Application of Tegeran (*Maclura cochinchinensis*) bark as natural tanning agent for the quality of tilapia fish skin

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ABSTRACT

Chrome is a tanning material that is very harmful to the environment hence its role is being replaced with vegetable tanning materials. One of the natural ingredients that contain tannin is Tegeran (*M. cochinchinensis*) wood. The aim of this study was to determine the effect of *M. cochinchinensis* as natural tanning agent for tilapia fish skin. Tannin contained in the *M. cochinchinensis* was being extracted using three solvents: water, ethanol, and water-ethanol (1:1). The composition of the material and the solvent was 1:4. It was heated in the waterbath at temperature 70 °C for 3 hours. The results showed that the use of *M. cochinchinensis* as natural tanning agent could at once gave unique color to the tanned fish skin. The average of shrinkage temperature was 78.11°C. Leather tanned with *M. cochinchinensis* that was extracted with water showed higher value of tensile strength and tear strength than those with ethanol and water-ethanol.

Keywords: leather tanning, *M. cochinchinensis*, tannin extraction, tegeran wood, tilapia.

INTRODUCTION

Leather industry needs various chemicals for the tanning process to convert skins and hides, by-products of the meat industry, into leather (Gil *et al.*, 2012; Onem *et al.*, 2015; Teng *et al.*, 2016; van Gerven *et al.*, 2016). The most common tanning agent used in leather industry is chromium sulphate base (Geier & Lessmann, 2012) because it can deliver soft leather and reduce leather tanning cost. Aside from chromium, other chemicals usually used in tannery are aluminium, formaldehyde, and synthetic tanning.

Whilst tannery is an important industry for environment because it utilizes slaughterhouse wastes, this industry also produces pollutants to the environment (Gil *et al.*, 2012; Cao *et al.*, 2017), particularly because chrome utilization can harm the environment. In chrome tanning process, 55–65% of chrome is not absorbed in the leather and become liquid wastes (Covington, 2009). The increase of awareness against environment and health issues nowadays (Aslan, 2009; Selvi *et al.*, 2013; Krishnamoorthy *et al.*, 2013) makes

tanneries compete in making environmentally friendly products.

Various vegetable tanning agents commonly used in tannery are mimosa, quebracho, chestnuts, divi-divi, and gambier. One of natural materials known as natural dyes in batik processing and commonly found in Indonesia is *M. cochinchinensis*. The plant has several names, such as Tegeran, *Cudrania javanensis*, *M. javanica*, *Cudraina cochinchinensis*, Kayu Kuning, Soga Tegeran, Kederang (Malaysia), and Kokompusa (Philippines) (Lemmens & Wulijarni-Soetjipto, 1991). *M. cochinchinensis* has a rough, gummy, and spiny stem with brownish color (Atika & Salma, 2017). As a dyeing agent, *M. cochinchinensis* produces yellow or yellowish green color.

Although *M. cochinchinensis* is commonly used as a coloring agent, no studies have shown that *M. cochinchinensis* can be used for leather tanning while study about its tannin content is very limited. Hence, before starting this research, *M. cochinchinensis* have extracted with water.

The result showed that the tannin content of *M. cochinchinensis* was 11.46%. This value is lower than the tannin content of mimosa (71-72.5%) (Kasmudjiastuti, 2014) which is commonly used for vegetable leather tanning. However, *M. cochinchinensis* produces a distinctive color that other dyeing agents do not have. Its use as tanning agent could at once give color to the leather, so the dyeing process can be eliminated.

Tannin contained in *M. cochinchinensis* has to be extracted in order to be used as leather tanning agent. Tannin extract derived from plants has been widely used in leather production in the world (Kardel *et al.*, 2013). Therefore, currently, there is an increasing demand for the development of effective and efficient techniques of natural material extraction (Sae-leaw *et al.*, 2013). Various kinds of extraction techniques are carried out to gain optimum extracts. The extraction result depends on the solvent used, method, time, and extraction temperature, as well as the composition and physical characteristics of the sample, such as texture (Tan & Kassim, 2011).

