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KERATIN HYDROLYSATE FROM WOOL BY-PRODUCTS AS AN ADDITIVE FOR DYEING BOVINE LEATHERS

Mariana Daniela BERECHET*, **Carmen GAIDĂU**, **Demetra SIMION**, **Claudiu ȘENDREA**

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KERATIN HYDROLYSATE FROM WOOL BY-PRODUCTS AS AN ADDITIVE FOR DYEING BOVINE LEATHERS

ABSTRACT. In this research, the aim was to obtain keratin hydrolysate from wool waste from sheep breeders and use it in technologies for dyeing bovine hides. The keratin hydrolysate (KerNa), obtained by alkaline hydrolysis with sodium hydroxide, was physico-chemically analyzed, determining the protein substance in the amount of 80.65%, highlighting the bands specific to peptides and compounds with sulfur by FTIR spectroscopy and particle size by DLS technique, obtaining majority populations at 161 nm and 615 nm. Bovine hides were treated with keratin hydrolysate, in different stages of the dyeing process, and an increase in the dyeing resistance to wet and dry rubbing and the dyeing resistance to water drops was obtained, as well as the improvement of the specific color parameters. Leathers dyed with the use of the KerNa additive showed an increase in the friction resistance of the dyeing (grade 5/5) and brighter colors according to ISO Brightness. Treatments based on protein-rich keratin hydrolysate, applied in various stages of the dyeing process, interact with the leather's collagen or tanning agents, giving the finished leathers improved properties of shade, shine and softness. The good results obtained in the applications of keratin hydrolysate in the leather industry show that the keratin extract can be the basis for obtaining new biomaterials with various applications. The utilization of wool waste from animal husbandry leads to a decrease in the amount of waste and the prevention of environmental pollution.

KEY WORDS: keratin hydrolysate, dyeing resistance, wool by-products

HIDROLIZATUL DE CHERATINĂ OBȚINUT DIN SUBPRODUSE DE LÂNĂ UTILIZAT CA ADITIV ÎN VOPSIREA PIEILOR DE BOVINE

REZUMAT. În această cercetare s-a urmărit obținerea unui hidrolizat de cheratină din deșeuri de lână de la crescătorii de ovine și folosirea în tehnologii de vopsire a pieilor de bovină. Hidrolizatul de cheratină (KerNa), obținut prin hidroliză alcalină cu hidroxid de sodiu, a fost analizat fizico-chimic, determinându-se substanța proteică în valoare de 80,65%, punându-se în evidență benzile specifice peptidelor și compușilor cu sulf, prin spectroscopie FTIR și dimensiunea particulelor prin tehnica DLS, obținându-se populații majoritare la 161 nm și la 615 nm. S-au tratat piei bovine cu hidrolizat de cheratină, în diferite etape ale procesului de vopsire și s-a obținut o creștere a rezistenței vopsirii la frecare umedă și uscată și a rezistenței vopsirii la picătura de apă, precum și îmbunătățirea parametrilor specifici de culoare. Pieile vopsite cu utilizarea aditivului KerNa au prezentat o creștere a rezistenței la frecare a vopsirii (nota 5/5) și culori mai strălucitoare conform ISO Brightness. Tratamentele pe bază de hidrolizat de cheratină bogat în proteine, aplicate în diverse etape ale procesului de vopsire interacționează cu colagenul pielii sau agenții tananți conferind pieilor finite proprietăți îmbunătățite de nuanță, strălucire și moliciune. Rezultatele bune obținute în aplicațiile hidrolizatului de cheratină în industria de pielărie arată că extractul de cheratină poate sta la baza obținerii de biomateriale noi cu aplicații diverse. Valorificarea deșeurilor de lână din zootehnie conduce la scăderea cantității deșeurilor și prevenirea poluării mediului înconjurător.

CUVINTE CHEIE: hidrolizat de cheratină, rezistența vopsirii, subproduse de lână

L'HYDROLYSAT DE KÉRATINE OBTENU À PARTIR DE SOUS-PRODUITS DE LAINE UTILISÉ COMME ADDITIF DANS LA TEINTURE DES PEAUX DE BOVINS

RÉSUMÉ. Dans cette recherche, l'objectif a été d'obtenir un hydrolysat de kératine à partir de déchets de laine d'éleveurs ovins et de l'utiliser dans les technologies de teinture des peaux de bovins. L'hydrolysat de kératine (KerNa), obtenu par hydrolyse alcaline à la soude, a été analysé physico-chimiquement, pour déterminer la substance protéique à hauteur de 80,65%, mettant en évidence les bandes spécifiques aux peptides et composés soufrés, par spectroscopie FTIR et la taille des particules par DLS, obtenant de populations majoritaires à 161 nm et 615 nm. Les peaux de bovins ont été traitées avec de l'hydrolysat de kératine, à différentes étapes du processus de teinture, et une augmentation de la résistance de la teinture au frottement humide et sec et de la résistance de la teinture aux gouttes d'eau a été obtenue, ainsi qu'une amélioration des paramètres de couleur spécifiques. Les cuirs teints avec l'utilisation de l'additif KerNa ont montré une augmentation de la résistance au frottement de la teinture (grade 5/5) et des couleurs plus vives selon la norme ISO Brightness. Les traitements à base d'hydrolysat de kératine riche en protéines, appliqués à différentes étapes du processus de teinture, interagissent avec le collagène de la peau ou les agents de tannage, conférant aux peaux finies des propriétés améliorées d'ombre, de brillance et de douceur. Les bons résultats obtenus dans les applications de l'hydrolysat de kératine dans l'industrie du cuir montrent que l'extrait de kératine peut être à la base de l'obtention de nouveaux biomatériaux aux applications variées. L'utilisation des déchets de laine issus de l'élevage entraîne une diminution de la quantité de déchets et la prévention de la pollution de l'environnement.

MOTS CLÉS : hydrolysat de kératine, résistance à la teinture, sous-produits de la laine

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INTRODUCTION

Keratin is used in various applications based on natural biomaterials. In addition to the potential of assembling into organized structures, keratin is also composed of bioactive elements suitable for the initiation of biocompatible interactions with various substrates [1]. Keratin-rich waste pollutes the environment and is released in increasing quantities as by-products from agro-industrial or leather processing operations [2-4]. Keratin from renewable sources from the leather industry is abundant, available and easily harvested. Extracted keratin hydrolysates can be processed into various products using established techniques specific to a wide range of fields [5, 6]. Keratinous materials have a high protein content consisting of at least 17 amino acids that can be used in animal feed or agricultural fertilizers. Degradation of keratin waste can therefore provide an inexpensive source of protein and amino acids [7]. Keratinous materials, formed by specifically organized keratinized cells, filled with proteins, mainly fibrous keratins, are natural polymeric composites that present a complex hierarchical structure that varies from nano to centimeter: polypeptide chain structure, filamentous matrix structure, lamellar structure, structure in sandwich-type layers. These fibrous keratins are the most abundant and have an average molecular mass in the range of 40-60 kDa [8-10]. On the other hand, keratinous materials have a high cysteine content that differentiates them from other biopolymers, they are usually durable, hard and non-reactive with the natural environment. They provide mechanical support and various protective functions in the adaptation of vertebrates to the external environment [11]. Matrix proteins have a high content of cysteine, glycine and tyrosine amino acids. Those fractions with a high content of cysteine have a molecular weight in the range of 11-26 kDa, and those fractions with a high content of glycine and tyrosine residues have a molecular weight between 6 and 9 kDa [10, 12]. Keratins and keratinized materials are often discussed in terms of α- and β-keratins. Keratins are classified into α-keratins (amorphous model) from keratinized tissues and β-keratins, which are found in bird feathers [13, 14]. Since ordered structures (α- or β-keratins) predominate, keratinized materials are conveniently distinguished by these components. In addition, the two usual secondary structures, α-helix and β-sheet, are the two major internal support structures in proteins [15]; therefore, they are usually used to classify keratins [13].

The preparation of keratin hydrolysates from the waste wool generated by sheep breeding contributes to the design of new biomaterials and to the prevention of environmental pollution. The obtained keratin hydrolysates can be used for the creation of new biomaterials with multiple applications, as well as for the design of new ecological treatments for hides and furs with different functionalities, which will lead to a reduction in the consumption of petroleum origin auxiliaries and synthethic dyes.

EXPERIMENTAL

Materials and Methods

Wool waste was purchased from seep breeders from Constanța County, ammonium and sodium carbonate was supplied by SC Cristal RChim SRL, sodium hydroxide was supplied by Lachner. The bovine wet-blue leathers were prepared in Leather Research Department by standard technology. Keratin hydrolysate was obtained from wool waste by alkaline hydrolysis in the presence of sodium hydroxide. All reagents used were analytical grade.

Obtaining Keratin Hydrolysate

The wool was degreased, chopped and hydrolyzed by the alkaline method in the presence of sodium hydroxide, at 80°C, for 4 hours, in a steel reaction vessel with automated control of stirring and temperature to obtain soluble keratin hydrolysates, according to the scheme presented in Figure 1.

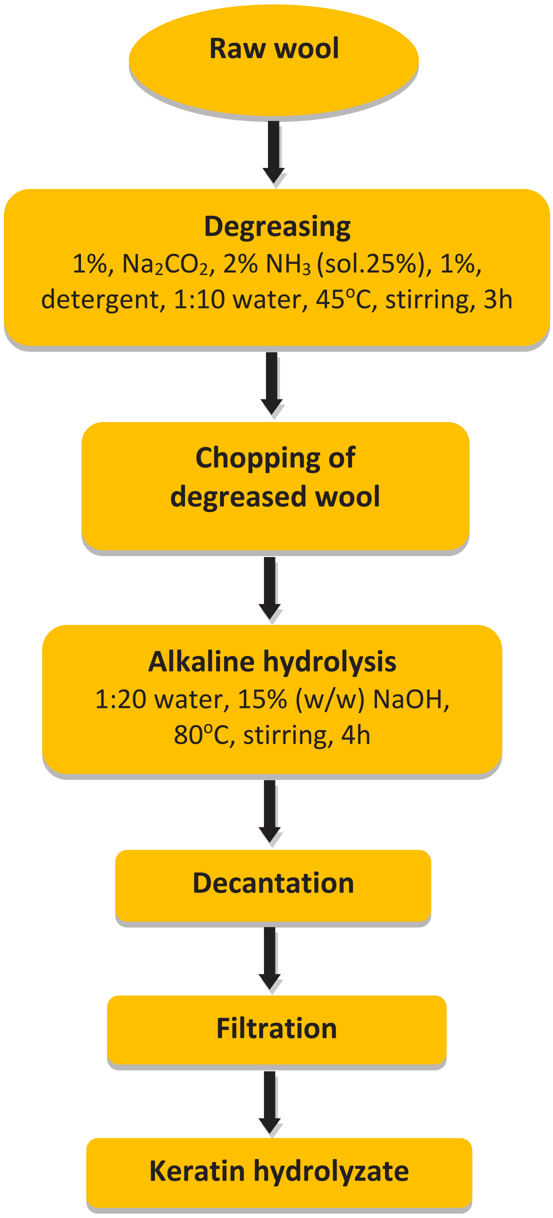


Figure 1. Technological scheme for obtaining keratin hydrolysate by alkaline hydrolysis

Characterization of Keratin Hydrolysate

The keratin hydrolysate obtained by alkaline hydrolysis was characterized by physico-chemical analyses regarding the content in dry substance (SR EN ISO 4684:2006), total ash (SR EN ISO 4047:2002), total nitrogen and protein substance (SR ISO 5397:1996), pH (STAS 8619/3:1990) and amino nitrogen (ICPI Method).

Determination of Particle Size by DLS Technique

The keratin hydrolysate obtained was analyzed using Malvern's Zetasizer Nano ZS equipment. Three measurements were made to determine the size of the particles and the Zeta potential.

Characterization of Keratin Hydrolysate by FTIR

Fourier Transform Infrared Spectroscopy (FTIR) spectra of samples were obtained using Nicolet iS50 FTIR spectrophotometer in the wave number ranging from 400 cm^{-1} to 4000 cm^{-1}, using attenuated total reflection (ATR).

Experiments on Leather Dyeing with Keratin Hydrolysate

The keratin hydrolysate was tested as additive for leather dyeing following the dosing stages presented in Table 2.

Analyses of Dyed Leathers Using Keratin Hydrolysate as Additive

The leather characteristics were assessed for colour fastness to cycles of to-and-fro rubbing (SR EN ISO 11640:2013), resistance to water drop (STAS 8259/3-68) and softness (SR EN ISO 17235:2002). The color characteristics were measured by using the Datacolor CHECK II portable spectrophotometer provided with a color analysis software.

RESULTS AND DISCUSSIONS

Physico-chemical Analysis of Keratin Hydrolysate

The physico-chemical characteristics of keratin hydrolysate obtained by alkaline hydrolysis with sodium hydroxide is rich in total nitrogen content (13.93%) and protein substance (80.65%), which can influence the results obtained in the treatment of bovine leathers in dyeing processes (Table 1).

Table 1. Physico-chemical characteristics of keratin hydrolysate

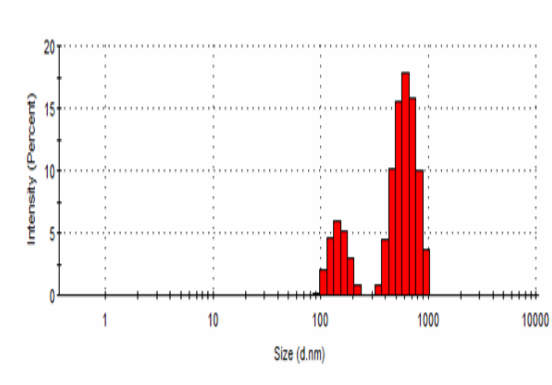
Characteristics	KerNa
Dry substance, %	15.72
Ash, %	9.73
Total nitrogen*, %	13.93
Protein substance*, %	80.65
pH, pH units	10.10
Aminic nitrogen**, %	0.49

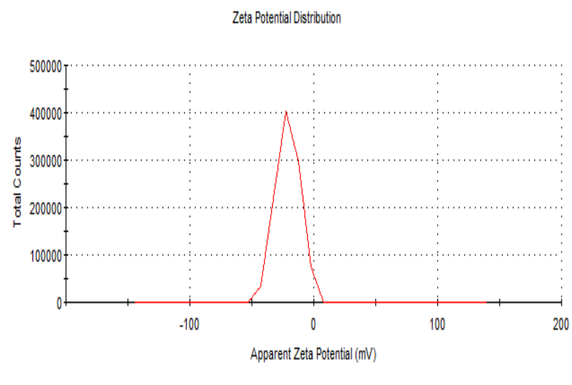
* reported to the dry substance.

** reported to the protein substance.

Determination of Particle Size by DLS Technique

Two major populations were highlighted at 164nm and 615 nm (Figure 2 (a)), with an average particle size of 776 nm and a polydispersity of 0.707. The measured Zeta potential has a value of -20.9mV (Figure 2 (b)).





(a) (b)

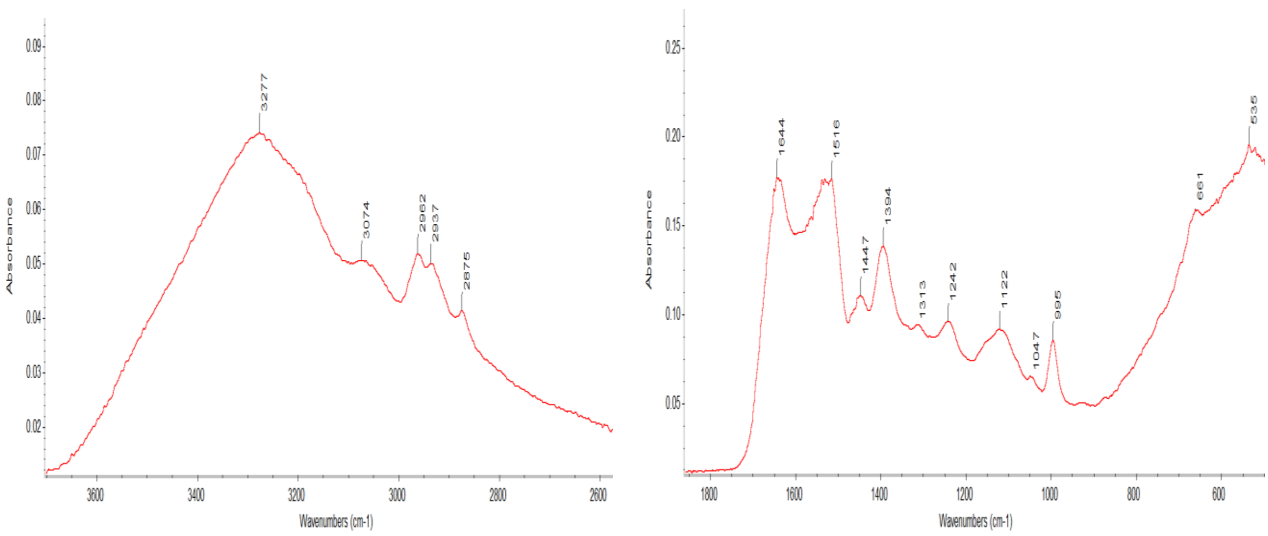
Figure 2. Histogram of particle sizes distribution (a), and Zeta potential (b) of keratin hydrolysate (KerNa)

Characterization of Keratin Hydrolysate by FTIR

The infrared absorption spectrum of keratin hydrolysate (KerNa) shows characteristic absorption bands attributed to peptides (-CONH), known as amide I, amide II, and amide III as well as sulfur compounds [16-18]. The broad band appearance indicates hydrogen bonding at 3277 cm^{-1}. Absorption bands at 3074 cm^{-1}, 2962 cm^{-1}, 2937 cm^{-1} can be attributed to the differences between O–H, N–H and stretching modes C -H [19-21].

Amides present in the IR spectrum absorption bands located at 1644 cm^{-1} and 1516 cm^{-1} due to the coupling between the valence vibration of the C=O bond and the deformation vibration of the N-H bond; the two bands are usually described as the amide I band (due mainly to the valence vibration of the C=O bond) and the amide II band (due to a vibrational coupling between an N-H bond deformation frequency and a C-N bond elongation frequency) [22-24].

The band at 1242 cm^{-1} corresponds to C-N stretching vibrations and C=O bending which are identified as amide III [17, 25, 26]. The fingerprint area (1400-400 cm^{-1}) of the IR spectrum contains numerous absorption bands that characterize the molecular structure as a whole (skeleton vibrations: deformation, combination, harmonics) [27, 28].



(a) (b)

Figure 3. FTIR spectrum of the keratin hydrolysate obtained with sodium hydroxide (KerNa), (a) 3600 cm^{-1} - 2600 cm^{-1}, and (b) 1800 cm^{-1} - 500 cm^{-1}

Thiols (R-SH) present in the IR spectrum a characteristic absorption band determined by the valence vibration of the S-H bond located at 2675 cm^{-1}. This band is of weaker intensity and less influenced by the association through hydrogen bonds. In thioethers (R-S-R), the absorption band determined by the valence vibration of the C-S bond appears at 661 cm^{-1} and 535 cm^{-1}, corresponding to the cross-linking disulfide group [17].

The valence vibration of the S=O bond (stretching vibration) produces a band located at 995 cm^{-1} characteristic of sulfoxides (R_2SO) and two bands at 1242 cm^{-1} and 1122 cm^{-1}, and 1313 cm^{-1} and 1394 cm^{-1}, respectively, characteristic of sulfones (R_2SO_2) [17, 29].

The valence vibration of the >C=S bond produces an absorption band at 1047 cm^{-1} [17, 29]. The band at 2675 cm^{-1} is in the area where the absorption bands appear due to the vibration of the -S-H bond (elongation vibration) in the structure of thiols [17].

Testing and Evaluating the Functionality of Keratin Hydrolysate with Applications in Bovine Leather Dyeing

Treatments with keratin hydrolysate obtained by hydrolysis with sodium hydroxide were applied in various stages of the dyeing operation on samples of bovine hides. Three samples of bovine leather were dyed in the presence of keratin hydrolysate in different stages of the dyeing operation compared to a control sample (Table 2). The experiments regarding the use of keratin hydrolysate as a dyeing additive were carried out according to the scheme and notations described in Table 2.

Table 2: Bovine leather samples obtained and application of the keratin hydrolysate in the technological process

No.	Samples obtained, notations	Description
1	V_0	Control sample (without keratin hydrolysate)
2	V_N	Treatment with keratin hydrolysate in the neutralization stage
3	V_1	Keratin hydrolysate treatment in the dyeing stage
4	$V_{1(5.2)}$	Treatment with keratin hydrolysate at pH=5.2, before fixing the dye

The dyed bovine leathers obtained (Figure 4) were analyzed for determining the fastness of the dyeing to dry and wet rubbing, measuring the softness and determining the resistance of the dyeing to water drop (Table 3).

Table 3: Fastness characteristics of dyed bovine leathers

Characteristics			U.M.	Samples / Determined values			
				V_0	V_N	V_1	$V_{1(5.2)}$
Colour fastness to cycles of to-and-fro rubbing	dry	20 cycles	marks	5/5		5/5	5/5
		50 cycles		5/4.5	5/4	5/5	5/5
		100 cycles		5/4.5		5/5	5/5
		500 cycles		5/3		5/4	5/4
	wet	20 cycles		4-5/3		5/4-5	5/4
		50 cycles		4/2	4/2-3	4-5/4	4/3-5
		80 cycles		2/1		3-4/4	3-4/3
Softness, ring opening Ø 25mm			-	2.0	3.0	3.9	3.3
				2.2	3.1	3.3	3.4
				2.2	3.2	3.0	3.5
				Average: 2.1	Average: 3.1	Average: 3.4	Average: 3.4
Resistance to water drop			marks	3	4	4-5	4

The fastness characteristics measured show an improved resistance of the dyeing, compared to the control.

Samples V_0 V_N V_1 $V_{1(5,2)}$

Figure 4. Bovine leathers dyed in the presence of KerNa hydrolysate

Measurement of Leather Color Characteristics with the Datacolor CHECK II Portable Spectrophotometer

With the help of the CIEL*a*b* and CIEL*C*h software systems, specific to the equipment, the chromatic coordinates of the color of each leather sample dyed in the presence of keratin hydrolysate were obtained. The determined color parameters are: L* represents the degree of lightness, the maximum value for L* is 100 (perfect white), and the minimum is 0 (perfect black); a* represents the shade between green (-a*) and red (+a*); the negative value b* is blue while a positive one is yellow; C* (chroma) provides indications regarding the purity (high values) or complexity (low values) of the mixture; h is the hue angle, it reflects the proportion between the chromatic components a* and b*.

The ISO Brightness Index is a parameter calculated from spectrophotometric data that describes the color change of a test sample. This test is most commonly used to evaluate color changes in a material caused by exposure to the open air, real or simulated, but also to determine the degradation produced by light [30].

The measurement of the ISO Brightness index shows an accentuated brightness for the samples obtained with KerNa treatment with a maximum in the case of the sample $V_{1(5,2)}$ (Figure 5).

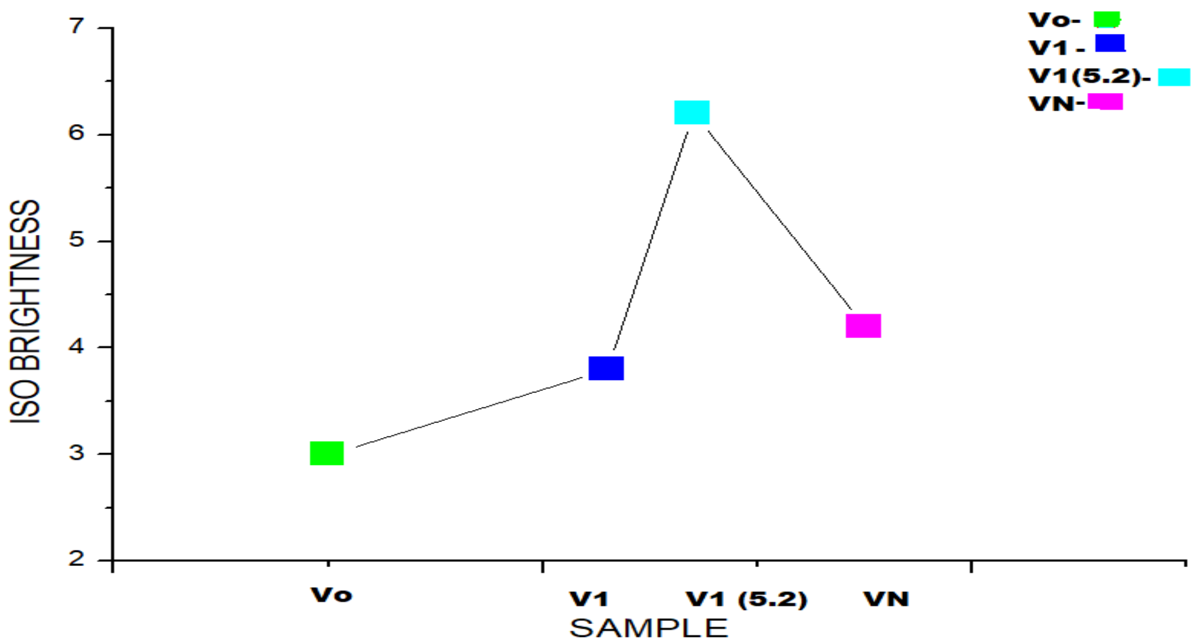


Figure 5. ISO Brightness index for bovine leathers

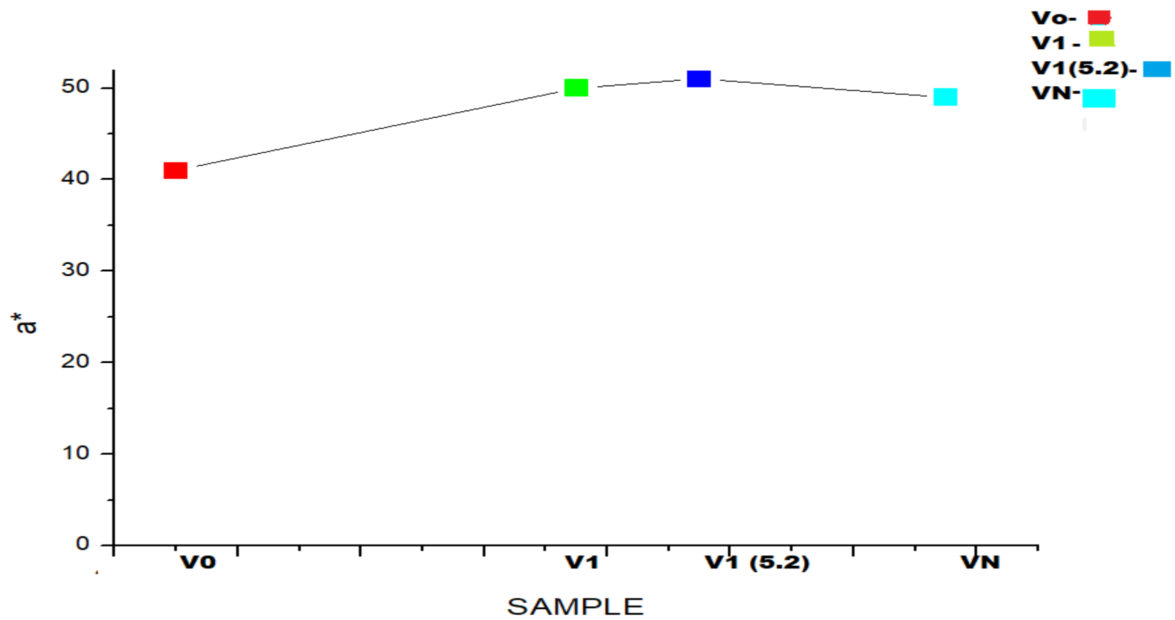


Figure 6. Chromatic component a* for bovine leather

The measurement of the chromatic component a* shows higher values (red component) for the bovine leather samples treated with KerNa compared to the control, V_0 (Figure 6).

