Jambolan fruit peels (*syzygium cumini l. skeels*) as substitute for synthetic acid base indicators: implementation of the ESD concept

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Abstract. Implementation of Education for Sustainable Development (ESD) can be done by implementing several strategies such as integrating the three pillars of ESD to learning material and adopting the principles of green chemistry in learning. In this study, the use of renewable materials with safe solvents to extract jambolan fruit peels as a substitute for synthetic indicators has been carried out. The results of measuring the absorbance value at wavelength 507-528 showed that the jambolan fruit peels was extracted optimally in the solvent mixture double distilled water : ethanol with a ratio of 1 : 2 at pH 2. Under these conditions, maceration was carried out 24 h three times and then evaporated and extracted using n-hexane and chloroform solvents. Extracts that have been tested under various pH, ranging from 1 to 14, and titration methods were then used in learning activities to determine the level of CH₃COOH in food vinegar on the topic of acid-base titration. The data generated in this study indicates that the natural indicator of jambolan fruit peels can be used as a substitute for synthetic indicators. Its use in learning provides knowledge to students regarding the chemicals that are more economical and environmentally friendly and support implementation of ESD concept in school.

1. Introduction

The concept of ESD (Education for Sustainable Development) has three pillars namely environmental, economic and social for future generations [1]. Chemistry education has an important role in ESD because many products in everyday life are based on chemistry as well as production processes and end products from the chemical industry that have great potential to focus on the environment [2]. One way to implement the ESD concept is to present four ESD strategies that can be implemented in formal chemistry education, namely: Adopting green chemistry, incorporating ESD content in learning, incorporating socio scientific issues, and utilizing chemistry learning as part of school culture [3].

The application of ESD concept by adopting some of the principles of green chemistry is done through using natural acid-base indicators on acid-base material instead of synthetic indicators. The use of synthetic indicators has limitations because the prices relatively expensive, some indicators are toxic and cause environmental pollution even though they are of little use [4]. Therefore, the use of synthetic indicators should be reduced and replaced with natural materials. Natural plants or materials that can be
used as acid-base indicators derived from plant pigments, either from flowers, leaves, fruit or peel, which contains anthocyanin compounds that can change color at each change in pH [5].

Indonesia as a tropical country has several unique plants such as jambolan plants. This plant bears fruit in September-January with purple-black peel if it is ripe, has a sweet and sour taste that contains a lot of anthocyanins and is known as an antioxidant and anti-inflammatory [6]. Unlike other natural acid-base indicators such as purple cabbage that must be purchased, jambolan peel is a plant that grows freely. Jambolan fruit that are ripe will fall so it is easy to take and get for free. This is expected to increase student awareness about the choice of using inexpensive and natural chemical compared to synthetic. Several studies have been carried out to extract jambolan fruit, such as the solvent effect on topical fruit peel extraction using water, ethanol and isopropyl solvents and various mixtures with the results of research using a mixture of water and ethanol to extract jambolan as the best solvent [7]. Another study conducted using ethanol solvent showed that jambolan extracts changed color when added hydrochloric acid (red), sodium hydroxide (olive green), acetic acid (reddish pink) and ammonia (green) solution [8]. In this study, the extraction process was optimized by varying the solvent and pH ratio. Then the extract was tested to distinguish solutions in pH 1-14 and as an indicator in acid-base titration to determine the effectiveness of jambolan fruit peel as an indicator.

