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CHARACTERISTICS OF POLLUTION AND CHANGES IN THE TANNING INDUSTRY

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ABSTRACT: The article outlines the range of specialized leather processing tanneries processes. They are the backbone of the leather industry. The difficulties these plants face are indicated, and wastewater parameters are given and compared with literature data, confirming that they are a problem for many plants. Good water and wastewater management practices to improve environmental aspects are also described. The data on the leather industry from recent years were analyzed in terms of economics, showing that the outlook for the industry is not optimistic. Rising costs are reducing profits, translating into business closures, and thus reducing the number of workers employed. All of the above factors contribute to the fact that the leather sector and its tanneries have been going through difficulties for many years.

KEYWORDS: tannery, industrial effluent, industrial production

Introduction

The tanning industry can be described as the initial stage and the basis of the leather industry, but many other industries are also based on using leather to produce certain goods. Leather manufactured in tanning plants, only in its final iteration and provided it possesses a certain quality, is fit for use in the production of clothing items, haberdashery, furnishings, and many other items of a utilitarian or luxury nature. Without tanning plants, we are left with untreated, raw hides as residues from the slaughtering processes. In this form, they are entirely unsuitable for production, due to unevenness in thickness, shape, or color, and, above all, due to the fact that they can quickly undergo biological decomposition. Despite the many benefits of treated leather and its resistance to degradation, the tanning industry produces effluent with high concentrations of chromium and is responsible for significant environmental pollution with this element (Lofrano et al., 2013; Celary & Sobik-Szołtysek, 2014). Tanning is an industry in which the generated wastewater is causing significant issues and, with smaller plants, can be the reason for halting, reducing, or even terminating production due to rising costs. Chromium from the tanning processes enters wastewater due to chromium tannins being most commonly used. A method of synthesizing them was first discovered in the 19th century, thus beginning the modern chromium tanning process (Famielec, 2014; Kubala & Przywara, 2014). When it is done well, the leather becomes incomparably resistant to biological degradation and is protected from its effects (Wieczorek et al., 2011). Leather processing, however, is not limited to chromium tanning only, as it consists of a series of operations performed in the dry, wet, and finishing workshops (Chmielowski, 2019; Lenort et al., 2017; Bartkiewicz & Umiejewska, 2010; Bień et al., 2019). The wet workshop is based on several processes carried out in water baths, with appropriately selected chemical compounds which are expected to produce a specific effect in a given part from the total molding.

Leather baking processes

In the first stage of the process, the hides undergo soaking. It involves restoring the leather to its original water content, by washing it of all impurities and using salt for its preservation. Wet leather is also more flexible and easier to work with. Wet operations are further supplemented by the first stage in the series of mechanical processing elements; de-molding. It is a process that removes excess subcutaneous tissue, meat, and fat fragments. It reduces the weight of the skin together with its thickness, making it easier to further process. In addition, the reduced weight results in a decreased need for chemicals to be used down the line. The defleshed hides are then returned to the drum – a cylindrical tank where wet operations are carried out – and remain there until the tanning is completed. The first stage of the following processes is liming, i.e. alkaline swelling of the leather by using alkaline compounds of lime. Consequently, there is an increase in the thickness of the skin, due to swelling. Hair follicles open up, and hair can be removed from the top of the skin. Once the hair is removed, the increased thickness of the skin is no longer desired. Therefore, another process is carried out which has the opposite effect. As a result, the thickness of the skin is reduced and restored to its original state. This process is referred to as decalcification. It reduces the pH of the bath and skin, leaching out calcium and other alkaline compounds that took part in the previous process. Gradually lowering the pH means that the hides are being prepared for tanning, which is carried out in an acidic environment. The decalcified hides are subjected to etching, during which proteolytic enzymes are used to refine the leather. Then, by adding salts and acids to the pickling process, the hides are finally prepared for the most crucial process: tanning. This stage, in order to progress correctly, requires a low pH, so that the tannin binding occurs. In most plants chromium serves as the tannin in this process. Introduced into the bath in excess, it guarantees proper tanning of the hides, filling them with tannin and protecting them from degradation. Because the amount of chromium significantly exceeds the required level, the remainder goes into the wastewater, raising the chromium pollution load (Kubala & Przywara, 2014). Tanning is the last stage of wet operations in a wet-tanning workshop. The hides are subsequently subjected to dry operations on mechanical processing machines. The tanned hides are wrung out to drain the water accumulated in them. Then, single pieces are divided into two parts to obtain two splits; face and flesh. The face part is the one from which the hair

