

# Mass Transfer of Natural Dye Extraction and the Degradation Rate

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**Abstract.** This research studied the effect of temperature on the mass transfer rate and degradation rate of natural dye extraction. As the representative, two natural dyes extracted from Senduduk and Susupan Gunung plants were employed. Senduduk and Susupan Gunung are weed plants that are often found in peatlands. Susupan Gunung is easily found in South Kalimantan, and local people use it as a natural dye for handicraft products. Senduduk is often found in the South Sumatra area also used as a natural dye for traditional fabrics. Senduduk and Susupan Gunung were extracted in a three-neck flask using water as a solvent at temperatures of 50°, 70°, and 90°C. Samples of the extract solution were taken at certain times until the tannin concentration was constant. The tannin concentration in the solution was analyzed using volumetric methods. Experimental data consists of tannin concentrations in solution at various times. The mass transfer coefficient, equilibrium constant, and tannin degradation rate constant were determined by minimizing the sum square of errors between experimental data and the model. Senduduk contains more tannin (0.0094 g/cm<sup>3</sup> solution) than Susupan Gunung (0.0079 g/cm<sup>3</sup> solution), and Senduduk has a higher mass transfer coefficient than Susupan Gunung. The higher the temperature, the greater the rate of tannin degradation. During the extraction process, extract of Senduduk and Susupan Gunung leaves are stable at 50°C, which tends to degrade faster at higher temperatures.

**Keywords:** Degradation Rate, Extraction Rate, Mass Transfer, Natural Dye, Senduduk, Susupan Gunung

## INTRODUCTION

Senduduk (*Melastoma malibathricum* L) and Susupan Gunung (*Mimosa pigra* L) usually grow in bushes and humid places. The chemical content of Senduduk includes flavonoids, tannins, phlobatannins, alkaloids, and saponins (Koodkaew et al., 2018), and the chemical content of the leaves, including

saparin, flavonoids, tannins, steroids, and glycosides (Liana et al., 2015). Several studies show that the content of flavonoids and tannins can produce natural dyes. Flavonoids produce red or orange, while tannins produce brownish colors (Liana et al., 2015; Mindaryani et al., 2023).

Tannins are classified into two categories: hydrolysable tannin and condensed tannin.

Hydrolyzed tannins can undergo molecular degradation or decomposition in water. The hydrolysis process involves breaking chemical bonds with the involvement of water molecules. When tannins are hydrolyzed in water, chemical reactions produce various substances. Water-soluble products of tannin hydrolysis include gallic acid, sugar, and protocatechuic acid. Gallotannin, or common tannic acid, is a well-known hydrolysable tannin. Weak bases or weak acids hydrolyze hydrolysable tannins to produce phenolic acids and carbohydrates. Tannin or tannic acid is widely used in the dye industry, for making gallic acid, ink, water purification, surface coatings, plastic resins, adhesive production, drilling fluids, mercury removal, wastewater treatment, etc. (Binti Rosli et al., 2019). Abilleira et al., (2021) studied the extraction of tannins from the bark of *Pinus pinaster* and *Acacia dealbata* with two methods, which were extraction with a soxhlet and extraction through heat and agitation at 85°C. The research shows that the highest yields obtained were 25.8 wt% for *P. pinaster*, and 29.5 wt% for *Acacia dealbata*. Ethanol (80-20 vol/vol) was the most efficient solvent agent compared to distilled water. Industry and small-scale businesses prefer to use water as a solvent, as it is environmentally friendly and cheap. Kilpeläinen et al., 2023, studied the optimization of tannin yield from spruce and pine bark using water and added chemicals at different temperatures (Kilpeläinen et al., 2023). The highest yields of tannins were found in spruce bark (47 mg/g). Pine bark showed significantly lower values, varying between 15 and 16 mg/g. Tannin yields increased along with the extraction temperature.

Senduduk and Susupan Gunung are sometimes utilized as craft dyes by local people, especially at South Kalimantan and

South Sumatra. Therefore, this plant has the potential to be a natural dye. This study was conducted to extract natural dye in Senduduk and Susupan Gunung plants to find the optimum operating conditions, mass transfer, and degradation parameters.



