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Comparison of Gravimetric Method with UV-Vis Spectrophotometry for Determination of Reaction Order in Natural Dyes Adsorption Process

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Abstract – The order of the reaction is the number of concentration factors that affect the speed of a chemical reaction. The reaction order can be used to determine how the adsorption process is in the colouring process based on determining the linear regression equation of the R square value. This study aims to compare the gravimetric method with the UV-Vis spectrophotometric method in determining the reaction order in chlorophyll samples of the natural dye papaya leaves. This study used a quantitative method to determine the value of the reaction order of the papaya leaf natural dye, with data analysis techniques including gravimetric method analysis to determine chlorophyll content, UV-Vis spectrophotometry to determine the value of chlorophyll absorbance and linear regression to determine the order of the reaction. The results showed that the two methods followed first order with an R-value of 0.951 for the gravimetric method and 0.994 for the UV-Vis spectrophotometric method.

Keywords: Adsorption; Natural Dyes; Gravimetry; UV-Vis Spectrophotometry.

INTRODUCTION

Natural dyes are dyes obtained from natural materials such as plants, animals and other mineral sources. Natural dyes can be used as alternative dyes that are non-toxic, renewable, easily degraded and environmentally friendly. Almost all types of plants, if we extract them, will produce dyes, such as fruit, flowers, leaves, and even roots, logs, seeds, and skin (Pujilestari, 2015). This natural dye reduces chemical residues harmful to the environment (Ribeiro, MGTC, et. al, 2010). Natural dyes must be used in chemistry learning, bearing in mind that there are still many uses for hazardous chemicals that can pollute the environment. Applying Green Chemistry and Education for Sustainable Development (ESD) is also essential so that students can use chemical concepts to solve environmental problems and create environmental awareness for future generations (Matitaputty, et al, 2022).

Banten is known for having an isolated tribe called the Baduy people, whose lifestyle is still natural. They use plants that can be used as natural dyes for natural colouring since ancient times passed down from generation to generation. This natural dye was found based on their search for several plants around that could be used as dyes. The colouring plants used by the Baduy people include renrang skin, mahogany skin, secang skin, embarrassed daughter, jengkol skin and areca nut, which require further ethno-chemical studies (Namirah, et al., 2019).

Papaya is a versatile plant that is often used in traditional medicine. The leaves are commonly used as natural dyes because they produce a green colour called chlorophyll. Chlorophyll is a green dye resulting from a response to reflected or absorbed light. The potential of these colouring pigments is carried out by analysing the optical properties in the form of transmittance analysis (T), which is the ratio of the intensity of absorbed radiation to the intensity of the radiation that comes out and also carried out absorbance analysis (A), which is the quantisation of how much light is absorbed by pigment particles in one solution. Regarding green chemistry, papaya leaves are used as a natural dye to reduce synthetic dyes, which are harmful to the environment (Khofya, & Aji, 2018).

In Aisy's research (2018), the chlorophyll in olives was obtained to produce a green colour by decomposing heat. The amount of time when heating, pressure, and temperature are factors that affect the decomposition process, so the chlorophyll in olives can be seen to have two types. Type of chlorophyll a, greenish-yellow (another example is red algae) and chlorophyll b, greenish blue (another example is green algae). Chlorophyll a is the primary photosynthetic pigment in green plants for the process of transferring light energy to chemical acceptors for photosynthesis and mostly absorbs at wavelengths of 430 nm and 660 nm (Aisy, 2018). Following are the differences in the structure of chlorophyll a and b; the difference is the alkyl bonded to each structure.

