CITRIC ACID AS AN EFFECTIVE AND SAFE FIXING AGENT IN VEGETABLE TANNING PROCESS OF GOATSKIN

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Received: 02.10.2022 Accepted: 05.12.2022 https://doi.org/10.24264/lfj.22.4.3

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ABSTRACT. Formic acid is known as a fixing agent in vegetable tanning process but this material is corrosive and irritant. Citric acid has the potential to be developed as an alternative fixing agent. This research aims to study the ability of citric acid as an alternative fixing agent in the tanning process, especially vegetable tanning of goatskin. The tanning process was carried out by the drum method. Pickled goatskins were tanned with mimosa and then fixed with citric acid. The concentration of citric acid varied from 1%; 1.5%; 2%; 2.5%; to 3%, to determine the optimum concentration. A fixing agent of 2% formic acid was used as a control. The results show that the control skin had similar characteristics to the treated skin. Physical properties of T4 have met the standard of SNI 0253-2009. It can be concluded that the optimal concentration of citric acid that can be used as an alternative fixing agent in vegetable tanning process of goatskin is 2.5%.

KEY WORDS: tanning, skin, fixing agent, citric acid

UTILIZAREA ACIDULUI CITRIC CA AGENT DE FIXARE EFICIENT ȘI SIGUR ÎN TABĂCIREA VEGETALĂ A PIEILOR DE CAPRĂ

REZUMAT. Acidul formic este cunoscut ca agent de fixare în procesul de tăbăcire vegetală, însă acest material este coroziv și iritant. Acidul citric are potențialul de a fi utilizat ca agent de fixare alternativ. Această lucrare de cercetare își propune să studieze capacitatea acidului citric ca agent alternativ de fixare în procesul de tăbăcire, în special la tăbăcirea vegetală a pielii de capră. Tăbăcirea s-a realizat în butoi. Pieile de capră piclate au fost tăbăcite cu mimosa și apoi fixate cu acid citric. Concentrația acidului citric a variat de la 1%; 1,5%; 2%; 2,5%; la 3%, pentru a determina concentrația optimă. S-a utilizat ca martor un agent de fixare pe bază de acid formic 2%. Rezultatele arată că pielea martor a avut caracteristici similare cu pielea tratată. Proprietățile fizice ale T4 au îndeplinit cerințele standardului SNI 0253-2009. În concluzie, concentrația optimă de acid citric care poate fi utilizată ca agent de fixare alternativ în procesul de tăbăcire vegetală a pieilor de capră este de 2,5%.

CUVINTE CHEIE: tăbăcire, piele, agent de fixare, acid citric

L'UTILISATION DE L'ACIDE CITRIQUE COMME AGENT DE FIXATION EFFICACE ET SÛR DANS LE PROCESSUS DE TANNAGE VÉGÉTAL DE LA PEAU DE CHÈVRE

RÉSUMÉ. L'acide formique est connu comme agent de fixation dans le processus de tannage végétal, mais ce matériau est corrosif et irritant. L'acide citrique a le potentiel d'être développé comme agent de fixation alternatif. Cette recherche vise à étudier la capacité de l'acide citrique comme agent fixant alternatif dans le processus de tannage, en particulier dans le tannage végétal des peaux de chèvre. Le processus de tannage a été effectué par la méthode du tambour. Les peaux de chèvre picklées ont été tannées au mimosa puis fixées à l'acide citrique. La concentration en acide citrique a été variée de 1 % ; 1,5 % ; 2 % ; 2,5 % ; à 3 %, pour déterminer la concentration optimale. Un agent de fixation à base d'acide formique à 2% a été utilisé comme témoin. Les résultats montrent que la peau témoin avait des caractéristiques similaires à la peau traitée. Les propriétés physiques du T4 ont satisfait à la norme SNI 0253-2009. On peut conclure que la concentration optimale d'acide citrique qui peut être utilisée comme agent de fixation alternatif dans le processus de tannage végétal de la peau de chèvre est de 2,5 %.

