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Microwave Assisted Extraction (MAE) Process of Tannin from Mangrove Propagules Waste as Natural Dye for Coloring *Batik tulis*

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Abstract. Mangrove propagule waste is one of the biomass wastes that decays fast, hence it can pollute the environment. Mangrove propagule contains 30.43% tannin, and thus it has high potential to be used as a natural dye for coloring *Batik Tulis*. Unfortunately, this raw material has not been utilized optimally. The objective of this study is to extract tannin substances from mangrove propagules by using Microwave Assisted Extraction (MAE) method. The effects of solvent types (i.e. ethanol and distilled water), material-solvent ratio, extraction time and temperature on the yield of tannin obtained have also been investigated. The extraction results were analyzed by FT-IR to determine the presence of tannin contained in the dyes. The extraction results showed that the optimum yield of etanol solvent was 27.5%, which occured at material-solvent ratio of 0.04 g/ml, extraction time of 30 minutes, and temperature of 60°C. Whereas, the distilled water produced 22.7% yield of tannin, which also occured at material and solvent ratio 0.04 g/ml, extraction time of 30 minutes, and temperature of 80°C. Additionally, FT-IR analysis of tannin extract from mangrove propagules with etanol and distilled water showed the presence of hydroxyl groups (O-H), groups (C-H), C = C groups, and C-O groups.

Introduction

Batik Tulis is one of the most well-known Indonesian cultural and traditional cloths. The dyes used in coloring *Batik Tulis* can be natural dyes and synthetic dyes. Synthetic dyes include Naptol, Remazol and Indigosol. The use of synthetic dyes containing chemicals has negative effect on the environment, e.g. water and soil pollution. The use of natural dyes for batik industry is an alternative substitute for synthetic dyes [1]. Natural dyes are produced by extracting various plant parts e.g. flowers, fruits, leaves, stems, and roots [2]. One of the plants that can be used as natural dye source is mangrove propagules.

Mangrove is vegetation that grows in puddles with high salinity. The growth of mangrove plants every year is approximately 100 thousand seeds. However, the propagule mortality ratio reaches 40%, hence a lot of propagules become biomass waste in the coastal area. The area of mangrove land in Tugu Rejo district, Semarang is approximately 220.96 hectares which covering an area of 7.5% of the total area of the district. Species from mangrove propagules that mostly grown in the mangrove land of Tugu Rejo district are *Rhizophora mucronata* [3]. *Rhizophora mucronata* has tannin levels of 30.43% [4]. Tannin contained in *Rhizopora mucronata* has the potential to be a natural coloring agent for *Batik Tulis*.

Extraction of tannin from mangrove propagules can be done using conventional and non-conventional methods. Conventional extraction includes extraction using soxhlet and maceration. The process is quite effective, but requires a longer time and the energy needed for heating is also high [5]. Another alternative that can be used is the Microwave Assisted Extraction (MAE) method. Microwave Assisted Extraction is an extraction method that utilizes heat from microwaves to accelerate selective extraction through solvents heating quickly and efficiently. This method is better than the conventional method due to the relatively fast extraction time, increased extraction yield, and less solvent requirements [6]. Based on the description above, it is necessary to investigate tannin

extraction from mangrove propagules as alternative natural dye for *Batik Tulis* using Microwave Assisted Extraction (MAE) method and compared the results with the conventional method (i.e. using soxhlet).

Experimental

Materials. The raw material used in this study was the mangrove propagules, which obtained from Tugu Rejo district, Semarang. The solvents used were ethanol (99.9%) from Merck (Germany) and distilled water. Variables used in this study include: material and solvent ratio, extraction time, and extraction temperature. Prior to the extraction, the mangrove propagules were dried under the sun for 2-3 days and heated at 80°C for 4 hours. Then the dried mangrove propagules were powdered using a blender and then screened using a 35 mesh shieve shaker. Fig. 1 shows the photographs of raw materials.

(a) (b)

Fig. 1 Photographs of a) Mangrove (*Rhizopora mucronata*), and b) Mangrove propagules.

