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EFFICIENCY OF ELECTROCOAGULATION METHOD TO REDUCE COD, BOD AND TSS IN TANNERY INDUSTRY WASTEWATER: APPLICATION OF THE BOX–BEHNKEN DESIGN

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EFFICIENCY OF ELECTROCOAGULATION METHOD TO REDUCE COD, BOD AND TSS IN TANNERY INDUSTRY WASTEWATER: APPLICATION OF THE BOX–BEHNKEN DESIGN

ABSTRACT. This study intends to assess the removal efficiency of the chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS) from raw tannery wastewater using electrocoagulation by aluminum electrodes as well as to determine the effects of its main operating factors. Therefore, the response surface methodology was applied through an experimental Box–Behnken design by considering the current intensity (I), treatment time (T), and pH levels as the factors. In addition, the BOD, COD, and TSS removal percentages were considered to be the response variables. The results indicate that the treatment time, current intensity, and pH level were significant for COD and TSS, whereas only the treatment time was significant at a confidence level of p-value < 0.05 for BOD. For COD, the optimal operating conditions were I = 3 A, T = 24 min, and pH = 8.4; for BOD, the optimal operating conditions were I = 3 A, T = 24 min, and pH = 5.5; and for TSS, the optimal operating conditions were I = 2.7 A, T = 19 min, and pH = 7.4. Under these conditions, removal efficiencies of 56.8%, 69.2%, 99.9% were observed for COD, BOD, and TSS, respectively. The results suggest that electrocoagulation is an effective method for removing the parameters under study; therefore, it is a viable alternative for reducing the pollution issues caused by the tannery industry.
KEY WORDS: tannery, electrocoagulation, aluminum electrodes, Box–Behnken design

EFICIENȚA METODEI DE ELECTROCOAGULARE PENTRU REDUCEREA CCO, CBO ȘI TSS DIN APELE UZATE ALE INDUSTRIEI DE PIELĂRIE: APLICAREA EXPERIMENTULUI BOX-BEHNKEN

REZUMAT. Acest studiu are obiectivul de a evalua eficiența reducerii consumului chimic de oxigen (CCO), consumului biochimic de oxigen (CBO) și a totalului materiilor solide în suspensie (TSS) din apele reziduale ale tăbăcăriilor, folosind electrocoagularea cu electrozi de aluminiu, precum și de a determina efectele principalilor factori de operare ai acestei metode. Prin urmare, metodologia suprafeței de răspuns a fost aplicată printr-un design experimental Box-Behnken, luând în considerare factori precum intensitatea curentului (I), timpul de tratament (T) și nivelul pH-ului. În plus, procentele de eliminare a CBO, CCO și TSS au fost considerate variabile de răspuns. Rezultatele indică faptul că timpul de tratament, intensitatea curentului și nivelul pH-ului au fost semnificative pentru CCO și TSS; pe de altă parte, doar timpul de tratament a fost semnificativ la un nivel de încredere al valorii p <0,05 pentru CBO. Pentru CCO, condițiile optime de operare au fost I = 3 A, T = 24 min și pH = 8,4; pentru CBO, condițiile optime de funcționare au fost I = 3 A, T = 24 min și pH = 5,5; iar pentru TSS, condițiile optime de funcționare au fost I = 2,7 A, T = 19 min și pH = 7,4. În aceste condiții, s-au observat valori ale eficienței de reducere de 56,8%, 69,2%, 99,9% pentru CCO, CBO și, respectiv, TSS. Rezultatele sugerează că electrocoagularea este o metodă eficientă pentru reducerea parametrilor studiați; prin urmare, este o alternativă viabilă pentru reducerea problemelor de poluare cauzate de industria de pielărie.
CUVINTE CHEIE: tăbăcărie, electrocoagulare, electrozi din aluminiu, experiment Box-Behnken

EFFICACITÉ DE LA MÉTHODE D'ÉLECTROCOAGULATION POUR RÉDUIRE LA DCO, LA DBO ET LES TSS DANS LES EAUX USÉES DE L'INDUSTRIE DU CUIR : APPLICATION DE LA CONCEPTION BOX-BEHNKEN

RÉSUMÉ. Cette étude vise à évaluer l'efficacité d'élimination de la demande chimique en oxygène (DCO), de la demande biochimique en oxygène (DBO) et du total des matières solides en suspension (TSS) des eaux usées de la tannerie en utilisant l'électrocoagulation par des électrodes en aluminium ainsi qu'à déterminer les effets de ses principaux facteurs de fonctionnement. Par conséquent, la méthodologie de la surface de réponse a été appliquée par le plan expérimental de Box-Behnken en considérant l'intensité du courant (I), le temps de traitement (T) et les niveaux de pH comme facteurs. De plus, les pourcentages d'élimination de la DBO, de la DCO et du TSS étaient considérés comme les variables de réponse. Les résultats indiquent que le temps de traitement, l'intensité du courant et le niveau de pH étaient significatifs pour la DCO et le TSS, alors que seul le temps de traitement était significatif à un niveau de confiance de valeur p <0,05 pour la DBO. Pour la DCO, les conditions de fonctionnement optimales étaient I = 3 A, T = 24 min et pH = 8,4 ; pour la DBO, les conditions de fonctionnement optimales étaient I = 3 A, T = 24 min et pH = 5,5 ; et pour TSS, les conditions de fonctionnement optimales étaient I = 2,7 A, T = 19 min et pH = 7,4. Dans ces conditions, des rendements d'élimination de 56,8%, 69,2%, 99,9% ont été observés pour la DCO, la DBO et la TSS, respectivement. Les résultats suggèrent que l'électrocoagulation est une méthode efficace pour réduire les paramètres étudiés ; par conséquent, c'est une alternative viable pour réduire les problèmes de pollution causés par l'industrie du cuir.
MOTS-CLÉS : tannerie, électrocoagulation, électrodes en aluminium, conception Box-Behnken

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INTRODUCTION

The tannery industry is an important activity in the economic development of Peru and this is due to the diversity of articles that are generated from leather and the international demand of tanned skins until wet blue state (wet tanned skin). However, tanneries have been mainly characterized by the usage of low-technology and poor production practices that exacerbate the environmental problems associated with this industry by generating large volumes of highly polluted wastewater, mainly discharged in an untreated manner directly into rivers or sewage networks. According to the Peruvian national leather production data, between 45 and 50 m^3 of effluents were produced for each ton of tanned leather in 2017, indicating the generation of approximately 30,000 m^3 of effluents. The pollutant load of these effluents contains high amounts of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS), sulfides, ammonium, chlorides, and heavy metals such as chromium. When high COD and BOD contents are reported in organic matter, water bodies lose a considerable amount of dissolved oxygen. This is harmful to aquatic organisms because it results in anaerobic activity that may release harmful gases. Therefore, the adoption of clean production and effluent treatment alternatives is of paramount importance. Estimates from the Center for Technological Innovation in Leather, Footwear, and Related Industries (CITEccal Lima) identified approximately 100 different tanneries in Lima. However, most of these tanneries have not yet implemented an effluent treatment system, which can ensure their compliance with the current environmental regulations, thus putting not only the environmental health but also the very existence of the industry at constant risk. Further, a possible solution to this issue may be the usage of electrocoagulation for treating raw tannery wastewater. In 2009, Ayhan Sengil *et al*. [1] applied electrocoagulation through steel and aluminum electrodes, achieving COD removal rates of 68%. In another study, Varank *et al*. [2] reported COD and TSS removal efficiencies of 82.2% and 85.5% when using aluminum electrodes and 67.4% and 86.2% when using steel electrodes, respectively, in 2014. Deghlesa *et al*. [3] also reported an optimal COD removal efficiency of 64.4% using aluminum electrodes. In 2017, Ufuk Durmaz *et al*. [4] determined the optimum operating values for COD and TSS removal through aluminum electrodes to be 18.9 mA/cm^2, 20 min of electrolysis time, and a pH level of 6.

Our study focuses on assessing the efficiency of the electrocoagulation process for removing the pollutants generated by the tannery industry expressed as BOD, COD, and TSS and on optimizing the process through the Box–Behnken (BBD) response surface methodology. Electrocoagulation offers many advantages over conventional treatments. In this process it is not necessary to add chemicals to the water, its reactors are more compact and simpler, and it has a high efficiency in the removal of various contaminants [5, 6]. In addition, as with any technology, it has some disadvantages, such as the periodic replacement of electrodes, the presence of high concentrations of aluminum and iron in the sewage sludge, and a high cost in places where there is no access to electrical energy [7]. Electrocoagulation is an electrochemical process in which metal plates, known as electrodes, are arranged in pairs, with one of the electrodes acting as the anode and the other acting as the cathode. Further, the cathode is oxidized, and the anode is reduced, generating hydroxide complexes acting as coagulants that allow the agglomeration of pollutants. Most of these agglomerates rise to the surface because of the fact that the hydrogen microbubbles perform a flotation process, whereas the rest are deposited in the bottom part of the water body [8]. Therefore, several types of electrodes, such as aluminum, iron, stainless steel, and platinum, have been tested [9]. In this study, we used aluminum electrodes as both the anode and the cathode, where reactions 1, 2 and 3 are generated [10].

At the anode:

$$Al \rightarrow Al^{3+} + 3e \qquad (1)$$

At the cathode:

$$3H_2O + 3e \rightarrow \tfrac{3}{2}H_2(g) + 3OH^- \qquad (2)$$

In the solution:

$$Al^{3+}(aq)+3H_2O \rightarrow Al(OH)_3+3H^+(aq) \qquad (3)$$

EXPERIMENTAL

Materials and Methods

Tannery Wastewater

Water was collected from the pilot treatment plant at the Center for Technological Innovation in Leather, Footwear, and Related Industries (CITEccal), which generates industrial effluents from its tanning processes, to recreate the actual treatment conditions. This type of water contains high amounts of organic matter, pollutants and exhibits high conductivity because of the low-technological tanning processes used by the industry. Table 1 displays the values obtained from the initial effluent characterization.

Table 1: Physicochemical Effluent Analysis

Parameter	Value
COD (mg/L)	4162.3
BOD (mg/L)	1825
TSS (mg/L)	1600
Conductivity (μS/cm)	10560
pH	8.5
Turbidity (NTU)	1330
Chromium (mg/L)	114.56

Electrocoagulation Reactor

For these purposes, a Bacth type reactor with the following dimensions was used: length: 30 cm; width: 20 cm; and height: 25 cm. The total volume of the reactor was 15 liters, with the capacity to treat 12 liters of wastewater and a free volume of 3 liters for the accumulation of sludge. In total, we used 8 aluminum electrodes (4 as the anode and 4 as the cathode, each 10 cm wide and 10 cm long with a total area of 100 cm^2). In addition, we used a series configuration, and the plates were spaced at 2 cm to reduce the demand of electric current owing to high water conductivity. Figure 1 displays a diagram of the reactor.

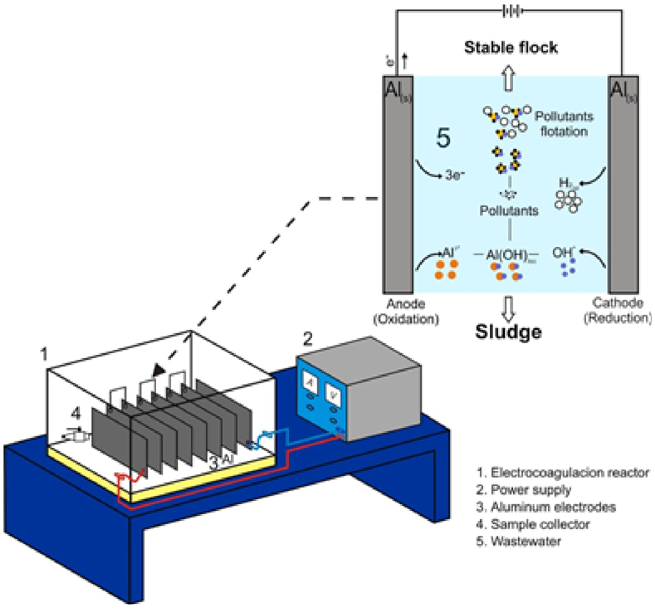

Figure 1. Electrocoagulation Reactor

Experimental Procedure

The experimental procedure proposes tests for three pH values of water (8.5, 7, and 5.5). In these three stages, different electric current intensities were applied (1, 3, and 5 A), and samples were obtained at different times (8, 16, and 24 min). To measure the pH and conductivity, an Oakcton CON450 field meter was used. In addition, COD (SMEWW-APHA-

AWWA-WEF Part 5220 D; 23rd), BOD (SMEWW-APHA-AWWA-WEF Part 5210 B; 23rd), and TSS (SMEWW-APHA-AWWA-WEF Part 2540-D; 23rd) were used to quantify the response variable. Finally, we used Equation 4 to determine the COD, BOD, and TSS removal percentages.

$$Y = \%R = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \qquad (4)$$

Here,

Y : Removal percentage of COD,BOD,and TSS
C_i: Concentration of COD,BOD,and initial TSS
C_f: Concentration COD,BOD,and final TSS

Box–Behnken Experimental Design

For this study, the response surface methodology with a Box–Behnken experimental design was used using three factors, each factor with three levels, and 13 experiments by considering two experiments to denote the central values. The factors considered in the design were the electric current intensity (x_1), treatment time (x_2), and pH level (x_3) (see Table 2). To develop a response surface regression model, a complete quadratic model was applied (see Equation 5), where the experimental observations of the response variable were the COD , BOD, and TSS removal percentages. For the statistical analysis, the Statgraphics Centurión XVI software was used, which reported an analysis of variance (ANOVA) at a 95% confidence level. The polynomial model was evaluated by the value of the correlation coefficient R^2 and R^2 adj.

$$y_i = b_0 + \sum_{i=1}^{n} b_i\, x_i + \sum_{i=1}^{n} b_{ii}\, x_i{}^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij}\, x_i x_j \qquad (5)$$

Table 2: Experimental Design Factors and Levels

Factors	Levels		
x_1 : Current Intensity (A)	1	2	3
x_2 : Time (min)	8	16	24
x_3: pH Level	5.5	7	8.5

RESULTS AND DISCUSSION

Effect of Current Intensity

Current intensity is one of the most critical parameters, which can significantly impact the effectiveness of the electrocoagulation process [8-11, 12]. As has been previously reported, as the intensity increases, the amount of anodic aluminum dissolution also increases, which leads to improved coagulation and pollutant removal [7]. For this study, we applied current intensities of 1, 2, and 3 A in a serial circuit to reduce energy consumption due to the high conductivity values presented by this type of wastewater. As the current intensity increases in Figures 2a, b; 4a, b; and 6a, b, it can be seen that the rate of removal of COD, BOD and TSS increases significantly. This is caused when a high current intensity is supplied to the reactor, generating a large number of monomeric and polymeric species according to Faraday's law, which reduces the amount of wastewater pollutants [8]. In Table 3 it can be seen that the highest removal values were obtained at 2 and 3 amps. With these current intensities a removal of COD, BOD and TSS of 54%, 66% and 97%, respectively, was achieved. These results are not consistent with the results reported by Feng Jing-Wei *et al*. [13] in 2007, which indicate COD removal rates of more than 68% when using Al electrodes under current intensities of 0 to 1 A. The BOD removal results from our study also deviated from the results reported by Kongjao *et al*. [14], and Benhadji *et al*. [15], who reported efficiency values of 96% and 90%, respectively. However, these differences may be attributed to the different characteristics of the tested effluents. In 2014, Thirugnanasambandham *et al*. [8] reported values similar to the values reported herein, where an efficiency of 56.98% was achieved when applying a current density of 20 mA cm^{-2} for 20 min. In addition, Espinoza *et al*. [16] obtained efficiencies of 50% and 65% for COD and TSS, respectively, when using a current density of 68 mA cm^{-2}. However, Ufuk Durmaz *et al*. [4] reported maximum removal efficiencies of 49% for COD and 42% for TSS when applying a current density of 22.7 mA/cm^{-2}, a pH level of 6, and a treatment time of 60 min. Tables 5 and 6 show the regression or slope coefficients of the model used. In the model for TSS, the regression coefficient of the current intensity is positive, which indicates that the percentage of TSS removal (response variable) increases by an average of approximately 29,1667. In contrast, for BOD and COD the percentage of removal increases by approximately 19.3333 and 2.91667, respectively.

Effect of pH

The metal hydroxide precipitations are controlled by pH variations, which remove the pollutants while acting as coagulants [8]. To assess their impact on the treatment efficacy, the pH was changed from 5.5 to 8.5. The results from these variations are presented in Table 3 and Figures 2, 4, and 6. These results are very similar to the results obtained by Espinoza *et al*. [16], where optimal COD and TSS removal rates were reported for pH values of 6.5–8.0 and 6.5–8.5, respectively. Based on these results, a reduction of the pH to 5.5 improves the removal of organic matter (COD and BOD), whereas this does not result in a noticeable removal of TSS. In 2015, Deghlesa *et al*. [3] reported optimal COD removal values at a pH of 7. By considering that pH only had a minimal impact on the efficiencies, the modification of this parameter is not justified in practical applications, generating reagent consumption expenditure savings. In addition, Ufuk Durmaz *et al*. [4] reported optimal efficiencies at a pH of 6 with a treatment time of 60 min.

Effect of Treatment Time

As known, the removal efficiency of pollutants increases as the electrolysis time increases due to the generation of metal ions and flocs [17-19]. The results for this parameter are shown in Table 3 and Figure 2, 4 and 6 which offer proof that the COD, BOD, and TSS removal rates increase as the treatment time progresses. These results are very similar to the ones reported by Tak *et al*. [20], which indicate an increase in efficiency after 10 to 20 min of treatment. In addition, Thirugnanasambandham *et al*. [8] reports that efficiencies may reach up to 72% after a treatment time of 20 to 60 min. Thus, determining the optimum treatment times becomes critical, especially when considering that very long treatment times generate high energy consumption and electrode wear [21], which would increase the treatment costs.

Results of the Box–Behnken Design

Table 3 presents the results obtained from the Box–Behnken factorial design for all 13 experiments with 2 central experiments using the pH, current intensity, and treatment time as independent variables.

Table 3: Box–Behnken Design for COD, BOD, and TSS removal

	Factors			Removal		
Exp. No	Current (A) x_1	Treatment Time (min) x_2	pH x_3	COD (%) y_1	BOD (%) y_2	TSS (%) y_3
1	1	16	5.5	36	57	74
2	2	8	5.5	43	60	79
3	2	24	5.5	54	66	85
4	3	16	5.5	51	63	89
5	1	8	7	24	43	76
6	1	24	7	30	45	89
7	3	8	7	36	48	94
8	3	24	7	46	54	97
9	1	16	8.5	22	57	81
10	2	8	8.5	23	59	86
11	2	24	8.5	36	63	95
12	3	16	8.5	35	63	96
13	2	16	7	37	46	96
14	2	16	7	38	47	97
15	2	16	7	36	46	96

An empirical relation was observed between the COD, BOD, and TSS removal efficiency percentages, and the influence of the variables on the process can be obtained by correlating the experimental results with the response functions using the Statgraphics Centurion XVI software program.

In addition, ANOVA yielded a 95% confidence level (see Table 4) by comparing the variation sources against the Fisher's distribution (F-test) to validate the viability of the regression model. Table 5 shows the regression coefficients for the second order response model. The response surface models are shown in Table 6. The coefficients of determination R^2 for COD (y_1), BOD (y_2), and TSS (y_3) are 98.5551%, 99.5823%, and 99.573%, respectively, which indicate a good model fit. Further, the results suggest that the treatment time, current intensity, and pH are significant for both COD and TSS, whereas only the treatment time was significant at a confidence level of p-value < 0.05 for BOD.

Table 4: ANOVA Table

	Variation Source	Sum of Squares	DF	MS	F-Test	P-Value
COD	x_1 : Current Intensity (A)	392.0	1	392.0	108.9	0.0001
	x_2 : Time (min)	200.0	1	200.0	55.56	0.0007
	x_3: pH Level	578.0	1	578.0	160.56	0.0001
	x_1^2	33.2308	1	33.2308	9.23	0.0288
	x_1x_2	4.0	1	4.0	1.11	0.3401
	x_1x_3	1.0	1	1.0	0.28	0.6207
	x_2^2	0.0	1	0.0	0.00	1.0000
	x_2x_3	1.0	1	1.0	0.28	0.6207
	x_3^2	14.7692	1	14.7692	4.10	0.0987
	Total error	18.0	5	3.6		
	Total (corr.)	1245.73	14			
	$R^2 = 98.5551\%$, Adj $R^2 = 95.9542\%$					
BOD	x_1 : Current Intensity (A)	84.5	1	84.5	115.23	0.0001
	x_2 : Time (min)	40.5	1	40.5	55.23	0.0007
	x_3 : pH Level	2.0	1	2.0	2.73	0.1296
	x_1^2	0.641026	1	0.641026	0.87	0.3927
	x_1x_2	4.0	1	4.0	5.45	0.0668
	x_1x_3	0.0	1	0.0	0.00	1.0000
	x_2^2	9.25641	1	9.25641	12.62	0.0163
	x_2x_3	1.0	1	1.0	1.36	0.2956
	x_3^2	732.333	1	732.333	998.64	0.0000
	Total error	3.66667	5	0.733333		
	Total (corr.)	877.733	14			
	$R^2 = 99.5823\%$, Adj $= 98.8303\%$					

TSS	x_1 : Current Intensity (A)	392.0	1	392.0	500.43	0.0000
	x_2: Time (min)	120,125	1	120,125	153.35	0.0001
	x_3: pH Level	120,125	1	120,125	153.35	0.0001
	x_1^2	68.0064	1	68.0064	86.82	0.0002
	x_1x_2	25.0	1	25.0	31.91	0.0004
	x_1x_3	0.0	1	0.0	0.00	1.0000
	x_2^2	34.1603	1	34.1603	43.61	0.0012
	x_2x_3	2.25	1	2.25	2.87	0.1509
	x_3^2	183.083	1	183.083	233.72	0.0000
	Total error	3.91667	5	0.783333		
	Total (corr.)	917.333	14			

R^2= 99.573%, Adj = 98.8045%

Table 5: Regression coefficients for the 2nd order response surface models

Term	COD removal (%)		BOD removal (%)		SST removal (%)		Confidence intervals - 95.0 %		
	Coefficient	P-value	Coefficient	P-value	Coefficient	P-value	Mean	Lower limit	Upper limit
Constant	88.2222	0.0192	348.37	0.0000	-129.185	0.0001	88.66	84.1559	93.0441
x_1	19.3333	0.0273	2.91667	0.4193	29.1667	0.0001	2.0	1.58138	2.41862
x_2	0.0833333	0.9194	-0.46575	0.1448	2.19271	0.0014	16.0	12.651	19.349
x_3	-18.1111	0.0370	-87.2963	0.0000	45.3981	0.0000	7.0	6.37207	7.62793
x_1^2	-3.0	0.0288	-0.416667	0.5623	-4.29167	0.0002	4.533	2.83461	6.23206
x_1x_2	0.125	0.3401	0.125	0.0493	-0.3125	0.0016	32.0	22.2362	41.7638
x_1x_3	-0.333333	0.6207	0	1.0000	0	1.0000	14.0	10.7811	17.2189
x_2^2	0	1.0000	0.0247396	0.0074	-0.047526	0.0010	290.113	181.415	398.852
x_2x_3	0.0416667	0.6207	-0.0416667	0.2532	0.0625	0.1219	112.0	86.2489	137.751
x_3^2	0.888889	0.0987	6.2596	0.0000	-3.12963	0.0000	50.2	41.3855	59.0145

x_1 (current intensity, A), x_2 (time, min), x_3 (pH).

Table 6: Response surface model for COD, BOD and TSS removal (%)

Response	Quadratic polynomial model		P-value
COD removal (%)	$y_1 = 88.2222 + 19.3333x_1 + 0.0833333x_2 - 18.1111x_3 - 3.0x_1^2 + 0.125x_1x_2 - 0.33333x_1x_3 + 0.0416667x_2x_3 + 0.888889x_3^2$	98.5551	0.0005
BOD removal (%)	$y_2 = 348.37 + 2.91667x_1 - 0.46575x_2 - 87.2963x^3 - 0.416667x_1^2 + 0.125x_1x_2 + 0.0247396x_2^2 - 0.0416667x_2x_3 + 6.25926x_3^2$	99.5823	0.0000
TSS removal (%)	$y_3 = -129.185 + 29.1667x_1 + 2.19271x_2 + 45.3981x_3 - 4.29167x_1^2 - 0.3125x_1x_2 - 0.047526x_2^2 + 0.0625x_2x_3 - 3.12963x_3^2$	99.573	0.0000

The effects of the process variables are presented in Figures 2, 3, 4, 5, 6 and 7, which represent the three-dimensional (3D) and contour (2D) response surface plots. These plots use the mathematical models developed in Equations 6, 7, and 8, where the COD, BOD, and TSS removal percentage variations may be observed according to the variation of their current intensity (x_1), treatment time (x_2), and pH (x_3). In addition, this allowed us to determine the optimum condition for each factor to maximize the COD, BOD, and TSS removal.

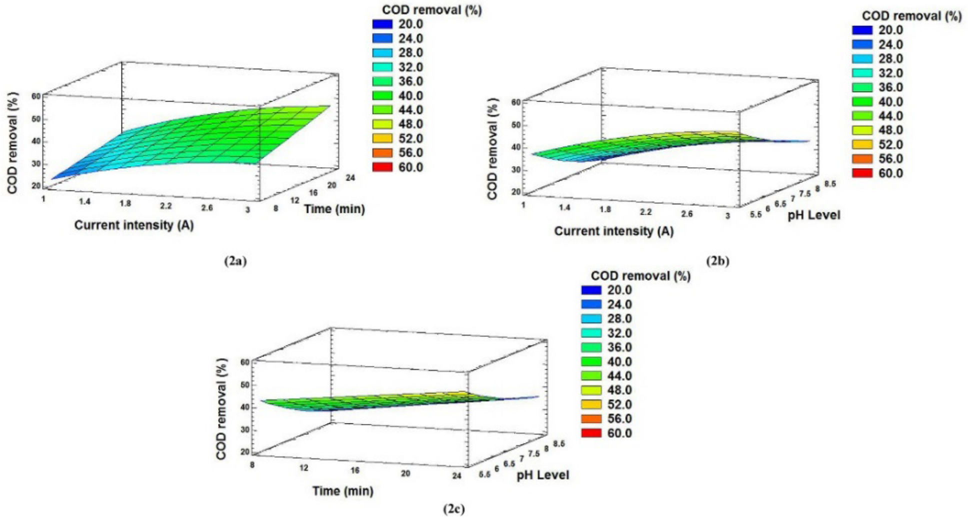

Figure 2. Three-dimensional (3D) response surface charts for COD removal percentages: 2a) current intensity and treatment time; 2b) current intensity and pH; and 2c) treatment time and pH

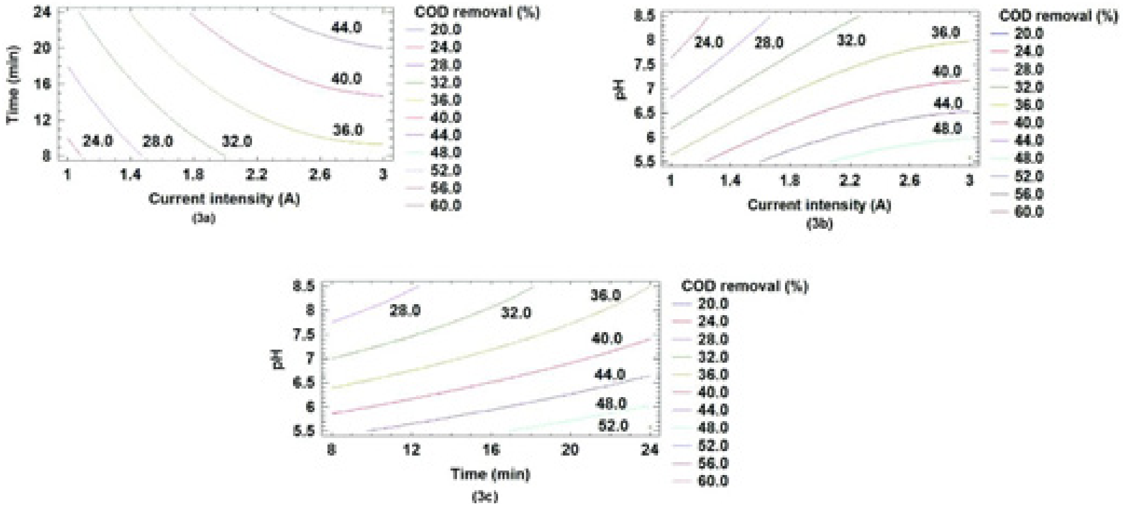

Figure 3. Two-dimensional (2D) response surface charts for COD removal percentages: 3a) current intensity and treatment time; 3b) current intensity and pH; and 3c) treatment time and pH

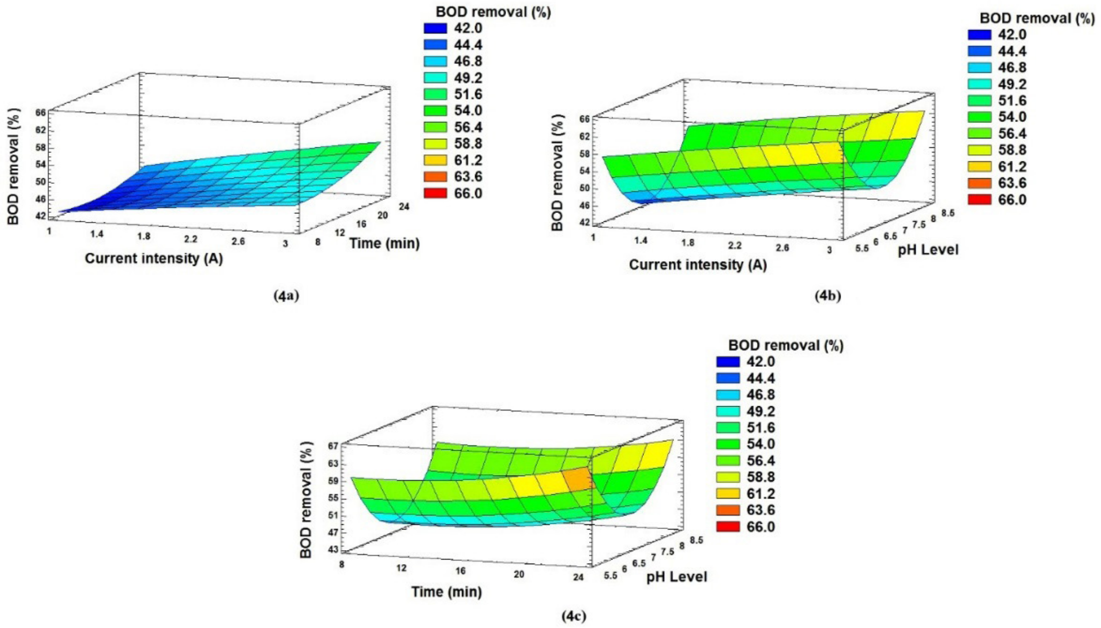

Figure 4. Three-dimensional (3D) response surface charts for BOD removal percentages: 4a) current intensity and treatment time; 4b) current intensity and pH; and 4c) treatment time and pH

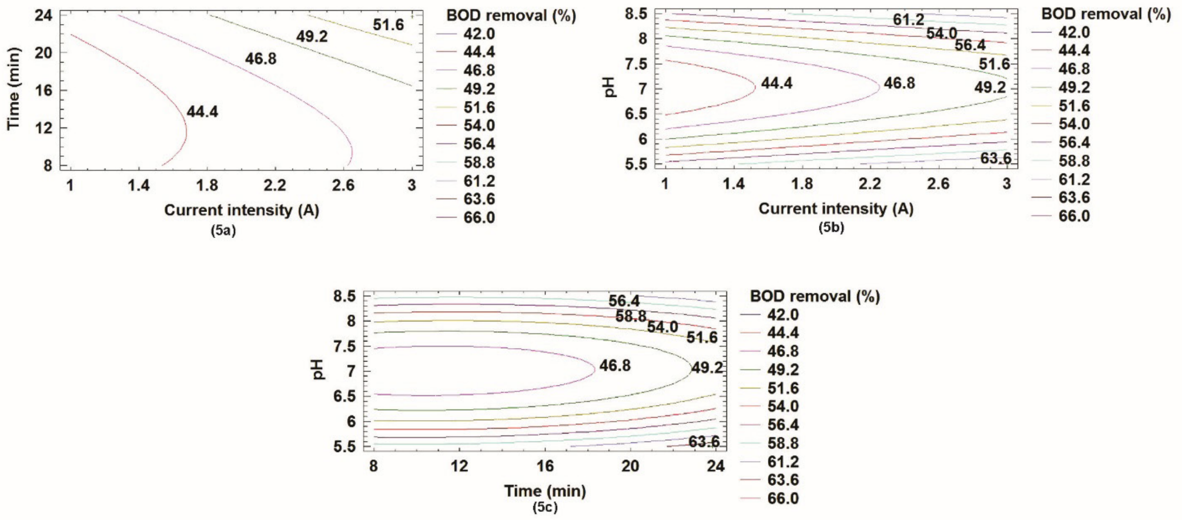

Figure 5. Two-dimensional (2D) response surface charts for BOD removal percentages: 5a) current intensity and treatment time; 5b) current intensity and pH; and 5c) treatment time and pH

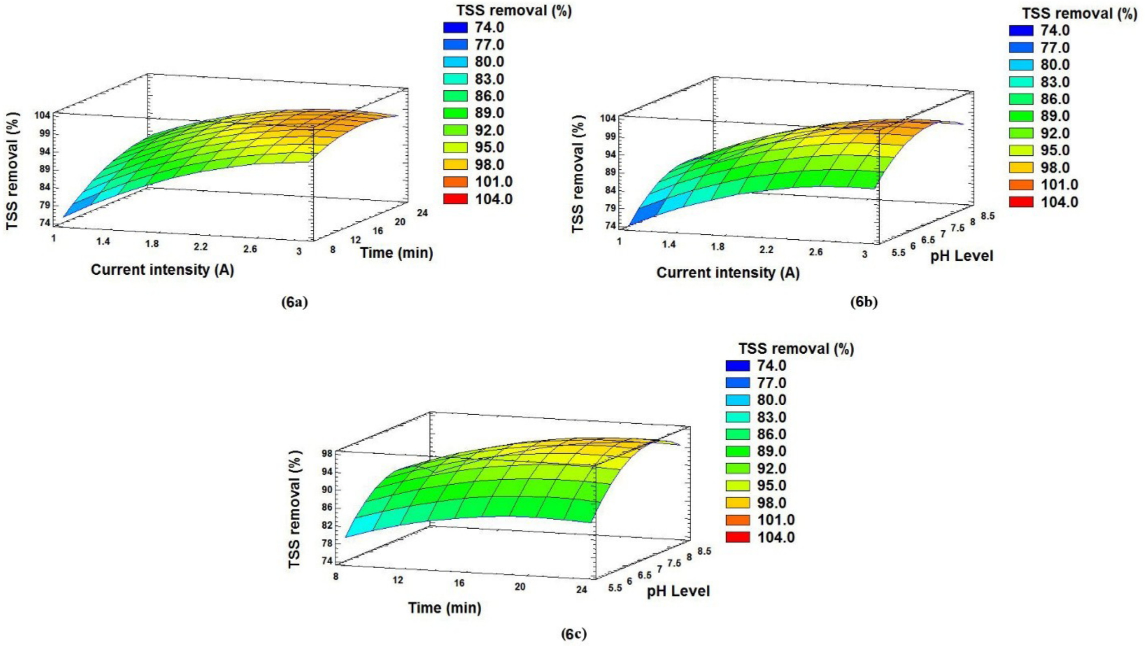

Figure 6. Three-dimensional (3D) response surface charts for TSS removal percentages: 6a) current intensity and treatment time; 6b) current intensity and pH; and 6c) treatment time and pH

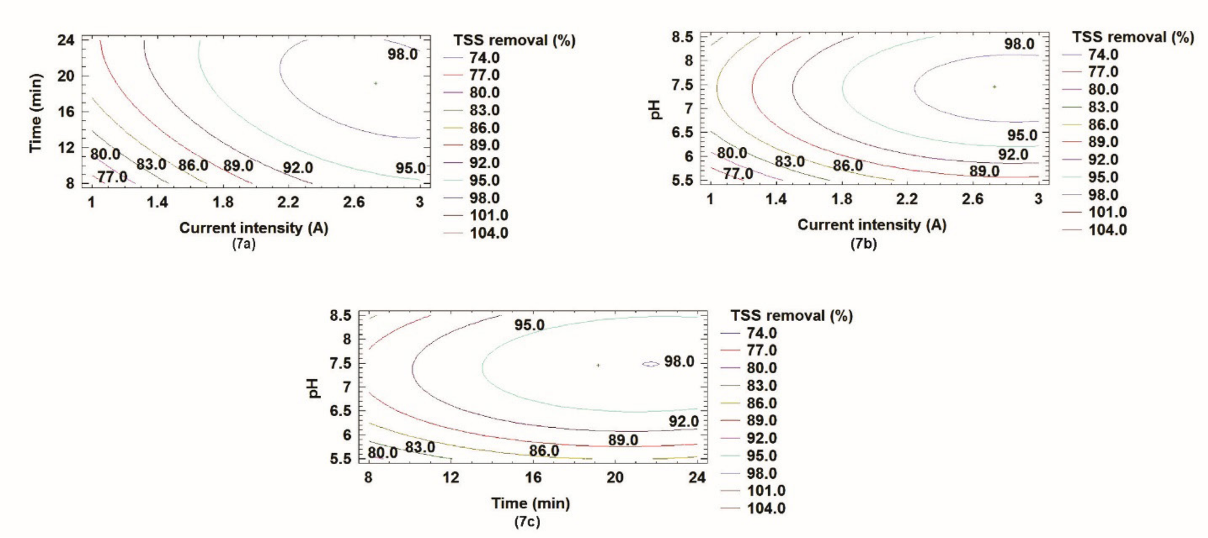

Figure 7. Two-dimensional (2D) response surface charts for TSS removal percentages: 7a) current intensity and treatment time; 7b) current intensity and pH; and 7c) treatment time and pH

CONCLUSIONS

This study proves that electrocoagulation by aluminum electrodes is effective for reducing COD, BOD, and TSS from tannery wastewater. As per the experimental design, all the factors (current intensity, treatment time, and pH) significantly affected COD and TSS, whereas only the treatment time significantly affected BOD. The correlation coefficient R^2 for COD, BOD, and TSS was 98.5551%, 99.5823%, and 99.573%, respectively, indicating a good model fit. For COD, the optimal operating conditions were established as I = 3A, T = 24 min, and pH = 8.4; for BOD, the optimal operating conditions were I = 3A, T = 24 min, and pH = 5.5; and for TSS, the optimal operating conditions were I = 2.7A, T = 19 min and pH = 7.4. Thus, optimum removal efficiencies of 56.8%, 69.2%, and 99.9% were achieved for COD, BOD, and TSS, respectively. Finally, it must also be emphasized that under actual treatment conditions, using reagents for changing pH would not be justified because the obtained efficiencies are very similar.

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AN IMPROVED HALO METHOD FOR EVALUATING THE ANTIBACTERIAL ACTIVITY OF LEATHER

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AN IMPROVED HALO METHOD FOR EVALUATING THE ANTIBACTERIAL ACTIVITY OF LEATHER

ABSTRACT. In order to evaluate leather antibacterial activity rapidly and accurately, an improved halo method was developed based on conventional halo method and the agar diffusion plate method. During the new method, there were two layers of medium, the bottom was sterile medium and the top was medium containing microbes; more than one leather sample could be tested in a culture dish. The antibacterial activities of leather treated by nano-silver, nano-ZnO and butyl paraben against *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* and *Rhodotorula mucilaginosa* were tested by the new method. The results indicated intraclass correlation coefficient values were greater than 0.7 but the P values were less than 0.05 during improved halo method testing, thus, the repeatability and reliability was comparable or even better than conventional method. Nano-silver showed excellent and broad antibacterial activity and the difference between each antibacterial agent could be observed clearly and intuitively during improved halo method testing. In sum, improved halo method was a fast, accurate, qualitative and quantitative testing method and would be a new choice for evaluating leather antibacterial activity.

KEY WORDS: leather, antibacterial activity, evaluation method, improved halo method

O METODĂ ÎMBUNĂTĂȚITĂ DE DETERMINARE A ZONEI DE INHIBARE PENTRU EVALUAREA ACTIVITĂȚII ANTIBACTERIENE A PIELII

REZUMAT. Pentru a evalua rapid și precis activitatea antibacteriană a pielii, a fost dezvoltată o metodă îmbunătățită pe baza metodei de determinare a zonei de inhibare convențională și metodei plăcilor de difuzie de agar. În cadrul noii metode, au existat două straturi de mediu, partea inferioară a reprezentat mediu steril și partea superioară un mediu conținând microbi; mai multe probe de piele pot fi testate într-un vas de cultură. S-a testat activitatea antibacteriană a pielii tratate cu nano-argint, nano-ZnO și butil paraben împotriva *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* și *Rhodotorula mucilaginosa* prin noua metodă. Rezultatele au indicat valori ale coeficientului de corelație intraclasă mai mari decât 0,7, dar valorile P au fost mai mici de 0,05 în cazul testării prin metoda îmbunătățită, astfel, repetabilitatea și fiabilitatea au fost comparabile sau chiar mai bune comparativ cu metoda convențională. Nano-argintul a demonstrat o activitate antibacteriană excelentă și pe scară largă, iar diferența dintre agenții antibacterieni a putut fi observată clar și intuitiv în timpul testării prin metoda îmbunătățită. În concluzie, metoda îmbunătățită de determinare a zonei de inhibare este o metodă de testare rapidă, precisă, calitativă și cantitativă și poate fi o alternativă pentru evaluarea activității antibacteriene a pielii.

CUVINTE CHEIE: piele, activitate antibacteriană, metodă de evaluare, metodă îmbunătățită de determinare a zonei de inhibare

UNE MÉTHODE AMÉLIORÉE DE DÉTERMINATION DE LA ZONE D'INHIBITION POUR L'ÉVALUATION DE L'ACTIVITÉ ANTIBACTÉRIENNE DU CUIR

RÉSUMÉ. Afin d'évaluer l'activité antibactérienne du cuir rapidement et avec précision, une méthode améliorée a été développée basée sur la méthode conventionnelle de détermination de la zone d'inhibition et la méthode de diffusion d'agar. Au cours de la nouvelle méthode, il y avait deux couches de milieu, la partie inférieure était un milieu stérile et la partie supérieure un milieu contenant des microbes ; plus d'un échantillon de cuir pourrait être testé dans une boîte de culture. Les activités antibactériennes du cuir traité par le nano-argent, le nano-ZnO et le butyl paraben contre *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger* et *Rhodotorula mucilaginosa* ont été testées par la nouvelle méthode. Les résultats ont indiqué que les valeurs des coefficients de corrélation intraclasse étaient supérieures à 0,7 mais les valeurs P étaient inférieures à 0,05 lors des tests de la méthode améliorée, ainsi, la répétabilité et la fiabilité étaient comparables ou même meilleures que la méthode conventionnelle. Le nano-argent a montré une excellente et large activité antibactérienne et la différence entre chaque agent antibactérien a pu être observée clairement et intuitivement lors de la méthode améliorée. En résumé, la méthode améliorée de détermination de la zone d'inhibition était une méthode d›essai rapide, précise, qualitative et quantitative et constituerait un nouveau choix pour évaluer l›activité antibactérienne du cuir.

MOTS CLÉS : cuir, activité antibactérienne, méthode d'évaluation, méthode améliorée de détermination de la zone d'inhibition

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INTRODUCTION

Leather mainly consists of cross-linked collagen after being processed by a huge amount of chemical and mechanical procedures. As there are abundant nutriments in leather, such as protein, carbohydrate, fat, leather is an ideal harbor for bacteria and fungi reproduction. Microbe growth leads to unpleasant odor, skin infection, low product quality and other related issues, therefore, there is necessary to develop leather with excellent antibacterial properties [1, 2].

In leather industry, there are many research studies on antibacterial agents and antibacterial leather, in which nano-silver is widely used [3]. A kind of nano-silver was prepared by using sodium borohydride as reductant and benzalkonium bromide as protective agent [4], and it had been used for producing antibacterial leather and fur [5-8]. Evaluation of the antibacterial activity of leather is one of the most important work and basis for applying and spread antibacterial leather, but the standard method for the tests is rare and method is a little bit complicated and time-consuming [9]. The most widely used methods for evaluation of antibacterial activity are minimum inhibitory concentration and halo method [10, 11]. Halo method can be used to evaluate leather antibacterial activity qualitatively, but only one sample is available per time. Microorganism inhibiting ring test could measure several samples during one experiment. The combination of halo method and microorganism inhibiting ring test would accelerate antibacterial activity evaluation efficiency.