MOTS CLÉS : tannage, peau, agent de fixation, acide citrique

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INTRODUCTION

Nowadays, environmental factors have become a big issue in leather tanning process. Even the leather tanning industry needs to have an eco-green technology label which shows that the industry is environmentally friendly [1]. The tanning process cannot be separated from the fixation stage which affects the formation of the bond between skin collagen and tanning agent. This stage needs a chemical as a fixing agent that can arrange the charge of skin so that the bond can be formed. Various fixing agents are used depending on the material that will bind to skin protein. Chromium(III) and polyamines can be used as fixing agents for dyes, while polyacrylate is used as a fixing agent for chromium(III) [2]. This is due to its ability to form complexes through carboxylate groups. Sodium edate, tetrasodium edate, and trisodium citrate have also been reported to be used as fixing agents for fabric dyeing agents, where the fabric has functional groups similar to that of skin [3-4]. Formic acid is known as a fixing agent that is often used in the tanning process, especially in vegetable tanning process [5-9]. Formic acid combined with mineral acid as a fixing agent during the post-tanning operation also has been reported in a previous study [10]. Formic acid produces hydrogen ions (H^+) in the solution, resulting in the breaking of the salt bridges in skin protein. From a health perspective, formic acid is a corrosive and irritant chemical that also may cause severe skin burns. This has led some regions to apply occupational exposure limit values as a precaution. In addition, formic acid is expensive from an economical perspective [10]. Therefore, a safer and more effective fixing agent in the tanning process is needed.

One acid material that is easily found is citric acid. Citric acid is a weak acid that can be produced synthetically or naturally from fruits and vegetables, especially citric fruits [11]. It also has properties that are safe for the human body so there is no tendency to burn or irritate the skin. The presence of H^+ ions in the citric acid causes this acid to be used as a fixing agent in the tanning process. Therefore, identification of the ability of citric acid as a fixing agent was carried out in this study.

EXPERIMENTAL

Materials and Methods

Materials

The materials used were 6 sheets of pickled goatskins, mimosa (Mimosa ME produced by SODA), mimosa sulphited (produced by SODA), naphthalene sulphonates (Coralon OT produced by STAHL), sulphited oil (Derminol OCS produced by STAHL), citric acid (PT Golden Sinar Sakti) and sodium bicarbonate ($NaHCO_3$).

Methods

The pickled goatskins were processed through vegetable tanning using the drum method. The formulation of the tanning process is shown in Table 1. Variation of fixing agent in this study was divided into 5 treatments: treatment 1 (T1; 1% citric acid), treatment 2 (T2; 1.5% citric acid), treatment 3 (T3; 2% citric acid), treatment 4 (T4; 2.5% citric acid), and treatment 5 (T5; 3% citric acid). Control (T0; 2% formic acid) was used as a comparison. The vegetable-tanned skins were then characterized, including FT-IR analysis, shrinkage temperature, tensile strength, elongation, and tear strength. Treatment skin with the best physical properties was then analyzed using SEM (Scanning Electron Microscope) and compared to control skin.

RESULTS AND DISCUSSIONS

Tanning Process

Fixation stage has a major role in the tanning process because it determines the skin charge that results in interaction with the tanning agent. In general, fixation in vegetable tanning process involves acid as a fixing agent. This acid donates hydrogen ions to the collagen skin so that the charge becomes positive. In addition, the acid will lower the pH of the system.

Vegetable tanning process conducted in this study was carried out using citric acid as a fixing agent. Citric acid lowers the pH of the solution so that the pH at fixation stage is below the isoelectric point of the skin. The pH at

Table 1: The stages of vegetable tanning process of goatskin

Stage Process	Chemical	Time (min)
pH Adjustment	200% Water	
	2.5% $NaHCO_3$	90
Pretanning	200% Water	
	4% Coralon OT	45
Tanning	10% Mimosa sulphited	60
	3% Derminol OCS	45
	15% Mimosa	120
	4% Coralon OT	15
Fixation	1; 1,5; 2; 2,5; 3% Citric acid or 2% Formic acid	30

fixation stage in this study is presented in Table 2. It describes the fixation done at a pH of 3.5 when using formic acid and in the pH range of 4.2 to 4.5 in the use of citric acid. It is proved in previous studies that the skin proteins have strong internal cross-links in the isoelectric point range of skin, which is around pH of 5 to 7 [12-13]. This is due to the opposite charge of the protein being at its maximum. In addition, the spatial conditions of the protein chains are interconnected to form strong internal links, both from salt bridges and coordinate cross-links of hydrogen bonds. The addition of acid can decrease the pH of the system so that some of the salt bridges are broken due to the protonation of the carboxyl ion (Figure 1). This also causes the breaking of hydrogen bonds as a result of further crosslinked groups. Therefore, a new coordination group is formed that can react with the tanning agent [13].