By extracting keratin from the wool waste through alkaline hydrolysis in the presence of sodium hydroxide, keratin hydrolysate (KerNa), rich in protein substance, was obtained, which, through specific treatments applied in leather dyeing technology, leads to improved characteristics of finished products. Bovine leathers were treated with keratin hydrolysate, KerNa, in different stages of the dyeing process and an increase in the dyeing fastness to wet and dry rubbing and the dyeing resistance to water drop was obtained, as well as the improvement of the specific color parameters.

CONCLUSIONS

The main conclusions of this research can be summarized as follows:

- Keratin hydrolysate (KerNa), obtained by alkaline hydrolysis with sodium hydroxide from wool by-products, was tested and evaluated in treatments on bovine leathers during the dyeing operations, obtaining an increase in the rubbing resistance of the dyeing (mark 5/ 5) and brighter colors given by ISO Brightness.
- Treatments based on protein-rich keratin hydrolysate, applied in various stages of the leather processing process, interact with the leather's collagen and tanning materials, giving it improved properties of color and softness.
- The good results obtained in the applications of keratin hydrolysate in the leather industry show that keratin extract can be the basis for obtaining new biomaterials with various applications.
- The utilization of wool by-products leads to a decrease in the amount of waste and the prevention of environmental pollution.

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REFERENCES

1. Singh, V., Wang, S., Ng, K.W., 2.25 Keratin as a Biomaterial, in: Reference Module in Materials Science and Materials Engineering, *Comprehensive Biomaterials II*, **2017**, 2, 542–557, https://doi.org/10.1016/B978-0-12-803581-8.09317-6.
2. Călin, M., Constantinescu-Aruxandei, D., Alexandrescu, E., Răut, I., Badea Doni, M., Arsene, M.L., Oancea, F., Jecua, L., Lazăr, V., Degradation of Keratin Substrates by Keratinolytic Fungi, *Electron J Biotechnol*, **2017**, 28, 101–112, https://doi.org/10.1016/j.ejbt.2017.05.007.
3. Lange, L., Huang, Y., Busk, P.K., Microbial Decomposition of Keratin in Nature — A New Hypothesis of Industrial Relevance, *Appl Microbiol Biotechnol*, **2016**, 100, 2083–96, https://doi.org/10.1007/s00253-015-7262-1.
4. Jin, H-S., Park, S.Y., Kim, K., Lee, Y-J., Nam, G-W., Kang, N.J., Lee, D.-W., Development of Akeratinase Activity Assay Using Recombinant Chicken Feather Keratin Substrates, *PLoS One,* **2017,** 12, e0172712, https://doi.org/10.1371/journal.pone.017271.
5. Kreplak, L., Doucet, J., Dumas, P., Briki, F., New Aspects of the α-helix to β-sheet Transition in Stretched Hard α-keratin fibers, *Biophys J*, **2004,** 87, 640–7, https://doi.org/10.1529/biophysj.103.036749.
6. Bragulla, H.H., Homberger, D.G., Structure and Functions of Keratin Proteins in Simple, Stratified, Keratinized and Cornified Epithelia, *J Anat*, **2009**, 214, 516–59, https://doi.org/10.1111/j.1469-7580.2009.01066.x.
7. Holkar, C.R., Jain, S.S., Jadhav, A.J., Pinjari, D.V., Valorization of Keratin Based Waste, *Process Saf Environ Prot*, **2017**, https://doi.org/10.1016/j.psep.2017.08.045.
8. Miserez, A., Guerette, P.A., Phase Transition-induced Elasticity of a-helical Bioelastomeric Fibres and Networks, *Chem Soc Rev*, **2013**, 42, 5, 1973–95, https://doi.org/10.1039/C2CS35294J.
9. Herrmann, H., Aebi, U., Intermediate Filaments: Molecular Structure, Assembly Mechanism, and Integration into Functionally Distinct Intracellular Scaffolds, *Annu Rev Biochem*, **2004**, 73, 749–89, https://doi.org/10.1146/annurev.biochem.73.011303.073823.
10. Vasconcelos, A., Freddi, G., Cavaco-Paulo, A., Biodegradable Materials Based on Silk Fibroin and Keratin, *Biomacromolecules*, **2008**, 9, 1299–1305, https://doi.org/10.1021/bm7012789.
11. Schweizer, J., Bowden, P.E., Coulombe, P.A., Langbein, L., Lane, E.B., Magin, T.M., Maltais, L., Omary, M.B., Parry, D.A.D., Rogers, M.A., Wright, M.W., New Consensus Nomenclature for Mammalian Keratins, *J Cell Biol*, **2006**, 174, 2, 169–74, https://doi.org/10.1083/jcb.200603161.
12. Plowman, J.E., Proteomic Database of Wool Components, *J Chromatogr B*, **2003**, 787, 63–76, https://doi.org/10.1016/S1570-0232(02)00211-8.
13. Wang, B., Yang, W., McKittrick, J., Meyers, M.A., Keratin: Structure, Mechanical Properties, Occurrence in Biological Organisms, and Efforts at Bioinspiration, *Prog Mater Sci*, **2016**, 76, 229–318, https://doi.org/10.1016/j.pmatsci.2015.06.001.
14. Fraser, R.D.B., Parry, D.A.D., The Structural Basis of the Filament-Matrix Texture in the Avian/Reptilian Group of Hard b-keratins, *J Struct Biol*, **2011**, 173, 2, 391–405, https://doi.org/10.1016/j.jsb.2010.09.020.
15. Lodish, H., Berk, A., Zipursky, S.L., Matsudaira, P., Baltimore, D., Darnell, J., *Molecular Cell Biology*, 4th ed. New York, W.H. Freeman and Company, **2000**.
16. Qin, X., Yang, C., Guo, Y., Liu, J., Johannes, H., Bitter, B., Scott, E.L., Zhang C., Effect of Ultrasound on Keratin Valorization from Chicken Feather Waste: Process Optimization and Keratin Characterization, *Ultrason Sonochem,* **2023**, 93, 106297,

https://doi.org/10.1016/j.ultsonch.2023.106297.
17. Alahyaribeik, S., Ullah, A., Methods of Keratin Extraction from Poultry Feathers and Their Effects on Antioxidant Activity of Extracted Keratin, *Int J Biol Macromol*, **2020**, 148, 449–456, https://doi.org/10.1016/j.ijbiomac.2020.01.144.
18. Pan, F., Xiao, Y., Zhang, L., Zhou, J., Wang, C., Lin, W., Leather Wastes into High-value Chemicals: Keratin-based Retanning Agents via UV-initiated Polymerization, *J Clean Prod*, **2023**, 383, 135492, https://doi.org/10.1016/j.jclepro.2022.135492.
19. Lambert, J.B., Shurvell, H.F., Verbit, L., Cooks, R.G., Stout, G.H. (Eds.), *Organic Structural Analysis*, Chapter 5, Macmillan, NY, **1976**.
20. Surewicz, W.K., Mantsch, H.H., Chapman, D., *Biochemistry*, **1993**, 32, 2, 389, https://doi.org/10.1021/bi00053a001.
21. Cardamone, J.M., Investigating the Microstructure of Keratin Extracted from Wool: Peptide Sequence (MALDI-TOF/TOF) and Protein Conformation (FTIR), *J Mol Struct*, **2010**, 969, 97–105, https://doi.org/10.1016/j.molstruc.2010.01.048.
22. Khosa, M.A., Ullah, A., In-situ Modification, Regeneration, and Application of Keratin Biopolymer for Arsenic Removal, *J Hazard Mater*, **2014**, 278, 360–371, https://doi.org/10.1016/j.jhazmat.2014.06.02.
23. Hill, P., Brantley, H., Van Dyke, M., Some Properties of Keratin Biomaterials: Kerateines, *Biomaterials*, **2010**, 31, 585–593, https://doi.org/10.1016/j.biomaterials.2009.09.076.
24. Staron, P., Banach, M., Kowalski, Z., Staron, A., Hydrolysis of Keratin Materials Derived from Poultry Industry, *Proceedings of ECOpole*, **2014**.

https://doi.org/10.1016/j.matpr.2021.09.377.

25. Vasconcelos, A., Freddi, G., Cavaco-Paulo, A., Biodegradable Materials Based on Silk Fibroin and Keratin, *Biomacromolecules*, **2009**, 10, 1019, https://doi.org/10.1021/bm9002927.
26. Wang, J., Gao, H., Qin, C., Zhao, Z., Yuan, H., Wei, J., Nie, Y., Experimental and Theoretical Study on the Extraction of Keratin from Human Hair Using Protic Ionic Liquids, *J Mol Liq*, **2022**, 368, 120626, https://doi.org/10.1016/j.molliq.2022.12062.
27. Tan, B.Y., Nguyen, L.T.H., Ng, K.W., Development of a Mechanically Stable Human Hair Keratin Film for Cell Culture, *Mater Today Commun*, **2022**, 30, 103049, https://doi.org/10.1016/j.mtcomm.2021.103049.
28. Idris, A., Vijayaraghavan, R., Rana, U.A., Fredericks, D., Patti, A.F., MacFarlane, D.R., Dissolution of Feather Keratin in Ionic Liquids, *Green Chem*, **2013**, 15, 525–534, https://doi.org/10.1039/c2gc36556a.
29. Fortunati, E., Aluigi, A., Armentano, I., Morena, F., Emiliani, C., Martino, S., Santulli, C., Torre, L., Kenny, J.M., Puglia, D., Keratins Extracted from Merino Wool and Brown Alpaca Fibres: Thermal, Mechanical and Biological Properties of PLLA Based Biocomposites, *Mater Sci Eng*, C 47, **2015**, 394–406, https://doi.org/10.1016/j.msec.2014.11.007.
30. Alexe, C.A., Gaidau, C., Stanca, M., Radu, A., Stroe, M., Baibarac, M., Mateescu, G., Mateescu, A., Stanculescu, I.R., Multifunctional Leather Surfaces Coated with Nanocomposites through Conventional and Unconventional Methods, *Mater Today: Proc*, **2022**, 54, 44-49,

PRODUCTION OF ELASTIC LEATHERS FROM HORSE RAW MATERIAL USING ACTIVATED AQUEOUS SOLUTIONS OF AGENT

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PRODUCTION OF ELASTIC LEATHERS FROM HORSE RAW MATERIAL USING ACTIVATED AQUEOUS SOLUTIONS OF AGENT

ABSTRACT. A step-by-step technology of formation of leather material made of horse raw materials using electrochemically activated aqueous solutions of chemical agents has been developed. Effective implementation of the leather raw material soaking process has been established due to the use of the optimal ratio of catholyte and anolyte. At the same time, environmentally hazardous agents are excluded from the process and its duration is reduced by two times compared to the current technology. The use of working solutions at the stages of liming and tanning with the use of catholyte and anolyte respectively, ensures the exclusion of environmentally hazardous chemical agents and the reduction of the processes duration. The developed technology of production of leather materials, unlike the existing ones, is characterized by simultaneous treatment of all anatomical areas of the hide.

KEY WORDS: horse hide, electrochemically activated water, activated agent solutions, technology, leather properties

REALIZAREA DE PIEI ELASTICE FOLOSIND CA MATRIE PRIMĂ PIELE DE CAL ȘI SOLUȚII APOASE CU AGENȚI DE ACTIVARE

REZUMAT. S-a dezvoltat pas cu pas o tehnologie de obținere a pielii folosind ca materie primă piele de cal și soluții apoase activate electrochimic de agenți chimici. Implementarea eficientă a procesului de înmuiere a pielii s-a datorat utilizării raportului optim de catolit și anolit. În același timp, agenții periculoși pentru mediu sunt excluși din proces, iar durata acestuia este redusă de două ori comparativ cu tehnologia actuală. Utilizarea soluțiilor de lucru în etapele de cenușărire și tăbăcire, folosind catolitul, respectiv anolitul, asigură excluderea agenților chimici periculoși pentru mediu și reducerea duratei proceselor. Tehnologia de obținere a pielii dezvoltată, spre deosebire de cele existente, este caracterizată de tratarea simultană a tuturor zonelor anatomice ale pielii.

CUVINTE CHEIE: piele de cal, apă activată electrochimic, soluții cu agent de activare, tehnologie, proprietăți ale pielii

FABRICATION DE CUIRS ÉLASTIQUES À PARTIR DE MATIÈRE PREMIÈRE DE CHEVAL À L'AIDE DE SOLUTIONS AQUEUSES AVEC DES AGENTS ACTIVANTS

RÉSUMÉ. Une technologie d'obtention du cuir a été développée étape par étape en utilisant le cuir de cheval comme matière première et des solutions aqueuses activées électrochimiquement par des agents chimiques. La mise en œuvre efficace du processus de trempage de la peau était due à l'utilisation du rapport optimal entre le catholyte et l'anolyte. Dans le même temps, les agents dangereux pour l'environnement sont exclus du processus et sa durée est réduite de deux fois par rapport à la technologie actuelle. L'utilisation de solutions de travail dans les étapes de pelanage et de tannage, utilisant respectivement le catholyte et l'anolyte, garantit l'exclusion des agents chimiques dangereux pour l'environnement et la réduction de la durée des processus. La technologie d'obtention de la peau développée, contrairement à celles existantes, se caractérise par le traitement simultané de toutes les zones anatomiques de la peau.

MOTS CLÉS : cuir de cheval, eau activée électrochimiquement, solutions avec des agents activants, technologie, propriétés du cuir

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INTRODUCTION

One of the effective ways to improve existing technologies is the use of new chemical agents, including activated water and its solutions. Various methods are used to obtain activated water [1, 2]: under the influence of thermal, magnetic, ultrasonic and electric fields. At the same time, electrochemically activated (ECA) water has advantages compared to the use of other types of liquid treatments in leather materials manufacturing technologies. This concerns the high redox potential, the thermodynamic imbalance of such technological solutions stored for a long time and causing intensification of biotechnological processes [3, 4]. Another advantage of ECA solutions is the possibility of effective regulation of their properties. The use of ECA water in technologies of leather and fur raw materials processing can be considered particularly effective. Taking into account the significant volume of working solutions and the need to protect natural raw materials from biological damage caused by microorganisms, the use of ECA solutions of agents in the multi-component and multi-stage technology of leather materials production can be considered promising. At the same time, an urgent issue is to reduce the consumption of environmentally harmful agents and the duration of individual step-by-step physical and chemical treatments via development of chemical composition of working solutions and the conditions for their effective use for production of high-quality leather materials.

ECA water is known to be used in medicine, electronic industry, agriculture, food and light industries, and other industries [5]. At the same time, many works use different fractions of ECA water: catholyte and anolyte that are characterized by specific properties in relation to pH, available chemically active radicals and ions, and high redox potential [1]. In works [6, 7], the authors identified effective bactericidal properties of anolyte in relation to the vital activity of pathogenic microorganisms. In this case, lack of habituation of microorganisms to such disinfectants despite their environmental safety has been shown. The authors [8] identified bactericidal properties of anolyte on test organisms. In the furfural synthesis technology, the authors [9] showed the possibility of using anolyte as a catalyst instead of acid agents.

In paper [10], peculiarities of ECA water diffusion into the structure of protein raw materials were studied. In this case, glycosaminoglycans and lipids are effectively removed from the structure of leather raw materials. At the same time, catholyte exhibits an intense extractive effect during the processing of plant raw materials [11]. The specific properties of the effect of ECA aqueous solutions on physical and chemical transformations of the collagen structure of rabbit skin tissue were studied in [12]. It was established that catholyte and anolyte significantly increase the volume formation and deformation characteristics of hide tissue. In paper [13], the plasticizing effect of catholyte on the structure of leather material during the formation of shoe products was established. At the same time, efficiency of using the material area increases. The authors [14] report the improvement of physical and mechanical as well as deformation characteristics of the hide after tanning processes: re-tanning, re-dyeing and greasing. However, re-tanning significantly reduces the elongation of the material, while the coefficient of its homogeneity decreased as a result of greasing. The use of THPS prior to plant tanning [15] reduces consumption of chromium compounds during tanning, increases heat resistance of the hide and the elastic and plastic properties of the dermis.

Thus, the analysis of scientific and technical references on the study of the properties and use of fractions of electrochemically activated water: anolyte and catholyte of different chemical composition in technological processes proves their high bactericidal and physicochemical properties. This gives grounds for the prospects of practical application in leather production technologies.

The aim of the research is to study the influence of electrochemically activated solutions of chemical agents on the processes of formation of elastic leather material from raw horsehide and its properties.

EXPERIMENTAL

Materials and Methods

The research is carried out using halves of wet-salted horsehide with a mass of 6.6 kg after fleshing in raw materials with a moisture content of 45.3–51.8 and a thickness of 1.7–6.2 in different anatomical areas of the hide (Table 1).

Table 1: Changes in content of moisture and dermis thickness by anatomical areas of horsehide

Area name	Moisture, % of dermis mass	Thickness, mm
Head	68.1 / 49.9	1.7
Neck	66.7 / 48.6	1.9
Back	63.9 / 45.3	4.1
Loin	64.7 / 46.8	5.4
Flank	69.2 / 50.1	3.3
Dock	64.6 / 46.4	6.1
Croup	65.3 / 46.9	5.7
Legs	70.1 / 50.8	2.8
Stifle	66.4 / 47.2	3.7
Barrel	71.3 / 51.8	2.3
Average	67.03 / 48.38	3.7

Note: The numerator and denominator show moisture content in the dermis of fresh hide respectively, without taking into account the hair preserved by brining

Table 1 shows that the maximum moisture content of fresh horsehide is observed in peripheral areas. Central anatomical areas are characterized by minimal moisture content. The uneven distribution of moisture in the anatomical areas of the horsehides stays even after they have been brined. The same refers to thickness distribution.

In research on the technology of formation of elastic hides from horse raw materials, two fractions of ECA water: anolyte and catholyte and a number of chemical agents of different composition were used. ECA fractions of water are obtained in the research laboratory of the National University of Food Technologies at the semi-production flow-type installation «Izumrud KFTO» (RF, Petersburg) with a capacity of 60-70 dm^3/h. Anolyte and catholyte are characterized by a pH of 2.7-3.6 and 9.0-10.8, respectively, and a redox potential of 300-1500 and –100…–700 mV. It should be noted that under the conditions of storage in closed rooms without an air layer, the hydrogen index and the redox potential of the catholyte and anolyte relax to a quasi-stable state within 50 hours by 3% and 16–18%, respectively [16].

Among the other technological agents, the following ones should be noted:

– technical pancreatin of polyfunctional action (OCT 49-167-81), which contains a number of proteolytic enzymes;

– chrome tanning agent (TU 2141-033-541386-2003) with a basicity of 35-42%;

– acrylic polymer Retanal RCN-40 from the company «Cromogenia-Units, S.A.» (Spain);

– Quebracho extract with a tannin content of 70% from the company «Plasma» (Ukraine);

– Trupol RA lubricating material as a mixture of sulfated and sulfited synthetic and natural anionic fats with an active substance content of 70%, pH 10% emulsion 7.5 manufactured by Trumpler company (Germany);

– potassium alum $KAl(SO_4)_2 \cdot 12H_2O$.

Unlike the developed technology of processing leather raw materials by the current technology [17], nonionic surfactant SPK-50 (TU 2484-014-22284995-99), sodium carbonate and sodium sulfide % of sample mass: 0.25, 0.45 and 0.3, respectively, are used at the soaking stage.

The water content in raw materials is determined by the gravimetric method at a temperature of 102 ± 2 °C; the pH of water and technological solutions is measured with a pH-meter of the pH-340 brand. Before weighing the samples on electronic scales (AXIS, AD200, Poland), surface moisture was carefully removed with filter paper.

Characterization of the samples of the obtained hides is carried out according to the complex of physical and chemical properties after their preliminary conditioning [18] by the exsiccation method under normal conditions at a temperature of 20±2 °C and a relative humidity of 65 ± 5%. Heat resistance of hide samples is characterized by hydrothermal shrinkage of collagen molecules during its denaturation (welding temperature), which is established by heating the sample at a rate of 2–3 °C/min in a mixture of glycerin and water with a weight ratio of 4:1 (ASTM D6076-18 and DSTU (National Standard of Ukraine) 2726- 94). The content of chromium tanning compounds in the semi-finished product is determined by iodometric titration and is expressed as the mass fraction of chromium (III) oxide. Substances extracted with organic solvents (SEOS) are determined in Zaychenko's apparatus using tetrachloromethane and trichloroethylene in a ratio of 1:1, followed by drying at temperatures of 128-130 °C for 1.5 and 1.0 hours, respectively.

Bound organic tannins (BOT) in leather are calculated by the formula:

$$BOT = LS - PS, \quad (1)$$

where LS = 100 – (TA + OS + OWS) is the mass fraction of leather substances calculated on the dry basis;

TA – the mass fraction of total ash (DSTU ISO 4047:2006);

OS – the mass fraction of organic substances, extracted with organic solvents (DSTU EN ISO 20344);

OWS – the mass fraction of organic water-soluble substances (DSTU ISO 4098:2020);

PS – the mass fraction of hide (protein) substance in the leather in terms of completely dry leather. It is determined by the nitrogen content by the Kjeldahl method (DSTU ISO 937:2005).

Hide density is determined by the ratio of its mass to the total volume. Mechanical properties of the leather samples are measured on the PM-250M tearing machine (RF) at a distance between the clamps of 50 mm with a deformation rate of 90 mm/min. The hide area is determined on an electromechanical action machine model 07484/P1 produced by the Svit company (Czech Republic).

RESULTS AND DISCUSSION

All technological processes of leather raw materials processing are carried out at Chinbar PJSC (Ukraine, Kyiv) using a drum of the Doze company (Germany) with a volume of 0.39 m^3. Soaking of horse raw materials with a significant difference in properties in different anatomical areas of the hide is carried out taking into account the results of previous studies and the use of anolyte and catholyte [19]. It should be noted that in the catholyte/anolyte mixture in the soaking processes, it is necessary to take into account the nature of the pH change and the antiseptic properties of the working solution.

The soaking process of canned raw materials is carried out in a catholyte/anolyte mixture under the conditions listed in Table 2.

To determine the optimal catholyte/anolyte ratio, a study of the effect of mixture composition on water absorption by the anatomical area: the croup, taking into account the high pH of the subsequent liming process was carried out. The choice of this area of hide is due to its increased density and the convenience of controlling the moisture content.

Table 2: Technology of soaking and liming, and tanning processes

Process	Agent/consumption, % of raw material mass	Mode
Washing	Water 26-28 °C – 150	60-min rotation; drain
Soaking	Catholyte /anolyte = 5/1-3/1 26-28 °C – 130	pH 8.2-9.5, rotation (rev.) 2 hrs.; then every hour revolutions 5 min for 4 hrs., drain
Liming	Catholyte 26-28 °C – 30 Calcium hydroxide – 0.7 Sodium hydrosulfide – 0.6 Sodium sulfide – 0.6 Calcium hydroxide – 0.4 Catholyte 28 °C – 80	 40 min. rev./ 20 min. idle/ 30 min. rev. 30 min. rev., pH ~ 12 30 min об. 10 min/hrs., 7,5-8 hrs., pH ~ 12.2
Washing	Water 24-26 °C – 2×150	2 times 15 min. Each
Fleshing	Fleshing machine	
Unusable areas removal	Table	Removal of unusable areas of hide
Doubling		Thickness of hide 2.2-2.3 mm
Identification of mass of hide		The entire batch is weighed
Washing	Water 32-34 °C – 150	20 min. rev. of the drum
Deliming-softening	Catholyte 36-38 °C= 5/1 – 20 Ammonium sulfate – 3.0 Pancreatin – 0.05	 60 min. rev.; pH 8.2-8.5 30 min. rev., drain
Washing	Water 18-20°C – 2×150	Two times 20 min. rev. each, drain
Pickling	Anolyte 25-27 °C – 40 Sodium chloride – 2.5 Sodium formate – 0.4 Sulfuric acid – 0.6 Formic acid 85% – 0.3	 15 min. rev. 30 min. rev. 3 hrs. rev., pH 2.6-2.8
Tanning	Chromium sulfate with a basicity of 37-42% – 4 Sodium formate – 0.25 Catholyte/anolyte 7/1 45 °C – 30 Magnesium oxide – 0.4	 2,5 hrs. rev. 4–4,5 hrs. rev., pH 3.6–3.8

According to the obtained data, the optimal catholyte/anolyte ratio corresponds to the minimum duration of reaching the moisture content as close as possible to its content in fresh hide after having been soaked for 5-6 hours. At the same time, there is no strip of dark color in thickness of the croup when it is cut near the rump, which indicates the completion of the process. Therefore, with a ratio of catholyte/anolyte of 7/1-5/1, the duration of the soaking process is reduced by 2.5 times when excluding environmentally hazardous agents.