In recent years, consumer preferences has been changed into non-conventional leather, such as tilapia fish skin (*Oreochromis niloticus*). As a waste of fillet industry, tilapia fish skin is not optimally utilized yet, because its utilization is limited into skin crackers with low economic value. Tilapia fish skin through tanning process can increase its value into fish skin product that has beautiful motif and similar quality to reptile skin. Hence, the aim of this study was to determine the effect of *M. cochinchinensis* wood extract as vegetable tanning agent.

MATERIALS AND METHODS

Materials

The material used in this study was *Tegeran* (*M. cochinchinensis*) bark obtained from Prawoto Shop, Yogyakarta. Tilapia fish skin used was in dry condition as industrial wastes of PT. Aquafarm Nusantara, Central Java, Indonesia. The chemicals used were ethanol 70%, $KAl(SO_4)_2 \cdot 12H_2O$, wetting agent, Na_2S , $Ca(OH)_2$, $(NH_4)_2SO_4$, NH_4Cl , bating agent, degreasing agent, $HCOOH$, H_2SO_4 , $NaHCO_3$, $Al_2(SO_4)_3$, fish oil, synthetic oil, and Sincal DR.

Equipments

The equipment used in this study were hammer, 100 ml beaker glass, 600 ml beaker

glass, measuring cylinder, Memmert waterbath, analytical scale, digital scale, 150 μm filter paper, experimental tanning drums, fleshing knives, easel, sculpting tools, staking tools, pH paper, plastic cups, and shrinkage temperature tester.

Methods

Preparation of *M. cochinchinensis*

Dried *M. cochinchinensis* wood was reduced in size using hammer. The solvent to extract the wood was varied into three types, i.e. water (NT-a), ethanol (NT-e), and water-ethanol (NT-ae). Water-ethanol solvent was prepared using 1:1 ratio. Then, 10 gram of wood was added by 40 ml of each solvent and heated in waterbath for 3 hours at 70 °C temperature. The extraction yield was filtered through two filtration stages, gauze filtration continued with filtration using 150 μm filter paper. Furthermore, the *M. cochinchinensis* extract was stored for a day before applied for tanning operation.

Tanning procedure

Three types of *M. cochinchinensis* extract were immediately applied to tilapia fish skin through tanning process with three replications. The codes used were NT-e; NT-a; and NT-ae which indicate the fish skins were tanned with *M. cochinchinensis* extracted in ethanol, water, and water-ethanol. The tanning procedure was carried out through several stages according to the tanning process by Pahlawan and Kasmudjiastuti (2012) with several modifications as showed in Table 1. Percentage of chemicals used was based on the weight of the skins (w/w).

After the tanned fish skin was hung, it was toggled for a day and stacked. Then, $HCOOH$ and H_2SO_4 were added 3 x 15 minutes that meant the chemicals were added step by step for every 15 minutes.

Testing of tanned tilapia skin quality

Quality assessment was conducted on physical quality of tilapia fish skin leather that has been tanned using *M. cochinchinensis* extract. The tests carried out were analysis of variance (anova), shrinkage temperature tensile strength and elongation tests based on the testing method in SNI 06-1795-1990 (BSN, 1990), as well as tear strength, and total ash content using the testing method in accordance with SNI 06-1794-1990 and SNI 06-0645-1989 (BSN, 1989) consecutively.

Table 1. Tilapia fish skin tanning process.

