The utilization of kesumba seeds for coloring Biawak (Varanus salvator) leather with dyeing and finishing methods based on environmentally friendly

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Abstract. The aim of the study was to utilize kesumba seeds (Bixa orellana L) for coloring Biawak (Varanus salvator) leather dyeing and finishing methods against color fastness based on environmentally friendly. The ingredients used are kesumba seeds, Biawak leather, binder from white part of egg. Using the experimental methods, with four phases: (1) extraction of kesumba seeds wet and dry, (2) dyeing methods variations: (a) dye concentration from kesumba seeds, (b) dyeing durations (c) temperature (°C), Rpm of the drum 12, and crust Biawak leather, (3) finishing method using binder from white part of egg, and (4) testing Absorption and color fastness test on wet and dry rubbing, the assessment standard uses a gray scale and staining scale. Data analysis using Analysis of variance. The results shows that there significant differences in color absorption in the flash asverages are 80-70% and nerf asverages are 60-40%, and results of Biawak leather fastness test for dyeing and finishing methods, dried kesumba seeds concentration 9%, dry rubbing discoloration 4-5 (good) fastness, orange-yellow color on the leather and wet kesumba seeds concentration 6%, 3-4 fastness (good enough), orange-red color on the leather and the results of wet rubbing are found to have an average color fastness value of 3 (enough) for wet and dry kesumba. It can be concluded that coloring from kesumba and binder material ingredients based on environmentally friendly can be used as a dyeing material and also for finishing as an alternative substitution of synthetic dyes in the Leather Industry.

1. Introduction
Pollution is a problem that is often found in the environment, especially in aquatic environments, without realizing the pollution comes from industrial activities, one of which is the leather tanning industry which processes raw leather (hides / skins) into tanned leather using tanner and coloring material. Leather tanning industry, there are 4 main phases of the process, namely: (1) beam house operation; (2) tanning; (3) post-tanning process and (4) finishing. Each stage consists of several types of processes, each process requires additional chemicals and generally requires water, depending on the type of raw leather used and the desired type of leather product [1]. Products that contain coloring chemicals are often used in the basic coloring dyeing process tanned leather by soaking and rotating it in a solution of dyes, with the aim of providing the basic color on the leather so that the use of coloring agents (finishing) will not be too thick, so it is not easily broken and added binder as a color binded [2].

Environmental effects of using synthetic dyes for example: Azo-Bensidin, p-Cresidine 4-Aminodiphenyl and 0-Toluidin, contain hazardous and toxic metals pigments, as dyeing and finishing
dyes. Carcinogenic compounds bensidin and biphenylamine which have a similar molecular structure that is an ammonia aromatic compound with planar molecules, so these compounds can interkolate into DNA, interaction with DNA bases and cause irreversible DNA damage that can trigger cancer and waste water can contaminate environment [3]. Although synthetic dyes have advantages such as more practical use which means time efficiency, as well as the appearance of colors that provide satisfactory results on finished leather products, but has a weakness the price is relatively too high, and has great potential to have impacts pollution to the environment.

Indonesia as a tropical country and has high soil fertility has the potential to produce coloring plants, most of which have not been widely used to be applied to the leather tanning industry. One of the natural dyes that can be used is the kesumba plant (*Bixa orellana* L), visually, the color produced from the seeds is Orange-yellow [4] Based on the introduction that the material can be used as a substitute for imported synthetic dyes with several advantages including: availability is quite a lot, environmentally friendly [5], and relatively easy to extract, but the weakness of the quality of the color or eternity of the color of most plant pigments easily fade, the color fades quickly when exposed to sunlight need to be added binder and dyeings and Finishing process, related to the background and problems as described by the researcher very interested to be done, The Utilization of Kesumba Seeds for Coloring Biawak (*Varanus Salvator*) Leather With Dyeing And Finishing Methods Based On Environmentally Friendly.

2. Methods

2.1 Materials

The ingredients used are wet and dried kesumba seeds, aquadest as solvents, biawak (*Varanus salvator*) crust leather, binder material (white part of egg) ingredients. The tools used for dyeing and Finishig drum coloring process and fastness test using Crockmeter, Gray scale, and Staining Scale tools.

2.2 Methods Extraction kesumba

Using the experimental methods with 4 phases: (1) Extracting kesumba wet and dry seeds, extraction process using kesumba seeds and aquades solvents with a ratio (material: solvent) w/v, extraction time variation at 80-100°C, to color density and rendemen, (2) The dyeing process of kesumba dyes on biawak crust leather with various concentrations (1.0; 3.0; 6.0; 9.0 and 12.0%), drum / Rpm rotations (4; 8; 12; 16 and 20) and temperature (<30°C; 40-60°C; 70-80°C; 90-100°C and> 100°C), (3) The finishing process with the addition of binders and (4) Testing of absorption and rubbing color fastness test ( wet and dry), the assessment standard uses a gray scale and staining scale. Color fastness test for rubbing (SNI 0288-2008). Data analysis using Analysis of variance.