At the same time, the need to exclude environmentally hazardous antiseptic agents from the working solution is taken into account. Shall the pH value in the soaking process according to the current technology decrease from 10.7, with available sodium sulfide, sodium carbonate, and surfactant to 7.3 (Table 3) upon completion of this process in 14 hours, according to the developed technology, at a lower initial pH value, this process is completed in 5.0-5.5 h without the use of an environmentally hazardous agent. When determining the optimal ratio, condition of the raw materials is taken into account. Completion of the soaking process takes place under control of the moisture content that should be close to the moisture content of the fresh raw material in the area of the croup.

Table 3: Change in pH of technological solution at soaking of horse raw hides

Working solution	pH from the start of soaking, hrs.				
	0	0.15	1.0	5	14
Catholyte/anolyte 1/0	10.6	8.4	7.6	7.2	7.2
1/1	6.7	7.1	7.1	7.1	7.1
5/1	8.3	7.7	7.3	7.1	7.1
7/1	9.5	8.2	7.4	7.2	7.2
Distilled water	6.6	7.0	7.1	7.1	7.1
Current technology	10.7	8.5	7.7	7.4	7.3

After the raw material has been soaked, it is limed (Table 2) using only catholyte, which creates a working environment when it is consumed, initially 30% of the mass of the raw material, and after 3.5 hours another 80% is added. The total duration of the process is 10.0-10.5 hours. After washing the received half-finished hides, its physicochemical properties are determined (Table 4).

Table 4: Properties of limed horse raw hides

Index	Researched technology		Current technology	
	Back	croup	back	croup
The temperature of the moisturized dermis, °C	49.0	56.0	52.0	59.0
The density of the semi-finished product, g/cm^3	1.019	1.113	1.032	1.125
Mineral substances, %	1.37	1.12	1.17	0.89

The obtained results indicate a higher content of mineral substances in the experimental samples both in the area of the croup and the back by 26.0% and 17.0% respectively, compared to the samples of the current technology. This proves increased activity of chemical agents during their interaction with collagen of the dermis with available catholyte, while their consumption is three times lower. This primarily concerns calcium hydroxide. Interaction of alkaline agents with collagen of the dermis is accompanied by a decrease in the welding temperature of the hide and its density. This may be the result of effective defibrillation of the hide structure when treated with an alkaline solution based on catholyte.

After washing, doubling, washing, de-liming-softening and washing, the obtained hide is pickled with available 40% of anolyte with a reduced consumption of sodium chloride by two times compared to the current technology and replacing 50% of sulfuric acid with 25% formic acid. The process of leather tanning is carried out on a spent pickling solution with the masking of the basic chromium sulfate with sodium formate, which contributes to its effective diffusion. At the same time, consumption of chromium compounds is reduced by 20% compared to the current technology. After 2.5 hours, a 30% catholyte/anolyte mixture and magnesium oxide base are added to continue tanning. Tanning is completed at the welding temperature of the samples of 107 °C.

Subsequently, the tanned semi-finished product is adjusted to a thickness of 1.1-1.2 mm, washed with 150% of water at a temperature of 35 °C. Further, the semi-finished product is doubled with available anolyte and basic chromium sulfate 100% and 1.6% of the mass of the semi-finished product respectively, neutralized with a mixture of formate and sodium bicarbonate in a ratio of 4:1 to pH 6.0-6.5. After washing the obtained semi-finished product with 150% of water at a temperature of 55 °C, the semi-finished product is filled with organic compounds with consumption of 4% of acrylic polymer Retanal RCN-40 and 4% of quebracho extract, and plasticized with 7% of Trupol RA lubricating material. Fixation of filling and plasticizing agents in the structure of the semi-finished product is carried out by 0.4-0.5% of aluminum-potassium alum to pH 4.2. The technology is completed by washing with 150% of water at a temperature of 30 °C. After drying and moisturizing processes, the samples of the obtained leather material are kneaded on a vibrating stretching and softening machine «Mollisa» produced by Svit company (Czech Republic).

The current technology [17] differs from the developed one by additional plasticization of the semi-finished product after neutralization and washing of the semi-finished product using an enzyme preparation and surfactant.

The obtained half hides were analyzed for chemical composition and physical and mechanical properties (Table 5) after the completion of drying and moisturizing treatments. A comparative analysis of leather samples of experimental and current technologies indicates a higher content of chromium tanning compounds and bound organic substances in the first case. At the same time, higher welding temperature, strength and deformation capacity of the samples are observed. This may indicate a more effective implementation of the chemical structuring process due to the use of activated aqueous solutions of agents for the technology of manufacturing leather material from horse raw materials. At the same time, compared to the current technology, there are 6.9 and 15% more of unbound fatty substances for the back and croup areas, respectively.

Table 5: Physical and chemical characteristics of leather

Index	Technology			
	researched		current	
	back	croup	back	croup
Mass share, %				
– chromium oxide (III)	4.21	3.58	4.02	3.37
– SEOS	8.67	6.76	8.11	5.86
– BOT	12.79	8.75	12.04	7.78
Welding temperature, °C	115.0	111.0	112.0	109.0
Density, g/cm^3	0.62	0.66	0.64	0.69
Breaking strength limit, MPa	18.6	23.1	16.9	21.3
Elongation under load 10 MPa, %	38.0	27.0	33.0	23.0
Elongation at break, %	66.0	49.0	61.0	45.0
Area output, dm^2/10 kg of raw material	153.0		146.2	

The higher content of fatty substances in the structure of the semi-finished product of the researched technology helps to increase the mobility of fibrillar structure of leather material during its deformation. This is confirmed by some decrease in density and increase in elastic and plastic properties of the hide. This especially applies to the strength and deformation capacity at low loads on experimental hides, which increase by 8.5-10.0 and 15.0-17.0%, respectively. This is also evidenced by the increase in the yield of leather by area by 6.8 dm^2 from 10 kg of raw material. According to the set of properties, the obtained leathers meet the DSTU requirements and can be used for the manufacture of footwear, clothing and haberdashery products, taking into account the properties of anatomical areas of horsehide.

CONCLUSIONS

A step-by-step technology for formation of leather material from horse raw materials using electrochemically activated aqueous solutions of chemical agents has been developed. A complex of physical and chemical properties in different anatomical areas of horsehide has been studied. The effect of the ratio of fractions of electrochemically activated aqueous solutions of catholyte and anolyte on the complex of physical and chemical properties of leather material at different stages of its formation has been determined. Effective implementation of leather raw material soaking process has been shown due to the use of the optimal ratio of catholyte and anolyte. At the same time, environmentally hazardous agents are excluded from the process; its duration is reduced by 2.5 times compared to the current technology.

The use of working solutions based on catholyte at the liming stage of leather raw materials ensures a three-fold reduction in the consumption of environmentally hazardous chemical agents. At the same time, when implementing the developed tanning process using anolyte, consumption of environmentally hazardous chromium compounds is reduced by 20% and the duration of the process is reduced by 1.7 times.

Taking into account the specific influence of different fractions of electrochemically activated aqueous solutions of chemical agents on the formation of leather material ensures obtaining a complex of increased elastic and plastic properties while saving natural raw materials by 4.6% compared to the current technology. At the same time, the developed technology of the production of leather materials, unlike the existing ones, is characterized by the simultaneous treatment of all anatomical areas of the hide. The obtained leather material meets the requirements of DSTU 3115-95 Leather for sewing products – General technical characteristics and ISO 9001:2008 international standard of quality management systems requirements and can be effectively used in manufacturing of a wide range of products. At the same time, we may recommend areas of the back and croup of horse leather to be used in production of shoe parts, and the remaining areas for haberdashery and accessories.

REFERENCES

1. Fidaleo, M., Moresi, M., Electrodialysis Applications in the Food Industry, *Adv Food Nutr Res*, **2006**, 51, 265-360, https://doi.org/10.1016/S1043-4526(06)51005-8.
2. Plutakhin, G.A., Mohammed, A., Koshchayev, A.G., Gnatko, Y.N., Teoreticheskie osnovy elektrokhimicheskoi obrabotki vodnykh rastvorov, *Nauchnyi zhurnal Kubanskogo gos. Agrarnogo univ.*, **2013**, 92(08), http://ej.kubagro.ru/2013/08/pdf/35.pdf.
3. Hsu, S.Y., Kao, H.Y., Effects of Storage Conditions on Chemical and Physical Properties of Electrolyzed Oxidizing Water, *J Food Eng*, **2004**, 65, 3, 465-471,

https://doi.org/10.1016/j.jfoodeng.2004.02.009.

4. Shirahata, S., Hamasaki, T., Teruya, K., Advanced Research on the Health Benefit of Reduced Water, *Trends Food Sci Technol*, **2012**, 23, 2, 124-131, https://doi.org/10.1016/j.tifs.2011.10.009.
5. Golohvast, K.S., Ryzhakov, D.S., Chajka, V.V., Gulkov, A.N., Perspektivy ispolzovaniya elektrkhimicheskoy aktivatsii rastvorov [Application potential of solution electrochemical activation] Voda: khimiya i ekologiya, *Water: Chemistry and Ecology*, **2011**, 2, 23-30 [in Ukrainian].
6. Cloete, T.E., Thantsha, M.S., Maluleke, M.R., Kirkpatrick, R., The Antimicrobial Mechanism of Electrochemically Activated Water against *Pseudomonas aeruginosa* and *Escherichia coli* as Determined by SDS-PAGE Analysis, *J Appl Microbiol*, **2009**, 107, 2, 379-384, https://doi.org/10.1111/j.1365-2672.2009.04233.x.
7. Robinson, G.M., Lee, S.W-H., Greenman, J., Salisbury, V.C., Reynolds, D.M., Evaluation of the Efficacy of Electrochemically Activated Solutions against Nosocomial Pathogens and Bacterial Endospores, *Lett Appl Microbiol*, **2010**, 50, 3, 289-294, https://doi.org/10.1111/j.1472-765X.2009.02790.x.
8. Goncharuk, V.V., Bahryi, V.A., Arkhipchuk, V.V., Chebotarev, R.D., Biotestirovanie elektrokhimicheski aktivirovannoi vody, *Khimiia I tekhnologiia vody*, **2005**, 4, 399-411 [in Ukrainian].
9. Kashkovskiy, V.I., Kamenskykh, D.S., Zastosuvannia aktyvovanoi vody v procesi kyslotnogo gidrolizuvannia roslynnykh vidkhodiv z vysokym vmistom pentozaniv, Instytut bioorganichnoi khimii ta naftokhimii NAN Ukrainy, **2012**, http:waste.ua/eco/2012/biomass/hydrolysis/ [in Ukrainian].
10. Lee, M.Y., Kim, Y.K., Ryoo, K.K., Lee, Y.B., Park, E.J., Electrolyzed-Reduced Water Protects against Oxidative Damage to DNA, RNA, and Protein, *Appl Biochem Biotechnol*, **2006**, 135, 2, 133-144, https://doi.org/10.1385/ABAB:135:2:133.
11. Shapovalenko, O.I., Tvtushenko, O.O., Momot, I.M., Gerashchenko, A.T., Perspektyvy vykorystannia elektroaktyvovanoi vody pry vyrobnytstvi kombikormiv, *Khranenie i pererabotka zerna*, **2011**, 5, 143, 40-42, http://dspace.nuft.edu.ua/jspui/handle/123456789/14133 [in Ukrainian].
12. Yefimchuk, H., Skidan, V., Nazarchuk, M., Seleznov, E., Yanovets, A., Multicriteria Compromise Optimization for Leather and Fur Skin Materials Tanning Technology, *Leather and Footwear Journal*, **2020**, 20, 2, 183-196, https://doi.org/10.24264/lfj.20.2.9.
13. Lutsyk, R.V., Matviyenko, O.A., Bovsunovskiy, O.B., Mozhlyvosti vykorystannia elektroaktyvovanoi vody v tekhnologicheskikh procesakh vzuttevogo vyrobnytstva, *Visnyk KNUTD*, **2005**, 2, 53-58 [in Ukrainian].
14. Nalyanya, K.M., Rop, R.K., Onyuka, A., Birech, Z., Sasia, A., Effect of Crusting Operations on the Physical Properties of Leather, *Leather and Footwear Journal*, **2018**, 18, 4, 283-294, https://doi.org/10.24264/lfj.18.4.4.
15. Plavan, V., Valeika, V., Kovtunenko, O., Širvaityte, J. THPS Pretreatment before Tanning (Chrome or Non-chrome), *J Soc Leather Technol Chem*, **2009**, 93, 5, 186-192.
16. Bordun, I., Ptashnyk, V., The Influence of Storage Condition on the Relaxation Processes in Electrochemically Activated Water, *East-Eur J Enterp Technol*, **2012**, 1/6, 55, 27-30, https://doi.org/10.15587/1729-4061.2012.3395.

17. Tekhnologichna metodika vyrobnytsva shkir riznomanitnogo asortymentu dlia verkhu vzuttia i pidkladky vzuttia, galantereinykh vyrobiv iz shkur velykoi rogatoi khudoby ta kinskykh, Kyiv: ZAT «Chynbar», **2003**, 11 p. [in Ukrainian].
18. Danylkovych, A.H., Praktikum z khimii I tekhnologii shkiry ta khutra, Kyiv: KNUTD, **1999,** 428 p. [in Ukrainian].
19. Danylkovych, A., Lishchuk, V., Romanyuk, O., Use of Electrochemically Activated Aqueous Solutions in the Manufacture of Fur Materials, *SpringerPlus*, **2016**, 5, 1, 214-224 [E-resource], https://doi.org/10.1186/s40064-016-1784-6.

INFLUENCE OF ATMOSPHERIC CONDITION ON THE POLYMER COMPOSITE BASED ON NBR RUBBER AND FUNCTIONALIZED PROTEIN WASTE

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INFLUENCE OF ATMOSPHERIC CONDITIONS ON THE POLYMER COMPOSITE BASED ON NBR RUBBER AND FUNCTIONALIZED PROTEIN WASTE

ABSTRACT. Technology has progressed a lot in the last 20 years, today it is possible to obtain new polymer composites that show performance properties. The ever-increasing demand for new high-performance materials has determined the appearance of new polymer structures based on elastomers and various wastes (protein, cellulosic, elastomeric, etc.) from various fields (shoes, leather goods, etc.). This paper describes the obtaining and characterization of polymer composites based on NBR rubber (butadiene-co-acrylonitrile) and protein waste from the footwear and leather goods industry, cryogenically ground to micrometric dimensions and modified with PDMS (polydimethyl siloxane). PDMS has the role of a plasticizer, but at the same time it improves the dispersion of protein waste mixed in the polymer matrix. The polymer composites were obtained by the mixing technique and tested from a physical-mechanical point of view according to the standards in force. The characterization in normal condition and accelerated aging at 70°C for 168 h (it was carried out hot, using the hot air circulation oven method) was carried out after the samples were subjected to conditioning for 24 h at ambient temperature. Also, the polymer composite samples were subjected for 365 days to atmospheric conditions (sun, rain, wind, hail, light, etc.) to see their influence on the properties of the obtained polymer composites.

KEY WORDS: NBR elastomer, polymer composite, leather waste, mechanical properties, functionalized

INFLUENȚA CONDIȚIILOR ATMOSFERICE ASUPRA COMPOZITULUI POLIMERIC PE BAZĂ DE CAUCIUC NBR ȘI DEȘEU PROTEIC FUNCȚIONALIZAT

REZUMAT. Tehnologia a progresat foarte mult în ultimii 20 de ani, astăzi fiind posibilă obținerea de noi compozite polimerice ce prezintă proprietăți performante. Cererea tot mai crescută de noi materiale performante au determinat apariția de noi structuri polimerice pe bază de elastomeri și diverse deșeuri (proteic, celulozic, elastomeric etc.) provenite din diverse domenii (încălțăminte, marochinărie, etc). Prezenta lucrare descrie obținerea și caracterizarea compozitelor polimerice pe bază de cauciuc NBR (butadien-co-acrilonitril) și deșeu proteic din industria de încălțăminte și marochinărie, măcinat criogenic la dimensiuni micrometrice și modificat cu PDMS (polidimetil siloxan). PDMS are rolul de plastifiant, dar în același timp îmbunătățește dispersia deșeului proteic amestecat în matricea polimerică. Compozitele polimerice au fost obținute prin tehnica amestecării și testate din punct de vedere fizico-mecanic conform standardelor în vigoare. Caracterizarea în stare normală și îmbătrânire accelerată la 70°C timp de 168 h (s-a realizat la cald, folosind o metodă de încălzire cu ajutorul etuvei cu aer circulant) s-a efectuat după ce epruvetele au fost supuse condiționării timp de 24 h la temperatură ambiantă. De asemenea, epruvetele de compozit polimeric au fost supuse timp de 365 zile la condiții atmosferice (soare, ploi, vânt, grindină, lumină etc.) pentru a se observa influența acestora asupra proprietăților compozitelor polimerice obținute.

CUVINTE CHEIE: elastomer NBR, compozit polimeric, deșeu de piele, proprietăți mecanice, funcționalizat

L'INFLUENCE DES CONDITIONS ATMOSPHÉRIQUES SUR LE COMPOSITE POLYMÈRE À BASE DE CAOUTCHOUC NBR ET DE DECHETS PROTÉIQUES FONCTIONNALISÉS

RÉSUMÉ. La technologie a beaucoup progressé au cours des 20 dernières années ; il est aujourd'hui possible d'obtenir de nouveaux composites polymères aux propriétés performantes. La demande toujours croissante de nouveaux matériaux performants a déterminé l'apparition de nouvelles structures polymères à base d'élastomères et de déchets divers (protéiques, cellulosiques, élastomères, etc.) issus de domaines variés (chaussure, maroquinerie, etc.). Le présent article décrit l'obtention et la caractérisation de composites polymères à base de caoutchouc NBR (butadiène-co-acrylonitrile) et de déchets protéiques issus de l'industrie de la chaussure et de la maroquinerie, broyés cryogéniquement aux dimensions micrométriques et modifiés avec du PDMS (polydiméthylsiloxane). Le PDMS a le rôle de plastifiant, mais améliore en même temps la dispersion des déchets protéiques mélangés dans la matrice polymère. Les composites polymères ont été obtenus par la technique de mélange et testés d'un point de vue physico-mécanique selon les normes en vigueur. La caractérisation en condition normale et vieillissement accéléré à 70°C pendant 168 h (effectuée à chaud, en utilisant la méthode du four à circulation d'air chaud) a été réalisée après que les échantillons aient été soumis à un conditionnement pendant 24 h à température ambiante. Aussi, les échantillons de composites polymères ont été soumis pendant 365 jours aux conditions atmosphériques (soleil, pluie, vent, grêle, lumière, etc.) pour voir leur influence sur les propriétés des composites polymères obtenus.

MOTS-CLÉS : elastomère NBR, composite polymère, déchets de cuir, propriétés mécaniques, fonctionnalisé

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INTRODUCTION

The development of new sustainable polymer composites, with predetermined properties, which are easy to recycle and ecological, with a low environmental carbon footprint, using concepts of the circular economy is a topical interest [1, 2]. The growing concern about the disposal of waste from the environment has led to the issuance of laws and regulations that take into account its management [3-6]. The main advantages of reusing waste of any type (elastomer, protein, plastic, glass, etc.) are to reduce environmental pollution, but also to protect human health. Also, through the use of new advanced and high-performance technologies, the turnover of economic agents increases. The reintroduction of a recycled material into a new composite requires certain modifications, such as grinding, putting it in contact with various precursors (modification with polydimethylsiloxane – PDMS) to improve their properties [7-9]. Grinding can be done coarsely or up to nanometric dimensions with the help of cryogenic mills, at various rotation speeds [10, 11].

Given that polymeric materials are not biodegradable, in order to obtain such composites, the current trends are to use natural fibers: protein, cellulosic fibers, eggshells, etc. [12, 13]. Natural protein waste can successfully replace inorganic fillers (silicon, carbon black, etc.) in elastomeric mixtures (vulcanized composites based on NBR). They also improve properties such as hardness, tensile modulus, etc., they do not sustain combustion, they have the ability to self-extinguish and are hygroscopic [13, 14]. We can thus say that the natural fibers (protein) added to the vulcanizates based on butadiene-co-acrylonitrile rubber bring improvements to their physical-mechanical properties [8, 9]. The NBR elastomer, due to its stability at temperatures between -40 and 108°C, is an ideal elastomer for the aeronautical industry, but it is also used in the footwear industry, and also to produce modular goods, sponges, expanded foams, floor mats, etc. NBR is an elastomer [15] (rubber) that shows resistance to oils and acids, also a superior strength, and by adding vulcanization accelerators such as tetramethylthiuram disulfide (Th), the physical and mechanical properties are improved. Antioxidants such as IPPD (N-isopropyl-N'-phenyl-p-phenylenediamine) are added to improve the aging (degradation) effect of vulcanizates under the action of atmospheric conditions: high temperatures, rain, wind, light, oxygen etc. [16, 17].

In this work, polymer composites based on NBR rubber and leather waste modified with PDMS were obtained by the mixing technique. Then they were tested rheologically and from a physical-mechanical point of view, under normal conditions at ambient temperature, accelerated aging at 70°C for 168 h, but also under atmospheric conditions (sun, rain, wind, hail, light, etc.) for 365 days to observe their influence on the properties of the obtained polymer composites [18, 19].

EXPERIMENTAL

Materials

The following materials were used in order to obtain polymer composites [18, 19]:

1) NBR rubber - butadiene-co-acrylonitrile rubber: acrylonitrile content - 34%; Mooney viscosity (100%) - 32±3; density - 0.98 g/cm^3;

2) Stearin - white flakes: moisture - 0.5% max; ash – 0.025 % max;

3) ZnO – zinc oxide microparticles: white powder, precipitate 93-95%, density – 5.5 g/cm, specific surface – 45-55 m^2/g;

4) SiO_2 - silicon dioxide: density: 1.9 - 4.29 g/cm^3, molar mass – 60.1 g/mol;

5) Kaolin - white powder, molecular weight 100.09;

6) PRW - protein waste: from the footwear and leather goods industry, cryogenically ground to micrometric sizes and modified with PDMS (polydimethylsiloxane);

7) PDMS - Polydimethylsiloxane fluid: has the role of plasticizer, but at the same time improves the dispersion of the protein waste mixed in the polymer matrix;

8) mineral oil;

9) IPPD 4010 – N-isopropyl-N'-phenyl-p-phenylenediamine: density – 1.1 g/cm^3, solidification point above 76.5°C, flat brown to dark purple granules;

10) S – Sulphur (vulcanization agent): fine yellow powder, insoluble in water, melting point: 115°C, faint odor;

11) Th – tetramethylthiuram disulfide (curing agent): density – 1.40g/cm^3, melting point <146°C, an ultrafast curing accelerator.

Methods

Preparation of Polymeric Composite

The stages of obtaining the polymer composites based on NBR rubber and protein waste (PRW) that were made using the mixing technique on an internal Brabender Plasti-Corder mixer are the following, Figure 1 [18, 19]:

1. collecting the protein waste (from the footwear and leather goods industry) and grinding it to a size of 0.35 mm using a cryogenic cyclone mill (Retsch ZM 200, Verder Scientific, Germany) at a speed of 12000-14000 rpm, in the presence of dry ice used as a cooling agent;

2. dosing the raw materials and obtaining the polymer composites on an internal Brabender Plasti-Corder mixer (Brabender GmbH&Co KG, Duinsburg, Germany) according to Table 1, [18] respecting the order of introducing the ingredients, Table 2, and the established working parameters;

3. obtaining a 3-4 mm thick sheet on a laboratory electric roller (Rolling mill machine, ZG-160 YRDB, Xiamen Ollital Technology Co, Ltd, Xiamen, China) after adding sulfur vulcanization activator and Th accelerators to the mixture [18] (relative to 100 parts plasticized rubber);

4. rheological testing (Monsanto R-100 Oscillating Disc Rheometer, MonTech GmbH, USA);

5. obtaining samples of standard sizes in the electric laboratory press (Fortune Press, TP/600 model, Fontijine Grotness Vlaardingen, Holland);

6. conditioning the samples for 24 hours at room temperature;

7. physical-mechanical tests on the elastomer testing equipment, according to the standards in force: under normal conditions, accelerated aging 168 h at 70°C [18] and exposure to atmospheric conditions for 365 days (then physical-mechanical tests are performed).

Table 1. Working method on the Brabender Plasti-Corder mixer [18, 19]

Order of introducing ingredients	Time (minutes)	Working speed, rpm	Working temperature, °C
NBR elastomer	1’ 30” (plasticizing elastomer)	40 rpm	36°C
Ingredients according to working formulation (Table 2) (without vulcanization agents)	4’	20 rpm	40°C
Homogenization of mixture	2’	80-100 rpm	60-100°C

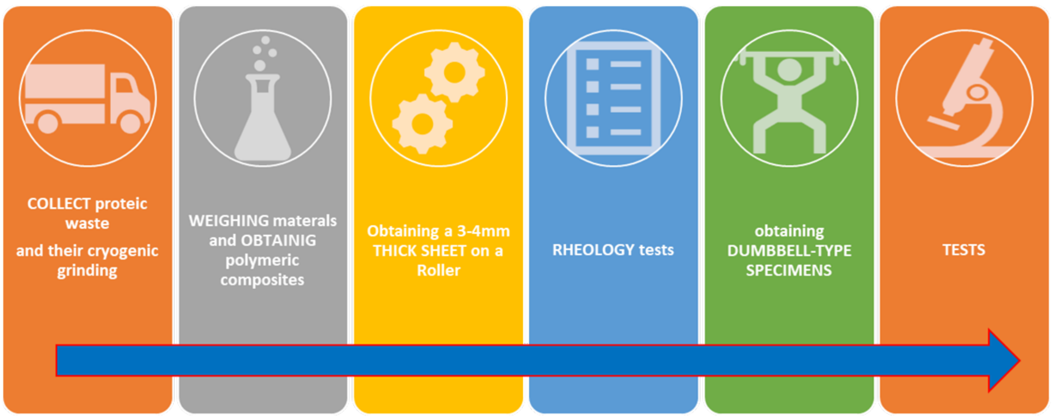

Figure 1. Stages of obtaining polymer composites based on NBR elastomer (butadiene-co-acrylonitrile rubber) and protein waste (PRW)

Table 2: Formulation of polymer composite based on NBR rubber and protein waste [18]

Materials	MU [g]	Symbol					
		Bo (control)	$BCPP_O$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Butadiene-co-acrylonitrile (NBR)	g	150	150	150	150	150	150
Stearin (flakes)	g	1.8	1.8	1.8	1.8	1.8	1.8
Zinc oxide (ZnO – active powder)	g	7.5	7.5	7.5	7.5	7.5	7.5
Silicon dioxide (SiO_2)	g	45	-	30	20	-	-
Kaolin	g	37.5	37.5	37.5	37.5	37.5	37.5
PRW functionalized with potassium oleate	g	-	-	15	30	45	75
Non-functionalized leather waste	g	-	45	-	-	-	-
Mineral oil	g	15	15	15	15	15	15
IPPD 4010	g	4.5	4.5	4.5	4.5	4.5	4.5
Sulfur (S)	g	2.25	2.25	2.25	2.25	2.25	2.25
Tetramethylthiuram disulfide (Th)	g	0.9	1.5	0.9	0.9	0.9	0.9

Modification (Functionalization) of the Protein Waste

The PRW (protein waste) from the footwear industry was modified in the first phase by grinding to a size of 0.35 mm at a speed of 12,000-14,000 rpm, with a cryogenic mill [9, 10] continuing with the functionalization of the powder with polydimethylsiloxane (PDMS), which also acts as a plasticizer. TRW functionalization was achieved by contacting 100 g of PRW waste with 20% PDMS and then placing it in an oven with circulating air, at a temperature of 70°C, for 4-6 hours, homogenizing the mixture every 20 -30 minutes.