In the study, a new method for evaluation of antibacterial activity of leather was proposed based on inhibition zone method and agar diffusion plate method with some modifications and improvements, named improved halo method, and the effect, accuracy, reliability and repeatability of improved halo method were compared with traditional halo method and agar diffusion plate method. The new method would be applied practically for measuring antibacterial activity of leather produced by nano-silver, nano-ZnO and butyl paraben. The new improved halo method would be new choice for evaluating leather antibacterial activity rapidly and precisely.

EXPERIMENTAL

Materials

The strains of bacteria and fungi used in this study were *Staphylococcus aureus*, *Escherichia coli*, *Rhodotorula mucilaginosa* and *Aspergillus niger*, which were all isolated from the shoes worn by children [12, 13]. *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus niger* and *Rhodotorula mucilaginosa* represented the gram-positive bacteria, gram-negative bacteria, mould and yeast, respectively. The beef extract peptone medium was used to culture the bacteria and the rose-bengal medium was used to culture the yeast and mould.

Nano-silver antibacterial agent with average particle size 26 nm and silver concentration 0.024 g/L [4], 0.1% w/w nano-ZnO antibacterial agent with average particle size 51.8 nm [14] and 60 g/L butyl paraben antibacterial agent [15] were prepared in laboratory. The chrome tanned pig shoe-lining leathers used in these tests were from a local tannery. Other reagents were research grade.

Sample Preparation

Preparation of Microbe Suspensions

5×10^5-5×10^6 cfu/mL bacterial suspensions: a 4 mm inoculating loop was used to scrape one loop of pure bacteria off the medium, and the bacteria were cultured in 100 mL fluid medium for 24 h, then 1 mL bacterial suspensions into 100 mL physiological saline solution (0.85%, w/w); finally, the bacteria solution with some glass balls were shaken in a vibrator at 37°C for 2 h until well dispersing.

5×10^5-5×10^6 cfu/mL fungi spores or yeast suspensions: a 4 mm inoculating loop was used to scrape five loops of pure spores off the medium, and the spores were shaken in a vibrator at 28°C for 2 h until well dispersing.

Preparation of Antibacterial Leather Samples

Antibacterial leather treated with nano-silver: Leather samples were completely soaked in nano-silver antibacterial agent solution at 25°C for 1.5 h, and then the samples were taken out by sterile and dried in the air.

Antibacterial leather treated with nano-ZnO: Leather samples were completely soaked in nano-ZnO antibacterial agent solution at 25°C for 18 h, and then the samples were taken out by sterile and dried in the air.

Antibacterial leather treated with butyl paraben: Leather samples were completely soaked in butyl paraben antibacterial agent at 25°C for 3 h, and then the samples were taken out by sterile and dried in the air.

Antibacterial Activity Evaluation Method

Halo Method

18 mL sterile medium was poured into 120 mm sterile culture dish until become solid, and then 0.2 mL different microbe suspensions was put onto the medium surface and dispersed by sterile glass rods. Leathers were cut into circular samples with a diameter of 18 mm and the samples were placed on center of the dish. The dish inoculated bacteria were cultured at 37°C for 24 h and the dish inoculated fungi and yeast was cultured at 28°C for 48 h, and then diameter of inhibition zone was measured.

Agar Diffusion Plate Method

The different kinds of microbe containing medium were prepared by blending 10mL different microbe suspensions with 150 mL corresponding media after being sterilized and cooled down to 45°C. 12mL sterile medium was added into a 120 mm sterile culture dish to form the bottom medium when it was solidified; then, 6 mL microbe containing medium was poured upon the surface of the bottom medium and shaken until dispersing uniformly to form the top medium. Leathers were cut into circular samples with a diameter of 18 mm and the samples were placed on center of the dish. The dish inoculated bacteria were cultured at 37°C for 24 h and the dish inoculated fungi and yeast was cultured at 28°C for 48 h, and then diameter of inhibition zone was measured.

Improved Halo Method

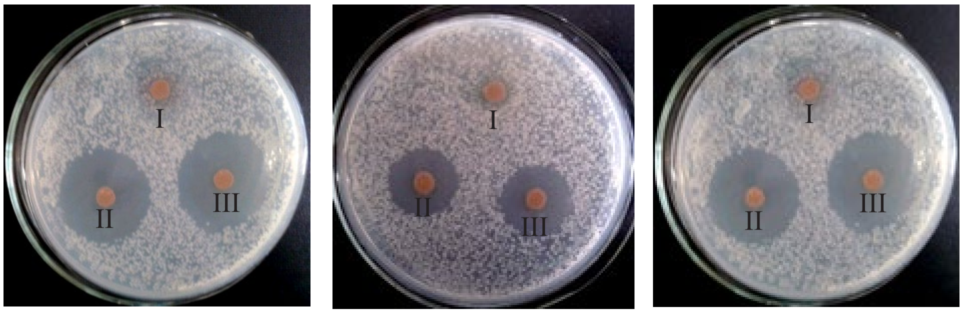
The different kinds of microbe containing medium were prepared by blending 10mL different microbe suspensions with 150 mL corresponding media after being sterilized and cooled down to 45°C. 12mL sterile medium was added into a 120 mm sterile culture dish to form the bottom medium when it was solidified; then, 6 mL microbe containing medium was poured upon the surface of the bottom medium and shaken until dispersing uniformly to form the top medium. Some marks were signed on the back of the plate; the spacing between each mark was larger than 25 mm and the distance from every mark to edge of the plate was greater than 15 mm. Leather were cut into circular samples with a diameter of 5 mm and the samples were placed on surface of the top medium, in addition, the center of each sample should coincide with the mark. The dish inoculated bacteria were cultured at 37°C for 24 h and the dish inoculated fungi and yeast was cultured at 28°C for 48 h, and then diameter of inhibition zone was measured.

Repeatability Analysis

Every experiment was repeated 6 times, and the data was analyzed by the statistical software of SPSS 17.0. The repeatability and the reliability were analyzed by the consistency and the intraclass correlation coefficient (ICC) value.

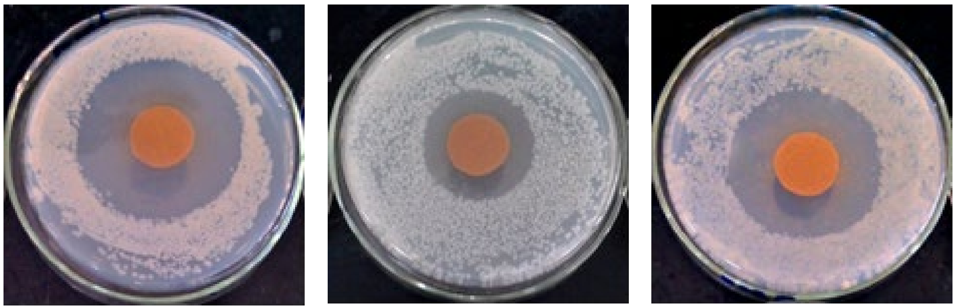
RESULTS AND DISCUSSION

Evaluation of Antibacterial Activity by Different Methods



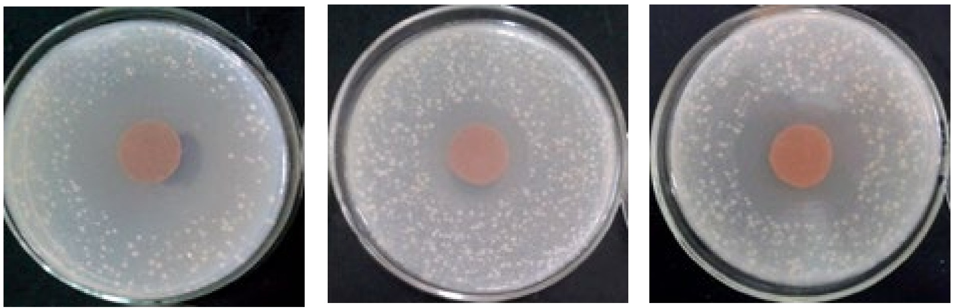
nano-silver butyl paraben nano-ZnO

Figure 1. Antibacterial activity against *Escherichia coli* evaluated by improved halo method (I: blank sample, II and III: antibacterial samples)



nano- butyl paraben nano-ZnO

Figure 2. Antibacterial activity against *Escherichia coli* evaluated by halo method



nano-silver butyl paraben nano-ZnO

Figure 3. Antibacterial activity against *Escherichia coli* evaluated by agar diffusion plate method

The antibacterial activity of different leathers treated by three kinds of antibacterial agent was evaluated by improved halo method, halo method and agar diffusion plate method, and the results are shown from Figure 1 to Figure 3. It is clear that there are obvious inhibition zones around leather samples treated by antibacterial agents with improved halo method but no inhibition zone around blank sample; therefore, the new method is valid. The improved halo method is upgraded based on halo method and agar diffusion plate method. In traditional halo method, bacteria or fungi are coated onto the surface of medium by hand; consequently, the distribution of microbes is not uniform during reproduction (Figure 2). In traditional agar diffusion plate method, microbes are mixed with media under shaking, but only one sample could be tested in one culture dish (Figure 3). It is not suitable for plenty of experiments. In improved halo method, microbes are distributed evenly onto medium and more than one leather sample could be evaluated in one dish simultaneously, both efficiency and accuracy would be improved.

Repeatability and the Reliability of Different Methods

Table 1: Repeatability and reliability analysis of improved halo method

Microbe	Antibacterial agent	Average (mm)	RSD (mm)	ICC	P
Escherichia coli	nano-Ag	32.55	0.98	0.884	0.001
	butyl paraben	19.62	0.71	0.733	0.019
	nano-ZnO	25.38	0.92	0.883	0.001
Staphylococcus aureus	nano-Ag	37.65	0.96	0.995	0.000
	butyl paraben	31.59	0.92	0.825	0.004
	nano-ZnO	42.79	0.90	0.723	0.022
Aspergillus niger	nano-Ag	35.52	0.84	0.976	0.000
	butyl paraben	10.66	0.79	0.927	0.000
	nano-ZnO	31.23	0.96	0.873	0.001
Rhodotorula mucilaginosa	nano-Ag	35.70	0.99	0.875	0.001
	butyl paraben	17.27	1.06	0.757	0.014
	nano-ZnO	39.24	0.87	0.988	0.000

Table 2: Repeatability and reliability analysis of halo method

Microbe	Antibacterial agent	average (mm)	RSD (mm)	ICC	P
Escherichia coli	nano-Ag	48.44	0.71	0.875	0.020
	butyl paraben	31.60	1.73	0.980	0.000
	nano-ZnO	45.60	0.94	0.853	0.028
Staphylococcus aureus	nano-Ag	56.63	1.09	0.901	0.012
	butyl paraben	36.69	0.80	0.814	0.044
	nano-ZnO	49.46	0.90	0.923	0.007
Aspergillus niger	nano-Ag	60.80	1.20	0.931	0.005
	butyl paraben	33.75	1.29	0.789	0.056
	nano-ZnO	63.22	1.06	0.808	0.047
Rhodotorula mucilaginosa	nano-Ag	52.74	0.50	0.555	0.198
	butyl paraben	39.08	1.30	0.841	0.032
	nano-ZnO	55.45	1.28	0.933	0.011

Table 3: Repeatability and reliability analysis of agar diffusion plate method

Microbe	Antibacterial agent	mean（mm）	RSD（mm）	ICC	P
Escherichia coli	nano-Ag	42.89	1.64	0.979	0.001
	butyl paraben	31.01	1.45	0.927	0.013
	nano-ZnO	41.08	1.57	0.977	0.002
Staphylococcus aureus	nano-Ag	46.09	1.31	0.888	0.028
	butyl paraben	34.27	1.84	0.988	0.000
	nano-ZnO	46.49	0.59	0.848	0.048
Aspergillus niger	nano-Ag	49.27	1.07	0.756	0.100
	butyl paraben	29.05	1.18	0.860	0.042
	nano-ZnO	54.16	1.63	0.971	0.002
Rhodotorula mucilaginosa	nano-Ag	52.09	1.93	0.951	0.006
	butyl paraben	35.93	1.64	0.847	0.048
	nano-ZnO	52.25	1.92	0.977	0.002

Antibacterial activities of leathers treated with three kinds of antibacterial agents were evaluated by improved halo method, halo method and agar diffusion plate method, and the results are listed from Table 1 to Table 3, in which average is inhibition zone diameter in different tests; RSD is relative standard deviation of test results; ICC is intraclass correlation coefficient; P smaller than 0.05 means results are statistically significant. The range of ICC is from 0 to 1, and higher value means better reliability. ICC lower than 0.25 means poor consistency; ICC from 0.25 to 0.49 means low consistency; ICC from 0.50 to 0.69 means poor medium consistency; ICC from 0.70 to 0.89 means good consistency; ICC from 0.90 to 1.00 means excellent consistency.

As is shown in Table 1, all ICC values are greater than 0.70 but all P values are less than 0.05, indicating the antibacterial activities results from improved halo method are reliable and repeatable. Compared with halo method (Table 2), the new method brings about higher ICC value but lower P value as the microbes are distributed evenly onto medium surface. The ICC value and P value in the new method is comparable with agar diffusion plate method (Table 3), so it could conclude that more than one samples tested in one culture dish would not impair evaluation accuracy.

The results in Table 1 to Table 3 also suggest that nano-silver brings about better antibacterial activities against *Escherichia coli* and *Staphylococcus aureus* and nano-ZnO results in better antibacterial activities against *Aspergillus niger* and *Rhodotorula mucilaginosa*. Since butyl paraben is poorly soluble in water, the antibacterial activity is the poorest.

Application of the Improved Halo Method

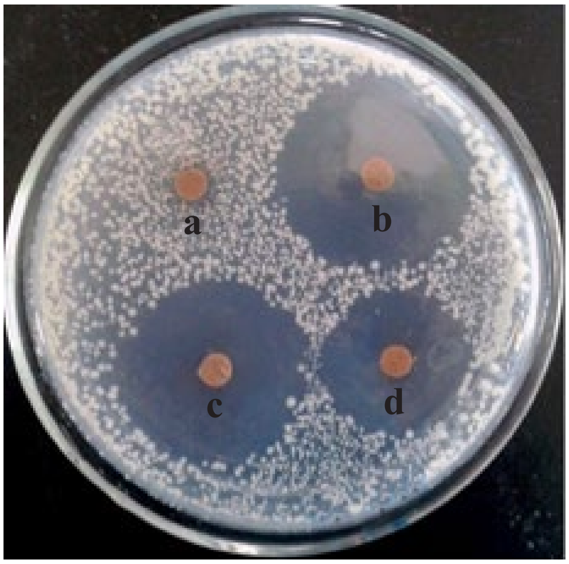


Figure 4. The antibacterial activity of different samples against *Escherichia coli* tested by improved halo method (a - blank; b - nano-silver; c - nano-ZnO; d - butyl paraben)

Figure 4 illustrates that four samples could be tested in one culture dish for evaluating antibacterial activities against *Escherichia coli*. The diameter of inhibition zone from big to small is nano-silver, nano-ZnO, butyl paraben and blank, and the difference between each sample is very clear and intuitive. Therefore, improved halo method could not only be used for evaluating leather antibacterial activity quantitatively but it is also a fast and qualitative analysis method.

CONCLUSIONS

An improved halo method was developed based on traditional halo method and agar diffusion plate method for evaluating leather antibacterial activity quickly, intuitively and precisely. In the method, microbes were blended with sterile medium directly and double layer medium was used to avoid error from uneven distribution of microbes, and more than one sample could be tested in one culture dish for evaluating antibacterial activity. Antibacterial activity against various bacteria, fungi and yeast could be evaluated by improved halo method, and antibacterial activity of leather treated by different antibacterial agents could be tested by the method too. Moreover, the repeatability and reliability of new method was excellent, and the results were not only quantitative but also intuitive. In sum, improved halo method would be a new choice for leather evaluating antibacterial activity rapidly and precisely.

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ANTIBACTERIAL COMPOUND BASED ON SILICONE RUBBER AND ZnO AND TiO_2 NANOPARTICLES FOR THE FOOD AND PHARMACEUTIC INDUSTRIES. PART II - BIOLOGICAL AND MORPHOLOGICAL CHARACTERIZATION

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ANTIBACTERIAL COMPOUND BASED ON SILICONE RUBBER AND ZnO AND TiO_2 NANOPARTICLES FOR THE FOOD AND PHARMACEUTIC INDUSTRIES. PART II - BIOLOGICAL AND MORPHOLOGICAL CHARACTERIZATION

ABSTRACT. The aim of this paper is the biological and morphological characterization of an antibacterial compound based on silicone rubber (Elastosil R701/70-OH), reinforced with ZnO and TiO_2 nanopowders (with antibacterial, antifungal and antimicrobial properties), charged (chalk), crosslinked with peroxide (dicumyl peroxide - powder 40% with calcium carbonate and silica, specific to the food, pharmaceutical, but also medical field). ZnO and TiO_2 nanopowders, by their homogeneous dispersion in the mass of the compound, have a determined role on its antibacterial and antimicrobial sterilization properties. The mixture of antibacterial compound based on silicone rubber was made on a laboratory roller, provided with cooling, in the form of a sheet (maximum thickness 5 mm), in strict compliance with the technological recipe and the established mode of operation. Subsequently, the mixture is processed into forming molds at predetermined parameters by determining the vulcanization time using the Monsanto rheometer (to determine the optimum temperature and vulcanization times), but also the biological and morphological characterization, according to current standards in specific food and pharmaceutical environments.
KEY WORDS: silicone elastomer, biological characterization, nanopowders, antibacterial

COMPOUND ANTIBACTERIAN PE BAZĂ DE ELASTOMER SILICONIC ȘI NANOPARTICULE DE ZnO ȘI TiO_2 PENTRU DOMENIUL ALIMENTAR ȘI FARMACEUTIC. PARTEA II – CARACTERIZARE BIOLOGICĂ ȘI MORFOLOGICĂ

REZUMAT. Scopul acestei lucrări este caracterizarea din punct de vedere biologic și morfologic a unui compound antibacterian pe bază de cauciuc siliconic (Elastosil R701/70-OH), ranforsat cu nanopulberi de ZnO și TiO_2 (cu proprietăți antibacteriene, antifungice și antimicrobiene), șarjat (cretă), reticulat cu peroxid (peroxid de dicumil - pulbere 40% cu carbonat de calciu și silice, specific domeniului alimentar, farmaceutic, dar și medical). Nanopulberile de ZnO și TiO_2 prin dispersia lor omogenă în masa compoundului au rol determinant asupra proprietăților de sterilizare antibacteriană și antimicrobiană ale acestuia. Amestecul de compound antibacterian pe bază de cauciuc siliconic s-a realizat pe un valț de laborator, prevăzut cu răcire, sub forma unei foi (grosime de maxim 5 mm), cu respectarea strictă a rețetei tehnologice și a modului de operare stabilit. Ulterior amestecul este prelucrat in matrițe de formare la parametrii prestabiliți prin determinarea timpului de vulcanizare cu ajutorul reometrului Monsanto (pentru stabilirea temperaturii și timpilor de vulcanizare optimi), dar și a caracterizării biologice și morfologice, conform standardelor în vigoare în medii specifice domeniului alimentar, dar și farmaceutic.
CUVINTE CHEIE: elastomer siliconic, caracterizare biologică, nanopulberi, antibacterian

COMPOSÉ ANTIBACTÉRIEN À BASE DE CAOUTCHOUC DE SILICONE ET DE NANOPARTICULES DE ZnO ET TiO_2 POUR LES INDUSTRIES ALIMENTAIRE ET PHARMACEUTIQUE. PARTIE II - CARACTÉRISATION BIOLOGIQUE ET MORPHOLOGIQUE

RÉSUMÉ. L'objectif de cet article est la caractérisation biologique et morphologique d'un composé antibactérien à base de caoutchouc silicone (Elastosil R701/70-OH), renforcé de nanopoudres de ZnO et TiO_2 (aux propriétés antibactériennes, antifongiques et antimicrobiennes), chargé (craie), réticulé au peroxyde (peroxyde de dicumyle - poudre à 40% avec carbonate de calcium et silice, spécifique aux domaines alimentaire, pharmaceutique et médical). Les nanopoudres de ZnO et TiO_2, par leur dispersion homogène dans la masse du composé, ont un rôle déterminant sur les propriétés de stérilisation antibactériennes et antimicrobiennes. Le mélange de composé antibactérien à base de caoutchouc silicone a été réalisé sur un rouleau de laboratoire, avec refroidissement, sous forme de feuille (épaisseur de maximum 5 mm), en respectant strictement la recette technologique et le mode de fonctionnement établi. Par la suite, le mélange est transformé en moules de formage à des paramètres prédéterminés en déterminant le temps de vulcanisation à l'aide du rhéomètre Monsanto (pour déterminer la température optimale et les temps de vulcanisation), mais aussi la caractérisation biologique et morphologique, selon les normes actuelles dans des environnements alimentaires et pharmaceutiques.
MOTS-CLÉS : élastomère de silicone, caractérisation biologique, nanopoudres, antibactérien

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INTRODUCTION

Silicone elastomers – silicone rubber is generally processed at high temperatures up to a maximum of +320°C (the processing temperature range is between -100°C to above +320°C), is indoor, non-toxic, has resistance to ozone, resistance to low temperatures and environments (-100°C) while maintaining its properties, also has excellent electrical insulation performance. Silicone rubber is preferred in food, pharmaceutical and medical fields due to these properties and its ease of processing and modeling, but also due to its sterilization properties, as a result of processing at high temperatures up to +320°C [1-7].

The development of new materials coated with various nanoparticles in order to inhibit bacterial adhesion to the substrate, thus eliminating their chance to trigger an infectious process has been intensively studied recently [8-10]. The nanoparticles normally have a high surface/volume ratio, ensuring a much more effective antibacterial and antifungal activity. So, their dispersion in elastomeric compounds have a decisive role in influencing the antimicrobial and antibacterial sterilization properties [11]. Due to their antimicrobial, antibacterial and antifungal activity, ZnO and TiO_2 nanoparticles are used for countless applications in everyday life, such as medical devices, dental implants, the textile industry, plastics, antibacterial coatings, building materials, etc. [12-16].

The aim of the paper was to characterize an antibacterial compound biologically, in specific environments (for the pharmaceutical and food industries: *Staphylococcus aureus* ATCC 25923; *Escherichia coli* ATCC 25992 and *Candida albicans* ATCC 10231) [17] and morphologically. The tested antibacterial compound is based on silicone elastomer (rubber Elastosil R701/70-OH – the majoritarian material), charged with chalk, stearin as plasticizer, crosslinked with dicumyl peroxide on silica support and reinforced with zinc oxide and titanium dioxide nanopowders in different percentages, obtained by the technique of mixing on an electric roller. The test specimens and the related characterizations were obtained in the electric press at vulcanization times and temperatures established from the rheological analysis [18-22].

EXPERIMENTAL

Materials

Materials used to obtained the antibacterial compound based on siliconic elastomer, reinforced with nanopowders are: Elastosil R701/70-OH (silicon rubber: polydimethylsiloxane with vinyl groups, dynamic viscosity over 9.000.000 mPa*s, in the form of paste, density – 1.32 g/cm^2, colour – opaque); stearin (white flakes, moisture - 0.5% max, ash – 0.025 % max); ZnO (microparticles: white powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g); ZnO (zinc oxide nanoparticles- white powder, size particles 20 nm, molecular mass – 98.87 g/mol, specific surface area – 23 m^2/g, density – 4.26 g/ml, and concentration – 99,5%); TiO_2 (titanium dioxide nanoparticles: white nanopowder, particle size 21 nm, molecular mass – 79.87 g/mol, specific surface area – 23 m^2/g, density – 4.26 g/ml, assay ≥ 99.5 % trace metals basis); chalk ($CaCO_3$ precipitate – white powder, molecular weight 100.09); PD (dicumyl peroxide, powder 40% with calcium carbonate and silica - Perkadox 14-40B (1.65 g/cm^3 density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%)).

For the biological characterization were used the following materials: *Staphylococcus aureus* ATCC 25923; *Escherichia coli* ATCC 25992; *Candida albicans* ATCC 10231. The above-mentioned strains come from American Type Culture Collection (ATCC, US).

Methods

Preparation of Antibacterial Compound

The antibacterial compound mixtures were made by the mixing on a laboratory roller provided with cooling, with strict observance of the technological recipe, Table 1, and the established mixing times (Figure 1) [21]. The silicone rubber - Elastosil R701/70-OH (elastomer) was plasticized between the rolls for approximately 2.5-3 minutes, then the stearin is added and the mixing is continued for 2 minutes. The ZnO microparticles were blended for a maximum of 2 minutes until the mixture became homogeneous, and the ZnO and TiO_2 nanopowders were added to the mass of the compound continuing the mixing for 3 minutes. Then mixing was continued for 3 minutes, then chalk was added, and after that the last ingredient was added - PD (dicumyl peroxide), continuing mixing for 3 minutes. The mixture is homogenized on the roll mill for maximum 2 minutes and taken off in the form of a 3-4 mm thick sheet. After the optimal vulcanization time is established, Figure 1 [21], the specimens are processed in the electric press, then subjected to physical-mechanical, chemical, biological and morpho-structural characterization, according to the standard in force, after their stabilization for 24 h at room temperature [21].

Table 1: Formulation of antibacterial compounds based on silicone rubber reinforced with TiO_2 and ZnO nanoparticles [21]

Symbol	MU [g]	CS_1 (control)	Sample 2	Sample 3	Sample 4
Silicone rubber (Elastosil R701/70-OH)	g	150	150	150	150
Stearin (flakes)	g	7.5	7.5	7.5	7.5
Zinc oxide (active powder)	g	6	4.5	3	1.5
Zinc oxide (nanopowder)	g	-	1.5	3	4.5
Titanium dioxide (nanopowder)	g	-	1.5	3	4.5
Chalk ($CaCO_3$ - powder)	g	15	15	15	15
Dicumyl peroxide (PD)	g	11.25	11.25	11.25	11.25

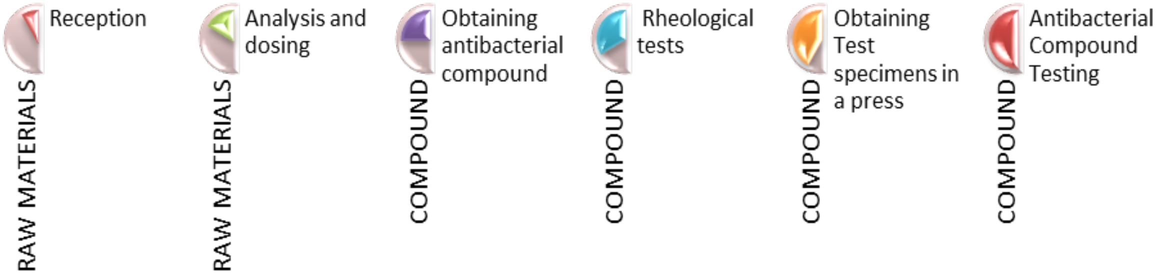
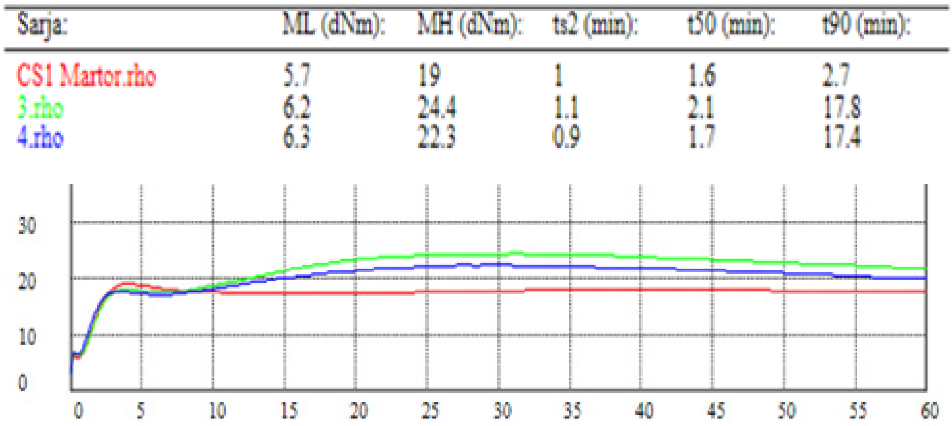


Figure 1. Technological process of obtaining the antibacterial compound reinforced with ZnO and TiO_2 nanopowders [21]



Sarja:	ML (dNm):	MH (dNm):	ts2 (min):	t50 (min):	t90 (min):
CS1 Martor.rho	5.7	19	1	1.6	2.7
3.rho	6.2	24.4	1.1	2.1	17.8
4.rho	6.3	22.3	0.9	1.7	17.4

Figure 2. Rheological analysis of sample CS_1 (control), sample 3, sample 4, to establish the curing time in the electrical press [21]

Biological Setup

To analyze the antimicrobial activity (biological setup), the antibacterial compound specimens based on silicone elastomer, reinforced with nanopowders with antifungal, antibacterial and antimicrobial properties, ZnO and TiO_2, were tested and characterized according to ASTM standard: E 2149-10. They were tested on the following strains: *Staphylococcus aureus* ATCC 25923; *Escherichia coli* ATCC 25992 and *Candida albicans* ATCC 10231 and preserved on glycerol medium, were seeded on nutrient gelatin agar medium and Sabouraud dextrose agar with chloramphenicol, to obtain 24 h cultures. All samples were sterilized and placed in six-well plates - Nunc with 200 µl microbial suspension (density 0.5 McFarland = 1.5 x 108 CFU/mL) and 2 ml broth for bacteria. For fungi, the microbial suspension had a density of 1 McFarland, i.e. 3 x 108 CFU/ml. Incubation took place at 37°C for 24 hours. After the incubation process the colonized materials were washed with sterile distilled water to remove non-adherent microorganisms, then they were introduced into Eppendorf tubes with 1 ml of physiological serum, also sterile (AFS). These were sonicated at maximum power for 15 seconds and then vortexed for 15 seconds at 300 rpm. Then, decimal dilutions were made, which were seeded in triplicate of 10 µl per nutrient agar medium, namely Sabouraud with chloramphenicol, to calculate the number of colony-forming units/ml - CFU.

Morphological Characterisation

The antibacterial compounds based on silicone rubber, reinforced with nanopowders with antifungal, antibacterial and antimicrobial properties and crosslinked with dicumyl peroxide, obtained by mixing technique, were morphologically tested by scanning electron microscopy - SEM. Microscopic analyses were performed using an electron microscope at 15\20 keV, in the primary electron beam, on specimens covered with a gold film, to highlight the degree of dispersion of nanopowders, but also changes in the surface of the elastomer. The microscope generates a flow of electrons that bombard the sample, allowing a clear view of the structure of the sample under analysis. The lower surface, the upper surface, but also the transverse one can be visualized.

RESULTS AND DISCUSSIONS

Biological Characterization of Antibacterial Compounds

There are different types of nanoparticles (nanopowders) that can be incorporated into the elastomer matrix, depending on their properties and their application. Thus, various studies have been performed for the development and use of new materials mixed with different types of nanopowders to limit bacterial adhesion to the surface, thus eliminating the possibility of triggering an infectious process.

The antibacterial compound based on silicone elastomer, reinforced with ZnO and TiO_2 powders (with antifungal, antibacterial and antimicrobial properties) was tested for 24 h at 37°C on:

- *Staphylococcus aureus* as a model for Gram positive bacteria,
- *Escherichia coli (E. coli)* as prototype for Gram negative bacteria,
- *Candida albicans* (*C. albicans)* as a representative of fungi.

This type of species is among the most frequently isolated species from infections, with an increased incidence in nosocomial ones. Thus, in this study, the antimicrobial, antibacterial and antifungal activity of the antibacterial compound surfaces mixed with ZnO and TiO_2 nanopowders was tested.

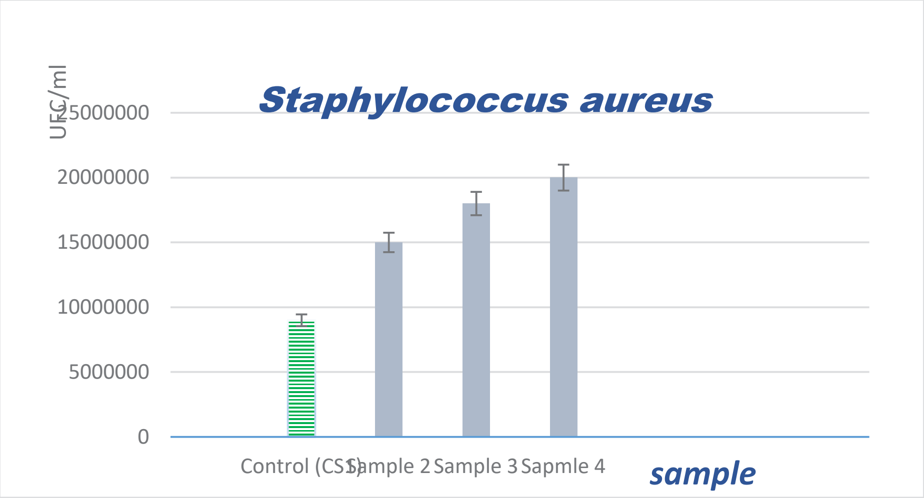


Figure 3. Biological characterization of antibacterial compound samples with ZnO and TiO_2 nanopowders on *Staphylococcus aureus* ATCC 25923 strains

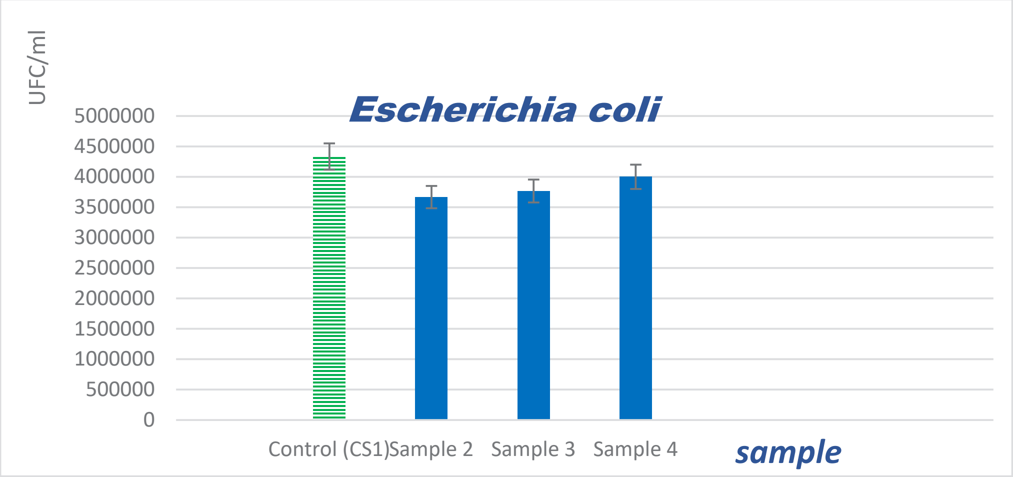


Figure 4. Biological characterization of antibacterial compound samples with ZnO and TiO_2 nanopowders on *Escherichia Coli* ATCC 25992 strains

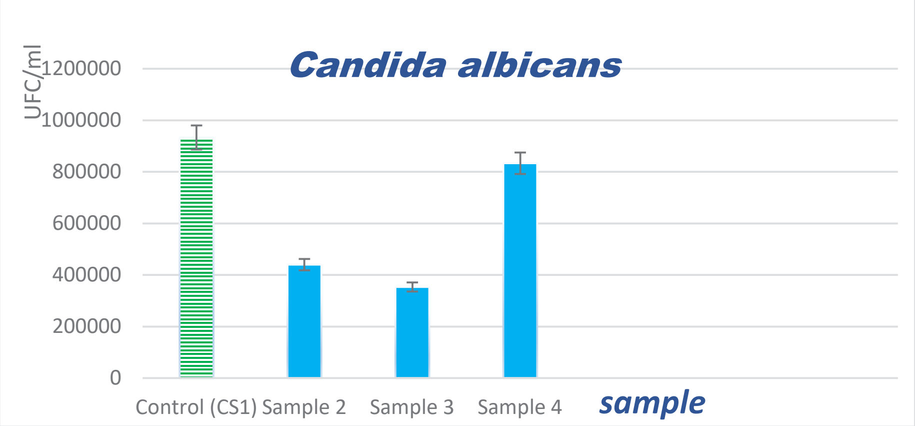


Figure 5. Biological characterization of antibacterial compound samples with ZnO and TiO_2 nanopowders on *Candida albicans* ATCC 10231 strains

Tests performed on these types of strains showed that the specimens with zinc oxide and titanium dioxide nanopowders show adhesion capacity compared to the CS_1 sample (control sample) depending on the concentration of nanopowders introduced in the antibacterial compound mixture.

The tests performed on fungi, *Candida albicans*, proved to be very effective in all the tested samples (Sample 2, Sample 3 and Sample 4), sample 3 showing the most effective values against the mentioned fungal species. Also in the case of Gram-negative bacterial strains - *Escherichia coli*, we can see that all samples, especially sample 2, show effective antimicrobial activity.

The antimicrobial activity tested against Gram-positive bacteria - *Staphylococcus aureus*, in this case favors bacterial adhesion on the tested samples, the CFU/ml values being high compared to the values recorded for the control sample - CS_1.

Morphological Characterization of Antibacterial Compounds

Elastosil R701/70 silicone rubber antibacterial compound specimens (which is the main component) reinforced with ZnO and TiO_2 nanoparticles were analyzed using the Hitachi S2600N electrocopic microscope at 15-20 keV in the primary electron beam, in cross-section, on samples covered with gold film. The SEM images are shown in Figures 6 and 7, where the dispersion of nanoparticles with antimicrobial, antifungal and antibacterial role in the obtained antibacterial compound can be observed.

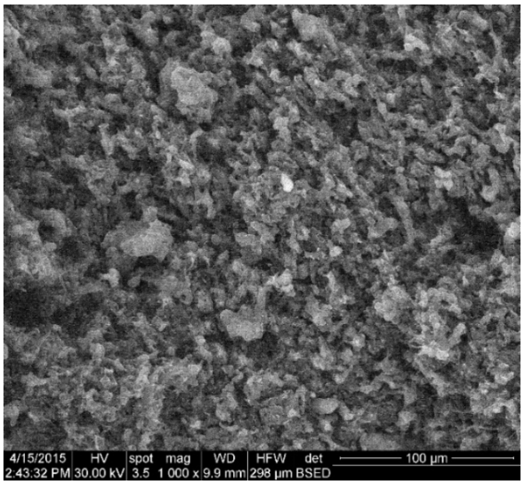


Figure 6. SEM image recorded for sample 2

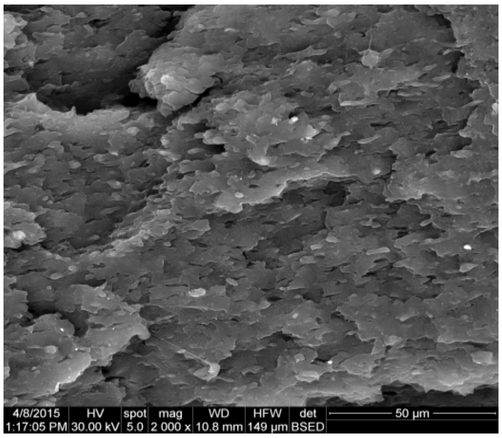


Figure 7. SEM image recorded for sample 3

The images of the samples recorded in cross section show a biphasic morphology, with ZnO and TiO_2 nanopowder particles evenly distributed in the elastomeric matrix (silicone rubber being the major component in which all other components are dispersed), thus leading to an improvement of characteristics of the compound (resistance, elasticity, increased microbial activity, etc.).

There is also a homogeneous dispersion of all components in the mass of the antibacterial compound, thus demonstrating that it was performed at optimal parameters according to the plan.

CONCLUSION

The paper presents the biological and morphological characterization of antibacterial compounds based on silicone rubber, reinforced with zinc oxide and titanium dioxide nanopowders and crosslinked with dicumyl peroxide. The biological characterization was performed on strains specific to the food and pharmaceutical field according to the standards in force, for 24 hours at 37°C. The three strains used are *Staphylococcus aureus* ATCC 25923, *Escherichia coli* ATCC 25992 and *Candida albicans* ATCC 10231. The standard used for the biological test of the antibacterial compound based on silicone rubber and ZnO and TiO_2 nanopowders was ASTM: E 2149-10 standard.

According to the biological characterization performed, samples 2 and 3 show effective antimicrobial activity against both fungi - *Candida albicans*, and Gram-negative bacteria - *Escherichia coli*.

The morphological characterization showed that the tested specimens were performed according to the vulcanization times and temperatures determined from the rheological analysis (using the Monsanto rheometer) and a homogeneous dispersion of both ZnO and TiO_2 nanopowders and other components used in the mass of the compound.

As a result of the biological and morphological characterization of antibacterial compounds based on sliconic elastomer we can say that they have potential applications in both the pharmaceutical and food fields, especially samples 2 and 3.

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GREEN PRODUCTIVITY IN THE INDONESIAN LEATHER-TANNING INDUSTRY

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GREEN PRODUCTIVITY IN THE INDONESIAN LEATHER-TANNING INDUSTRY

ABSTRACT. Green productivity (GP) is a strategy by which production processes are improved by efficiently using resources and materials and adverse impacts on the environment are reduced. This study aims to measure GP of an Indonesian leather-tanning industry and develop alternatives to current processes that would improve its environmental and economic impacts. Two small to medium tanneries (Tanneries A and B) in two provinces were used as a case study. Data were collected through direct observation, measurements, in-depth interviews, and activity documentation. Material flow was analyzed using a green material flow map to determine the six sources of green wastes and the environmental indicators. The GP Index (GPI) was used to measure GP. The best method by which to improve GP was determined using GPI to a ratio of GP along with expert analysis using an analytical hierarchy process. GPI at Tannery A, located in West Java, was 0.14 with economic and environmental indicators of 1.44 and 10.41, respectively. GPI at Tannery B, located in Central Java, was 0.16 with economic and environmental indicators of 1.60 and 9.99, respectively. GP in both tanneries was low because of their suboptimal use of water. High water consumption can lead to a high discharge of liquid waste. Six alternatives for Tannery A and four for Tannery B were created. According to GPI, GP ratio, and expert opinion, the best strategy by which to improve GP was water recycling in the soaking and liming processes. This strategy increased GPI at Tannery A to 0.18 and at Tannery B to 0.20.

KEY WORDS: Green productivity, Green productivity index, Green productivity ratio, Indonesian leather-tanning industry

PRODUCTIVITATEA ECOLOGICĂ ÎN INDUSTRIA DE PIELĂRIE DIN INDONEZIA

REZUMAT. Productivitatea ecologică (GP) este o strategie prin care procesele de producție sunt îmbunătățite prin utilizarea eficientă a resurselor și a materialelor, reducând impactul advers asupra mediului. Acest studiu își propune să măsoare GP a industriei de pielărie din Indonezia și să dezvolte alternative la procesele actuale care ar îmbunătăți impactul asupra mediului și economiei. S-au utilizat două tăbăcării mici spre medii (Tăbăcăriile A și B) din două provincii ca studiu de caz. Datele au fost colectate prin observație directă, măsurători, interviuri detaliate și documentarea activității. Fluxul de materiale a fost analizat folosind o hartă a fluxului ecologic de materiale pentru a determina cele șase surse de deșeuri ecologice și indicatorii de mediu. Indicele GP (GPI) a fost utilizat pentru a măsura productivitatea ecologică. Cea mai bună metodă prin care s-a îmbunătățit GP a fost determinată folosind GPI raportat la GP împreună cu analiza experților folosind un proces de ierarhie analitică. GPI al Tăbăcăriei A, situat în Java de Vest, a fost 0,14; indicatorii economici și de mediu fiind de 1,44, respectiv 10,41. GPI al Tăbăcăriei B, situat în Java Centrală, a fost 0,16, indicatorii economici și de mediu fiind de 1,60 și, respectiv, 9,99. În ambele tăbăcării GP a fost scăzută din cauza utilizării apei sub nivelul optim. Consumul mare de apă poate duce la eliminarea unei cantități mari de deșeuri lichide. Au fost create șase alternative pentru Tăbăcăria A și patru pentru Tăbăcăria B. În conformitate cu GPI, raportul GP și opinia experților, cea mai bună strategie pentru a îmbunătăți GP a fost reciclarea apei în procesele de înmuiere și cenușărire. Această strategie a crescut GPI în cazul Tăbăcăriei A la 0,18, iar în cazul Tăbăcăriei B la 0,20.

