A Kinetic study on Color Degradation during Application of Dried Colorant from Roselle Extract with Foaming Agent

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Abstract. Roselle extract is known as the source of red pigment (anthocyanins). The anthocyanins are potential as the food colorant that safer than synthetic colorant and gives benefit to human health. This research was to study the effect of pH and storage temperatures on the kinetic degradation of color in application as the food colorant from dried roselle extract with foaming agent. The food colorant was applied in jelly. During the application, the color changes in jelly were observed every 7 days for 28 days. The color changes during application were fitted to several kinetic models of color degradation. Result showed that the color degradation was faster in higher pH and higher storage temperatures. The color retention can be well estimated using the zero order kinetic model.

Keywords: food colorant; degradation; kinetic; roselle

1. Introduction

Color affects the perception of the quality and taste of food [1]. In food processing, color degradation often occurs so the food colorants are added. Some reasons for adding food colorant such as (1) Increasing color intensity in food (2) Changing degraded colors during the process (3) Minimizing variations in one batch of production (4) Equip food with nutrition [2,3]. There are two types of food colorant that added to food products, namely synthetic colorant and natural colorant. Around of 42% of the food coloring market uses synthetic colorant because of cheaper prices, attractive appearance, and better color resistance [1,4]. However, synthetic food colorant such as tartazine can cause intolerant reactions in some individuals [5]. In addition, the use of synthetic food colorant indirectly contributes to hyperactivity disorders in children or commonly called Attention Deficit Hyperactivity Disorder (ADHD) [6,7]. Based on the chemical structure of natural food coloring, it can be classified into six types namely heme, carotenoids, chlorophyll, betalain, flavonoids, and other dyes [3]. Generally this natural color pigment is less stable and the color changes during processing [8]. Color changes in the pigment one of them occur due to oxidation. Heme can change from red to purplish and chlorophyll can change from green to brown [3].

One of the anthocyanin pigment sources is roselle. Roselle is produced in China, India, Sudan, Uganda, Indonesia, Malaysia and Mexico. Around 6.23% of the world's total roselle production is produced in
Indonesia [9]. The main types of anthocyanins found in roselle flower are delphinidin-3-sambubioside (71.4%) and cyanidin-3-sambubioside (26.6%) [10]. Anthocyanin content in roselle flowers varies depending on the method of planting, extraction method, type of solvent, and material size [9]. Extraction can take the anthocyanin content of roselle flowers [11,12]. Roselle extract needs to be dried to produce stable anthocyanins and facilitate storage. Several studies have examined the drying process of roselle extract and its relation to nutrient degradation during the drying process. Drying roselle extract with foaming agent is the option to form the stable natural colorant with high nutrition [13]. However, based on literature studies, it is hard to find the study application for dried roselle extract in food applications. The aim of this research is to study the effect of storage conditions like pH and temperature on kinetic degradation of color during application of dried roselle extract with foaming agent.

2. Materials and Methods

2.1. Materials
Dried roselle colorant was obtained through lab scale production [13]. Jelly powder was purchased from local market in Semarang, Indonesia. All of the chemicals that were used from chemicals suppliers.

2.2. Methods
This research was consisted in several steps that involved roselle production of natural food colorant (dried roselle extract), material formulation, analysis of color and structure using FTIR and fitting kinetic model for color degradation.

2.2.1 Natural food colorant production. Dried roselle extract as the food colorant was obtained through extraction and drying process. Extraction process was conducted using 50 gram of roselle calyces and 500 ml of water as the solvent [11]. The roselle extract was then dried with addition of foaming agents for 145.3 minutes in drying temperature 40°C as studied in previous research [13].

2.2.2 Material formulation. The dried roselle extract with foaming agents was applied as the natural food colorant in jelly. The material formulations can be seen in the Table 1. Amount 500 ml of water was added in 100 gram of materials. Then the solution was mixed and heated up. The jelly was then placed in different storage condition, refrigerator condition (5°C) and environmental condition (28°C). The pH of the jelly was adjusted using buffer solution. The color of jelly was observed every 168 hours for 672 hours.

| Material               | Weight (gram) |
|------------------------|---------------|
| Sucrose                | 84            |
| Jelly powder           | 15            |
| Dried food colorant    | 0.15          |
| Citric acid            | 0.85          |

2.2.3 Color analysis. The color changes of jelly were observed using a Chroma Meter (CR-300, Minolta Co., Ltd., Osaka, Japan). The scale of color was identified as Hunter L (Lightness), a (redness and greenness) and b (yellowness and blueness) value. The L, a and b was then calculated as the ΔE value (Equation 1) and color combination of L×a×b [14].

$$\Delta E = \sqrt{(L_t - L_0)^2 + (a_t - a_0)^2 + (b_t - b_0)^2}$$ (1)

2.2.4 FTIR analysis. FTIR spectrometer (Frontier FT-IR 96681 from PerkinElmer, America) was recorded from 4000 to 1048 cm⁻¹. The sample measurements were replicated three times.
2.2.5. Kinetics of color degradation. The kinetic of color degradation was described using three kinetic models, such as order 0 (Equation 2), order 1 (Equation 3), and order 2 (Equation 4). The model with the highest value of $R^2$ was selected to describe the color degradation during the storage. The color jelly was described using combination of of $L \times a \times b$ [14].