Characterization of the Polymer Composite

The polymer composites based on NBR elastomer and PRW were characterized according to the standards in force, in normal state, as well as in terms of behavior after accelerated aging. After the samples were conditioned at room temperature, samples were punched for each individual determination with standardized devices (punch knives), three samples for each determination. The hardness was determined according to ISO 48-4:2018 – Sh°A (for elastomers); elasticity (%) ISO 4662:2017; tensile strength, N/mm^2 – ISO 37-2020; accelerated aging was carried out in heat, using the hot air circulation oven method and in atmospheric and weather conditions (rain, wind, sun, light, etc.) for 1 year according to ISO 188/2011 [9].

RESULTS AND DISCUSSIONS

Physical-Mechanical Characterization

The following physical-mechanical characteristics of the polymer composites were determined: hardness, elasticity, tensile strength, elongation at break and residual elongation after conditioning for 24 hours at room temperature, in normal state, accelerated aging at 70°C for 168 h, Table 3 [18], and atmospheric conditions and weather for 365 days, Table 4.

Following the determinations, it is observed that the hardness of the polymer composites, both in normal conditions and accelerated aging at 70°C and 168 h, increases with the amount of leather waste functionalized with PDMS added to the mixture. For the samples $BCPP_3$ and $BCPP_4$ where the active filler – SiO_2 – is replaced with leather waste, the hardness increases by up to 12°Sh A. The elasticity decreases by up to 5.55% in the case of the samples where the active filler is totally replaced with PRW modified with PDMS. PDMS has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein waste in the polymer matrix [9, 10].

Table 3: Physical-mechanical characterization of polymer composites based on NBR, in normal state and accelerated ageing at 70°C [18]

	Sample					
Physical-mechanical characterization	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Normal State						
Hardness, °Sh A	61	70	66	69	71	73
Elasticity, %	18	18	21	20	19	18
Tensile strength, N/mm^2	11.3	3.44	9.4	8.1	3.97	1.7
Elongation at break, %	180	500	960	800	420	420
Residual elongation, %	80	36	56	56	28	26
Accelerated aging at 70°C and 168 h						
Hardness, °Sh A	66	73	69	72	75	75
Elasticity, %	24	22	26	24	23	22
Tensile strength, N/mm^2	14.47	3.30	9.31	6.96	2.98	1.49
Elongation at break, %	980	540	880	680	420	380
Residual elongation, %	60	28	60	40	28	26

The tear resistance values both in normal condition and accelerated aging decrease as the active layer of silicon dioxide is replaced by the leather waste. For the samples $BCPP_3$ and $BCPP_4$ containing PRW modified with PDMS tensile strength shows a decrease of 64.86 up to 84.95%, and after the accelerated aging process due to the replacement of the active filler with leather waste it decreases significantly by up to 89.7%, and presents values between 1.749 -9.31 N/mm^2.

The elongation at break in normal state for the samples that have in the mixture both leather waste and active filler ($BCPP_1$ and $BCPP_2$) increases by values between 344.4-433.3%, and for those in which the active filler is completely replaced by the leather waste modified with PDMS ($BCPP_3$ and $BCPP_4$), it also increases by up to 133.3%. After the accelerated aging process at 70°C and 168 h compared to the control BO sample, the elongation at break values decrease significantly by up to 61.22%.

For the samples that have in their composition PRW modified with PDMS, as well as SiO_2, $BCPP_1$ and $BCPP_2$, both in normal state and accelerated aging, the residual elongation decreases by 30% (normal state) and 33.33% (accelerated aging). For the samples containing only PRW modified with PDMS, $BCPP_3$ and $BCPP_4$, the values decrease significantly compared to the BO control sample by up to 67.5% in normal condition, and 56.66% after the accelerated aging process.

For all the samples, following the tests performed, according to ISO 188/2011, changes in their values can be observed, after being subjected to atmospheric conditions and weather (rain, wind, sun, light, etc.) for 365 days, Table 4.

Table 4: Physical-mechanical characterization of polymer composites based on NBR, under atmospheric conditions and weather for 365 days

	Sample					
Physical-mechanical characterization	BO (control)	$BCPP_0$	$BCPP_1$	$BCPP_2$	$BCPP_3$	$BCPP_4$
Atmospheric conditions for 365 days (sun, rain, wind, hail, light, UV radiation)						
Hardness, °Sh A	72	75	76	77	77	75
Elasticity, %	22	18	20	18	17	16
Tensile strength, N/mm^2	8.23	3.36	6.21	4.63	3.05	1.71
Elongation at break, %	700	180	500	260	140	200
Residual elongation, %	44	24	32	22	24	22

After exposure to atmospheric conditions for 365 days, the hardness increases by 5-8° Sh A, and the elasticity values decrease. For the samples containing PRW functionalized with PDMS and SiO_2, the elasticity decreases by 9.09%, and 22.72%, respectively, and in the case of the samples where the active filler was totally replaced with PRW, the values decrease by 22.72% for the $BCPP_3$ sample, and by 27.28% for the $BCPP_4$ sample, respectively.

The tensile strength has values between 1.71-6.21 N/mm^2 and decreases significantly in the case of samples in which the active filler is totally replaced with leather waste (PRW) modified with potassium oleate. Elongation at break decreases depending on the percentage of waste added to the mixture. For the samples in which SiO_2 is totally replaced by PRW modified with PDMS, $BCPP_3$ and $BCPP_4$, the values are influenced by the presence of waste and decrease significantly by up to 80%, and 71.42%, respectively. The residual elongation decreases by values between 27.27-50% for all samples subjected to atmospheric conditions for 365 days.

CONCLUSION

The ever-increasing demand for new high-performance materials has determined the emergence of new polymer structures based on elastomers and various types of waste (protein, cellulosic, elastomeric, etc.) from various fields (shoes, leather goods, etc.). By reusing waste of any type (elastomer, protein, plastic waste, glass, eggshells, etc.) and transforming it through different processing methods into new products with added value, we can reduce environmental pollution and at the same time protect people's health by reducing toxicity in the working environment.

The polymer composites based on elastomer and protein waste (PRW) were obtained by the mixing technique according to the working formulation, respecting the order of introduction of the ingredients and the established work parameters. The leather waste from the footwear and leather goods industry was cryogenically ground, and carbonic ice was used as a cooling agent in the form of 3-5 cm pellets and modified with PDMS in order to activate it. PDMS has the role of a plasticizer, but at the same time it improves the dispersion of mixed protein waste in the polymer matrix. The characterization of the polymer composites based on NBR rubber and leather waste was carried out on the specific equipment for elastomers according to the standards in force, after the samples were conditioned for 24 h at ambient temperature. After subjecting the samples to atmospheric conditions for 365 days, following the physical-mechanical characterizations, it is found that the values obtained show changes. Compared to accelerated aging at 70°C and 168 h, the values obtained for the physical-mechanical characteristics of the samples, after being subjected to atmospheric conditions for 365 days, are not very different. This fact shows that subjecting the samples to atmospheric conditions did not have a major impact on the properties of the polymer composites based on NBR elastomer/leather waste, and neither on the environment.

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REFERENCES

1. Moktadir, Md.A., Ahmadi, H.B., Sultana, R., Zohra, F.-T., Liou, J.J.H., Razaei, J., Circular Economy Practices in the Leather Industry: A Practical Step towards Sustainable Development, *J Clean Prod*, **2020**, 251, 119737, https://doi.org/10.1016/j.jclepro.2019.119737.
2. Geissdoerfer, M., Savaget, P., Bochen, N.M.P., Hultink, E.J., The Circular Economy – A New Sustainability Paradigm, *J Clean Prod*, **2017**, 143, 757-768, https://doi.org/10.1016/j.jclepro.2016.12.048.

3. Nations Environment Programme, Global Waste Management Outlook, **2015**, available at: https://www.unenvironment.org/resources/report/global-waste-management-outlook.
4. Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June **2006** on shipments of waste.
5. Plastic Recyclers Europe, Increased EU Plastics Recycling Targets: Environmental, Economic and Social Impact Assessment – Final Report, Deloitte, **2015**, available at: https://www.plasticsrecyclers.eu/plastics-recyclers-publications.
6. Plastics, The Facts, “An Analysis of European Plastics Production, Demand and Waste Data. Plastics Europe”, **2017**, available online: the_facts_2017_FINAL_for_website_one_page.pdf (accessed on 5 December 2018), https://www.plasticseurope.org/application/files/5715/1717/4180/Plastics
7. Alexandrescu, L., Deselnicu, V., Sönmez, M., Georgescu, M., Nițuică, M., Deselnicu, D.C., Pang, X., Biodegradable Polymer Composite Based on Recycled Polyurethane and Finished Leather Waste, *IOP Conf Ser: Earth Environ Sci*, **2019**, 401, 012006, https://doi.org/10.1088/1755-1315/401/1/012006.
8. Stelescu, M.D., Airinei, A., Bargan, A., Fifere, N., Georgescu, M., Sönmez, M., Nițuică, M., Alexandrescu, L., Stefan, A., Mechanical Properties and Equilibrium Swelling Characteristics of some Polymer Composite Based on Ethylene Propylene Diene Terpolymer (EPDM) Reinforced with Hemp Fibers, *Materials*, **2022**, 15, 19, 6838, https://doi.org/10.3390/ma15196838.
9. Nițuică, M., Oprea, O., Stelescu, M.D., Sönmez, M., Georgescu, M., Alexandrescu, L., Motelica, L., Polymeric Biocomposite Based on Thermoplastic Polyurethane (TPU) and Protein and Elastomeric Waste Mixture, **2023**, 16, 15, 5279, https://doi.org/10.3390/ma16155279.
10. Stelescu, M.D., Sönmez, M., Alexandrescu, L., Nițuică, M., Gurau, D.F., Georgescu, M., Structure and Properties of Blends Based on Vulcanized Rubber Waste and Styrene–Butadiene–Styrene Thermoplastic Elastomer, *J Rubber Res*, **2022**, 25, 4, 421-434, https://doi.org/10.1007/s42464-022-00187-y.
11. Alexandrescu, L., Georgescu, M., Sönmez, M., Nițuică, M., Biodegradable Polymeric Composite Based on Recycled Polyurethane and Rubber Wastes: Material Green Shoe Manufacturing, *Leather and Footwear Journal*, **2020**, 20, 3, 323-331, https://doi.org/10.24264/lfj.20.3.10.
12. Lee, B.H., Kim, H.J., Yu, W.R., Fabrication of Long and Discontinuous Natural Fiber Reinforced Polypropylene Biocomposites and Their Mechanical Properties, *Fibers Polym*, **2009**, 10, 1, 83–90, https://doi.org/10.1007/s12221-009-0083-z.
13. Mohammed, L., Ansari, M.N.M., Pua, G., Jawaid, M., Islam, M.S., A Review on Natural Fiber Reinforced Polymer Composite and Its Applications, *Int J Polym Sci*, **2015**, 243947, https://doi.org/10.1155/2015/243947.
14. Pickering, K.L., Efendy, M.C.A., Lee, T.M., A Review of Recent Development in Natural Fiber Composites and Their Mechanical Performance, *Compos Part A-Appl S*, **2015**, 1-15, https://doi.org/10.1016/j.compositesa.2015.08.038.
15. Alexandrescu, L., Sönmez, M., Nițuică, M., Gurău, D., Popa, N., Hybrid Polymeric Structures Based on Butadiene-co-Acrylonitrile and Styrene-Butadiene Rubber Reinforced with Nanoparticles, *Leather and*

Footwear Journal, **2014**, 14, 1, 39-52, https://doi.org/10.24264/lfj.14.1.4.

16. Dobrinescu, A., New Types of Elastomers for Special Purposes (in Romanian), Ministry of Light Industry, Centre for Documentation and Technical Publications, Bucharest, **1971**.
17. Mirici, L.E., Thermoplastic Elastomers (in Romanian), Art. Press & Augusta, Timisoara, **2005**.
18. Nițuică, M., Sönmez, M., Georgescu, M., Stelescu, M.D., Alexandrescu, L., Gurau, D., Biodegradable Polymer Composites Based on NBR Rubber and Protein Waste, *Leather and Footwear Journal*, **2021**, 21, 4, 229-236, https://doi.org/10.24264/lfj.21.4.3.
19. Nițuică, M., Sönmez, M., Georgescu, M., Stelescu, M.D., Alexandrescu, L., Gurau, D., Pantazi-Bajenaru, M., Polymer Composite Based on NBR Rubber Compounded with Rubber Waste Functionalized with Potassium Oleate, *Leather and Footwear Journal*, **2022**, 22, 1, 45-52, https://doi.org/10.24264/lfj.22.1.5.

OCCUPATIONAL EXPOSURE OF FOOTWEAR ROUGHING DUST DURING FOOTWEAR MANUFACTURING PROCESS

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OCCUPATIONAL EXPOSURE OF FOOTWEAR ROUGHING DUST DURING FOOTWEAR MANUFACTURING PROCESS

ABSTRACT. Footwear roughing dust (FRD) is generated from roughing operations involved in footwear manufacturing. The dust is created by the friction of emery paper against the grain surface of finished leather. FRD coming from finished leather is likely to contain chromium, which is widely used for leather processing. Generally, chromium is found in two forms in the leather industry, namely Cr (III) and Cr (VI), of which the latter has an evident and adverse effect on human health. This study aims to identify the major effects of FRD on workers' health and to find out the correlation with the factors influencing those adverse health effects. In this study, a survey among 30 roughing operators from eight footwear factories in Bangladesh was conducted. The major health effects of FRD are eye irritation, skin itching, chest pain, coughing, and fatigue. This study constructed three hypotheses to investigate whether human health is affected by FRD with working experience, the age of workers, and the use of personal protective equipment (PPE). The results showed that working experience and use of PPE have distinct influences on the health effects caused by FRD, whereas workers' age has no impact on their health effects. Finally, some recommendations are formulated to prevent or mitigate workers' adverse health effects in order to ensure a better working environment in the footwear industry.

KEY WORDS: footwear roughing dust, health safety, occupational exposure, personal protective equipment

EXPUNEREA OCUPAȚIONALĂ LA PRAFUL REZULTAT ÎN URMA ȘLEFUIRII PIELII ÎN PROCESUL DE FABRICARE A ÎNCĂLȚĂMINTEI

REZUMAT. Praful rezultat în urma șlefuirii încălțămintei derivă din operațiunile de șlefuire prezente în procesul de fabricare a încălțămintei. Praful este generat de frecarea hârtiei abrazive pe suprafața granulată a pielii finisate. Praful rezultat din șlefuirea pielii finite este foarte probabil să conțină crom, care este utilizat pe scară largă în prelucrarea pielii. În general, cromul se regăsește în industria de pielărie sub două forme, și anume, Cr (III) și Cr (VI), cel din urmă având un efect evident și negativ asupra sănătății umane. Acest studiu își propune să identifice efectele majore ale prafului de la șlefuire asupra sănătății lucrătorilor și să găsească o corelație cu factorii care influențează aceste efecte adverse asupra sănătății. În acest studiu, s-a efectuat un sondaj în rândul a 30 de lucrători din opt fabrici de încălțăminte din Bangladesh. Efectele majore asupra sănătății ale prafului de la șlefuire sunt iritația ochilor, mâncărimea pielii, durerea în piept, tusea și oboseala. În acest studiu s-au construit trei ipoteze pentru a investiga dacă sănătatea umană este afectată de prafului de la șlefuire, și anume experiența de lucru, vârsta lucrătorilor și utilizarea echipamentului individual de protecție (EIP). Rezultatele au arătat că experiența de lucru și utilizarea EIP au influențe distincte asupra efectelor cauzate de praful de la șlefuire asupra sănătății, în timp ce vârsta lucrătorilor nu are niciun impact asupra acestor efecte. În cele din urmă, s-au formulat câteva recomandări pentru a preveni sau atenua efectele adverse asupra sănătății lucrătorilor în vederea asigurării unui mediu de lucru mai bun în industria de încălțăminte.

CUVINTE CHEIE: praf de la șlefuirea încălțămintei, securitate și sănătate, expunerea la locul de muncă, echipament individual de protecție

EXPOSITION PROFESSIONNELLE À LA POUSSIÈRE RÉSULTANT DU POLISSAGE DU CUIR DANS LE PROCESSUS DE FABRICATION DE CHAUSSURES

RÉSUMÉ. La poussière résultant du polissage des chaussures provient des opérations de polissage présentes dans le processus de fabrication des chaussures. La poussière est générée par le frottement du papier abrasif sur la surface granuleuse du cuir fini. La poussière issue du polissage du cuir fini contient très probablement du chrome, largement utilisé dans le traitement du cuir. Le chrome se trouve généralement dans l'industrie du cuir sous deux formes, à savoir Cr (III) et Cr (VI), ce dernier ayant un effet évident et négatif sur la santé humaine. Cette étude vise à identifier les principaux effets de la poussière sur la santé des travailleurs et à trouver une corrélation avec les facteurs influençant ces effets néfastes sur la santé. Dans cette étude, une enquête a été menée auprès de 30 travailleurs de huit usines de chaussures au Bangladesh. Les principaux effets sur la santé de la poussière résultant du polissage sont l'irritation des yeux, les démangeaisons cutanées, les douleurs thoraciques, la toux et la fatigue. Dans cette étude, trois hypothèses ont été construites pour déterminer si la poussière affecte la santé humaine, à savoir l'expérience de travail, l'âge des travailleurs et l'utilisation d'équipements de protection individuelle (EPI). Les résultats ont montré que l'expérience professionnelle et l'utilisation d'EPI ont des influences distinctes sur les effets sur la santé de la poussière, alors que l'âge du travailleur n'a aucun impact sur ces effets. Enfin, certaines recommandations sont formulées pour prévenir ou atténuer les effets néfastes sur la santé des travailleurs afin d'assurer un meilleur environnement de travail dans l'industrie de la chaussure.

MOTS CLÉS : poussière résultant du polissage des chaussures, sécurité et santé, exposition professionnelle, équipement de protection individuelle

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INTRODUCTION

Roughing is regarded as one of the major and critical operations in the lasting department of any footwear manufacturing unit. In order to attach the upper to the corresponding sole, it is necessary to 'scrape' a thin layer of material off the upper surface so that glue can penetrate the leather and adhere properly, which is called 'roughing' [1]. This task contributes to producing leather and sole material fibres, dust, or small scraps, which represent 5–15% (w/w) of the solid wastes generated by shoe-making companies [2]. A major portion of these dusts are big particles (greater than 50 µm) [3], which are collected by a dust collector attached to a roughening machine (a bag where dusts are collected from the air by using the extractor hood with a cyclone system). However, a significant portion of small or tiny particles (<1 µm to 13 µm) [4, 5] of these dusts spread out during roughing and affect the surrounding workers. A study found that concentrations of these airborne particles may vary from 0.07 to 1.01 mg/m^3, and the amount of insoluble and hexavalent chromium may vary from 0.10-0.32 and 0.01-0.0811g/m^3, respectively [6]. To manage this solid waste, the FRD is conventionally dumped in the open environment for landfilling purposes [2], which results in an unpleasant odour and severe impact on the environment due to the leaching of chromium ions and the generation of toxic emissions including nitric oxide [7]. Some of the roughing dusts are incinerated [8], which may create hexavalent chromium through an oxidation process [9]. This hexavalent chromium causes an increased risk of bone, prostate, lymphomas, Hodgkin's, leukaemia, stomach, genital, renal, and bladder cancers in the human body once taken up [10]. Therefore, the dust particles generated from leather can cause several health hazards like cancer, respiratory diseases, and central nervous system abnormalities once they are entered into the human body through any route of exposure [7]. However, the nature and magnitude of these effects may vary from factory to factory and person to person depending on various factors such as working experience, age and use of Personal Protective Equipment (PPE), frequency of personnel exposed, contact time, route of exposure, immune system of the host, etc. Against this backdrop, this study was conducted on the identification of associated factors of health hazards emanating from the FRD. It also aimed to find out the possible adverse effects of FRD on human health and test several hypotheses regarding health hazards related to FRD. Also, this study proposes several recommendations that should be followed to alleviate the adverse health impacts brought by the FRD. In this line, this study sets the following objectives:

i. To identify the major effects of FRD on workers' health.
ii. To identify the factors that influence adverse health effects emanating from the FRD.
iii. To propose necessary recommendations to prevent or mitigate the adverse health effects caused by the FRD.

EXPERIMENTAL

Materials and Methods

This is a survey work that aims to explore the influencing factors for adverse health effects on the workers of the footwear lasting department in Bangladesh. This study took 30 workers as a sample, both for the experimental and control groups. As the survey was conducted during the COVID-19 pandemic and the minimum sample size of 30 confirms normal distribution in statistics [11], this study took 30 respondents as the sample. The experimental group was composed of 30 roughing operators (28 males and 2 females) selected from the lasting department. The age range of the participants was from 19 to 35 years, and the working experience was from 3 to 17 years. On the other hand, the control group was formed with 30 workers (28 males and 2 females) from random working sections (e.g., cutting and sewing department, human resource department (HR), management department, marketing department, merchandising department, etc.) except the lasting department, with the same age range and working experience as the experimental group. This study followed a purposive sampling technique to select footwear factories, and a simple random sampling technique was followed to select respondents. A total of eight footwear factories were selected purposively from the Dhaka and Chittagong divisions. The sampling technique is illustrated in Figure 1. A survey questionnaire was developed to collect data from the respondents. The duration of data collection was from November 1, 2021, to November 27, 2021. Face-to-face interviews were conducted to collect primary data from the selected factories. In order to validate the responses of the respondents regarding their health effects, this study formed an expert panel of four members, consisting of two medical officers and two industrial experts. The model of the used roughing machine in the footwear factories was a Volber 152. For the data analysis, appropriate graphical analysis was conducted to find out the health effects on workers due to FRD. Using STATA software, a T-test is carried out for the hypothesis test.

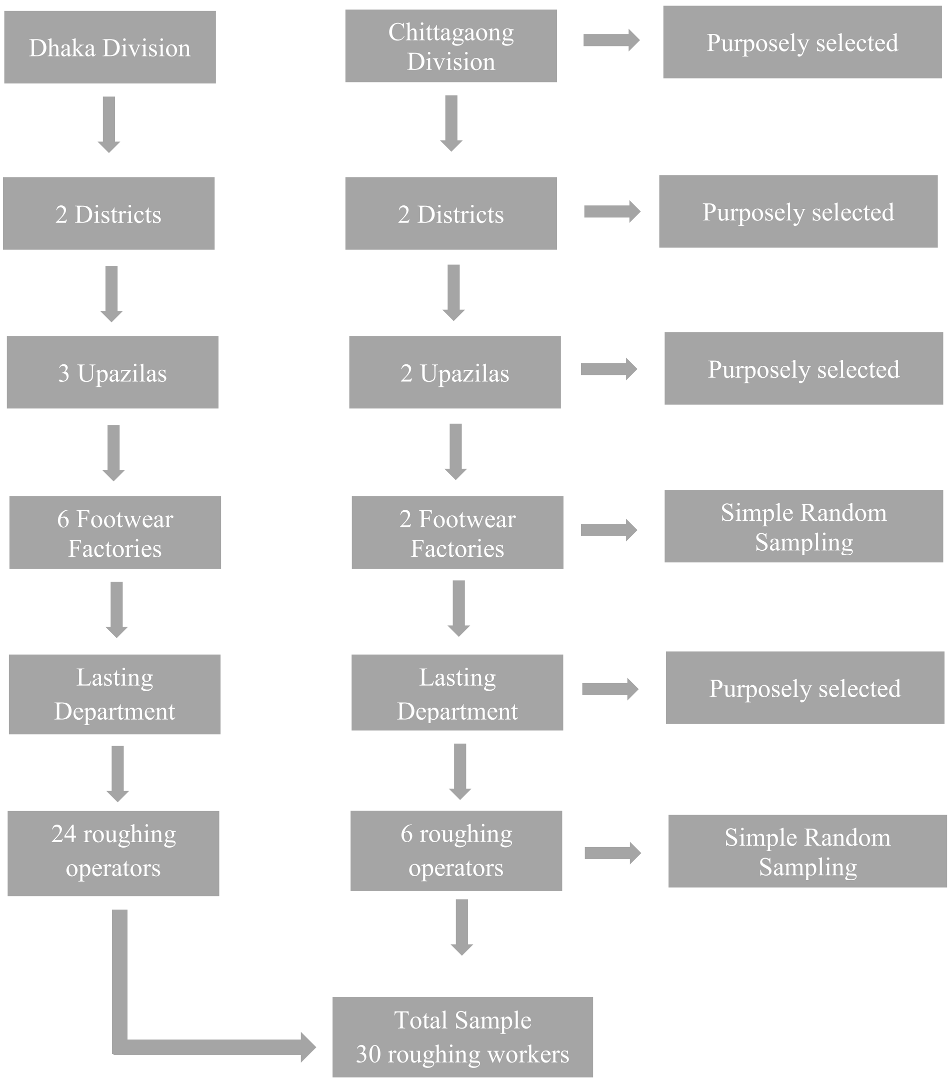

Figure 1. Schematic diagram of sampling technique

For data analysis, three Hypotheses were formulated in this study as follows:

Hypothesis 1: The working experience of the roughing operator influences the health effects caused by footwear roughing dust.

Hypothesis 2: The age of the roughing operator influences the health effects caused by footwear roughing dust.