3. Results and Discussion

3.1 Natural dyes kesumba seeds extraction

The extraction from kesumba wet and dried seeds with water solvent and extraction time of 60 minutes, on color density there were increases and decreases, obtained an optimum 4.26°Be for extracting wet kesumba (KB3), temperature 100°C, ratio 4: 30b / v, and obtained the lowest 1,53°Be in the extraction of dried kesumba (KK1), temperature of 40°C, ratio of 1:30 b / v, in dried kesumba (KK1), can be seen in Figure 1.
Figure 1. The relation between extraction kesumba seeds and color density

This difference is not only influenced by the extraction temperature but also the stirring speed, the greater the stirring speed, the better the results, while if the stirring speed is small then the results obtained are less concentrated, because the contact between solvent and solute is less than perfect [4]

Figure 2. The relation between extraction kesumba seeds and yield

The extraction of wet and dry kesumba seeds on yields with a time of 60 minutes, an increase and a decrease occurred, obtained an optimum yield of 8.28% (KB3) at extraction temperature of 100°C, ratio of ingredients: solvent (5:30), and obtained in dry kesumba the lowest yield was 4.45% (KK1) in temperature extraction (40°C), ratio of ingredients: solvent (1:30). In Figure 2. This difference is caused by the higher ratio of the weight of the material and solvent, the more the dyestuff material is used so that more dyes can dissolve, because the extracted solids the results obtained are greater, because contact is more frequent with solvents whose amount more, and it appears that the liquid has begun to saturate with dyes so that the yield starts to be constant, [6]

Figure 3. The relation between duration extraction kesumba seed and color density

Shows that the extraction of kesumba seeds extraction time of 90 minutes at a temperature of 100°C, obtained the optimum color density of 4.22°Be in dried kesumba (KK), and optimal color density of 4.95°B in wet kesumba seeds (KB). See Fig 3. This increase and decrease is thought to be
due to extraction time, the longer the extraction time the greater the results obtained, because the contact between the solvent and the extracted material will also cause the solvent to be enriched more solely, and diffuse from the simplicia to the solvent, the length of the extraction process, the more active substances can be extracted, until a saturation point occurs from the diffusion process [7].

Figure 4. The relation between duration extraction kesumba seed and Yield

The dye extraction from wet and dry kesumba seeds extraction time was 90 minutes and the temperature was 100°C, the ratio of ingredients: solvent (5: 3) b / v, obtained optimum yield of 9.25% from wet kesumba seeds (KB), and optimum yield of 8.28% from dried kesumba seeds (KK), see Fig. 4. This difference is caused, the extraction time determines the number of active substances that can diffuse out of solid simplicia into the solvent. The longer the extraction time, the more active substances are extracted, so that saturation / saturation can occur in the maceration process towards the solvent the longer the extraction time, the more active substances are extracted, so that saturation can occur in the maceration process [8]

3.2 Dyeing Process

3.2.1 Effect of Concentration. It was shown that the effect of the concentration of kesumba dyes was optimum absorption of 70.0% (nerf biawak leather, 6% wet kesumba / KB dye concentration) and 40% (nerf biawak leather, 9% dried kesumba / KK dye concentration). The optimum color fiber power is 80% (in the flash monitor lizard skin, 6% wet kesumba / KB dye concentration) and 70% (flash biawak leather, 9% dried kesumba / KK dye concentration). Can be seen in table 1.

Table 1. The result of dyeing process kesumba concentration variable for % absorption.

| Kode | The relation concentration and % absorption on Nerf and Flash | Biawak leather |
|------|---------------------------------------------------------------|----------------|
|      | 1% | 3% | 6% | 9% | 12% |
| KB   | Nerf | 31,0 | 50,9 | 52,2 | 72,7 | 70,0 | 80,0 | 68,3 | 78,2 | 65,1 | 76,4 |
| KK   | Nerf | 24,3 | 33,5 | 27,8 | 56,3 | 32,7 | 62,2 | 40,0 | 70,0 | 38,5 | 68,0 |

This difference is caused by kesumba dyes are acidic and contain bixin, an acidic type containing anion groups will bind anionically with cationic amino acid groups from skin proteins. In principle, chromium salts in crust biawak leather will bind carboxylic acid groups from skin proteins, so that the tanned (chrom) skin tends to increase the amount of cationic charge. Furthermore, the salt will be hydrolyzed by releasing acid which will increase the acidity of the tanned skin, so that the bonds occur very quickly when using acid dyes. The fast bonding on the surface of the skin can result in an uneven coloring process and very low penetration of dyes into the skin [5].