Table 2: pH value of solution in fixation stage

Materials	pH of solution
T0	3.5
T1	4.5
T2	4.5
T3	4.2
T4	4.2
T5	4.2

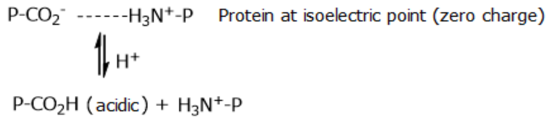


Figure 1. The effect of acid addition on the breaking of salt bridges in skin protein

Formic acid has a different pKa than citric acid. Formic acid in aqueous solution undergoes one stage of ionization (pKa = 3.74), while citric acid undergoes three stages of ionization ($pK_{a1} = 3.13$; $pK_{a2} = 4.77$; $pK_{a3} = 6.40$) [14]. According to Table 2, it is known that the fixation using citric acid was carried out at a pH below the pKa of formic acid for the control skin and below the pKa_2 of citric acid for the treated skin. This explains that fixation occurs with the help of H^+ ions resulting from the ionization of formic acid and citric acid. This phenomenon is in accordance with Gustavson's (1954) explanation above which states that the addition of acid can cause the skin to react with tanning agents [13]. Therefore, citric acid can also be used as a fixing agent in vegetable tanning process.

Mimosa is a condensed vegetable tanning material. This type of tanning material can react with collagen through hydrogen bonds and quinoid species to produce covalent bonds [2]. Therefore, a model of the structure of vegetable-tanned skin that is possible to form is shown in Figure 2.

The optimum concentration of citric acid that can react with the protein of the skin is 2% (Figure 3). An increase in the amount of reacted citric acid was observed at concentrations of 1% to 2%. This phenomenon states that the number of H^+ ions required for the fixation reaction is not sufficient at a concentration of 1%. Meanwhile, the amount of citric acid that reacts with the skin tends to be constant if the concentration of citric acid used is greater than 2%. This can happen because the number of H^+ ions needed has reached the saturation point. Therefore, the addition of citric acid concentration did not significantly affect the fixation reaction.