2. Methods

2.1 Materials and tools

The research was conducted at University State of Jakarta laboratory and implemented in acid-base titration topic at SMAK 7 PENABUR Jakarta, which details are as follows. Jambolan fruit peels is obtained from the backyard of SMAK 7 PENABUR Jakarta, Indonesia. All chemicals used are pro-quality qualified; CHCl$_3$, HNO$_3$, HCl, CH$_3$COOH, CH$_3$COONa, NH$_3$, NH$_4$Cl, NaOH, PP and MM synthetic indicators and pH four buffer (Merck), double distilled water (pro injection). 95% ethanol and n-hexane (technical) were used for extraction without purification, and all water used to make a solution using distilled water. To measure the pH of all solutions used a pH meter (Hanna Type 98107) which has been calibrated with a pH four buffer solution, Eyela 1000as Evaporator used for evaporation extract from jambolan fruit peels and Shimadzu 1240 UV-VIS spectrophotometer to measure the wavelength and absorbance of the extract.

2.2 Optimization jambolan fruit peels extract preparation

Jambolan fruit is washed, and the peel is taken then dried at room temperature to reduce water content as shown in Figure 1. The extraction was prepared by macerating 0.8 gram jambolan fruit peel with 30 mL various solvents namely double distilled water, ethanol, double distilled water : ethanol (2 : 1), double distilled water : ethanol (1 : 1), double distilled water : ethanol (1 : 2). Maceration with each solvent for 24 hours at room temperature in a dark bottle. The resulting extracts were measured using a UV-VIS spectrophotometer at a wavelength of 300-550 nm. The absorbance value of extracts from various solvents which produced the highest absorbance was chosen as the optimal solvent.

![Figure 1. Jambolan Fruit Peels](image-url)
room temperature in a dark bottle. The extraction obtained was measured by its absorbance at a wavelength of 500-600 nm. The highest absorbance value was selected as the optimal pH condition for extracting anthocyanin in jambolan fruit peels.

2.3 Jambolan fruit peel extraction preparation

The jambolan fruit peels extract was prepared by macerating 16 grams of jambolan fruit peels in 160 mL of double distilled water solvent : ethanol (1 : 2) pH 2 for 24 hours at room temperature in a dark bottle. The extraction process was carried out 3 times so that the filtrate was ±480 mL. The filtrate is then concentrated using an evaporator at a temperature of 60°C until it is thick purple (66 mL). The evaporation results were then extracted with n-hexane solvents 4 times with a volume of 20 mL each until the color of the n-hexane solvent was clear. Extraction was continued with chloroform solvent 3 times with a volume of 20 mL to the color of clear chloroform solvent. The extract is then stored in a dark bottle in the refrigerator.

The resulting extract was then tested in various pH solutions by reacting 6 mL of pH 1-14 solution with six drops of jambolan fruit peels extract on a transparent glass bottle. Testing jambolan fruit peels extract as an indicator of acid base titration carried out by titrating HCl solution with NaOH solution, CH$_3$COOH solution with NaOH solution, CH$_3$COOH solution with NH$_3$ solution and titrating NH$_3$ solution with HCl solution. Titration was carried out using three drops of methyl red and phenolphthalein indicators as synthetic indicators and six drops of jambolan fruit peel extract as a natural indicator.

3. Result and Discussion

3.1 Solvent and pH optimization

Anthocyanin can be extracted in semipolar to polar solvents, the more similar the anthocyanin polarity with the solvent, the more anthocyanin extracted by solvent. The best solvent for extracting anthocyanin is acidified methanol [9], but in addition to the toxic methanol properties, many studies have stated that there is no definite solvent to extract anthocyanin, the solvent to extract certain plant anthocyanins maximally does not necessarily extract other plants equally well [10]. Therefore, optimization of solvent is done to find out the best solvent extracting jambolan fruit peels.

Based on observations (Figure 2) it appears that the intensity of red in the double distilled water: ethanol (1:2) solvent is more concentrated so that it indicates more anthocyanin extracted in the solvent. This is supported by measuring the absorbance of solvent optimization (Table 1) which shows that the largest absorbance value is 0.638 at a wavelength of 524 nm. This shows that the jambolan fruit peels extracted maximally in a mixture of double distilled water and ethanol (1:2) which are included in the five safest solvents. This is in accordance to the principles of green chemistry, namely the use of safe solvents.

