J. T. K. L.
JURNAL TEKNIK KIMIA DAN LINGKUNGAN

J. Tek. Kim. Ling. 2025, 9 (1), 31-37
p-ISSN : 2579-8537, e-ISSN : 2579-9746
http://jurnal.polinema.ac.id/index.php/jtkl
DOI: http://dx.doi.org/10.33795/jtkl.v9i1.6169

Utilization of Red Dragon Fruit (*Hylocereus polyrhizus*) Peel Waste as an Alternative Indicator for Acid - Base Titration

Noor Isnaini Azkiya*, Shafara Najla Marinda Sukmawanta, Cucuk Evi Lusiani

Department of Chemical Engineering, Politeknik Negeri Malang, Jl. Soekarno Hatta No. 9, Malang 65141, Indonesia

ABSTRACT

Titration indicators are organic (generally) or inorganic compounds used in titrations to determine and indicate the end point of a titration. Indicators that are widely used in acid-base titrations are synthetic indicators such as phenolphthalein (PP), methyl red (MM), methyl orange (MO), and phenol red (MF). Apart from being relatively expensive, the use of these indicators also produces chemical waste which can pollute the environment. The solution to overcome this problem is to utilize natural ingredients as a substitute for synthetic indicators. The natural indicator used in this research was the peel of red dragon fruit (*Hylocereus polyrhizus*). Red dragon fruit peel contains flavonoid compounds, one of which is anthocyanin. Anthocyanins are polar so they can be dissolved in polar solvents such as ethanol. This research aims to determine the effect of the type of solvent and length of maceration time in anthocyanin extraction as an indicator for strong acid-strong base titration, and to determine the effect of storage time on the stability of red dragon fruit peel extract. In the maceration process, a variable ratio of solvent to red dragon fruit peel was used 1:5 (w/v). The solvents used were ethanol, methanol, and acetone acidified with 5 mL of HCl 1% (v/v). Identification of anthocyanin compounds was carried out using FT-IR and UV-Vis. In this study, the highest anthocyanin content was found in the acetone solvent $9x10^{-4}$ mg/100 g and the lowest was in the methanol solvent at $6x10^{-4}$ mg/100 g. Furthermore, the most similar application to a commercial titration indicator is the use of methanol and acetone solvents with a 24-hour extraction time.

Keywords: anthocyanins, natural indicators, red dragon fruit peel, titration.

1. INTRODUCTION

The pH indicator is very important, especially in the field of chemistry where it is used for volumetric analysis. One method of this analysis is acid-base titration or neutralization titration [1]. This titration involves adding an indicator that functions to help determine the equivalence point which is marked by observing the color change at the end of the titration. The indicators used in neutralization titrations are called acid-base indicators. Indicators are very special chemicals that can change the color of a solution with changes in pH after adding an acid or base. Acid-base indicators tend to react with excess acid or base during titration to produce a color change. Until now, the indicators that are widely used in acid-base titrations are synthetic indicators such as phenolphthalein (PP), methyl red (MM), and methyl orange (MO) [2]. Apart from being relatively expensive, the use of these indicators also produces chemical waste which can pollute the environment. The solution to overcome this problem is to utilize natural ingredients as a substitute for synthetic indicators. Natural indicators are dyes or pigments that can be isolated from various plants, fungi, and algae [3,4].

Dragon fruit is an imported fruit that is popular with the public because it has properties and benefits as well as quite high nutritional value [5]. Red dragon fruit is

*Corresponding author:
E-mail: noorisna@polinema.ac.id (Noor Isnaini Azkiya)

Received : August 29, 2024
Accepted : November 23, 2024

known to have components composed of phenolic and non-phenolic compounds which have antioxidant activity. The peel of red dragon fruit (*Hylocereus polyrhizus*) has a color and characteristics similar to the flesh of the fruit because it also contains high levels of antioxidant components such as phenolic compounds and flavonoids. This is also supported by previous research which states that red dragon fruit peel extract contains vitamin C, tannins, alkaloids, anthocyanins, steroids, and flavonoids [6]. Dragon fruit peel contains flavonoid compounds, one of which is anthocyanin. This anthocyanin can change color as the pH value changes so it can be applied as an acid-base indicator [7-9].

Anthocyanins are a class of flavonoid compounds that are broadly divided into plant polyphenols. Flavonols, flavon-3-ols, flavones, flavanones, and flavanols are additional classes of flavonoids that are in the oxidation of anthocyanins [10,11]. This pigment plays a role in the appearance of red to blue colors in some flowers, fruit, and leaves. Anthocyanins are polar so they can be dissolved in polar solvents such as ethanol, acetone, and water. The color of anthocyanin is greatly influenced by the structure of the anthocyanin and the degree of acidity (pH). Anthocyanins tend to be colorless in the neutral pH area, in solutions with a very acidic pH (pH < 3) they give a maximum red color, while in alkaline solutions (pH 10.5) the anthocyanin pigment changes color to blue [12]. The nature of anthocyanins, which can change color at different pH levels, makes it possible to apply them as indicators for acid-base titrations.