follicles have been removed along with the hair, and the flesh part is the underside which was de-muscled. Depending on the expected final product, each is subjected to planning, obtaining pieces of a specific, even thickness over its entire surface. Skins prepared in this way can then return to the wet department. Again, the hides are given their expected characteristics, such as water resistance, in water baths by applying specific fats. The skins are also given a preset color during this part of production. It can be their final coloring, or just an undercoat. Two semi-finished leather products can already be of commercial value and be used in manufacturing. These are wet-blue leather, tanned leather, crust leather, or tanned and off-tanned leather. Wet-blue can be used in plants that are prepared for further self-tanning of hides, and where it is impossible to individually tan them, for example, due to the lack of chrome wastewater management facilities. Crust leather, conversely, can be a material for leather parts, despite their aesthetic value being of a lower market value.

Characteristics of tannery wastewater

Several wet and dry processes are carried out using the correct sequence of actions and by applying supporting chemicals that interact directly with the skin to achieve its preset properties. They involve managing wastewater generated during that stage (Ascón-Aguilar et al., 2019). In addition, almost every action is preceded by a rinsing process. Each rinse represents an additional mass of water that becomes contaminated due to mixing with wastewater and leaching leftover chemicals from the skins. The rinse water introduced into the tanks increases their overall volume, but reduces the overall load. The high water demand also varies by plant (Dymaczewski, 2011). As the technological development of each plant increases, it is possible to reduce the use of water and especially any points where it is lost through failures or leaks. Reducing water use should be the goal to be achieved in all plants (Rüffer & Rosenwinkel, 1998), but it is not an easy task, due to technological limits and financial constraints (Bień et al., 2017). Good plant organization and the technical condition of both machinery and floors contribute to the limitations in the use of water, for example, for washing surfaces or rinsing machinery. The better the condition of the machines, the easier it is to clean them. These volumes of water compared to the total used in processing are negligible but, with larger plants (and thus bigger scale of production), they may already represent a certain amount whose reduction will be noticeable. The total volume of wastewater can be as high as 60 m³/t of rawhide (Mendrycka & Stawarz, 2012). Dziadel et al. (2022a), based on one of the plants located in Podlasie, determined that the volume of wastewater generated was about 30m³. On the other hand, Szalińska (2002) and Ferdous et al. (2023) report similar values of 30 to 60 and 35 to 56 m³ of wastewater per ton of hides. These volumes can be described as similar and reproducible, since the idea of production in different plants will be similar. In contrast, the degree of technological development, the ability to maintain adequate plant water management, or the ability to manage wastewater will differ and thus directly affect the results obtained.

In the case of tanning plants, a policy of separation of wastewater management in terms of pollutants is applied mainly due to the presence of chromium. The main wastewater stream is collected separately, with leachate from processes other than tanning. Wastewater enriched in chromium, on the other hand, should be discharged into a separate tank. It is essential because of the quality of wastewater and its treatment capacity. Chromium wastewater contains high concentrations of this element, due to excess proportions needed in the tanning process. It has a measurable impact of increasing the certainty that tanning is carried out correctly, but creates a more contaminated leachate as a result. A positive aspect of that considerable accumulation of chromium in wastewater is the possibility of its recovery. Developed wastewater treatment technologies and separate lines associated with chromium recovery require higher concentrations of chromium already at the entrance to the treatment plant. The higher the chromium load, the greater the amount of chromium that can be returned and reused during tanning. Another way to manage chromium wastewater is to reuse the broiled wort. It again involves a large amount of chromium already present in it. Then, a certain amount of fresh tannin must be supplied to the returned wort to replenish it. It causes the chromium to be reused from the previous process, and the additional amount of chromium is only a supplement and can serve as an excess, safeguarding the process and guaranteeing proper tanninization.

In addition to chromium, other chemical compounds are used in the leather processing. Salt, used in the first stage, is also used during tanning, and it is from those two processes that the most significant amount goes into wastewater. As a result of the use of ammonium sulfate at the decalcification stage and sulfuric acid during tanning, the wastewater is also enriched in sulfate. In turn, the liming process is a source of sulfides. It is also the source of the highest suspended matter loads, BOD₅ and COD. Nitrogenous compounds, such as nitrogen, accumulate due to the decomposition of proteins removed from the skin. This is due to the liming and decalcification processes, which are also responsible for a large amount of ammonia. (Rydin et al., 2013). High pollution means that wastewater must be managed and treated before entering the environment (Malovanyy et al., 2020). The compounds present are typical, and their contents in raw and treated wastewater are determined, while some supporting compounds like surfactants, lubricants, and wetting agents are also used. Ultimately, about 15% of the chemistry used remains in the final product, with the remainder going into the wastewater (Rydin et al., 2013).