**Fig. 1:** Senduduk or Senggani (*Melastoma malabathricum*)



**Fig. 2:** Susupan Gunung (*Mimosa pigra L*)

Extraction is a physical process in which tannins are transferred from solid leaves to a solvent, typically water. During the extraction process, tannin degradation can occur. The duration of heating applied to the extract leads to a reduction of the extract, primarily due to tannin degradation within the extract. Generally, the solubility of flavonoids and tannins increases with rising temperature. However, it is crucial to consider the extraction temperature; excessively high temperatures can affect the hydroxyl (O-H) and carboxyl (C=O) groups in tannins and flavonoids, influencing their properties and

functions. These functional groups may undergo damage and degradation at very high temperatures, leading to alterations in the molecular structure of tannins. The damage to these groups can reduce the hydrophilic properties of tannins and their ability to form hydrogen bonds with other molecules. Conversely, the extraction process may be suboptimal if the temperature is too low. A previous study on the effect of temperature on the degradation of Merbau natural dye showed that the tannin degradation was not affected by the drying temperature (60°C to 90°C), based on the titration method and FTIR analysis (Mindaryani et al., 2023). Sari, et.al. (2022) compared the maceration and sonication method for extracting of flavonoids from mango leaves and studied the effect of solvent ratio on yield. The sonication process was set at 40°C, and took 30 minutes; on the other hand, the maceration method at room temperature took 36 hours. The maceration method requires a long process and is not feasible for the industry to apply. Yuniati et.al. (2023) studied the optimization and characterization of the colorant extraction process from *sappan* wood using the ultrasound-assisted extraction method. The research identified the optimum operating conditions for the extraction of *sappan* wood and the use of 60% ethanol solvent were obtained using a frequency of 40 kHz, a temperature of 60 °C, a ratio of 0.0050 g mL<sup>-1</sup>, and an extraction time of 20 min. Febriana et.al., 2016, studied the effect of temperature on the extraction of *Swietenia Mahagoni* by ultrasound-assisted extraction (UAE) method. The result shows that by applying UAE method at low temperatures, the extraction time was faster than conventional extraction, and the yield improvement is 9.27% from 30°C to 50°C. This research used the

conventional method to be applied in small-scale industries and applied water as a solvent to be environmentally friendly.

## MATERIALS AND METHODS

Senduduk and Susupan Gunung leaves were supplied by Eco Sasirangan, the farmer group from South Kalimantan. Senduduk's and Susupan Gunung's leaves were ground and sieved with 30 mesh sieves. Distilled water, all chemicals were purchased from Merck, Germany: KMnO<sub>4</sub> (99% purity), indigo carmine (C173015), and H<sub>2</sub>SO<sub>4</sub> (95 - 97% purity).

Details of the experiment are as follows. The three-neck flask was filled with 800 mL of water as a solvent, heated to a temperature of 50°C, added with 80 g of ground Senduduk leaves, and stirred at a speed of 250 rpm. Samples were taken at certain times until the tannin concentration was constant. The same procedure was repeated for extraction temperatures of 70 and 90°C. Based on the initial experiment, the extraction time was too short, so samples were taken more frequently at the initial extraction stage, and finished at 80 minutes. The same experiment procedures were carried out for ground Susupan Gunung leaves extraction.

To determine the tannin content in the extract, 5 mL of the sample was taken and then centrifuged to separate the solution from solid. The extract was analyzed for its tannin content by using a titration method. The color changed from blue to reddish brown. The tannin solution sample 5 mL was added with 20 mL of indigo carmine solution, then was diluted into 200 mL with distilled water. This solution was titrated with 0.1 N KMnO<sub>4</sub> solution until its color turned from dark blue initially into reddish brown. A blank solution (without any tannin sample) was also

titrated using the same procedure. Tannin concentration was calculated with the following:

$$C_{Af} = \frac{(V_s - V_b) \times 0.004157}{V_{ms}} \quad (1)$$

where  $V_s$  is the titrated volume of the sample ( $\text{cm}^3$ );  $V_b$  is the titrated volume of the blank ( $\text{cm}^3$ );  $V_{ms}$  is the sample volume (5 mL). The analysis was carried out twice for each sample.

The yield of tannin in the extraction process is affected by solid to solvent ratio and temperature. The mass transfer rate of tannin from solid to solvent is affected by the mass transfer area, which is the diameter of the solid and the stirring speed. The higher temperature, the higher yield, but tannin is easily degraded by high temperatures. Therefore, it is important to optimize the extraction temperature. Based on the previous experiment, tannin is degraded faster at higher temperatures.

$$N_A = k_c a (C_{Af}^* - C_{Af}) \quad (2)$$

The equilibrium equation is then estimated with the following;

$$C_{Af}^* = K_{Hs} X_A \quad (3)$$

Batch extraction is carried out in the experiment at a certain temperature and stirring speed. Mass balance of tannin is applied in the isothermal extraction system.

