Combination chrome and mangrove (*Rhizophora mucronata*) bark crude extract on *Epinephelus* sp. leather quality

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Abstract. Almost all tanning leather industry used chrome sulphate mineral because it has a high tannic power and produce tanned leather with good quality. However, as much as 25% chrome in tanning is wasted as liquid waste. Chrome waste product from tanning process is categorized as dangerous waste which is toxic to the environment. The aim of this study was to determine the effect of combination chrome and mangrove bark crude extract on tanned *Epinephelus* sp. skin. The results showed that the best grouper skin was tanned on 8% tanner extract, which was demonstrated a tensile strength value by 228.91 kgf/cm², tear strength by 23.43 kgf/cm, elongation by 24.03%, and shrinkage temperature by 55.23° C. This studied promised application of mangrove extract could replace chrome as tanned agent for greenly method.

1. Introduction

Grouper (*Epinephelus* sp.) is an important economic fishery commodity in fish trade because it has export demand and high prices in the world market [1]. The Ministry of Maritime Affairs and Fisheries explained that within 5 years (2011-2016) the volume of grouper exports increased by an average of 30.75% per year and the export value of 16.42 million US dollars in 2017. Grouper production continued to increase but it product will produces waste that is not used optimally.

Fisheries processing industry wastes include head, scales, skin, fins, and bones[2]. The waste of grouper skin produced from the processing industry is 15% of the total weight of the entire body part of the fish [3]. Utilization of fish skin is currently only used as food ingredients such as skin crackers which have low selling value. The use of fish skin to increase selling value is one of them by making leather [4]. Currently, 85-90% of the leather industry the world is doing the tanning process to use chromium mineral as tanning materials [5]. This reason because chrome has a high tanning power by binding to the carboxyl group of the skin so that the structure of the skin becomes more compact and strong [6]. However, the process of tanning waste chromium contributes to environmental pollution. The 25 % of chrome used in tanning process is wasted in liquid form[7].

The chrome waste was categorized as toxic waste because contain a heavy metal that cannot degraded and accumulated in the soil. Mangroves can be used as vegetable tanners because they contain a variety of phenolic derivatives, especially tannins [8]. Tannin as a vegetable tanner contains hydroxyl groups and carboxyl groups to form strong complex bonds with other protein and macro molecules[9]. The use of tannins as a vegetable tanner is expected to reduce the use of chromium compounds which are not environmentally friendly materials.
2. Materials and methods

Grouper (Epinephelus sp.) skin was gift from PT. Alam Jaya Surabaya, Indonesia. Mangrove bark Rhizophora mucronata was collected from drying bark mangrove at Wonorejo, Surabaya, Indonesia. Mangrove bark were extracted using 70% ethanol (1:10) at a temperature of 70 °C. Leather production was followed procedure described previous work [10].

The stages of the tanning process include: soaking, liming, fleshing, deliming, degreasing, batting, pickling, tanning, retaining, dyeing, fatliquoring, and finishing. The tanners used are chrome, mangrove bark extract, and a combination of both. The treatment of tanners is 8% chrome, 6% chrome 2% mangrove, 4% 4% chrome mangrove, 2% mangrove chrome 6%, and 8% mangrove. This study was using completely randomized design (CRD) with 5 treatments and 4 replications. The tanned skin parameters were determined by physical quality includes tensile strength, strong tear, elongation, and shrinkage temperature. The physical properties data were analyzed using Analysis of Variance (ANOVA) then continued analysis using Duncan’s Multiple range test (α=0.05).

3. Results and Discussion

3.1 Tensile Strength

| Treatment         | Mean ± Standard Deviation |
|-------------------|---------------------------|
|                   | Tensile Strength (kgf/cm²) | Tear Strength (kgf/cm) | Elongation (%) | Shrinkage Temperature (℃) | Chrome Bonded (%) |
| 8% chrome         | 228.91 ± 12.10             | 26.48 ± 4.28            | 46.49 ± 4.83     | 92.90 ± 0.25               | 2.84 ± 0.01       |
| Chrome 6%         | 214.54 ± 10.22             | 18.49 ± 6.94            | 43.29 ± 9.13     | 80.23 ± 0.29               | 1.77 ± 0.01       |
| Mangrove 2%       | 141.33 ± 10.99             | 11.36 ± 1.36            | 42.37 ± 5.39     | 83.03 ± 1.86               | 1.01 ± 0.01       |
| 4% Mangrove Chrome 4% | 140.20 ± 13.28          | 16.54 ± 2.92            | 26.70 ± 1.93     | 71.23 ± 1.20               | 0.68 ± 0.01       |
| 2% Mangrove Chrome 6% | 220.14 ± 14.78           | 23.43 ± 8.34            | 24.03 ± 3.85     | 55.23 ± 0.49               | -                |

Note: Superscript differences indicate the effect of treatment (p <0.05)

The skin has two different functional groups such as carboxylic (COO⁻) and amino (NH₃⁺). Both groups of functions can be active in different environments. The carboxylic group is active under acidic conditions, while the active amino group is in alkaline conditions. This condition is adjusted to the tanner used. The process of binding tanners with functional groups of skin cannot occur in inappropriate loads [11].