This study will be conducted to use anthocyanin compounds from red dragon fruit peel extract as an acid-base indicator by determining the best solvent, length of maceration time, and length of storage time for the extract, identifying anthocyanin compounds based on functional groups, determining pH trajectory, determining anthocyanin concentration, and developing natural acid-base indicators. It is believed that the research findings would provide information on other acid-base markers that can be developed independently.

2. RESEARCH METHODS

2.1. Red Dragon Fruit Peel Extraction

The red dragon fruit peel was dried outdoors in the absence of sunshine for two 24-hour periods. After drying, the red dragon fruit skin was crushed with a blender. The pulverized red dragon fruit peel was then macerated for 12 hours, 24 hours, and 36 hours in a solvent at a 1:5 (w/v) ratio. The solvents employed in this study were 500 mL of ethanol, methanol, and acetone, each acidified with 5 mL of 1% HCl. After maceration, the extract was filtered through 20-25 µm filter paper prior to distillation. The concentrated filtrate obtained from distillation was then ready to be employed as an indicator of strong acids and bases.

2.2. Identification of Anthocyanin Compounds

a. Preparation of pH 1 and pH 4.5 solutions

A total of 0.186 g of KCl was placed in a glass beaker, followed by 100 mL distilled water. Concentrated HCl is then gradually added to the solution until it reaches pH 1. A pH 4.5 solution was prepared by weighing 5.7 mL of 1 M CH_3COOH and pouring it into a glass beaker with 100 mL of pure water. Then, 2.5 grams of 0.3 M CH_3COONa was added to the solution dropwise until the pH reached 4.5.

b. Determination of Total Anthocyanin Concentration Using the Differential pH Spectrophotometric Method

A total of 1 mL of anthocyanin extract was dissolved in 9 mL of pH 1 solution, followed by the same procedure at pH 4.5. After dissolution, the absorbance of anthocyanins at pH 1 and pH 4.5 was determined using UV-Vis

spectrophotometry at 530 and 700 nm, respectively [13].

c. Identification of Anthocyanin Compounds Based on Functional Groups

The material was combined with KBr powder until homogenous before being shaped into pellets. The results of FT-IR characterization of red dragon fruit peel extract are shown graphically. The spectrum shown in the graph was then compared to the literature to determine the functional groups of red dragon fruit peel extract.

2.3. Application of Red Dragon Fruit Peel

A total of 15 mL of 0.1 M HCl was mixed with 5 drops of concentrated red dragon fruit peel extract indicator, then titrated with standardized 0.1 M NaOH. The color change of the solution was observed until the endpoint was reached. The titration was carried out in triplicate, and the amount of NaOH required was reported. Titrations were brought out utilizing phenolphthalein (PP) and methyl orange (MO) as indicators.

3. RESULTS AND DISCUSSION

3.1. Characterization of Red Dragon Fruit Peel Extract

The research used the maceration process to extract the dragon fruit peels (Figure 1). Since most solvents used for anthocyanin extraction are polar alcohol group chemicals such ethanol, methanol, and acetone, they are acidified with 1% HCl. Anthocyanin molecules are more stable at low pH (acidic conditions) than in neutral or alkaline solutions, hence 1% HCl solution is the most effective acidifying solution [14-16].

The anthocyanin levels in red dragon fruit peel extract were assessed using the differential pH spectrophotometric method. This technique measures the difference in absorbance of visible light at two different pH levels, 1.0 and 4.5. The theoretical maximum wavelength of anthocyanin is in the wavelength range 505-545 nm. In this study, the maximum wavelength of previous research was used, namely 530 nm, which is the wavelength of the anthocyanin compound cyanidin-3-glucosidase with a molar absorptivity (ε) of 26,900. This wavelength can optimally identify the content of anthocyanin compounds in the form of flavylium cations. The 700 nm wavelength is used to correct turbidity or other contaminants that are still in the sample and to control whether the test has been carried out correctly.

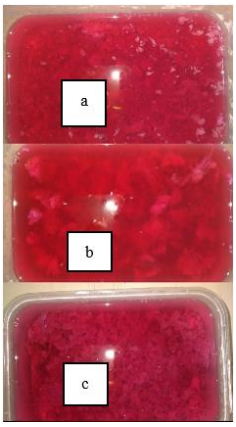

Figure 1. Maceration of red dragon fruit peel using solvents (a) ethanol, (b) acetone, (c) methanol.