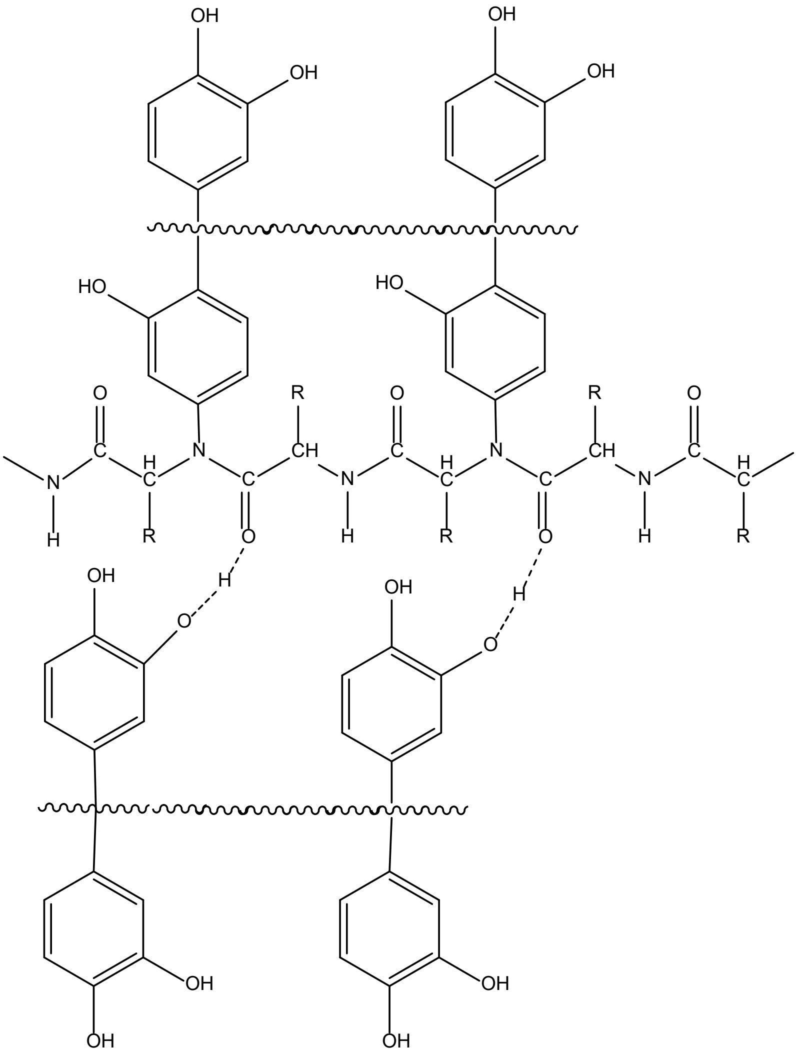


Figure 2. Hypothetical structure of vegetable-tanned skin

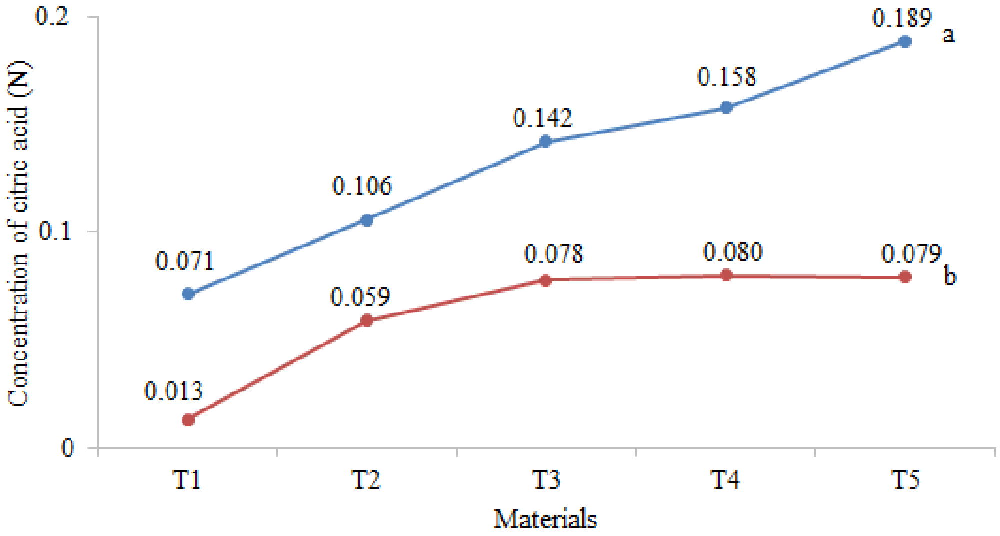


Figure 3. The concentration of citric acid (N): (a) added in the fixation stage and (b) reacts with collagen skin

Functional Groups

The vegetable-tanned skin is then characterized by FTIR spectrophotometer to identify the functional groups in the product. The result of infrared absorbance shows that the vegetable-tanned skin exhibits the characteristic absorbances of hydroxyl, methylene, and amide (Figure 4). The stretching vibrations of O-H are observed at 3398 cm^{-1} and 563 cm^{-1} [15]. Those bands are abroad due to the presence of hydrogen bonding. The vibration band at 2932 cm^{-1} comes from the asymmetric stretching vibration of C-H. Furthermore, the methylene group is detected at 1335 cm^{-1} [16-17]. Containing collagen, the absorbance of amide is observed at 1636 cm^{-1} from the stretching vibration of carbonyl collagen of amide I. The bending vibration of -OH also occurs at this wavenumber range, resulting in overlapping bands. Characteristic absorption of amide II is shown at 1543 cm^{-1} coming from stretching vibration of C-N and overlapping with N-H bending vibration band [15, 18-20]. Moreover, absorption of C-N is also detected at 1450 cm^{-1}. The absorption band at 1234 cm^{-1} proves the presence of amide III [19]. Whereas stretching vibration of C-O-C is observed at a wavenumber range of 1034-1111 cm^{-1} [16].

