

Economic efficiency of leather treated with zeolite after the pickling process

Ekonomska učinkovitost kože obrađene zeolitom nakon procesa pikljanja

Scientific paper / Znanstveni rad

Franka Žuvela Bošnjak^{1*}, Sandra Flinčec Grgac², Kristina Maršić¹

¹University of Zagreb, Faculty of Textile Technology, Study in Varaždin, Hallerova aleja 6, 42000 Varaždin, Croatia

²University of Zagreb, Faculty of Textile Technology, Department of Textile Chemistry and Ecology, Prilaz baruna Filipovića 28a, 10000 Zagreb, Croatia

*Correspondence: franka.zuvela.bosnjak@tff.unizg.hr

Abstract

Raw bovine leather (hide) undergoes a series of manufacturing processes to obtain a finished leather or semi-finished leather, which as such can last for a long period without damage to the hide. The damage by bacteria in the tannery is almost entirely restricted to the soaking operation, but some damages occur under poor storage conditions after pickling and in a wet stage after tanning. Protection against microorganisms is still needed because long periods of storage in moisture and heat create conditions suitable for the rapid growth of microorganisms, which can cause considerable hide damage. The development of microorganisms causes damage that affects the final quality and usability of the leather. In order to avoid damage, the hide undergoes a process of washing and removing microorganisms, before the tanning process. This paper studies and compares the costs of protection from microorganisms of hide treated with bath containing zeolite and citric acid, after the process of pickling, in relation to the costs of removing microorganisms that occur due to poor storage conditions. The costs are one of the elements for determining economic efficiency. This comparison provides an insight into the costs of these processes and their cost-profitability.

Keywords: economic efficiency; costs; hide; leather; zeolite; microorganisms.

Sažetak

Sirova goveđa koža prolazi kroz niz proizvodnih procesa da bi se dobila gotova ili polugotova koža koja, kao takva, može trajati dugi period bez pojave oštećenja na koži. Oštećenje sirove kože bakterijama je gotovo u potpunosti ograničeno na proces namakanja, ali neka oštećenja nastaju zbog loših uvjeta skladištenja nakon procesa pikljanja i u mokroj fazi nakon štavljenja. Zaštita od mikroorganizama je i dalje potrebna jer dugi period skladištenja u vlažnim uvjetima i toplom prostoru stvara uvjete povoljne za rast i razvoj mikroorganizama, što može uzrokovati znatna oštećenja. Razvoj mikroorganizama uzorkuje oštećenja koja utječu na konačnu kvalitetu i upotrebljivost gotove kože. Da bi se oštećenja izbjegla koža prolazi kroz proces pranja i eliminiranja mikroorganizama prije nego se podvrgne procesu štavljenja. U ovom radu proučavaju se i uspoređuju troškovi zaštite kože od mikroorganizama koja je obrađena otopinom zeolita i limunske kiseline, nakon procesa pikljanja, u odnosu na troškove obrade uklanjanja mikroorganizama koji nastaju zbog loših uvjeta skladištenja. Troškovi su jedan od elemenata za određivanje ekonomske učinkovitosti. Ova usporedba daje uvid u troškove navedenih procesa i njihovu isplativost.

Ključne riječi: ekonomska učinkovitost; troškovi; koža, zeoliti; mikroorganizmi.

1. Introduction

When leathers (wet blue, wet white, vegetable tanned, or crust) is held on store for a period of time in wet condition it is necessary and important to add fungicide during any steps in the leather making process. Otherwise, the development of bacteria and mould occurs, and thus the collagen fibre is damaged. Leather contains adequate nutrition and industry environmental conditions are typically favourable for fungal growth [1]. In addition to high humidity, hides are rich in fats, proteins and carbohydrates, which significantly favour the growth of microorganisms, especially bacteria and fungi. These microorganisms produce enzymes that can break down macromolecules into smaller units that can be absorbed through cell membranes and used as nutrients and energy. They can infect the leather from the slaughter stage through the leather production processes [2-5]. Fungi can attack salted hides, pickled hides, vegetable tanned leather, chrome tanned leather and finished leathers. Semiprocessed leathers like wet blue and

wet white are extremely sensitive to fungal attack due to their high water content and acidity.