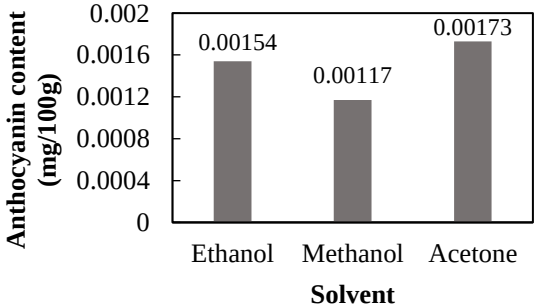

Figure 2. Anthocyanin content in red dragon fruit peel extract varies depending on the solvent used.

In this study, the highest anthocyanin content was achieved with acetone as the solvent, reaching a level of 0.00173 mg per 100 grams (Figure 2). This is due to acetone's moderate polarity, which is effective at dissolving polar compounds like anthocyanins. Additionally, acetone can break hydrophobic interactions and enhance

the solubility of anthocyanins in the solvent, leading to a more efficient extraction compared to other solvents [17].

The results of FT-IR characterization of red dragon fruit peel extract are displayed in Figure 3 and Table 1. The infrared spectrum of dragon fruit peel extract using ethanol, methanol, and acetone as a solvent was obtained in the form of a transmittance spectrum.

The frequency unit used on a horizontal line is expressed as a wave number. The spectrum of red dragon fruit peel extract from the three solvent variations has the same spectrum pattern, namely the hydroxyl group (O-H) which appears at wave numbers 3600-3200 cm^{-1}, C-H aldehyde which appears at wave numbers 2843-2841 cm^{-1}, the carbonyl group (C=O) which appears at wave numbers 1637 cm^{-1}, the ester group C-O which appears at wave numbers 1016 cm^{-1}, C-H alkene and C-H aromatic which appears at wave numbers 800-400 cm^{-1}.

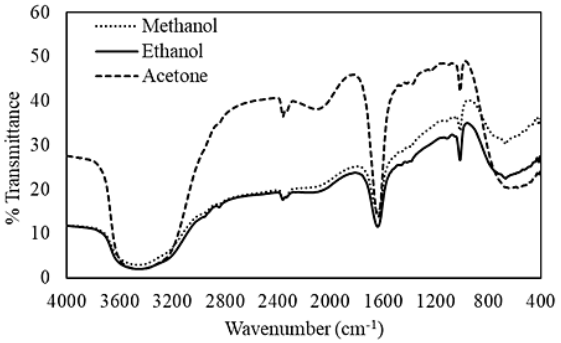

Figure 3. Infrared spectrum of concentrated extract of dragon fruit peel in (a) Ethanol, (b) Acetone, and (c) Methanol solvent.

The spectrum results of red dragon fruit peel extract from the three solvent variations showed the presence of active compounds in the alkaloids, flavonoids, tannins, saponins, steroids, and terpenoids. This is indicated by the strong intensity of the stretching vibrations of the absorbed O-H groups. In the O-H functional group, the peak broadens due to hydrogen bonds between molecules and a shift to a lower wave number. The hydroxyl group appears in the spectrum with a very strong intensity because it has the smallest %T value compared to other functional groups. The higher the %T value, the smaller the absorption intensity, and vice versa, the smaller the %T value, the greater the absorption intensity.

Table 1. Interpretation of infrared spectrum data for the three solvent variations.

Wavelength (cm^{-1})		Functional Groups
Result Study	References [18]	
3600-3200	3385-3370	O-H
2843-2841	2841-2840	C-H alifatic
2350-2330	-	COC
2085-2040	-	>CO
1637	1660-1654	C=C aromatic
1016	1026	C-O
800-400	677-675	C-H aromatic

The widened shape of the absorption band for the O-H functional group indicates the presence of alkaloid compounds containing the N-H functional group. The presence of stretching vibrations from the C-H alkane functional group that was detected proves the existence of the N-H functional group because the C-H alkane functional group indicates the presence of sufficient intensity to induce non-polar compounds such as steroids and terpenoids to appear as vibration bands. The C-O functional group strengthens the presence of tannins in red dragon fruit peel extract. The presence of a carbonyl group (C=O), is a general characteristic of flavonoid compounds, namely tannin. The C=O functional group has a quite strong intensity apart from the O-H functional group because the %T is small. The C-H alkene and C-H aromatic functional groups indicate the presence of flavonoid compounds.

The identification results from the FT-IR test show that red dragon fruit peel extract contains anthocyanins and anthocyanidins. The dominant type of anthocyanin is cyanidin because the peel of dragon fruit is

red. The color of anthocyanidin pigments is influenced by the substitution pattern of the hydroxyl group (-OH) [19]. Anthocyanins are part of secondary metabolites that are widely distributed in nature known as flavonoids. Anthocyanidins are anthocyanin aglycones that are formed from acid hydrolysis [20]. Anthocyanins and anthocyanidins share a common characteristic that they both carry a positive charge.