Process	Materials	Amount (%)	Time (minute)
Soaking	Water	1000	
	Teepol	2	240
Fleshing			
Weighing			
Liming	Water	1000	
	Na ₂ S	2	30
	Ca(OH) ₂	3	60
Deliming,	Water	300	
Degreasing,	(NH ₄) ₂ SO ₄	2	60
Bating	Teepol	1	
	Palcobate	1	
	Water	100	30
Pickling	NaCl	10	
	HCOOH	1	3 x 15
	H ₂ SO ₄	0,5	3 x 15
Pre-tanning	NaHCO ₃	0,5	2 x 15
	KAl(SO ₄) ₂ · 12H ₂ O	10	180
Tanning	<i>M. cochinchinensis</i>	1.000	8 x 30, overnight
Fatliquoring	Water 50 °C	50	
	Fish oil	5	30
	Synthetic oil	4	
	Water 50 °C		30
	HCOOH	1	3 x 15
	Sincal DR	1	15
Washing	Water	2000	10
Hanging	-	-	-

RESULTS AND DISCUSSION

Shrinkage Temperature

The anova result showed that the F_{count} was greater than the F_{table} in the significance of 95%. Thus, it indicates that the solvent of the extraction influenced on the leather's shrinkage temperature. The solvent used to prepare *M. cochinchinensis* would affect the tannin content of the extraction, that the tannin linked to the collagen since shrinkage temperature shows the crosslink degree and hydrothermal stability (Kasmudjiastuti *et al.*, 2015).

M. cochinchinensis wood which was extracted with water, ethanol, and their combination resulted the leather with a shrinkage temperature of 78.19 °C (Figure 1). This result indicates that *M. cochinchinensis* extract has the ability to provide a good vegetable-tanned leather. Even though, the figure has different result compare to those tanned with gambier as vegetable tanning agent which reached more than 100 °C (Setiawan *et al.*, 2015). According to BASF (2004), vegetable-tanned leather has shrinkage temperature 70 – 85 °C. Shrinkage temperature is one of critical point in manufacturing of leather which will determine the quality of leather.

Shrinkage temperature expresses the temperature reached when the leather started to shrink against heat 2 °C/min. in aqueous medium (Carşote *et al.*, 2016). This study evaluated the crust leather as the object. Different solvents were used for the extraction of *M. cochinchinensis* and then the result were used for tanning. In order to investigate the effect of different solvent of the extract in the tanning process on the shrinkage temperature of tilapia fish crust leather, analysis of variance (anova) is needed.

Figure 1. The shrinkage temperature of tanned-skin with different tannin extract.

Figure 2. Model of the reaction between plant polyphenol and collagen (Covington, 2009).

Tannin could make a bond with collagen fiber due to its reactive group and has suitable molecule size in binding several collagen fibers at once. The sum of crosslinking bond depends on the molecule size of polyphenol and the amount of -OH groups (small molecules, $M < 500$, and big molecules, $M > 300$ does not have tanning effect) (Combalia *et al.*, 2016). The reaction between plant polyphenol and collagen of leather is presented in the Figure 2.

The results of shrinkage temperature test showed that the tannin extracted from *M. cochinchinensis* wood with ethanol (NT-e) and a combination of water-ethanol (NT-ae) provided higher shrinkage temperature than that with water (NT-a). Higher tannin bound in the skin fiber resulted in higher shrinkage temperature of tilapia tanned-skin sample.

Tensile Strength

According to analysis of variant test for tensile strength with 95% of significance level, the F_{count} (12.477) was greater than the F_{table} (5.143). It can be concluded that different solvent used in the extraction process has a significant effect on the tensile properties of tilapia fish leather. Tilapia fish skin tanned with *M. cochinchinensis* wood extract, which was extracted with water, ethanol, and the combination of both, has the tensile strength value of 123.21 kg/cm², 80.46 kg/cm², and 79.91 kg/cm², respectively (Figure 3). The tensile strength value represents the strength of bond between collagen fibers and the tannin. Tilapia fish skin which was tanned with *M. cochinchinensis* wood extract (NT-a) has the greatest tensile properties value.

Figure 3. The effect of extraction solvent on tensile strength of the resulted leather.