The use of formic acid as a fixing agent in control leather does not significantly affect the absorption band pattern of the skin. Likewise, for the use of citric acid in sample leather, the absorption bands resulted show that the leather has the same functional groups as skin. This is due to the fixing agents, both formic acid in control leather and citric acid in the sample, do not change the functional groups of the leather. The intensity of the absorption band of sample T1 is lower than that of other samples. This should be due to the fact that the amount of citric acid is not sufficient so that the mimosa could not be maximally fixed into the skin.

If the citric group is attached to the material, it will result in the absorption of asymmetric stretching of COO^{-}, symmetric stretching of COO^{-} and stretching of CH, respectively at 1629 cm^{-1}, 1383 cm$^{-1,}$ and 1054 cm^{-1} [21]. The presence of these absorption bands is difficult to observe due to the overlapping band of other functional groups. However, the similarity of the absorption bands between unfixed tanned leather and fixed tanned leather, indicates that the citric group is not bound to the skin. This confirms that only the H^{+} ion of acid is involved in the fixation stage.

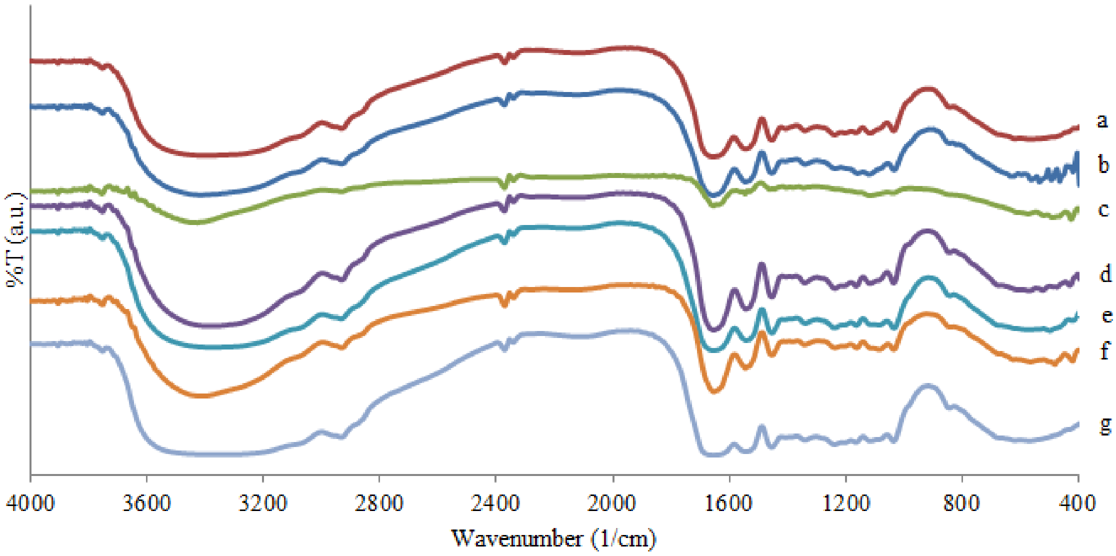


Figure 4. Infrared spectra of goatskins: (a) before fixation, (b) T0, (c) T1, (d) T2, (e) T3, (f) T4, (g) T5

Shrinkage Temperature

Shrinkage temperature is the temperature when the collagen structure of the skin begins to shrink by heating in a water medium [22]. Shrinkage temperature of the skin was measured to identify its stability to heat. Because of the same fixation reaction mechanism in the control skin as in the treated skin, there is no significant difference between the two (Table 3). The difference in shrinkage temperature shows the difference in the strength of the interaction between collagen and mimosa. This is following the statement of Covington (2009) that the difference in shrinkage temperature is influenced by the different types of reactions that occur [2]. Based on the structural model in Figure 2, it is known that collagen can bind to mimosa in two ways. The first way is the formation of hydrogen bonds, while the second is the formation of covalent bonds. The stronger covalent bond than the hydrogen bond causes the sample that has more covalent bonds to have a higher shrinkage temperature. This happens because it takes higher energy to break the covalent bond. The optimum shrinkage temperature is obtained when using 1.5% citric acid. This concentration is smaller than the required formic acid concentration (2%). This is possible because citric acid is a triprotic acid so it has a higher number of H^+ ions that can be donated than formic acid. Meanwhile, the number of cross-links also depends on the size of the polyphenolic molecule and the number of -OH groups of tannin molecules present [23].