3.2.2 Effect of drum speed (Rpm). It shows that the coloring process with the influence of drum (Rpm) of kesumba dyes obtained optimum color absorption of 76.2% (Nerf Biawak leather, 12 rpm, wet
kesumba dye / KB) and 68.1% (Nerf biawak leather, 12 rpm dye) kesumba Dry / KK). Optimum color fiber power of 85.3% (in the flash portion of biawak leather, wet dye 12 rpm / KB) and 74.4% (Flash biawak leather, dried kesumba dye 12 rpm / KK). Can be seen in table 2.

| Code | 4 | 8 | 12 | 16 | 20 |
|------|---|---|----|----|----|
| Nerf | 38.3 | 55.8 | 58.3 | 60.7 | 76.2 |
| Flash | 85.3 | 73.8 | 80.3 | 69.4 | 76.2 |
| KK | 27.4 | 43.2 | 47.4 | 46.3 | 68.1 |
| Nerf | 74.4 | 63.4 | 56.8 | 40.0 | 66.5 |

This difference is strongly influenced by the histology structure of biawak (varanus salvator) and drum rotational speed, and also the effect of dye concentration for each liter of water, using dyes in the dyeing process based on the heavy percentage of crust biawak leather, the greater the percentage of color on the leather, because the amount of water used fixed ranges from 100 -150% of crust biawak leather weight [9].

3.2.3 Effect of temperature. The coloring process with the influence of the temperature 70-80°C of the coloring agent kesumba at a concentration of 9%, the nerf part of the biawak leather obtained optimum color absorption 75.4% in the dye wet kesumba (KB), and 65.2% in the dried kesumba (KK), and in part flash obtained optimum color absorption capacity of 80.5% in wet kesumba dyes (KB), and 70.4 in dried kesumba dyes (KK). See table 3

| Code | <30°C | 40-60°C | 70-80°C | 90-100°C | >100°C |
|------|-------|---------|---------|----------|--------|
| Nerf | 48.3  | 65.8    | 75.4    | 75.2     | 74.0   |
| Flash | 68.3  | 70.7    | 80.5    | 83.3     | 80.4   |
| KK   | 37.4  | 63.2    | 65.2    | 70.4     | 73.2   |
| Nerf | 73.0  | 75.8    | 73.2    | 70.5     |        |

This difference is due to the method used to dissolve the dye into paste is to add a little water to the coloring powder until evenly distributed, then add boiling water 20 times the amount of the dye added. The increase in temperature will also increase the effect. The use of mordant in coloring can reduce the cationic properties and coloring can be more evenly distributed, it can also increase penetration, but the color is increasingly pale. Secondary variance in the kesumba dye will be attenuated by rising temperatures, and high temperatures can break down the dye molecules, this causes good solubility in these dyes. With the higher temperature will make the dye more easily dissolve, the condition will cause penetration and the distribution of coloring agents on the skin the better, but the binding capacity is low [10].

3.3 Finishing process

Finishing process uses natural kesumba dyes by adding an adhesive (binder) from white part of egg protein with variations (1.0; 1.5; 2.0; 2.5 and 3 %) to the weight of crust. In table 4. It shows that the color sharpness is optimal in the addition white part of egg protein binder intervals of 2.0-2.5%, with a score of 3 which means the color is very sharp.

| Code | Add white part of egg binder to kesumba dyes (%) |
|------|-----------------------------------------------|

Table 2. The results of dyeing process Rpm variable for % absorption

Table 3. The results of dyeing process temperature variable for % absorption

Table 4. The results finishing process binder variable material for color sharpness
Description: Color sharpness: value 1 = less sharp color, sharp color = 2 and very sharp color = 3.

This difference is due to adhesives (binders) from egg protein as a medium that connects kesumba dyes to the dyeing process and components of kesumba dyes in the finishing process with the surface of the skin. The binder is also a film forming substance that can polish the skin in the glasing process, softener (softener, plastizer), so that the finishing coloring agent is not easily broken, soft and elastic, the dye used is added to the softener material will form a hard film so it does not break easily or crack. The coloring agent for this finishing process does not bind chemically to the skin but is only physically bound.

Table 5. Color fastness values of kesumba dyes on crust biawak leather

| Concentration (%) w/v | Dry rubbing | Web rubbing |
|-----------------------|-------------|-------------|
|                       | Web Kesumba | Dried Kesumba | webKesumba | Dried Kesumba |
| 1.0                   | Nerf 1      | Flash 1     | Nerf 2      | Flash 2     |
| 1.5                   | Nerf 2      | Flash 2     | Nerf 3      | Flash 3     |
| 2.0                   | Nerf 3      | Flash 3     | Nerf 3      | Flash 3     |
| 2.5                   | Nerf 3      | Flash 3     | Nerf 2      | Flash 2     |
| 3.0                   | Nerf 2      | Flash 2     | Nerf 3      | Flash 3     |

Figure 5. The results finishing process of application kesumba dyes on biawak (Varanus salvator) Leather

The results of the application of dyes in wet and dry biawak leather (fig.5), organoleptic test found orange-yellow color from dried kesumba (KK), and orange-red color from wet kesumba (KB), according to the purpose of finishing process to beautify appearance the leather by strengthening the color and gloss (color sharpness), smoothing the appearance of the surface tanned and covering the defects or color appearance in the dyeing process which is uneven, and protects the surface tanned from damage due to friction, heat, rain and sunlight [3].