The results of solvent optimization showed that jambolan fruit peels anthocyanin content was delphinidin-3,5-diglucoside, petunidine-3,5-diglucoside, malvidin-3,5-diglucoside, cyanidin-3,5-diglucoside, and peonidin-3,5-diglucoside [11] has a polarity similar to the double distilled water: ethanol (1:2). The results of this study are in accordance with the foregoing which states that the extracted anthocyanin concentration is optimal in the combination of water and ethanol solvents [7].

pH optimization results in very concentrated color intensity at pH 1 and decreases at higher pH (Figure 3), while the highest absorbance value is at pH 2 with an absorbance value of 3.690 at a wavelength of 528 nm and decreases at pH 3 (Table 2). This is because at low pH the content of red flavylium cations is very dominant and decreases at higher pH [12].

3.2 Jambolan fruit peel extraction

The use of dry samples in this study is because dry samples contain more flavonoids [13], while the maceration process is carried out at room temperature in dark bottles to prevent the occurrence of anthocyanin degradation by light which can lead to reduced anthocyanin content [14].
Extraction using nonpolar n-hexane solvent was carried out to separate nonpolar compounds such as lipids, carotenes, chlorophyll pigments and other nonpolar compounds, while extraction with chloroform aims to separate semipolar compounds from extracts. Extraction using n-hexane and chloroform solvents produces polar extracts in accordance with anthocyanin properties and can produce brighter colors in the identification of various pH solutions.

Table 1. Absorbance of Jambolan Fruit Peels Extract at Various Solvents

| Solvent                  | Wavelength (nm) | Abs  |
|--------------------------|-----------------|------|
| Etanol                   | 343             | 4,000|
|                          | 266             | 4,000|
| Double distilled water   | 507             | 0,315|
| Double distilled water : Etanol (1 : 2) | 524 | 0.638 |
| Double distilled water : Etanol (1 : 1) | 520 | 0.293 |
| Double distilled water : Etanol (2 : 1) | 525 | 0.394 |

Table 2. Absorbance of Jambolan Fruit Peels Extract at Various pH

| pH  | Wavelength (nm) | Abs  |
|-----|-----------------|------|
| 1   | 572             | 2,357|
| 2   | 528             | 3,690|
| 3   | 528             | 0,383|
| 4   | 528             | 0,336|

Figure 2. Jambolan Fruit Peels Extraction Color
(1) Ethanol Solvent; (2) Double distilled water : Ethanol (2 : 1); (3) Double distilled water : Ethanol (1 : 1); (4) Double distilled water : Ethanol (1 : 2); (5) Double distilled water

3.3 Jambolan Fruit Peels Effectiveness Test

The effectiveness test of jambolan fruit peels is done with two parameters; testing with various pH solutions and testing by the titration method. The results of testing the extract with a pH 1-14 solution produce the color as shown in Figure 4. At pH 1-2, the extract is red and fades at pH 3-7, at pH 8 the extract is purple and green at pH 9-11, then turn yellow at pH 12-14. This result is not much different from previous studies that the intensity of red decreases with increasing pH [15]. This occurs because anthocyanin forms a red flavinium cation at pH 1, at pH 2-4 anthocyanin in the form of a mixture of flavinium and quinoidal cations, at pH 5-6 there are two colorless compounds namely pseudobasa carcino1 and chalcone [16]. Under acidic conditions, the pigment form is the cation of flavium and the cation flavium nucleus, where the number of electrons in the cation flavium nucleus is small so it is very
reactive. Increased pH causes flavylium cations to become unstable and easily undergo structural transformation into chalcone compounds. Further increase in pH causes loss of protons rapidly from the hydroxyl group of flavillium cations to produce a blue quinonoidal form [10]. The anthocyanin color intensity of jambolan fruit peel at various pH makes it can be used as an acid-base indicator.