3.2. Application of Red Dragon Fruit Peel Extract as a Titration Indicator

This dragon fruit peel extract indicator was applied to the strong acid-strong base titration of HCl samples with NaOH as a secondary standard solution. This sample was selected because based on the results of the pH trajectory test, the resulting color change showed that the dragon fruit peel extract had a color change area at pH 8-10 with a color change from orange to colorless. The results of the titration using the indicator red dragon fruit peel extract and synthetic indicators (phenolphthalein and methyl orange) in the strong acid-strong base titration are shown in Figure 4. When using red dragon fruit peel extract as an indicator, titrating an HCl solution with an NaOH solution reached an equivalence point at pH 7, indicating that it can serve as a natural indicator for strong acid-strong base titrations.

In observations of strong acid-strong base titrations using red dragon fruit peel extract as an indicator, the most accurate titration endpoint was achieved with a24-hour maceration for all three solvent variations. The titration endpoints in different solvents were 13.4 mL with ethanol extract, 13.2 mL with methanol extract, and 13.3 mL with acetone extract. For comparison, the endpoint with phenolphthalein was 13.8 mL, while with methyl orange, it was 13.5 mL. The observed color changes for the different indicators were phenolphthalein changed from colorless to pink, methyl orange transitioned from dark red to pink, and red dragon fruit peel extract changed from orange to colorless.

The maceration times of 12 and 36 hours may have caused significant errors during titration because of differences in the number of active components extracted. A shorter maceration time (12 hours) might not extract enough pigment, while a longer time (36 hours) could lead to degradation of the active components or extraction of additional substances that affect the stability of the extract's color. This variability could cause differences in the volume of NaOH needed, affecting the titration results.

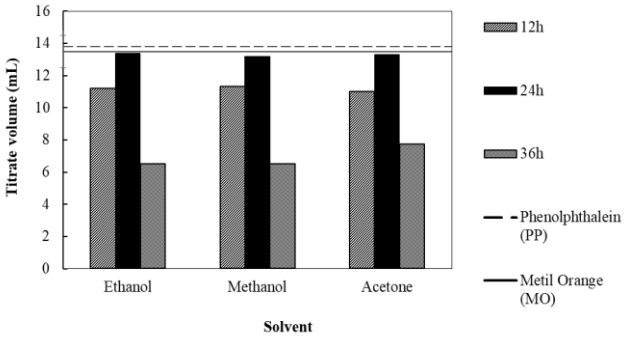

Figure 4. Results of titration using red dragon fruit peel extract as an indicator compared to phenolphthalein (PP) and methyl orange (MO) indicators.

3.3. The effect of Storage Time on the Stability of Red Dragon Fruit Peel Extract

Based on the results of the analysis using a UV-Vis spectrophotometer (Figure 5), it showed that there was a decrease in anthocyanin levels in the three solvent variations along with the length of storage time of the extract. This is because the longer the storage, the more it will damage the color intensity due to the effects of free radicals that damage the anthocyanin color pigment [21]. The average total anthocyanin concentration was $7x10^{-4}$ mg/100g in ethanol solvent, $6x10^{-4}$ mg/100g in methanol solvent, and $9x10^{-4}$ mg/100g in acetone solvent. The stability of the total anthocyanin content is influenced by many factors such as changes in pH, temperature, sample preparation process, conditions and

storage period of samples that are too long so that anthocyanin compounds can be degraded [21].

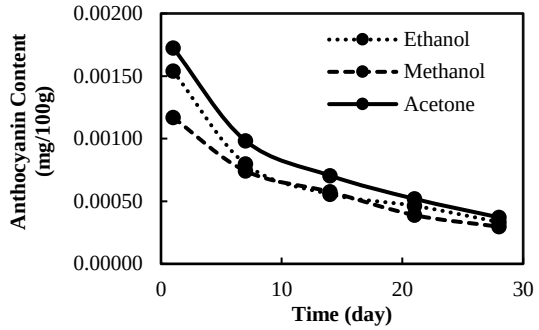

Figure 5. The effect of Storage Time on the Stability of Red Dragon Fruit Peel Extract.

4. CONCLUSION

The type of solvent influences anthocyanin extraction as an indicator for strong acid-strong base titrations with the highest anthocyanin content found in the acetone solvent at 9x10-4 mg/100 g and the lowest in the methanol solvent at 6x10-4 mg/100 g. The length of maceration time has an influence on anthocyanin extraction as an indicator for strong acid-strong base titration as evidenced by the best maceration time at 24 hours.

ACKNOWLEDGMENT

The author expresses his gratitude to State Polytechnic of Malang which has funded this research through the Regular Research scheme of DIPA Polinema in 2023.

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