Extraction Process. In this study, the extraction of dyes was carried out by Microwave Assisted Extraction (MAE) method with several variables. The variables were as follow: solvents (i.e. 0.01, 0.02, 0.04, 0.06, 0.08, 0.1 g/ml), extraction time (i.e. 5, 10, 30, 60, 90, 120 minutes) and extraction temperatures for ethanol (i.e. 50, 60, 70, 80°C), while distilled water (i.e. 60, 70, 80, 90°C). The volume of the solvents used was constant at 250 mL. Fig. 1 shows the schematic illustration of Microwave Assisted Extraction (MAE) method. For the extraction process, the mangrove propagules powder (according to the variable) and solvent were put into the extractor apparatus. Afterward, the temperature of the extractor was set (according to the variable) and heated until specified temperature. The extraction time started after the specified temperature was reached. The extract was separated by a distillation device to separate the solvents and the natural dyes. The resulted dyes were dried at temperature according to the boiling point of the solvent until the weight is constant, and then calculated for the yield.

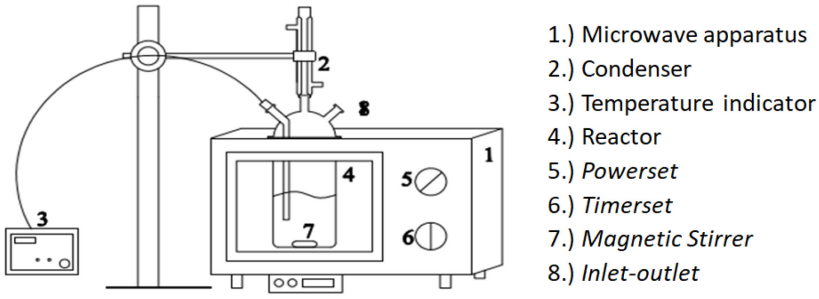

Fig. 2 Schematic illustration of the Microwave Assisted Extraction (MAE) method.

Results and Discussion

Effect of Ratio Raw Material and Solvent. The aim of studying the effect of ratio of raw materials to solvents on the yield of natural dyes was to determine the optimal conditions of extraction process in term of ratio of ingredients to solvents. The effect of ratio of ingredients to solvents to the yield of dyes is presented in Fig. 3a. As seen in the figure, the ratio of raw materials to solvents 0.01-0.04 g/ml increased the yield of the natural dyes. In other hand, ratio of raw materials to solvents 0.04-0.1 g/ml produced lower yields or tends to decrease. The optimum ratio of raw material to solvent for both the solvents (i.e. ethanol and distilled water) was 0.04 g/ml. While, the yields of natural dye produced were 23% and 19.14% for ethanol and distilled water, respectively. This result is in agreement with the study of Song et al. [7], which reported that the higher the ratio of raw material to solvent (to certain ratio) the higher the transfer of dye compounds from the raw material to the solvent, causing the yield to increase. This result is supported by the statement of [8], in which the increase of ratio of raw material to solvent could extract more target compounds to certain condition until finally there was a decrease of yield when the ratio increased.

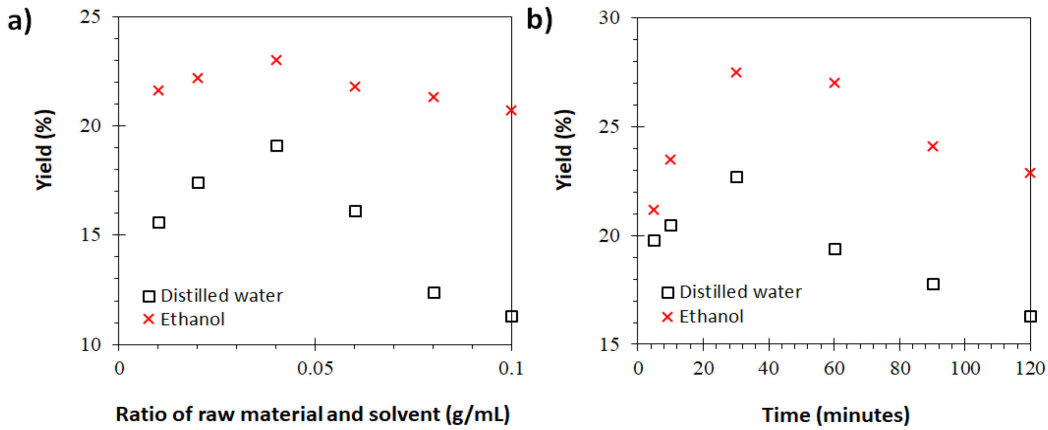

Fig. 3 Effect of a) Ratio of raw material and solvent, and b) Extraction time on the yield.