CUVINTE CHEIE: productivitate ecologică, indice de productivitate ecologică, raport de productivitate ecologică, industria de pielărie din Indonezia

PRODUCTIVITÉ ÉCOLOGIQUE DANS L'INDUSTRIE INDONÉSIENNE DU TANNAGE DU CUIR

RÉSUMÉ. La productivité écologique (GP) est une stratégie par laquelle les processus de production sont améliorés en utilisant efficacement les ressources et les matériaux et en réduisant l'impact négatif sur l'environnement. Cette étude vise à mesurer la GP de l'industrie indonésienne de tannage du cuir et à développer des alternatives aux procédés actuels pour améliorer l'impact sur l'environnement et l'économie. Deux petites et moyennes tanneries (Tanneries A et B) dans deux provinces ont été utilisées comme étude de cas. Les données ont été collectées par observation directe, mesures, entretiens approfondis et documentation des activités. Les flux de matières ont été analysé à l'aide d'une carte des flux de matières vertes pour déterminer les six sources de déchets verts et les indicateurs environnementaux. L'indice GP (GPI) a été utilisé pour mesurer la productivité écologique. La meilleure méthode pour améliorer GP a été déterminée en utilisant GPI sur un ratio de GP avec une analyse d'experts utilisant un processus de hiérarchie analytique. Le GPI de la Tannerie A, située dans la province de Java occidental, était de 0,14 avec des indicateurs économiques et environnementaux de 1,44 et 10,41, respectivement. Le GPI de la Tannerie B, située dans la province de Java central, était de 0,16 avec des indicateurs économiques et environnementaux de 1,60 et 9,99, respectivement. La GP dans les deux tanneries était faible en raison de leur utilisation sous-optimale de l'eau. Une consommation d'eau élevée peut entraîner un rejet élevé de déchets liquides. Six alternatives pour la Tannerie A et quatre pour la Tannerie B ont été créées. Selon le GPI, le ratio GP et l'opinion d'experts, la meilleure stratégie pour améliorer la GP était le recyclage de l'eau dans les processus de trempage et de chaulage. Cette stratégie a augmenté le GPI de la Tannerie A à 0,18 et de la Tannerie B à 0,20.

MOTS CLÉS : productivité écologique, indice de productivité écologique, ratio de productivité écologique, industrie indonésienne du tannage du cuir

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INTRODUCTION

Indonesia is the largest leather producer in Southeast Asia, and leather and footwear products are some of its main exports. Figure 1 compares annual leather production from several countries and clearly indicates Indonesia's rank as top producer from 1999 to 2015 [1]. The average growth of leather, leather product and footwear industries in 2010–2015 reached 5% and accounted for 0.26% of Indonesia's Gross Domestic Product (GDP) in 2013, which was equivalent to $237 billion [2].

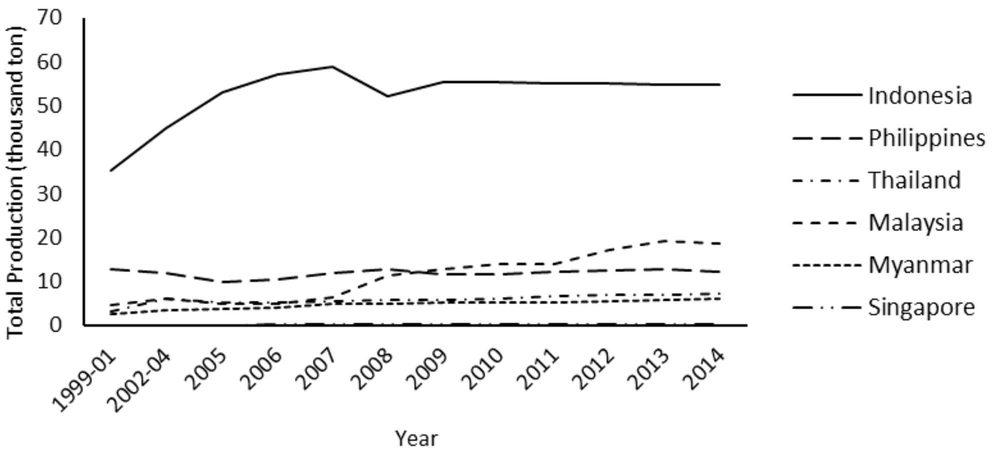

Figure 1. Total production of bovine heavy leather and bovine light leather

The Indonesian leather-tanning industry has experienced considerable growth. Data from Statistics Indonesia showed that the annual growth of leather, leather and footwear production for a large- to medium-scale industry was 6.6% and for a small-scale industry was 7.7% during 2010–2017 [3]. The export volume was growing as well by nearly 12.84% in 2013–2015 [2]. The agreement by the Association of Southeast Asian Nations Free Trade Area since 2015 has continued to incite competition in the global leather market. To thrive among the competition, a company must have business advantages and imperatives, such as maximum productivity in its operation management system. The challenges for the industrial world are dynamically increasing following various types of pressure, such as market globalization, standardization, regulations, and policy [4]. If the first operating system focuses only on low-cost production, the world would expect the industry to consider sustainable developments, including environmental impacts, ecofriendly technology, and renewable resources.

The leather-tanning industry is widely known as non-ecofriendly [5]. The tanning process results in various wastes, both solid and liquid, that can seriously damage the environment if not properly handled [6, 7]. The amount of solid waste from a tannery varies depending on the technology and type of end product. Some sources have estimated that 1 tonne of raw skin could result in 439–600 kg solid waste, of which 25% contained chrome and the remaining 75% was chrome-free solid waste or became a suspended solid in liquid waste, and that only 250–300 kg was converted into leather [8, 9].

According to the Indonesian Tanners Association, 75% of all tanneries in Indonesia are classified as small and medium enterprises (SMEs). These SMEs have limitations that hinder their environmental management efforts. SMEs tend to be more harmful to the environment than the larger enterprises because of their poor production techniques [10]. SME tanneries in developing countries face serious waste management problems and many are being shut down because they are not able to meet the required waste management standards [11]. This situation is similar in Indonesia, where there is a lower rate of adoption of green tanning practices [12]. This contradicts a recognition by the industry of the importance of building an ecofriendly tannery to thrive in the global market. An approach to green productivity (GP) must surface to achieve that objective.

GP is a strategy by which to improve productivity as well as the economic aspects, environmental quality, and socioeconomic development of an industry. This approach improves production processes by more efficiently utilizing resources and materials to reduce negative impacts on the environment. A GP strategy maintains that a healthy environment and competitive economic factors are mutually influential [13]. To design a productivity-improvement strategy in Indonesia's tanneries, it is essential to first measure their GP index (GPI). This value aids a business in gaining a better understanding of the factors involved, such the costs and benefits of the actions taken and the limitations and opportunities that surround them. This would help the industry to better understand its GP goals and assist it in formulating its objectives and ways by which to achieve them [14].

The GP strategy applied in various industries has improved product quality; reduced scrap, pollution, and risk; reduced materials and costs; and increased yield without sacrificing the environment [15, 16]. In addition, GP promotes systematic assessment by reporting on and planning for environmental protection efforts [17]. The aim of this research was to map and analyze GP in the Indonesian leather-tanning industry and examine efforts by which to increase GP in these industries using case studies in two SME tanneries.

EXPERIMENTAL

Framework

GP in the Indonesian leather-tanning industry was measured using a systems approach that began with collecting data through direct observation, measurements, in-depth interviews, activity documentation, and analyses of solid and liquid waste samples by an accredited test laboratory. System identification was conducted using mass balance analysis and six green wastes at each stage of the production process. In the next stage, the environmental and economic indicators were used to calculate GP. GP is increased by minimizing or eliminating the use of resources that have an impact on environmental conditions. The best alternatives for increasing productivity are created using the GPI method, GP ratio, and analytical hierarchy process (AHP) technique.

The best GP improvement strategy is determined in two ways. First, a GPI calculation is simulated for each of the proposed alternatives, with the highest GPI being the alternative that provides the best improvement in GP. Second, the most applicative alternative is determined using AHP, which involves three expert opinions from academic, industry practice, and business sectors.

Data Collection and Analyses

Qualitative and quantitative data in the form of primary and secondary data were used in the analyses. Primary data were obtained through direct observation, measurements, in-depth interviews, activity documentation, and analyses of solid and liquid waste samples by an accredited test laboratory. Secondary data were obtained from the opinions of experts who were academics, practitioners, and businesspeople. Secondary data were also obtained from related studies published in scientific articles, scientific journals, and reference books and on the Internet. GP data together with influential indicators were calculated and analyzed using Microsoft Excel 2010. The best alternatives by which to increase GP were analyzed using Expert Choice 11. A summary of the data, characteristics of the data, data sources, collection procedures, and data analyses are presented in Table 1.

Table 1: Data, data characteristics, data sources, and data collection sources

No.	Data	Data Characteristics	Data Sources	Data Collection Source
1	Production process flow	Secondary	Tannery A and B	Field survey, interview and literature review
2	Economic: total production costs; total production; selling price;	Secondary	Tannery A and B	Field survey, interview and literature review
3	Six green waste generated	Secondary	Tannery A and B	Field survey, and literature review
4	Solid and liquid waste quality in Tannery A and B	Primary	Accredited laboratory	Testing in laboratory
5	Alternative solution to increase green productivity	Primary	Experts (academic, practitioner, and businessman)	Interview and questionnaire

Identification of Production Process and Material Requirements

The production process was analyzed using mass balance analysis and Green Value Stream Mapping (GVSM). Mass balance analyses identified the amount of waste generated in the production system; GVSM identified seven sources of green waste. The seven sources of green waste were defined as an excessive use of energy, water, material, waste, transport, emissions, and damage to biodiversity [18]. In this study, biodiversity loss was not calculated because of the limited information available from the tanneries.

Green Productivity Index

GPI is the ratio of economic benefits to environmental impacts and is represented by the following equation [19]:

$$GPI = \frac{Economic\ Indicator}{Environmental\ Indicator} = \frac{SP/PC}{EI} \qquad (1)$$

where GPI = green productivity index, SP = selling price, PC = production cost, and EI = environmental impact.

Economic Indicator

An economic indicator is the ratio of the selling price to production cost for producing a one-unit of product. In this research, the production cost was based on the cost to process 1.5 tons salted-hide. The total costs were the sum of the fixed and variable costs.

$$Economic\ Indicator = \frac{Revenue}{Total\ Cost} \qquad (2)$$

$$Total\ Cost = Fixed\ Cost + Variable\ Cost \qquad (3)$$

$$TC = \frac{FC}{X} + VC \qquad (4)$$

where TC = total cost (IDR/h), FC = fixed cost (IDR/year), VC = variable cost (IDR/h), and x = estimated working hours per year (h/year).

Environmental Impact Indicator

The value of the environmental impact indicator depends on multiplying the sum of the weight of the GP indicator and the amount of waste produced during the production process for each type of indicator. A high environmental impact value indicates poor environmental management. The indicator weight was derived from the 2005 Environmental Sustainability Index (ESI) [17] using the weight equalization aggregation method. ESI measures a country's ability to protect the environment for decades to come and integrates 76 sets of data into 21 indicators of environmental sustainability [20]. Table 2 shows an important ESI indicator used in this study. The 2005 ESI water quality indicators include variables such as of dissolved oxygen value, phosphorus concentration, electronic conductivity, and suspended solids. Phosphorus is important because it plays a role in the eutrophication process in waterbodies [21, 22].

GPI comprises three indicators as follows: gaseous waste generation (GWG), water consumption (WC), and solid waste generation (SWG). Table 2 presents the derivation of six weighted ESI indicators into the three GPI environmental variables. GWG, WC, and SWG are weighted as 0.33, 0.5, and 0.17, respectively; therefore, the environmental impact during the tanning production process is presented in Equation 5.

$$EI = 0.33\,GWG + 0.5\,WC + 0.17\,SWG \tag{5}$$

Table 2: Derivation of three environmental indicators of the green production index (GPI) in the leather-tanning process

GPI Indicators	Equivalent with ESI Indicators	Wight in ESI	Weight merging (x)	Weight (x) in GPI (x/0.30)
Gaseous wastes generation (GWG)	Reducing air pollution	0.05	0.10	0.33
	Greenhouse gas emission	0.05		
Water consumption (WC)	Water quality	0.05	0.15	0.5
	Water quantity	0.05		
	Reducing water stress	0.05		
Solid wastes generation (SWG)	Reducing waste & consumption pressure	0.05	0.05	0.17
Total			0.30	1

Emissions from Liquid and Solid Wastes

Liquid waste emissions were calculated based on chemical oxygen demand (COD) values. The methane value was then converted to a carbon dioxide (CO_2) equivalent. Solid waste emissions from the open dumping/landfill area were calculated using the Landfill Gas Emissions Model (LandGEM) v.3.02. LandGEM is an automated approximating tool with a Microsoft Excel interface that can be used to estimate emission levels for total landfill gas, CH_4, CO_2, non-CH_4 organic compounds, and other air pollutants from the landfill. This tool was issued by the United States Environmental Protection Agency's (USEPA) Clean Air Technology Center. Solid waste emissions from open burning were calculated following the Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories chapter on waste incineration and open burning. IPCC is an international body created to scientifically assess climate change. IPCC was established in 1988 by the World Meteorological Organization and the United Nations Environment Program. The calculation of CO_2 gas emissions from combustion of shaving scraps is as follows:

$$CO_2\ Emission = (SW \times dm \times CF \times FCF \times OF) \times \frac{44}{12} \tag{6}$$

where SW = total amount of solid waste (kg), dm = dry matter content in the waste (%), CF = fraction of carbon in the dry matter/total carbon (%), FCF = fraction of fossil carbon in the total carbon (%), OF = oxidation factor (%), and 44/22 = conversion factor from C to CO_2. The dm value was obtained from the analysis of the sample used in the laboratory, while CF, FCF, and OF values were derived from the default data for CO_2 emission factors according to IPCC Guidelines for National Greenhouse Gas Inventories [23].

Selection of Alternatives

The selection of alternatives was based on the future GPI and then expanded using AHP to determine those most applicable. The GPI value in GP were obtained from the ratio of the GPI alternative (GP_{alt}) to the GPI initial condition (GP_{cur}) [19]. The GPI ratio formula is presented as follows:

$$GP_{ratio} = \frac{GP_{alt}}{GP_{cur}} = \frac{(SP_{alt}/PC_{alt})/EI_{alt}}{(SP_{cur}/PC_{cur})/EI_{cur}} = \frac{(Sp_{alt} \times PC_{cur})}{(SP_{cur} \times PC_{alt})} \times \frac{EI_{cur}}{EI_{alt}} \tag{7}$$

where GP_{ratio} = GPI ratio; SP_{alt} = selling price of the alternative; PC_{alt} = production costs of the alternative; SP_{cur} = the selling price of the initial condition; PC_{cur} = production cost of initial conditions; EI_{alt} = environmental impacts of the alternative; and EI_{cur} = environmental impact of the initial conditions.

AHP is an analytical method used in decision making to determine the best decisions from various alternatives. There are four basic principles of AHP according to Marimin *et al*. (2014) [24]. First, problems should be identified to compile a hierarchy. The preparation begins with deconstructing a complex problem into its main components. Then, the main components are further broken down and the process continues to form a hierarchy. Second, each level in the hierarchy is assessed through pairwise comparisons. Scales 1–9 are best for expressing opinions [25]. Third, pairwise comparisons are made at each level in the hierarchy to determine priorities. A pair of elements is compared based on specific rules, and the intensity of preferences between the elements is considered. Each hierarchical level, either quantitative or qualitative, can be compared according to a predetermined protocol for judgment so that weights and priorities are generated. Fourth, a logical consistency must be ensured. Assessments that are highly consistent are necessary for accurate decision making. The consistency ratio should be ≤10%. If not, the assessment is considered to be random and must be corrected.

RESULTS AND DISCUSSIONS

Industries Profile

The GP measurement for the Indonesian leather-tanning industry was conducted at two sites located in different provinces—Tannery A in Bogor, West Java, and Tannery B in Magetan, East Java. Both are SMEs. Tannery B is located in a specialized area for small-medium-sized tanneries called Lingkungan Industri Kulit (LIK), which is supervised by the Magetan Industry and Trade Office. Tannery A is not located in a specifically industrial area. Both Tanneries A and B produce custom products according to customer specifications. Some of the final products are gloves, upper shoes, and leather articles for bags. Tannery A uses salted goatskin for the raw material and Tannery B uses salted bovine hide.

Production Process

There are four main processes in both tanneries—beamhouse, tanning, post-tanning, and finishing. Beamhouse and tanning consume large amounts of water. The beamhouse process consists of soaking, liming, fleshing, deliming, and pickling. Fleshing at both tanneries was done manually. The tanning process consists of tanning and retanning. Post-tanning processes include dyeing, fatliquoring, and fixation. Finishing includes vacuum drying and toggling.

Calculation of Environmental Impact Indicators

We calculated the value of the environmental impact indicator from the accumulation of waste generated from the production process. GVSM was used to analyze the amount of waste generated from each stage of the process. There were seven sources of green waste found for each stage of the production process [18]; however, only six of these were taken into account for this study. Biodiversity loss was not calculated because of the limited amount of data available at the observed tanneries. The six sources of green waste were energy consumption, water consumption, material consumption, solid waste generation, transportation, and emissions, and their measured results from the tanning process at both Tanneries A and B are presented in the current state of GVSM in Figure 2 and

Figure 3, respectively. Water consumption was the highest among all sources of green waste at both tanneries, with washing (40%) and soaking (28%) being the biggest contributors.

Each tannery produced two types of waste—solid waste from liquids and liquid waste from solids. Green waste in the transportation category was zero because, at each tannery, materials and goods were moved manually. Emissions were derived from only liquid and solid wastes. Solid waste and wastewater management at Tannery A was poor. There is a simple wastewater treatment plant separates sludge using chemical coagulated materials and treats biowastes using bacteria; however, these practices do not meet the requirement standards for wastewater treatment plant (WWTP) effluent. Solid waste from fleshing was discharged into an open-dumping area and scraps from the shaving process were open burned behind the facility.

Waste management at Tannery B was relatively good. Liquid waste was treated in a communal WWTP managed by a government-owned agency before being discharged to the local waterbody. WWTP operational costs came from government subsidies and fees paid by each tannery in the area. The tariff was calculated based on raw hide.

Four types of solid waste were also generated from the tanneries. Waste from Tannery B came namely from scraps after trimming, fat and meat residues, scraps from splitting, and scraps from shaving. Very little of this waste has any economic value. Scraps from trimming are used in kikil (traditional food), scraps from splitting are made into skin cracker (food), and scraps from shaving were used as filler in footwear production. The remaining fat and meat residues are deposited into the landfill.

Scraps from shaving contributed 64% to total emissions generated from Tannery A. An interview with the owner revealed that the current waste management methods were used because they were cheap and easy. The owner of Tannery A was conscious of violating the regulations; however, there were not many alternative methods based on economics. Tannery A’s strategic location, which is adjacent to a waterbody, made it extremely easy to directly dispose of the wastewater. The wastewater was discharged during rainy days because the high volume of rain and flow rate dissolved and moved the wastewater very quickly. Similar problems were encountered in tanneries in other countries, such as Bangladesh [26], Albania [27], Pakistan [28], and India [29].

Based on the analysis of six sources of green waste, Tannery A generated 0.42 tons GWG, 19.97 tons WC, and 1.68 tons SWG; Tannery B generated 0.02 tons GWG, 19.77 tons WC, and 0.58 tons SWG. Using Equation (5), the EI value for the production process in Tanneries A and B were 10.41 and 9.99, respectively. The amounts of GWG and SWG in Tannery B was were smaller than in Tannery A because the former had good liquid waste management and solid waste utilization management protocols.

Calculation of Economic Indicators

The production cost for 1500 kg raw hide was used as a basis to calculate the economic indicators. Calculations of production costs for Tanneries A and B are presented in Table 3 and Table 4. Using the Equation (2), the current economic indicator for Tanneries A and B were 1.44 and 1.60, respectively. The value of the economic indicator for Tannery B was higher than that for Tannery A because of several factors, such as cheaper labor wages, shorter production times, and income from the sale of the by-products (scraps from trimming and splitting).

Table 3: Calculation of production costs and acceptance at Tannery A

	Item	Amount (IDR)
Production cost		
Fixed cost	Labor wages	23,534,259
	Depreciation of machinery and equipment	10,533,930
	Maintenance of machinery and equipment	526,697
Variable cost	Raw materials and auxiliary	32,697,168
	Utilities	615,313
Total production cost		67,907,367

Item	Amount (IDR)
Acceptance	
Product (sq ft)	4,900
Price per sqft	20,000
Total acceptance	98,000,000

Table 4: Calculation of production costs and acceptance at Tannery B

	Item		Amount (IDR)
Production cost			
Fixed cost	Labor wages		6,420,000
	Depreciation of machinery and equipment		1,410,000
	Maintenance of machinery and equipment		70,500
Variable cost	Raw materials and auxiliary		35,331,651
	Utilities		421,094
	WWTP fee		225,000
Total production cost			43,653,242
Acceptance			
Item	Weight	Price (IDR/unit)	Amount (IDR)
Product	2700 sqft	17,500	47,250,000
Scraps from trimming	120 kg	9,500	1,140,000
Scraps from splitting	561.06 kg	38,000	21,321,040
Total acceptance			69,711,040

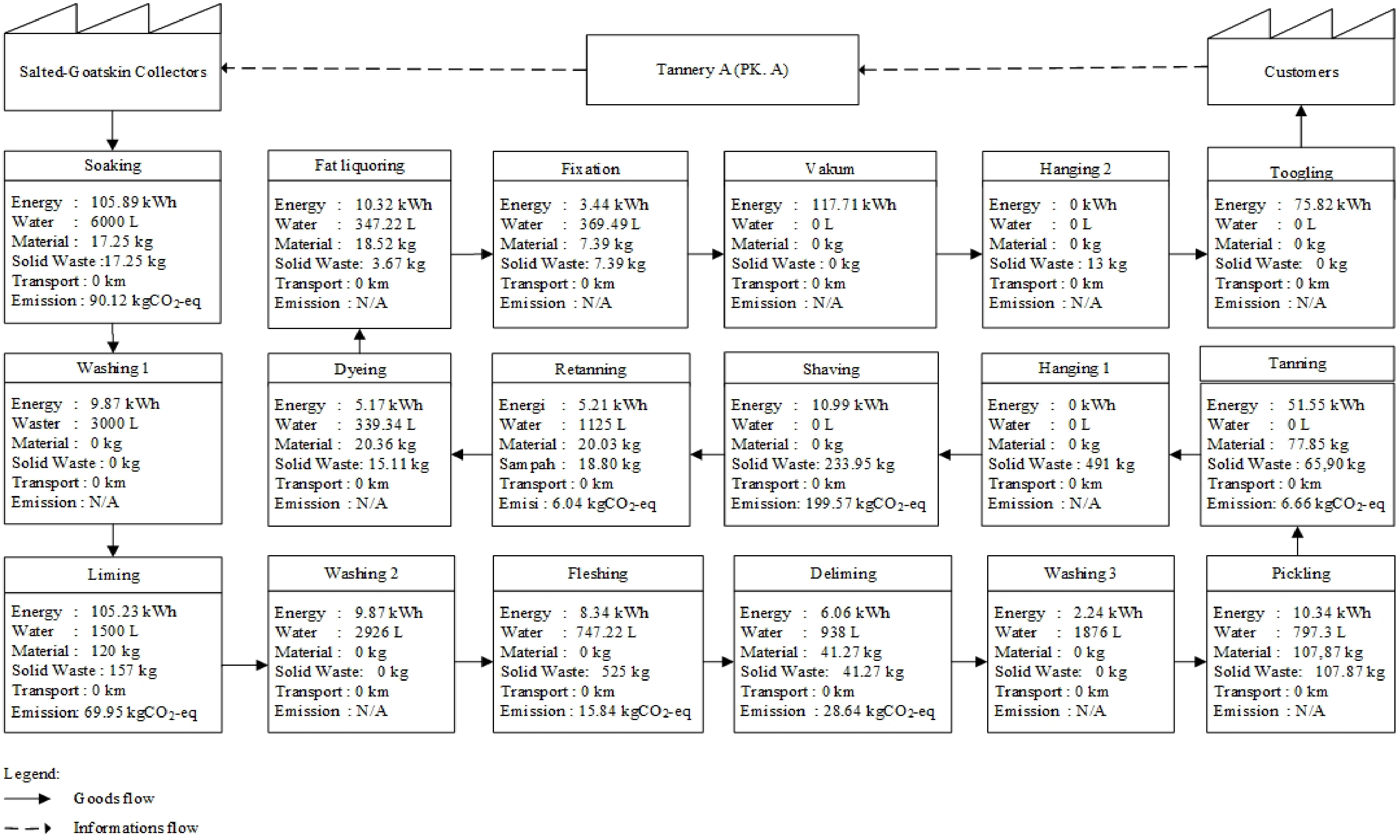

Figure 2. Current Green Value Stream Mapping (GVSM) at Tannery A

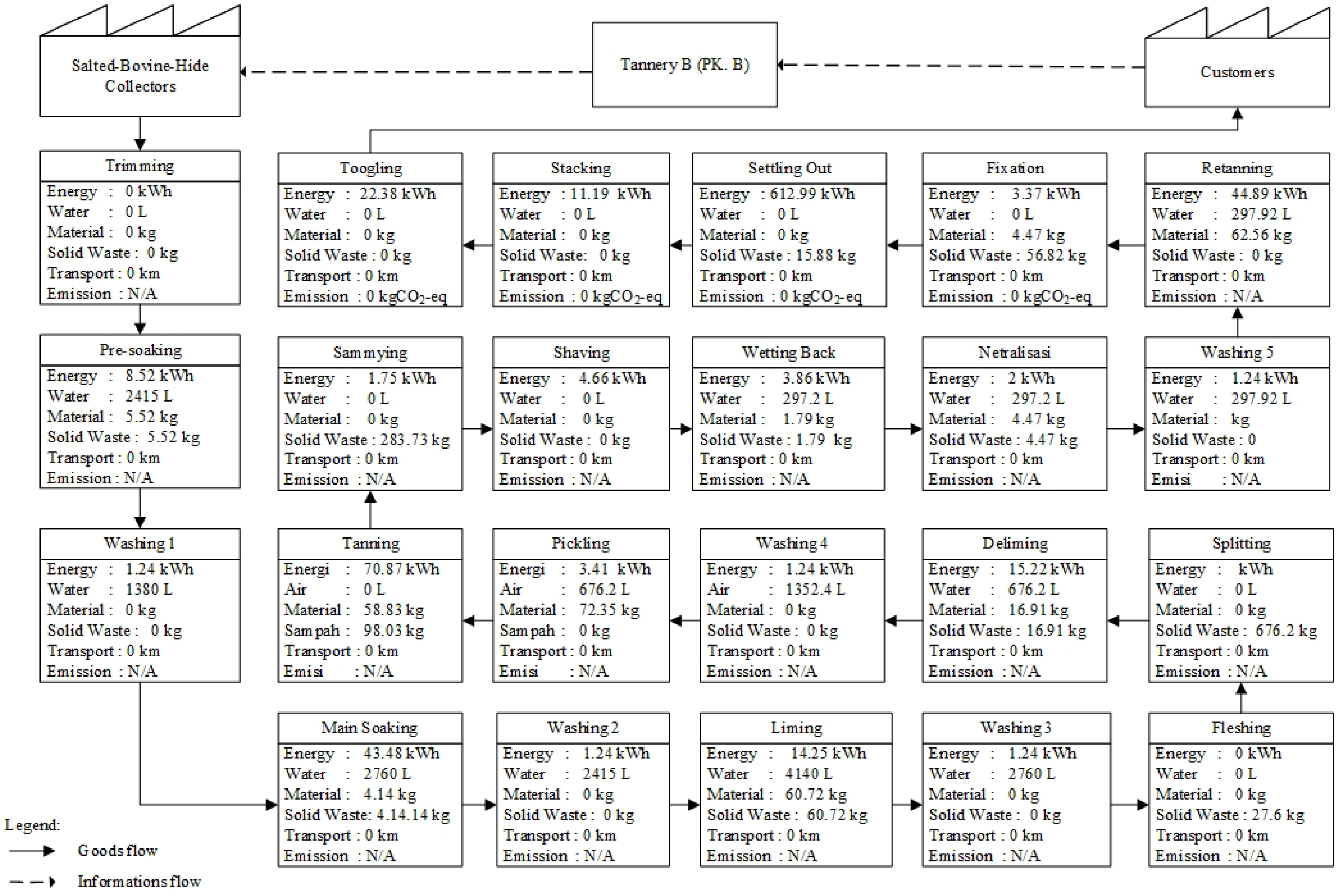

Figure 3. Current Green Value Stream Mapping (GVSM) at Tannery B

Calculation of Green Productivity Index

GPI was derived from the ratio of economic to environmental indicators. By using Equation (1), we obtained an initial GPI value at Tannery A of 0.14 and at Tannery B of 0.16, which indicated that Tannery B had a greater GP value. Good environmental management practices at Tannery B were the reasons behind its higher value. In addition, the communal WWTP in LIK helped small tanneries to properly manage their wastewater. The existence of government support through advice from experts in management systems followed by subsidized operational costs helped Tannery B to become more environmentally friendly.

Based on Figure 4, the environmental impact values at both tanneries were significantly higher than the economic indicator, which means that the environmental impacts exceeded the economic impacts. This suggests that poor management of factory performance has hindered the achievement of GP in Tanneries A and B. Based on the histogram, Tannery A had the highest environmental impact value (10.41) with an economic impact value of 1.44. Tannery A was at the same level of GPI as another tannery studied. The measurements taken by Hasanah *et al*. (2016) [30] at Tannery XYZ had a GPI value of 0.204 with an environmental indicator of 8.78 and an economic indicator of 1.79. Nevertheless, the environmental indicators in both research findings are still far above the economic impacts.

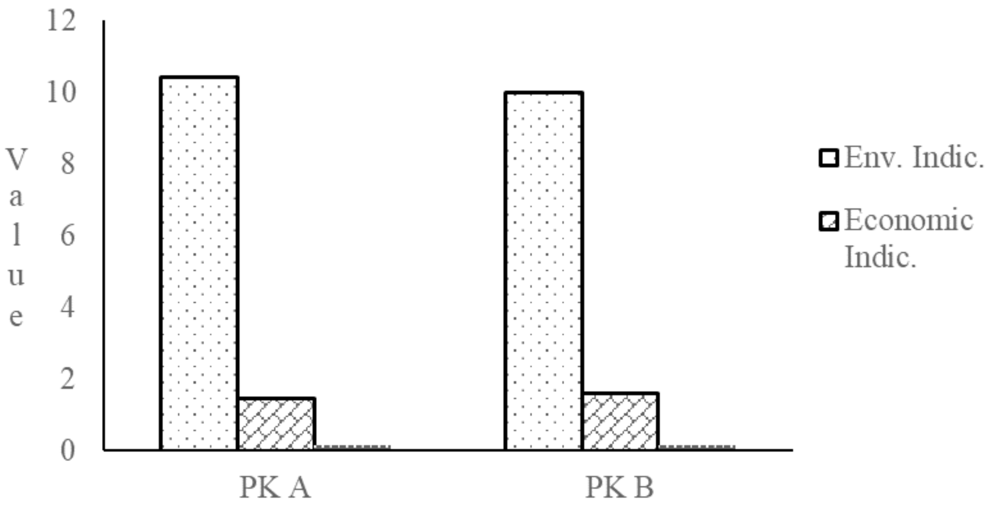

Figure 4. Environmental indicator, economic indicator, and green productivity index (GPI) of Tanneries A and B

Alternative Strategies for Green Productivity Improvement

A GP improvement strategy is derived from chosen alternatives to waste management based on the GPI value. Based on the literature study, five such alternatives that would improve the GPI value in Tanneries A and B were formulated. The alternatives are described in the following sections.

Alternative 1: Water Recycling

Water consumption in the beamhouse and during the tanning process comprises ~50% of total tannery water consumption [31]. Soaking and liming processes are the highest water consumers and accounted for 37% in Tannery A and 47% in Tannery B; therefore water-recycling techniques must be implemented to rationalize total water consumption by the tannery. In addition, reducing water consumption will reduce the volume of liquid waste. Countercurrent recycling techniques at the soaking stage can decrease water usage by up to 67% of its total water consumption. The physical properties of the leather produced using this method are proportional to the leather processed using the current processes [31, 32]. Hides move in a direction opposite that of the water. Counter-soaking schemes at Tanneries A and B are presented in Figure 5. Water recycling during the liming process also promotes a decrease in water consumption. Money and Adminis (1974) [33] conducted a study in which they reused water containing lime and sodium sulfite from the liming process more than 20 times and showed that there was a 20-fold overall reduction in water consumption. Nazer *et al.* (2006) [34] used the same technique with four cycles and reduced COD emissions by 24%, and saved water, sulfite, and sulfate by 50%, 46–76%, and 26–73%, respectively.

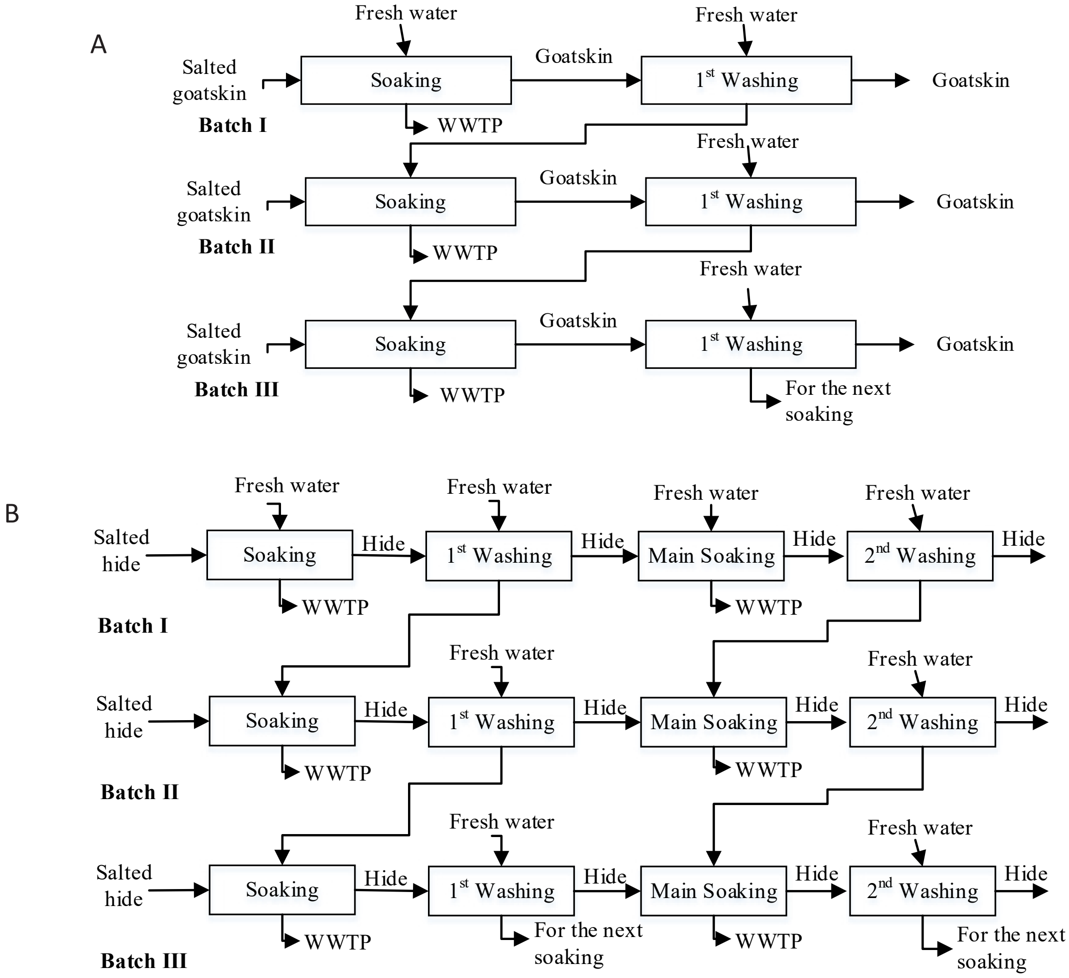

Figure 5. Countercurrent soaking scheme at Tannery A and Tannery B

According to IUE (2008) [32], this technique can save ≤40% of sodium sulfide and ≤50% lime while reducing COD by 30–40% and the nitrogen in liquid waste by 30%; however, the application is labor intensive because it requires a high level of control. In addition, this technique requires filtrating suspended materials, adjusting the temperature, and adding lime, sulfite, and water. The quality of the resulting leather could be negatively affected if there is any lack of control during this procedure because the suspended melanin and insoluble pieces of cuticle from the soluble part of the hair would be pushed into the grain by the equipment, resulting in a dirty product [32,33].

According to Rao *et al.* (2003) [31], countercurrent techniques can be applied to the liming process. In this technique, the water to be reused comes from washing the previous batch, while the used water from the liming process is directly discharged to WWTP. This technique is convenient because the washing process is done only by adding water; therefore, the water is easier to use in the liming process. By applying this technique, water consumption would be reduced by 50%. The schemes for implementing countercurrent water recycling during liming at Tanneries A and B is are shown in Figure 6. By applying this alternative at Tannery A, it is predicted that the value of environmental indicators would be reduced to 8.126. This reduction would be the result of reduced water consumption and a decrease in the total value of COD in the effluent, both of which have significant effects on decreasing environmental impacts. The GPI calculation for this alternative at Tannery A is 0.178. At Tannery B, this alternative is predicted to reduce the value of the environmental impact to 8.087 and increase the GPI value to 0.197.

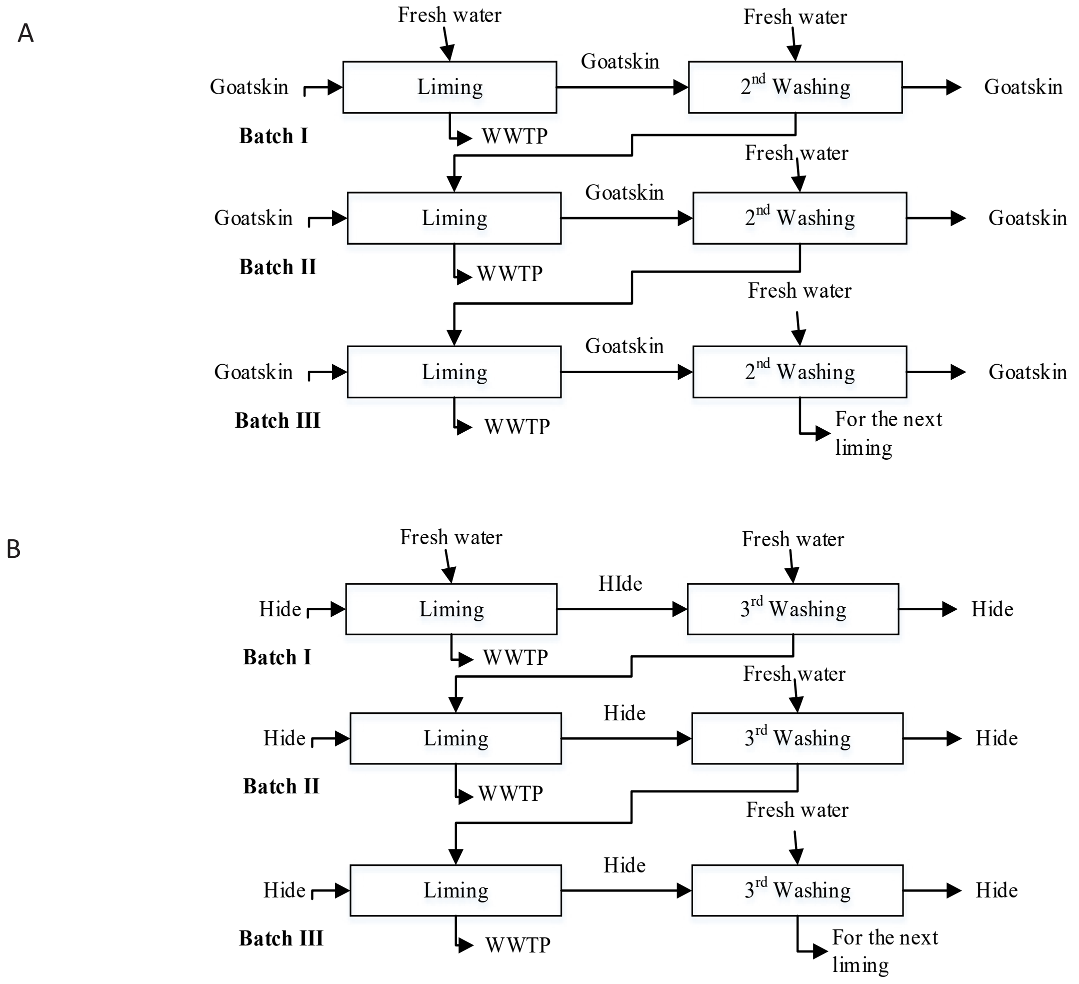

Figure 6. Countercurrent liming at Tannery A and Tannery B

Alternative 2: Using the Shaving Scraps

Scraps from shaving contribute 47% to total emissions at Tannery A, which is a result of these wastes not being fully utilized and being openly burned. According to Mardliyan (2014) [35], shaving scraps can be sold to a leather board manufacturer for Rp1500/kg. If this alternative is adopted at Tannery A, there would be a reduction in the environmental impact indicator to 10.341 and a slight improvement in the economic indicator to 1.449; however, the overall improvement in the future GPI value that would be very small compared with that of only 0.140 under initial conditions. This option is not necessary at Tannery B because the shaving scraps are used as filler in manufacturing footwear.

Another possible solution is to incorporate the shaving scraps into other products to add value and realize a more significant economic improvement. Leather scraps are composed of collagen, which can be extracted into collagen hydrolysate. Collagen hydrolysate has high economic potential and can be used in various products [36, 8], such as polycondensate adhesive substitute [37], biodegradable film [38], microencapsulated polymers [39], and superabsorbent hydrogels [40-42]; however, there is no company that performs hydrolysis; therefore, collagen hydrolysate cannot yet be efficiently extracted from the scraps for using in making these various products.

Alternative 3: Chrome Recovery

Tanneries A and B use chromium tannin as the main tanning chemical. For a one-time production process with a capacity of 1500 kg salted hides, Tannery A consumes ~65 kg chromium while Tannery B consumes ~47 kg. The results of research by Wiegant *et al*. (1999) [43] showed that only ~70% of the chromium can bind to the hide's collagen, leaving ~30% that is dissolved and discharged with liquid waste. The chromium(III) oxide (Cr_2O_3) contained in the wastewater is not toxic; however, if not immediately treated, it can oxidize into chromium(IV) dioxide (CrO_2), which is carcinogenic under acidic conditions, when exposed to heat and sunlight [44], and when reacting with oxidizing agents, such as MnO_2 [45] and chlorine, to then contaminate the groundwater [46]. From one production batch, 19.7 kg chromium waste is produced at Tannery A and 14.2 kg at Tannery B. With the chrome tanning price of ~Rp20,000/kg, it is worth Rp394,000 at Tannery A and Rp284,000 at Tannery B.

Cr_2O_3 in liquid tanning waste can be recovered for the next tanning process using a fairly simple treatment. Using this approach, Wiegant *et al*. (1999) [43] recovered and reused chromium in the tanneries in the Kanpur region of India. First, the liquid waste from the tanning process is filtered to separate the impurities. Organic materials contained in tanning wastes (fats, syntans, and high-fixation auxiliaries) can sometimes cause problems, such as grayish shades and color inconsistency, in high-quality leather production; therefore, the production staff must ensure that the fat content is within the maximum range of 45 mg/L. The dissolved chromium in the liquid waste is precipitated by adding magnesium powder or slurry at pH 8–9 and stirring for ~3 h, after which the sludge formed is separated from the liquid. The sludge is then dissolved in sulfuric acid concentrate and reused in the next tanning process [47]. This technique has also been tested by [47] and [48] using wet blue leather that has the same quality as the normal process, with 70% chrome recovery and 30% fresh chrome. A simple flow chart of this process is shown in Figure 7. The total number of chromates that could be recovered from this technique is ~23.3% of total chromium consumption [47].