Clusters of collagens bind to active groups of tanning agents to form stable skin and can be used in the long term or called leather tanning. The tanning process occurs chemically and mechanically [5]. According to [11] tanning using chrome occurs in two stages. The first stage of chrome will diffuse through the skin pores to form ionic bonds. During the tanning process the adjustment of the media pH around 3.8-4.0 causes the binding of irreversible chrome salts to skin proteins via coordinate covalent bonds[12]. This results in chrome tanned skin having an elastic structure and not easily broken (high tensile strength).

Tanner material factor has a significant effect on tensile strength. Based on our study, the tensile strength value exceeds the standard in all treatments. The tensile strength standard is in accordance with [13], which is a minimum of 101.9721 kgf/cm². The tensile strength of 8% chrome tanner has the same value as 8% mangrove tanner.

3.2 Tear Strength

The value of tear strength is directly proportional to the value of tensile strength. The strong tear standard showed same accordance with [13] which is a minimum of 16.5078 kgf/cm. All treatments
have values above the standard except for 4% Mangrove 4% chrome treatment which were 11.36 kgf/cm. The highest yield of the highest tear was obtained at 8% chrome treatment of 26.48 kgf/cm.

Tannin extract is a mixture of complex polyphenols. Vegetable tannins are classified as condensed tannins, hydrolyzed, and flavonoids. Tannins contain hydroxyl groups and carboxyl groups to form strong complex bonds with proteins and other macro molecules [9]. Based [14] the tanner made from vegetable contain active group on the protein fibers (\(-\text{NH}_2^+\)), binds to the active substance group tanner (OH\(-\)), which will form hydrogen bonds. Tannin which is bound to the tanning process will coat the collagen fibers of fish skin. Vegetable tanners could fill empty spaces between collagen fibers to produce denser and stiff skin [6].

3.3 Tear Strength
The highest elongation value was 46.49%, showed by 8% chrome concentration. The standard of elongation of leather product was showed a maximum of 30% [13]. Treatment of 2% chromium 6% and 8% mangrove in accordance with the standards of 26.70% and 24.03%. Based on the results of the study, the higher the concentration of mangrove extract used showed the lower the value of elongation. The number of bonds formed between tanneries and collagen produces a rigid skin structure. A low elongation value indicates a less elastic skin structure. However, the high value of elongation (very elastic) will produced unbeautiful skin if used as a product.

3.4 Shrinkage Temperature and Chrome bond
Shrinkage temperature has 92.90 C at a concentration of 8% chromium. The lowest value of wrinkle temperature was 55.23 C in 8% mangrove wood extract tanner. The use of chromium as a tanner can produce a high wrinkle temperature value compared to vegetable tanners.

The results of the study were in accordance with the references which show that tanned fish skin using chrome has a high wrinkle temperature value. In contrast to vegetable tanners which have low wrinkle temperature values. Trivalent chrome (Cr III) component as tanner agent reacts with skin collagen fibers so that the skin becomes stable against heat and water [15]. Whereas in vegetable tanner’s hydroxyl groups of tannins form hydrogen bonds with skin collagen peptide groups [16]. The bond between tannins and skin collagen depends on the size of the molecule and the number of -OH groups. The covalent bond between collagen and tanneries plays an important role in increasing the skin shrinkage temperature of the skin [17]. The toxicity of chromium particles depends on the oxidation state. Toxic compounds can enter the body through 3 routes, such as inhalation, the digestive tract, and direct skin contact. International specifications for the disposal of chrome waste in the tanning process are 0.1-2 ppm [9].

4. Conclusion
The results showed that the combination of chrome as tanner and mangrove bark extract had a significant effect on the quality of tanned grouper skin. The 8% mangrove treatment was showed the best result in terms of physical parameters with a tensile strength by 228.91 kgf/cm², tear strength 23.43 kgf/cm, elongation 24.03%, wrinkle temperature 55.23 °C and safer because it was not contamination of chrome.

5. References
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