The result of tensile strength were contradictory with the shrinkage temperature, where the water solvent provided the tanned-skin with the highest tensile strength but lowest shrinkage temperature. Tensile properties indicates how strong the maximum torque needed to stretch the leather sample until it breaks into two pieces, and expresses in kg/cm² or N/cm² unit. According to Kholifah *et al.* (2014), tensile strength is one of indicator that determine the quality of leather where it represents the bond between hides/skin's collagen fibers and tannin.

Tensile strength of leather could also be influenced by the fat content of the leather. The fat content in leather could increase the tensile strength (Kholifah *et al.*, 2014). Another thing that is also suspected to affect the tensile strength of the leather is the quality of raw skin and process during leather tanning, such as the preserving method of skin, liming process, bating process, fatliquoring, and the process of toggling (Pahlawan & Kasmudjiastuti, 2012).

According to Indonesian National Standard 06-4586-1998 (BSN, 1998), minimum tear strength of finished leather from freshwater snakes leather tanned with chrome is 102 kg/cm² (Figure 3). Hence, only fish skin tanned with *M. cochinchinensis* extracted with water that met the tensile strength requirements. Tanin is polar and can dissolve in polar solvent. High polarity solvent could extract organic compound better than the low ones. Thus, extraction using water could produce less yield but higher quality (Kasmudjiastuti, 2017).

Figure 4. The elongation of resulted leather tanned with different extract.

Elongation at Break

Leather's elongation is closely related to the elasticity of the resulted leather. The leather becomes soft due to the reduction of elastin during the liming and bating process. The anova test results for elongation with a confidence level of 95% indicates that $F_{\text{count}} (0.900) < F_{\text{table}} (5.143)$. This shows that different solvent used to extract did not significantly affect the elongation of tilapia fish skin. The results of the elongation test in this study showed that *M. cochinchinensis* wood extracted using water, ethanol, and water-ethanol has the elongation at 39.49%, 46.93%, and 46.37%, respectively (Figure 4).

Indonesia National Standard 06-4586-1998 (BSN, 1998) stated that maximum elongation of finished leather from freshwater snakes leather tanned with chrome is 30% that all of the samples did not meet the requirements.

Tear Strength

Tear strength is the maximum limit for the skin to be torn (Kholifah *et al.*, 2014). The anova test results for tear strength with a confidence level of 95% indicates that $F_{\text{count}} (7.061) > F_{\text{table}} (5.143)$. It shows that the solvent used for extraction has significant effect on the tear strength of the tanned fish skin. *M. cochinchinensis* wood extracted using water, ethanol, and water-ethanol resulted crust leather with tear strength of 20.76, 12.91, and 15.84 kg/cm² (Figure 5). Indonesia National Standard 06-4586-1998 (BSN, 1998) stated that minimum tear strength of finished leather from freshwater snakes leather tanned with chrome is 15 only fish skin tanned with water that met the

Figure 5. The tear strength of resulted leather with different tannin extract.

requirements. In addition to the tanning agent used in the tanning process, the tear strength can also be affected by the structure of the skin tissue, where the collagen bundle has irregular interwoven.

CONCLUSION

Tilapia fish skin tanned with *M. cochinchinensis* extracted with water showed higher value of tensile strength and tear strength than those with ethanol and water-ethanol, whereas tilapia fish skin tanned with *M. cochinchinensis* extracted with ethanol showed higher value of shrinkage temperature and elongation than others. Based on Indonesia National Standard 06-4586-1998 about the quality requirements of freshwater snake skin tanned chrome, only the tilapia fish skin tanned with *M. cochinchinensis* extracted with water that met the tensile strength requirements, while for elongation, all the samples were not met the requirements. The use of *M. cochinchinensis* as natural tanning agent could at once give unique color to the tanned fish skin. This study is a preliminary research that needs to be improved with another extraction methods of *M. cochinchinensis* or tanning agent combination to meet the better tanned fish skin quality.

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