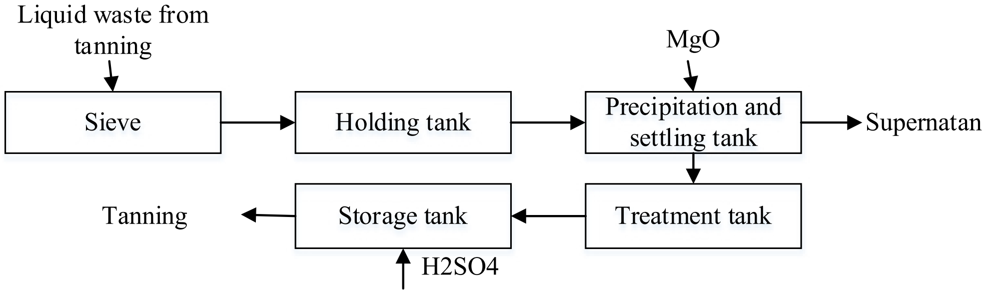

Figure 7. Flow diagram of chrome recovery

Applying this alternative is estimated to save ~Rp301,415/batch at Tannery A and ~Rp225,012/batch at Tannery B. In addition, there would be a slight increase in economic indicators to 1.451 at Tannery A and 1.492 at Tannery B. There would also be a slight decrease in environmental indicators to 10.403 at Tannery A and 9.983 at Tannery B. The environmental indicator value would not be significantly different from that under initial conditions so that an increase in GPI value would be nearly negligible or remain at 0.139 at Tannery A and 0.161 at Tannery B.

Alternative 4: Salt Recovery

Salting is the most widely used technique throughout the world to preserve hide and skin. Salt is generally inexpensive, widely available, and has good dehydration properties. Salt dispersed onto the surface of the skin/hide is expelled during soaking and discharged along with the liquid waste, which contributes to an increase in total dissolved solids (TDS). An alternative is to thresh the hide before soaking to remove some of the salt. The salt remaining after threshing the salted hide before soaking can be reused in the pickling process. This will beneficially reduce the amount of TDS in the liquid waste.

Salt was recovered from salted hide by tanneries in India during 1997–1998 under the United Nations Industrial Development Organization (UNIDO) program. Finished leather from the utilization of residual salt in the pickling process was of the same quality as that made from fresh salt. There are two ways that salt can be threshed form the skin—by using the conventional method and by using a DODECA table designed by UNIDO. Manual threshing involves holding the side of the hide and hitting it two or three times on the surface of a table. According to the workers, this technique is uncomfortable and exhausting [49]. Threshing using a DODECA table is done in a similar way; however, the DODECA surface is designed in such a way that makes it easier to remove the salts, resulting in an increase in salt release from 5% to 8%.

The salt recovery for the pickling process can reducing the consumption of fresh salt by ≤50%. The residual salt obtained from this process is first purified by preparing a 12% solution and then filtered to separate hair, tissue, sand, and other insoluble materials. The filtrate is then mixed with 300 mg/L polyaluminum chloride and 2 mg/L polyelectrolytes and allowed to stand for 4–6 h. This solution can be used in the pickling process up to 50%. The process must be controlled to ensure that the salt concentration is at 80° Bé. The recovery of residual salt is highly feasible and the process has been done at tanneries in India. If this alternative is implemented, it is estimated to save Rp117,250/batch at Tannery A and Rp194,050/batch at Tannery B. There would be a slight increase in economic indicators to 1.446 at Tannery A and 1.603 at Tannery B and a decrease in the environment indicator to 10.399 at Tannery A and 9.979 at Tannery B; however, GPI value would remain the same as that under current conditions.

Alternative 5: Constructed Wetlands for Wastewater Treatment

Treating wastewater using a constructed wetland (CW) system is a technique that can potentially be applied at Tannery A, which is without WWTP, because it is efficient, inexpensive, and powerful [50]. CW have been widely used to treat various forms of liquid waste, such as industrial, rural household, urban household, and nonpoint-source pollutants [51-53]. Tannery A is classified as an SME; therefore, a simple and inexpensive treatment for liquid waste is needed. A CW system connected to a plant is an important element that plays a role in processing liquid waste. Together with animals and microorganisms that live in the water and filler, CW has a unique flora and fauna environments. When liquid waste flows into a CW system, it is purified through filtration, adsorption, sedimentation, ion exchange, plant absorption, and microbial decomposition [50].

The wastewater from a tannery is usually turbid and malodorous because it generally contains meat and blood remnants, lime slurry, fluff, dissolved protein, salt residue, acids, residual paints, and Cr_3O_2. Cr_3O_2 can be oxidized to CrO_2, which has a toxicity rate 10–100 times that of Cr_3O_2 [54]. USEPA has classified CrO_2 as one of 17 chemicals toxic to humans, and it is considered to be one of 20 contaminants that must be addressed before being discharged into the environment.

CW plants play an important role in processing wastewater. Various plant species are known to have the ability to absorb and accumulate various types of toxic metals, phenolic compounds, azo dyes, and various other organic and inorganic contaminants. Among the CW plants, *Typha domingensis* and *Borassus aethiopium* have the highest chromium removal efficiency of 99%, *Phragmites australis* has the highest ammonium removal efficiency of 82.5% [55], and *Phragmites* (reeds) species have the highest COD removal efficiency 85% [56]. Research by Calheiros *et al*. (2007) [57] has shown that *T. latifolia* and *P. australis* propagation is highly adaptable in liquid waste from a tannery. The horizontal subsurface flow type of CW systems is recommended for use with tanneries because it is able to tolerate input fluctuations, including excess input. This characteristic is very important because, in general, the production capacity of SME tanneries in Indonesia fluctuates throughout the year. If this option is implemented and COD is reduced by 70%, the environmental indicator would increase to 8.902, but GPI would remain the same as that under current conditions.

Selection of GP Improvement Strategy Using the GP Ratio

The GP ratio is an instrument that could be useful in the process of decision making to improve GP by helping to determine whether one alternative is superior to current conditions and other alternatives. GPI and GPI ratio calculations for each alternative at Tanneries A and B are presented in Table 5.

Table 5: Comparison of the alternatives by green productivity index value

Alternatives	Tannery A				Tannery B			
	EI	Env. Indicator	GPI	GP_{ratio}	EI	Env. Indicator	GPI	GP_{ratio}
Current condition	1,44	10,41	0,14	-	1,60	9,99	0,16	-
Alternative 1	1,44	8,13	0,18	1,28	1,60	8,09	0,20	1,23
Alternative 2	1,45	10,34	0,14	1,01	-	-	-	-
Alternative 3	1,45	10,40	0,14	1,00	1,61	9,98	0,16	1,01
Alternative 4	1,45	10,40	0,14	1,00	1,60	9,98	0,16	1,01
Alternative 5	1,44	10,36	0,14	1,00	-	-	-	-
Combination	1,46	8,03	0,18	1,31	1,61	8,08	0,20	1,24

Based on the calculations, the GP ratio for all alternatives except alternative 4 is >1 at Tannery A. It expected that applying these alternatives would improve green productivity at both tanneries. The same method is applied in the calculation of the economic indicator ratio (EI ratio) and the environmental indicator ratio (Env. I ratio), as presented in Table 6.

Table 6: Comparison of alternatives by green productivity (GP) ratios

Alternatives	Tannery A			Tannery B		
	EI *ratio*	Env. I *ratio*	GP *ratio*	EI *ratio*	Env. I *ratio*	GP *ratio*
Alternative 1	1,000	0,781	1,281	1,000	0,810	1,231
Alternative 2	1,004	0,994	1,007	-	-	-
Alternative 3	1,006	1,000	1,000	1,005	0,999	1,006
Alternative 4	1,002	0,999	1,000	1,004	0,999	1,006
Alternative 5	1,000	0,995	1,000	-	-	-
Combination	1,011	0,772	1,309	1,009	0,809	1,244

Recycling the water (alternative 1) at both tanneries improves the environmental performance but not the economic performance because the EI ratio is 1. On the other hand, using shaving scraps more efficiently (alternative 2) at Tannery A improves both the economic and environmental performance, although still lower than that of alternative 1. Applying a combination of all alternatives at both tanneries results in the highest GP ratio with a higher increase in economic and environmental performance.

The GP portfolio or GP ratio is illustrated by plotting the EI and Env ratios. The GP portfolio is helpful for identifying the strengths and weaknesses of the existing alternatives [58]. Figure 8 and Figure 9 show the GP portfolio for Tanneries A and B, respectively, where the reciprocal ratio of environmental performance between the alternative and the current process is plotted against the ratio of economic performance between the alternative and the current process. If an alternative solution lies above the dotted curve, it is considered to be better than the current practice. An alternative that is located in quadrant 1 is considered to be favorably profitable from an economic and environmental perspective. The most favorable alternative is located in the upper right quadrant and the most unfavorable is located in the lower left quadrant of the portfolio [20].

In the GP portfolios for both tanneries, all alternatives are located in quadrant 1, which means that these are positive alternatives to current operations from an economic and environmental perspective. The most advantageous alternative is located at the top of the right quadrant and the least advantageous in the bottom left quadrant. These alternatives are more favorable from an environmental perspective than an economic perspective because they lie above the diagonal line in quadrant 1. Alternatives 1 and 5 at Tannery A and alternative 1 at Tannery B predict an improvement in environmental impacts but no improvement in economic impact, which means that they would increase environmental performance but not economic performance. On the other hand, alternatives 2, 3, and 4 at Tannery A and alternatives 3 and 4 at Tannery B would result in improvements of both environmental and economic performance, but it is still lower than alternative 1 at both tanneries. From both portfolios, we can conclude that alternative C, which is a combination of all alternatives, at both Tanneries A and B is the best solution because it improves both environmental and economic performance.

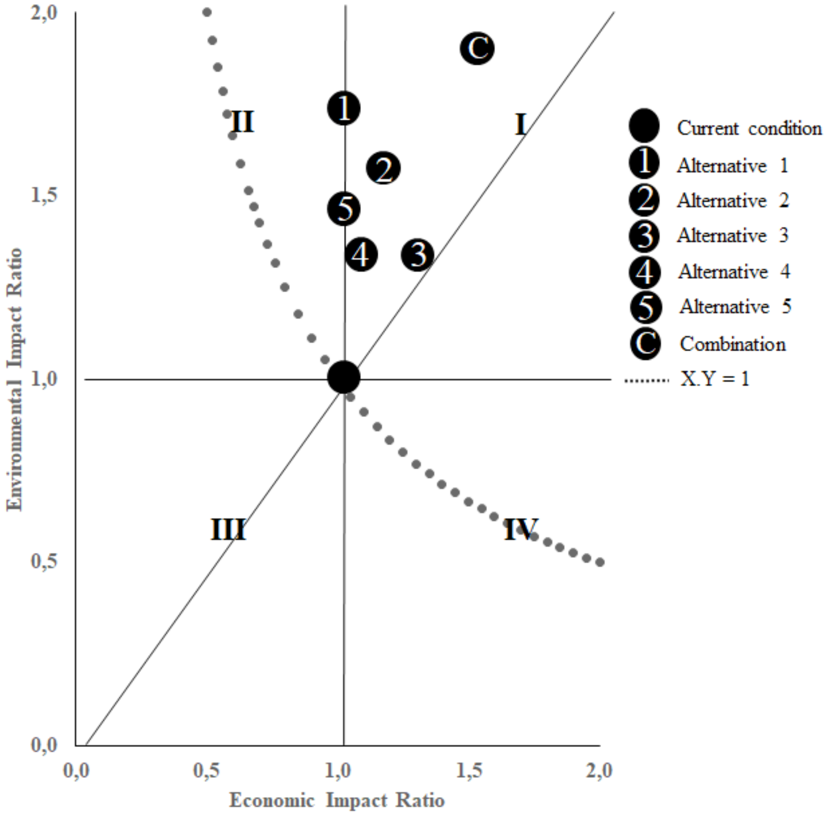

Figure 8. Green productivity portfolio of alternatives at Tannery A

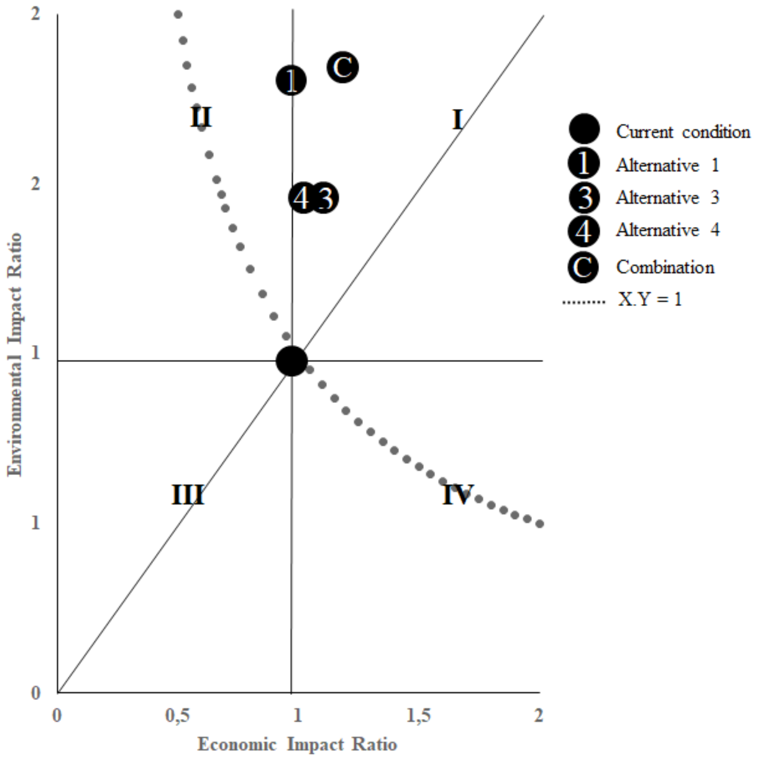

Figure 9. Green productivity portfolio of alternatives at Tannery B

Green Productivity Improvement Strategy for Small to Medium Tannery

AHP was used to determine the most applicable alternative for the SME tanneries. The AHP model can be used to calculate the weights of each quantitative and qualitative criterion [59]. Its development comprised four levels—goals, objectives, criteria, and alternatives. The most applicable alternative based on expert opinion is water recycling. Water recycling contributes more to increasing GP at the tanneries than any other alternative. Nevertheless, the other alternatives, even though they have a lower weight, might also increase GP; however, the impact would be lower compared to those from the selected alternatives.

The results of the AHP method and the GP portfolio for selected alternatives are not the same. In the opinion of experts, alternative C has the lowest weight and would require a high investment and high maintenance costs. This alternative would be too difficult for SMEs to implement. The GPI and GP ratio measurements show that water recycling provides the second highest improvement after alternative C. When independently compared to each alternative, water recycling has the highest impact on reducing environmental impacts; therefore, it is the best alternative for improving GP at both tanneries.

CONCLUSIONS

The leather-tanning processes at Tannery A result in 535.81 KWh energy consumed, 19,965.57 L water consumed, 430.54 kg material used, 1,584.21 kg garbage produced, 0 km transportation, and 416.82 kg emissions. The GPI calculation at Tannery A was 0.14. The leather-tanning processes at Tannery B result in 355.48 KWh energy consumed, 19,765 L water consumed, 291.76 kg material; 575.63 kg garbage produced, 0 km transportation, and 24.25 kg emissions. GPI at Tannery B was 0.16. The GP levels at both tanneries were insufficient because many resources, especially water, were not being optimally utilized. Using large quantities of water has an impact on the amount of liquid waste that is generated.

To increase the GPI value at both tanneries, six alternatives were developed for Tannery A and four for Tannery B as follows: water recycling in soaking and liming, using shaving scraps, recovering chromium, recovering salt, constructing CW for liquid waste treatment, and a combination of all of these strategies. Based on the highest GPI ratio, alternative C was chosen for Tanneries A and B. By applying this selected alternative, the GPI value at Tannery A would increase to 0.18 and to 0.20 at Tannery B. In the future, studies are needed on the implementation of the selected GP improvement strategies in the leather industry.

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KERATIN HYDROLYSATES EXTRACTED FROM SHEEP WOOL WITH POTENTIAL USE AS ORGANIC FERTILIZER

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KERATIN HYDROLYSATES EXTRACTED FROM SHEEP WOOL WITH POTENTIAL USE AS ORGANIC FERTILIZER

ABSTRACT. Keratin hydrolysates were obtained from sheep wool by alkaline hydrolysis at different concentrations of KOH (3%, 5% and 8%) and temperatures (75°C, 85°C, 95°C and 99°C) of the reaction medium. The protein content of the keratin extracts was between 65.54% and 87.10%. Particle measurements showed a decrease in particle size with the increase of concentration and temperature of the reaction medium. The ATR-FTIR spectra revealed specific bands to proteins and sulfur originated from keratin amino acids. The keratin hydrolysate type KerK8_{95} was further investigated as organic fertilizer for two types of wheat seeds. The results showed that the use of 5% KerK8_{95} led to the increase of the wheat stems lengths by 10.7% for Mirastar wheat and 18.3% for Tamino wheat, respectively, compared to control sample. Keratin hydrolysates are promising biopolymers as organic fertilizers in agriculture applications.

KEY WORDS: keratin hydrolysates, protein substance, organic fertilizer

HIDROLIZATE DE CHERATINĂ EXTRASE DIN LÂNĂ DE OAIE CU POTENȚIAL DE UTILIZARE CA FERTILIZATOR ORGANIC

REZUMAT. Hidrolizele de cheratină au fost obținute din lână de oaie prin hidroliză alcalină la diferite concentrații de KOH (3%, 5% și 8%) și temperaturi (75°C, 85°C, 95°C și 99°C) ale mediului de reacție. Caracteristicile fizico-chimice ale cheratinelor au arătat valori ale substanței proteice între 65,54% și 87,10%. Măsurătorile mărimii particulelor au indicat o scădere a dimensiunii particulelor odată cu creșterea concentrației și cu creșterea temperaturii mediului de reacție. Spectrele ATR-FTIR au prezentat benzi spectrale specifice proteinelor și compușilor cu sulf proveniți de la aminoacizii din cheratină. Hidrolizatul de cheratină KerK8_{95} a fost utilizat ca fertilizant pentru două tipuri de semințe de grâu. S-a obținut o creștere a lungimii tulpinii grâului cu 10,7% pentru soiul Mirastar și 18,3% pentru soiul Tamino în cazul aplicării a 5% KerK8_{95}, în comparație cu proba martor. Hidrolizatele de cheratină sunt biopolimeri cu potențial pentru utilizare ca fertilizanți organici cu aplicații în agricultură.

CUVINTE CHEIE: hidrolizate de cheratină, substanță proteică, fertilizant organic

HYDROLYSATS DE KÉRATINE EXTRAITS DE LA LAINE DE MOUTON AVEC UNE UTILISATION POTENTIELLE COMME ENGRAIS ORGANIQUE

RÉSUMÉ. Les hydrolysats de kératine ont été obtenus à partir de la laine de mouton par hydrolyse alcaline à différentes concentrations à 3%, 5% et 8% de KOH et à différentes températures à 75°C, 85°C, 95°C et 99°C du milieu réactionnel. Les caractéristiques physico-chimiques des kératines ont montré des valeurs de la substance protéique entre 65,54% et 87,10%. Les mesures de la taille des particules ont montré une diminution de la taille des particules avec l'augmentation de la concentration et avec l'augmentation de la température du milieu réactionnel. Les spectres ATR-FTIR ont montré des bandes spectrales spécifiques aux protéines et aux composés soufrés de la kératine. L'hydrolysat de kératine KerK8_{95} a été utilisé comme engrais pour deux types de blé. Une augmentation de la souche de blé a été obtenue de 10,7% pour le blé Mirastar et de 18,3% pour le blé Tamino lorsque 5% de KerK8_{95} ont été appliqués, par rapport à l'échantillon témoin. Les hydrolysats de kératine sont des biopolymères susceptibles d'être utilisés comme engrais organique en agriculture.

MOTS CLÉS : hydrolysats de kératine, substance protéique, fertilisant organique

INTRODUCTION

Wool keratin has a distinct three-dimensional structure and contains approximately 95% protein, 0.5% minerals, 5% lipids [1-3]. This structure of keratin consists (protein fibers: 50.5 wt% C, 22.0 wt% O, 16.5 wt% N, 6.8 wt% H, 3.7% S, and 0.5 wt% ash) of 2 polypeptide chains composed of different amino acids, connected with inter and intramolecular bonds [2]. Disulfide, hydrogen and ionic bonds are characteristic for the keratin structure and these lead to its stability and strength increase, and resistance to dissolution in various solvents [4, 5]. Keratins are insoluble in most solvents such as organic solvents, water, weak acids, alkaline solutions and enzymes, such as trypsin or pepsin. This biopolymer contains glycine, proline, serine and cysteine in high concentrations, while the lysine, methionine and histidine are found in a low content [6]. The ionic bonds between carboxylic anions and ammonium cations depend mainly on the pH and at the isoelectric point, at pH = 4.9, they are strong. These ionic bonds are weak in extreme conditions of acidity or alkalinity. At low pH values these bonds can

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be reduced by the protonating of carboxylic group, while the deprotonating of amino group occurs at high pH levels [7]. The solubilization of the wool structure occurs mainly by disturbing the complex structure of keratin [8]. Commonly used methods for the solubilisation of keratin are: reduction [9], oxidation [10], alkaline extraction [11], microwave irradiation [12], steam treatment [13] and ionic liquids [14]. Various biomaterials containing keratin have been manufactured and researched for their application in the field of biomedical sciences in the form of hydrogels [15-17], films [18], fibers, sponges, scaffolds [19-20] and wound patches [24]. For these applications, keratin biomaterials have demonstrated biocompatibility [25-27], unique chemical structure [28], and biodegradability [29-31]. In addition, the cheap raw materials such as wool and hair are renewable resources of this biopolymer extraction [32, 33]. In a previous paper, we demonstrated the stimulating growth effect of new emulsions, based on collagen and keratin additives, on the Tamino and Mirastar wheat seeds [34]. The aim of this paper is to investigate the influence of different concentrations of KOH and temperatures conditions for the extraction of keratin hydrolysate from sheep wool, to analyze the physical-chemical properties of keratin extracts and the potential use of keratin extract as organic fertilizer for stimulating the growth of wheat plants. As compared to other reported research [35] we have used KOH as hydrolysis agent for its nutritional potential for plant growth.

EXPERIMENTAL

Materials and Methods

Materials

Potassium hydroxide (flakes KOH) from Lachner, Neratovice, Czech Republic, ammonia solution (NH_3 25%), and anhydrous sodium carbonate (Na_2CO_3) from Chimreactiv SRL, Bucharest were used in this experiment. Sheep wool was purchased from local sheep farmers.

Extraction of Keratin Hydrolysates

Keratin hydrolysates were obtained by alkaline hydrolysis with KOH. First, the sheep wool was degreased in a solution of 1g/L NH_3 25%, 1g/L anionic detergent and 1g/L Na_2CO_3 by stirring for 6h at 40°C. After the wash process, the wool was dried in open space and then cut into small pieces (2-4 mm). Two series of keratins were obtained in varied conditions of temperature or concentration during the production process. One series of keratins was obtained at constant temperature of 99°C and with 3% ($KerK3_{99}$), 5% ($KerK5_{99}$) and 8% ($KerK8_{99}$) KOH (w/w). Second series of keratins was obtained at a constant concentration of KOH 8% (w/w) and three different temperatures, 75°C ($KerK8_{75}$), 85°C ($KerK8_{85}$), and 95°C ($KerK8_{95}$). All alkaline extraction processes were performed under mechanical stirring for 3h.

Characterization of Keratin Hydrolysates

The physical–chemical characteristics of keratin hydrolysates were analyzed according to standardized and in-house methods: SR EN ISO 4684:2006 (dry matter), SR EN ISO 4047:2008 (ash content), SR ISO 5397:1996 (total nitrogen and protein). The size particles and Zeta potential of keratins were measured by Dynamic light scattering (DLS) technique with Zetasizer Nano-ZS device from Malvern (Malvern Hills, UK). The results of the analyses were expressed as the average values of three determinations.

ATR-FTIR Spectroscopy

ATR-FTIR analysis was performed with a FT-IR/ATR spectrometer - Jasco 4200 operating in the range of 4000 to 550 cm^{-1}, with a spectral resolution of 0.5 cm^{-1}.

Wheat Seeds Treatment

Two concentrations of KerK8_{95}, 3% and 5% (w/v) in water were applied to Tamino and Mirastar wheat seeds and the growth of stems was observed up to 10 days by measurement of stems' length and compared to control sample (treated with water).

RESULTS AND DISCUSSIONS

Physical-Chemical Analyses

The main physical-chemical characteristics of keratins hydrolysate extracts obtained with 3%, 5% and 8% KOH and at constant temperature of 99°C are shown in Table 1.

Table 1: Physical-chemical characteristics of KerK3_{99}, KerK5_{99} and KerK8_{99} keratin hydrolysates

Characteristics	KerK3_{99}	KerK5_{99}	KerK8_{99}
Dry matter, %	1.71 ± 0.02	7.01 ± 0.03	7.17 ± 0.04
Ash*, %	12.22 ± 1.4	11.41 ± 1.8	11.12 ± 0.23
Total nitrogen*, %	12.86 ± 2.45	13.41 ± 0.2	14.12 ± 0.45
Protein*, %	77.77 ± 3.47	81.31± 0.46	85.49 ± 2.7
pH, units of pH	9.49 ± 0.58	9.92 ± 0.12	10.05 ± 0.68

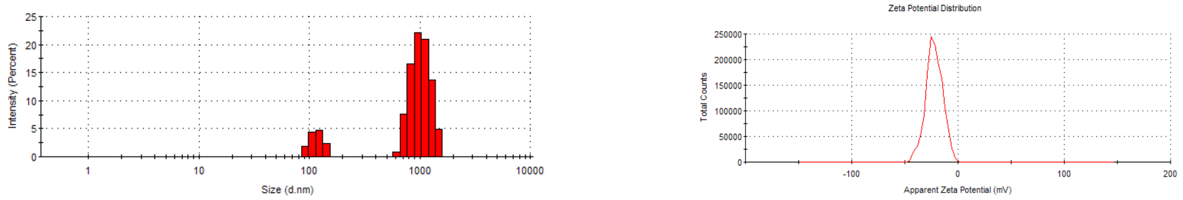
* Values are reported at dry substance.

The main physico-chemical characteristic values of the keratins reported in Table 1 increased with the increase of the concentration of KOH, from 3% to 5% and 8%. Thus, the total nitrogen values increased from 12.86% in the case of KerK3_{99} to 13.41% in KerK5_{99} and to 14.12% in KerK8_{99}; also, the protein concentration increased from 77.77% in KerK3_{99}, to 81.31% in KerK5_{99} and to 85.49% in KerK8_{99}, respectively (Table 1).

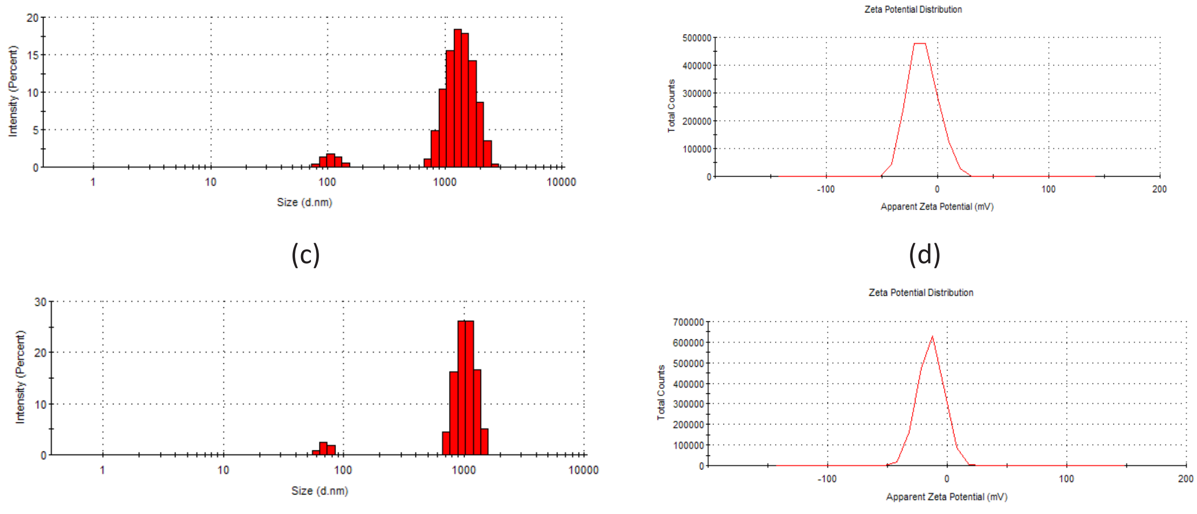
Table 2: Particle sizes, polydispersity and Zeta potential of KerK3_{99}, KerK5_{99} and KerK8_{99} keratin hydrolysates

Keratin hydrolysate	Particle populations (%) and size (nm)				Average dimension, nm	PdI	Zeta potential, mV
	Majority population 1		Majority population 2				
	Size	%	Size	%			
KerK3_{99}	116.1	13.3	1024	86.7	892.9	0.668	-22.3
KerK5_{99}	107.5	5.3	1401	94.7	1025	0.326	-13.3
KerK8_{99}	70.35	5.2	1050	94.8	1256	0.377	-13.7

DLS analysis shows the appearance of small particle sizes from 116.1 nm in KerK3_{99} to 107.5 nm in KerK5_{99}, and to 70.35 nm in KerK8_{99}, which decrease in size as the concentration of the extractive medium increases. The value of the Zeta potential is between -22.3 mV and -13.7 mV (Table 2, Figure 1) showing a decrease of their stability even the polydispersity values indicate more homogenous composition.



(a) (b)



(c) (d)

(e) (f)

Figure 1. Histograms of particle size distribution and Zeta potential in KerK3$_{99}$ (a, b), KerK5$_{99}$ (c, d), and KerK8$_{99}$ (e, f)

Physical-chemical characteristics for the second series of keratin hydrolysate extracts obtained at temperature of 75°C, 85°C, 95°C and a concentration of 8% KOH are shown in Table 3.

Table 3: Physical-chemical characteristics of KerK8$_{75}$, KerK8$_{85}$ and KerK8$_{95}$ keratin hydrolysate extracts

Characteristics	KerK8$_{75}$	KerK8$_{85}$	KerK8$_{95}$
Dry matter, %	1.48± 0.02	2.64± 0.1	4.03± 0.05
Ash*, %	17.75± 2.4	17.05± 0.98	12.16± 1.42
Total nitrogen*, %	10.81± 3.7	13.64± 1.21	14.39± 2.7
Protein*, %	65.54± 2.6	82.58 ± 1.1	87.10± 5.04
pH, units of pH	11.85± 1.04	11.19 ± 0.20	10.35± 0.89

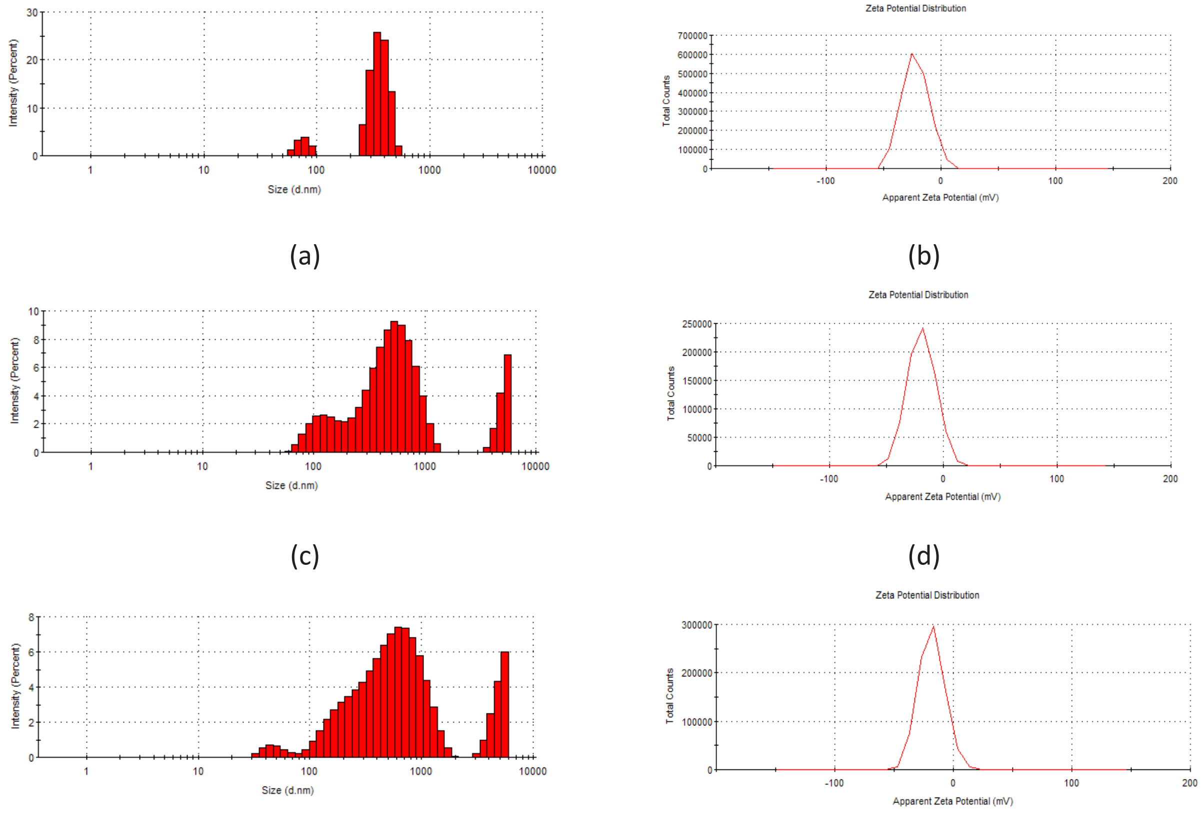
* Values are reported at dry substance.

The keratin extracts obtained at the concentration of 8% KOH in the reaction medium and temperatures of 75°C, 85°C and 95°C are characterized by total nitrogen values that increase from 10.81% in KerK8$_{75}$, to 13.64% in KerK8$_{85}$ and to 14.39% in KerK8$_{95}$ and protein values increasing between 65.54% to 87.10% (Table 3).

Table 4: Particle sizes and Zeta potential of KerK8$_{75}$, KerK8$_{85}$ and KerK8$_{95}$ keratin hydrolysate

Keratin hydrolysate	Particle populations (%) and size (nm)						Average dimension, nm	PdI	Zeta potential, mV
	Majority population 1		Majority Population 2		Majority population 3				
	Size	%	Size	%	Size	%			
KerK8$_{75}$	75.80	10.5	362.4	89.5	-	-	787.7	0.673	-22.3
KerK8$_{85}$	128.1	15.7	546.5	71.5	5086	12.8	462.4	0.764	-19.1
KerK8$_{95}$	50.22	3	575.5	83	4901	13.9	478.5	0.757	-18.2

Particle size measurement for the KerK8$_{75}$, KerK8$_{85}$ and KerK8$_{95}$ keratins shows dimensions between 50.22 nm and 128.1 nm for the first majority population, between 362.4 nm and 575.5 nm for the second majority population and between 4901 nm and 5086 nm for the third majority population. Histograms of particle size distribution show an increase in the particle size spectrum with the increase in temperature of the hydrolysis process (Figure 2). The value of the Zeta potential is between -22.3 mV and -18.2 mV (Table 4, Figure 2).



(a) (b)

(c) (d)

(e) (f)

Figure 2. Histograms of particle size distribution and Zeta potential in KerK8$_{75}$ (a, b), KerK8$_{85}$ (c, d), and KerK8$_{95}$ (e, f)

DLS analyses show that the process of hydrolysis with 8% KOH at temperature between 75-95°C, leads to more dispersed keratin hydrolysates with three majority populations and average size ranging between 787.7 nm and 462.4 nm, lower than the series of keratin hydrolysates obtained at 99°C with 3-8% KOH, having an average size between 1256-892.9 nm.

FT-IR Analyses

Figure 3 represents the ATR-FTIR spectra of hydrolysated keratin at different concentrations of KOH, while Figure 4 shows the ATR-FTIR spectra of hydrolysated keratin at different temperatures.

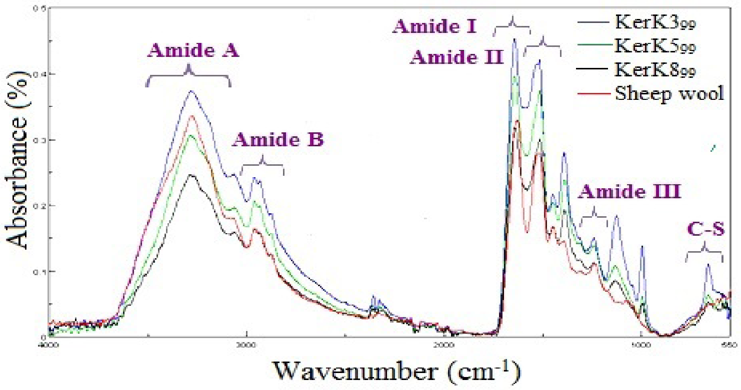


Figure 3. ATR-FTIR spectra of KerK3$_{99}$, KerK5$_{99}$, KerK8$_{99}$, and sheep wool

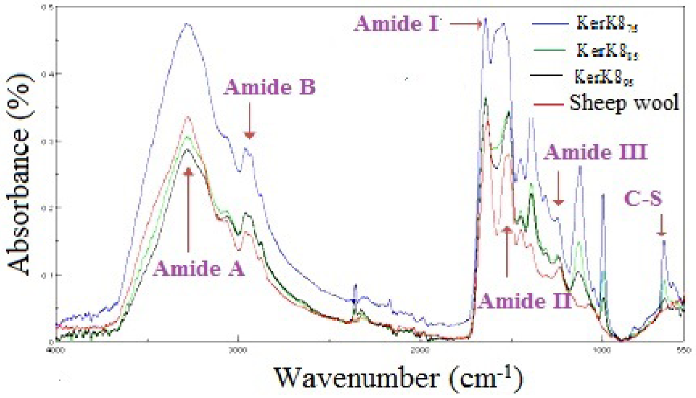


Figure 4. ATR-FTIR spectra of KerK8$_{75}$, KerK8$_{85}$, KerK8$_{95}$, and sheep wool

Keratin is easier to break into smaller peptide fragments after hydrolysis of S-S bonds between macromolecular chains [35-38]. The spectral band from 3282-3288 cm^{-1} can be attributed to the stretching vibration of -O-H and -N-H (Amide A) [39]. The absorption peak between 2960-2962 cm^{-1} is attributed to the asymmetric extent of -CH$_2$- (Amide B). The specific band from 1630-1643 cm^{-1} is assigned to the extension -C=O (Amide I) [40-42]. The absorption peaks around 1515-1517 cm^{-1} and 1237-1245 cm^{-1} correspond to the N-H band coupled to the C-H (Amide II) range and the C-H (Amide III) range, respectively. The absorption bands around 670 cm^{-1} and 578–541 cm^{-1} can be attributed to the extension of the C-S bond and the S-S bond, as well as to the deformation of the C-C bond corresponding to keratin specific sulfur compounds [35, 43–46]. The ATR-FTIR spectra show higher intensities of the specific bands for keratin hydrolysate obtained with 8% KOH at 99°C and at 95°C (Figures 3 and 4), these also having the highest concentration of protein (Table 1).

Bioactive Properties of Keratin Hydrolysate for Growth Stimulation of Wheat Plants

Based on the results presented in Tables 1 and 3, the KerK8$_{95}$ shows the higher content of nitrogen (14.39%) and relatively low particle size, compared to the other keratin extracts. For this reason, the KerK8$_{95}$ was selected as potential organic fertilizer to treat the Tamino and Mirastar wheat seeds and to monitor the plants growth over a 10-day period. The experiments were performed in laboratory conditions, as follows:

25 seeds for each type of wheat were put in contact with control (without keratin, treated only with water), 3% KerK8$_{95}$ and 5% KerK8$_{95}$, respectively. The preliminary results obtained by measuring the wheat stem length from day 7 to day 10 are plotted in Figures 5 and 6.

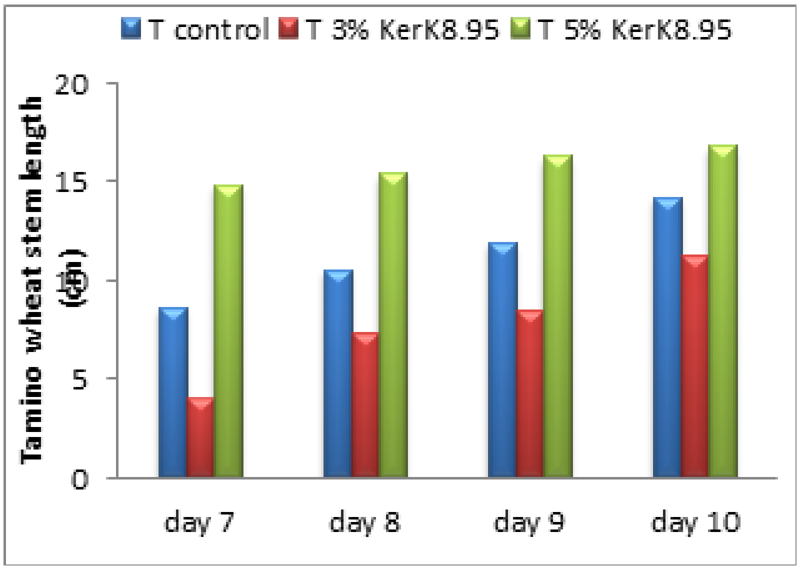


Figure 5. The effect of KerK8$_{95}$ on the increase in Tamino wheat stem length (cm) compared to control

Figure 5 shows the growth of Tamino wheat stems treated with 3% and 5% KerK8$_{95}$ during seven to ten days of the experiment. It is observed that the wheat seeds treated with 5% KerK8$_{95}$ led to the higher increase, from 14.8 cm to 16.8 cm, while in the case of Tamino wheat treated with 3% KerK8$_{95}$, the increase was smaller, between 4 cm to 11.2 cm. The seeds treated without keratin extract showed a stem development from 8.6 cm to 14.2 cm. The keratin hydrolysate KerK8$_{95}$ was used in these experiments to stimulate the development of Tamino wheat stem, obtaining the highest increase with 18.3% in the case of the treatment with 5% KerK8$_{95}$ compared to control sample.

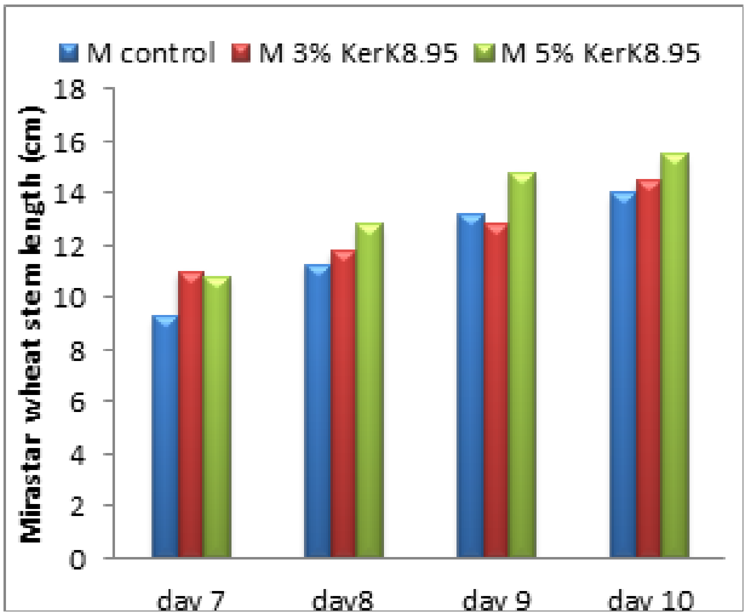


Figure 6. The effect of KerK8$_{95}$ on the increase in Mirastar wheat stem length (cm) compared to control

Figure 6 shows the growth of Mirastar wheat seeds treated with 3% and 5% $KerK8_{95}$ during seven to ten days of the experiment. It is observed that the Mirastar wheat seeds treated with 5% $KerK8_{95}$ led to the higher increase, from 10.8 cm to 15.8 cm, while in the case of seeds treated with 3% $KerK8_{95}$, the increase was between 11 cm to 14.5 cm. The keratin hydrolysate $KerK8_{95}$ was used in these experiments to stimulate the development of Mirastar wheat stem, obtaining the highest increase with 10.7% in the case of 5% $KerK8_{95}$ compared to control sample. However, all keratin extracts show nitrogen and sulfur in their structures, so they are likely to be used as potential organic fertilizer for plant growth stimulation. The next experiments will investigate in detail the influence of hydrolysed keratin on wheat seeds according to standardized procedure.

CONCLUSIONS

Keratin hydrolysates were obtained from sheep's wool by alkaline hydrolysis at different concentrations of KOH, i.e. 3%, 5% and 8% and different temperatures, i.e.75°C, 85°C, 95°C and 99°C of the reaction medium. The physical-chemical characteristics of the keratins show values of the protein substance between 65.54% and 87.10%. Particle size measurements show a decrease in particle size with the increase of concentration and temperature of the reaction medium. ATR-FTIR analyses confirmed the protein structure with increased intensities for specific bands in the case of more concentrated keratin hydrolysates and with specific bands for sulfur originated from cysteine amino acid. The keratin hydrolysate coded $KerK8_{95}$ was used in preliminary experiments as organic fertilizer to facilitate the growth of two wheat types. The results showed an increase with 10.7% of stem length for Mirastar wheat and 18.3% in the case of Tamino wheat seeds treated with 5% $KerK8_{95}$, compared to control sample. Results showed that the keratin hydrolysates obtained from sheep wool could be promising biomaterials for use as organic fertilizer in agriculture.