The results of titration with the indicator of jambolan fruit peels extract, and synthetic indicators are shown in Table 3. In alkaliometri titration using a natural indicator, there are two times the color change, red to faded red, almost colorless and green, while the acidimetri titration with the color change from green to brownish red. Color changes occur due to equilibrium reactions between molecules and ions from acid-base indicators.

The working principle on the three indicators is represented by the PP indicator with the reaction: HPh (colorless) $\rightleftharpoons$ H$^+$ + Ph$^-$ (pink). In an acidic state, the equilibrium will shift towards the formation of HPh so that the color of the solution is colorless, in addition to the base, OH$^-$ will bind H$^+$ so that the equilibrium shifts towards the formation of Ph$^-$ which causes the indicator color to pink. This is when the indicator will change color and the titration is stopped which is known as the end point of the titration.

![Figure 4. Colors of Jambolan Fruit Peels Extract in Standard Solution Various pH](image)

**Table 3. Titration Results Using Synthetic and Natural Indicators**

| Titrant (mL) | Titrate (mL) | Indicators         | Color changes         |
|--------------|--------------|--------------------|-----------------------|
| HCl          | NaOH         | PP                 | Colorless-Pink        |
| 10           | 9.6          | PP                 | Red-Green             |
| 10           | 9.967        | Jambolan indicator | Colorless-Pink        |
| CH$_3$COOH   | NaOH         | PP                 | Red-Green             |
| 10           | 10,467       | PP                 | Colorless-Pink        |
| 10           | 10,767       | Jambolan indicator | Red-Green             |
| CH$_3$COOH   | NH$_3$       | PP                 | Colorless-Pink        |
| 10           | 5.033        | PP                 | Red-Green             |
| NH$_3$       | HCl          | Jambolan indicator | Yellow-Red            |
| 10           | 22.8         | MM                 | Yellow-Red            |
| 10           | 22.33        | Jambolan indicator | Green-Brown to Red    |

Based on the ratio of the volume titrant needed to titrate titration to the end point of the titration it can be concluded that the natural indicator of jambolan fruit peels can be used as an acid base indicator because it shows the volume of the endpoint of titration that is not much different from using synthetic indicators. The use of jambolan fruit peels indicator in learning was done to determine CH$_3$COOH levels in kitchen vinegar using 0.1 M NaOH through the titration method. The results showed that CH$_3$COOH levels obtained by students were not much different from the levels stated in kitchen vinegar bottles (25%). Some of the opinions of students about the use of jambolan fruit peel indicators are as follows:

"*It's better to use natural indicators because it's environmentally friendly and inexpensive*"

(Student 21, April 26, 2019)
"The ESD principle in learning is maintaining the environment. It is proven that natural indicators that are more environmentally friendly are also just as beneficial as syntheses, so perhaps many are aware not to use synthetic ingredients if they can be replaced with natural ingredients" 
(Student 14, April 26, 2019)

Based on these results it can be said that the use of a natural indicator of jambolan fruit peels can be used in learning as a substitute for synthetic indicators. The application of education for sustainable development in schools is done by using chemicals that reduce solvent emissions and reduce waste, use renewable materials and use safe solvents. In addition, the selection of jambolan fruit that is easily obtained as raw material raises awareness in students to choose to use materials that are economically beneficial but also pay attention to the environment.

4. Conclusion
The application of the concept education for sustainable development by adopting the principles of green chemistry done by replacing synthetic indicators with natural indicator of jambolan fruit peels which are renewable materials, using safe solvents, reducing solvent emissions and reducing waste. The study showed that jambolan fruit peels was extracted optimally in the solvent mixture double distilled water: ethanol with a ratio of 1:2 at pH 2. The same effectiveness between the synthesis indicators and jambolan fruit peels proves that natural ingredients can be utilized in learning. It can be concluded that jambolan fruit which highly available and environmentally friendly may serve as an alternative for chemicals used as acid base indicators.

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