Fungal growth on salted hides may cause severe damage such as looseness or loss of grain layer, weak fibre, weak grain, pitted grain and stains on leather that has gone through the process of pickling or tanning, the development of fungi causes uneven colouring. There are different shades of the same colour on one piece of leather that are visible to the naked eye. Such leather must be subjected to additional dyeing in order to correct errors. The addition of fats to the structure of the leather affected by fungi leads to non-uniform absorption, which is also manifested in the form of spots on the leather [2,6-7]. Damages on leather surface can cause significant direct and indirect costs such as staining, non-uniformity in further processing, grain damage, changes in physical parameters, organizational costs related to re-work, and customer complaints. The impact on workers' health should not be ignored, as well as the costs that problems of this type entail. High

levels of fungal spores can cause allergic reactions. Some types of fungi present in leather production under certain conditions produce microtoxins, which can cause severe and long-term consequences [1,6].

In recent years, the application of zeolite in leather production has been studied. Sun, Xiao Dan et. al. used modified nano NaY zeolite as pretanning agent additive in leather industry for the first time in order to decrease the chromium content in leather waste liquor and enhance the mechanical properties of leather [8].

Ciambelli, P et.al. investigated synthetic Na-zeolites (NaA, NaX, NaAX) as tanning agents in leather production from sheepskin and calfskin pelts [9]. Esquerra-Resa, Salvadoret. al. investigated new biodegradable tanning process based on zeolites in two steps was studied. A procedure for tanning sheep and beef hides was developed. Three types of retanning processes were studied [10]. Gurler Karaman, D. et.al. implemented various tanning combinations among alkali aluminosilicates to specify whether alkali aluminium silicates have tanning effect or not, and which combination provides the most appropriate results as for tanning quality [11].

To ensure the quality of the final product the correct use of antimicrobial agent is necessary for the conservation of hides and leather. Commercial agents that prevent the development of bacteria and fungi are an additional burden on wastewater.

Modern business success is linked to the basic economic principle of rationalization, which expresses the effort to achieve maximum benefits for the company with the available resources (factors, production factors) and means of work. In order for the company to be able to comply with the principle of rationalization in its operations, it must achieve the greatest possible "benefit" with as less investment as possible [12]. Economy, as a basic measure of business efficiency, expresses the cumulative relationship of all created effects and consumed elements in the work process over a certain period of time [13].

Every economic activity causes certain expenses it creates some kind of costs. The business result, as the outcome of the operation of a business entity, always ends with a business profit or business loss. Profit and loss are quantities measured by the amount of realized income and the amount of expenses. Revenues are the economic benefits of business, and costs can be defined as the monetary amount of funds used to achieve a certain goal.

This work follows the size of costs in leather processing; their basic division is also explained. Costs can be divided according to the function and according to the deadline. Costs according to the function they perform in business and in company can be divided on costs of production, sales, procurement, marketing, administration and other costs. Costs according to maturity can be divided on: short-term, medium-term and long-term costs. All mentioned costs can be divided according to the criterion of business dynamics into: a) fixed costs and b) variable costs.

The dynamics of business depends on the economic branch to which the company belongs. Fixed costs are costs that do not change with changes in the volume of production capacity, while variable costs clearly depend on the amount of production [14,15].

In a manufacturing company whose main activity is related to the process of leather production (tanning and processing), the division according to dynamics would include fixed costs such as the wages of workers, depreciation costs, rents, licenses and other contracted fixed allowances. Variable costs include costs such as raw materials and resources used in the production process, various overhead costs (water, gas, fuel) and the costs of semi-finished products and finished products, as well as the variable part of salaries.

The result obtained from the aforementioned analysis represents the degree of economy. The principle of economy is based on the economy of all resources that go into production and requires the maximum result.

Since costs are one variable for calculating the efficiency coefficient ($E = \text{revenues/costs}$) this paper studies and compares the size of costs

of protection from microorganisms of pickled hides treated with zeolite (an eco-friendly agent) after the process of pickling in relation to the costs of removing microorganisms that occur due to poor storage conditions. With the aim of using zeolites as an eco-friendly agent and comparing the costs of zeolite treatment with the costs of regular mould and fungus removal from regular production.

2. Experimental part

2.1. Materials and methods

In order to obtain usable leather for various products, animal hides are processed in several stages; pretanning (liming, bating and pickling), tanning and post tanning and finishing. The preparatory operations of soaking, liming, delimiting and pickling were carried out under industrial conditions according to the standard procedure.