The degradation of tannin is regarded to occur in the solution, with the degradation reaction rate being first-order,

$$r_A = k_r C_{Af} \quad (4)$$

The mass balance of tannin in the solution is formulated as follows:

$$V \frac{dC_{Af}}{dt} = k_c a (C_{Af}^* - C_{Af}) V - k_r C_{Af} V \quad (5)$$

$$V \frac{dC_{Af}}{dt} = k_c a (K_{Hs} X_A - C_{Af}) V - k_r C_{Af} V \quad (6)$$

The mass balance of tannin in solid is as follows:

$$M_s \frac{dX_{Af}}{dt} = -k_c a \cdot V (K_{Hs} X_A - C_{Af}) \quad (7)$$

Where  $M_s$  is total mass of solid.

$$t = 0, C_{Af} = C_{Afo} = 0, X_A = X_{Ao} \quad (8)$$

$$t = t, C_{Af} = C_{Af}, X_A = X_A \quad (9)$$

With a certain ratio of solid per solvent volume,  $M_s$  g/V  $\text{cm}^3$ , and the predicted  $k_c a$ ,  $K_{Hs}$ , and  $k_r$  values, the differential equation can be solved, and  $C_{Af}$  versus time for the model can be calculated. Mass transfer coefficient  $k_c a$  and equilibrium constant  $K_{Hs}$  and degradation rate constant  $k_r$  can be determined by fitting method where the experimental data  $C_{Af}$  versus time is known. Sums of Square of Errors (SSE) minimization was employed in this case.

$$SSE = \sum (C_{Af,calc} - C_{Af,data})^2 \quad (10)$$

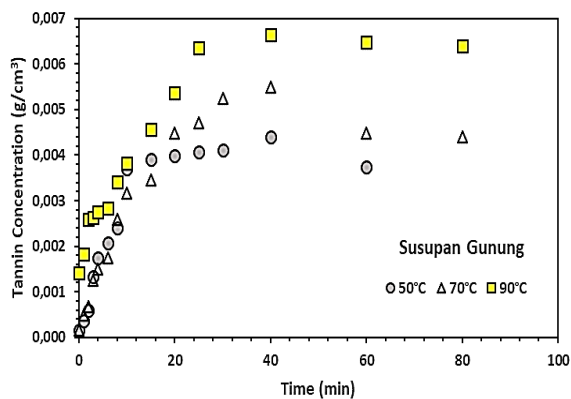
## RESULTS AND DISCUSSION

### Extraction Profiles of Natural Dyes

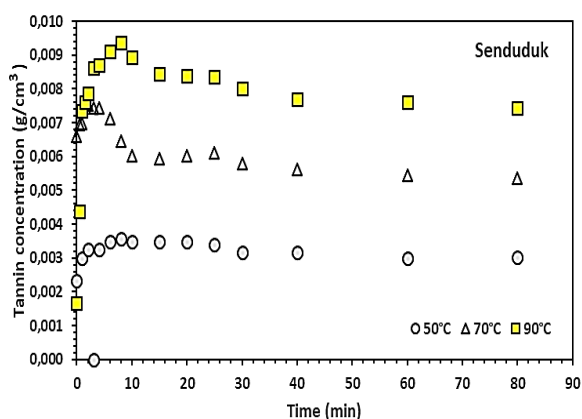
The experimental data are shown in Figure 3 and Figure 4 for Susupan Gunung and Senduduk leaf extraction.

From Figures 3 and 4, the extraction process of Senduduk leaves is faster than the Susupan Gunung, and the tannin content of Senduduk is also higher than that of Susupan Gunung tannin content. This is based on the highest extract concentration at 90°C, where Senduduk extract concentration is 0.0094 g/cm<sup>3</sup> and that of Susupan Gunung is 0.0079 g/cm<sup>3</sup>. Both plants show that the tannin is more stable at the extraction temperature of 50°C, but at the higher temperature, the tannin content decreases. For Susupan Gunung, the tannin content decreased after

40 minutes of the extraction process, and for Senduduk, it was even faster, decreasing after 10 minutes.