Table 3: Shrinkage temperature of vegetable-tanned skins

Materials	Shrinkage temperature (°C)
T0	79
T1	76
T2	82.3
T3	76
T4	77
T5	80

In order to tan using vegetable extracts, the hides must be in contact with the extracts for a considerable time. The reason for this is that vegetable extracts are not simple products; they are composed of organic molecules of different molecular sizes [24]. It may be possible that the number of -OH groups of tannin molecules present in T2 is greater than others. This explains the different shrinkage temperatures even in similar fixation pH.

Tensile Strength, Elongation, and Tear Strength

Physical properties of tanned goatskin including tensile strength, elongation, and tear strength were tested. Tensile strength is the amount of load needed to pull tanned goatskin until the collagen fibers are broken. Meanwhile, elongation is a measure of the stretch characteristics of tanned goatskin produced by a tensile load. The tear strength indicates the maximum limit of the skin to be torn. The results are presented in Table 4.

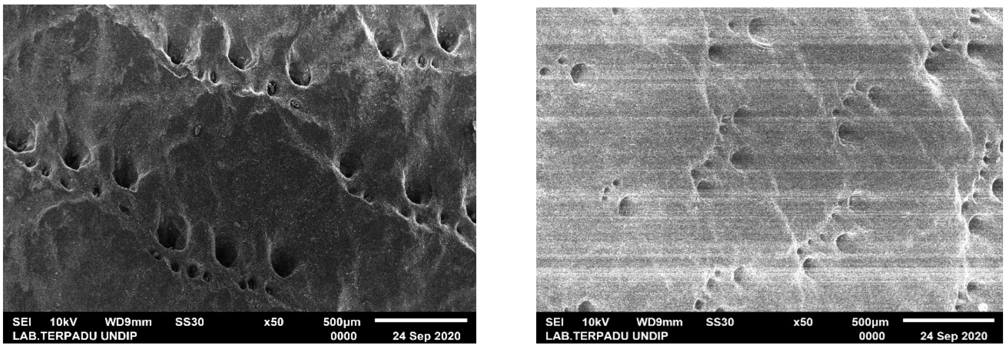
Table 4: Physical properties of vegetable-tanned skins

Materials	Tensile strength (N/cm^2)	Elongation (%)	Tear strength (N/cm)
T0	2163.23	30.42	112.03
T1	1257.52	40.12	94.56
T2	1521.2	25.78	81.3
T3	2402.12	26.92	111.9
T4	1604.97	48.44	167.44
T5	1787.94	26.20	91.66

The test result in Table 4 shows that there is no definite trend between the difference in the amount of citric acid and the physical properties. In addition, it is also known that the physical property values of the sample revolve around its control, indicating similar strength interaction on skin. When compared to SNI 0253-2009 [25], not every skin meets the standard. This indicates that the skins need to be further processed in post-tanning to obtain the appropriate properties. Among these skins, the skin that has met the SNI 0253-2009 standard is T4.

Surface Morphology

SEM analysis was employed to observe the surface morphologies of the control and sample (T4). The results are shown in Figure 5. It can be seen that the grain surface of the sample is flatter and fuller compared to the control. This is possible due to the filling effect resulting from the interaction of collagen and citric acid. Citric acid, which is a triprotic acid, provides a higher pH value in the system than formic acid. This allows the reaction between collagen and mimosa to be slower, resulting in a more flat and fuller tanned skin.



(a) (b)

Figure 5. Surface morphology of vegetable-tanned skins: (a) T0 and (b) T4

CONCLUSIONS

Citric acid can be used as an alternative fixing agent to substitute formic acid in vegetable tanning process. The control skin had similar characteristics to the treated skin. The optimal concentration of citric acid as a fixing agent is 2.5%, which has met the standard of SNI 0253-2009.

Acknowledgements

This work was supported by Politeknik ATK Yogyakarta through Research Grant of Riset Pembinaan, No. 178/SK/BPSDMI/ ATK/XII/2019.

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