**Order 0**

$$C_t = C_0 - kt \quad (2)$$

**Order 1**

$$\ln C_t = \ln C_0 - kt \quad (3)$$

**Order 2**

$$\frac{1}{C_t} = \frac{1}{C_0} - kt \quad (4)$$

Where $C_t$ was the color of jelly at t hours, $C_0$ was the color of jelly at 0 hours, $k$ was constant rate of color degradation, $t$ was storage time (hours)

3. Results and Discussion

3.1. The effect of pH on color stability

The $\Delta E$ (the total color difference) value along storage time was observed. The total color difference was used to determine the stability of the color by its value changes. The different pH resulted in different value of $\Delta E$ (Figure 1). At storage time 168 hours, the $\Delta E$ value reached higher than 3.5 in jelly with pH 6. It is indicated that the color difference is noticeable for human eye. While in pH 2 and pH 4, at the same time the value of $\Delta E$ less than 3.5. At pH 2 and pH 4, the color difference was noticeable at storage time 336 hours.

![Figure 1](image)

**Figure 1.** The value of total color difference ($\Delta E$) at various pH of jelly under temperature storage 28°C

The pH affected the anthocyanin structure and color, also lead to different stability of color during storage. At lower pH storage, the jelly resulted higher color stability (Figure 1) and based on FTIR analysis, the absorbance value was higher (Figure 2). Based on the FTIR analysis there was two peak
that appeared, OH group appeared at wavelength of 3567-3837 cm\(^{-1}\) and C=O group at wavelength of 1637-1638 cm\(^{-1}\). That two group is the major group in anthocyanin structure [10]. Delphinidin-3-sambubioside and cyanidin-3-sambubioside are two main anthocyanins compound contained in roselle calyces [10]. Delphinidin and cyanidin have high stability in lower pH and degradation occurs at higher pH [15]. At pH 2, the anthocyanin was red and in the form of flavylium cations. In pH range between 4 and 6, there are four possible structure of anthocyanin: flavylium cation (red), chalcone (yellow), quinonoidal base (purple) and carbinol base (colorless) [16].

![FTIR spectra of jelly with different pH](image)

**Figure 2.** FTIR spectra of jelly with different pH at frequency of 1048–4000 cm\(^{-1}\) at storage temperature 28°C

3.2. The effect of storage temperatures on color stability
The natural food colorant form dried roselle extract with foaming agents was applied in jelly. The effect of storage temperature was observed (Figure 3 and Figure 4). During the storage time, the redness value (a) decreased. The lightness (L) increased and the blueness (b) decreased.

![Color changes during the storage time](image)

**Figure 3.** The color changes during the storage time at storage temperature 28°C
The ΔE (the total color difference) value increased along the storage time. At the 168 hours, the ΔE value of jelly at storage temperature 5°C was less than 2, indicated that the color difference was lowest and did not noticeable by the human eye. While in the same time, the ΔE value of jelly at storage temperature 28°C was 3.5 (medium color difference). The noticeable color difference was approached when the ΔE value higher than 3.5. At storage temperature 5°C, the visible color changes was observed at 336 day. While, at storage temperature 28°C after 168 hours. Higher storage temperature lead to color degradation, was indicated by the redness value (a) reduction and the lightness (L) increation [17,18]. This result was comparable with synthetic, the synthetic colorant at storage temperature 5°C was able to retain the color 2 times longer [19].

![Figure 4. The color changes during the storage time at at storage temperature 5°C](image)

3.3. Kinetics of color degradation
Kinetics of color degradation during the storage depends on temperature and pH. The zero, first, and second order of kinetic model were used to predict the value of constant rate of color degradation at different temperatures and pH. The zero order kinetic and the first order kinetic were comparable since several variable gave the highest value of $R^2$ (Table 2). But the zero order kinetic was favorable model since the average value of $R^2$ was the highest. The value of constant rate of color was higher in higher storage temperature and pH. This result was appropriate with the result above. The value of kinetic constant can be used for predicting the color retention in longer storage time.
Table 2. Kinetic model for color degradation under different pH and storage temperature

| T (°C) | pH  | Kinetic Model  | Equation         | R²   |
|-------|-----|---------------|------------------|------|
| 5     | 2   | Order 0       | C = -4.9667t + 43971 | 0.7787 |
| 6     | 4   |               | C = -14.09t + 13409 | 0.9442 |
| 2     | 6   |               | C = -16.777x + 12439 | 0.9789 |
| 28    | 4   | Order 1       | ln (C) = -0.0001x + 0.011 | 0.7792 |
| 6     | 2   |               | ln (C) = -0.0019x + 0.0521 | 0.8909 |
| 28    | 4   | Order 2       | 1/C = 7.10^{-7}t + 2.10^{-5} | 0.8184 |
| 6     | 4   |               | 1/C = 3.10^{-7}t + 5.10^{-5} | 0.7701 |
| 2     | 6   |               | 1/C = 3.10^{-9}t + 2.10^{-5} | 0.7797 |
| 28    | 2   |               | 1/C = 7.10^{-8}t + 8.10^{-5} | 0.9449 |
| 4     | 6   |               | 1/C = 3.10^{-8}t + 2.10^{-5} | 0.8906 |

4. Conclusion
The stability of natural food colorant from dried roselle extract with foaming agent was affected by pH and storage temperature. The pH related to structure and color of anthocyanin. Delphinidin and cyanidin is stable in lower pH. In storage temperature 5°C, the jelly showed a good color until 336 hours. Higher storage temperature reduce the redness and increase the lightness of jelly. Zero order kinetic was favorable model and can be used to predict the color degradation during the storage and predict the color retention in longer storage time.

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