Effect of Extraction Time. The effect of extraction time on the yield of tannin was also investigated. The results of the analysis are presented in Fig. 3b. As seen in the figure, there was a tendency that the longer the extraction time, the yield obtained tend to increase and reached the maximum at 30 minutes, then gradually decreased. At the optimum time, the yield produced by ethanol solvent was 27.5%, while by distilled water was 22.7%. The decreasing yield at extended extraction time was because the amount of dye in the raw material was limited and the solvent used had the ability to dissolve the existing dye compound. Therefore, though the extraction time was extended, the ability of solvent to extract the dye in the raw material was limited. Instead, the prolonged exposure time may degrade the extracted compounds and reduces the yield of extract produced [9].

Effect of Extraction Temperature. The effect of extraction temperature on the yield of dye is presented in Fig. 4. As seen in the figure, the increasing temperature resulted in increasing yield of dye and decreased after reached the optimum temperature. The optimum temperature for ethanol solvent was 60°C with a yield of 27.5% and in distilled water was 80°C with a yield of 22.7%. The increasing temperature increased the ability of solvent to extract the dye from the raw material. In other hand, temperatures that are too high may damage or degrade the tannin compounds in the material. This was likely the cause why the extract obtained decreased at high temperatures, i.e. > 60°C for ethanol and > 80°C for distilled water [10].

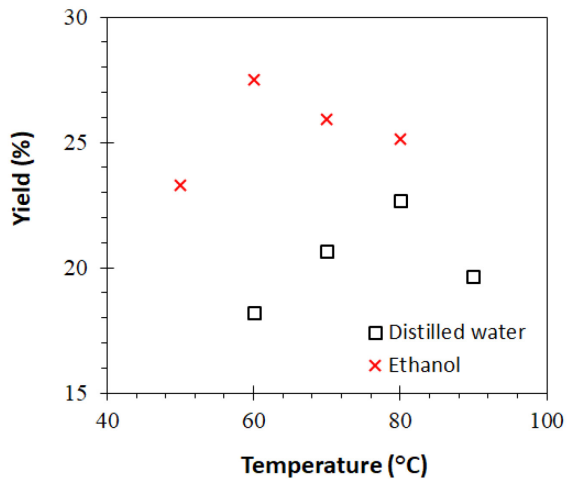

Fig. 4 Effect of extraction temperature on the yield of the dye.

Soxhlet Extraction vs Microwave Assisted Extraction (MAE). In this study, the results of Microwave Assisted Extraction (MAE) were compared with the extraction result using soxhlet, and were listed in Table 1. As seen in the table, the Microwave Assisted Extraction method produced a greater yield than the extraction by using soxhlet. It can be concluded that the extraction of tannin (dye) using the Microwave Assisted Extraction method was more effective and efficient since it required a shorter time and produced the optimum color. The higher yield of tannin by microwave extraction was caused by the activity of solvent molecules that triggered swelling of plant material due to microwave heating [9]. In term of extraction time, the conventional method using soxhlet requires long extraction time due to long time needed for the rupture of cells in the powder pore mangrove propagules until the solvent extracts the solute (i.e. dye compound). When the solvent dissolves the solute and diffuses from the solute solid into the solvent liquid takes a long time because there is no driving force from inside pore [11]. In other hand, with the use of Microwave Assisted Extraction, the time needed for rupture of pore cells in the mangrove propagule powder was short due to microwaves heating. Once the pores in the powder of mangrove propagules open, the solvent diffusion rate from within the liquid was faster. Thus, the extraction of dye compound obtained from mangrove propagules was higher by using Microwave Assisted Extraction with a more efficient time.

Table 1 Comparison of optimal conditions and results obtained by Microwave Assisted Extraction (MAE) method dan Soxhlet extraction.

Method and solvent	MAE		Soxhlet	
	Distilled water	Ethanol	Distilled water	Ethanol
Time (hour)	0.5	0.5	2	1.5
Temperature (°C)	82	62	100	78
Yield (%)	22.7	27.5	8.8	8.8

Fourier Transform Infra-Red (FT-IR) Spectroscopy Analysis. FTIR analysis was carried out to determine the functional groups of tannin in powdered dye. This analysis was carried out using infrared spectroscopy at wave numbers 400-4000 cm^{-1} [12]. Fig. 5 shows the FT-IR analysis results of the extracted dye obtained by ethanol and distilled water at the ratio of material to solvent of 0.04 g/mL, extraction time of 30 minutes, extraction temperature of 60°C (ethanol) and 80°C (distilled water).