Hypothesis 3: Awareness of using Personal Protective Equipment (PPE) influences the health effects caused by footwear roughing dust.

For testing hypothesis 1, roughing operators are divided into two groups: Group 1: Working experience is up to 5 years, and Group 2: Working experience is more than 5 years. For testing hypothesis 2, roughing operators are divided into two groups: Group 1: Age is up to 25 years, and Group 2: Age is more than 25 years. On the other hand, for testing hypothesis 3, roughing operators are divided into two groups: Group 1: Operators who have the awareness of using PPE; and Group 2: Operators who do not have the awareness of using PPE. A paired sample T-test was carried out between Group 1 and Group 2 using STATA software.

RESULTS AND DISCUSSION

This study mainly focused on finding out the possible health hazards of the 30-roughing operators from 8 footwear manufacturing units due to FRD exposure. The health effects on the participants of the selected footwear units are illustrated in Figure 2. In total, 10 health related issues were identified from the survey among roughing operators. Some of them are major, and some can be considered minor based on their intensity in the collected survey data. From the bar chart below, the major health effects in correlation to exposure to FRD are eye irritation, skin itching, chest pain, coughing, and fatigue, which were experienced by 90%, 83%, 53%, 33%, and 33% of the total respondents, respectively. Other minor health problems faced by workers in these 8 factories are hair itching, breathing problems, dizziness, hair hardening, and insomnia. Although all workers in the experimental group were involved with the same type of operation for 8 hours per day, they did not experience the same degree of health effects created by the FRD.

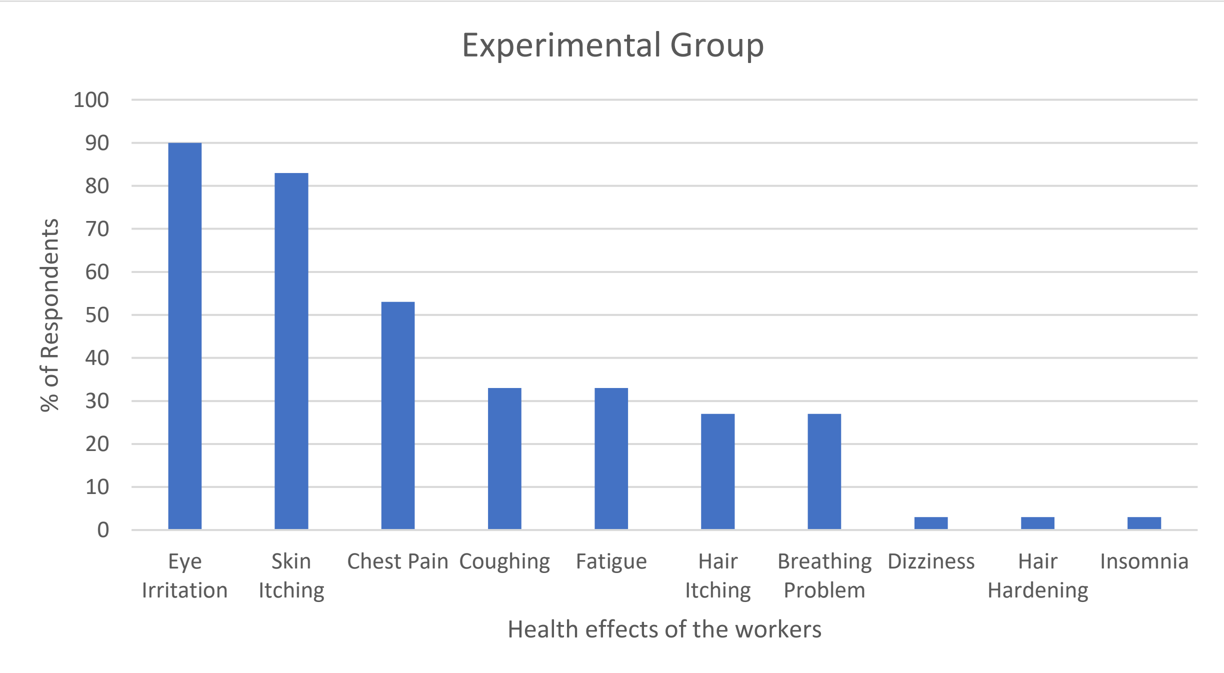

Figure 2. Different health effects and their intensity among the respondents caused by FRD (Experimental group)

On the other hand, only 13.33% of respondents in the control group reported that they experienced skin itching problems. The remaining 86.67% of respondents did not experience any health-related issues, as shown in Figure 3.

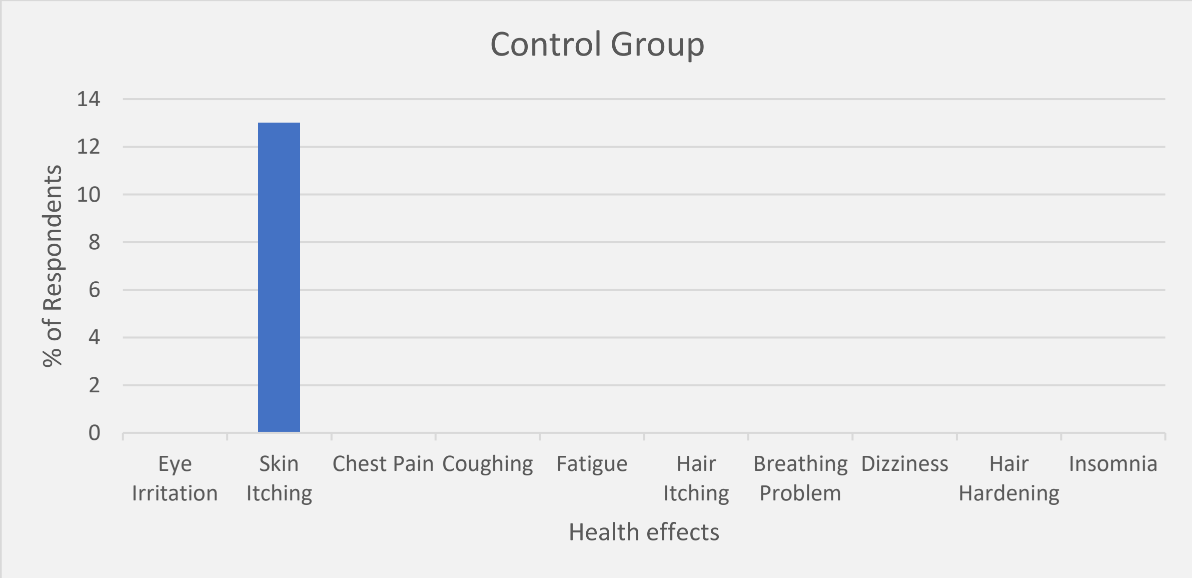

Figure 3. Different health effects and their intensity among the respondents (control group)

From the findings between the control and experimental groups, it can be concluded that a roughing operator is more likely to be affected by the FRD than workers in other departments.

Table 1: Testing hypothesis between working experience and health effects

	Obs.	Mean1	Mean2	Dif.	St Err	t value	p value
Group 1 – Group 2	13	4	5.231	-1.231	.612	-2	.067

Table 2: Testing hypothesis between workers' age and health effects

	Obs.	Mean1	Mean2	Dif.	St Err	t value	p value
Group 1 – Group 2	14	4.072	4.643	-.571	.542	-1.05	.311

Table 3: Testing hypothesis between awareness of using PPE and health effects

	Obs.	Mean1	Mean2	Dif.	St Err	t value	p value
Group 1 – Group 2	14	3.143	5.500	-2.357	.52	-4.55	.001

The results of hypothesis test 1, 2, and 3 are provided in Tables 1, 2, and 3, respectively. Here, the t value is -2. As | t | > 1.96, there is a significant difference between Group 1 and Group 2. So, the null hypothesis is rejected. Therefore, highly experienced operators have a higher chance of being affected by roughing dust as their exposure time to this dust is higher. Table 2 shows that the t value is -1.05. As | t | < 1.96, there is no significant difference between Group 1 and Group 2 for Hypothesis 2. So the null hypothesis is accepted. Therefore, the operator's age does not influence the health effects caused by roughing dust. Alternatively, Table 3 shows that the t value is -4.55. As | t | > 1.96, there is a significant difference between Group 1 and Group 2 for Hypothesis 3. So the null hypothesis is rejected in this regard. Therefore, operators who are aware of using Personal Protective Equipment (PPE) are less likely to be affected by rouging dust.

Generally, necessary personal protective equipment (gloves, safety glasses, shoes, earplugs or muffs, hard hats, respirators, coveralls, vests, and full body suits) is provided to the workers by the authority in order to ensure primary safety. However, this study found only 3% of roughing operators were aware of using this PPE during their working hours. As a result, workers' clothes, hair, and other uncovered parts of the body easily get involved with the dust particles. This practice enables the workers to absorb smaller dust particles through their eyes and skin. Since workers are not concerned about wearing safety gloves, their palms are found to have scars, rough and dusty in appearance, which may lead to several skin diseases. In addition, more than 80% of the respondents in the experimental group were seen taking foods without cleaning their hands properly, which allows the FRD to reach up to the metabolic organ systems and eventually cause severe health issues. Besides, due to not being aware of wearing safety masks, a distinct inhalation of FRD takes place among the roughing operators, which ultimately causes the breakdown of the effectiveness of the respiratory system of any worker of any age, according to the medical officers. This opinion is relevant to the findings of the second hypothesis, i.e., operator age does not influence the health effects caused by roughing dust. Overall, a common scenario of continuous inhalation and ingestion of the FRD was observed among the workers of all the 8 footwear manufacturing units during the entire study, which is related to fragile and poor health conditions.

According to the expert panel, roughing operators are not able to realize the adverse effects created by roughing dust on their health. Sometimes they are affected by some of those adverse effects, but they do not take them seriously. Even they cannot express it properly, whether they are facing any problems or not. The workers possess a higher chance of suffering from permanent health complications (e.g., skin diseases, various lung diseases like asthma, chronic bronchitis, decreased efficiency, fragile health, etc.) in respect of having a longer period of work experience in the lasting department, which leads to their low life expectancy. This opinion supports the finding of the first hypothesis of this study, i.e., that highly experienced operators have a higher chance of being affected by roughing dust as their exposure time to this dust is higher. The expert panel also stated that most of the roughing operators do not have enough knowledge of Occupational Health and Safety (OHS). Similarly, the authorities of the respective plant are not strict in adopting this safety manner over the workers. To conclude, they suggested using personal protective equipment (PPE), which may control the rate of adverse effects on health associated with the findings of the third hypothesis of this study.

Some recommendations are made in this study to prevent or reduce the adverse effects on workers' health caused by FRD. The opinions of the expert panel are also considered in making these recommendations. The following recommendations are made, both for workers and the industry:

1. Occupation-based personal protective equipment (PPE) should be used by the roughing operators during roughing machine operation. For example, hand gloves to protect the palm of the hand from the roughing dust, an apron to protect the body from the roughing dust, safety goggles to protect the eye from the roughing dust, a hairband to protect the hair, an earplug to protect from the noise of the machine, and finally, an appropriate mask to protect the respiratory organs from entering the roughing dust should be practiced.
2. Hands, mouth, and nose should be washed properly after finishing the job. During working hours, compressed air can be used frequently to clean the dirty parts of the body.
3. Job rotation or rest can be introduced among roughing operators during working hours to reduce work fatigue.
4. Access to safe drinking water should be ensured by the practitioners of the footwear industry. Meanwhile, the habit of drinking adequate water should be developed among the roughing operators. However, before drinking water, one must rinse the mouth with gurgling.
5. Fluorides, povidone iodine, and endodontic chemicals containing mouthwash, toothpaste, and prophylactic gels should not be used by the roughing operators. Fluorides, povidone iodine, and endodontic chemicals are strong oxidants, and they easily oxidize Chromium Cr (III) to Chromium Cr (VI), which is more toxic and carcinogenic to human health.
6. A periodic awareness campaign for ensuring the occupational health and

safety of workers should be conducted by the top management of the footwear factory.

7. Strict and regular monitoring should be carried out by the concerned authority of the footwear factory to ensure workers health and safety. Rewards and recognition for obedient workers can also be introduced.

In general, the common scenario in the footwear industry represents that occupational health and safety (OHS) rules are not properly maintained in the leather and footwear industries in Bangladesh, which is responsible for causing injuries, accidents, and workers' adverse health effects [12]. A study conducted by Deb *et al*. found adverse health effects among the 400 workers of 20 footwear factories, where frequent headache (41.5%), stomachache (18.5%), eye problems (11%), and pain in joints (9.5%) were the most reported problems by the respondents [13]. In this study, respiratory problems, skin irritation, coughing, and ear problems were also found at a noticeable level.

CONCLUSION

Roughing is a critical and sensitive operation in the lasting department of any footwear manufacturing unit. This operation should be carried out with proper care, as faulty roughing may occur, which increases the defect rate and reduces the quality of the footwear. Although modern roughing machines have a dust collector and some particles are large in size, a significant portion of the roughing dust spreads out around the rotating wheel of the machine and affects the roughing operator's health. The aims of this study were to figure out the potential health effects on roughing workers due to exposure to FRD and to identify the factors that influence the potential health effects. In this regard, the total respondents were divided into two groups: the control group, which was composed of 30 workers from random working sections other than lasting, and the experimental group, which was consisted of 30 roughing operators from only lasting department. This research was carried out with the assistance of an expert panel consisting of four members, including two medical officers and two industry experts, in order to validate the responses of the respondents. This study found several adverse health effects, such as eye irritation, skin itching, chest pain, coughing, fatigue, hair itching, breathing problems, dizziness, hair hardening, and insomnia, that were experienced by the respondents in the experimental group. Based on the information obtained from hypothesis analysis, the degree of the impact on workers' health varies depending on working experience and use of Personal Protective Equipment (PPE) whereas workers' age has no influence on the degree of health effects. Apart from that, maximum workers were found having not even a minimum knowledge about the basic safety and hygiene manner, for example, they were unwary of cleaning their hands during taking food inside the manufacturing plant. In order to mitigate the potential adverse effect, using necessary protective equipment, a periodical awareness campaign, work rotation, and active monitoring are strongly recommended. However, this study has some limitations. The emission of roughing dust may vary depending on a few factors, for example: type of upper materials (e.g., leather, synthetic, polymer, etc.) and types of footwear (e.g., Oxford, Derby, Moccasin, Casual, Boot, Sandal, Court Shoe, etc.), which were not considered in this study. Also, only 30 roughing operators from eight footwear factories were considered for the survey, which could be extended in any future study. A future study can be carried out to find out the impact of volatile organic compounds on human health utilized in the production of footwear.

Conflicts of Interest

The authors declare no conflict of interest.

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REFERENCES

1. Jatta, F., Zanoni, L., Fassi, I., Negri, S., A Roughing/Cementing Robotic Cell for Custom Made Shoe Manufacture, *Int J Comput Integr Manuf*, **2004**, 17, 7, 645–652, https://doi.org/10.1080/09511204200027 3212.
2. Ferreira, M.J., Almeida, M.F., Freitas, F., Formulation and Characterization of Leather and Rubber Wastes Composites, *Polym Eng Sci*, **2011**, 51, 7, 1418-1427, https://doi.org/10.1002/pen.21643.
3. Hobson, T., Particle Size Helps in Selecting Dust Collector | Aerodyne, **2020**, https://blog.dustcollectorhq.com/particle-size-helps-in-selecting-dust-collector (accessed Mar. 01, 2023).
4. Prochon, M., Marzec, A., Dzeikala, O., Hazardous Waste Management of Buffing Dust Collagen, *Materials* (Basel), **2020**, 13, 7, 1498, https://doi.org/10.3390/ma13071498.
5. Stroszejn-Mrowca, G., Szadkowska-Stańczyk, I., Exposure to Dust and Its Particle Size Distribution in Shoe Manufacture and Repair Workplaces Measured with GRIMM Laser Dust Monitor, *Int J Occup Med Environ Health*, vol. 16, no. 4, pp. 321–328, 2003.
6. Uuksulainen, S.O., Heikkilä, P.R., Olkinuora, P.S., Kiilunen, M., Self-reported Occupational Health Hazards and Measured Exposures to Airborne Impurities and Noise in Shoe Repair Work, *Int J Occup Environ Health*, **2002**, 8, 4, 320–327, https://doi.org/10.1179/oeh.2002.8.4.320.
7. Greenwell, M., Sarker, M., Rahman, P.K.S.M., Biosurfactant Production and Biodegradation of Leather Dust from Tannery, *Open Biotechnol J*, **2016**, 10, 1, 312–325, https://doi.org/10.2174/18740707016100 10312.
8. Kabir, A., Khan, K., Jhahan, E., Khan, M.I.H., A Study on Incineration from the Wastages of Footwear Industries in Bangladesh, *Int J Sci Eng Investig*, **2017**, 6, 68, 53-58.
9. Flores, T.M., de Simas Koller, T., Auler, S.H., de Souza, J., Characterization of Animal Leather Dust Waste from the Footwear Industry, *Int J Eng Sci*, **2020**, 10, 8, 27-31.
10. Costa, M., Toxicity and Carcinogenicity of Cr(VI) in Animal Models and Humans, *Crit Rev Toxicol*, **1997**, 27, 5, 431–442, https://doi.org/10.3109/10408449709078 442.
11. Krithikadatta, J., Normal Distribution, *J Conserv Dent*, **2014**, 17, 1, 96–97, https://doi.org/10.4103/0972-0707.124171.
12. Senthil, R., Hemalatha, T., Kumar, B.S., Uma, T.S., Das, B.N., Sastry, T.P., Recycling of Finished Leather Wastes: A Novel Approach, *Clean Technol Environ Policy*, **2014**, 17, 1, 187–197, https://doi.org/10.1007/s10098-014-0776-x.
13. Deb, A.K., Chowdhury, M., Hossain, M.I., Azam, F.A.B., Workers' Health and Workplace Condition Evaluation (WCE) Of the Footwear Industries in Bangladesh Extraction of Lac Dye and Its Application in Shoe Upper leather Dyeing, *IOSR J Environ Sci Toxicol Food Technol*, 2018, 12, 8, 7–13.

PERSONAL DESIGN, THE NEW FASHION TREND WITH APPLICATIONS OF INNOVATIVE TECHNOLOGIES

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PERSONAL DESIGN, THE NEW FASHION TREND WITH APPLICATIONS OF INNOVATIVE TECHNOLOGIES

ABSTRACT. The development of 3D technology has brought opportunities and challenges to the shoe industry, as people's living standards have improved due to economic development, and people have increasing requirements for shoe design. They have become more critical, active and informed. They pursue customized products/services and like to be involved in the design process. Additive manufacturing technologies enable this customization of products and new business models should embrace these trends to differentiate themselves and gain competitive advantage. The application of 3D technology is widespread in various fields, including footwear production. From a physical model, it is possible to create a digital model using 3D scanning technology for redesign purposes. The use of 3D printing technology can enable faster modeling of footwear products, enrich the shape of footwear and meet the aesthetic needs of footwear designers. Therefore, the article studies and analyzes the top technologies in fashion, 3D shoe printing technology.
KEY WORDS: fashion, innovative technologies, 3D printing

PERSONAL DESIGN, NOUL TREND ÎN MODĂ CU APLICAȚII DE TEHNOLOGII INOVATIVE

REZUMAT. Dezvoltarea tehnologiei 3D a adus oportunități și provocări pentru industria încălțămintei, deoarece standardele de viață ale oamenilor s-au îmbunătățit datorită dezvoltării economice, iar oamenii au cerințe tot mai mari pentru designul încălțămintei. Au devenit mai critici, activi și informați. Ei urmăresc produse/servicii personalizate și le place să fie implicați în procesul de proiectare. Tehnologiile de fabricație aditivă permit această personalizare a produselor și noile modele de afaceri ar trebui să îmbrățișeze aceste tendințe pentru a se diferenția și a obține avantaje competitive. Aplicarea tehnologiei 3D este larg răspândită în diferite domenii, inclusiv în producția de încălțăminte. Dintr-un model fizic, este posibil să se creeze un model digital folosind tehnologia de scanare 3D în scopuri de reproiectare. Utilizarea tehnologiei de imprimare 3D poate permite modelarea mai rapidă a produselor de încălțăminte, îmbogăți forma încălțămintei și poate satisface nevoile estetice ale designerilor de încălțăminte. Prin urmare, articolul studiază și analizează tehnologiile de top în modă, tehnologia de imprimare 3D a încălțămintei.
CUVINTE CHEIE: modă, tehnologii inovative, imprimare 3D

PERSONAL DESIGN, LA NOUVELLE TENDANCE DE LA MODE AVEC DES APPLICATIONS DE TECHNOLOGIES INNOVANTES

RÉSUMÉ. Le développement de la technologie 3D a apporté des opportunités et des défis à l'industrie de la chaussure, car le niveau de vie des gens s'est amélioré en raison du développement économique et les gens ont des exigences croissantes en matière de conception de chaussures. Ils sont devenus plus critiques, actifs et informés. Ils recherchent des produits/services personnalisés et aiment être impliqués dans le processus de conception. Les technologies de fabrication additive permettent cette personnalisation des produits et les nouveaux modèles commerciaux doivent adopter ces tendances pour se différencier et acquérir un avantage concurrentiel. L'application de la technologie 3D est répandue dans divers domaines, y compris la production de chaussures. A partir d'un modèle physique, il est possible de créer un modèle numérique en utilisant la technologie de numérisation 3D à des fins de reconception. L'utilisation de la technologie d'impression 3D peut permettre une modélisation plus rapide des produits chaussants, enrichir la forme des chaussures et répondre aux besoins esthétiques des créateurs de chaussures. Par conséquent, l'article étudie et analyse les plus nouvelles technologies de la mode, la technologie d'impression 3D de chaussures.
MOTS CLÉS : mode, technologies innovantes, impression 3D

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INTRODUCTION

Fashion and technology go very well together. And this is just the beginning, because high tech will continue to transform what we wear, in many ways, in the years to come. 3D printing technology is still in its early stages, but it has already made its way into the world of fashion.

In the future we will see more and more shoes with a unique design. Product development activity and innovation are important components of the design process. Following the stages of the design process, after the new product concept has been defined, it is necessary to diversify (develop) this product idea. Diversification techniques (product development) aim to obtain a sufficient number of models within the same family (concept), models to be subjected to an analysis aimed at defining the optimal variants, both for the consumer and for the producer.

Technology has progressed enormously in the last 20 years and as a result of this progress, 3D printers are no longer used only for creating prototypes, but even for finished products.

3D printers allow designers to produce a prototype in a very short time. Consequently, the prototype can be tested and remodeled quickly. Designers can obtain, with the help of 3D printers, shoe components with extremely complex shapes. Today, the technology is present in most of the research laboratories owned by the institutions concerned with the development of fashion design.

Fashion design does not only express a new idea in the creation of a product, but also an identification of it with the person who wears it. This is how the notion of personal design appears, which we will encounter more and more often in the coming years.

Everything will become a cultural communication through the message of the product idea, a technological communication through the technical sketch of the product, a commercial communication through the collection catalogue and an advertising one through the fashion illustration.

As one of the largest industries in the world, expected to rake in up to $3.3 trillion by 2030 [1], it is surprising to learn that the way fashion works today has not changed that much in the last twenty years. However, growing concerns about pollution, as well as the need to satisfy today's hyper-connected consumers, have given way to new technologies. We live in the "age of technology".

People want instant access to the latest trends as soon as new shoe designs hit the catwalks, thanks to social media. Also, younger generations looking to stand out from the crowd are looking for products that can be tailored to their specific needs and preferences. In addition, "mass produced" or "fast fashion" footwear seems to be losing its appeal.

Many designers must embrace the latest technologies to push the boundaries of manufacturing, marketing and wearability as customers' real lives become more intertwined with the digital world.

TOP TECHNOLOGICAL PROGRESS IN FASHION

Artificial Intelligence

In recent years, shoe companies have used artificial intelligence to improve their customers' shopping experience, analyze data, increase sales, forecast trends and provide inventory data. Chatbots and touch screens are used in stores to improve the customer experience through personalized product suggestions. Real-time inventory tracking has become essential for businesses as it saves time and ensures efficient warehouse management and operations. In addition, if we combine inventory tracking with powerful predictive tools, companies could have a significant competitive advantage. Instead of significant competitive advantage. Instead of relying solely on traditional ways of forecasting trends—which require observation and data collection from fashion designers and trend spotters—companies can have instant access to data that allows them to plan the right styles and quantities in a timely manner.

British fashion company STITCH FIX has an automated wardrobe planning tool that, using analytics, records its customers' purchases and enters them into a virtual wardrobe [2]. The platform allows women to create looks from their wardrobe and even choose from over 10,000 stores. Also, the TRUEFIT customization platform uses an online matching engine that helps users find a proper fit with brands and new styles on the market [3]. Another interesting example is the INTELLIGENCE NODE, which allows users to track trends in real time [4]. Customers can enter specific keywords, user browsing patterns, price limits, and more. Intelligence Node's AI-based search platform allows users to find exact or closest matches to the desired product. Fashion trend forecasting relied solely on past trends to predict the future. New technologies like HEURITECH are defining audience panels on social networks [5]. To predict future trends, it applies image recognition technology from social media to access shapes, prints, colors and material characteristics (Fig. 1).

Figure 1. Image recognition technology that predicts style trends. Source: Heuritech

Google also implemented a similar experiment in partnership with German fashion brand ZALANDO. The neural network understands style preferences, colors and textures. After that, the algorithm was used to create models based on users' style preferences (Fig. 2). There is also a collaborative project between IBM and the Fashion Institute of Technology, known as "Reimagine Retail", which uses IBM's high-tech AI tools to indicate real-time trends in the fashion industry in shapes, colors, etc.

