extract displayed the major absorption peak at λ_{max}= 529 nm and the transition intensity is 0.924 a.u on hydrochloric acid (HCl). This assigned by the electronic transition from the electron which was stabilized by the cation of flavylium on the Oxygen atom. It was indicate a characteristic of anthocyanin compounds. Anthocyanin from Gayo Arabica coffee husk was stable at 35^{o}C and 50^{o}C, which has a main absorption peak at λ_{max} = 529 nm and transition intensities of 1.547 a.u and 1.49 a.u. of 35^{o}C and 50^{o}C, both of which have major absorption peaks at λ_{max}= 529 nm and transition intensities of 1.547 a.u and 1.49 a.u. Then, it was red at pH 1 and 3, almost colorless at pH 5, 8 and 10, and yellowish color at pH 12. Anthocyanin pigment in coffee fruit extract is very stable at pH 1 where λ_{max} = 524.5 nm with a transition intensity of 0.474 au.

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