Process of soaking, liming, delimiting and pickling was carried out in conventional industrial conditions. Treatment with Bath I was performed in a laboratory device Mathis. The amount of agents is dosed according to the weight of water. The sample is washed in a water ratio of 50% by weight of pickled hides. In bath 1 was added: Citric acid (Sigma Aldrich, St. Louies, USA), 70 gdm-3; Zeolite 5A 65 gdm-3 and wetting agent Felosan RG-N (CHT, Swicerland) 1 gdm-3. The sample was treated in Bath 1 for 3 hours at a temperature of 30°C. After processing, the sample was tested for *Staphylococcus aureus* (S.aure.), *Escherichia coli* (E.coli) and *Candida albicans* (C.abic). Tests were performed according to EN ISO 20645:2018 Textile fabric – Determination of antibacterial activity – Agar diffusion plate test. The results show that the pickled hides treated with bath 1 has some resistance to the mentioned microorganisms. The processing recipe was used for profitability calculations as stated in the paper. Processing effect is not the subject of this paper.

Pickled hides that gets damage in the form of mold and fungus as a result of being stored on the grain side undergoes a washing process before further processing (tanning). The hide is washed in water ratio of 200% by weight of hides. In bath is added surfactant 0,15 % Borron SAF (TFL, Germany) at 30°C for 60 minutes. After the drain, clean water is poured in, 0,15% Formic acid (Ivero, Croatia) and 0,15 % fungicide Busan 1401 WB (Buckman, Belgium) are added.

Costs are very important for controlling the efficiency of conducting business activities in the company, and for evaluating past, present and future activities at all levels in the business organization.

This is precisely why we start from cost analysis as a measure to determine the efficiency of certain leather processes before placing it on the market. Calculation is a computational procedure for calculating costs or cost price [16].

The main goals of creating calculations are related to determining prices (selling prices and cost prices), controlling operations and results, and determining the company's business policy [12]. This paper work is related to the first objective of the calculation, i.e. the calculation of the cost price of the leather processing after pickling.

The cost of pickled hides treatment with Bath I was compared to the cost of washing the hides after the appearance of mold and stains on the hides due to storage [17].

3. Results and discussion

Table 1 shows the consumed amounts of agents used in the process of treating pickled leather with Bath I. The calculation was made on 1000 kg of raw hides. Distinguish are wholesale prices of agents and the price of industrial water with associated fees for wastewater (Croatia, July 20, 2022).

The total costs listed in the Table 1 and Table 2 do not include all variable costs (electricity and other overhead costs related to the production process) nor fixed costs (determined wages of workers), but only direct variable costs defining the process.

The amount of total costs of the process in Table 1 are 149,85 € per 1000 kg of leather, or 0,15 € per 1 kg of leather. The total duration of the process is 180 minutes, and the cost per minute is 0,83 €.

Table 1. Costs of agents used in Bath I for 1000 kg of pickled leather.

Resources / agents	Amount of agents/1000 kg	Processing time	Temperature	Price per unit of measure	Cost of used resources / agents
water	500 l			3,32 €/m ³	1,66 €
citric acid	35 kg	180 min	30°C	3,29 €/kg	115,43 €
Zeolite 5A	32,5 kg			0,97 €/kg	31,59 €
wetting agent	0,5 kg			2,34 €/kg	1,17 €
				total cost	149,85 €

Table 2. Processing costs for leather washing after the appearance of mould and stains due to storage on 1000 kg pickled leather.

Resources / agents	Amount of agents/1000 kg	Processing time	Temperature	Price per unit of measure	Cost of used resources / agents
water	2000 l	135 min	30°C	3,32 €/m ³	6,64 €
wetting agent	15 kg			2,34 €/kg	35,01 €
water	2000 l			3,32 €/m ³	6,64 €
ant acid	15 kg			1,66 €/kg	24,89 €
fungicide	15 kg			8,84 €/kg	132,61 €
				total cost	205,87 €

The amount of total costs of the process in Table 2 are 205,87 € per 1000 kg of leather, or 0,21 € per 1 kg of leather. The total duration of the process is 135 minutes, and the cost per minute is 1,58 €.

The cost of processing pickled leather with Bath I is 27.19% (55,27 €) cheaper than the regular costs of removing mould and fungus.

Therefore, it can be concluded that the use of Bath I in the treatment process to protect the hides from microbes and mould contributes to the economic efficiency of the company due to lower processing costs. It should not be disregarded that a smaller amount of water (80%) was used for the treatment with Bath I compared to the regular process, which is of great importance for environmental protection. Reduced water consumption results in a reduction of wastewater.