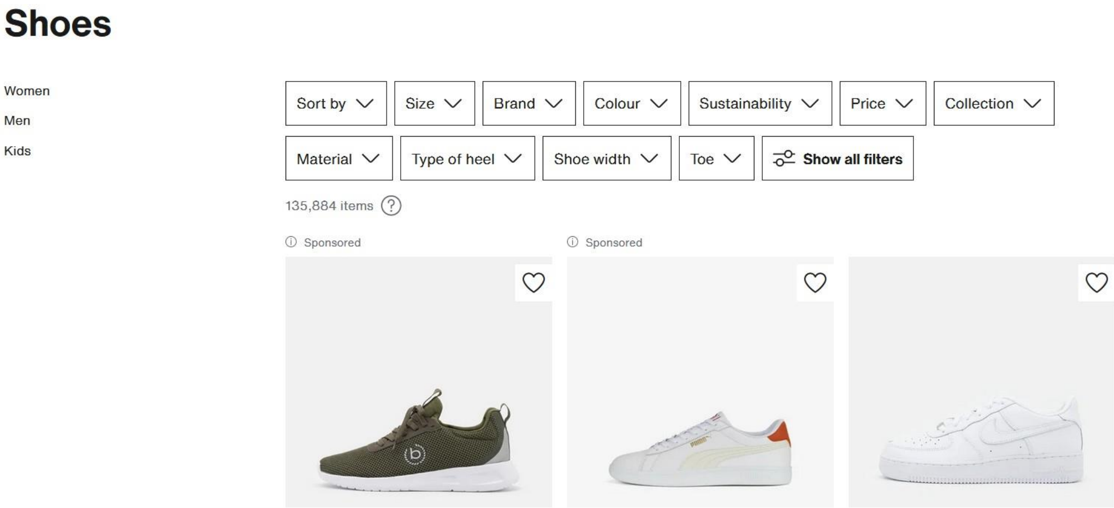

Figure 2. ZALANDO Algorithm, source: Zalando

These technologies highlight how AI is the bulwark of future developments in the fashion industry, shaping everything from trend forecasting to how consumers can actually view and buy products.

New Materials

New materials are undoubtedly the future of fashion, another way for designers to distinguish themselves. All the facts point to the idea that ecological leather is not a very sustainable option [6]. Startups like MODERN MEADOW are fighting this by creating lab-grown leather without harming animals [7]. Also, companies like BOLT THREADS and ENTOGENETICS are innovating very strong spider silk [8].

The latest applications of printed objects that change colors include a system created by MIT researchers called ColorFab 3D. This technology prints 3D objects with “photochromic inks” that change color when exposed to certain wavelengths of UV light. [9] One of their first items produced was the ring that can be programmed in a number of customizable colors.

Google fans could soon be wearing clothing made by the digital tech giant. Project Jacquard [10], from Google’s ATAP (Advanced Technology and Projects) lab, is a collection of conductive threads for weaving touch-sensitive textiles such as clothing, tablecloths, carpets, or anything else made of fabric. The team behind Project Jacquard also makes it possible to change color with Ebb. It is a technology that changes the color of the fabric. The color can be programmed to change our mood or decor. Ebb materials could even help us perform many activities we currently do on our phones using color signals. For example, when we receive a call, the color of the cuff changes. This highlights how new materials will literally reshape the clothing and footwear we wear.

Internet of Things (IoT)

IoT describes a network of objects – “things” – that are embedded in technology to enable the exchange and connection of data over the Internet. This is one of the most exciting emerging technology trends in the fashion market. Year after year, everyday fashion continues to improve to reflect the realities of our everyday lives. From a great emphasis on comfort to the use of new materials, the fashion industry has had to keep up in adapting to the demands of contemporary life. This has been seen most clearly in advances in wearable technology and wearable gadgets. These have come to influence the way we interact with the environment, with others, with our bodies, giving the word “comfort” a whole new meaning.

As our “real” lives become more and more blended with a virtual existence, many designers have experimented and pushed the boundaries of what wearability means. The Internet of Things (IoT) enables data sharing, inventory management, security, increased efficiency and productivity. Some of the most exciting IoT innovations are related to health. For example, the NADI X yoga pants (Fig. 3) have built-in sensors to correct users’ posture through vibrations while they perform yoga exercises [11]. HEXOSKIN, for example, tracks heart rate and temperature. They also make socks that count steps, measure calories, etc. Nike has released a pair of lace-up sneakers (Fig. 4) that can adapt to the unique shape of the wearer’s foot and can be controlled via a smartphone. The needs of the foot change at any moment, depending on the sport, its duration and the specific movements. When users wear the IoT shoes, it appears that a customized system senses the foot tension and the shoe adjusts [12].

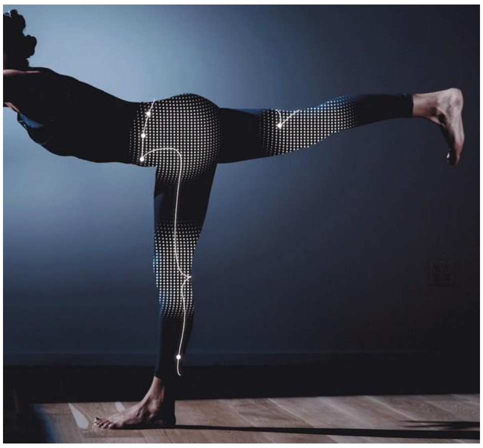

Figure 3. NADI X Yoga pants.
Source: Zalando

Figure 4. Nike customizable shoes

Virtual and Augmented Reality (VR and AR)

A widespread use of VR allows customers to try on clothes virtually. This provides greater accuracy due to custom measurement functionality and also uses augmented reality technology. It also means customers may be more likely to buy products they feel like trying. Some companies are making the most of AR and VR technology. One user of AR/VR technology is EFI Optitex, which has greatly improved the costly and time-consuming process of finding a suitable fit. They showed how to take the essential components of a design, such as sketches and technical models, which can then be turned into simulated 3D renderings. Other new 3D rendering technologies include CLO. The tool allows companies to edit models and make changes instantly.

3D Printing

Additive manufacturing technologies, also known as 3D printing or rapid prototyping, have had a rapid development in the last decade, being considered technologies of the future. With their help, you can create different products with a complex geometric shape, different conceptual models or functional prototypes that can be tested, checked and revised repeatedly before sending the new product into production. Since the advent of 3D printers, many companies, both large and small, have looked at the possibilities they offer for on-demand production [13]. This will create new avenues for customization, durability and creativity. Thus, many fashion companies have adopted 3D printing technology in their collections in 2022, from accessories to finished products. Even though it takes more time to create, less waste results. On-demand garment printing reduces material waste by approximately 35% [14].

One of the pioneers of 3D printing in the fashion industry is Iris Van Herpen. The Dutch designer has an extensive body of 3D printing work dating back to 2010. One of her most notable pieces is the “Crystallization” top, which was 3D printed from white polyamide. Van Herpen is perhaps the only designer who has presented at the prestigious Haute Couture fashion weeks in Paris, using sophisticated technologies for her garments and presentations.

3D printing also takes fashion to a new level of conceptual art. Anouk Wipprecht’s incredible Spider dress has mechanical arms that move based on the proximity of other people. This 3D printed dress combines cutting edge scientific technology and haute couture fashion, demonstrating the versatility of this new technology. Digital knitting has also made great strides in the world of 3D printing and offers a wealth of customization possibilities. For example, manufacturers like Shima Seiki can turn cones of yarn into a seamless garment in less than an hour.

The Advantages of 3D Printing

In footwear production, the traditional technological process is mainly: designing, modeling, cutting, sewing and soling. The whole production process takes a long time and is very complicated. The combination of 3D design technology and 3D printing technology can quickly achieve the initial mold production and check the result, thereby reducing the time and improving the competitiveness of footwear enterprises in the fierce market competition [15, 16, 17]. The use of software and 3D technology to obtain the shoe allows the creation and modification of its shape in accordance with the design requirements. 3D printing technology is needed to faster and better integrate fashion elements [18, 19].

The main advantages are:

- reducing the costs of planning, designing, making and putting a new product on the market by checking the design and functionality at an early stage, respectively, by eliminating some preliminary stages belonging to the series production process, allowing at the same time to make the required changes much faster and at lesser costs;
- optimizing the design, the possibility of customization, obtaining objects with a high degree of complexity;
- decreasing the time of launching the new product on the market (from a few weeks/months to a few hours or days);
- promoting the principle of sustainability – because the products can be made to order, depending on the needs, without consuming excess resources, the materials used are generally easy to recycle, they are ecological and compatible with the environment [20].

3D PRINTED SHOES

3D printing can be used in any field, and fashion is no exception. It is possible to create 3D printed shoes, original designs, insoles, soles, heels, etc., make rapid prototypes and try new manufacturing processes. Everything is possible thanks to 3D printing technology.

Designers and 3D Printing

3D printing allows designers to create clothing. But its usefulness in fashion technology does not stop there, as it is also possible to create shoes. For example, Zoe Jia-Yu Dai, a shoe designer from Taiwan, created “Breaking the 3D Mould” (Fig. 5), a collection of shoes with 3D printed parts [21]. This technology allows designers to go further with designing structures. It is a way to change the manufacturing process. It is easier to create organic structures with additive manufacturing than with a traditional process.

Figure 5. “Breaking the 3D Mould”

It is obviously a good way to create prototypes. Some designers only focus on shoe design. The “Melissa” shoes are an excellent example of the possibilities offered by 3D printing technology when it comes to design [22]. The “Melissa” shoes are among the most amazing examples of what 3D printing can do for style and design (Fig. 6-8). This Brazilian footwear company produces shoes using injection molding and 3D printing. They are made of a patented plastic called Melflex. The production process is quite green and tends towards a cradle-to-cradle model, as the remaining material is used to create new shoes. The design and production process of “Melissa” models requires experimentation. The brand works with architects and designers to propose a futuristic and unique shoe design.

Figure 6. Designer Andreia Chaves created the “Invisible shoes”

Figure 7. The Brazilian duo Campana Brothers designed a mini-collection

Figure 8. Swedish designer Naim Josefi created these shoes that fit perfectly. The buyer's foot is scanned in the store and the shoes are made on demand.

3D Printed Shoes – Attempting a New Manufacturing Process and New Materials

Rethinking Production

As in other sectors, 3D printing can be used to develop new manufacturing processes. It can provide more possibilities and opportunities to any company. For example, Feetz is an American startup that makes shoes to order, easy to wear and with an appealing style. In addition, Feetz is committed to protecting the environment. They developed their own 3D printer, using a fused filament manufacturing technique and their own 3D printing material – a proprietary polymer. They wanted to rethink the entire manufacturing process, to make it more sustainable. Feetz uses recycled and recyclable materials, is water-free and has reduced its carbon footprint by 60%. In addition, there is no material waste, because with 3D printing you only use the amount you need [23]. The use of 3D printing in their manufacturing process shows that it is possible to change the way the footwear industry affects the environment.

High Performance Materials for 3D Printing

New high-performance materials are now available on the market and are specially adapted to the creation of footwear parts such as midsoles. The perfect example is thermoplastic polyurethane (TPU). Objects printed with thermoplastic polyurethane offer advanced properties, which is perfect for obtaining durable, strong and flexible parts (Fig. 9).

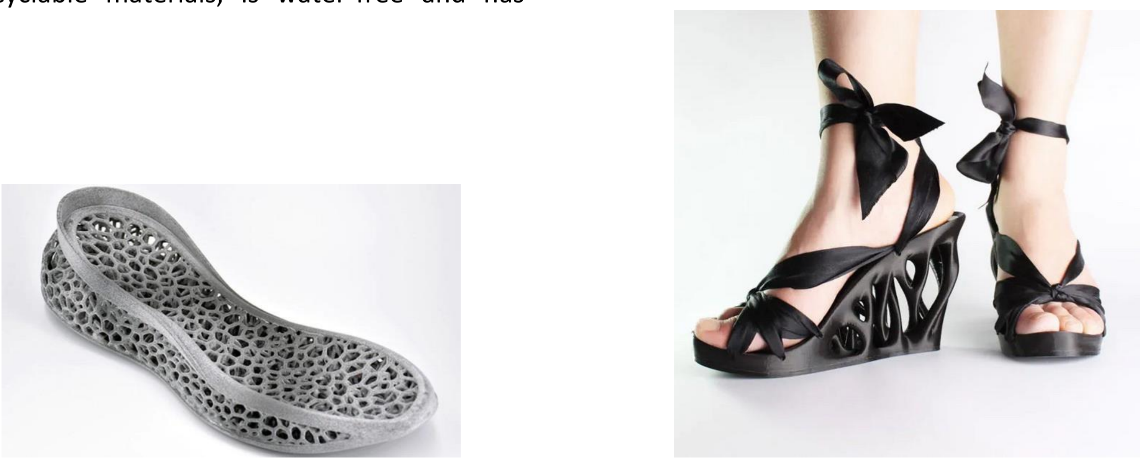

Figure 9. 3D-printed TPU soles [23]

CONCLUSIONS

3D printing can be used in any field, and fashion is no exception. It is possible to create 3D printed shoes, original designs, insoles, soles, heels, etc., make rapid prototypes and try new manufacturing processes. Everything is possible thanks to 3D printing technology.

3D printing takes fashion to a new level of conceptual art. Designers will continue to work with 3D printing because it allows the creation of incredible designs with a lot of freedom. The footwear industry is more connected to 3D printing than we might think. All these examples show that there are different ways to create shoes. You can push the boundaries of design or change manufacturing methods by finding an environmentally friendly way to produce, or even get shoes or insoles custom-made for more comfort.

Fashion innovation is critical to commercial value and longevity. It is central to how we shape the industry. Fashion innovation can help replace existing materials with sustainable alternatives. Innovation in fashion will enable us to function and interact in a digital world. The only way forward is to innovate, develop and adapt fashion.

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REFERENCES

1. Dimovski, A., 28 Trendy Fashion Industry Statistics for a Luxurious 2023, *GoRemotely*, **2023**, available at: https://goremotely.net/blog/fashion-industry-statistics/?ref=techpacker.com
2. https://www.stitchfix.com/
3. https://www.truefit.com/business
4. https://www.intelligencenode.com/
5. Poncelin, C., How Heuritech forecasts fashion trends thanks to AI, *Heuritech*, **2020**, available at: https://www.heuritech.com/articles/fashion-solutions/how-heuritech-forecasts-fashion-trends-thanks-to-artificial-intelligence/?ref=techpacker.com
6. Thomas, L., Is Vegan Leather a More Sustainable Option? The Answer is Complicated, *The Good Trade*, **2021**, available at: https://www.thegoodtrade.com/features/vegan-leather-vs-animal-leather/.
7. https://www.modernmeadow.com/
8. https://boltthreads.com/technology/microsilk/
9. Chow, D., These 3D-printed Accessories Change Color Whenever You Want, **2018**, available at: https://www.nbcnews.com/mach/science/these-3d-printed-accessories-change-color-whenever-you-want-ncna845581
10. https://atap.google.com/jacquard/
11. https://www.wearablex.com/pages/how-it-works
12. White, M., IoT Shoes Can Adapt to Individual Users and Be Controlled via a Smartphone, *The Manufacturer*, **2019**, available at: https://www.themanufacturer.com/articles/iot-shoes-can-adapt-to-individual-users-and-be-controlled-via-a-smartphone/.
13. McDowell, M., Fashion Brands Embrace 3D Design, *Vogue Business*, **2020**, available at: https://www.voguebusiness.com/technology/fashion-brands-embrace-3d-design.
14. Kochar, S., Top 9 Technology Trends Reshaping the Fashion Industry in 2023, *Techpacker*, **2023**, available at: https://techpacker.com/blog/design/top-9-fashion-technology-trends/
15. Clarke, T.E., Frederick, E.C., Hamill, C.L., The Effects of Shoe Design Parameters on Rearfoot Control in Running, *Med Sci Sports Exerc*, **1983**, 15, 5, 376–381, https://doi.org/10.1249/00005768-198315050-00006.

16. Backes, E.H., Pires, L.D.N., Beatrice, C.A.G., Costa, L.C., Passador, F.R., Pessan, L.A., Fabrication of Biocompatible Composites of Poly (Lactic Acid)/Hydroxyapatite Envisioning Medical Applications, *Polym Eng Sci*, **2020**, 60, 3, 636–644, https://doi.org/10.1002/pen.25322.
17. Chantelau, E., Gede, A., Foot Dimensions of Elderly People with and without *Diabetes mellitus* - A Data Basis for Shoe Design, *Gerontology*, **2002**, 48, 4, 241–244, https://doi.org/10.1159/000058357.
18. Daneshmand, A., Hosseini Hashemi, B., Performance of Intermediate and Long Links in Eccentrically Braced Frames, *J Constr Steel Res*, **2012**, 70, 167–176, https://doi.org/10.1016/j.jcsr.2011.10.011.
19. Hennig, E.M., Sterzing, T., The Influence of Soccer Shoe Design on Playing Performance: A Series of Biomechanical Studies, *Footwear Sci*, **2010**, 2, 1, 3–11, https://doi.org/10.1080/19424281003691999.
20. Cicala, G., Giordano, D., Tosto, C., Filippone, G., Antonino, R., Blanco, I., Polylactide (PLA) Filaments a Biobased Solution for Additive Manufacturing: Correlating Rheology and Thermomechanical Properties with Printing Quality, *Materials*, **2018**, 11, 7, 1191, https://doi.org/10.3390/ma11071191.
21. Dai, Z.J.Y., Breaking the 3D Mould, Virtual Shoe Museum, available at: https://Virtualshoemuseum.Com/Zoe-Jia-Yu-Dai/Breaking-The-3d-Mould/
22. ***, 3D Printing for Green Fashion – Melissas' Footwear Experiments, **2012**, available at: https://www.sculpteo.com/blog/2012/03/29/3d-printing-for-green-fashion-melissas-footwear-experiments/
23. ***, 3D Printed Shoes: How 3D Printing Revolutionizes the Footwear Industry, available at: https://www.sculpteo.com/en/3d-learning-hub/applications-of-3d-printing/3d-printed-shoes/

ENVIRONMENTAL SUSTAINABILITY: A CHALLENGE FOR LEATHER INDUSTRY

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ENVIRONMENTAL SUSTAINABILITY: A CHALLENGE FOR LEATHER INDUSTRY

ABSTRACT. Adopting pollution prevention strategies (PPS) can ensure environmental sustainability (ES) in the leather industry and can help the industry achieve several sustainable development goals (SDGs). In order to ensure the ES of the leather industry, there is a need for research to identify a comprehensive list of PPS. This research aims at identifying the most effective PPS for the leather industry, which are categorized into 4R (reduce, reuse, recycle, and recover) dimensions. This is a case study where four leather processing companies from Bangladesh were purposively selected. Through an extensive literature review and experts' opinions, 21 PPS are identified for the leather industry's ES. Also, this study shows several benefits of PPS through which various SDGs can be achieved in the leather industry. This study will certainly guide the leather industry managers to ensure the ES of the leather industry and, consequently, assist in achieving several SDGs.

KEY WORDS: 4R strategies, environment sustainability, leather industry, pollution prevention, sustainable development goals

SUSTENABILITATEA MEDIULUI: O PROVOCARE PENTRU INDUSTRIA DE PIELĂRIE

REZUMAT. Adoptarea strategiilor de prevenire a poluării poate asigura sustenabilitatea mediului în industria de pielărie și poate ajuta industria să atingă mai multe obiective de dezvoltare durabilă (ODD). Pentru a asigura sustenabilitatea mediului în industria de pielărie, este nevoie de cercetare pentru a identifica o listă cuprinzătoare de strategii de prevenire a poluării. Această cercetare își propune să identifice cele mai eficiente strategii de prevenire a poluării pentru industria de pielărie, pe principiul 4R (reducere, reutilizare, reciclare și recuperare). În acest studiu de caz s-au selectat intenționat patru companii de prelucrare a pielii din Bangladesh. Printr-o analiză extinsă a literaturii de specialitate și a opiniilor experților, s-au identificat 21 de strategii de prevenire a poluării pentru sustenabilitatea mediului în industria de pielărie. De asemenea, acest studiu arată câteva beneficii ale strategiilor de prevenire a poluării prin care pot fi atinse diverse ODD-uri în industria de pielărie. Acest studiu va ghida cu siguranță managerii din industria de pielărie pentru a asigura sustenabilitatea mediului în industria de pielărie și, în consecință, pentru a ajuta la atingerea mai multor ODD.

CUVINTE CHEIE: strategii 4R, sustenabilitatea mediului, industria de pielărie, prevenirea poluării, obiective de dezvoltare durabilă

LA DURABILITÉ ENVIRONNEMENTALE : UN DÉFI POUR L'INDUSTRIE DU CUIR

RÉSUMÉ. L'adoption de stratégies de prévention de la pollution peut garantir la durabilité environnementale dans l'industrie du cuir et aider l'industrie à atteindre plusieurs objectifs de développement durable (ODD). Pour garantir la durabilité environnementale dans l'industrie du cuir, des recherches sont nécessaires pour identifier une liste complète de stratégies de prévention de la pollution. Cette recherche vise à identifier les stratégies de prévention de la pollution les plus efficaces pour l'industrie du cuir, basées sur le principe des 4R (réduire, réutiliser, recycler et valoriser). Quatre entreprises de transformation du cuir au Bangladesh ont été délibérément sélectionnées dans cette étude de cas. Grâce à une analyse approfondie de la littérature et des avis d'experts, 21 stratégies de prévention de la pollution pour la durabilité environnementale dans l'industrie du cuir ont été identifiées. En outre, cette étude montre certains avantages des stratégies de prévention de la pollution grâce auxquelles divers ODD peuvent être atteints dans l'industrie du cuir. Cette étude guidera sûrement les responsables de l'industrie du cuir pour assurer la durabilité environnementale dans l'industrie du cuir et contribuera par conséquent à atteindre plusieurs ODD.

MOTS CLÉS : stratégies 4R, durabilité environnementale, industrie du cuir, prévention de la pollution, objectifs de développement durable

INTRODUCTION

The leather processing companies known as tanneries produce huge amounts of pollutants during preservation to finished leather production. During 1,000 kg of hides or skins processing into leather, 30-40 m^3 of wastewater and 800-850 kg of solid wastes are generated, which contain 300 kg of hazardous chemicals [1]. Bangladesh has huge potential for developing this sector as it has an abundant supply of quality raw materials and cheap production costs. However, the country is lagging behind in the competition due to the lack of environmental sustainability (ES) of its tanneries [2]. Nowadays, ES has become a burning issue for the leather industry due to global warming and the worsening of the environmental ecosystem [3-4]. Moreover, most consumers and reputed buyers are giving

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priority to outsourcing leather and leather products from sustainable tanneries. Therefore, the need for adopting sustainable practices has become a major priority for the leather processing industry in every country. However, most of the tannery owners in Bangladesh consider adopting sustainable practices an expensive and complex process, which will increase the cost of manufacturing. As a result, ES has become a massive challenge for the leather industry in Bangladesh. In the previous literature, researchers have tried to find a better way to shape the leather industry as more sustainable. In this vein, Marrucci *et al*. (2022) argued that life cycle assessment is a necessary approach to ensure a circular business model in the leather industry for ensuring a zero-carbon future [5]. Huang *et al*. (2022) developed chrome-free eco-friendly leather to mitigate the environmental pollution from chrome-tanned leather processing [6]. Karuppiah *et al*. (2021) conducted a review article to find out the inhibitors of circular economy practices in the context of the leather industry [7]. China *et al*. (2020) performed a review study on possible alternative technologies rather than the widely used chrome tanning process to prevent environmental pollution [8]. Islam *et al*. (2020) identified the challenges of sustainable supply chain management for the Bangladeshi leather industry [9]. Moktadir *et al*. (2020) identified the challenges to implementing circular economy practices in the Bangladeshi leather industry for achieving ES [10]. Kanagaraj *et al*. (2015) and Dixit *et al*. (2015) have explored various cleaner technologies for mitigating the environmental footprint of the leather industry [11-12]. Gupta *et al*. (2018) conducted a case study on a leather processing company in India to explore the firm performance between pollution prevention and control strategies and its benefits over the triple bottom line (TBL) approach [13].

From an extant literature review, it is evident that there were various studies that focused on the implementation of cleaner technologies in leather processing and the identification of the challenges of circular economy practices and sustainable supply chain management in the leather industry. However, there was a scarcity of literature on a summarized comprehensive list of pollution prevention strategies (PPS) for the leather industry. To the best of our knowledge, no prior research was carried out on the existing state of adoption of various PPS for achieving ES of tanneries and their prospective benefits on achieving several sustainable development goals (SDGs). Therefore, this research is intended to fulfill the following objectives:

1. To identify the pollution prevention and control strategies for the leather industry under the 4R (Reduce, Reuse, Recycle, and Recover) dimensions and explore the environmental benefits of those strategies.
2. To find out the current status of practicing the identified 4R practices for the selected four case leather companies in Bangladesh.
3. To suggest practical implications for achieving SDGs and environmental compliance certification (e.g., Leather Working Group) for the leather industry in the way of ensuring environmental sustainability.

Literature Review

An Overview of the Leather Industry in Bangladesh

Bangladesh has a good reputation for manufacturing excellent quality leather around the world at competitive prices due to low labor costs, availability of raw hides/skins, and government incentives for export [14]. The country has 200 tanneries and 165 leather goods and footwear companies, which are contributing to the country's export market. According to the Export Promotion Bureau of Bangladesh, in the last fiscal year 2021-2022, Bangladesh exported $ 1.245 billion in leather, leather goods, and leather footwear with a positive growth of 32.31% against that of the previous year, achieving the 2nd export earning sector in the country [15]. Currently, Bangladesh is contributing less than 0.5% of the total world demand for leather, leather goods, and leather footwear. The major barrier to escalating the export volume of the leather industry is a lack of ES. The absence of proper waste management, inferior technologies, traditional methods of leather processing, lack of facilities for improvement, and unwillingness for adopting eco-friendly practices have created a negative environmental impression for the leather industry in the international business environment [12]. This industry creates a huge amount of hazardous and toxic pollutants degrading the surrounding environments, creating serious health problems among the employees working in the leather processing companies, and thus lowering the living standards of the community people. Due to severe environmental pollution, degraded human life in the Hazaribagh area (a residential zone in Dhaka city), and simultaneous pressurization from the environmental protection agencies, pollution control bodies, buyers, well-known brands, etc., the Bangladesh government took an initiative of relocating all the leather processing units from Hazaribagh to the Tannery Industrial Estate, Hemayetpur, Savar. This specialized estate has a Central Effluent Treatment Plant (CETP) system that can treat 30,000 m^3 effluents in a single day with extra facilities for chrome recovery, water treatment, and sludge treatment [16]. Though solid wastes are the major wastes of this industry, there is no solid waste management plant in the Tannery Industrial Estate so far. Also, at the Tannery Industrial Estate, the central effluent treatment plant (CETP) system is not functional at the required scale [17-18]. Due to the improper installation of some pre-planned facilities, and improper regulations from the authority, the Dhaleaswari river near the CETP plant, has been polluted and thereby, the surrounding environment is destroying a great deal [19-21]. If this situation continues to degrade the ecosystems at this devastating rate, this will turn into a death trap for the leather industry. Therefore, more research is needed to make a guideline on how to implement sustainable leather processing for ensuring ES in the Bangladeshi leather industry.