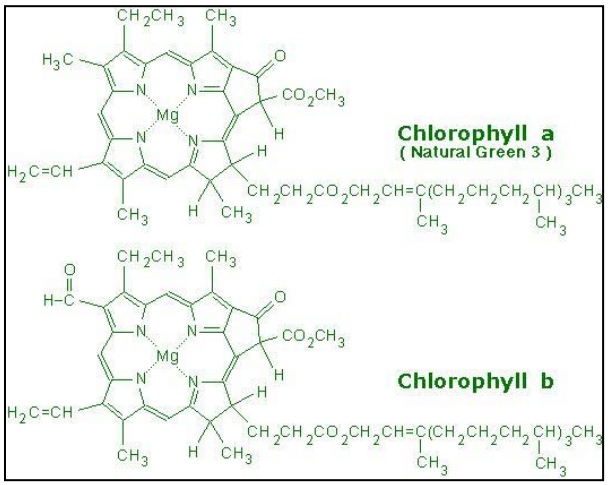

Figure 1. Structure of chlorophyll a and b

Adsorption is a process that occurs when a fluid (liquid or gas) is bound to a solid and eventually forms a thin layer on the surface of the solid. The adsorption process is divided into two processes, namely physical adsorption caused by force *Van der Waals*, and chemically caused by a chemical

reaction between the adsorbate molecules and the atoms making up the surface of the adsorbent. Factors affecting adsorption include contact and agitation time, sufficient contact required to reach adsorption equilibrium and surface area of the adsorbent. The greater the surface area of the adsorbent, the greater the adsorption is carried out (Saputra, 2008).

This study aimed to compare the gravimetric method with the UV-Vis spectrophotometric instrument in determining the reaction order in the adsorption process of chlorophyll samples of the natural dye papaya leaves. By determining this order, we can determine the optimal time for the adsorption process of natural dyes to determine whether adsorption can be carried out mono or in bilayers. The gravimetric and UV-Vis spectrophotometric methods are easy to perform even in a simple laboratory, so they are efficient, but the results are still valid.

METHODS

Research Materials

The papaya material sample used in this study came from the Inpres 15 market, Larangan, Tangerang City, Banten, picked directly from the tree. The materials used in this study were papaya leaves, 60% ethanol, distilled water and filter paper. The tools used are a digital balance and instrument UV-Vis Spectrophotometer model 752 N.

Preparation of Natural Dyes Samples

Natural dyes were made from papaya leaves with the following procedure: (1) Papaya leaves were cut into small pieces and then weighed 12.5 g, 25 g, 37.5 g, 50 g and 62.5 g, respectively. (2) Dissolving papaya leaves with 50 mL of distilled water, then heating using a bath with a temperature of 40°C. (3) 100 mL of 60% acetone was added to the solution and then filtered. (4) The natural dye solution filtrate is allowed to settle overnight. (5) The chlorophyll content of the natural dye samples was calculated using the gravimetric method, and the absorbance value using UV-Vis spectrophotometry.

Calculation of Chlorophyll Rate

Chlorophyll content was calculated using the formula: % Content = (mass of substance ÷ mass of sample) × 100%. (1) The natural dye is poured slowly into the funnel until it is completely filtered. (2) Place the filter paper containing the chlorophyll precipitate onto the watch glass. (3) Put the filter paper containing the chlorophyll precipitate into the oven at 105°C. (4) Cool the crucible, weigh it.

Calculation of Chlorophyll Absorbance Value

Data was also collected using a UV-Vis spectrophotometer with a wavelength of 645 nm. The absorbance strength is calculated by the absorbance value using the formula: A = abc. Then both gravimetric and UV-Vis spectrophotometric data were analysed by linear regression to determine the reaction order using Excel and SPSS applications.

RESULT AND DISCUSSIONS

Preparation of Natural Dyes Samples

Based on research conducted by Aisy (2018), extraction was carried out using a temperature of 50°C, and the optimal length of time for sampling was obtained at 60 minutes with the highest chlorophyll content of 0.4654 mg/L. Based on research by Azizah & Utami (2016), papaya leaves have the potential as a natural dye by producing a green colour on cotton cloth. The higher the temperature during the heating process in making natural dye samples from papaya leaves, the less chlorophyll pigment is contained.