3.4 Fastness testing of biawak (Varanus salvator) leather

The color fastness values of wet kesumba (KB) and dried Kesumba (KK) dyes in the coloring process using throuth dyeing and finishing methods can be seen (Table 5).
Shows biawak leather fastness test results for dyeing and finishing methods, for 9% dried kesumba dye, on Rpm 12 drum, dry rubbing color the score (4-5) fastness mean excellent, orange-yellow color and the wet kesumba seeds dry rubbing color the score (3-4) fastness mean good, orange-red color and the result of wet rubbing results in an average color fastness score value 3 fair fastness for wet and dry kesumba seeds.

4. Conclusion
1) The result significant difference extracting kesumba seeds with a ratio (4:20), pigment coloring material, containing bixin, acidic coloring, color density (4.03°Be) and yield (6.48%) higher than dried kesumba seeds color density value (2.76 °Be) and yield (3.59%), and the color obtained is yellow-orange, so that it can be used as an alternative coloring material for the tanning process.
2) Dyeing process obtained optimum absorption in the coloring process with the influence of the temperature of the kesumba dyes at a concentration of 9%, the portion of the monitor lizard skin obtained optimum color absorption 75.4% in the wet kesumba dye (KB), and 65.2% in the dye dry kesumba (KK), and in the flash section optimum optimum color absorption of 80.5% in wet kesumba (KB) dyes, and 70.4 in dried kesumba dyes (KK).
3) Finishing Process Optimal color sharpness on the addition of egg white protein binders finishing at concentrations (2.0-2.5)%, organoleptic test with a score of 3 means very sharp colors.
4) The color fastness test results of 9% dried kesumba dye, on a Rpm 12 drum drum, dry rubbing color change test for 4-5 excellent fastness, orange-yellow color, and wet kesumba seed material resistant value 3-4 good fastness, orange-red color and the results of wet rubbing have an average color fastness value of 3 fair fastness for wet and dry kesumba seeds.

References
[1] Xiaolei Z, 2012. An overview of wax utilization in China. *European Chemical Bulletin*. Vol 1(6), 210-211 DOI: 10.17628/ECB.2012.1.210
[2] Covington, D, Anthony, and Tony. 2009, Tanning Chemistry: The Science of Leather, Cambridge: The Royal Society of Chemistry. RSC Publishing, United Kingdom, pp 281-285
[3] Daniels, R and W. Landmann, 2008, Pre-Finishing and Finishing, *World Leather*, Vol.21, No.21 pp 42-43.
[4] Paryanto, Kriyantoro, and R. Prabowo, Y.S., (2015). Pembuatan Zat pewarna Alami berbentuk bubuk (powder) dari biji kesumba (Bixa orellana L), Journal ekulilibrium, Vol.14. No1, ISSN: 1412-912: pp 13-16
[5] Sembiring, B.Br. 2014. Kesumba Keling (Bixa orellana) sebagai pewarna ramah lingkungan. Ballitro. Jurnal Warta Lingkungan dan Pengembangan Tanaman Industri 20(2)): pp 27-30.
[6] Putri, A.R, Tavita, G.E, and Muflihati, (2016), Ekstrak Biji Kesumba (Bixa orellana L) sebagai pewarna alami kayu sengon (Paraserianthes falcata Linn), Jurnal Hutan Lestari, Vol 4(3): pp 306-313
[7] Kurniati, N, 2012, Ekstraksi dan uji Stabilitas Zat Warna Brazilin, *Journal of Chemical Science*, Volume V, p 56.
[8] Sitompul, J., Widayat, P., and Soerawidjaja, T. H. (2012). Evaluation and modification of processes for bioethanol separation and production. Int. J. Renew. Energ. Develop., 1: 15-22 (12)

[9] Abrahart, E.N, 2005. Dyes and Their Intermediates, Second Edition, London, Edward Arnold.

[10] Darmawati, E, Sudarmadji, Santoso, U. 2016. The Application of Affal Parchment Leather as Souvenir Materials Using Secang Bark Dye Color Fastness, Proceedings ICTIS, ITP PRESS DOI 10.21063/ICTIS.2016.1015: pp 88-93.