Environmental Sustainability (ES)

Elkington first used the phrase 'triple bottom line', a way of measuring a company's sustainability, in his book named *Cannibals with the Fork: The Triple Bottom Line of 21st-Century Business* [22]. The author explained in that book that a sustainable company will not only preserve and use natural and energy resources but also give importance to human rights with keeping the best interest of the company's economic condition. In other words, the sustainability of an organization is branched into three dimensions, i.e., environmental, social, and economic sustainability. Sutton *et al*. (2014) defined environmental sustainability as the capability to maintain things or qualities that are valued in natural and biological environments [23]. It is a way of conserving natural resources and protecting the ecosystem for current and future generations [24]. Broadly, it is a state of balancing resiliency and interconnectedness that allows human society to satisfy its needs neither by exceeding the capacity of its supporting ecosystems to continue to regenerate the services necessary to meet those needs nor by our actions diminishing biological diversity [25-26]. As leather processing operations are extremely polluting, sustainable practices can lead this industry to achieve ES [11,13]. The International Council of Tanners (ICT), an organization of the world's leather trade association has described ES for the leather industry in the following contexts: whole compliance with environmental regulations that include water and air emissions, and solid wastes; obedience to energy efficiency; processing life cycle assessment and identification of the environmental footprint of leather processing; commitment to doing the operations towards best practices in processing to predict ever-increasing environmental controls and carbon reduction targets and to practice due diligence.

ES can be achieved by practices such as adopting clean production practices in leather processing, efficient usage of energy, effective waste minimization techniques, proper waste management practices, reduction of natural resources consumption, better usage of raw materials and processing chemicals, reduction of the quantity of the pollutants emitted, and reduction of the environmental cycle of products [27-29]. In addition, adopting environmentally sustainable practices influence organizational performance creating economic, environmental, and social benefits and improving the company's image among the supply chain members [27, 30-32]. An environmentally sustainable leather processing company can lead to several environmental benefits represented in Table 1, which will not only improve any company's business but also ensure the overall protection of the environment.

Table 1: Potential Environmental Benefits from 4R Practices [33]

Environmental benefits	
1.	Reduction of water, chemical, raw materials, and energy consumption.
2.	Less generation of the air pollutants emissions such as carbon products, nitrogenous products, VOC (volatile organic chemicals), particulate matter, smoke, dust, heat, etc.
3.	Almost no or less generation of hazardous pollutants such as heavy metals, chemical oxygen demand (COD), biological oxygen demand (BOD), pH values, nitrogenous and phosphorous compounds, suspended solids, etc., in the wastewater and releasing clean water into the environment.
4.	Less generation of solid wastes and usage of the solid wastes into value-added products.

4R Strategies for Pollution Prevention and Pollution Control

Pollution prevention is the process of reducing the amount of generation of wastes including source reduction, and efficient use of raw materials and energy resources, whereas pollution control, is the process of managing the pollutants after it is emitted by recycling and recovering them in order to reduce the impact of pollutants on the environment [34-35]. Pollution prevention, i.e., source reduction, cleaner technology, etc., may seem a costly process at the initial stage of adaptation in the leather industry but in the long run, it will benefit this industry by reducing the risk of liability, saving the operating cost, lowering the housekeeping cost, increasing the productivity and process efficiency, reducing the environmental impacts of the wastes, protecting the eco-system and resources [32, 36]. Both pollution prevention and pollution control strategies can improve the industry's current deteriorating situation, which can effectively aid the leather industry of Bangladesh in thriving. 4R, i.e., Reduce, Reuse, Recycle, and Recover strategies are widely used in waste management, which is a great tool for minimizing, managing, and recovering reusable materials from both solid and liquid wastes. A brief description of the 4R strategies is given below:

- ***Reduce***

Reducing means minimizing the consumption of any resources (e.g., chemicals, energy) and lowering the generation of waste during any stage of leather processing [37].

- ***Reuse***

Reuse means the usage of tannery wastes as raw materials or products either in the same function or in other functions [37].

- ***Recycle***

Recycling means the conversion of tannery wastes into useable products or the usage of these wastes as raw materials in another process after simply treating them by collection, separation, and suitable modification while all the physical and chemical characteristics remain similar to the wastes [37].

- ***Recover***

Recover means the usage of tannery wastes as raw materials or products after technical treatment while the main physical and chemical properties of these wastes change to their prior conditions [37].

There were very few studies based on 4R practices of waste management for pollution prevention and control in the leather processing industry in the previous literature. Leather processing involves many unit operations using a lot of chemicals that emit many hazardous and carcinogenic pollutants posing a serious threat to the ES of this industry [38]. The negative impact on the environment and high dissipation of energy of this industry can be mitigated by adopting a closed-loop economy or zero-waste technologies rather than depending on the linear economy of waste management where wastes will be recovered and recycled and reused in the same industry or other similar industries [39]. Cleaner production can be introduced in the leather processing industry by changing raw materials and production processes in beam house operations, using alternatives to chrome tanning, increasing the uptake of chrome in the tanning process, recovering and reusing chromium, and direct chromium recycling [40]. Waste utilization might also be beneficial for this industry as many solid wastes can be altered into biodiesel/biomass [41], composite sheets [42], electromagnetic interference shielding [43] mixing with other materials; buffing dust can be used as a filler in the production of rigid polyurethane foams [44] and for the fabrication of composite sheet [45], leather solid wastes can be also turned into new leather by solid-state shear milling technology by incorporating thermoplastic polyurethane [46]. Additionally, recovered protein hydrolysate from chrome shaving dust can be utilized as a filler/fat-liquoring agent, free from any toxic chemicals in the re-chroming/ fat-liquoring operation that will produce high-quality leather [47]. Also, these protein hydrolysates are applicable in agriculture, feed, adhesives, bio-plastic, construction, cosmetics, pharmaceutical industries, and bone and tissue engineering combined with several polymer composites or matrixes [48].

However, all these studies indicate the pilot application and theoretical exploration of the waste minimization, waste management, and waste utilization techniques that can be applied to the leather industry aiming at achieving ES. The real-life observations of these techniques and methods have not been explored in the context of the leather industry of Bangladesh. Against this backdrop, this study first focuses on the identification of a comprehensive list of pollution prevention strategies (PPS) for the leather industry's sustainability. Second, this study finds the current practices of adopting PPS in the leather industry. Finally, this study also highlights the gaps in why the practitioners of this industry are not adopting PPS for ensuring ES. This study contributes to the existing literature in the following ways. This study will identify the PPS under the 4R dimensions of waste management, which will be feasible to implement in leather processing operations. The findings of this study will particularly help industry practitioners achieve ES and thereby ensure several sustainable development goals (SDGs).

Table 2: Potential 4R Practices in leather processing from literature review and experts' opinions

4R dimensions	Pollution prevention strategies (PPS)	References
Reduce	1. Usages of green or raw hides/skins	49
	2. Usage of silica gel/boric acids/SMB (sodium chloride and sodium meta bi-sulfite method)/phytochemical preservation/bacteriocin solution in preservation stages of leather processing	11
	3. Usage of green fleshing	49
	4. Practicing short float operations	37
	5. Ammonium-free deliming	50
	6. Usage of sulfur stripping in dehairing and liming	49
	7. Enzymatic dehairing operations using proteolytic and lipolytic enzyme or using enzyme hydrogen peroxide	51
	8. Hair-saving methods in dehairing operations	52
	9. Usage of water-based liquor in finishing operations	49

4R dimensions	Pollution prevention strategies (PPS)	References
	10. Alternatives of chromium salts in tanning systems such as fleshing-acrylate composite, nanoparticle dispersion (NPD), phosphonium-based tanning agents, Nanoparticle polymer (NPP), and combination tanning using vegetable tannins and aluminium sulphate	11, 13, 53
	11. Mass balance in the process and Zero Liquid Discharge (ZLD) in the tannery	Proposed in this article
Reuse	1. Usage of the same float in soaking and liming operations	37
	2. Usage of pre-deliming float in the liming and reliming operations	54, 55
	3. Usage of bating float in the pre-diming, liming, and bating operations	
	4. Usage of the tanning liquors after screening and biological/chemical treatment in the pickling and tanning operations	
	5. Usage of the recovered chrome from the tanning effluents in percentage with fresh chrome salts in tanning operation	
Recycle	1. Conversion of solid wastes (raw trimmings, fleshings, chrome shaving) into by-products (composite leather sheet, glue, gelatin, biodiesel, etc.)	56
	2. Recycling of waste liquor such as liming, pickling, and tanning liquors and reusing it in a loop system	Proposed in this article
Recover	1. Energy recovery from different solid wastes (raw trimmings, pre-fleshings, limed fleshings, buffing dust, chrome shavings, etc.)	57-59
	2. Chrome recovery by various economic methods and usage of the recovered chrome in the tanning operation	58, 60, 61
	3. Recovering protein hydrolysate from raw trimmings, buffing dust, and chrome shaving dust and usage of it in the re-chroming/fat-liquoring process as a filler/fat-liquoring agent, surface up-gradation of the leather, brick, and concrete manufacturing process, composite materials formation	45, 57, 62

Methodology

This study used a qualitative case study. The case study was chosen because it is a proper method for investigating a specific problem in any industry [32]. Case study often leads to new, creative, and in-depth insights about any problem, develop a new, novel, testable, and analytically valid theory, and present real-life situations about the subjects of interest [49]. In order to get in-depth and real-life data, the case study was selected for this particular study. In this study, a non-probability sampling technique was used to choose an expert panel of 17 members. In the expert panel, the faculty members of the Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh, Khulna University of Engineering and Technology, Bangladesh, and tannery experts of Bangladesh who have at least 5 years of working experience were targeted as the samples for finalizing the potential 4R practices at the first step. A total of 21 potential PPS were identified from a literature review. Then, the PPS were validated by the expert panel. The validated PPS are presented in Table 2, in which there are 11 practices under the reduce section, 4 for reuse, 2 for recycling, and 3 for the recover sections. Later, a survey questionnaire and an interview protocol were developed to capture the data from the expert panel about 4R practices regarding PPS in the context of the leather industry's ES. For the case study, four tanneries were purposively selected to explore the current status of adopting the identified 21 PPS. Figure 1 represents the research framework that was followed for this study.

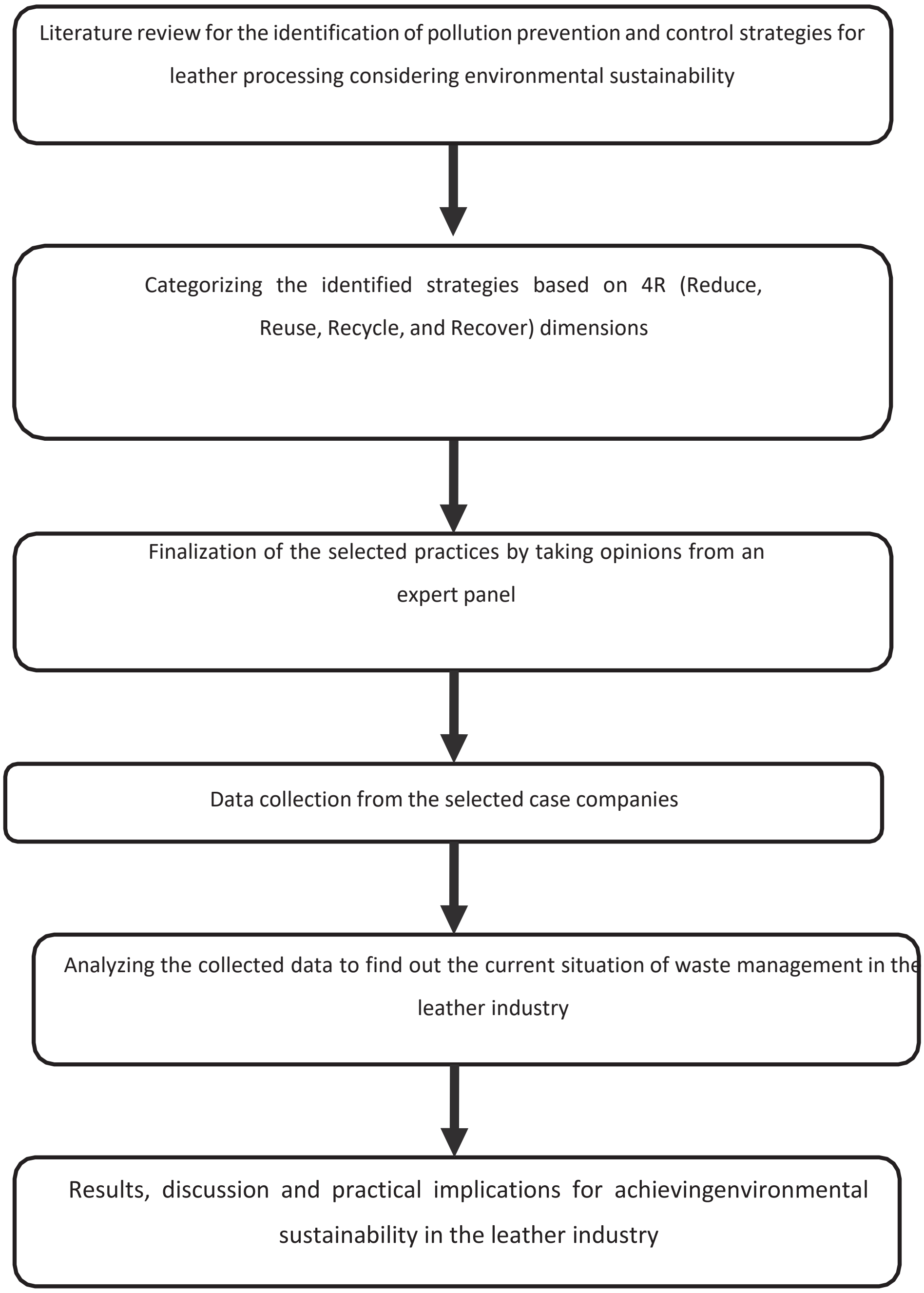

Figure 1. Research framework of this study

Case Study and Data Collection

The previous literature showed that purposive sampling has gained popularity among researchers in the case study [4]. Therefore, in this study, purposive sampling was used to select the four case tanneries in Bangladesh. The selected four leather processing companies (LPC) are referred to as LPC 1, LPC 2, LPC 3, and LPC 4 in this article. The general manager of each tannery was interviewed about their 4R practices based on the questionnaire focusing on 21 PPS as shown in Table 2, the benefits of 4R practices to the environment, and what approaches they are willing to take in the future were asked. The recorded data are presented in Table 3 and Table 4.

Table 3: The practical scenario of case companies against 4R practices for pollution prevention and control

4 R dimension	Potential practices	LPC 1	LPC 2	LPC 3	LPC 4
Reduce	1. Raw materials	Salted hides/skins	Salted hides/skins	Salted hides/skins	Salted hides/skins
	2. Preservation techniques	Salt curing	Salt curing	Salt curing	Salt curing
	3. Green fleshing utilization	No	No	No	No
	4. Practicing of short float in beam house operations	Moderate float	Moderate float	Moderate float	Yes
	5. Deliming procedure	Convention al	Conventional	Conventional	Conventiona
	6. Dehairing procedure	Convention al	Conventional	Conventional	Modern
	7. Usage of water-based liquor in the finishing process	Depending on the final finished leather requirements	Depending on the final finished leather requirements	Depending on the final finished leather requirements	Depending on the final finished leather requirement
	8. Tanning salts used in tanning operation	Basic chrome salts	Basic chrome salts	Basic chrome salts	Basic chrom salts
	9. Utilization of mass balance and zero-liquid discharge (ZLD)	No	No	No	No
	10. Any special method/techniques that reduce the generation of the wastes	No	No	No	Yes, hair separati on from liming operation.
Reuse	1. Usage of the same float in soaking and liming operation	No	No	No	No
	2. Usage of pre-deliming float in the liming and reliming operations	No	No	No	No
	3. Usage of bating float in the pre-deliming, liming, and bating operations	No	No	No	No
	4. Usage of the tanning liquors after screening and biological/chemical treatment in the pickling and tanning operations	No	No	No	No
	5. Usage of the recovered chrome from the tanning effluents in percentage with fresh chrome salts in the tanning operation	No	No	No	No
	6. Any special techniques/methods that include reusing the solid/liquid wastes	No	No	No	No

4 R dimension	Potential practices	LPC 1	LPC 2	LPC 3	LPC 4
Recycle	1. Conversion of solid wastes (raw trimmings, fleshings, chrome shaving) into by- products (composite leather sheet, glue, gelatin, biodiesel, etc.)	No	No	No	No
	2. Recycling of waste liquor such as liming, pickling, tanning liquors and reusing it in a loop system	No	No	No	No
	3. Any method/technique the company has implemented that recycle the wastes	No	No	No	Trying to implem ent
Recover	1. Energy recovery from different solid wastes (raw trimmings, pre fleshings, limed fleshings, buffing dust, chrome shavings, etc.)	No	No	No	No
	2. Chrome recovery from tanning effluents	No	No	No	Yes
	3. Recovering the protein hydrolysate from raw trimmings, buffing dust, chrome saving/tanned saving	No	No	No	No
	4. Any special method/techniques that recover value-added products from wastes	No	No	No	Yes, hair separation from liming operation

Table 4: Environmental benefits from sustainable leather processing practices

Environmental benefits from PPS	LPC 1	LPC 2	LPC 3	LPC 4
1. Reduction of the water, chemical, raw materials, and energy consumption	Agree	Agree	Agree	Agree
2. Less generation of the air pollutants emissions such as carbon products, nitrogenous products, VOC (volatile organic chemicals), particulate matters, smoke, dust, heat, etc.	Agree	Agree	Agree	Agree
3. Almost no or less generation of the hazardous pollutants such as heavy metals, COD, BOD, pH values, nitrogenous and phosphorous compounds, suspended solids, etc. in the wastewater and releasing clean water into the environment	Agree	Agree	Agree	Agree
4. Less generation of the solid wastes and usage of the solid wastes into value-added products	Agree	Agree	Agree	Agree

RESULTS AND DISCUSSION

Analysis of the Data

From the collected data, it is found that the case companies did not follow much of the 4R practices even though they agreed on the fact that adopting 4R practices result in benefitting the environment and human life. In the reduce section, 10 questions were asked to get the practical approaches for reducing the generation of waste. For raw materials, all of the selected case companies used salted hides/skins. Salt curing was used as preserving the raw hides/skins. The green fleshing from the salted hides/skins was dumped in the open areas. During beam-house operations, moderate floats were generally used. For deliming operations, ammonium sulfate and ammonium chloride were used. Mixtures of lime and sodium sulfides were used in the unhairing/dehairing operation. Depending on the customer's or buyer's requirements, water-based liquors were used in the finishing operation whereas generally solvent-based liquors were preferred. Basic chrome salts were utilized in the tanning process. In any of the processes, mass balancing and zero-liquid discharge methods were also not employed. Three of the companies do not have any special techniques for reducing the generation of waste while LPC 4 was using hair separation techniques from the liming operation. 6 questions were interrogated in the reuse section. Usage of the same float in the soaking and liming was not utilized in the case companies. Utilization of the pre-deliming float in the liming and re-liming operations, bating float in the pre-deliming, liming, and bating operations were not followed. Finally, usage of the tanning liquors after treatment in the next tanning/pickling operation and usage of the recovered chrome from tanning effluents in certain percentage with fresh chrome salts were not utilized. Currently, the selected companies are not performing any special methods/techniques for reusing waste. In the recycling criteria, 3 questions were posed. Conversion of solid wastes (raw trimming, fleshing, chrome shaving) into by-products (composite leather sheet, glue, gelatin, biodiesel, etc.) were not performed in those companies. Recycling the waste liquors i.e., liming, pickling, tanning, and reusing in the loop system was not utilized. Furthermore, case companies do not have any method involved in recycling the waste. 5 questions were asked in the recovery criteria. All four of them did not recover energy from different solid wastes (raw trimmings, pre-fleshing, limed fleshing, buffing dust, chrome shavings, etc.). Chrome from the tanning effluents and protein hydrolysate from raw trimmings, buffing dust, and chrome saving/tanned saving were not recovered as well for the 2 case companies whilst among them, LPC 4 were using chrome recovery techniques. LPC 4 company was just separating chrome from waste liquors, it was not processing this recovered chrome waste for further use in any other operations. Moreover, the three case companies did not have any special chrome recovery techniques. The general manager from LPC 1, LPC 2, LPC 3, and LPC 4 were requested to share their opinions about the benefits the leather processing company may provide to the environment through adopting those potential 4R practices. All of them agreed on the point that adopting the 4R practices in leather processing will result in less generation of air pollutants emissions such as carbon products, nitrogenous products, VOC (volatile organic compounds), particulate matter, smoke, dust, heat, etc. They also agreed that 4R practices will generate almost no or less amount of hazardous pollutants such as heavy metals, decreased chemical oxygen demand (COD), decreased biological oxygen demand (BOD), standard discharged pH values, reduced nitrogenous and phosphorous compounds, reduced suspended solids in the wastewater, and releasing nearly pure water into the environment. In addition, less generation of solid wastes and usage of the solid wastes into value-added products will be induced by 4R practices. Moreover, they agreed that 4R practices can reduce the amounts of chemicals, raw materials, energy consumption, and different wastes during leather processing.

From this case study of the leather processing companies, it is clear that the Bangladeshi leather industry is still far behind in achieving ES. Due to the inefficient CETP in the Hemayetpur area, the collected effluents from the local leather processing companies are not treated properly. Hence, the effluents that are discharged into the Dhaleshwari river from the CETP, are polluting the river with highly contaminated with chromium and other heavy metals [50] and surrounding because of the dumping of the solid wastes in the open yards. From Table 3, it is visible that the case leather processing companies are not concerned about adopting the PPS in their companies. This study finds that three of the four tanneries did not have any effluent treatment system, which is a prerequisite condition for sustainable leather processing. The main reason for that is the lack of investment in cleaner processing technologies, advanced machinery, and equipment. Though practitioners of the leather industry believe in several environmental benefits from the enlisted PPS, they are not interested in investment for change management in their organizations. They believe any further investment to ensure environmental compliance issues will increase their manufacturing costs, which may lose their competitiveness in the international market. However, from the interview with the top management of the LPC 4 case company, it is visible that if any leather company invests in ensuring environmental compliance issues, it will increase its competitiveness in the international market where the company can demand a higher price than the traditional leather processing companies. In LPC 4 company, their market shares and unit price of leather has been increased so much after the establishment their own ETP. Nowadays, international buyers of leather, leather goods, and leather footwear are sourcing leather from environmentally compliant tanneries. Therefore, practitioners of the leather industry should come forward with their own ETP and proper PPS to increase their market share.

Among the case companies, unlike LPC 1, LPC 2, and LPC 3, LPC 4 have practiced some of the PPS and thinking of implementing some other practices, which are beneficial for the company in achieving ES. For reducing water consumption and generation of toxic pollutants, LPC 4 practices short float in beam house operations. Additionally, it has modern dehairing techniques to reduce the COD and BOD values in the discharged wastewater. The company (LPC 4) has taken modern steps of separating the hair from liming effluents also, which is mitigating the generation of suspended waste from this tannery. For recycling, they are planning to implement some methods soon. As for recovery criteria, they are utilizing chrome recovery methods, which are helping the company discharge the lowest level of chromium imprint in the environment.

Usage of green hides might seem possible although in the context of Bangladesh, most of the hides/skins are collected and stored on the occasion of Eid-ul-Adha. For preservation techniques, salt curing is preferable as it is a cheap method in comparison with other preservation techniques. The usage of short float in processing operations can be practiced. Green fleshing is not utilized because of the lack of technologies and equipment. For deliming and dehairing of the hides/skins, the companies use conventional chemicals and methods. Advanced technologies, e.g., ammonium-free deliming, enzymatic dehairing, the hair-saving method in dehairing, sulfur stripping dehairing and liming operations are not performed as these practices require skilled human resources, improved machinery, and equipment, maintenance, etc. Though chrome tanning has several adversities in the environment, any other alternative tanning methods are not practiced as chrome tanning is a fast and cheap method of producing great quality leather. As per buyers' requirements, water-based liquors are occasionally used in the finishing operation. The remaining options for reduction environmental pollution load are not feasible in the industry as zero-liquid discharge and mass balancing require improved machinery, equipment, maintenance, skilled human resource, etc. From this study, it is clear that Lack of affordability, lack of awareness, and lack of willingness play a major role not to adopt newer and more efficient technologies in this industry regarding the identified 21 PPS.

In the reuse criteria, the major barrier for not adopting reuse practices is the requirements of advanced equipment and technologies. Most of the leather processing companies use traditional drums for processing operations. For reusing the waste liquors, e.g., pre-deliming, bating, tanning, and soaking, the liquors should be first stored in a container or pit and then the liquors should be conditioned for further using in the next operations. So, advanced technology will have to be introduced, which is considered a costly and troublesome process for this industry practitioners.

The first three case companies depend on the CETP for their wastewater treatment, having no practices of recycling of their own wastes. Recycling the waste liquors and using them in a loop system and converting the solid wastes for creating by-products require an individual effluent treatment plant, improved machinery, extra cost for processing and maintenance, skilled and additional human resources, which will increase the cost of manufacturing that is not preferable by the practitioners.

Updated technologies, skilled human resources, and affordability is required for recovering valuable materials from different wastes. The government's project about solid waste utilization is under development. So, there is a hope that the solid waste utilization project will improve the waste-to-wealth approach in this industry.

Environmental Benefits and Implications for Achieving Several SDGs

All of the above PPS under 4R practices will benefit the environment in many ways by ensuring a safe ecosystem, improved human life, etc. Reduction practices, i.e., usage of green hides/skins, eco-friendly preservation process instead of salt curing, ammonium-free de-liming, enzymatic dehairing, sulfur stripping in dehairing and liming operations, hair-saving dehairing method, switching to alternative eco-friendly tanning methods rather than basic chromium sulfate (BCS) tanning agent, water-based liquors in the finishing operation will generate fewer pollutants, e.g., reduced carbon products, nitrogenous and phosphorous compounds, VOC, particulate matters, heavy metals, smoke, dust, suspended solids, etc. As a result, COD, BOD, and other pollution load values of wastewater, degradation of land due to unethical landfilling, and the quantity of air pollutants emission will be reduced a great deal. The application of zero liquid discharge (ZLD), mass balancing will decrease the pollutants load in the air, water, and soil. These practices will preserve water quality for aquatic lives and people and air quality for people and animals, which will help in achieving SDG Goal 6: Ensuring clean water and sanitation, SDG Goal 14: Life below water, SDG Goal 11: Sustainable cities and communities.