**Fig. 3:** Experimental data for Susupan Gunung at various temperatures



**Fig. 4:** Experimental data for Senduduk at various temperatures

Research on the extraction of Indian medicinal plants and mashua conducted by Lim and Murtijaya (2007) and Silva et al. (2007) showed that heat may have the ability to increase the yield of phenolic compounds such as tannins, where higher extraction temperatures can show much higher amounts of phenolic compounds in these compounds. Al-Farsi and Lee (2008) proved the same phenomena, especially for the phenolic group. Increasing the extraction temperature encourages high extraction of active compounds, where the diffusion

coefficient and solubility of the solid in the solvent also increase, leading to greater extraction of active compounds. The extraction efficiency of tannin, when high heat is applied to the extraction solvent, will also enable it to break the cell walls, thereby releasing phenolics, which results in a higher phenolic yield in the extract. On the other hand, exposure or treatment at high temperatures for a long period can also cause degradation of the active compound. Some compounds are not resistant to high temperatures, so they will cause damage to the active compounds (Wang et al., 2007). The degradation is probably caused by a reaction of polyphenol with oxygen (from air), in which polyphenol is known as an antioxidant.

The extraction efficiency and quality of tannins depend on the duration of extraction (Hussain et al., 2020; Luo et al., 2019), when long extraction duration results in higher amounts of tannin. Plant cell structures break down over time in solvents, and tannin extraction yields increase (Petchidurai et al., 2019), but quality can decrease over time.

### Model Parameters of Extraction of Natural Dyes

Figure 5 and Figure 6 show the experimental data and the calculated tannin concentration in solution versus time.

Figure 6 shows that the tannin concentration from the model fits all the experimental data for Susupan Gunung extraction at 50°, 70° and 90°C. However, for the Senduduk extraction, the tannin concentration from the model slightly fits the 70°C extraction data and the experimental data at 50° and 90°C. The mass transfer coefficient was determined using the experimental data from the initial step of the extraction process when an unsteady state

condition occurred. Yuniati et.al., 2023, applied the Ultrasonic Assisted Extraction Method to *sappan* wood, and the result shows that there was an increase in the extraction yield until the system reached the optimum condition at 20 min extraction and similar to this research, which is shown in Figures 5 and 6.

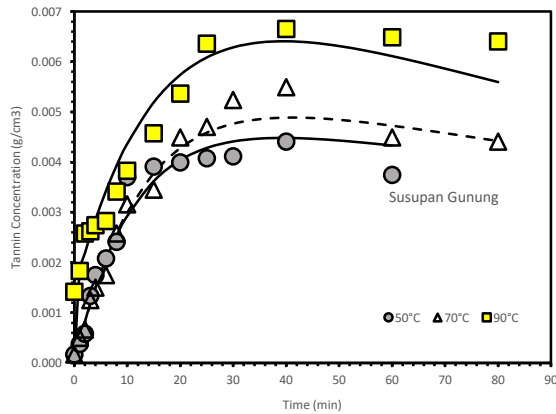


Fig. 5: Fitting method for Susupan Gunung

The fitting method determines the mass transfer coefficient, equilibrium constant, and degradation rate constant, where Table 1 shows the calculation result. The tannin concentration in the solution versus time is used to determine parameters, namely the mass transfer coefficient,  $k_c a$ , the equilibrium constant,  $KH_s$ , and degradation rate constant,  $k_r$  chosen when the Sum Square of Error between the calculated concentration and

the experimental concentration is the smallest.

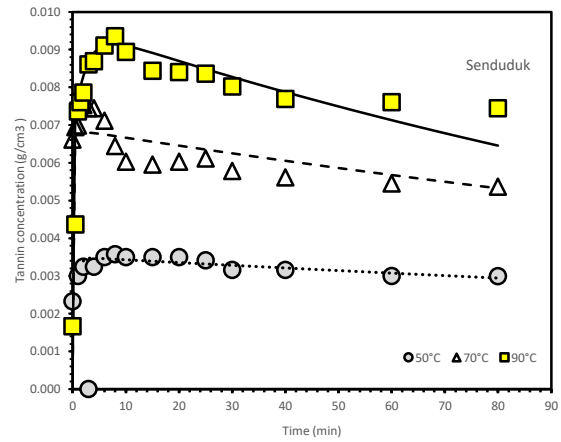


Fig. 6: Fitting method for Senduduk

Table 1 shows that (volumetric) mass transfer coefficient ( $k_c a$ ) of Senduduk is higher than that of Susupan Gunung, although the extraction condition is the same. The value of mass transfer coefficient  $k_c$  of Senduduk and Susupan Gunung leaves is theoretically the same. On the other hands, the specific surface  $a$  ( $\text{cm}^2/\text{cm}^3$ ) of ground Senduduk leaves seems higher than that of ground Susupan Gunung leaves. This is due to the nature of Senduduk leaves, which are softer than Susupan Gunung leaves. When both leaves are ground, Senduduk leaves produce smaller particles than Susupan Gunung leaves.