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TECHNOLOGY OF FREE CHROME TANNING PROCESS: OPTIMAL LEVEL OF FORMALDEHYDE AS TANNING AGENT FOR MONDOL STINGRAY (*Himantura gerrardi*)

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TECHNOLOGY OF FREE CHROME TANNING PROCESS: OPTIMAL LEVEL OF FORMALDEHYDE AS TANNING AGENT FOR MONDOL STINGRAY (*Himantura gerrardi*)

ABSTRACT. Chrome (VI) has a high level of toxicity. Formaldehyde is potential to be developed as a substitute of chrome tanning agent. The aims of this study are to explain the amount of formaldehyde bound, shrinkage temperature, tensile strength, and tear strength on Mondol stingray (*Himantura gerrardi*) leather. Pickled mondol stingray has been used as raw material. The study was divided into 4 treatments, that is P.I (formaldehyde 2%), P.II (formaldehyde 4%), P.III (formaldehyde 6%), and P.IV (formaldehyde 8%). The method used is drum tanning. Shrinkage temperatures, tensile strength and tear strength of P.I and P.II are significantly different from P.III and P.IV, but P.I is not significantly different from P.II, whereas P.III is not significantly different from P.IV. P.III is shown to improve the quality of leather stingray more than P.I and P.II, and has fulfilled the requirements of leather stingray according to SNI. 06-6121-1999. It can be concluded that the optimal level of formaldehyde tanning agent that can be used as a chrome tanning agent substitute in tanning Mondol stingray skin is formaldehyde 8% (P.III).

KEY WORDS: free chrome tanning agent, formaldehyde, *Himantura gerrardi*

TEHNOLOGIA PROCESULUI DE TĂBĂCIRE FĂRĂ CROM: NIVELUL OPTIM DE FORMALDEHIDĂ UTILIZATĂ CA AGENT DE TĂBĂCIRE PENTRU PIELEA DE PEŞTE STINGRAY (*Himantura gerrardi*)

REZUMAT. Cromul (VI) are un nivel ridicat de toxicitate. Formaldehida are potențial de utilizare ca substitut pentru agentul de tăbăcire pe bază de crom. Scopul acestui studiu este de a determina cantitatea de formaldehidă legată, temperatura de contracție, rezistența la rupere și rezistența la sfâșiere a pielii de pește stingray (*Himantura gerrardi*). Ca materie primă s-a folosit piele de pește stingray piclată. Studiul a fost împărțit în 4 tratamente, și anume: P.I (formaldehidă 2%), P.II (formaldehidă 4%), P.III (formaldehidă 6%) și P.IV (formaldehidă 8%). Metoda folosită este tăbăcirea în butoi. Temperaturile de contracție, rezistența la rupere și rezistența la sfâșiere a P.I și P.II sunt semnificativ diferite de P.III și P.IV, dar P.I nu este semnificativ diferit de P.II, în timp ce P.III nu este semnificativ diferit de P.IV. Este cunoscut faptul că P.III îmbunătățește mai mult calitatea pielii de pește decât P.I și P.II și îndeplinește cerințele referitoare la pielea de pește stingray conform SNI. 06-6121-1999. Se poate concluziona că nivelul optim de tăbăcire cu formaldehidă care poate fi utilizată ca substitut pentru agentul de tăbăcire pe bază de crom pentru pielea de pește stingray este de 8% formaldehidă (P.III).

CUVINTE CHEIE: agent de tăbăcire fără crom, formaldehidă, *Himantura gerrardi*

TECHNOLOGIE DU PROCESSUS DE TANNAGE SANS CHROME : LE NIVEAU OPTIMAL DE FORMALDÉHYDE COMME AGENT DE TANNAGE POUR LA PEAU DE RAIE (*Himantura gerrardi*)

RÉSUMÉ. Le chrome (VI) a un haut niveau de toxicité. Le formaldéhyde est susceptible d'être développé comme substitut de l'agent de tannage au chrome. Les objectifs de cette étude sont de déterminer la quantité de formaldéhyde lié, la température de retrait, la résistance à la traction et la résistance à la déchirure de la peau de raie (*Himantura gerrardi*). La peau de raie picklée a été utilisée comme matière première. L'étude a été divisée en 4 traitements, à savoir P.I (formaldéhyde 2%), P.II (formaldéhyde 4%), P.III (formaldéhyde 6%) et P.IV (formaldéhyde 8%). La méthode utilisée est le tannage au tambour. Les températures de retrait, la résistance à la traction et la résistance à la déchirure de P.I et P.II sont significativement différentes de P.III et P.IV, mais P.I n'est pas significativement différente de P.II, tandis que P.III n'est pas significativement différente de P.IV. Il est connu que P.III améliore davantage la qualité des peaux de raie que P.I et P.II, et satisfait les exigences des peaux de raie selon SNI. 06-6121-1999. On peut conclure que le niveau optimal d'agent de tannage au formaldéhyde qui peut être utilisé comme substitut d'agent de tannage au chrome pour la peau de raie est le formaldéhyde à 8% (P.III).

MOTS CLÉS : agent de tannage sans chrome, formaldéhyde, *Himantura gerrardi*

INTRODUCTION

The skin tanning process is a process to convert raw skin into tanned skin or leather [1], this process has a major role in increasing the stability of triple helix structures from the collagen matrix [2]. All skin types can be processed into leather [3]. Fish skin has been widely used as a variety of leather products that have high economic value. The favorite skin type of fish is stingray skin because of its skin structure which has fine stones, resulting in leather with special and exotic features, and can reach widths up to 30 inches [4].

Currently, the leather tanning industry is required to have an eco green technology label [5], which is an environmentally friendly industry. The big challenge facing the leather tanning industry in Indonesia in applying the eco green technology label is the dominance of the use of chrome tanning agents. Chrome is a tanning agent which has very high toxicity, especially in the form of chrome (VI) [6]. Therefore, an

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Some chrome substitute tanning agents have been developed, such as zirconium (VI) and aluminum (III) that have high durability and water resistance. Besides, there are also phosphonium, several types of syntans, and aldehydes that are more environmentally friendly and have biodegradable properties [7]. One type of aldehyde that has the potential to be developed as a chrome substitute tanning agent is formaldehyde. Formaldehyde tanning from formalin has been widely used in the leather tanning industry especially for wet white leather [8]. Formaldehyde tanning agents can easily bind to skin collagen, by forming strong complexes so that the skin becomes denser [9]. The use of chromium-formaldehyde combination tanning agents provides good effects on tensile strength, tear strength and thickness [10].

Formaldehyde has applications in many industrial processes [11], and it still permitted to be used as tanning material with a limit to the number identified in leather, where in each country has different limits [12]. Maximum formaldehyde limits detected in tanned skin for adults and direct contact with skin is 75 mg/kg, for tanned skin that is not in direct contact with the skin is 300 mg/kg, while for tanned skin which is intended for children is of maximum 20 mg/kg [13].

Some leather tanning companies have used formaldehyde as a tanning agent, with a concentration of 8-10% formalin use [3], so research that examines the optimal level of use of formaldehyde tanning agents on stingray skin so that formaldehyde use can be controlled. Therefore, this study aims to explain the amount of formaldehyde that can be bound to the skin of the mondola stingray (*Himantura gerrardi*) and the shrinkage temperature, tensile strength, and shrinkage strength that can be achieved by using formaldehyde tanning agents. Then, the results are compared with the Indonesian standards for fish skin leather (SNI. 06-6121-1999).

EXPERIMENTAL

Materials and Methods

Instruments

Thermometer, pH indicators, BCG indicators, small cutting knives, bucket, and process drums (RPM: 10-12).

Materials

40 sheets of pickled stingray skin, H_2O, NaCl, MgO, $NaHCO_3$, and formalin (with 80% formaldehyde level).

Tanning Process

This study was divided into 4 treatments: treatment I (2% formaldehyde), treatment II (formaldehyde 4%), treatment III (formaldehyde 6%), and treatment IV (8% formaldehyde). Each treatment consisted of 10 sheets of stingray skin. The pre-tanning process flow is shown in Figure 1. The tanning method uses drum tanning and formulation refers to [3] shown in Table 1.

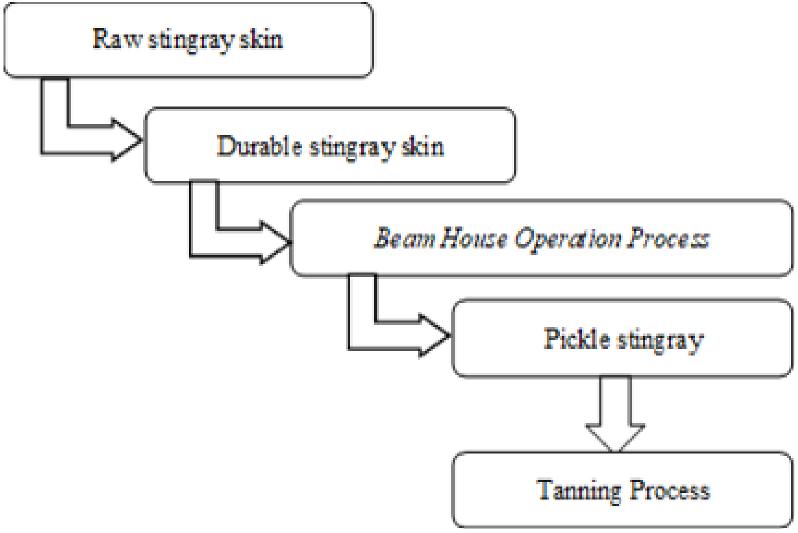

Figure 1. Scheme of pre-tanning process

Table 1: Formulation of the formaldehyde tanning process

Process	%	Chemicals	Control		
			Time (minutes)	pH	Temperature (^{0}C)
Tanning	75	H_2O			
	10	NaCl			
	P.I; P.II; P.III; P.IV	Formalin	150’		32^{0}C
	1	MgO			
	0,25	$NaHCO_3$	15’	7	
Washing	0,5	$NaHSO_3$	30’		
	2	H_2O_2	10’	6,5	
Drain					
Drying					

Data Analysis

The data obtained were analyzed using SPSS version 17.0 for Windows [14]. The analysis used is the compare means analysis (One Way ANOVA) to compare each treatment with significant value is P<0,05 [15]. Further results from wet blue stingray skin were analyzed using FTIR (Fourier Transmitted Infra Red).

RESULTS AND DICUSSION

Formaldehyde Levels

Based on the results of the analysis of formaldehyde, the levels of bound formaldehyde and free formaldehyde of stingray skin for each treatment are known (Table 2).

Table 2: Levels of formaldehyde bound

% Use of formaldehyde	Bound formaldehyde (mg/kg)	Free formaldehyde (mg/kg)
2	2136.67	0.32
4	2433.33	0.40
6	1933.33	0.27
8	2833.33	0.20

The results obtained showed that each treatment gave different results in % formaldehyde bound. The highest level of formaldehyde bound was 8% in formaldehyde use, the skin was able to bind the aldehyde as much as 2833.3 mg/kg. This shows that commonly the more formaldehyde used, the more the amount of the aldehyde will bind to the skin amine group. The most dominant reaction between formaldehyde and skin protein is the skin amine group from the amino acid lysine. The reaction between amines and formaldehyde forms a formation called methylol derivatives [16]. Aldehydes can further react with tannins from vegetable tanning agents, then form vegetable tannins to form cross-bonds with skin collagen when there are high-activity nucleophilic sites in tannin molecules [17].

Besides formaldehyde bound, the analysis of free formaldehyde was also carried out. It was known that the highest level of free formaldehyde was reached at 4% use of formaldehyde. This shows that at this level of use, the skin is able to bind a great level of formaldehyde but it also releases quite a lot of formaldehyde. The lowest level of free formaldehyde was found in 8% use of formaldehyde. This clarifies that the use of 8% formaldehyde in tanning of stingray skin yields the leather with the highest of formaldehyde bound and the lowest of free formaldehyde.

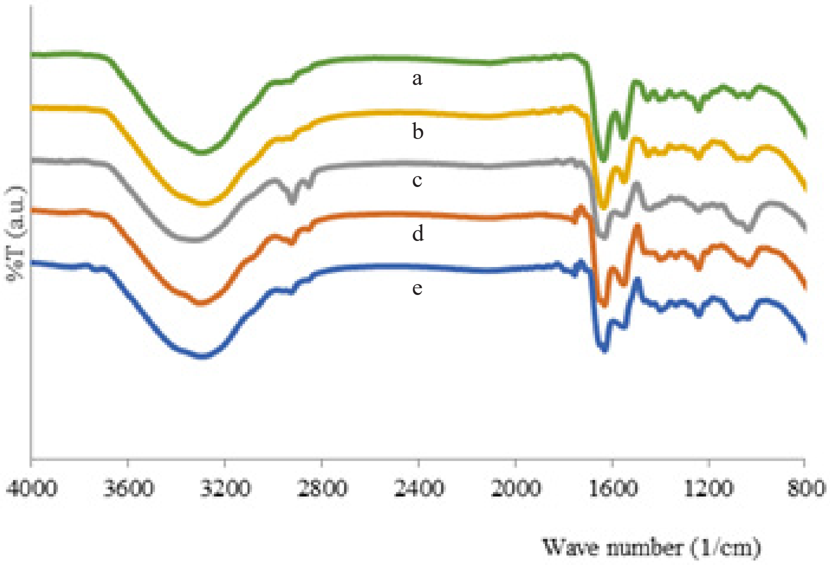

Figure 2. Infrared spectra: (a) shell skin; formaldehyde leather (b) 2%; (c) 4%; (d) 6%; (e) 8%

Analysis of sample FTIR uptake is shown in Figure 2. Pellicle has several characteristic absorption bands. The absorption band at wave number 1035 cm^{-1} appears as a bending vibration of the aromatic group of vegetable tanning agents [18]. The presence of a methylene group (-CH$_2$-) in skin collagen was identified at wave numbers 1339 and 1452 cm^{-1} as wagging vibrations and bending vibrations. Vibration of the -NH group from amide III resulted in absorption at the wave number region 1241 cm^{-1} [19, 20]. Uptake at wave number 1553 cm^{-1} is a bending vibration -NH$_2$ and a stretching vibration of CN in amide group II. The uptake of the amide group I is seen in the wave number region 1630 cm^{-1} as stretching vibration C = O [21]. The binding of N-H to amino acid groups results in uptake in the area of 3300 cm^{-1} [18].

The success of the tanning process of stingray skin with formalin is proven through infrared absorption analysis. If viewed from its absorption of infrared radiation, there was no significant change between the pellet skin absorption band with formalin tanned skin. This is due to the type of bond that is formed is not too different between the skin of the particles with formalin tanned leather. The mechanism of the reaction that occurs is shown in Figure 3. Based on the reaction it is known that the tanning process produces a Schiff base. The C = N bond on formalin tanned skin was detected through absorption bands at the wave number region 1547-1551 cm^{-1} [22]. This absorption band overlaps with bending vibrations $-NH_2$ and CN stretching vibrations on amide II groups of proteins [20]. Uptake of the CH bond causes the appearance of absorption bands at the wave number region 1440-1450 cm^{-1} as stretching vibrations of the groups $-CH_2-$ and 2853-2927 cm^{-1} as stretching vibrations of C-H asymmetry [22]. Vibration of N-H from amino acid groups was detected in regions of 3300 cm^{-1} [9]. The difference in the concentration of formalin used in the tanning process was not observed significantly in the infrared absorption band. This shows that there are no differences in the types of bonds formed due to various concentrations.

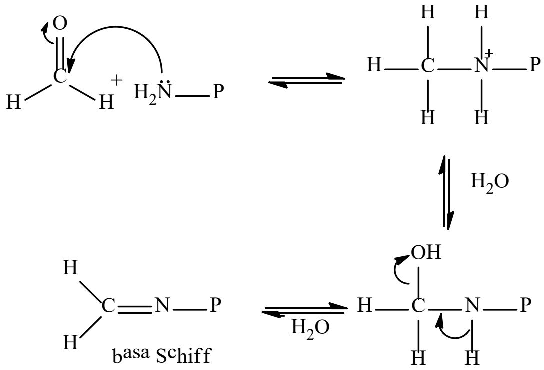

Figure 3. The mechanism of the reaction between the skin of the particles and formaldehyde (P = protein)

Formalin on the market generally contains 80% formaldehyde and has the chemical formula H_2CO_3 [23]. Formaldehyde can react with the functional group $-NH_2$ perfectly so that it can change the physical properties of collagen proteins.

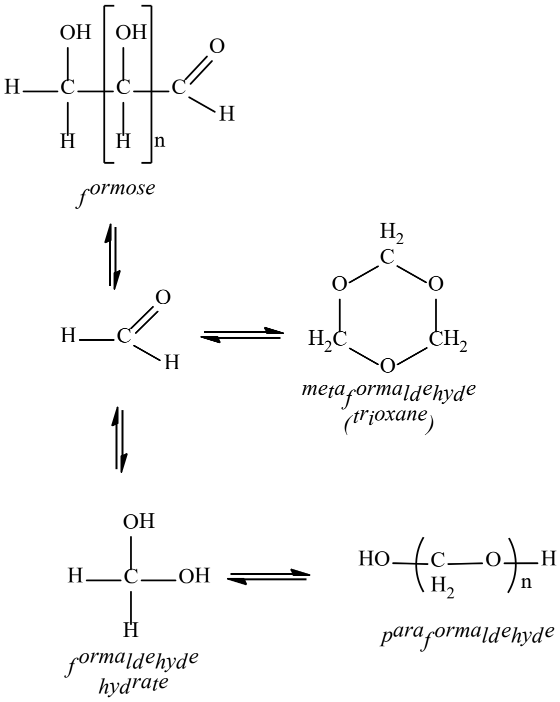

Figure 4. Structure of formaldehyde [5]

Formaldehyde is an aldehyde tanning agent with a simple structure that has 1 aldehyde group [16]. The chemical structure of formaldehyde is shown in Figure 4. Formaldehyde can be found in the polymerized form depending on the type of sample used. In addition, formaldehyde can be in the form of hydration, but generally formaldehyde species are dominated by paraformaldehyde [24]. The presence of a hydroxyl group (-OH) in formaldehyde causes tanned skin to have hydrophilic properties, so it is often used for gloves articles. Hydrophilic properties are the effects of the polymeric properties of tanning substances, which encourage separate fiber structures, and the presence of hydrogen bonding groups in polymers.

Some studies show formaldehyde reactions using NMR spectroscopy. The reaction with gelatin shows that lysine is a group favored by the aldehyde then arginine. Unexpected modifications are found in peptides containing free N-terminal amino groups or arginine residues. Adduction of formaldehyde reacts with the N tip through two steps: the N tip forms imidazolidinone, and then glycine is attached via the methylene bridge. Two covalent modifications occur in arginine-containing peptides: (i) attachment of one glycine molecule to arginine residue through two methylene bridges, and (ii) merging two glycine molecules through four methylene bridges. It is known that formaldehyde does not produce crosslinking between molecules between two primary amino groups [25].

Shrinkage Temperature

Table 3 presents the results of observations on increasing the shrinkage temperature of the results of stingray skin tanning.

Table 3: Temperature shrinkage of Mondol stingray skin (*Himantura gerrardi*)

% Use of formaldehyde	Shrinkage temperature (°C)
2	63.041 ± 0.107^a
4	66.050 ± 0.100^a
6	76.750 ± 1.405^b
8	77.333 ± 1.505^b

a and b show real differences (p < 0,05)

Shrinkage temperature is the temperature of the skin when the collagen structure shrinks by heating in a water medium or the point where the skin of the host begins to shrink at a certain temperature. This shrinkage occurs because the folds of the polypeptide chain due to the strength of the woven collagen fibers break up by extreme conditions such as heating at high temperatures [10]. The skin consists of a bundle of three-dimensional collagen fibers, and the main component of skin forming is collagen which is a well-structured fibrous protein. Skin tanning plays a major role in increasing the stability of the helical triple structure of the collagen matrix. The tanning material has varied efficiency in the stability of collagen. Thermal stability of leather is known from conventional shrinking test (CST) method and differential scanning calorimetry (DSC) method [2]. The standard shrinkage temperature used in this study is the temperature when the sample begins to experience 150 µm shrinkage [26].

Based on the results in Table 3, it is known that the use of formaldehyde with levels of 2% and 4% produces tanned skin with a shrinkage temperature (°C) that is significantly different (P <0.05) compared to formaldehyde use of 6% and 8%. The more amount of formaldehyde used increases the shrinkage temperature (°C) of tanned stingray skin. The use of 2 and 4% formaldehyde tanning agents has not been able to increase the shrinkage temperature to 70 °C on stingray skin, while the use of 6 and 8% have been able to give the effect of increasing the shrinkage temperature to more than 70 °C. This is possible because the more amount of formaldehyde is used, the higher the bond between the aldehyde and the skin amine group, so that the shrinkage temperature rises.

The tanning treatment using formaldehyde at 6% and 8% have met the SNI 06-0234-1990 standard, namely, the minimum wrinkle temperature that must be achieved by stingray skin for leather goods is 70 °C. It was known that the shrinkage temperature achieved in 6% formaldehyde use was able to increase the shrinkage temperature of tanned fish skin to 76.750 ± 1.405 °C, the results were not significantly different ($P < 0.05$) with 8% formaldehyde use which was able to increase shrinkage temperatures to 77.333 ± 1.505 °C. This shows that the use of 6% formaldehyde has been optimal for increasing the shrinkage temperature of tanned fish skin, because it gives results that are not significantly different from the use of 8% formaldehyde. Although the tanning material still provides a lower shrinkage temperature than the chrome tanner, formaldehyde has been able to give an effect of increasing shrinkage temperature according to SNI, which is at least 70 °C.

It is difficult for formaldehyde to form cross bonds with amino acid groups rather than chrome, so the shrinkage temperature achieved is not as high as when using chrome tanning material [24]. Several studies have stated that the maximum shrinkage temperature that can be achieved with formaldehyde tanning agents is 80 °C.

Formaldehyde also has a lower shrinkage temperature when compared with glutaraldehyde [27]. D-Lysine uptake is found more when the use of glutaraldehyde is increased in tanning. The amino groups both lysine and hydroxyproline are involved in the glutaraldehyde tanning reaction. It is possible that D-Lysine has improved hydrothermal stability. Increased shrinkage temperature showed increased stability of wet white skin [5].

Tensile Strength

Tensile strength is the amount of load needed to pull tanned fish skin (N/cm^2) until the collagen fibers are cut off, this study produced the tensile strength presented in Table 4.

Table 4: Tensile strength of Mondol stingray skin (*Himantura gerrardi*)

% Use of formaldehyde	Tensile strength (N/cm^2)
2	2084.803 ± 14.974^a
4	2093.982 ± 9.858^a
6	2533.022 ± 2.027^b
8	2564.758 ± 32.757^b

a and b show real differences ($p < 0,05$)

Based on the test results presented in Table 4, the concentration of formaldehyde use of 2 and 4% gave the value of tensile strength of tanned stingray skin at 2.084.803 ± 14.974 N/cm^2 and 2.093.982 ± 9.858 N/cm^2, these results were significantly different ($P < 0.05$) with formaldehyde use of 6 and 8%, which are 2.533.022 ± 2.027 N/cm^2 and 2.564.758 ± 32.757 N/cm^2. The tensile strength of tanned stingray skin in this experiment shows a value that tends to increase in line with the increase in the concentration of formaldehyde tanning agent. All treatments provide tensile strength values that meet the SNI 06-6121-1999 standard for tanned stingray skin, which is a minimum of 2.000 N/cm^2. Every tanned skin must meet the minimum SNI value because it becomes a benchmark for the manufacture of leather products [27].

Goat skin tanned with aldehyde tanner produces higher tensile strength than those tanned with chrome [28]. When viewed from the level of density, this can be caused because formaldehyde tanned leather has a higher density level than chrome tanned leather, but has a lower elongation [10]. The use of non-formaldehyde melamine resin as a retanning agent has the effect of increasing the attractiveness of the nail than formaldehyde melamine resin [29].

The main tensile strength of tanned skin is influenced by the size of fibril diameter and collagen fibers, therefore the skin that comes from older animals tends to have higher tensile strength than young animal skin because collagen fibers become increasingly stable [30]. Mondol stingray skin tanned by formalin with a concentration of 8% had a tensile strength of 2,397.85 (N/cm^2) [10], this result was lower than that reported in this study, however, the two results of this study had met SNI standards about tanned stingray skin. This is probably due to the differences in the age of stingrays used as samples in the study so that it is necessary to further study the effect of age on the tensile strength of stingray skin.

Tear Strength

Tearing strength is an important factor in determining skin quality because it shows that the maximum limit of the skin can be torn [31]. The results obtained from testing the strength of the rays of stingray skin tanned using formaldehyde tanners with different concentrations are shown in Table 5.

Table 5: Tear strength of Mondol stingray skin (*Himantura gerrardi*)

% Use of formaldehyde	Tear strength (N/cm)
2	447.174 ± 1.486^{a}
4	457.790 ± 2.998^{a}
6	627.771 ± 0.358^{b}
8	610.687 ± 2.489^{b}

a and b show real differences ($p < 0,05$)

The use of 2 and 4% formaldehyde tanners produced a tear strength of 447.174 ± 1.486 N/cm and 457.790 ± 2.998 N/cm, these results were lower than the strength of the rind skin which was tanned with formaldehyde 6 and 8% namely 627.771 ± 0.358 N/cm and 610.687 ± 2.489 N/cm with values that have met SNI 06-6121-1999 (minimum 300 N/cm). This study showed that the stingray skin was tanned with a tendency of tear strength to increase in line with the increase in the concentration of formaldehyde tanning agent.

Based on the above results it is known that the increase in the concentration of 4% formaldehyde to 6% formaldehyde had a significantly different effect, and did not differ when the formaldehyde concentration was increased to 8%. This shows that 6% formaldehyde concentration has been able to produce tear strength with a value similar to 8% formaldehyde, even in the use of 8% formalin gave a lower tear strength value of 371.52 ± 2.10 N/cm [10]. Therefore, it can be suggested that the level of use of formaldehyde used in several tanning industries will be reduced.

In addition to producing tanned leather which has a shrinkage temperature, tensile strength and strong tear that meets the SNI 06-6121-1999 standard, tanning with formaldehyde produces tanned white leather so that it is suitable for use in articles of natural color leather products. Some industries have applied tanning with formaldehyde tanners especially for woolskin and gloves articles with high sweat resistance [27].

Even though until now, chrome is still considered a “perfect” tanning agent to produce the desired tanned skin, but the use of tanning material must be stopped immediately because of its impact on health and the environment. Several studies have examined alternative tanning substitutes, including iron, aluminium, titanium, zirconium, polyphenols, polymers, aldehydes, carbohydrates. Therefore, this study has examined the optimal levels of formaldehyde use as an alternative tanner substitute for chrome.

Formalin is still freely used in the leather tanning industry; it is important to remember that formalin is a type of toxic and dangerous material. Formalin is known to interfere with the respiratory tract [32]. The glutaraldehyde aldehyde has a high level of toxicity indicated by inhibition of the growth of *Aspergillus niger* sp. [33]. Therefore, the use of formaldehyde needs to be limited including in the leather tanning industry, one of which is the determination of the maximum amount of formalin use as tanning material.

CONCLUSIONS

Formaldehyde tanning agent can be used to replace chrome. Optimal level of use of formaldehyde tanning agent is 8%, it can reach shrinkage temperatures, tensile strength and tear strength that have met the minimum standards set by SNI. 06-6121-1999.

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PREPARATION AND APPLICATION OF MODIFIED MONTMORILLONITE DISPERSION FOR CHROME-LESS TANNING OF LEATHER

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PREPARATION AND APPLICATION OF MODIFIED MONTMORILLONITE DISPERSION FOR CHROME-LESS TANNING OF LEATHER

ABSTRACT. The properties of modified montmorillonite dispersions for their use in the chrome-less leather tanning method were investigated. It is proposed to modify montmorillonite with aluminum compounds and to combine the obtained dispersions with chromium compounds for leather treatment. Modification of montmorillonite dispersions by aluminum compound within 5.0-7.0% $Al2O3$ of the weight of the mineral contributes to obtaining the most stable positively charged montmorillonite dispersions. The use of the obtained montmorillonite dispersions is effective for stabilizing the collagen structure and increasing the temperature resistance of collagen. The use of modified montmorillonite dispersions combined with a chromium tanning agent contributes to the introduction of chrome-less tanning. 0.75% of $Cr2O3$ and 3.0% of modified dispersion of montmorillonite of the weight of the pelts in conversion for mineral weight are considered the optimal consumption of chromium tanning agent.

KEY WORDS: tanning, montmorillonite, potassium aluminum sulfate, modification, dispersion, collagen, leather properties.

PREPARAREA ŞI APLICAREA UNEI DISPERSII DE MONTMORILONIT MODIFICATE PENTRU TĂBĂCIREA FĂRĂ CROM A PIELII

REZUMAT. S-au investigat proprietățile dispersiilor de montmorilonit modificate pentru utilizarea acestora într-o metodă de tăbăcire a pielii fără crom. Se propune modificarea montmorilonitului cu compuși din aluminiu și combinarea dispersiilor obținute cu compuși de crom pentru tratarea pielii. Modificarea dispersiilor de montmorilonit cu compusul de aluminiu în proporție de 5.0-7.0% $Al2O3$ relativ la greutatea mineralului contribuie la obținerea celor mai stabile dispersii de montmorilonit încărcate pozitiv. Utilizarea dispersiilor de montmorilonit obținute este eficientă pentru stabilizarea structurii colagenului și pentru creșterea rezistenței la temperatură a acestuia. Utilizarea dispersiilor de montmorilonit modificate combinate cu un agent de tăbăcire pe bază de crom contribuie la introducerea metodei de tăbăcire fără crom. Proporțiile de 0,75% $Cr2O3$ și 3,0% dispersie de montmorilonit modificată din greutatea pieilor gelatină relativ la greutatea mineralului sunt considerate consumul optim de agent de tăbăcire.

CUVINTE CHEIE: tăbăcire, montmorilonit, sulfat dublu de aluminiu și potasiu, modificare, dispersie, colagen, proprietățile pielii

PRÉPARATION ET APPLICATION D'UNE DISPERSION MODIFIÉE DE MONTMORILLONITE POUR LE TANNAGE DU CUIR SANS CHROME

RÉSUMÉ. Les propriétés des dispersions modifiées de montmorillonite pour leur utilisation dans la méthode de tannage du cuir sans chrome ont été étudiées. Il est proposé de modifier la montmorillonite avec des composés d'aluminium et de combiner les dispersions obtenues avec des composés de chrome pour le traitement du cuir. La modification des dispersions de montmorillonite par le composé d'aluminium dans la proportion de 5.0 à 7.0% d'$Al2O3$ par rapport au poids du minéral contribue à obtenir les plus stables dispersions de montmorillonite chargées positivement. L'utilisation des dispersions de montmorillonite obtenues est efficace pour stabiliser la structure protéique et augmenter la résistance à la température du collagène. L'utilisation de dispersions modifiées de montmorillonite combinées d'agent de tannage au chrome contribue à l'introduction du tannage sans chrome. Les proportions de 0.75% de $Cr2O3$ et 3.0% de dispersion modifiée de montmorillonite par rapport au poids de la peau en termes de poids minéral sont considérés comme l'utilisation optimale d'agent de tannage au chrome.

MOTS CLÉS : tannage, montmorillonite, disulfate d'aluminium et de potassium, modification, dispersion, collagène, propriétés du cuir

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INTRODUCTION

The tanning process is essential in stabilizing the collagen structure of the derma [1]. A variety of mineral and organic tanning agents are used for the tanning of the leather. Chrome tanning is the traditional option. The basic chromium sulfate is used in the production of 80% of leather in use. It is a coordination compound that effectively forms the structure of the derma. Stabilization of collagen structure by chromium compounds occurs through the formation of coordination bonds with carboxyl groups of the protein [2].

A peculiarity of chromium tanning turns out to be an inefficient use of chromium compounds, since almost 40% of tannins remain in wastewater [3]. Considering the disadvantages of using chromium compounds, scientific research on the replacement and use of rather eco-friendlier substances has been conducted for a long time. Although many papers have been written in this field of research [4-6], this type of research remains relevant due to a wide range of leather materials. Therefore, it is the environmental factor that determines the need to develop and apply chrome-less or chrome-free tanning.

One of the directions of ecologization of leather manufacturing is the use of modified montmorillonite dispersions in various technological processes such as tanning, filling, dyeing, fat-liquoring, etc. [7-9]. This is due to the special colloid-chemical properties of montmorillonite, as the main mineral of bentonite clays. Montmorillonite is an aluminosilicate and has a high exchange capacity [10]. The disorder of the crystal lattice of montmorillonite explains the high ability to disperse its aggregates and to acquire nanoscale particles. Montmorillonite has a well-developed adsorption surface, and its modification with various chemical compounds significantly changes the colloid-chemical properties of its dispersions. As a result of the modification, it is possible to obtain nanocomposites with the required charge, the nature of surface and pH to ensure effective changes in the structure of the leathers derma.

Thus, studies [11-12] proved the wastewater condition improvement at a leather tannery and the increase of environmentally-friendly manufacturing [11], and the improvement of physical-mechanical properties of leather [12], which testifies to the prospect of the use of montmorillonite for leather treatment.

In the study [13], the authors suggest the use of nanocomposite for leather tanning. The nanocomposite was prepared on the basis of acrylic acid monomers and acrylic aldehyde. Combined use of 6.0 % nanocomposite and chromium tanning agent with a consumption of 0.5 % Cr_2O_3 for tanning helps to increase the yield of experimental leather samples in thickness, tensile strength, and reduce the elastic elongation under load.

The effectiveness of leather tanning with the combined use of compositions based on modified montmorillonite dispersions and basic chromium sulfate was investigated in study [14]. To obtain the tanning composition [14], the modification of aqueous dispersion of montmorillonite with sodium carbonate and basic chromium sulfate was carried out. This method of combined tanning helps to reduce the use of chrome tanning agent by 20-25%. The positive effect of using chromium-modified montmorillonite dispersions for tanning [15] indicates the feasibility of their use for the chrome-less tanning. In order to improve the chrome-less tanning of leather, this paper proposes modification of montmorillonite dispersions by aluminum compounds, which will reduce the chromium tanning agent to a greater extent and ensure a higher level of environmental friendliness of the tanning process.

To tackle this problem, studies on the interaction of aluminum sulfate with derma collagen were performed in study [16]. According to the results of previous studies [17], it was found that modification of montmorillonite with aluminum compounds contributes to the change of structural and charge characteristics of mineral dispersions, provides the formation of stable complexes of Al (III) with carboxyl groups of collagen. With further studies, it is advised to determine the optimum consumption of aluminum compounds to modify montmorillonite dispersions and to develop an effective method for chrome-less tanning.

EXPERIMENTAL

Materials and Methods

Bentonite clays from Dashukivsky deposit (Ukraine, Cherkasy oblast) were used for the research. The content of montmorillonite in bentonite clays was 85 %.

Potassium aluminum sulfate (aluminum tanning agent), $AlK(SO_4)_2$ x$12H_2O$, – (Ukraine, Dnipro) – crystals of clear texture, colorless and water soluble crystals (aluminum oxide (III) content - 20.1%).

The basic chromium sulphate (chromium tanning agent), basicity OH/Cr=1.5, $Cr_2(SO_4)_n(OH)_{6-2n}$, – (Kazakhstan, Aktiubinsk plant of chromium compounds) is a green powder, well soluble in water. The content of chromium oxide (III) is 25.6 % and the dry residue is 89.49 %.

Gelatin acid method of production, whose amino acid composition is close to collagen was used as model preparation for the study of chemical interactions of the modified dispersions of montmorillonite with the functional groups of collagen. Gelatine of SER (Ukraine, Lisichanskiy Gelatin Factory) was used for the investigation. The properties of gelatin (GOST 11293-89): particle size < 5 mm; pH in soluble state in amount of 1.0 % = 5.6 ± 0.1 %, protein content = 83.32 ± 0.03 %; ash = 1.38 ± 0.01 %; moisture content = 15.3 ± 0.1 %.

Preparation of Modified Montmorillonite Dispersion

Montmorillonite dispersions were modified sequentially. Initially, it was planned to convert the Ca-form of montmorillonite to the Na-form of montmorillonite to disperse mineral aggregates. Next, modification by hydroxocomplexes of multicharged metals was carried out in order to change the sign of the charge on the montmorillonite surface and to give the necessary nature to its surface. Firstly, the aqueous dispersion of montmorillonite at a concentration of 100 g/l was treated with sodium carbonate. The consumption of sodium carbonate was 6 % of the weight of the dry mineral. Sodium carbonate was added to the aqueous dispersion of montmorillonite as a 10 % solution. The montmorillonite dispersion was thoroughly stirred at 50–60°C for 3 hours· The stirring speed on a mechanical stirrer was 1500 rpm· The pH of the dispersion of montmorillonite sodium form (MMTNa) was 7.0–7.5. Secondly, potassium aluminum sulfate of the weight of dry mineral in conversion for Al_2O_3 was added to the dispersion of montmorillonite sodium form. The montmorillonite dispersions treated with the aluminum compounds were mixed thoroughly and left for 24 h to complete the ion exchange processes, the pH of the modified montmorillonite dispersions (MMT_{Al}) is 3.5–4.0.

Rheological Properties of Montmorillonite Dispersion

The efficiency of sequential modification of montmorillonite and the change in the colloid-chemical properties of its modified dispersions were investigated by rheological characteristics. The rheological measurements of mineral dispersions were performed on a rotational coaxial viscometer Rheotest-2 (Germany) in the range of shear rates γ=0–1312 c^{-1} at temperatures of 20 ± 0.5°C. Montmorillonite dispersions were prepared for the experiment, the modification of which was carried out by potassium aluminum sulfate in conversion for Al_2O_3 (0.5; 1.0; 2.0; 4.0; 7.0; 10.0) % of the weight of the mineral. The structural changes of the modified montmorillonite dispersions MMT_{Al} were evaluated by the change in plastic viscosity.

Adsorption Aluminum Compounds on Surface of Montmorillonite

The adsorption of aluminum compounds on MMT_{Na} was studied using a ULAB 102UV spectrophotometer (China). To the same sample (0.5 g) MMT_{Na} in the form of 20 % paste, was added to 50 ml of potassium aluminum sulfate solution. Consumption of potassium aluminum sulfate was (1.0; 2.0; 4.0; 7.0; 10.0; 20.0) % Al_2O_3 of the weight of the mineral. Dispersion systems were periodically shaken for 24 hours. The solid phase was separated from the liquid using an OPN-8 centrifuge at a speed of 8000 rpm/min. The equilibrium concentration of Al_2O_3 in solution was then determined using a previously obtained calibration curve. The amount of adsorption (A) was calculated by the formula (1):

$$A = \frac{(C_0 - C_e) \times V}{m}, \qquad (1)$$

where, C_0 and C_e - are the initial and equilibrium concentrations of Al_2O_3 g/l;

V - volume of solution, l; m - is the mass of montmorillonite, g.

The Melting Temperature of the Gelatin

The influence of MMT_{Al} on structural transformation of the derma was investigated by the melting temperature of gelatin. The melting temperature of gelatin was used to justify the potential tanning effect of modified montmorillonite dispersions. A 5 % of gelatin solution was prepared for the study. The gelatin solution was introduced into heat-resistant tubes and then added tannins of various types and costs, shaken thoroughly and left to solidify. After freezing, the jelly gelatin was heated in a water bath at a rate of 3°C/min and the melting temperature of the jelly gelatin was fixed.

Exploration of the melting temperature of gelatin of the following samples was performed in order to compare the tanning effect of aluminum compounds and modified montmorillonite dispersions: gelatin after treatment with potassium aluminum sulfate (G+Al); gelatin after treatment with potassium aluminum sulfate and sodium formate for fixing tannins of aluminum compounds (G+Al+HCOONa); gelatin after treatment with modified montmorillonite dispersions (G+MMT_{Al}).

Consumption of potassium aluminum sulfate in conversion for Al_2O_3 for experiments G+Al and G+Al+HCOONa was formed (0; 1.0; 2.0; 4.0; 7.0; 10.0; 20.0) % of the weight of gelatin. For the G+MMT_{Al} experiment, MMT_{Al} consumption (in conversion for dry mineral) was 2.5 % of the weight of gelatin. The consumption of potassium aluminum sulfate for modifying the montmorillonite dispersion in conversion for Al_2O_3 was (0; 1.0; 2.0; 4.0; 7.0; 10.0; 20.0) % of the weight of the mineral.

IR-Spectroscopy

IR-spectroscopic research was carried out on the Fourier– IR-spectrometer TENSOR-37 (BRUKER, Germany) within 4000–400 cm^{-1}. The character and effectiveness of the interactions of functional groups of montmorillonite with active gelatin groups were evaluated by the change of intensity of light absorption of the corresponding absorption bands. According to sources [18–21], the analysis of vibration bands of absorption in the IR-spectra of resulting substances and the products of their interaction according to frequencies of vibration of characteristic groups of atoms was performed.

The identification of characteristic bands was performed for gelatin (G), gelatin treated with modified montmorillonite dispersions (G+MMT_{Al}), gelatin treated with chromium tanning agent and modified montmorillonite dispersions (G+Cr+MMT_{Al}).

Tanning Application

Four groups of four samples of goat pelts from 8×15 cm in size were formed for tanning and determined the effectiveness of the use of modified montmorillonite dispersions. The studied groups of samples were formed using the asymmetric fringe method (pieces of leather were taken from different regions of the leather). The treatment of the pelts was performed on the waste pickling liquid (density - 1.035 g/cm^3, pH - 2.8). The type of materials and their consumption are presented in Table 1.

Table 1: Consumption of materials for processing goat pelt

Material and consumption	Variant of treatment			
	1 control	2	3	4
Basic chromium sulfate, % Cr_2O_3	1.5	1.0	0.75	0.5
Montmorillonite*, % of the weight of the pelt	-	2.5	3.0	3.5
Potassium aluminum sulfate for modification of montmorillonite, % Al_2O_3 of the weight of the mineral	-	5.0	5.0	5.0

* – in conversion for the material weight

Treatment of the pelts samples for the control and studied options was carried out according to the parameters set out in the Table 2. Treatment option 1 was considered a control sample. The tanning for the control group was carried out by typical technology [22]. Only basic chromium sulfate was used, the consumption of Cr_2O_3 formed 1.5 % of the weight of the pelts (Table 2).

The option of treatments 2, 3, 4 was considered experimental and performed in stages. In the first stage of processing basic chromium sulfate with appropriate consumption was used (Table 1). Treatment of the pelts samples was within 60 minutes. In the second stage of tanning, a dispersion of MMT_{Al} was added to the liquid with the consumption of the dry mineral weight (Table 1).

Table 2: Parameters of the tanning process

Process	Chrome Tanning		Chrome-Less Tanning		Temp, ºC	Time, min	pH	Remarks
	Materials	Dosage, %	Materials	Dosage, %				
Pickling	Water* Sodium* Chloride* Sulfuric Acid*	80 8 1.2	Water Sodium Chloride Sulfuric Acid	80 8 1.2	25	25 60	2.5-2.8	
Tanning	Chrome tanning agent (in conversion forCr_2O_3)	1.5	Chrome tanning agent (in conversion for Cr_2O_3)	0.5-1.0**	25	60		
			Modified montmorillonite dispersions	2.5-3.5**	25	120		
Basification	Sodium bicarbonate	1.5	Sodium bicarbonate	1.5	25	2×20+30	3.7-4.0	overnight

* – All materials dosage used were based on limed pelts after weight

** – Dosing of materials was carried out according to the variant of treatment of the Table 1.

The Degree of Absorption of Chromium Compounds in the Wastewater

The degree of absorption of chromium compounds in the wastewater was determined using a ULAB 102UV spectrophotometer (China). For this purpose, 10 ml of tanning wastewater was selected and initial (C_0) and final (C_f) concentrations of Cr_2O_3 in the working fluid were evaluated using a previously obtained calibration curve. The degree of absorption of chromium compounds (%) during tanning was calculated by the formula (2):

$$x = \frac{C_0 - C_f}{C_0} \times 100\ \%, \qquad (2)$$

where C_0 - is the initial concentration of Cr_2O_3, g/l;

C_f - is the final (equilibrium) concentration of Cr_2O_3, g/l.