Furthermore, practicing short float in leather processing operations will reduce water and chemical consumption. Reusing the same liquors several times in an operation, the chemical and water consumption will be reduced. In addition, recovered products can be completely or partially substituted with various chemicals, i.e., usage of recovered chrome in the tanning operation with fresh chrome salts, usage of recovered protein hydrolysates in the re-chroming/fat-liquoring operations as a filler/fat-liquoring agent. In this way, chemical and water consumption will be reduced. Recycling the waste liquors from different stages of leather processing, e.g., liming, pickling, tanning, etc. by different chemical or biological treatments and reusing them in the loop system will reduce water and chemical consumption. Recycling operations will reduce water consumption and lessen the effects of pollutants by releasing nearly pure water into the environment. Conversion of the different solid wastes into by-products will reduce chemical and energy consumption. Thereby, the industry can assist in achieving SDG Goal 12: Responsible consumption and production. Usage of green fleshing will reduce the solid waste's load and biofuel can be generated from these wastes, which can another source of energy in the leather industry. Thus, this biofuel production from leather solid wastes can aid in achieving SDG Goal 7: Affordable and clean energy.

Glue, gelatin, and composite sheets can also be generated from different wastes of the leather industry. Recovering chrome and protein will reduce the quantity of waste produced. Moreover, these recovered products can be reused in different operations in the same industry reducing the total cost of materials consumed, and can be utilized in other industries to generate profits for the leather industry. In this way, there will be less generation of solid wastes from the leather processing industry, which will create a decent environment for employees' well-being. Alternatively, the conversion of leather solid wastes into value-added products can increase the yearly revenue for the leather industry. Thus, the industry can attain SDG Goal 3: Good health and well-being, and SDG Goal 8: Decent work and economic growth.

The current CETP plant of the Savar Industrial Estate is not functioning properly. As a result, it has become very tough for the leather industry practitioners to ensure environmental compliance issues. Moreover, the practitioners are indifferent to adopting innovative technologies to update the traditional tanning system. Therefore, developing the required infrastructure for the current CETP system as well as the development of individual ETP for every tannery is very urgent for this industry, which will help the leather industry to achieve SDG Goal 9: Industry, innovation, and infrastructure. Being one of the most polluting industries in the world, the leather industry is highly responsible for global warming and for any other climatic change. Proper implementation of the enlisted 21 PPS in this study can mitigate the climate change caused by the leather industry, which will help in achieving SDG Goal 13: Climate action 13.

In order to ensure technology-transfer and knowledge sharing, the leather industry of Bangladesh should work with numerous international organizations and nations, which will allow for the establishment of cleaner processing techniques as well as cutting-edge machinery and equipment for leather processing in a more sustainable way. By bolstering the international partnership as stated in SDG Goal 17: Partnerships for the goals, the leather industry will be able to ensure ES in its product cycle.

Conclusions and Future Scope for Research

This study identified the most relevant and potentially feasible set of 4R practices by a literature review and industry experts' opinions for ensuring ES in the leather industry. This study will certainly guide the practitioners of the leather industry to adopt the identified 21 PPS under reduce, reuse, recycle and recover dimensions with a clear understanding of how these practices can bring several environmental benefits for achieving ES. The findings of this research show that the case leather processing companies did not practice most of the PPS in their operations due to unwillingness in investment for advanced technologies and advanced machinery and equipment. The three case companies did not have any ETP for waste reduction whereas one company had its own ETP that was reducing its environmental impact. The yearly revenue of the LPC 4 companies showed that adopting some sustainable practices can not only bring environmental benefits but also, they can increase any company's economic growth. This study also guides how sustainable practices can help in achieving several SDGs in the leather industry. This study has some limitations that can act as scopes for any future research. The study was limited as the focus of the study was based on the case study of only four leather processing companies. Hence, in the future, more leather processing companies can be taken into account in other case study to compare the 4R practices and to analyze the performance gaps of those companies in the context of ES. Quantitative data could be included for conducting a cost-benefit analysis for estimating the strengths and weaknesses of environmentally sustainable 4R practices to obtain the best approach for achieving ES in the leather industry.

Conflicts of Interest

The authors declare no conflict of interest.

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REFERENCES

1. Ricky, R., Shanthakumar, S., Ganapathy, G.P., Chiampo, F., Zero Liquid Discharge System for the Tannery Industry—An Overview of Sustainable Approaches, *Recycling*, **2022**, 7, 3, 31, https://doi.org/10.3390/recycling7030031.
2. Asian Development Bank, Developing the Leather Industry in Bangladesh, ADB Briefs NO. 102, **2018**, 102, 1–8, https://dx.doi.org/10.22617/BRF189645-2.
3. Omoloso, O., Mortimer, K., Wise, W.R., Jraisat, L., Sustainability Research in the Leather Industry: A Critical Review of Progress and Opportunities for Future Research, *J Clean Prod*, **2021**, 285, 125441, https://doi.org/10.1016/j.jclepro.2020.125441.
4. Sarker, M.R., Ali, S.M., Paul, S.K., Munim, Z.H., Measuring Sustainability Performance Using An Integrated Model, *Meas: J Int Meas Confed*, **2021**, 184, 109931, https://doi.org/10.1016/j.measurement.2021.109931.
5. Marrucci, L., Corcelli, F., Daddi, T., Iraldo, F., Using a Life Cycle Assessment to Identify the Risk of "Circular Washing" in the Leather Industry, *Resour Conserv Recycl*, **2022**, 185, 106466, https://doi.org/10.1016/J.RESCONREC.2022.106466.
6. Huang, Y., Xiao, H., Pu, H., Xue, N., Hao, B., Huang, X., Shi, B., Self-Driven Directional Dehydration Enabled Eco-Friendly Manufacture of Chrome-Free Leather, *J Leather Sci Eng*, **2022**, 4, 1, 1–12. https://doi.org/10.1186/S42825-022-00089-0.
7. Karuppiah, K., Sankaranarayanan, B., Ali, S.M., Jabbour, C.J.C., Bhalaji, R.K.A, Inhibitors to Circular Economy Practices in the Leather Industry Using an Integrated Approach: Implications for Sustainable Development Goals in Emerging Economies, *Sustain Prod Consum*, **2021**, 27, 1554-1568, https://doi.org/10.1016/J.SPC.2021.03.015.
8. China, C.R., Maguta, M.M., Nyandoro, S.S., Hilonga, A., Kanth, S.V., Njau, K.N., Alternative Tanning Technologies and Their Suitability in Curbing Environmental Pollution from the Leather Industry: A Comprehensive Review, *Chemosphere*, **2020**, 254, 126804, https://doi.org/10.1016/j.chemosphere.2020.126804.
9. Islam, M.H., Sarker, M.R., Hossain, M.I., Ali, K., Noor, K.M.A., Towards Sustainable Supply Chain Management (SSCM): A Case of Leather Industry, *J Oper Strateg Plan*, **2020**, 3, 1, 81–98, https://doi.org/10.1177/2516600X20924313.
10. Moktadir, M.A., Ahmadi, H.B., Sultana, R., Zohra, F.T., Liou, J.J.H., Rezaei, J., Circular Economy Practices in the Leather Industry: A Practical Step Towards Sustainable Development, *J Clean Prod*, **2020**, 251, 119737, https://doi.org/10.1016/J.JCLEPRO.2019.119737.
11. Kanagaraj, J., Senthilvelan, T., Panda, R.C., Kavitha, S., Eco-Friendly Waste Management Strategies for Greener Environment Towards Sustainable Development in Leather Industry: A Comprehensive Review, *J Clean Prod*, **2015**, 89, 1–17, https://doi.org/10.1016/j.jclepro.2014.11.013.
12. Dixit, S., Yadav, A., Dwivedi, P.D., Das, M., Toxic Hazards of Leather Industry and Technologies to Combat Threat: A Review, *J Clean Prod*, **2015**, 87, 39–49, https://doi.org/10.1016/j.jclepro.2014.10.017.
13. Gupta, S., Gupta, S., Dhamija, P., Bag, S., Sustainability Strategies in the Indian Leather Industry: An Empirical Analysis, *Benchmarking*, **2018**, 25, 3, 797–814, https://doi.org/10.1108/BIJ-06-2017-0140.
14. Paul, H.L., Antunes, A.P.M., Covington, A.D., Evans, P., Philips, P.S., Bangladeshi Leather Industry: An Overview of Recent Sustainable Developments, *J Soc Leather Technol Chem*, **2013**, 97, 1, 25–32.
15. Halder, S., Export of Leather Goods Hits Decade High, *The Daily Star*, 07 July, **2022**, https://www.thedailystar.net/business/economy/news/export-leather-goods-hits-decade-high-3065886.

16. The Asia Foundation, **2020**, https://asiafoundation.org/category/in-asia/page/16/
17. Gosh, P.K., Hossain, M.D., Assessment of Tannery Effluent: A Case Study of Dhaleshwari River in Bangladesh, Proceeding of International Conference on Planning, Architechture and Civil Engineering (ICPAC 2019), 07-09 February, **2019**, Rajshahi, Bangladesh, 461–464.
18. Hasan, R., CETP At Savar Tannery Industrial Estate: Colossal Failure, Misuse of Public Funds, *The Daily Star*, 08 March, **2022**, https://www.thedailystar.net/news/bangladesh/news/cetp-savar-tannery-industrial-estate-colossal-failure-misuse-public-funds-2977956.
19. Hasan, M.M., Ahmed, M.S., Adnan, R., Shafiquzzaman, M., Water Quality Indices to Assess the Spatiotemporal Variations of Dhaleshwari River in Central Bangladesh, *Environ Sustain Indic*, **2020**, 8, 100068, https://doi.org/10.1016/J.INDIC.2020.100068.
20. Islam, M.A.S., Hossain, M.E., Majed, N., Assessment of Physicochemical Properties and Comparative Pollution Status of the Dhaleshwari River in Bangladesh, *Earth*, **2021**, 2, 4, 696-714, https://doi.org/10.3390/earth2040041.
21. Masum, S.A., Islam, M.S., A Case Study on Predicting the Environmental Impacts of Untreated Effluent Generated from Tannery Industrial Estate in Dhaka, Bangladesh, *Geo Environ Sustain*, **2020**, 13, 3, 22–31, https://doi.org/10.24057/2071-9388-2019-127.
22. Elkington, J., Partnerships from Cannibals with Forks: The Triple Bottom Line of 21st-Century Business, *Environ Qual Manag*, **1998**, 8, 1, 37–51, https://doi.org/10.1002/tqem.3310080106.
23. Sutton, P., A Perspective on Environmental Sustainability?, Victorian Commissioner for Environmental Sustainability, **2004**, 1-32, http://www.green-innovations.asn.au/.
24. Bob, U., Padayachee, A., Gordon, M., Moutlana, I., Enhancing Innovation and Technological Capabilities in the Management of E-Waste: Case Study of South African Government Sector, *Sci Technol Soc*, **2017**, 22, 2, 332–349, https://doi.org/10.1177/0971721817702293.
25. Morera, J.M., Bartolí, E., Chico, R., Solé, C., Cabeza, L.F., Minimization of the Environmental Impact of Chrome Tanning: A New Process Reusing the Tanning Floats, *J Clean Prod*, **2011**, 19, 17–18, 2128–2132. https://doi.org/10.1016/j.jclepro.2011.07.018.
26. Dutta, N., Narayanan, K., Impact of Environmental Regulation on Technical Efficiency, *Sci Technol Soc*, **2011**, 16, 3, 333–350, https://doi.org/10.1177/097172181101600305.
27. Omoloso, O., Wise, W.R., Mortimer, K., Jraisat, L., Corporate Sustainability Disclosure: A Leather Industry Perspective, *Emerg Sci J*, **2020**, 4, 1, 44–51, https://doi.org/10.28991/esj-2020-01209.
28. Severo, E.A., De Guimarães, J.C.F., Dorion, E.C.H., Nodari, C.H., Cleaner Production, Environmental Sustainability and Organizational Performance: An Empirical Study in The Brazilian Metal-Mechanic Industry, *J Clean Prod*, **2015**, 96, 118–125, https://doi.org/10.1016/j.jclepro.2014.06.027.
29. Tiwari, V., Thakur, S., Environment Sustainability Through Sustainability Innovations, *Environ Dev Sustain*, **2020**, 23, 5, 6941–6965, https://doi.org/10.1007/S10668-020-00899-4.
30. Chin, T.A., Tat, H.H., Sulaiman, Z., Green Supply Chain Management, Environmental Collaboration and Sustainability Performance, *Procedia CIRP*, **2015**, 26, 695–699, https://doi.org/10.1016/j.procir.2014.07.035.
31. de Sousa Jabbour, A.B.L., Frascareli, F.C.D.O., Jabbour, C.J.C., Green Supply Chain Management and Firms' Performance: Understanding Potential Relationships and The Role of Green Sourcing and Some Other Green Practices, *Resour Conserv Recycl*, **2015**, 104, 366–374, https://doi.org/10.1016/j.resconrec.2015.07.017.

32. Gupta, S.K., Gupta, S., Gayathiri, S., "Pollution Prevention" Is the Key to Drive Sustainability: Preliminary Findings from a Tannery Unit in India, *Manag Environ Qual*, **2018**, 29, 3, 416–426, https://doi.org/10.1108/MEQ-10-2017-0124.
33. Ahmad, S., Wong, K.Y., Rajoo, S., Sustainability Indicators for Manufacturing Sectors: A Literature Survey and Maturity Analysis from The Triple-Bottom-Line Perspective, *J Manuf Technol Manag*, **2019**, 30, 2, 312–334, https://doi.org/10.1108/JMTM-03-2018-0091.
34. da Cunha e Silva, D.C., de Oliveira, R.A., Simonetti, V.C., Toniolo, B.P., Sales, J.C.A., Lourenço, R.W., Creation of an Environmental Sustainability Index for Water Resources Applied to Watersheds, *Environ Dev Sustain*, **2022**, 1–21, https://doi.org/10.1007/S10668-022-02527-9.
35. Elleuch, B., Bouhamed, F., Elloussaief, M., Jaghbir, M., Environmental Sustainability and Pollution Prevention, *Environ Sci Pollut Res*, **2018**, 25, 19, 18223–18225, https://doi.org/10.1007/s11356-017-0619-5.
36. Petraru, M., Gavrilescu, M., Pollution Prevention, A Key to Economic and Environmental Sustainability, *Environ Eng Manag J*, **2010**, 9, 4, 597–614, https://doi.org/10.30638/eemj.2010.083.
37. Hu, J., Xiao, Z., Zhou, R., Deng, W., Wang, M., Ma, S., Ecological Utilization of Leather Tannery Waste with Circular Economy Model, *J Clean Prod*, **2011**, 19, 2–3, 221–228, https://doi.org/10.1016/j.jclepro.2010.09.018.
38. Kanagaraj, J.K., Panda, R.C., Vinodh Kumar, M., Trends and Advancements in Sustainable Leather Processing: Future Directions and Challenges—A Review, *J Environ Chem Eng*, **2020**, 8, 5, 104379, https://doi.org/10.1016/J.JECE.2020.104379.
39. Chojnacka, K., Skrzypczak, D., Mikula, K., Witek-Krowiak, A., Izydorczyk, G., Kuligowski, K., Bandrów, P., Kułażyński, M., Progress in Sustainable Technologies of Leather Wastes Valorization as Solutions for The Circular Economy, *J Clean Prod*, **2021**, 313, 127902, https://doi.org/10.1016/J.JCLEPRO.2021.127902.
40. Al-jabari, M., Sawalha, H., Pugazhendhi, A., Rene, E.R., Cleaner Production and Resource Recovery Opportunities in Leather Tanneries: Technological Applications and Perspectives, *Bioresour Technol Rep*, **2021**, 16, 100815, https://doi.org/10.1016/j.biteb.2021.100815.
41. Lazaroiu, G., Pană, C., Mihaescu, L., Cernat, A., Negurescu, N., Mocanu, R., Negreanu, G., Solutions for Energy Recovery of Animal Waste from Leather Industry, *Energy Convers Manag*, **2017**, 149, 1085–1095, https://doi.org/10.1016/J.ENCONMAN.2017.06.042.
42. Teklay, A., Gebeyehu, G., Getachew, T., Yaynshet, T., Sastry, T.P., Conversion of Finished Leather Waste Incorporated with Plant Fibers into Value Added Consumer Products – An Effort to Minimize Solid Waste in Ethiopia, *Waste Manag*, **2017**, 68, 45–55, https://doi.org/10.1016/J.WASMAN.2017.07.024.
43. Zeng, S., Huang, Z.X., Jiang, H., Li, Y., From Waste to Wealth: A Lightweight and Flexible Leather Solid Waste/Polyvinyl Alcohol/Silver Paper for Highly Efficient Electromagnetic Interference Shielding, *ACS Appl Mater Interfaces*, **2020**, 12, 46, 52038–52049, https://doi.org/10.1021/acsami.0c16169.
44. Członka, S., Bertino, M.F., Strzelec, K., Strąkowska, A., Masłowski, M., Rigid Polyurethane Foams Reinforced with Solid Waste Generated in Leather Industry, *Polym Test*, **2018**, 69, 225–237, https://doi.org/10.1016/J.POLYMERTESTING.2018.05.013.
45. Hashem, M.A., Nur-A-Tomal, M.S., Tannery Solid Waste Valorization Through Composite Fabrication: A Waste-To-Wealth Approach, *Environ Prog Sustain Energy*, **2018**, 375, 1722–1726, https://doi.org/10.1002/EP.12860.
46. Liu, B., Li, Y., Wang, Q., Bai, S., Green Fabrication of Leather Solid

Waste/Thermoplastic Polyurethanes Composite: Physically De-Bundling Effect of Solid-State Shear Milling on Collagen Bundles, *Compos Sci Technol*, **2019**, 181, 107674, https://doi.org/10.1016/j.compscitech.2019.06.001.

47. Yorgancioglu, A., Onem, E., Basaran, B., Preparation, Characterization and Application of Lubricating Protein Filler for Sustainable Leather Production, *J Nat Fibres*, **2020**, 18, 11, 1946-1956, https://doi.org/10.1080/15440478.2020.1751374.
48. Parisi, M., Nanni, A., Colonna, M., Recycling of Chrome-Tanned Leather and Its Utilization as Polymeric Materials and in Polymer-Based Composites: A Review, *Polymers*, **2021**, 13, 3, 1–23, https://doi.org/10.3390/polym13030429.
49. Hoque, A., Clarke, A., Greening of Industries in Bangladesh: Pollution Prevention Practices, *J Clean Prod*, **2013**, 51, 47–56, https://doi.org/10.1016/j.jclepro.2012.09.008.
50. Ariram, N., Sathish, M., Madhan, B., Chemical/Water-Free Deliming Process Using Supercritical Carbon Dioxide: A Step Toward Greener Leather Manufacture, *ACS Sustain Chem Eng*, **2020**, 8, 31, 11747–11754, https://doi.org/10.1021/ACSSUSCHEMENG.0C03867.
51. Andrioli, E., Petry, L., Gutterres, M., Environmentally Friendly Hide Unhairing: Enzymatic-Oxidative Unhairing as an Alternative to Use of Lime and Sodium Sulfide, *Process Saf Environ Prot*, **2015**, 93, 9–17, https://doi.org/10.1016/J.PSEP.2014.06.001.
52. Valeika, V., Širvaitytė, J., Bridžiuvienė, D., Švedienė, J., An application of Advanced Hair-Save Processes in Leather Industry as The Reason of Formation of Keratinous Waste: Few Peculiarities of Its Utilization, *Environ Sci Pollut Res*, **2019**, 26, 6, 6223–6233, https://doi.org/10.1007/S11356-019-04142-0.
53. Maguta, M.M., Nyandoro, S.S., Hilonga, A., Kanth, S.V., Njau, K.N., Alternative Tanning Technologies and Their Suitability in Curbing Environmental Pollution from The Leather Industry: A Comprehensive Review, *Chemosphere*, **2020**, 254, 126804, https://doi.org/10.1016/j.chemosphere.2020.126804.
54. Khan, K., Khan, I.H., Khan, I.I., Mahmud, A., Hossain, D., Recovery and Reuse of Chromium from Spent Chrome Tanning Liquor by Precipitation Process, *Am J Eng Res (AJER)*, **2018**, 7, 1, 346–352.
55. Selvakumar, A.M., Vimudha, M., Lawrance, I., Sundaramoorthy, S., Ramanaiah, B., Saravanan, P., Recovery and Reuse of Spent Chrome Tanning Effluent from Tannery Using Electro-Oxidation Technique, *Desalination Water Treat*, **2019**, 156, 323–330, https://doi.org/10.5004/dwt.2019.23825.
56. Kale, R.D., Jadhav, N.C., Utilization of Waste Leather for The Fabrication of Composites and to Study Its Mechanical and Thermal Properties, *SN Appl Sci*, **2019**, 1, 1231, 1-9, https://doi.org/10.1007/s42452-019-1230-9.
57. Jadhav, N.C., Jadhav, A.C., Waste and 3R's in Footwear and Leather Sectors, *Leather and Footwear Sustainability*, Springer Singapore, **2020**, https://doi.org/10.1007/978-981-15-6296-9_10.
58. Kokkinos, E., Proskynitopoulou, V., Zouboulis, A., Chromium and Energy Recovery from Tannery Wastewater Treatment Waste: Investigation of Major Mechanisms in the Framework of Circular Economy, *J Environ Chem Eng*, **2019**, 7, 5, 103307, https://doi.org/10.1016/J.JECE.2019.103307.
59. Vidaurre-Arbizu, M., Pérez-Bou, S., Zuazua-Ros, A., Martín-Gómez, C., From the Leather Industry to Building Sector: Exploration of Potential Applications of Discarded Solid Wastes, *J Clean Prod*, **2021**, 291, 125960. https://doi.org/10.1016/J.JCLEPRO.2021.125960.
60. Mohammed, K., Sahu, O., Recovery of Chromium from Tannery Industry Waste Water by Membrane Separation Technology: Health and Engineering Aspects, *Sci Afr*, **2019**, 4, 96,

https://doi.org/10.1016/j.sciaf.2019.e00096.

61. Shukla, A., Mahmood, Z., Singh, L.K., Studies on Recovery of Heavy Metals from Tannery Wastewater, *Int J Eng Sci Technol*, **2021**, 13, 1, 76–80, https://doi.org/10.4314/ijest.v13i1.11S.
62. Ammasi, R., Victor, J.S., Chellan, R., Chellappa, M., Amino Acid Enriched Proteinous Wastes: Recovery and Reuse in Leather Making, *Waste Biomass Valorization*, **2019**, 11, 11, 5793–5807, https://doi.org/10.1007/S12649-019-00912-6.

EUROPEAN RESEARCH AREA

Press Release from the IULTCS

7th July 2023

XXXVII IULTCS Congress 2023 Heidemann Lecture Presenter Announcement

The XXXVII IULTCS Congress Organizing Committee is extremely pleased to announce that Professor Yujia Xu will be the Heidemann Lecture Presenter at the XXXVII IULTCS Congress that will be held from 17th to 20th October 2023 in Chengdu, China.

The Heidemann Lecture is a keynote presentation that is held in memory of Professor Dr. Eckhardt Heidemann (1925-1999). Heidemann made significant practical contributions to the science of leather manufacture and he held a lifelong interest in the structure and properties of the collagen molecule. It is typical for the Host Society to invite a high-profile guest lecturer to make this keynote presentation of 30 – 45 minutes, as the opening lecture of the Scientific Program.

Professor Yujia Xu received her doctorate degree in Biophysics from the University of Connecticut, and conducted her postdoctoral research in the field of protein folding in the School of Medicine at the University of Pennsylvania. She started her collagen related research as a research associate with Prof. Barbara Brodsky and Prof. Jean Baum in the University of Medicine and Dentistry of New Jersey, and Rutgers university. She is currently an Associate professor in the Department of Chemistry at Hunter college of the City University of New York.

Prof. Xu’s main research interest has been the molecular mechanisms of the biological functions of collagen. Using protein design and recombinant technology her lab pioneered the strategy to develop triple helical peptides that can further self-assemble into collagen-like fibrils using modular amino acid sequences. These fibril-forming collagen mimetic peptides (FCMPs) are effective molecular tools for collagen research including the investigation of molecular interactions that stabilize collagen fibrils, which is among one of the fundamental research projects pioneered by Prof. Heidemann several decades ago. The FCMPs are also being used to develop novel biomaterials for biomedical applications.

The organizing committee are delighted that Professor Yujia has accepted the invitation to present the 2023 Heidemann Lecture.

Press Release from the International Council of Hides Skins & Leather Traders Associations

8th September 2023

ICHSLTA Meets at ACLE Shanghai; Elects Officers

The International Council of Hides, Skins, and Leather Traders Association (ICHSLTA) held its 94th Annual General Meeting at the ACLE fair in Shanghai on August 29th. At the meeting, ICHSLTA members reviewed a number of issues related to the trade of hides and skins globally, and more particularly the misuse of the word leather to describe non animal sourced material.

The Council also held its election for officer positions. The Council re-elected Toni Baltes from German Wirtschaftsverband Häute/Leder e.V. as their President as well as Dennis King from Australian Hides Skins and Leather Exporters Association and Nick Winters from French Hides Association as their Vice Presidents. Lénaïg Manéat of the French Hides Association – Federation Française des Cuirs et Peaux in France continues managing the organisation.

Toni Baltes is also the current President of the German Hides Association and Managing Director of A+B HIDES GmbH & Co. KG.

He began working in the raw hide trade with an apprenticeship in his parents' business. After that he completed further training at both national and international raw hide processing facilities and leather factories. He has gained more than 40 years of experience in the trade.

Toni Baltes:

"It was a pleasure to be able to hold our AGM in Shanghai and shake hands with our friends and colleagues from around the world. Our industry has changed in the aftermaths of the pandemic and the final consumers' expectations, often driven by "so-called" more ethical, sustainable consumption choices. One of our objectives over the next couple of years will be to restore the good reputation of leather, that it deserves. Leather is among the most natural, sustainable and beautiful materials available to manufacturers of all kinds of products. As President of ICHSLTA I look forward to working towards our common goal and would like to thank my colleagues for their renewed trust."

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