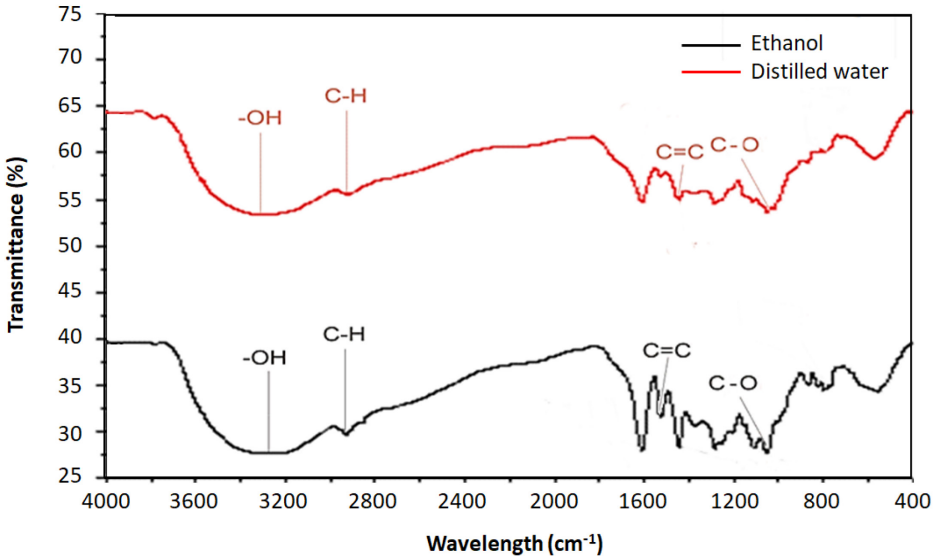

Fig. 5 FT-IR spectrum of tannin extracted by ethanol and distilled water.

As seen in Fig. 5, the FT-IR spectrum of tannin extracted by ethanol solvent showed the presence of hydroxyl (OH) groups in the area of 3277.31 cm^{-1}, aromatic groups (CH) in the area of 2926.29 cm^{-1}, the C-O group in the area of 1284.67 cm^{-1}, and the C=C group in the area of 1525.949 cm^{-1} [12]. Whereas, the tannin FT-IR spectrum with distilled water showed the presence of hydroxyl (O-H) groups in the 3304.06 cm^{-1} area, the aromatic group (C-H) in the area of 2856.33 cm^{-1}. group (C-O) in the area of 1286.45 cm^{-1}, and the C=C aromatic group in the area of 1519.8 cm^{-1} [12]. The FT-IR analysis results of this study was in agreement with other literature study [13]. Pantoja-Castro et al. [13] reported that in tannin there was hydroxyl (OH) group in the area of 3400 cm^{-1}, aromatic group (CH) in the area of 2920 cm^{-1}. Whereas, area of 1050 cm^{-1} was atrributed to CO group, while area of 800 cm^{-1} was attributed to C=C. The data in Table 2 shows the list of functional groups on tannins obtained by ethanol and distilled water, such as hydroxyl, carbonyl and other groups. The main elements in tannins are hydroxyl group, and carboxyl group. These groups indicate the presence of tannin in the natural dye extracted from mangrove propagules, which can be used for coloring *Batik Tulis*.

Table 2 Functional groups of extracted natural dye detected by FT-IR analysis.

Functional groups	Tannin (ethanol) (cm^{-1})	Tannin (distilled water) (cm^{-1})
O-H	3277.31	3304.06
C-H	2926.29	2856.33
C=C	1525.95	1519.8
C-O	1284.67	1286.45

Conclusion

In this study, the extraction of dyes from the mangrove propagules with ethanol and distilled water as solvents using microwave assisted extraction method was studied. The optimum operating conditions were obtained for ethanol solvent at the ratio of ingredients and solvents 0.04 g/mL, extraction time 30 minutes and temperature 60°C with yields of 27.5%, while aquades solvent at the ratio of ingredients and solvents 0.04 g/mL, extraction time 30 minutes and temperature 80°C with a yield of 22.7%. The FT-IR analysis results showed that the natural dye extracted from mangrove propagules with ethanol and distilled water solvents contained hydroxyl (OH) groups, groups (CH), groups (C = C), and groups (CO). These functional groups showed the presence of tannin in the extracted natural dye. In other hand, the optimum condition of extraction mangrove propagules using soxhlet was obtained with ethanol solvent at 2 hours with 8.8% yield, while the distilled water gave 8.8% yield at 14 hours. Therefore, it can be concluded that the extraction of tannins using the

Microwave Assisted Extraction method is more effective and efficient because it requires a shorter time and produces the optimum dye yield.

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