Table 1. Equilibrium Constant, Mass transfer coefficient, and degradation rate coefficient based on fitting method

	Susupan Gunung			Senduduk		
	50°C	70°C	90°C	50°C	70°C	90°C
<b>KHs gram solid/cm<sup>3</sup></b>	0.0514	0.0643	0.1030	0.0323	0.0494	0.0860
<b><math>k_c a</math>, 1/min</b>	0.0531	0.0415	0.0279	0.9040	0.4600	0.2105
<b><math>k_r</math>, 1/min</b>	0.0097	0.0108	0.0116	0.0089	0.0098	0.0109
<b>SSE</b>	$1.32 \times 10^{-6}$	$9.81 \times 10^{-7}$	$5.17 \times 10^{-6}$	$1.66 \times 10^{-7}$	$4.85 \times 10^{-5}$	$1.20 \times 10^{-4}$
<b>Error (%)</b>	11.26	7.88	10.14	3.04	6.42	7.80

A comparison of the mass transfer coefficient with other literatures is given in Table 2.

**Table 2.** Comparison of mass transfer coefficient

	Temperature	$k_c a$ (min <sup>-1</sup> )
Guerrero et al., 2008.	40° – 50°C	0.332 – 0.924
Susanti et al., 2019.	50° – 70°C	0.0358-0.0676
Nurwahyuwono et al., 2021.	65°C	0.0024-0.0042
This research	50°-90°C	0.0279 - 0.904

Although the value of  $k_c a$  depends on the condition of the extraction process, it is apparent that the results of this research are within the range of other researchers' results, as shown in Table 2.

The degradation rate constants of tannin from Senduduk and Susupan Gunung leaves show within the range of 0.009 – 0.012 min<sup>-1</sup> at a temperature of 50° – 90°C. This shows that tannin degradation is essentially not affected by the source of tannin itself. The degradation rate constant for both leaves can be expressed by equation:

$$k_r = 0.0525 \cdot \exp\left(-\frac{4651}{RT}\right) \text{ min}^{-1}$$

with activation energy = 4651 J/mol and temperature T in K.

## CONCLUSIONS

The Extraction of Senduduk and Susupan Gunung leaves is stable at 50°C, but the yield decreases after 30 minutes of extraction process at 70°C and 90°C. The higher the extraction temperature, the higher the extraction yield. Senduduk has higher tannin content (0.0094 g/cm<sup>3</sup> solution) than Susupan Gunung (0.0079 g/cm<sup>3</sup> solution) as well as its mass transfer coefficient. The

degradation rate constant is greater at higher extraction temperatures, with its value within the range of 0.009 – 0.012 min<sup>-1</sup> at 50° – 90°C.

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## NOMENCLATURE

- $k_c a$  : tannin volumetric mass transfer coefficient from solid to solvent [min<sup>-1</sup>]  
 $k_c$  : tannin mass transfer coefficient from solid to solvent [cm min<sup>-1</sup>]  
 $k_r$  : degradation rate [min<sup>-1</sup>]  
 $N_A$  : mass transfer rate of tannin from solid to solvent [g cm<sup>-2</sup> min<sup>-1</sup>]  
 $C_{Af}^*$  : the tannin concentration in the solution is in equilibrium with the tannin content in the solid [g cm<sup>-3</sup>]  
 $C_{Af}$  : tannin concentration in solution [g cm<sup>-3</sup>]  
 $K_{Hs}$  : equilibrium constant [g of solid cm<sup>-3</sup> of solvent]  
 $X_A$  : tannin content in solid [g tannin / g solid]  
 $V$  : volume of solvent [cm<sup>3</sup>]  
 $V_s$  : titrated volume of the sample (cm<sup>3</sup>)  
 $V_b$  : titrated volume of the blank (cm<sup>3</sup>)  
 $V_{ms}$  : sample volume (5 cm<sup>3</sup>)  
 $M_s$  : solid mass [g]



$C_{Afo}$  : initial tannin concentration in solvent [g tannin  $\text{cm}^{-3}$ ]  
 $X_{Ao}$  : initial content of tannin in solid [g tannin / g solid]  
 $t$  : time [min]

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