Gravimetric Analysis

Natural dye samples were quantified using the gravimetric analysis method. The following is the calculation data for chlorophyll content extracted from papaya leaf natural dyes:

Table 1. Chlorophyll Levels of Natural Dyes Solutions

Papaya leaf mass	Mass of chlorophyll extracted	Extracted chlorophyll content
12,5 g	3,445 g	27,56%
25 g	4,46 g	17,84%
37,5 g	6,237 g	16,632%
50 g	6,87 g	13,74%
62,5 g	7,364 g	11,782%

After the trial, the more papaya leaf mass extracted, the more chlorophyll mass produced. The more chlorophyll mass is used, the more chlorophyll will be bound (adsorbed) to the fabric. This shows that the reaction tends to be first order because it has a value that is directly proportional to the mass extracted and the mass of chlorophyll produced. Chlorophyll dyes that are absorbed into the fabric fibres will undergo an adsorption process and be bound by reactive groups on the fabric cellulose fibres in the form of hydroxyl groups (-OH) and form hydrogen bonds. Events that occur when the process of dyeing cloth into a natural dye solution of papaya leaves is also called swelling, namely swelling so that the pores of the fabric fibres will open and the chlorophyll dye can enter the fabric fibres together with the dye solution (Manurung, 2012). This is also reinforced by the UV-Vis Spectrophotometer measurements below.

Data from UV-Vis Spectrophotometer Measurement Results

Data was also collected using a UV-Vis spectrophotometer with a wavelength of 645 nm. Following are the results of the UV-Vis spectrophotometer test:

Table 2. Molar Absorptivity Calculation Results

Papaya Leaf Sample	absorbance	Concentration (M)	Molar Absorptivity
12,5 g	0,13	0,026	33,283
25 g	0,232	0,034	45,814
37,5 g	0,303	0,047	42,896
50 g	0,424	0,052	54,392
62,5 g	0,491	0,056	58,808

The concentration of an analyte can be determined by measuring the absorbance or transmittance of the analyte solution. The main requirement is that this analyte must be completely dissolved and the solution is coloured or can be coloured. Once the absorbance is known by measurement, the concentration of this analyte solution can be plotted onto a calibration curve or by direct comparison. In this experiment, by calculating the concentration by comparing the absorbance value with the molar absorptivity using the formula: A = abc.

Linear Regression Data

Linear regression is a statistical method that functions to test the causal relationship between the causative factor (X) and the consequent variable (Y). In addition to carrying out a linear regression test using Excel, a linear regression test was also carried out using the SPSS program to make the resulting data more accurate. Based on the attached graph, shows that the more papaya leaf mass extracted, the more chlorophyll mass produced. R value^2 on the graph of chlorophyll extraction of 0.951 and chlorophyll absorbance of 0.994. From the linear regression data, the chlorophyll content extracted from papaya leaf natural dyes using the gravimetric method produces the following graph:

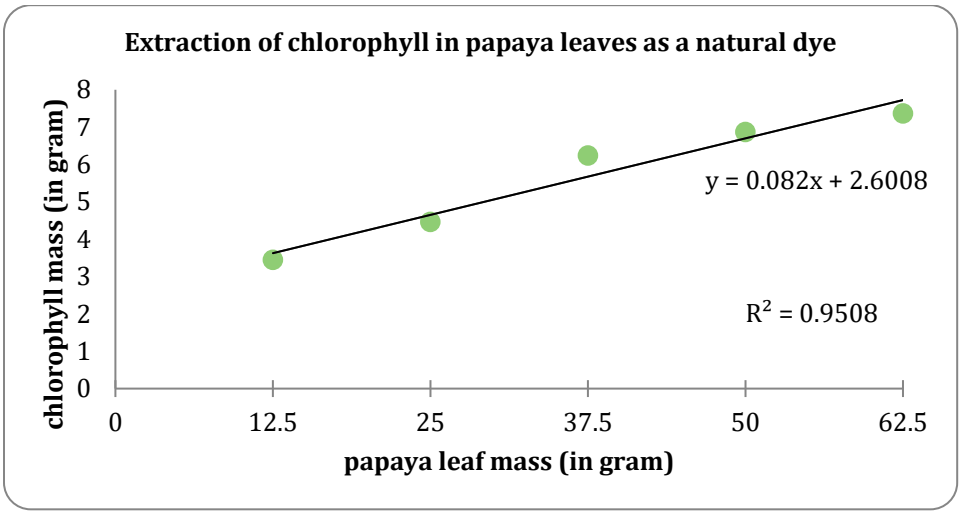

Figure 2. Papaya Leaf Mass on the Results of Chlorophyll Extraction

Because there is a tendency for the reaction order to follow the first order, we will prove this by making a linear graph to get a line equation and a linear regression result of 0.9508. These results will be strengthened by linear regression data on chlorophyll content extracted from papaya leaf natural dyes using the UV-Vis Spectrophotometry method, which shows a linear regression value of 0.9932 as follows:

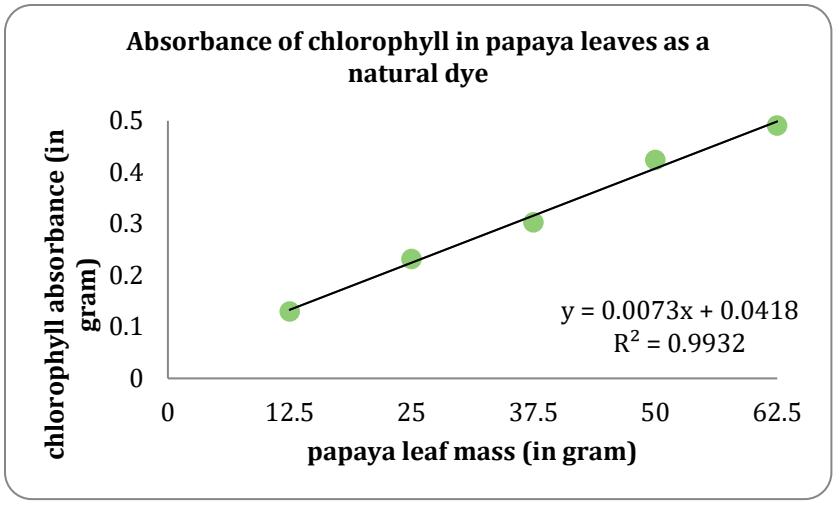

Figure 3. Natural dye chlorophyll absorbance

Based on the percentage of chlorophyll content, it shows that, although the mass of chlorophyll produced increases as the mass of extracted papaya leaves increases, the increase is not too much. From previous research conducted by Fauziah & Wakidah (2019), data was obtained that using a sample of 5 g and a solvent in the form of 96% ethanol, as much as 200 mL was extracted for 3 hours at 40°C, the amount of chlorophyll extracted would be obtained. as much as 0.5201%. These results are used to compare the results obtained in this study. Then the R Square value in the table shows the percentage where the independent variable affects the dependent variable. From the data generated using SPSS, the effect of the mass of papaya leaves on the mass of chlorophyll extracted was a value of 0.951, and the mass of papaya leaves on the absorbance of chlorophyll was a value of 0.994.
R square value, according to Sugiyono (2011). guidelines to provide an interpretation of the correlation coefficient as follows:

0.00 - 0.199 = very low

0.20 - 0.399 = low

0.40 - 0.599 = moderate

0.60 - 0.799 = strong

0.80 - 1.000 = very strong

The research results obtained were compared with previous studies. The following is a comparison of the results of the researchers with the results of other studies:

Table 3. Comparison of Previous Research Results

Researcher	Variable	Research result
[8]	Method: Collision, Solvent: Acetone 99.5%. T: 40°C	The absorbance of chlorophyll at a wavelength of 645nm is 0.082

CONCLUSION

Based on the results of the research that has been done, namely comparing the gravimetric method with the UV-Vis spectrophotometric instrument in determining the order of the reaction in the chlorophyll samples of the natural colouring of papaya leaves, the results show that the values of the two do not have much difference, namely the gravimetric method of 0.951 and the UV-Vis spectrophotometry of 0.994 and follows the first order reaction rate.

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