The Analysis of the Leathers after Chrome and Chrome-less Tanning

The analysis of the leather has been conducted using the official (IULTCS – International Union of Leather Technologists and Chemists Societies) methods.

The effect of MMT_{Al} dispersion on the stabilization of the derma collagen structure was evaluated by the yield of the leather by area, thickness, yield of weight and hydrothermal stability (shrinking temperature).

The Thickness and the Area of Leather and Yield of Weight of Leather

The thickness and the area of the leather were measured after chrome-tanning for control samples and after chrome-less tanning by the various experimental treatments (Table 1). The determination of leather thickness was performed according to (ISO 2589: 2019) and area (ISO 11646: 2014).

The thickness or area of experimental leather samples can be calculated based on the fact that the thickness or the area of control leather samples were 100 %.

The yield of weight of leather can calculated as the equation (3):

$$x = \frac{m}{l \times S}, \tag{3}$$

where, m - is the mass of the samples, g; l - is the average thickness of the samples, cm; S - is the area of the samples, cm^2.

Shrinking Temperature

The shrinking temperature of the leather samples was tested according to the International Standard Test Method (ISO 3380:2015).

Chemical and Physical-Mechanical Properties

Indicators of chemical and physical-mechanical properties of the leather were evaluated according to standard methods [23] and regulatory requirements for the upper shoe leather [24] (Table 3).

Table 3: Indicators of chromium tanning leather

№	Indicator	Value
1	Content in leather, %:	
	- moisture	10.0-16.0
	- chromium oxide (III)*	no less 3.7
	- substances extracted with organic solvents*	3.7-10.0
2	Tensile strength, $^{\times}10$ MPa	no less 1.4
3	Elongation at 9,8 MPa load, %	15-35

**- % on absolutely dry substance*

Content of Moisture, Minerals, Protein and Chromium Oxide

Determination of the moisture, protein and mineral content was tested according to the light industry standard methods [23]. The content of chromium oxide in the leather samples was determined according to ISO 5398-1.

Tensile Strength and Elongation at Load of Leather

The tensile strength and elongation at load of all the leathers were tested in accordance with the ISO 3376:2011.

Air Permeability and Water-Absorption by Capillary Action

Analysis of the leather samples' air permeability was tested according to the light industry standard methods [23]. Analysis of the leather water-absorption by capillary action according to (ISO 19074:2015).

RESULTS AND DISCUSSIONS

Rheological Properties of Montmorillonite Dispersion

The characteristic rheological properties of modified montmorillonite dispersions are manifested in changes in viscosity and pH levels from the consumption of the modifiers (Figure 1).

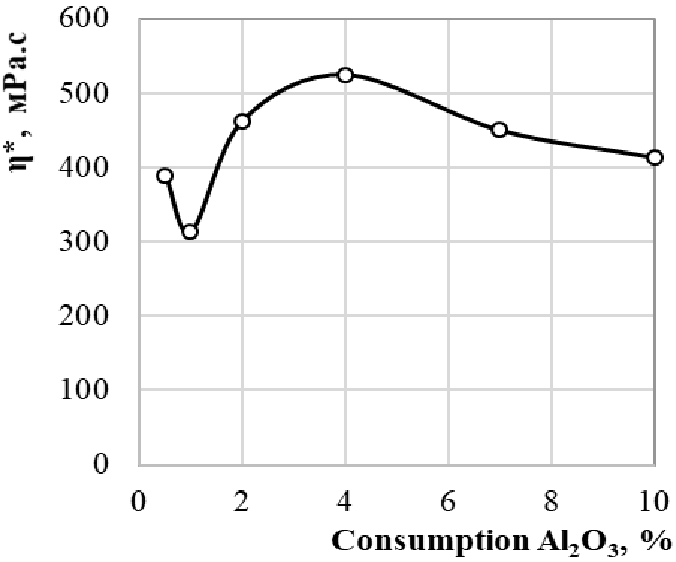


Figure 1. The curve of dependence of plastic viscosity on the concentration of Al_2O_3, 0.5; 1.0; 2.0; 4.0; 7.0; 10.0 %

The results of the plastic viscosity of the montmorillonite dispersion indicate that with increasing consumption of Al_2O_3 up to the level of 4.0 %, the mineral exchange capacity of the mineral is completely saturated. Further increase of Al_2O_3 concentration to 7.0 % is characterized by a sharp decrease in viscosity, which indicates the peptization of the dispersion. Given the above, it can be noted that at low concentrations of Al_2O_3 on the surface of the particles of montmorillonite, a gradual adsorption occurs (Figure 1). Aluminum cations first neutralize the charge of the surface of the mineral particles (consumption 0.5 - 4.0 % of Al_2O_3), and then recharge the surface to the cationic form (consumption 5.0 - 10.0 % of Al_2O_3).

Obtaining the most stable, peptized dispersions of montmorillonite occurs at the expense of aluminum compounds in conversion for Al_2O_3 within 5.0–7.0%. Increase of the aluminum compounds consumption to 10.0 % of Al_2O_3 results in a significant peptization of the dispersions and a decrease in the viscosity of the modified dispersions. At the same time, the modified dispersions are characterized by a stable pH level within 3.0–3.5 at the corresponding Al_2O_3 consumption. Such positively charged rarefied MMT_{Al} dispersions will be used in further studies.

Adsorption Aluminum Compounds on Surface of Montmorillonite

The modification of montmorillonite dispersions by aluminum compounds not only alters the rheological behavior but also affects the adsorption properties of the mineral. According to the results of studies (Figures 2, 3) it is revealed that a rapid increase of adsorption on the surface of montmorillonite at the consumption of aluminum compounds up to 7.0 % of Al_2O_3. In addition, the adsorption feature of aluminum compounds is in accordance to the Langmuir isotherm [25]. It can be assumed that the ion-exchange substitution of Na^+- ions initially occurs in the dispersion of hydroxo-cations of Al^{+3} on the surface of the mineral particles. As a result, charge neutralization and surface cation of the montmorillonite particles occur and subsequent adsorption of aluminum compounds occurs.

Further increase in the consumption of aluminum compounds up to 10-20 % of Al_2O_3 causes a slight increase in adsorption, which can be confirmed by the increase of complex formation on the surface of the modified montmorillonite and in solution.

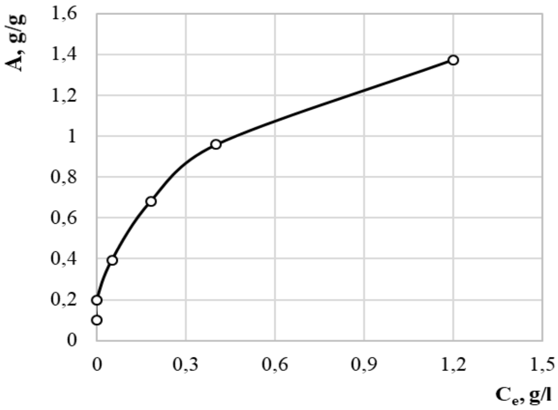


Figure 2. The adsorption level of aluminum compounds on the surface montmorillonite depending consumption of Al_2O_3

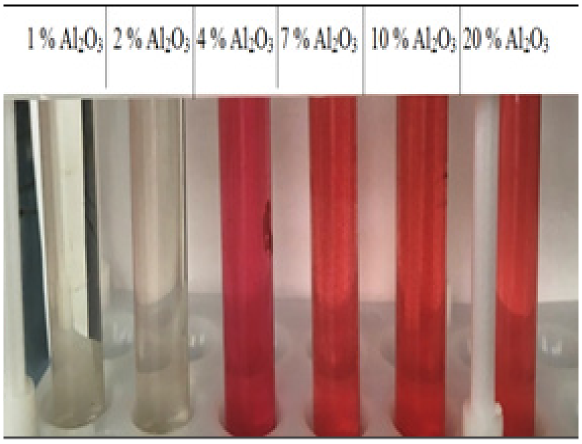


Figure 3. The adsorption of aluminum compounds on the surface montmorillonite depending consumption of Al_2O_3

A visual study of the modified montmorillonite dispersions with different consumption of aluminum compounds (Figure 3), shows that at a concentration of 1.0-2.0 % of Al_2O_3, the full saturation of the exchange capacity of montmorillonite is ensured. The coloration of the solutions by adding an aluminon indicator in bright red at a consumption level of 7.0-20.0 % of Al_2O_3 indicates that the complete saturation of the exchange capacity of montmorillonite is reached and the aluminum compounds are found to be in excess. The presence of excessive amounts of aluminum compounds in the montmorillonite dispersion may contribute to additional action tannin on the derma collagen during tanning.

At the same time, 5.0–7.0 % Al_2O_3 of the weight of the mineral can be considered the optimal consumption of potassium aluminum sulfate for modified montmorillonite dispersion. Under these conditions, diluted positively charged montmorillonite dispersions are obtained, which can be effectively applied in the tanning process.

Interaction of Modified Montmorillonite Dispersion with Collagen of Derma

Interaction of Modified Montmorillonite Dispersions on Melting Temperature of Gelatin

The results of the studies show an increase in the level of melting temperature of gelatin after treatment of aluminum compounds with tannins (Figure 4) and modified montmorillonite dispersion (Figure 5), which indicates a change in the state of the internal structure of gelatin. The results of melting temperature studies are presented in Figures 4–5.

Analysis of the results of the melting temperature for the G+Al and G+Al+HCOONa experiments indicates two distinctive features. At a consumption of 1.0-4.0 % of Al_2O_3 of the weight of gelatin for the G+Al experiment, the melting temperature rises to 45.6°C. However, a further increase of Al_2O_3 consumption in the range of 7.0-20.0% of Al_2O_3 of the weight of gelatin leads to a gradual decrease of the indicator to the level of 40.8-37.8°C, which is 17 % less than the maximum value. The melting temperature of gelatin without treatment with aluminum compounds was 36.7°C.

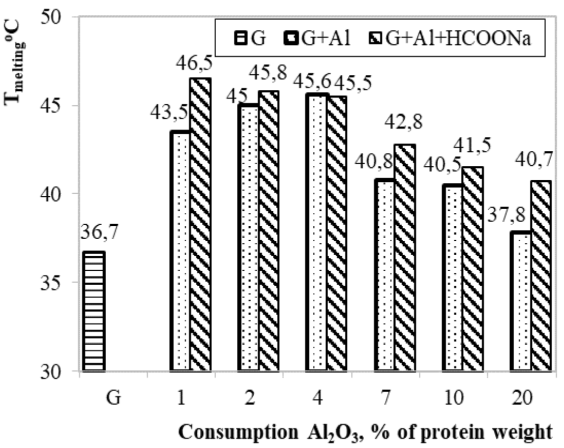


Figure 4. Melting temperature of gelatin after treatment of aluminum compounds and with fixing sodium formate

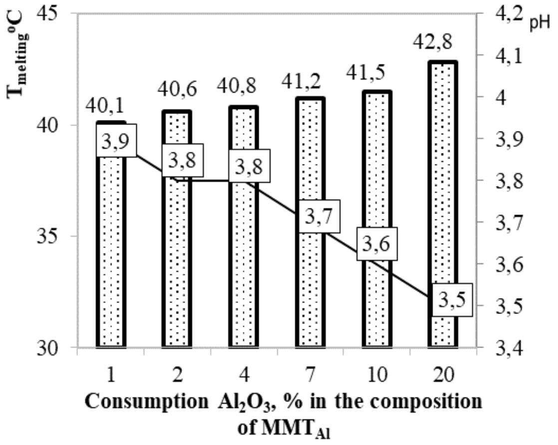


Figure 5. Dependence of the melting temperature of G+MMT$_{Al}$ and pH on the consumption of aluminum compounds

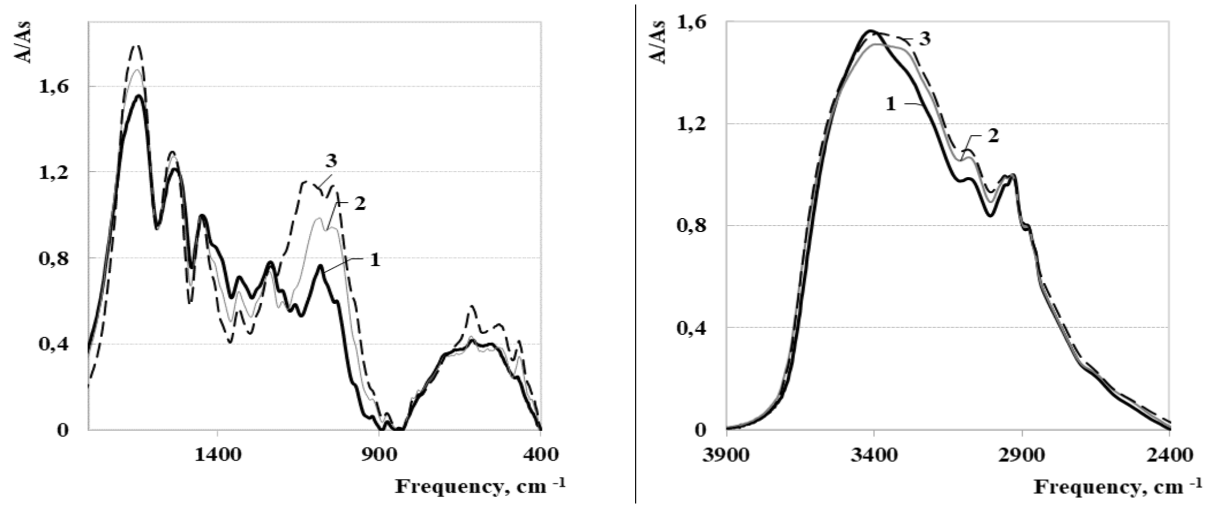
For G+Al+HCOONa experiments, an increase in the level of gelatin melting temperature compared to G+Al experiment was observed, indicating an increase in the complexation in the protein system [16]. In general, increasing the consumption of aluminum compounds more than 7.0 % of Al_2O_3 of the weight of gelatin is not advised, since there is a decrease in the melting temperature of gelatin in all situations. This may be due to the destabilization of the gelatin structure and the decrease in the pH of the medium owing to the presence of a large number of sulfogroups in the potassium aluminum sulfate, which causes a peptization of the gelatin system.

A study of the melting temperature of the G+MMT$_{Al}$ experiments (Figure 5) shows that the use of MMT$_{Al}$ dispersion promotes an increase in the melting temperature of gelatin. There is a structuring of gelatin at consumption above 7.0 % of Al_2O_3 of the weight of the mineral. Given that 2.5 % of the mineral dispersion was used to process gelatin in conversion for mineral weight, and the consumption of modifying montmorillonite was 1.0-20.0 % of Al_2O_3, the result of calculating the consumption of Al_2O_3 of the weight of gelatin was only 0.025-0.5 %. Thus, even at such minimum consumption of aluminum compounds, it is possible to increase the melting temperature of gelatin by 10-14 % compared to untreated gelatin. The introduction of modified montmorillonite dispersions promotes complex transformation of the collagen structure. This creates the formation of chemical bonds between collagen, chromium tanning agent, aluminum tanning agent and montmorillonite.

The pH is at 3.5-3.9, which is optimal for tanning. Therefore, the results of the analysis of the melting temperature of the gelatin after treatment with MMT$_{Al}$ dispersions indicate the possibility of their use for leather tanning. In order to more effectively structure and increase the level of derma collagen resistance in the process, it is advised to use modified montmorillonite dispersions with other tannins. Considering that aluminum tanning does not provide high hydrothermal resistance of derma [20], it is advised to use combined tanning using chromium compounds.

Identification of Chemical Interactions between Collagen Derma and Modified Montmorillonite

Spectra of G+MMT$_{Al}$ (Figure 6) are different from the spectra of the G+Al sample in the range of valence –NH fluctuations of nitrogen-containing groups of gelatin and valence vibrations of structuring hydroxyl groups $Al(OH)_3$. The band of 3462 cm^{-1} is related to OH-vibrations of the molecules of absorbed water that take part in hydrogen bonds. Appearance of the medium peak at 3387 cm^{-1} and more intensive at 3354 cm^{-1} for the sample G+MMT$_{Al}$ indicate the interlayer exchange cations and are proved by the existence of maximum in the IR-range at 3080 cm^{-1}.



a *b*

Figure 6. Characteristic absorption bands of G (1), G+MMT$_{Al}$ (2), G+Cr+MMT$_{Al}$ (3) in the frequency range: a – 3900 – 2400 cm^{-1}; b – 1900 – 400 cm^{-1}

The bands of valence fluctuations of Amides I, II and III for the G+MMT$_{Al}$ sample reveal a certain influence on the structure of gelatin. In this case, the area under the peaks of 1663 cm^{-1}, 1532 cm^{-1} and 1241 cm^{-1} decreases in comparison with maxima in the spectrum of the G sample.

In the spectral range of 1161–1016 cm^{-1}, valence fluctuations of CN-groups, sulfogroups and NH$_3^+$ vibrations of gelatin, valence fluctuations of Si(OH)Al, as well as vibrations of free surface deformation of OH-groups of SiO vibrations are manifested for the sample G+MMT$_{Al}$.

In the range of spectrum of 780–615 cm^{-1} for the G+MMT$_{Al}$ sample, there are the bands of valence fluctuations and deformation vibrations of peptides (Amide V and Amide VI) and the aluminum complex. In the spectrum of the G+MMT$_{Al}$ sample, the wide absorption band is divided into four maxima at 780 cm^{-1}, 699 cm^{-1}, 659 cm^{-1} and 615 cm^{-1}. This can indicate the participation of OH-groups in the formation of hydrogen interaction Si–OH···O–C.

Appearance of peaks of 525 cm^{-1} and 426 cm^{-1} for the G+MMT$_{Al}$ sample, which characterize deformation vibrations of C=O-groups, O–Si–O and valence fluctuations of Al–O may indicate the formation of hydrogen bonds between the functional groups of gelatin and MMT$_{Al}$ of the Si–O....H–N type with NH-groups of protein and Si–O....H–C with CH-groups of protein [18].

For the spectrum of the sample of G+Cr+MMT$_{Al}$ (Figure 6), valence fluctuations of OH-groups in the range of 3400 cm^{-1} are the most sensitive to the presence of hydrogen bonds. Their location depends on the concentration of water, conditions of obtaining the spectra that are easily separated from the absorption bands of other groups [21].

In the IR-spectrum of the G+Cr+MMT$_{Al}$ sample, adsorption moisture is characterized by wide absorption bands in the interval of 3500–3000 cm^{-1}. A wide adsorption band with two peaks at 3391 and 3379 cm^{-1} shifted to the low-frequency region, but with a larger area in comparison with the G+MMT$_{Al}$ sample, is caused by valence vibrations of H-bound OH-groups and their compactness. This fact is proved by a decrease in the sample of weakly bound moisture, characterized by the peak maximum at 3077 cm^{-1} (Figure 6a).

Results of analysis of the spectra of the G+Cr+MMT$_{Al}$ have more active coordination bonds between chrome and OH-groups of protein. It is also proved by the interval of the spectrum of 1667–1242 cm^{-1}, which characterizes the existence of valence groups of Amides I, II and III (Figure 6b). At the same time, bands of 1119–1041 cm^{-1} correspond to vibrations C–N of valence groups, NH and NH$_3^+$ deformation vibrations, as well as sulfogroups of chromium and aluminum complexes.

The shift of the peak of 1041 cm^{-1} by 25 cm^{-1} to the high-frequency range, as well as the shift of the bands of 754 and 609 cm^{-1} and an increase in their area, which is characteristic of COO$^-$, Me–O groups (Figure 6b), can indicate the formation of coordination bonds mainly between the ions of chromium and carboxylic groups –COOH of the side chains of gelatin. Also, the predicted strengthening of the structure of the treated gelatin may be a manifestation of the increase in siloxane groups caused by the hydroxo-complex ions Cr (III) and Al (III) located between the silicate layers of the mineral due to compression of the OH groups. As a result of a comprehensive study of the chemical interactions of modified montmorillonite dispersions with collagen, it is possible to state the feasibility of using modified montmorillonite dispersions for leather tanning.

Results of the Tanning Performance

An analysis of the degree of absorption of chromium compounds during tanning (Table 4) indicates that the highest absorption level at 86.9 % is distinctive to treatment option 3. The control treatment 1 is characterized by a lower absorption rate of 65.8 %. For option 4, the absorption rate was 82.2 %. Meanwhile, the initial consumption for chromium compounds was 3 times lower than that of the control treatment. The use of the modified montmorillonite changes the mechanism of chromium tanning. The spatial structure of the mineral and its large specific surface area create additional active centers for the chemical interaction of aluminum and chromium compounds with collagen of the derma. Montmorillonite particles enhance the adsorption and fixation of chromium compounds in the structure of the derma, which increases their degree of absorption in the derma.

Table 4: Analysis of wastewaters

Index	Variant of treatment			
	1 control	2	3	4
The degree of absorption of chromium compounds, %	65.8	81.5	86.9	82.2

For the control and experimental samples, an organoleptic analysis was performed. It was found that all the experimental samples (treatment options 2-4) were fuller, more elastic and softer compared to the control samples.

After modification the dispersion of montmorillonite contain polydisperse particles. Nano- (53.8-67.7 nm) and micro- (388.0-472.1 nm and 913.8-1128.0 nm) particles are present in the dispersion [26]. The modified montmorillonite dispersions can provide the formation of the derma structure at the level of fibrils and fibers [27]. At the same time screening of the structural elements of the derma is happening, which prevents them from sticking together, increases the area, thickness of the leather and improves the formation of the volume of the derma (Table 5).

Indicators of structure formation of the obtained leather are presented in Table 5 and estimated by the level of yield of leather thickness, area and shrinking temperature (Table 5).

Table 5: Indicators of structure formation of the derma

Index	Variant of treatment			
	1 control	2	3	4
Yield of leather, %				
– area	100.0	104.4	105.9	102.6
– thickness	100.0	104.4	108.5	108.4
Yield of weight, g/cm^3	0.462	0.497	0.511	0.485
Shrinking temperature, ˚C	103	102	102	101

An analysis of the derma structure formation indices (Table 5) shows that all prototypes have increased yield of leather area and yield of leather thickness. The biggest increase in thickness corresponds to the treatment options 3 and 4. The sample 3 is characterized by an increase of 5.9 % of the area output. This may be connected with the use of modified montmorillonite tannin composition on its effect on the formation of derma collagen structure.

Furthermore, almost identical hydrothermal stability as in the control of 103°C is achieved for all experimental options of treatment at lower consumption of chromium compounds during the tanning process. In this case, the decrease of consumption of chromium tanning agents by 33-67% in the experimental treatment will facilitate the rational use of chromium compounds and ecologization of the leather manufacturing.

The analysis of the chemical composition of the samples (Table 6) shows that the moisture content in all the experimental samples meets the standard requirements [24]. Due to the use of montmorillonite dispersions during the tanning process, the content of mineral substances is higher in the experimental samples and forms 11.0–11.6% compared to the control samples. In addition, in the control samples, the content of the protein substance was 2.4–3.1% higher than in the experimental samples. This can serve as evidence of better structuring and formation of the derma using a modified montmorillonite.

Analysis of the content of Cr_2O_3 in the leather shows that all samples meet the standard requirements (Table 3). In this case, the control samples contain 4.4 % of chromium oxide (Table 6) and have a low degree of adsorption of chromium compounds during tanning (Table 4). It should be noted that the content of Cr_2O_3 in leather from variants of treatment 3 and 4 is quite high at 50-67 % lower consumption of chromium tanning agent at the beginning of tanning compared to the control. The high content of chromium compounds in leather is the result of a more effective interaction of chromium compounds with the collagen of the derma. This is due to the presence of additional active centers of modified montmorillonite, which enhance the chemical interaction of the tanning agents.

As a consequence, chromium compounds in the derma structure are better bonded and fewer compounds get into the wastewater.

Table 6: Indicators of the chemical composition of the leather

Indicator	Variant of treatment			
	1 control	2	3	4
Content in leather, %:				
– moisture	14.5	14.2	14.1	13.8
– mineral substances*	10.7	11.6	11.0	11.1
– Cr_2O_3*	4.4	4.1	4.2	3.8
– protein substance*	64.7	62.3	62.0	61.6
– substances extracted with organic solvents *	6.7	6.8	6.5	6.4

* *in conversion for absolutely dry substance*

Moreover, the physical-mechanical properties of the obtained leather samples were investigated. According to the test results (Table 7), the control and experimental samples meet the standard requirements [24].

Table 7: Indicators of physical-mechanical properties of leather

Indicator	Variant of treatment			
	1 control	2	3	4
Tensile strength, ×10 MPa	1.85	1.95	2.01	1.92
Elongation at 9,8 MPa load, %	35,6	29,4	31,5	31,3
Specific elongation at rupture, %	57.4	49.0	51.8	54.4
Conditional modulus of elasticity, H/m^2	0.43	0.32	0.26	0.29
Rigidity, H	5.1	4.9	4.8	4.9

The data analysis in Table 7 shows that the level of tensile strength in the experimental samples is higher by 3.8–8.7% than that of the control. In addition, the use of the modified montmorillonite dispersion during the tanning reduces the elongation at 9.8 MPa load of on 11.5–17.4% and at rupture of 5.2–14.6% for the experimental samples compared with the control samples. Experimental samples have a lower level of rigidity and conditional modulus of elasticity compared to the control, which confirms the effectiveness of the use of the modified montmorillonite dispersion.

It is proved that the use of modified montmorillonite dispersion for tanning also affects the formation of hygienic properties of the leather (Table 8). As a result of the introduction of modified montmorillonite dispersion, the resistance to water-absorption by capillary action fractionally increases (except for the option 2). All samples have a high level of relative air permeability.

Table: 8 Hygienic properties of the leather

Indicator	Variant of treatment			
	1 control	2	3	4
Water-absorption by capillary action, %:				
– after 2 hours	182.3	188.6	175.1	169.3
– after 2 and 24 hours	191.3	191.6	179.8	177.9
Relative air permeability, cm^3/ cm^2 × hours	1570	1390	1450	1430

As a consequence of the leather quality analysis, 0.75 % of Cr_2O_3 and 3.0 % of the modified montmorillonite dispersion in conversion for the mineral content of the weight of the pelts (variant of treatment 3) can be considered the optimal consumption of chromium tanning agent. The use of modified montmorillonite combined with tanning basic chromium sulphate (III) allows to obtain leather with increased yield in area and thickness, sufficient level of structuring, required indices of physical-mechanical properties and chemical composition, reduced rigidity and increased resistance.

CONCLUSION

The paper is devoted to the study of modified montmorillonite dispersion properties in order to develop a chrome-less method of tanning. It is proposed to modify montmorillonite with aluminum compounds and to combine the obtained dispersions with chromium compounds.

It is proved that modification of montmorillonite dispersions by aluminum compounds within 5.0-7.0 % Al_2O_3 of the weight of the mineral contributes to obtaining the most stable positively charged montmorillonite dispersions. The obtained dispersions are characterized by a stable pH level in the range of 3.5-4.0, which is predicted to allow an efficient tanning process.

Analysis of the temperature resistance of gelatin indicates that the use of montmorillonite dispersions is effective for stabilizing collagen structure. To increase the level of derma collagen resistance in the process, it is advised to use modified montmorillonite dispersions in combination with other tannins.

Conducted studies on the chemical interactions between collagen of derma and modified montmorillonite dispersions have revealed the formation of chemical bonds involving aluminum between the collagen side chains and the hydroxyl groups of molecules of already bound peptides of pre-chromed gelatin. A combination of chemical interactions enables the formation of hydrogen, ionic and covalent bonds, which increases the efficiency of collagen structuring.

It has been confirmed that the use of montmorillonite modified using the aluminum compound for tanning contributes to the effective structuring of the derma and the formation of the required leather quality. The use of modified montmorillonite dispersions combined with a chromium tanning agent contributes to the introduction of chrome-less tanning. At the same time, 0.75 % of Cr_2O_3 and 3.0 % of modified montmorillonite dispersion of the weight of the pelts in conversion for mineral weight are considered the optimal consumption of chromium tanning agents. The developed chrome-less tanning results in soft leather with increased yield of leather area, reduced rigidity, sufficient resistance to water-absorption and increased hydrothermal resistance. Meanwhile, the consumption of chromium compounds for tanning and their content in wastewater are reduced by approximately 20%. This indicates that the use of modified montmorillonite dispersions increases the efficiency of chromium tanning use and promotes ecologization of leather manufacturing.

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INTEGRATING ROMANIAN FOOTWEAR COMPANIES IN A SUSTAINABLE APPRENTICESHIP SYSTEM - EXAMPLE OF GOOD PRACTICE FROM PILOTING WORK BASED LEARNING

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INTEGRATING ROMANIAN FOOTWEAR COMPANIES IN A SUSTAINABLE APPRENTICESHIP SYSTEM AND EXPERIENCE FROM PILOTING WORK BASED LEARNING

ABSTRACT. The Work Based Learning (WBL) pilot stands on a Locally Developed Curriculum elaborated within a partnership consisting of an Educational Institution (Technical high school), Economic operator (Footwear company) and a Public institution (University) and serves as a good apprenticeship model for both, VET providers and footwear companies. The goal of this study is to describes the apprenticeship experience and the stages of implementing WBL in Romanian footwear company, namely: selection of apprentices, WBL pilot planning, tutors training on WBL, WBL pilot implementation, and formative quality assurance. WBL pilot programme in Romania was applied at Papucei footwear company and involved three young apprentices from "Ion Holban" Technical College of Iasi with background in Textile and Clothing field. During one year, according to the developed WBL pilot program and guided by previously trained tutors from Papucei and TUIASI, the apprentices followed all the Core Spheres (Cutting, Pre-stitching, Stitching, Pre-lasting, Lasting, Assembly and Finishing) and Peripheral Spheres (Technical Development, Production planning, design and Quality Assurance) specific to industrial footwear manufacturing. The apprentices' achievements were evaluated by the responsible tutors using the special designed Matrices found in the Manuals developed by ICSAS to support tutors involved in WBL process. The entire apprenticeship experience was then investigated and evaluated by relevant stakeholders using SWOT analysis to highlight the strengths, weaknesses, opportunities and threats.

KEY WORDS: apprenticeship, Work Based Learning (WBL), industrial footwear manufacturing, VET system, locally developed curriculum

INTEGRAREA COMPANIILOR ROMÂNEȘTI PRODUCĂTOARE DE ÎNCĂLȚĂMINTE ÎNTR-UN SISTEM SUSTENABIL DE UCENICIE ȘI PREZENTAREA EXPERIENȚEI DE PILOTARE A PROGRAMULUI DE ÎNVĂȚARE LA LOCUL DE MUNCĂ

REZUMAT. Pilotarea programului de învățare la locul de muncă (WBL - Work Based Learning) se bazează pe un curriculum dezvoltat local elaborat în cadrul unui parteneriat format dintr-o instituție de învățământ (liceu tehnic), operator economic (companie de încălțăminte) și o instituție publică (universitate). Programul de ucenicie servește drept exemplu de bune practici atât pentru formatorii VET, cât și pentru companiile producătoare de încălțăminte. Scopul acestei lucrări este de a descrie experiența programului și etapele implementării WBL într-o companie producătoare de încălțăminte din România, și anume: selecția ucenicilor, planificarea pilotării, instruirea tutorilor, implementarea pilotării și asigurarea formativă a calității. Pilotarea programului WBL în România s-a desfășurat în cadrul companiei Papucei și a implicat trei tineri ucenici de la Colegiul Tehnic „Ion Holban" din Iași, cu studii în domeniul Textile și Îmbrăcăminte. Pe parcursul unui an, în conformitate cu programul dezvoltat și sub îndrumarea profesorilor și a tutorilor din cadrul Papucei și TUIASI, ucenicii au parcurs toate sferele de bază (croit, pregătit-cusut, cusut, pregătit tras-tălpuit, tras, tălpuit, finisat) și sferele periferice (dezvoltarea tehnică, planificarea producției, proiectarea și asigurarea calității) specifice fabricării industriale a încălțămintei. Progresul ucenicilor a fost evaluat de către formatorii responsabili aplicând matricele de evaluare concepute în acest scop și integrate în manualele elaborate în cadrul proiectului ICSAS pentru a sprijini tutorii implicați în procesul WBL. Întreaga experiență de ucenicie a fost apoi examinată și evaluată de părțile interesate folosind analiza SWOT și a evidențiat punctele tari, punctele slabe, oportunitățile și amenințările programului.

CUVINTE CHEIE: ucenicie, învățare la locul de muncă, fabricarea industrială a încălțămintei, sistemul de formare profesională, curriculum în dezvoltare locală

INTÉGRATION DES ENTREPRISES ROUMAINES DE FABRICATION DE CHAUSSURES DANS UN SYSTÈME D'APPRENTISSAGE DURABLE ET PRÉSENTATION DE L'EXPÉRIENCE DE PILOTAGE DU PROGRAMME D'APPRENTISSAGE SUR LE LIEU DE TRAVAIL

RÉSUMÉ. Le pilotage du programme d'apprentissage sur le lieu de travail (WBL - Work Based Learning) s'appuie sur un curriculum développé localement et créé en partenariat comprenant un établissement d'enseignement (lycée technique), un opérateur économique (entreprise de chaussures) et un établissement public (université). Le programme d'apprentissage est un exemple de bonne pratique pour les formateurs d'EFP et les entreprises de chaussures. Le but de cet article est de décrire l'expérience du programme et les étapes de la mise en œuvre du WBL dans une entreprise de chaussures en Roumanie, à savoir : la sélection des apprentis, la planification du pilotage, la formation des tuteurs, la mise en œuvre du pilotage et l'assurance qualité formative. Le pilotage du programme WBL en Roumanie a eu lieu au sein de l'entreprise Papucei et a impliqué trois jeunes apprentis du Collège technique « Ion Holban » de Iași, avec des études dans le domaine du textile et de l'habillement. Pendant un an, selon le programme développé et sous la direction d'enseignants et de tuteurs de Papucei et TUIASI, les étudiants ont parcouru toutes les sphères de base (découpe, préparation pour la couture, couture, préparation pour le tirage-montage, tirage, montage semelle, finition) et les domaines périphériques (développement technique, planification de la production, conception et assurance qualité) spécifiques à la fabrication industrielle de chaussures. Les progrès des apprentis ont été évalués par les formateurs responsables appliquant les matrices d'évaluation conçues à cet effet et intégrées dans les manuels développés dans le cadre du projet ICSAS pour soutenir les tuteurs impliqués dans le processus WBL. L'ensemble de l'expérience d'apprentissage a ensuite été examiné et évalué par les parties

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prenantes à l'aide de l'analyse SWOT et a mis en évidence les forces, les faiblesses, les opportunités et les menaces du programme.

MOTS CLÉS : apprentissage, apprentissage sur le lieu de travail, fabrication industrielle de chaussures, système de formation professionnelle, programme de développement local

INTRODUCTION

The Report on Experience and SWOT from piloting Work Based Learning in Romania serves as "apparent good practice" for other footwear companies.

WBL pilot of apprenticeship is based on a Locally Developed Curriculum (LDC) [1], named "Footwear manufacturing technologies", elaborated by "Ion Holban" Technical College of Iasi (Educational Institution), SC Angela International SRL – Papucei (Economic operator), and "Gheorghe Asachi" Technical University of Iasi (Public institution - consultant) according to all Romanian Regulations [2-12].

WBL pilot programme in Romania was implemented at Papucei footwear company, lasted one year, starting from October 2018, and involved three apprentices from "Ion Holban" Technical College of Iasi [13].

The apprentices faced real work processes specific to the main spheres of activity of industrial footwear manufacturing:

- Core spheres (582h): Cutting, Pre-stitching, Stitching, Pre-lasting, Lasting, Assembly and Finishing;
- Peripheral sphere (72h): Technical Development, Production planning, design and Quality Assurance.

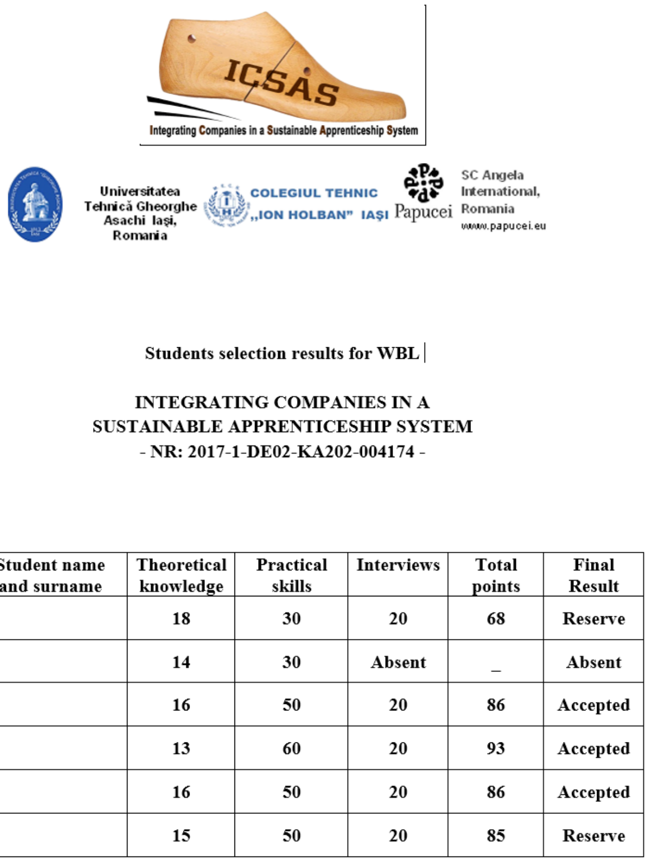
The apprentices' achievements were evaluated by the responsible tutors and their progress was documented and to further improve the WBL activity, the apprentices were asked to answer to a set of questions during an open interview to evaluate the atmosphere of the learning process.

The results of implementing WBL in Romania were shared and analysed during a workshop that gathered representants from TUIASI, Papucei, "Ion Holban" Highschool and CNDIPT (Romanian National Centre for the Development of Vocational and Technical Education). The experts shared their opinions regarding the implementation of WBL, the progress made by trainees, benefits and future collaborations. The results of the WBL pilot were evaluated through a SWOT analysis and are presented in the final chapter of this report.

IMPLEMENTING WORK BASED LEARNING IN ROMANIA

Selection of Apprentices

Apprentices engaged in the Work Based Learning have a background in Textile and Clothing and were selected from "Ion Holban" Technical High School from Iasi in collaboration with Papucei and TUIASI. Apprentices were evaluated in three stages: theoretical knowledge in the field, practical skills and interviews. From an initial number of six apprentices, the top three were selected based on their total score, as presented in Figure 1.



ICSAS
Integrating Companies in a Sustainable Apprenticeship System

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Students selection results for WBL

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- NR: 2017-1-DE02-KA202-004174 -

No.	Student name and surname	Theoretical knowledge	Practical skills	Interviews	Total points	Final Result
1.		18	30	20	68	Reserve
2.		14	30	Absent	_	Absent
3.		16	50	20	86	Accepted
4.		13	60	20	93	Accepted
5.		16	50	20	86	Accepted
6.		15	50	20	85	Reserve

Figure 1. Apprentices selection results for WBL piloting in Romania

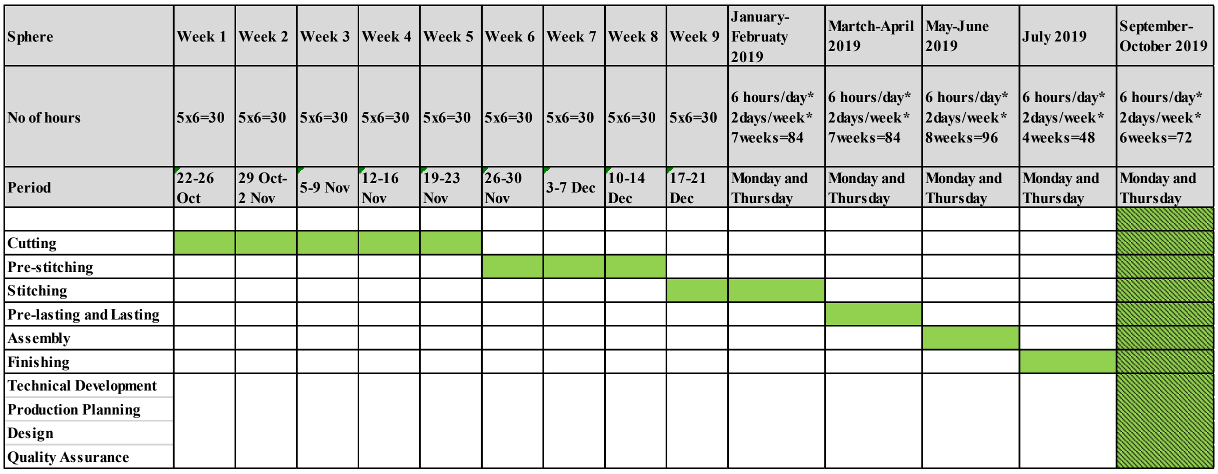
WBL Pilot Planning

The piloting phase had a duration of one year, scheduled during October 2018 - October 2019. The apprentices passed through all spheres of activity and started on 22nd October 2018. Considering learning-teaching activities of each sphere, Papucei and TUIASI decided on the following distribution (Table 1):

Table 1: Spheres distribution for piloting WBL

Learning spheres	Learning content	Time distribution	Total hours
Core Spheres	Cutting	October - November 2018 5 weeks, 5 days/week, 6 h / day	150
	Pre-stitching	November – December 2018 3 weeks, 5 days/week, 6 h / day	90
	Stitching	December 2018 - February 2019 1 week, 5 days / week, 6 h / day + 7 weeks, 2 days / week, 6 h / day	115
	Pre-lasting and lasting	March - April 2019 7 weeks, 2 days/week, 6 h / day	84
	Assembly	June 2019 8 weeks, 2 days/week, 6 h / day	96
	Finishing	July 2019 4 weeks, 2 days/week, 6 h / day	48
Peripheral spheres	Design Technical development Quality assurance Production planning	September - October 2019 6 weeks, 2 days / week, 6 h / day	72

The detailed schedule of the WBL is presented in the following chart (Figure 2):



Sphere	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	January-Februaty 2019	Martch-April 2019	May-June 2019	July 2019	September-October 2019
No of hours	5x6=30	5x6=30	5x6=30	5x6=30	5x6=30	5x6=30	5x6=30	5x6=30	5x6=30	6 hours/day* 2days/week* 7weeks=84	6 hours/day* 2days/week* 7weeks=84	6 hours/day* 2days/week* 8weeks=96	6 hours/day* 2days/week* 4weeks=48	6 hours/day* 2days/week* 6weeks=72
Period	22-26 Oct	29 Oct-2 Nov	5-9 Nov	12-16 Nov	19-23 Nov	26-30 Nov	3-7 Dec	10-14 Dec	17-21 Dec	Monday and Thursday	Monday and Thursday	Monday and Thursday	Monday and Thursday	Monday and Thursday
														▨
Cutting	🟩	🟩	🟩	🟩	🟩									▨
Pre-stitching						🟩	🟩	🟩						▨
Stitching									🟩	🟩				▨
Pre-lasting and Lasting											🟩			▨
Assembly												🟩		▨
Finishing													🟩	▨
Technical Development Production Planning Design Quality Assurance														▨

Figure 2. WBL pilot schedule in Romania

Tutors Training Workshop on WBL

The role of tutors is at the heart of apprenticeship programmes:

- passing on practical skills alongside with theoretical know-how;
- tutoring = internal knowledge management (& transfer) system;
- coaching apprentices = social responsibility;
- dealing with emotional ups and downs of teens.

Before the start of WBL pilot program in Romania, Tutors from Papucei footwear company were trained by representatives from TUIASI regarding the role of the tutors, the aim of the pilot activity, Train the Trainers manuals [14], Learning-Teaching Exercises [15], spheres of activity and WBT planning and coordination (Figure 3).

Figure 3. Train the Tutor workshop in Romania

WBL Pilot Implementation

According to the agreed WBL pilot program and guided by tutors from Papucei and TUIASI the apprentices followed all the Core Spheres (Figure 4) and the Peripheral Spheres (Figure 5) specific to industrial footwear manufacturing.

Core Spheres – 582 h

Cutting, Pre-stitching, Stitching, Pre-lasting, Lasting, Assembly and Finishing.

Cutting   Pre-stitching

Stitching

Pre-lasting Lasting

Finishing

Figure 4. Apprentices' during Core spheres WBL at Papucei

Peripheral Spheres – 72 h

Technical Development, Production planning, design and Quality Assurance.

Design Technical development

Production planning Quality Assurance

Figure 5. Apprentices' during Peripheral spheres WBL at Papucei

Regular Work Meetings at TUIASI

Additionally, WBL practical activities were backed up by regular meetings with the apprentices at TUIASI facilities (Figure 6) where tutors provided counselling, asked for feedback to constantly improve the training and provided additional theoretical explanations of the tasks.