4. Conclusions

The objective of this work was to determine the economics of processing pickled hides with baths containing zeolite and citric acid and to compare them with the costs of removing microbes and moulds according to the current production recipe.

The variable cost structure presented is determined under the ceteris paribus condition based on fixed wholesale prices for the unit of measure and the individual resources used. The zeolites in leather processing have cumulative economically justifiable costs. From the point of view of cost analysis, there is a financial profitability, which can have a positive impact on the efficiency of the operation and increase income.

From an environmental point of view, it is important to mention that the use of Bath I is more economically justifiable than that of fungicides. Water consumption and the amount of wastewater are significantly reduced. The risk of handling hazardous chemicals is reduced, which may be associated with an improvement in working conditions.

Previous studies have shown that the use of zeolite in the tanning process improves the mechanical properties of leather [9], which opens the possibility of testing the mechanical properties of pickled hides treated with baths containing zeolite.

Literatura

- [1] Zugno L. et al: Fungal Growth on Wetblue: Methods to Measure Impact on Leather Quality, Journal of the American Leather Chemists Association **106** (2011.) 1, 1-17.
- [2] Fontoura J.T., Gutterres M.: Damage of pickled hides, wet-blue leather and vegetable tanned leather due to biodeterioration, Journal of the American Leather Chemists Association **110** (2015.) 5, 134-144.
- [3] Orlita A.: Microbial biodeterioration of leather and its control: a review, International Biodeterioration & Biodegradation **53** (2004.) 3, 157-163.
- [4] Hauber C.: Microbicide applications in the leather industry, Directory of microbicides for the protection of materials, Springer 2005, 317-324.
- [5] Bryant S.D. et al: A New Antifungal Agent for the Leather Industry: S-Hexyl-S'-Chloromethyl-cyanodithiocarbamate (CHED), Journal of the Society of Leather technologists and Chemists **95** (2011.) 1, 7-10.
- [6] Birbir M. et al: Mold strains isolated from unfinished and finished leather goods and shoes, Journal of the American Leather Chemists Association **89** (1994.) 1, 14-19.
- [7] Bitlisli B.O. et al.: The effect of conservation defects on the suede quality of double-face, Journal of the American Leather Chemists Association **99** (2004.) 12, 494-501.
- [8] Sun XD. et al: New application of nano NaY zeolite in acrylic polymer pretanning agent, Microporous and Mesoporous Materials **328** (2021.) 1387-1811.
- [9] https://www.researchgate.net/publication/251457708_Zeolite-chrome_tanning_From_laboratory_to_pilot_scale, Pristupljeno: 2022-09-15.
- [10] Esquerra-Resa S. et al: Study of the Biodegradability of Leather Tanned with Sodium Aluminosilicate, Journal of the American Leather Chemists Association **117** (2022.) 6, 251-261.
- [11] Gurler Karaman D., Gulumsar G.: Possibilities of usage of alkali aluminosilicates as tanning material in chromium-free leather production, Tekstil ve Konfeksiyon **26** (2016.) 1, 117-124.
- [12] Dvorski S., Kovšca V.: Ekonomija za poduzetnike, Tiva tiskara Varaždin 2011, 421.

- [13] Maršić K., Hunjet A.: Analysis of the Croatian textile industry based on efficiency measurements using relative indicators of Croatian textile industry, 61st International Scientific Conference on Economic and Social Development – "Corporate social responsibility in the context of the development of entrepreneurship and small businesses", Milkovic M., Hammes K., Bakhtina O. (ed.), Sveučilište Sjever, Varaždin 2020, 1849-7535.
- [14] Santini I: Troškovi u poslovnom odlučivanju, Hibis d.o.o., Zagreb, 1999.
- [15] Majcen Ž: Troškovi u teoriji i praksi, Informator d.d., Zagreb, 1981.
- [16] Shnaishel T.S. et al: Evaluation of cost approach from the viewpoint of employees of the general company for leathers industries, World Economics & Finance Bulletin (WEFB) **12** (2022.) 12-31.
- [17] Babić M.: Makroekonomija, Mate d.o.o., Zagreb, 1996.

"The paper was published in the Book of Proceedings of the 10th International Textile, Clothing & Design Conference: Magic world of textiles (ITC&DC) 2022, Dubrovnik, Croatia".