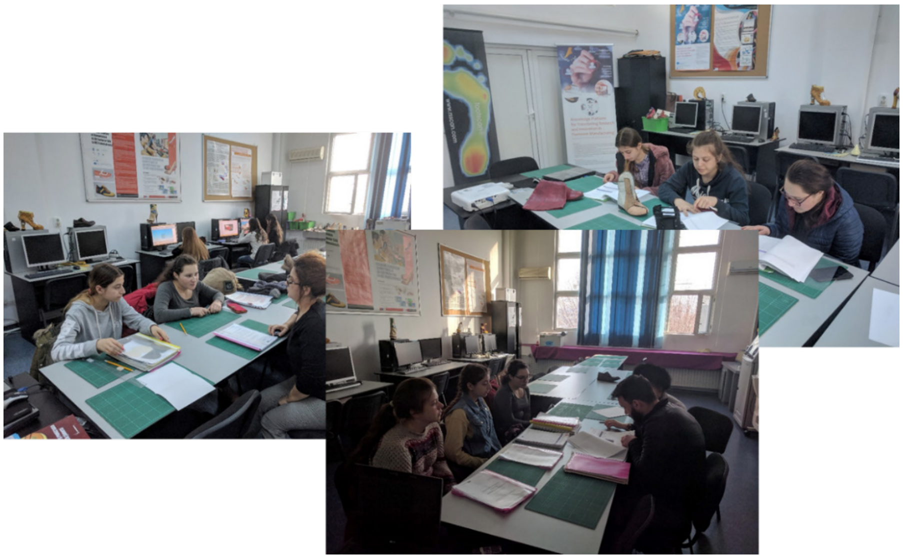


Figure 6. Apprentices' during regular meetings at TUIASI

Apprentices' Notebooks

Additionally, the apprentices documented all their work in individual notebooks (Figure 7) containing drawings, samples explanations and observations.

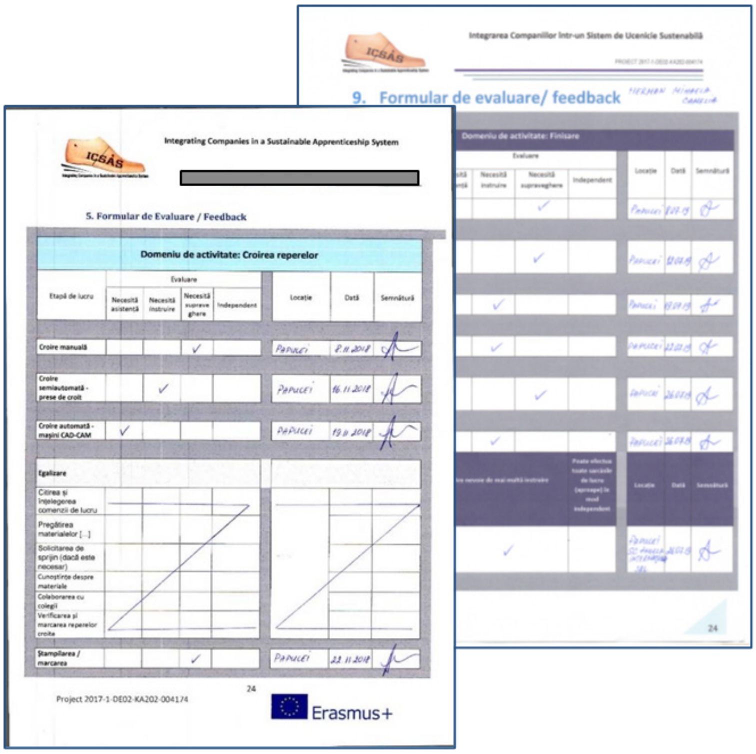
Figure 7. Apprentices notebooks and footwear prototypes

Formative Quality Assurance

Learning Outcomes Feedback

For each sphere of activity, at the end of the training in that sphere, the apprentices' achievements were evaluated by the responsible tutors from TUIASI and Papucei by using the Matrices found in the Manuals developed by ICSAS to support tutors involved in WBL process [16].

For all learning spheres, the apprentices need instruction or supervision to perform the respective work tasks. None of the apprentices managed to receive the highest possible rating "Can perform all work tasks (almost) independently". This is justified by the age of the apprentices (16-17 years old), their learning pace in an actual work environment being slower compared with the learning pace of an adult and their limited theoretical knowledge in the field of Footwear industrial manufacturing. Therefore, it is recommended to adapt the number of allocated hours for WBL according to the age of the students and their theoretical knowledge. An example of filled matrices is presented in Figure 8.



Integrarea Companiilor într-un Sistem de Ucenicie Sustenabilă

9. Formular de evaluare/ feedback

Domeniu de activitate: Finisare

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[redacted]

5. Formular de Evaluare / Feedback

Domeniu de activitate: Croirea reperelor

Etapă de lucru	Evaluare				Locație	Dată	Semnătură
	Necesită asistență	Necesită instruire	Necesită supraveghere	Independent			
Croire manuală			✓		Papucei	8.11.2018	
Croire semiautomată - prese de croit		✓			Papucei	16.11.2018	
Croire automată - mașini CAD-CAM	✓				Papucei	19.11.2018	
Egalizare							
Citirea și înțelegerea comenzii de lucru							
Pregătirea materialelor [...]							
Solicitarea de sprijin (dacă este necesar)							
Cunoștințe despre materiale							
Colaborarea cu colegii							
Verificarea și marcarea reperelor croite							
Ștampilarea / marcarea			✓		Papucei	22.11.2018	

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Figure 8. Example of filled matrices from Cutting and Finishing

The main findings of the Romanian apprentices learning outcomes assessment are presented in the following table (Table 2):

Table 2: Learning outcomes feedback main findings

Learning sphere	Findings
Cutting	All apprentices need instructions and supervision for performing the requested tasks for manual cutting and die-cutting and that they need assistance for automatic cutting.
Pre-stitching	Apprentices can read and understand work orders independently need additional instructions and supervision for making the adjustments on the skiving and splitting machines and that they need to be supervised during performing the majority of the pre-stitching operations.
Stitching	Apprentices need additional instructions and supervision for performing the majority of the stitching operations.
Pre-lasting and lasting	Apprentices can read and understand work orders independently, can perform the majority of operations independently or under supervision but need more practice to achieve the required quality. Regarding Lasting, due to the high complexity in operating the lasting machines the apprentices need further training in operating those machines.
Assembly	Apprentices can perform the majority of operations under supervision;
Finishing	Apprentices can perform the majority of operations but need supervision and additional practice to achieve the required quality.
Design	Allocated time was only sufficient to understand the main principles; therefore, apprentices need additional training in peripherical departments.
Technical development	
Quality assurance	
Production planning	

Interviews with the Apprentices

To further improve the WBL activity, after their stay at each learning station, the apprentices were asked to answer a set of questions during an open interview to evaluate the atmosphere of the learning process. Example of interview with apprentices is presented in Figure 9.

The following questions were used during the interviews:

- Which LS (Learning Station) have you just completed?
- How long did you stay there?
- Was the time frame adequate or rather too long or too short? If it was not adequate, why?
- Do you feel proficient at this LS now? If not, why?
- Did you feel well prepared for this LS? If not, what was missing?
- Do you think that the entire learning potential of the LS was used? If not, why?
- Did the tutor support you in an adequate way? If not, why?
- Do you think that communication with colleagues was cooperative? If not, why?
- Were you part of a team or were you working on your own?
- Would you recommend your learning experience at this LS to other learners? Why?
- What could be improved?
- What was the most difficult task at this learning station?
- Were you able to put your theoretical knowledge from vocational school into practice at this LS? Did this LS help you to reinforce your understanding of theoretical knowledge?

Main findings:

- All learning spheres were recommended as being dynamic and interesting;
- Tutors provided adequate support and explained in detail all the operations;
- Allocated time was considered sufficient to learn main operations;
- More time to be allocated for exercising activities with a higher degree of complexity;
- Additional training and practice regarding machinery setup;
- The practice helped them to improve their understanding of theoretical knowledge;
- Experienced colleagues were always open to provide support and assistance.

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[redacted]

- În ce stație de învățare ați fost?

Pregătire pentru asamblare prin coasere

- Cât timp ați petrecut acolo?

Aproximativ 6 ore pe zi, 5 zile pe săptămână, în perioada 26 noiembrie-14 decembrie.

- Timpul petrecut în cadrul stației de învățare a fost prea scurt, prea lung sau suficient? De ce?

În mare, timpul alocat a fost suficient, dar cred că pentru operațiile precum subțiere și egalizare timpul a fost un pic scurt (luând în calcul faptul că mașinile au reglaje specifice).

- Ați avut o pregătire de bază înaintea începerii activității în această stație?

Am avut o pregătire făcută în cadrul fabricii înainte de a începe activitatea.

- Credeți că s-a folosit întregul potențial de învățare în cadrul acestei stații? De ce?

Cred că în cazul operației de subțiere nu s-a folosit întregul potențial de învățare.

- Comunicarea cu colegii a fost cooperativă? De ce?

Da, colegii au fost cooperativi, ajutându-mă la învățarea modelului de efectuare a operațiilor.

- Ați fost integrat într-o echipă de lucru sau ați lucrat individual?

Am lucrat individual, fiind supravegheată și asistată de operatori.

- Ați recomanda experiența dvs. de învățare în acest departament pentru alți ucenici? De ce?

Da, pentru că a fost o atmosferă de lucru plăcută, iar operațiile efectuate mi s-au părut ușor de învățat.

4

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Integrarea companiilor într-un sistem de ucenicie sustenabilă

- Ce ar putea fi îmbunătățit?

Timpul alocat pentru învățarea operației de egalizare și subțiere.

- Care a fost cea mai dificilă parte în cadrul acestei stații de învățare?

Cea mai dificilă parte mi s-a părut reglarea mașinii de subțiat.

- Ați reușit să vă puneți în practică cunoștințele teoretice din școala profesională sau activitatea practică v-a ajutat să îmbunătățiți cunoștințele teoretice?

Activitatea practică m-a ajutat să îmbunătățesc cunoștințele teoretice.

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Figure 9. Example of Interview with apprentices

SWOT Analysis of WBL in Romania

The implementation of WBL in Romania was analysed during a workshop that gathered 12 representatives from TUIASI, Papucei, “Ion Holban” Highschool and CNDIPT (Romanian National Center for the Development of Vocational and Technical Education) that shared their opinions regarding the implementation of WBL, the progress made by trainees, benefits and future collaboration. The results of the SWOT analysis [17] made during the workshop is presented in the following table (Table 3):

Table 3: Learning outcomes main findings

Strengths
• CDL objectives were achieved (CDL – locally developed curriculum, a component of National Curriculum, includes allocated hours for the development of school-specific curriculum in partnership with private companies) – the CDL was developed in implemented successfully, the trainees followed and passed all WBL spheres of activity and can be employed in a footwear company; • The project facilitated the collaboration between Technical school - Industry - University • Training Manuals and Learning-Teaching manuals have great value, both for the company and the school; • Portfolios elaborated by the trainees have didactic use; • Social impact: comparison between school ateliers and factory; integration in work teams, contact with workers from the company. • Students learn how to follow a schedule, respect hierarchy, to be punctual, to communicate with colleagues, to follow work tasks; • The training program and manuals are very useful for both school and companies.
Weaknesses
• Estimated and allocated hours for some of the departments: too many or too few hours; for example: were too many hours for the cutting and stitching departments while for the lasting department more hours would be required; The main explanation for this is represented by differences in the degree of difficulty between departments and the age of the trainees (very young, 15-16 years old). The maximum number of hours imposed by the national legislation has to be respected but hours can be reallocated between departments; • Peripherical spheres: just a general introduction on these departments should be made, with few hours and the remaining hours should be allocated to the other departments. For example, to be proficient in Footwear Design or Technical development, a lot more hours are needed.
Opportunities
• The WBL programme can be successfully implemented in other footwear companies and technical schools from other regions from Romania. • Papucei and “Ion Holban” Highschool will continue to develop and strengthen their collaboration in the next years; • “Ion Holban” Highschool will use the project results to promote their educational offer to attract students from secondary school;
Threats
• Changes in Romanian legislation are unpredictable; • The DUAL Romanian education system is not fully functional; • The motivation of the young Romanian generation is generally low and their interest is hard to capture and maintain;

CONCLUSIONS

WBL pilot of apprenticeship based on a Locally Developed Curriculum (LDC) implemented at Papucei footwear company during one year and which involved three apprentices from "Ion Holban" Technical College of Iasi has received very positive feedback from the relevant stakeholders, including representatives from the footwear industry, experts in education, teachers, and tutors.

The results of implementing WBL in Romania demonstrate a sustainable model for adapting the professional training of youngsters through a complete training program covering all phases of footwear manufacturing.

The ICSAS apprenticeship model applied in Romania offers supportive resources for the development of the tools necessary for the application of dual training system. The presented apprenticeship-like scheme promises a relevant impact in the Romanian VET system and could be implemented by VET schools in partnership with the footwear companies. The training resources (curricula, sectoral framework, training manuals, tools for exercises and assessment, etc.) and agreement models are easy to be adapted to various particular situations and fields which makes it more valuable and sustainable.

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THE BEHAVIOR OF SHEEP LEATHER PARCHMENT TO ARTIFICIAL AGEING

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THE BEHAVIOR OF SHEEP LEATHER PARCHMENT TO ARTIFICIAL AGEING

ABSTRACT. Parchment used for restoration, book binding and art requires special performance on physical-chemical, organoleptic and aesthetic characteristics, but also good long-term stability. In this sense, the parchment is ecologically processed, with features that ensure firmness, fullness, light resistance, dimensional stability, thermal stability, malleability, flexural/pressure bending resistance. For a good behaviour in time and to artificial ageing, it is found that in the case of parchments made/obtained from sheepskin, the fat or volatile matter content must be as low as possible. The parchment with these qualities allows for the creation of new covers or historical replicas, complements for the integration of old covers, hot and/or cold stamping modelling, incision, entrainment, deposition of gold and silver foil, colouring and decoration with pigments and dyes. Some niche areas such as book bindings and art require a dedicated craftsmanship that promotes the survival of artisanal forms of production and the perpetuation of local creativity and identity. The parchments have undergone artificial ageing treatments based on the concomitant action of temperature and relative humidity for up to 16 days. Chemical (volatile matter, extractable substances, total ash, total nitrogen, dermal) and physical-chemical (measurement of colour variation and shrinkage temperature) analyses were performed to evaluate colour parameters and collagen hydrostability. The fat content of the parchment leads to oxidation reactions that cause the bathochromic effect, closing the colour, but also the deterioration over time of the fibrillar structure by depreciating the contraction temperature.

KEY WORDS: parchment, heritage object, colour change

COMPORTAMENTUL LA ÎMBĂTRÂNIRE ARTIFICIALĂ A PERGAMENTULUI DIN PIELE DE OAIE

REZUMAT. Pergamentul utilizat pentru restaurare, legătoria de patrimoniu și de artă necesită performanțe speciale privind caracteristicile fizico-chimice, organoleptice și estetice, dar și o bună stabilitate pe termen lung. În acest sens, pergamentul se prelucrează ecologic, cu caracteristici care asigură proprietăți de fermitate, plinătate, rezistență la radiațiile luminoase, stabilitate dimensională, stabilitate termică, maleabilitate, rezistență la flexiune/îndoire sub presiune. Pentru o bună comportare în timp și la îmbătrânire artificială se constată că în cazul pergamentelor realizate/obținute din piei de oaie, conținutul în grăsime sau materii volatile trebuie să fie cât mai mic. Pergamentul cu aceste calități permite realizarea de coperți noi ori replici istorice, completări pentru integrarea coperților vechi, modelare prin poansonare tip timbru sec la cald și/sau la rece, incizare, intarsie, depunere de foiță de aur și argint, colorare și decorare cu pigmenți și coloranți. Pergamentele au fost supuse unor tratamente de îmbătrânire artificială bazate pe acțiunea concomitentă a temperaturii și a umidității relative timp de până la 16 zile. S-au efectuat analize chimice (materii volatile, substanțe extractibile, cenușă totală, azot total, substanță dermică) și fizico-chimice (de măsurare a variației culorii și temperaturii de contracție) pentru evaluarea parametrilor de culoare și a hidrostabilității colagenului. Conținutul de grăsime din pergament conduce la reacții de oxidare care favorizează efectul batocrom, de închidere a culorii, dar și deteriorarea în timp a structurii fibrilare prin deprecierea temperaturii de contracție.

CUVINTE CHEIE: pergament, obiecte de patrimoniu, modificarea culorii

LE COMPORTEMENT AU VIEILLISSEMENT ARTIFICIEL DU PARCHEMIN EN CUIR DE MOUTON

RÉSUMÉ. Le parchemin utilisé pour la restauration, la reliure héritage et des œuvres d'art nécessite des performances particulières en ce qui concerne les caractéristiques physico-chimiques, mécaniques, organoleptiques et esthétiques, mais également une bonne stabilité à long terme. Dans ce sens, le parchemin est traité de manière écologique, avec des caractéristiques qui assurent les propriétés de fermeté, de plénitude, de résistance au rayonnement lumineux, de stabilité dimensionnelle, de stabilité thermique, de malléabilité, de résistance à la flexion sous pression. Pour un bon comportement dans le temps et un vieillissement artificiel, on constate que dans le cas de parchemins réalisés/obtenus à partir de peau de mouton, la teneur en matières grasses ou en matières volatiles doit être la plus faible possible. Ces qualités permettent la création de nouvelles couvertures ou de répliques historiques, des ajouts pour l'intégration des anciennes couvertures, la modélisation par poinçonnage à chaud et à froid, la gravure, la marqueterie, le dépôt de feuille d'or et d'argent, coloration et décoration avec des pigments et des colorants. Les parchemins ont été soumis à des traitements de vieillissement artificiels basés sur l'action concomitante de la température et de l'humidité relative pendant 16 jours. Des analyses chimiques (matières volatiles, substances extractibles, cendres, azote total, substance dermique) et physico-chimiques (pour la mesure de la couleur et de la température de retrait) ont été effectuées afin d'évaluer les paramètres de couleur et l'hydrostabilité du collagène. La teneur en matière grasse du parchemin conduit à des réactions d'oxydation qui favorisent l'effet bathochrome, assombrissant, mais aussi endommagent dans le temps la structure fibrillaire en dépréciant la température de retrait.

MOTS-CLÉS : parchemin, objets de patrimoine, changement de couleur

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INTRODUCTION

Roman historian Plinius reports that the origin of the use of parchment as a support for writing is attributed to the existing cultural competition between the king of Pergamon (now Turkey), Eumenes II (197-159 BC) and Ptolemy V of Egypt. The king of Egypt, fearing that Eumenes II will create a library that could overshadow the fame of Alexandria, suspended the export of papyrus. The king of Pergamon was forced to find alternative writing materials; this is supposed to have led to the invention of the parchment [1]. The parchment was mainly used for writing, initially on rolls - as is still the case in Israel - and from the second-century in the form of a book. The advantages of this material relative to the other supports was its durability, whiteness and flexibility. In addition, the processed skin absorbs less ink than the papyrus and could be written on both sides, the corrections were lighter, and several parchments could be sewn together; for these reasons, the use of parchment as a support for writing has become more and more frequent. Thus, parchment was the main support for writing from the Roman Empire to the Middle Ages. The development of the Christian Church played a fundamental role in its adoption throughout Europe. It is supposed that between the tenth and the sixteenth centuries, the use of parchment was predominant in Europe and its production qualities were the best. During this period, parchment was used for ecclesiastical texts, for legal and financial records, and for royal courts and for book covers [2-6].

Heritage objects from parchments kept in old monasteries, libraries, archives and museums are most often exposed to uncontrolled environmental conditions. Unsuitable environmental conditions are a serious threat for the artefacts' conservation and greatly reduce their lifespan as frequently the induced damage may remain invisible for a long period, while the inner structures may already have been seriously weakened. Therefore, their conservation condition requires a strict monitoring.

Parchment preservation has been an important concern in the work of modern researchers and conservators. There are numerous studies in literature [7-16] of artificial ageing that contain information about the various structural damages that occur in parchment. These are highlighted through complex micro-destructive or non-destructive analyses. Moreover, Ghioni *et al.* [17] show, by complex methods (X-ray diffraction, gas chromatography, solid state NMR), that the fats (lipid fraction) of the parchments causes in time the deterioration of the hierarchical structure of collagen. Compared to the data presented in the literature, this study brings in addition to accelerated ageing, a correlation of the amount of fat from parchments with the decrease of their shrinkage temperature but also a change of colour.

EXPERIMENTAL

For this study, 5 parchments were prepared at the Leather and Footwear Research Institute (ICPI), Division of the National Research and Development Institute for Textiles and Leather (INCDTP), Bucharest. The sheepskins were processed according to a traditional recipe of obtaining parchment. The skins preserved by salting were soaked in clean water of about 22°C to rehydrate the skins to a minimum, at least equal to the time of skinning. After soaking and fleshing, the recipe is using solution of lime for 3-4 days for removal of hair. The fleshing operation is used before the second liming operation (2-3 days). Then, other operations are deliming, washing and at the end the skin is stretched tensioned on a wooden frame and left to dry [18-20]. Frequently, during the processing of the sheepskins, the entire amount of fat cannot be removed because the fibrillar structure of the dermis is very fine and dense (it also depends on the breed of the animal, the type and state of preservation of the raw hides).

Samples were cut from the sheep parchments (Table 1) from the spine area and marked from 1 to 5, i.e. S1, S2, S3, S4 and S5. The parchment samples underwent artificial ageing treatments based on synergic action of relative temperature and humidity. The artificial ageing treatments have the following parameters:

- Duration: one day, 2 days, 4 days, 8 days and 16 days;
- Temperature: 85°C;
- Relative humidity: 60%.

The samples exposed to the artificial ageing treatment were subjected to chemical tests, shrinkage temperature and colour determination and assessment.

Chemical characteristics were determined according to standardised methods for obtaining volatile matter, extractable substances, total ash, total nitrogen and dermal substances [21-24].

Shrinkage activity was evaluated using a recently developed automated instrument (imageMHT) incorporating image analysis and diagnostic software [25]. The fibres samples, about 0.1-0.2 mg, taken from the corium side, were conditioned with demineralized water, for 10 minutes on a concave microscope glass. After separation of the skin fibers, the glass covered with a cover glass was inserted into the hot table and heated. The temperature rise rate was kept constant (2°C/min), and the maximum temperature level was set at 100°C. Collagen fibres' shrinkage activity was recorded and the Ts was measured. By heating in water, the fibers contract in different temperature intervals, their contraction depends on the quality and the degree of deterioration of the collagen structure.

In order to determine and assess colour changes, parchment samples were measured using a portable Datacolor CHECK II spectrophotometer, equipped with software for colour measurement [26, 27]. Using CIEL*a*b* and CIEL*C*h dedicated software, chromaticity coordinates were obtained for each parchment sample.

The significance of the parameters is as follows:

- L* represents the lightness, the maximum value for L* is 100 (perfect white), while the minimum is 0 (perfect black);

- a* represents the shade between green (-a*) and red (+a*);

- the negative value of b* is blue, while the positive one, yellow;

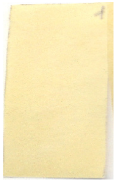
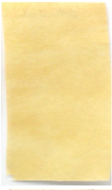
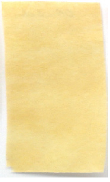
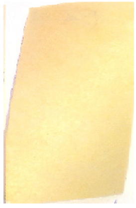
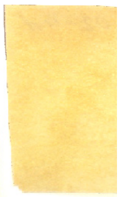
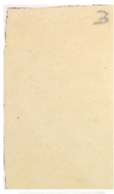
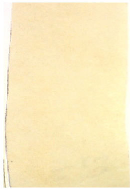
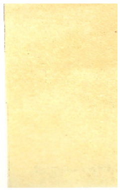
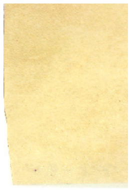
- C* (chroma) provides clues on purity (higher values) or complexity (lower values) of the mixture;

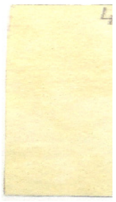
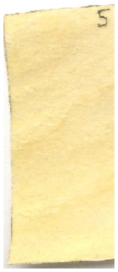
- h is the hue angle, reflects the proportion of the chromatic components a* and b*.

RESULTS AND DISCUSSIONS

The behaviour of the parchment samples after the artificial ageing cycles can be seen in Table 1.

Table 1: Images of S1-S5 sample parchments before and after ageing cycles

No.	Initial parchment	Artificially aged parchment				
		1 day	2 days	4 days	8 days	16 days
Sheep 1						
Sheep 2						
Sheep 3						

No.	Initial	Artificially aged parchment				
	parchment	1 day	2 days	4 days	8 days	16 days
Sheep 4						
Sheep 5						

Any changes that occur in the parchment during the technological process are related to the changes that occur in its constituent substances. Therefore, in order to understand the processes, the chemical composition of the parchment and the properties of its component parts must be known. With the help of chemical analysis, the following can be determined directly or indirectly: volatile matter and values for total ash, total nitrogen and dermal substances.

Table 2: Chemical characteristics of sheep parchments

No.	Characteristics	MU	Sample code/Values					*	Method
			S1	S2	S3	S4	S5	Uncertainty	Standard
1	Volatile matter	%	13.89	15.09	14.72	14.43	13.70	± 0.42	SR EN ISO 4684 – 2006
2	Extractable substances	%	6.61	2.39	3.69	5.83	8.81	± 0.87	SRENISO 4048 – 2008
3	Total ash	%	7.30	4.27	5.61	4.22	4.83	± 0.27	SR EN ISO 4047 – 2002
4	Total Nitrogen	%	15.29	14.76	14.38	14.48	14.42	± 0.66	SR ISO 5397 – 1996
5	Dermal substance	%	89.45	86.35	84.12	84.71	84.36	± 2.26	SR ISO 5397 – 1996

**Values for extracts are reported as free from volatile matter and values for total ash, total nitrogen, dermal substances are reported as free from volatile matter and extracts.*

From Table 2 it is observed that the big value variations of extractable substances, and the samples S1, S4 and S5 presents bigger amounts than S2 and S3 samples. The other chemical characteristics have similar values.

The variation of the shrinkage temperature is shown in Fig. 1.

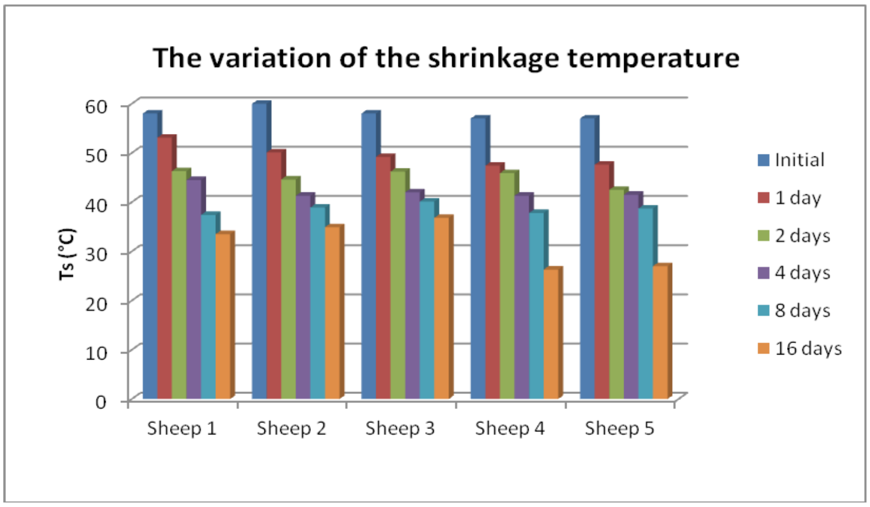


Figure 1. Variations of the shrinkage temperature after the ageing treatments

Shrinkage temperatures, Ts, showed a rather good hydrothermal stability for the untreated parchment samples, in good agreement with the data in the literature [15]. All samples show a major decrease of 5-9°C in the shrinkage temperature after a day of artificial ageing. In the following periods/ageing cycles, an approximately linear decrease of the shrinkage temperature is observed, by approximately 3-4°C. After the ageing period of 16 days at 80°C and RH 60%, there is an accentuated decrease of the shrinkage temperature for samples S4 and S5, according to Fig. 1 and at the same time, the images presented in Table 1.

The variations of the a* parameter is reported in Table 3 and in Fig. 2.

Table 3: Colour values of a* parameter for sheep parchments

Sample/Days of ageing	S1	S2	S3	S4	S5
			Parameter: a		
0-Initial	-0.28	-0.08	-0.18	-1.29	-1.09
1 day	2.36	4.15	-0.11	3.95	5.49
2 days	3.63	5.43	1.78	4.52	6.35
4 days	6.07	10.16	2.44	5.47	9.28
8 days	11.39	10.74	5.35	12.96	14.9
16 days	11.13	10.27	5.25	15.73	13.87

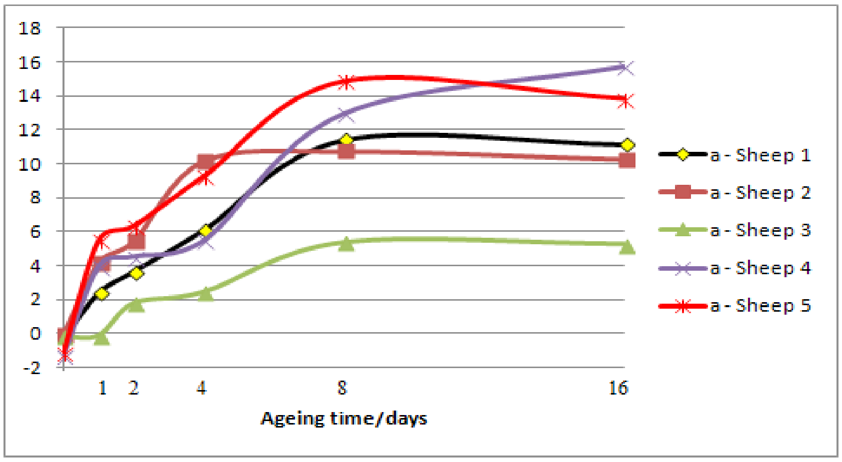


Figure 2. Variations of the a* parameter after the ageing treatments

According to Fig. 2, the smallest changes of the parameter a* were obtained for samples S3 and S2, both at 8 days and at 16 days of artificial ageing. For samples S1, S4 and S5 there is an intensification of the colour from yellowish white in initial state to creamy yellow after 4 days, and after 8 and 16 days to brownish cream, simultaneously with the deformation, embrittlement and rupture of the samples.

For the other measured colour parameters changes are presented in Fig. 3, 4, 5 and 6.

The variation of the colour parameter b* (from blue to yellow) during artificial ageing is shown in Fig. 3.

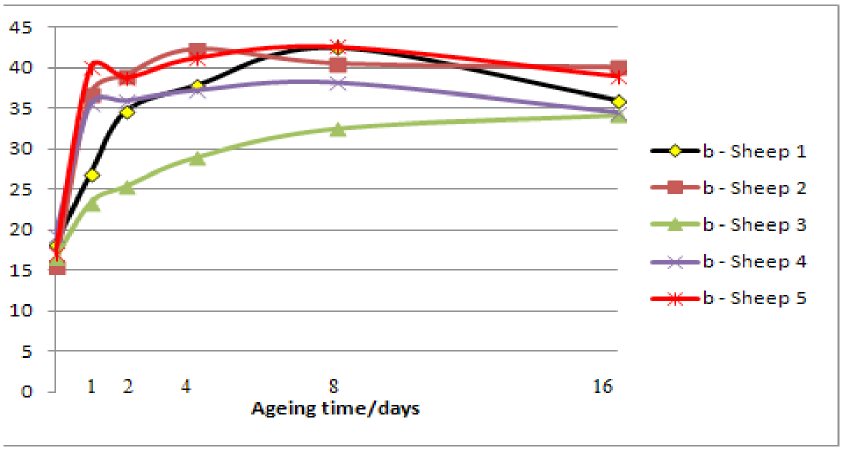


Figure 3. Variations of the b* parameter after the ageing treatments

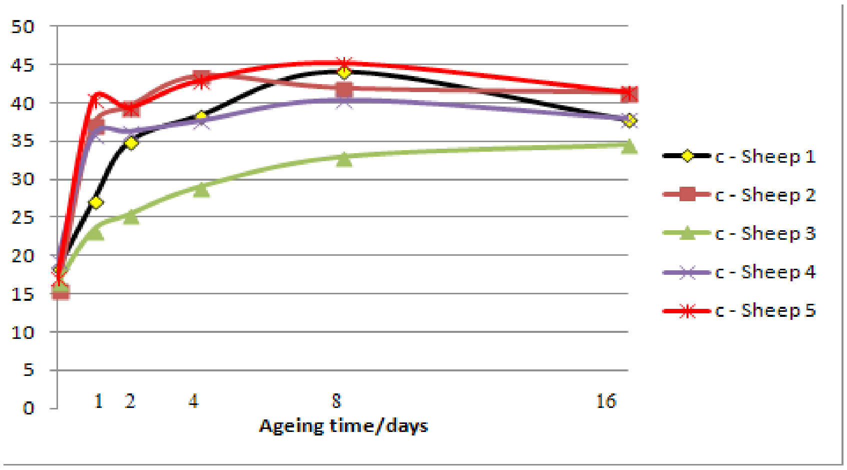


Figure 4. Variations of the c* parameter after the ageing treatments

The variations of the c* parameter after the ageing treatments is reported in Fig. 4.

From Fig. 4 it is observed that the best behaviour, from the point of view of c* parameter, is shown by sample S3, which has a small increase. Also, the significant growth takes place in the first period of artificial ageing, respectively after 1 day to 4 days inclusive.

The variations of the h parameter after the ageing treatments is reported in Fig. 5.

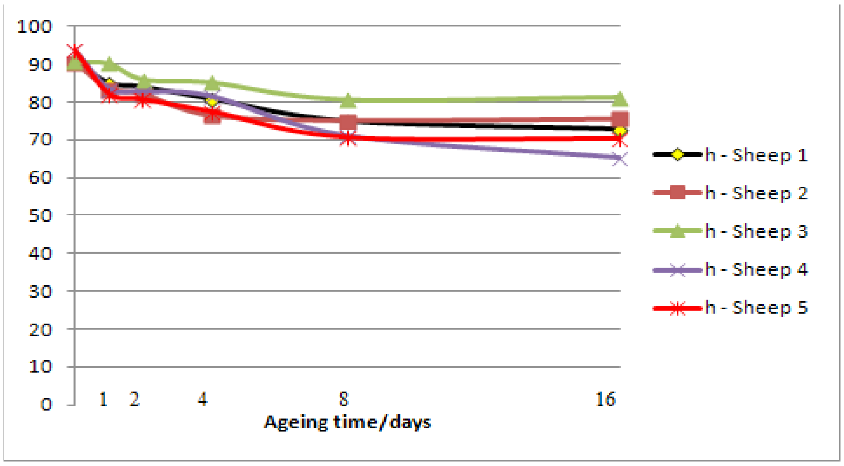


Figure 5. Variations of the h parameter after the ageing treatments

Fig. 5 shows that the parameter h for samples S2 and S3 has the smallest changes, which attests the good behaviour of these parchments during artificial ageing. The variations of the L parameter after the ageing treatments is reported in Fig. 6.

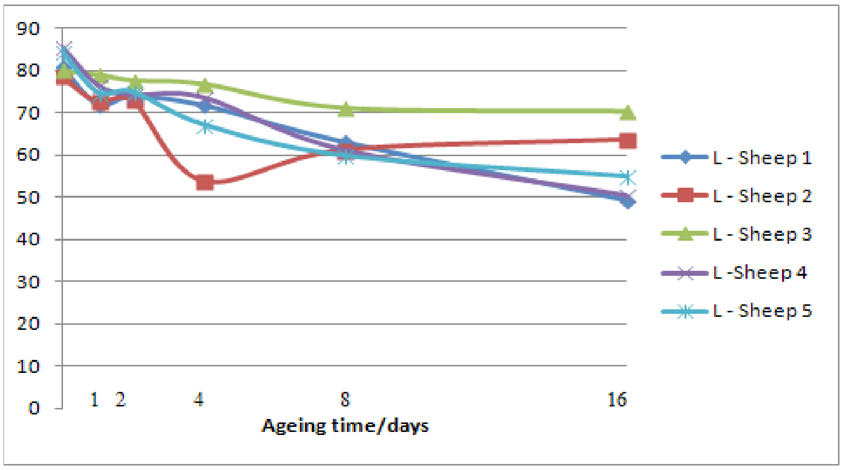


Figure 6. Variations of the L parameter after the ageing treatments

And from Fig. 6, as in the case of Fig. 5, it is observed that parameter L for samples S2 and S3 has the smallest changes after 16 days of artificial ageing, which confirms the good behaviour of these parchments during artificial ageing.

Because the 5 parchments obtained from 5 sheepskins were processed by the same process, it was expected that the results would show the same trend. However, the results obtained by evaluating the shrinkage temperature and colour parameters, resulted in a different behaviour after artificial ageing. This required correlations in terms of volatile matter (especially fats) and parchment's thickness. From our practice, it is known that the "quality" of parchment obtained from sheepskin is influenced by the fat content during the life of the animal, which cannot be completely eliminated during processing by specific chemical and mechanical operations.

In order to highlight the characteristics that influence the change of parchment colour during artificial ageing, a correlation of chemical and physical characteristics was performed, respectively the ratio of extractable substances (which are especially fats) and the thickness of parchments and colour parameters obtained by using CIE L*a*b* and CIEL*C*h, according to Table 4.

Table 4: Correlations between the ratio of extractable substances and the thickness of the parchments and the colour parameters obtained by using CIE L*a*b* and CIEL*C*h for the 16 days of ageing treatment

Sample	Volatile matter, %	Thickness, mm	Extractable substances/ Thickness	CIE L*a*b* and CIEL*C*h parameters				
				a*	b*	c*	h	L*
S1	6.61	0.28	23.607	11.13	36.05	37.72	72.84	49.23
S2	2.39	0.29	8.2414	10.27	40.04	41.34	75.61	63.7
S3	3.69	0.26	14.192	5.25	34.11	34.51	81.25	70.22
S4	5.83	0.29	20.103	15.73	34.46	37.88	65.47	50.51
S5	8.81	0.34	25.912	13.87	39.05	41.44	70.45	54.88

From the point of view of the colour changes we can conclude that after 16 days of accelerated ageing it is observed that for h parameter, the highest difference was recorded for sample 4, followed by sample 5 and sample 1. The smallest difference was recorded for sample 3. In the case of b and c parameters, the highest differences after 16 days were recorded for samples 2 and 5 followed by samples 1, 4 and 3.

After 8 days of accelerated ageing, the parameter a of the sample S5 is the biggest difference with a fat content of 8.81 and a thickness of 0.34, followed by the S4 sample with 5.83 grams and 0.29 thick, S1 sample with 6.61 fat and 0.28 thickness, S2 sample with 2.39 grams and 0.29 grams and sample 3, the smallest change with 3.69 grams and 0.26 thick.

For b and c parameters the greatest difference was recorded for the S1 and S5 samples with the highest fat content followed by the S2, S4 and S3 samples.

For parameter h, the largest variation was recorded in the S4 and S5 samples and the smallest difference was recorded for the S3 sample.

CONCLUSION

In this study we investigated the influence of accelerated ageing treatments on parchment samples exposed to 85°C temperature and 60% relative humidity with duration of one day, 2 days, 4 days, 8 days and 16 days and assessed the generated effects. The 5 sheepskins were technologically processed in the same way. The artificial ageing treatments affected the treated parchment samples compared to the untreated samples.

The chemical characteristics have similar values for all the parchment samples, except for the big value variations of extractable substances which showed great differences due to the way of preserving the skins by salting and to the biological characteristics of animals. Shrinkage temperatures, Ts, showed a rather good hydrothermal stability for the untreated parchment samples, but all samples show a major decrease of 5-9°C in the shrinkage temperature after a day of artificial ageing and continued to decrease in correlation with the exposure time. The most damaged samples were S4 and S5 after 16 days of ageing treatment. The results obtained by evaluating the shrinkage temperature and colour parameters, culminated in a different behaviour after artificial ageing. While the shrinkage temperature caused an accentuated decrease in Ts, the colour changes analyses results reported small differences in b*, c*, h parameters and substantial changes in a* and L* parameters for the samples S1, S4 and S5. We can conclude that the best behaviour to the artificial ageing was the sample S2 which presented small difference in colour in correlation with the smaller quantity of extractable substances (fat content).

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BIODEGRADABLE POLYMERIC COMPOSITE BASED ON RECYCLED POLYURETHANE AND RUBBER WASTES: MATERIAL FOR GREEN SHOE MANUFACTURING

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BIODEGRADABLE POLYMERIC COMPOSITE BASED ON RECYCLED POLYURETHANE AND RUBBER WASTES: MATERIAL FOR GREEN SHOE MANUFACTURING

ABSTRACT. This paper presents the process of obtaining biodegradable polymeric composites based on post-consumption thermoplastic polyurethane and post-consumption vulcanized rubber waste, in various ratios (5, 10, 20, 30, 50%), cryogenically ground to min. 100 nm, and maleic anhydride grafted polyethylene as compatibilizer between the two phases. This composite will be formed into a low-density product, with low cost, recovery and reuse of waste, containing post-consumption polymers, and last but not least, biodegradable. The methodology for making the new materials involves the following steps: sorting waste, grinding, functionalization and compounding. These operations are easy to manage and do not involve new equipment. Compounding, the most important operation, will be carried out on a corotating twin-screw extruder-granulator with the possibility to adjust parameters such as temperature and speed depending on the material, having a screw ratio (L/D-35). The tested biodegradable composites were characterized structurally and physico-mechanically. Waste transformation (ground and functionalized) into new value-added products will lead to remarkable improvements in the life cycle of raw materials and the responsible use of this waste, contributing to sustainability, improving eco-efficiency and economic efficiency and reducing the "pressure" of waste on the environment.

KEY WORDS: biodegradability, polymeric composite, post-consumption, green footwear

COMPOZIT POLIMERIC BIODEGRADABIL PE BAZĂ DE POLIURETAN RECICLAT ȘI DEȘEURI DE CAUCIUC: MATERIAL PENTRU FABRICAREA ÎNCĂLȚĂMINTEI ECOLOGICE

REZUMAT. Această lucrare prezintă procesul de obținere a unor compozite polimerice biodegradabile pe bază de poliuretan termoplastic post-consum și deșeuri post-consum de cauciuc vulcanizate, în proporţii variate (5, 10, 20, 30, 50%), măcinat criogenic la dimensiuni de min. 100 nm și compatibilizator, polietilenă grefată cu anhidridă maleică, între cele două faze. Acest compozit va fi utilizat la realizarea unui produs cu densitate scăzută, cu cost redus, cu recuperarea și reutilizarea deșeurilor, cu conținut de polimeri post-consum, și nu în ultimul rând, biodegradabil. Metodologia de obținere a noilor materiale implică următorii pași: sortarea deșeurilor, măcinarea, funcționalizarea și compoundarea. Aceste operațiuni sunt ușor de gestionat și nu presupun echipamente noi. Compoundarea, cea mai importantă operațiune, va fi realizată pe un extruder-granulator cu dublu șnec cu posibilitatea de a adapta parametri ca temperatura și viteza în funcție de material, având un raport al șnecului (L/D-35). Compozitele biodegradabile experimentate au fost caracterizate structural și fizico-mecanic. Transformarea deșeurilor (măcinate și funcționalizate) în produse noi cu valoare adăugată va conduce la îmbunătățiri remarcabile ale ciclului de viață a materiilor prime și la utilizarea responsabilă a acestui deșeu, contribuind la sustenabilitate, la îmbunătățirea eco-eficienței și eficienței economice și la reducerea „presiunii" deșeurilor asupra mediului.

CUVINTE CHEIE: biodegradabilitate, compozit polimeric, post-consum, încălțăminte ecologică

COMPOSITE POLYMÉRIQUE BIODÉGRADABLE À BASE DE POLYURÉTHANE RECYCLÉE ET DE DÉCHETS DE CAOUTCHOUC : MATÉRIEL POUR LA FABRICATION DES CHAUSSURES ÉCOLOGIQUES

RÉSUMÉ. Cet article présente le processus d'obtention des composites polymères biodégradables à base de polyuréthane thermoplastique post-consommation et de déchets post-consommation de caoutchouc vulcanisé, dans diverses proportions (5, 10, 20, 30, 50%), broyés cryogéniquement à min. 100 nm et polyéthylène greffé anhydride maléique comme compatibilisant entre les deux phases. Ce composite sera transformé en un produit de faible densité, avec un faible coût, en récupérant et réutilisant des déchets, contenant des polymères post-consommation, et enfin et non des moindres, biodégradable. La méthodologie d'obtention des nouveaux matériaux comprend les étapes suivantes : tri des déchets, broyage, fonctionnalisation et compoundage. Ces opérations sont faciles à gérer et n'impliquent pas de nouveaux équipements. Le compoundage, l'opération la plus importante, sera réalisé sur une extrudeuse bi-vis corotative avec la possibilité d'ajuster des paramètres tels que la température et la vitesse en fonction du matériau, ayant un rapport de vis (L/D-35). Les composites biodégradables expérimentés ont été caractérisés structurellement et physico-mécaniquement. La transformation des déchets (broyés et fonctionnalisés) en nouveaux produits à valeur ajoutée conduira à des améliorations remarquables du cycle de vie des matières premières et à l'utilisation responsable de ces déchets, contribuant à la durabilité, améliorant l'éco-efficacité et l'efficacité économique et réduisant la « pression » des déchets sur l'environnement.

MOTS CLÉS : biodégradabilité, composite polymère, post-consommation, chaussures écologiques

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INTRODUCTION

In 2015, the European Commission adopted the new Circular Economy Action Plan to stimulate Europe's transition from a linear towards a circular economy. This ambitious initiative: "Closing the loop - An EU action plan for the Circular Economy" is promoting the transition to a more circular economy, where the value of products, materials and resources is maintained in the economy for as long as possible and the generation of waste is minimized, being an essential contribution to the EU's efforts to develop a sustainable, low carbon, resource efficient and competitive economy. By maintaining the value of the materials and energy used in products in the value chain for the optimal duration and by minimising waste and resource use, the circular economy can promote competitiveness, innovation, a high level of protection for humans and the environment, and bring major economic benefits, thus contributing to growth and job creation. It can also provide consumers with more durable and innovative products that lead to monetary savings and an increased quality of life. Nowadays, the circular economy is an irreversible, global trend. It was foreseen that the proposed actions would contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy [1-4].

The paper presents a recycling route for post consumption shoe soles and wood wastes in order to obtain biodegradable composites for green shoe manufacturing. Reusing and recycling of polymer waste are valid options to reduce the amount of waste and, implicitly, the environmental impact, as required by Directive 2008/98/EC. A possible alternative is the transformation of polymer waste with a long lifespan into biodegradable polymeric composites. The worldwide trend toward using cheap, atoxic and durable materials from renewable resources contributes to sustainable development. Thus, the investigation of the potential use of rubber wastes as reinforcing agent in polymeric composites has gained new significance [5]. The global overuse of the synthetic polymer materials has brought some significant issues due to their negative impact on the environment during the past years [6]. Most synthetic polymers made from petroleum and its allied components are not degradable after they are transformed into waste. Today, more and more scientists have shifted their attention to the eco-friendly polymeric materials [7]. Advances in polymer waste management in recent years have made used tires be perceived as a potential source of energy or new raw materials. [8]. Analysis reports of the tire recycling market show that vulcanized rubber powder from tires is mainly used as a filler agent and modifiers in various types of compositions and polymer composites [9-12]. Discarded tires and other rubber waste (containing high quality natural and synthetic rubbers) have become the source of materials for obtaining "environmentally-friendly" composites with useful properties. The benefits of using such materials include the sustainable management of large quantities of used polymer items that are currently burdening the environment and the cost reduction of composite materials produced from cheap polymeric waste [13, 14]. The increase in the level of consumption of rubber recycling products shows that rubber powder is used in the rubber industry as a raw material for obtaining composites with useful practical properties and in an economical way. For high quality and durable rubber products, the use of rubber powder is limited. Therefore, rubber composites obtained by using rubber powder are used in practice for the manufacture of cheap items, where strength is not a priority, such as: flooring materials, windshield wipers, washers, conveyor belts, moulds, cable insulators and shoe soles [15]. Powders obtained from rubber waste can be used to obtain various types of new rubber-polymer composites with elastomeric and thermoplastic matrices. It is known in the literature that the properties of rubber powder depend on the method of obtaining it (cryogenic grinding or at ambient temperature), granule size, crosslinking, filler content, and the type of natural or synthetic rubber that the original products had. The mechanical properties and performance of polymer composites manufactured from rubber powder obtained from waste depend on the type of polymer matrix used and therefore the nature of the interactions between the matrix, the type and size of rubber granules and their quantity in composites [14, 15]. Thermoplastic polyurethane (TPU) is a preferred choice of polymer to produce engineering products because it has good physical and chemical characteristics, TPU can be processed with extrusion, injection, blow and compression molding equipment. In addition to that, TPU is well suited for a wide variety of fabrication processes [16]. There are previous studies reporting on TPU composites used with several different fibres, for instance TPU reinforced with synthetic fibres such as glass [17] and carbon fibre [18], with other natural fibres [19] such as curaua fibre [20], kenaf fibre [21] and rossele fibres [22]. The literature shows that no study has been carried out on post-consumption thermoplastic polyurethane (WTPU) / post-consumption rubber waste composites. The aim of this paper is to study the properties of WR reinforced WTPU composites with differential rubber waste content (5, 10, 20, 30 and 50 wt%). Tensile strength, tear strength, elasticity, hardness, elongation of break, attrition, melt flow index and morphological study (FT-IR) of WTPU/WR composites were examined.

EXPERIMENTAL

Materials and Methods

Materials

Materials used to obtain the polymer composites based on recycled polyurethane and rubber wastes are as follows: all composites contain post-consumption thermoplastic polyurethane waste (WTPU) compounded with compatibilizing agent, polyethylene grafted with maleic anhydride (PE-G-MA) from Sigma Aldrich and post-consumption butadiene-styrene rubber waste (WR), cryogenically milled at 10,000 rpm for 15 s and sieved through a 100 nm mesh sieve.

Preparation of Various Types of Biodegradable Polymer Composite

WTPU, PE-g-MA and WR were mechanically mixed in Brabender Plasti-Corder PLE 360 at 175°C and 80 rpm for 3 minutes, to melt the plastomer, and for 2 min. at 170°C for homogenisation. The total time was 7 min. Table 1 shows tested formulations from the Brabender mixing diagrams presented in Figure 1.

Table 1: Formulations of TPU waste with butadiene-styrene rubber waste and compatibilizing agent

	TPU waste + SBR powder + PE-g-MA					
Components	TPU 0	TPU 1 (5%)	TPU 2 (10%)	TPU 3 (20%)	TPU 4 (30%)	TPU 5 (50%)
TR waste	300	285	270	240	210	150
SBR Powder	0	15	30	60	90	150
PE-g-MA	0	15	15	15	15	15

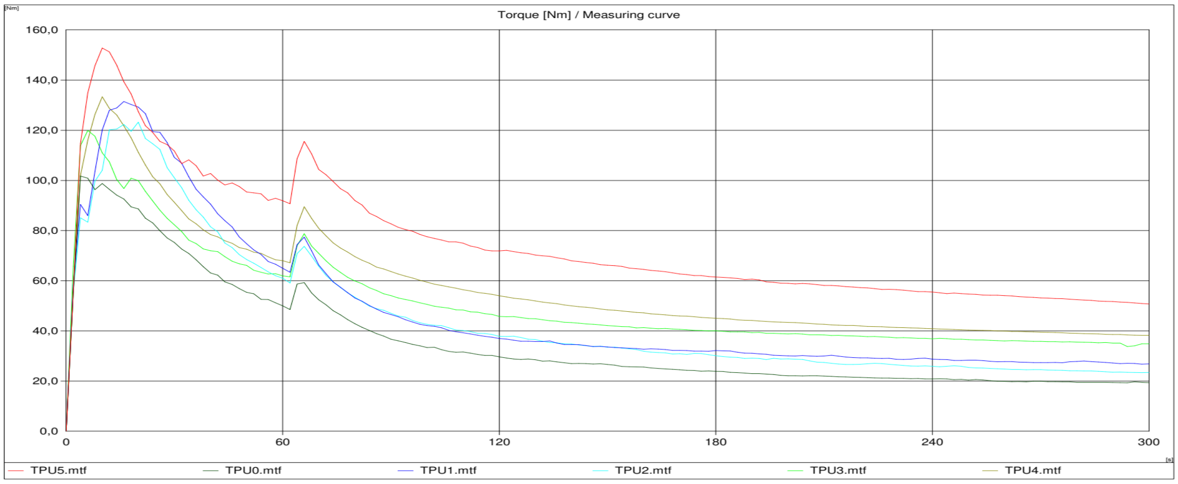

Figure 1. The overlapping Brabender mixing diagrams of control sample (WTPU – TPU0) and TPU-1-5 polymeric composites of TPU waste with butadiene-styrene rubber waste and compatibilizing agent

From the diagrams shown in Figure 1 it is observed that the temperature in the mixing chamber increases, depending on the percentage of rubber waste added to the polymer composite (starting from 175°C, it decreases to 120-144°C then increases as follows: TPU1-183°C, TPU2-185°C, TPU3-187°C, TPU4 -192°C and TPU5-205°C, the latter being the composite with a percentage of 50% elastomeric waste). Also, the mixing forces increase proportionally with the percentage of elastomeric waste in the composite starting at a temperature of 175°C and reaching a maximum at 30 seconds of mixing of 120 Nm for the TPU1 sample and increasing proportionally up to 157 Nm for the TPU5 sample. The maximum force is reached when the WTPU plasticizes and the dispersion of WR particles begins. After reaching the maximum force, it decreases evenly, the last minute being constant, which indicates the homogenization of the mixture. Table 2 shows the processing characteristics presented in the Brabender diagrams, for each processed composite.

Table 2: The characteristics, presented in the Brabender processing diagrams, for WTPU/PE-g-MA/WR polymer composites

Compound/ Characteristics	TPU1 (5%WR)	TPU2 (10%WR)	TPU3 (20%WR)	TPU4 (30%WR)	TPU5 (50%WR)
Loading peak temperature, °C	123	127	134	138	144
Inflection point temperature, °C	178	183	157	159	165
Maximum temperature, °C	178	183	160	162	168
Loading peak energy, Nm	67.2	77.0	18.0	18.1	22.4
Maximum energy, kNm	36,2	19.8	102,7	116.6	156.8
Gelation area energy, J	1,3	0.0	0.8	1.1	1.2
Specific energy (W/Sample mass), kJ	0.3	0.3.5	0.4	0.4	0.6
Gelation speed, Nm/min.	8.1	7.1	372,5	447.6	537.6

The compounds were then compression-molded (using an electrically heated laboratory press) to obtain a sheet of about 2 mm thick. Press parameters: preheating 3 min.; pressing 4 min.; cooling 13 min.; pressure 300 kN; temperature 170°C. The sheet was then cooled down to room temperature under the same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Testing Methods

Tensile tests of the samples were carried out according to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was measured by Shore "A" Durometer according to SR ISO 7619-1:2011.

Abrasion resistance was carried out according to ISO 4649/2010, the cylinder method, using a pressure of 10 N. Abrasion resistance was expressed by relative volume loss in relation to calibrated abrasive paper. A wearing tester with abrasive cloth having granulation of 212–80 mm (PE 80). The samples used were obtained from rolled blends and pressed into sheets, then cutting with a rotating die and have cylindrical shape, with a diameter of 16 mm and height of min. 6 mm.

Repeated flexions - Ross Flex - SR ISO 132/2018 is the test that determines the resistance of the specimens to the appearance and propagation of cracks when they are subjected to repeated flexions at an angle of 90°, on a mandrel with a diameter of 10 mm, up to 30,000 cycles or until the crack appears or the material breaks.

FT-IR spectroscopy was done using the FT-IR 4200 JASCO, Herschel series instrument, equipped with ATR having diamond crystal and sapphire head within the spectrometric range 2000-530 cm^{-1}.

RESULTS AND DISCUSSIONS

Physical-mechanical tests were carried out in the Investigation laboratory from INCDTP - Division ICPI, accredited by RENAR, and materialized in the determination of hardness, elasticity, tensile and tear strength, attrition, residual elongation and elongation at break for thermo-oxidative aging (168h x 100°C) and normal state, and melt flow index (see Tables 3 and 4).

Table 3: Physical-mechanical test results of formulations: TPU waste with butadiene-styrene rubber waste and compatibilizing agent

Property / test method	TPU0	TPU1	TPU2	TPU3	TPU4	TPU5
Hardness, °Sh A, SR ISO 7619-1:2011	79	80	81	81	81	78
Elasticity, %, ISO 4662:2009	24	24	24	24	24	20
Modulus, 100 %, ISO 4662:2009	3.53	3.53	3.57	3.43	3.31	2.84
Modulus, 300 %, ISO 4662:2009	6.23	5.29	-	-	-	-
Tensile strength, N/mm2, SR ISO 37:2012	7.9	5.64	4.82	4.29	3.8	3.52
Elongation at break, %, SR ISO 37:2012	480	340	280	220	200	180
Residual elongation, %, SR ISO 37:2012	96	56	34	24	20	18
Tear strength, N/mm, SR EN 12771:2003	49.8	52.6	44.67	41	32.22	25.84
Density, g/cm3, SR ISO 2781:2010	1.18	1.17	1.17	1.17	1.16	1.16
Abrasion, mm3, SR ISO 4649/2010	90.42	100.68	153.3	177.04	189.06	200.25
Ross Flex - repeated flexions SR ISO 132/2018	Withstands up to 150,000 cycles			90000 cycles-cracks appear, withstands cracks up to 109.000 cycles		3600 cycles-cracks appear, withstands cracks up to 25300 cycles

Table 4: Physical-mechanical test results of formulations: TPU waste with butadiene-styrene rubber waste and compatibilizing agent, after accelerated ageing 70°C x 168 h

Sample/Characteristic	TPU0	TPU1	TPU2	TPU3	TPU4	TPU5
Hardness, °Sh A, SR ISO 7619-1:2011	77	78	79	80	81	79
Elasticity %, ISO 4662:2009	30	26	26	24	24	22
Modulus,100 % ISO 4662:2009	3.41	-	-	-	-	3.64
Modulus, 300 % ISO 4662:2009	5.81	3.61	3.52	3.57	3.45	-
Tensile strength, N/mm^2, SR ISO 37:2012	6.65	5.05	4.28	3.57	3.62	3.64
Elongation at break, %, SR ISO 37:2012	460	300	280	180	160	140
Residual elongation, %, SR ISO 37:2012	60	34	28	20	20	20
Tear strength, N/mm, SR EN 12771:2003	58.5	50.5	45	38	34	25.5

Hardness

In the initial state of the control sample, TPU1, hardness value is 79-80°Sh A and increases to 81°Sh A for TPU3 and TPU4 samples, proportional to the rubber waste content. The increase of 2°Sh A is due to the loss of plasticizer in the compounding process at temperatures of 175°C. Regarding the TPU5 sample, with 50% elastomeric waste, the decrease to 78°Sh A occurs due to the large amount of waste, which initially had a hardness below 70°Sh A. After accelerated aging, in the control sample and the first three samples (5-20% elastomeric waste content) the hardness decreases by 1°Sh A due to the plasticization of the WTPU matrix and in those with high content of elastomeric waste, increases by 1°Sh A, due to losses of plasticizer from the elastomeric waste dispersed in the plastic mass.

Tensile Strength

The tensile strength falls in the range from 5.64-3.52 N/mm^2, for normal state and 5.05-3.64 N/mm^2 after aging. The values are comparable to those of thermoplastic polyurethane waste (TPU0) -7,9 N/mm^2 and decreases proportionally with the WR content introduced into the composite. Compared to the normal state, accelerated aging modifies the tensile strength values only by 1-2%.

Elasticity

The elasticity values are the same with the control sample (TPU0), respectively 24%

in all samples, except the composite with 50% elastomeric waste, for which the value is four units lower than the others, due to the high percentage of waste dispersed in the mass of WTPU. The values fall within the specific standards. At the accelerated aging, the values are lower than characteristic of the control sample - 30%, but higher than the characteristic values of the composites tested in normal state and non-uniform.

Tear Strength

Tear strength is an index with performance values, maintaining the same values (52.6-25.84 N/mm) due to tested elastic-plastic composites morphology (Table 3) and decreases proportionally with the amount of composite rubber waste compared to the control sample value of 49.8 N/mm. In the case of accelerated aging, the value of the control sample increases by approximately 20% (from 49.8 N/mm to 58.5 N/mm) compared to the values obtained for the composites that have an increase of 1-2 units, the composite with the higher proportion of rubber waste being practically equal. This is due to the rubber waste which is already aged and no longer influences the test values.

Abrasion Resistance

The values of abrasion resistance increase slightly from 90.42 mm^3 for the control sample up to 100.68 mm^3 for the sample with the 5% rubber wastes and increases with the amount of rubber waste up to 200.25 mm^3 for the TPU5 sample with 50% rubber waste. The values fall within the requirements imposed by the standards.

Density

Density values do not change when the rubber waste particles are added to the compound.

Repeated Flexions – Ross Flex

The current footwear standards specify for thermoplastic polyurethane footwear values of 30,000 cycles when determining repeated flexions. The values presented in Table 3 show that only the TPU5 composite with a rubber waste content of 50% does not fall into this value (25,300 cycles). The others have values five and three times higher, respectively, than the values imposed by the standard.

FT-IT Spectroscopy

IR spectrum represents the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wave length or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 µm. IR domain for usual organic chemistry is between 2.5 and 25 µm. The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm^{-1}, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid-state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the polyurethane waste and elastomeric waste spectrum. The FTIR spectra of the analyzed materials are presented in Fig. 2.

After the tests were carried out, the following were found:

- These figures clearly show the interaction between urethane groups and WF. The FTIR analysis confirmed the presence of functional groups characteristic for the TPU. The urethane moieties of WTPUs are confirmed by the presence of the main characteristic absorption bands. They are well represented by the characteristic ν(C=O) vibration region (1725 cm^{-1}), ν(N-H) stretching vibration region (3326 cm^{-1}) [15] and δ(N-H) bending vibration absorption peak at 1529 cm^{-1} [16]. It should be pointing out that with increasing content of WR in the reaction mixture the carbonyl peak at 1725 cm^{-1} decreases (Figure 2).
- The decrease of the absorption band from 1725 cm^{-1} specific to WTPU is associated with the decrease of the amount of WTPU from the tested composites and the increase of the elastomeric waste content. As the WR content in the polymer mixture increases, the WR-specific signal strength increases.

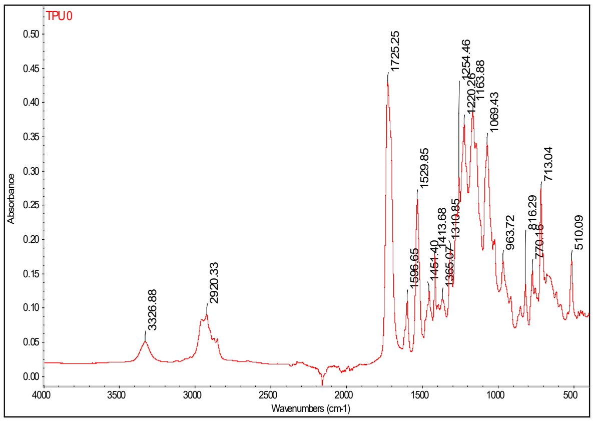

Figure 2. FTIR spectra for WTPU

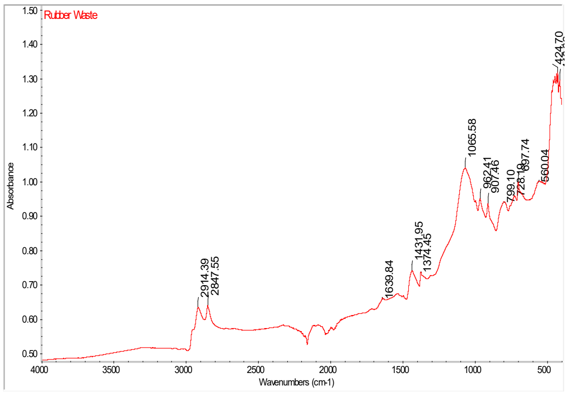

Figure 3. FTIR spectra for WR

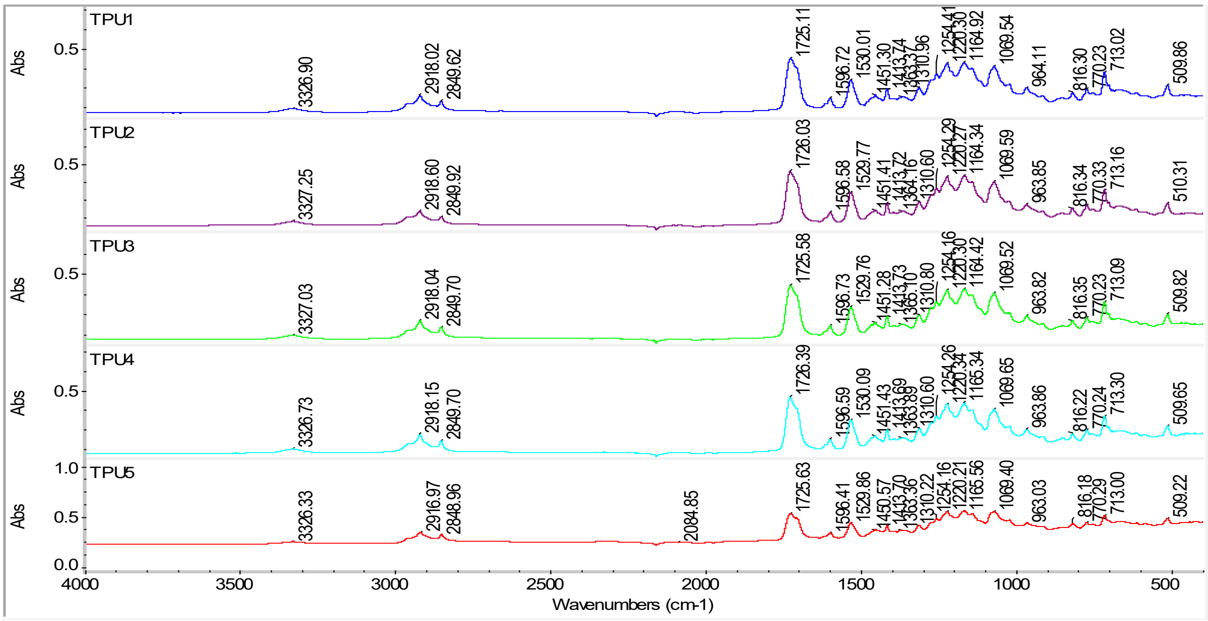

Figure 4. FTIR spectra for WTPU/PE-g-MA/WR polymer composites

- The presence of specific PE-g-MA groups does not appear in the spectra due to the small amount of material.

CONCLUSIONS

Post-consumption thermoplastic polyurethane (WTPU) waste is compounded with cryogenically ground post-consumption rubber waste (WR). These polymeric composites were processed in a twin-screw extruder-granulator using elastomeric waste of different proportions (5, 10, 20, 30, 50%) and compatibilizer based on maleic anhydride grafted polyethylene (PE-g-MA). Polymer composite samples with percentages of 5, 10, 20% post-consumer elastomeric waste showed the best physical and mechanical performance compared to those with higher percentages of elastomeric waste (30, 50%), characteristics that fall in the specific values of standardized thermoplastic polyurethane. Properties such as elongation at break and elasticity showed a slight reduction compared to WTPU, and the hardness increased by 1-2 units. The tensile strength of the composition decreased by half compared to WTPU. Thus, the WTPU / PE-G-MA / WR composite has a great potential for use in the footwear industry. Thus, the use of thermoplastic polyurethane and post-consumer rubber waste in polymer composites could contribute to sustainable development in the near future.

Acknowledgements

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Disclaimer

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EUROPEAN RESEARCH AREA

COTANCE NEWSLETTERS

Starting with January 2019, the COTANCE Council will issue a monthly COTANCE Newsletter with the purpose of promoting an improved image of leather to relevant decision makers and domestic stakeholders including Members of the European and National Parliament, Governmental authorities, Ministerial officers, Customers of the leather industry, Brands, Retail chains, Relevant NGOs, Designers, etc. The monthly newsletters present topics that tell the truth about a controversial aspect or a fact that is not well known by the general public to bring about a better understanding of leather and the European leather industry, as well as a positive predisposition to legislate in favor of the leather industry. The newsletters are available in seven languages at https://www.euroleather.com/index.php/newsletter, and were also published in the 2019 issues as well as the first 2020 issues of Leather and Footwear Journal. Newsletters 6 & 7 are given below.

NEWS 6/2020

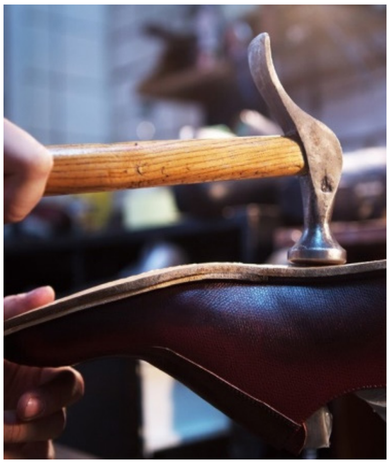
Original ways to use post-consumer leather

The leather value chain is a perfect example for the famous 3 Rs of the waste hierarchy: Reduce - Reuse – Recycle.

Indeed, tanners reduce biological waste from the meat sector, reusing the animal’s hides and skins for creating a new material, through their recycling into leather.

While this is true, there is still more that can be achieved through the circularity of leather and its sustainability.

What other “Rs” does leather bring to address the challenges of the 21st century?



Repairing

Leather articles can be repaired if they break! This feature is unique, something that substitute materials cannot offer. Think of how often one can re-sole shoes or repair the leather strap of your favourite leather bag, etc.

Reinventing

Although leather is designed for durability, it does not mean you cannot be in a mood for a change. Leather’s longevity allows leather articles to have a second or even a third life. Second-hand shops do good business with vintage leather articles, as they become trendy, generation after generation.

Reducing

Some leather articles are may be too small or no longer suitable for a new use. But even when leather is close to its end-of-life, useful applications can be found. For instance, shredded leather has been used and is still being used as a bedding in horse riding arenas; Either alone or in combination with wood or wood and paper residues, it cushions the impact of hooves on the ground.

Repurposing

Certain leather articles need to be replaced from time to time. This happens with office furniture or train and airplane seating or similar goods. Major companies have found creative ways to recover and reuse the leather from seating and produce other leather articles. An example is Amtrak, the US train company which has decided to turn their leather seating into appealing backpacks.

BiodegRadation

What happens at the very end of the lifecycle of leather? Well, leather is a natural material and with time and the appropriate environmental conditions, it will biodegrade. Leather is not like plastic that ends up as microparticles in our oceans and eventually enters the food chain. If we can still find leather in archaeological findings it is because the circumstances and conditions (temperature, relative humidity, light, exposure to air, absorption of natural preserving substances, etc.) were favourable for its preservation.

Picture of archeological finding taken from Djed Medu’s blog

Leather is not done surprising us! We need to look out for new collaborations with private and public partners, where the combination of the versatility and qualities of leather could reveal new uses for it. Why not thermal insulation in the buildings? End-of-life leather in the construction of highways? etc.

You may have a good idea. If so, share it with us and we may help you bring it to life.

Let’s continue re-inventing leather!

edited by

COTANCE

in collaboration with

CURTIDORES
ESPAÑOLES
SPANISH
TANNERS

NEWS 7/2020

How do we assess leather quality?

Tanning involves performing successive, interconnected chemical and mechanical operations. Water and various chemicals are used in precise quantities, at exact temperatures. Imposed treatment times and mechanical operations have strict settings. Leather quality requires monitoring, control, and human intervention. These processes impart the qualities that are desired in the finished leather.

In short, leather quality is a set of characteristics: resistance to physical-mechanical stress; comfort and safety during use/wear; durability and repair possibilities; aesthetics.

Let us go a little more into detail:

Authenticity

Leather is unique. "Leather-like" is not leather!

To avoid being deceived, before all else check the label and don’t trust any advertisement using oxymorons; the association of the term leather with a qualifier that makes no sense, such as apple, pineapple, wine, cactus, artificial, synthetic, vegan or similar indicates that they are fakes.

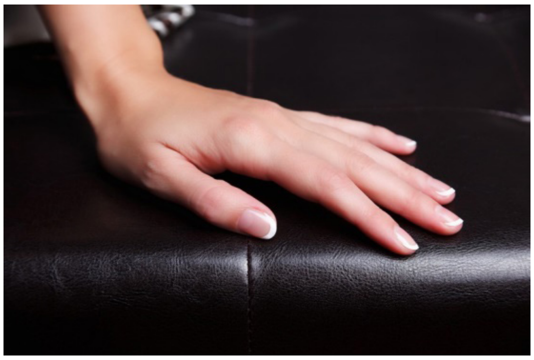
Restricted Substances

Restricted substances are chemicals which are strictly controlled.

Restrictions are stipulated by laws and regulations (such as the EU REACh Directive) and are complemented by lists of unwanted chemicals set by global brands, ecolabels, and NGOs, e.g. Restricted Substance Lists, Product Restricted Substance List or Manufacturer Restricted Substance List). In all cases, limit values are specified and test methods recommended.

Look, Touch & Smell

The look of leather is determined by the raw material and the tanning process. When leather is left as natural as possible, the original grain, the pattern of the dermis (hair follicles, fish or reptile scales) as well as any scars from the animal's life can be observed with the naked eye. If sanded with abrasive paper, you get nubuck or suede. By embossing with various patterns, you can mimic a different natural grain or create a totally new design. When covered with finishing films or coatings, you get coated leather and, if it has a mirror-like appearance, it becomes patent leather.



Touch and smell are sensations felt by the user. The touch can be dry, waxy, oily. The smell is the trace of a range of chemicals used to process the hides and skins. Some of them impart to the leather their own specific aroma. This is the case of vegetable tannins as well as oils. It is a specific odour, peculiar, but not at all unpleasant.

Resistance to Physical and Mechanical Stress or to Environmental and Use Conditions

Resistance is the property derived from the original fibrous structure of the material and what gives durability to the leather. It refers to tensile strength and tearing load. The surface doesn't crack with bending and elongation, and elasticity gives comfort when worn.

Leather resists water, sunlight, temperature, wet and dry rubbing, abrasions, repeated flexing, as required by the intended use.

Comfort

Leather provides thermal insulation, elasto-plasticity, which allows the product to keep its shape and not feel rigid the next time it is worn. Leather absorbs perspiration and releases it in the interval between uses. This is particularly relevant in footwear.

To conclude:

Since leather talks to your senses, it had better keep its promises!

All the above quality characteristics are routinely assessed by tanners and their customers, with test methods that the leather industry has developed over time and which are standardised in IULTCS, ISO and CEN.

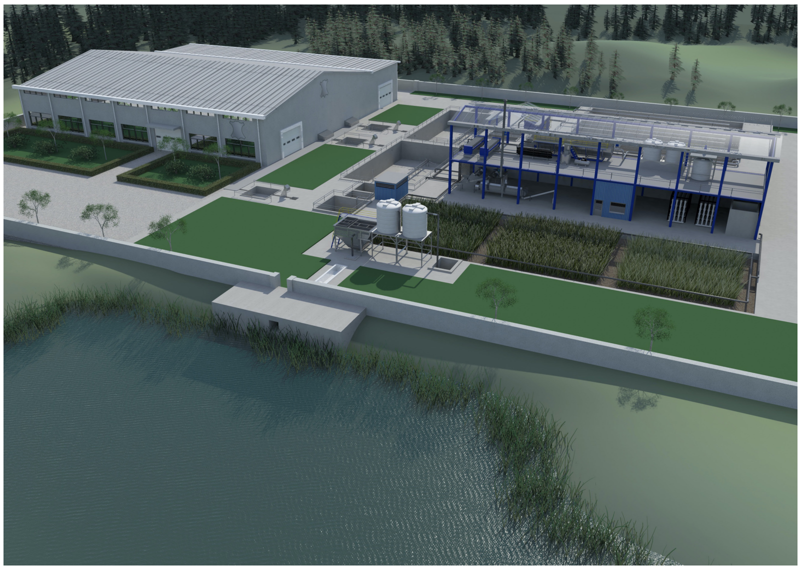
European leather assures consumers of its unequalled quality credentials.

edited by COTANCE

in collaboration with APPBR

NEWS RELEASE FROM THE IULTCS

New Videos Introducing Key Technologies for Tannery Effluent Treatment



The IULTCS is pleased to announce the addition of an animated introduction to 'Key Technologies for Tannery Effluent Treatment and Solid Waste Handling' to the IUE webpage of the Environmental Commission. The videos give an introduction to each treatment technology and describe the function and what potentially can be achieved. http://www.iultcs.org/effluent.php

The animated treatments are part of the environmental training courses of W2O Environment, which were made available by the company to be shared on the webpage of the IUE commission. W2O Environment Ltd was founded in 2005 and is an internationally recognised environmental company, supporting the leather industry worldwide, which provides environmental engineering of tannery effluent treatment and sludge handling plants and environmental training at Universities, for organisation and for the overall leather sector.

Dr Wolfram Scholz, Chair IUE Commission

News Release from the IULTCS

10 July 2020

EEthiopia to Host Global Leather Industry Events in 2021

As the world experiences the full impact of COVID-19 the global leather industry looks forward to the time when we have the opportunity to meet again, share our knowledge and renew old friendships. We also look towards countries where we are seeing investment in the industry and the enthusiasm to embrace innovation and adopt new technologies. The launch of “9 Days of Leather” in Addis Ababa, Ethiopia couldn’t be more pertinent.

Events will commence on 01 November 2021 with the 5th World Leather Congress (WLC) organised by the International Council of Tanners and COMESA LLPI with the theme ‘Leather – a Gift of Nature’.

Delegates can then move on to the major leather science and technology event the XXXVI IULTCS Congress which will be held from 03-05 November 2021 and will be exploring the theme of ‘Greening the Leather Value Chain’. The call for Congress abstracts will open shortly and abstracts will be able to be uploaded to the website.

The Congress venue will be the Ethiopian Skylight Hotel, close to the International airport in Addis Ababa.

The final three days, 06-09 November 2021 will then be dedicated to the All Africa Leather Fair (AALF) - Africa´s largest international exhibition dedicated to leather, accessories, components, footwear, leather goods, automotive and furniture.

Prof. Mwinyi Mwinyihija, IULTCS Congress President and Executive Director Africa Leather and Leather Products Institute (ALLPI) extends a warm welcome to leather industry friends from around the world as Africa opens the doors in 2021.

LEATHER: EUROPEAN SOCIAL AND ENVIRONMENTAL REPORT 2020

Program: EU Social Dialogue
Project: VS/2019/0009
Duration: February 2019 – October 2020
Coordinator: COTANCE
Co-coordinator: IndustriAll European Trade Union
Partners: ACEXPIEL (Spain), AHLI (Hungary), APIC (Portugal), APPBR (Romania), FFTM (France), FV TBSL (Austria), SG (Sweden), UKLF (UK), UNIC - Concerie Italiane (Italy), VDL (Germany)
Website: https://euroleather.com/news/projects/european-social-environmental-report

Objective and Short Description

The reflection of the performance of the European tanning sector regarding social indicators and environmental parameters which demonstrate the continuous striving of this towards excellence in the mentioned fields. The results of the Social and Environmental Report (SER 20) follows up on the exercise done in 2012.

The project will collect company data on some 37 social indicators and about 39 environmental parameters that reflect the performance of the tannery. Company data will be anonymised and aggregated at national level before being centrally computed at European level for drawing the conclusions. The Report will be completed with the activities developed by the Social Partners together or individually between 2012 and 2019 and in particular those related to projects such as *Leather is my Job!, A Future for Leather!, or Due Diligence for Healthy Workplaces in the Tanning industry*, as well as to the development by COTANCE of the *Product Environmental Footprint Category Rules (PEFCR) for Leather*, to Animal Welfare, to Traceability and to all the initiatives to improve the image of leather and develop education and training in the European Leather industry.

The initiative also includes the implementation of national workshops aimed at promoting the exercise and addressing hot topics related to Social or Environmental issues affecting the image of the leather industry.

A Final Conference where the results and SER 2020 will be presented and largely disseminated will conclude the initiative.

Project's Main Activities

- Drafting of the questionnaire (social indicators & environmental parameters)
- Translations of the questionnaire in the partners' languages
- Collection of national data
- Anonymisation / compilation at national level
- Agglomeration of data at European level and report
- National SD workshops
- Infographic video
- Translations (report) in the partners' languages
- Final conference
- Dissemination

Management of the project has included also:

- EU social partners (COTANCE and industriAll) Kick-off Meeting – 7 February 2019
- 4 Steering Committee (representatives of all partners) Meetings

27 February 2019, the first Steering Committee Meeting - The delegates from ACEXPIEL (ES), AHLI (HU), APPBR (RO), FFTM (FR), UKLF (UK), UNIC (IT) and VDL (DE) met in Brussels at the COTANCE headquarters and, since this first meeting was open to observers, were joined by a representative of BDSZ, the Hungarian Trade Union and a representative of industriAll European Trade Union.

Romanian Participation in the Project

APPBR (Asociatia Producatorilor de Piele si Blana din Romania / Romanian Leather and Fur Producers Association) is representing Romanian leather industry in the framework of the COTANCE - industriAll Social Dialogue project “Leather: Social and Environmental Report - 2020”.

APPBR has participated in all activities of the project and, according to the planned actions, on the 5th of December 2019 has organized in Bucharest, with the support of INCDTP-ICPI, the **NATIONAL WORKSHOP ROMANIA** on the topic: **CIRCULAR ECONOMY AND LEATHER INDUSTRY**.

In the SER 2020 Romanian National Workshop have participated 18 persons, as follows:

- 1 representative of COTANCE – Mr. Gustavo Gonzalez Quijano, Secretary General;
- 5 Romanian leather companies, represented by 6 participants;
- 1 representative of CONFPELTEX Trade Union;
- 3 representatives of APPBR; the President, Mr. Dorel Acsinte has represented the PIELOREX Tannery too;
- 8 senior researchers from Leather and Footwear Research Institute (INCDTP-ICPI), including Ms. Dana Gurau who provided the simultaneous interpretation.

The Workshop Program included the following 5 speeches/presentations:

1. Short presentation of SER 2020 project and APPBR’s activities - Luminita ALBU
2. Circular economy and sustainability - Priorities at EU level - Luminita ALBU, Gheorghe COARA
3. Circular economy - Solutions for leather industry - Gheorghe BOSTACA, Dorel ACSINTE
4. Strong employers’ organisations for the European Leather Industry - The importance of the Social Sectoral Dialogue - A presentation of COTANCE - Gustavo GONZALEZ-QUIJANO
5. Leather - Example of circular economy - Gustavo GONZALEZ-QUIJANO

Pictures from the SER 2020 – Romanian National Workshop

The Final Report and Dissemination

The new **Social and Environmental Report of the European Leather Industry (SER 2020)** is based on an intensive survey amongst European tanneries, led by COTANCE and industriAll-European Trade Union; company data on social indicators and environmental parameters that reflect the performance of the tanning sector were collected for each year of the reference period (2016 – 2017 – 2018). Companies' data, anonymised and aggregated at national level and centrally computed at European level are presented and analysed, versus 2012 data, where appropriate (in terms of average values).

Once the operation of agglomeration of data, from the national tanneries of partners, was completed, the elaboration of Draft Report by UNIC started. This has been completed at the end of February 2020. This contained:

- The EU tanning industry: Economic overview
- Social Footprint of the EU Tanning Industry
- Environmental Footprint of the EU Leather Industry
- Sustainability Priorities / Ethical Issues for the Value Chain
- Objectives and Challenges for the Future
- Methodological Note
- Glossary
- Partnership

The draft in question was sent to all partners for analysis and completions.

In the last Steering Committee meeting, on the 2nd of April 2020 (organized online), discussions were made on chapters, starting from the comments and additions proposed by the partners and the final form of the Report has been adopted. Subsequently the Final Report was sent to all partners to be translated into their national languages. For large-scale dissemination, the Report will be available in English, French, German, Hungarian, Italian, Portuguese, Romanian, Spanish and Swedish in electronic form (web and memory stick) and in a limited number of printed brochures.

The Cover for Social and Environmental Report 2012 (EN) and 2020 (RO)

On the 24th of April 2020, COTANCE and industriAll-Europe announced that, due to the Covid-19 pandemic, the Final Conference of the EU-sponsored "Leather: Social and Environmental Report 2020" project, initially scheduled in Vienna on 16 June 2020, has been postponed to the last quarter of 2020.

The Final Conference where the SER 2020 will be largely disseminated will take place online on December 1st 2020.; till then, the paper *“SER 2020 – A comparative approach proving the EU tanning industry’s continuous striving towards sustainable development”*, authors: G. Gonzalez-Quijano, D. Acsinte, Gh. Bostaca will be presented during ICAMS 2020 (1 – 3 October 2020, Bucharest, Romania).

Project Partners:

Coordinator / Co-coordinator:

COTANCE

industriAll EUROPEAN TRADE UNION

Partners:

APPBR

CURTIDORES ESPAÑOLES SPANISH TANNERS

leather from portugal

FRANCE F.F.T.M.

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ASSOCIATION OF HUNGARIAN LIGHT INDUSTRY

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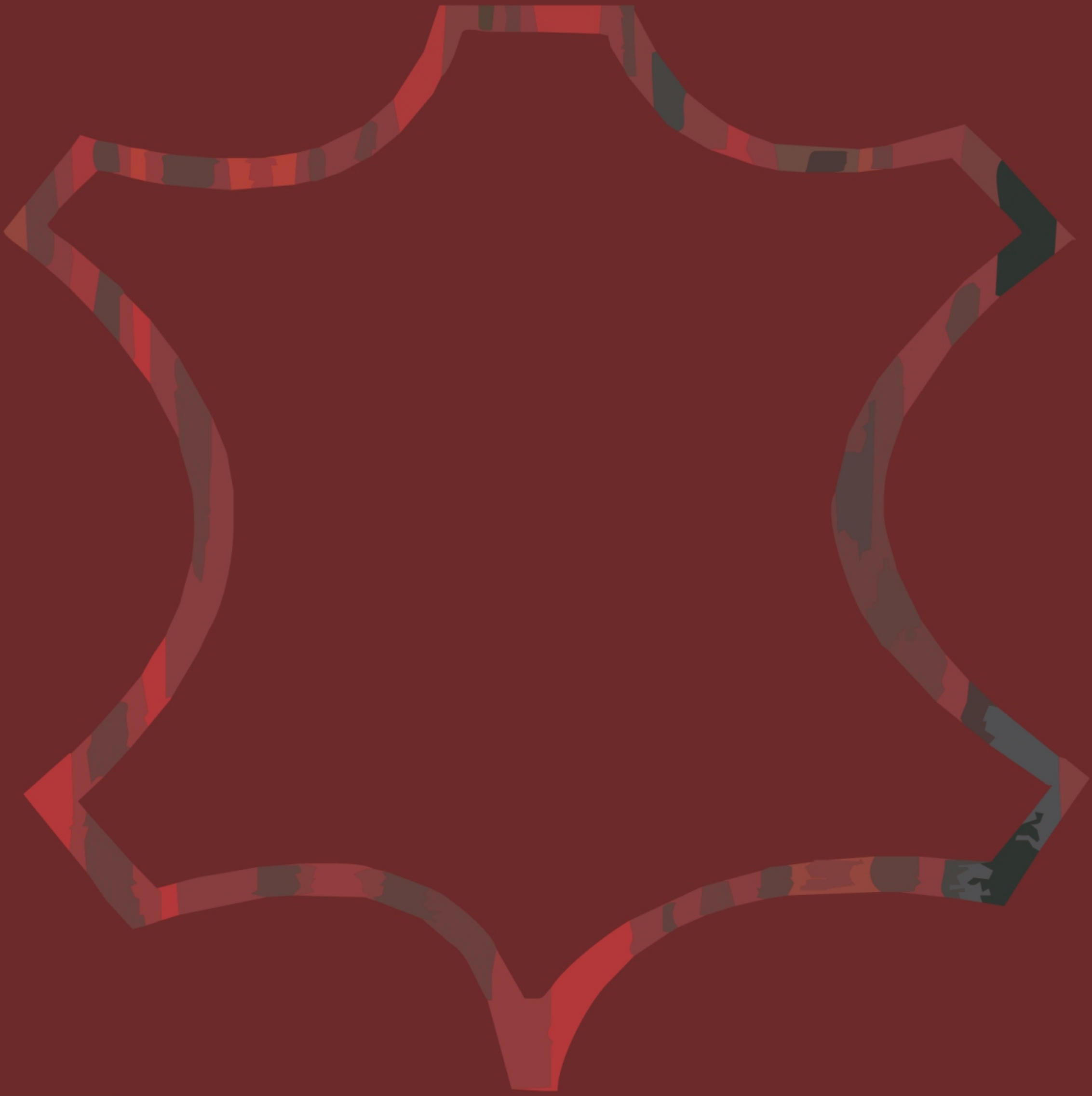

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