Table 1 shows the average parameters of tannery wastewater according to tests conducted on wastewater from a tannery plant located in Podlasie (The research was carried out as part of research work no. WI/WB-IIŚ/10/2023 at the Bialystok University of Technology and financed from a subsidy provided by the Ministry of Education and Science.), and Table 2 shows wastewater parameters obtained through good practices (Dziadel & Ignatowicz, 2022a; Rydin et al., 2013).

Table 1. Average pollution parameters of tannery wastewater from a plant located in Podlaskie Province

Type of wastewater	Indicator							
	Suspension	pH	Conductivity	Ammonium nitrogen	COD	BOD ₅	Chlorides	Chrome
	g/dm ³	-	µSm/cm	mgN /dm ³ _{NH4}	mgO ₂ /dm ³	mgO ₂ /dm ³	mgCl/dm ³	gCr/dm ³
Mixed from soaking processes	3.23	6.70	64.80	109.00	14500	2000	27300	-
Mixed from soaking and liming processes	1.16	9.08	44.60	14.90	14300	1900	1800	-
Wastewater from the decalcification process	1.496	8.91	27.504	33.20	6620	1200	1200	-
Mixed effluent from all processes before tanning	3.30	8.46	34.50	278.02	10180	2400	3500	-
Effluent after tanning	1.61	3.67	61.60	-	8290	-	17700	2.20

Source: authors' work based on Dziadel and Ignatowicz (2022a).

Table 2. Parameters of wastewater before disposal obtained through good practices

Indicator	Wetting	Process			
		Dehairing	Decalcification	Pickling-gargling	
Water consumption	m ³ /t	2	5	2.5	0.5
Suspension	kg/t	10	19	6	7
	g/m ³	5.0	3.8	2.4	14.0
BOD	kg/t	12	20	5	3
	g/dm ³	6.0	4.0	2.0	6.0

Indicator Wetting		Process			
		Dehairing	Decalcification	Pickling-gargling	
COD	kg/t	23	45	12	8
	g/dm ³	11.5	9.0	4.8	16.0
Ammonium nitrogen	kg/t	0	0.3	0.2	0.1
	g/dm ³	0.0	0.14	0.012	0.0
Chlorine	kg/t	5	3	1	28
	g/dm ³	2.5	0.6	0.4	56.0
Chrome	kg/t	-	-	-	0.1
	g/dm ³	-	-	-	0.2

Source: authors' work based on Rydin et al. (2013).

Table 3. Comparison of average values of pollutant parameters in tannery wastewater in outflows from soaking and dewatering processes

Parameter	Unit	Value			
		Source			
		Lofrano et al. 2013		Chowdhury et al. 2015	
Wetting					
pH	-	6	7.7		8.18
COD	[mg O ₂ /dm ³]	5000	31000	3000	10560
BOD ₅	[mg O ₂ /dm ³]	2000	-	-	1200
Suspension	[g/dm ³]	2.3	-	25	6.08
NH ₄ ⁺	[mg N-NH ₄ /dm ³]	-	850	-	-
Chlorides	[mg Cl/dm ³]	17000	-	15000	-
Decalcification					
pH	-	6	8.6	-	6.5
COD	[mg O ₂ /dm ³]	2500	5325	-	4200
BOD ₅	[mg O ₂ /dm ³]	1000	-	-	700
Suspension	[g/dm ³]	2.5	-	-	11
NH ₄ ⁺	[mg N-NH ₄ /dm ³]	-	3800	-	-
Chlorides	[mg Cl/dm ³]	2500	-	-	-

Source: authors' work based on Lofrano et al. (2013) and Chowdhury et al. (2015).

Since the data presented by Dziadel et al. (2022a) refer to mixed wastewater, averaged over time with successive processes, only the parameters of samples taken after soaking and decalcification processes can be compared. The pollutant parameters presented in the reference document refer to wastewater after specific processes and per ton of leather treated (Rydin et al., 2013). Similarly, the data are summarized in Table 3.

One can notice a similarity to the changes in impurities depending on the process. According to Tables 1 and 2, the amount of suspended solids is about half as much after the decalcification process relative to soaking. On the contrary, these values were presented by Chowdhury et al. (2015), where they were almost twice as high. In each case, the values for parameters such as BOD₅ and COD, which were lower after the decalcification process in each source, change similarly. The results differ only in

terms of determined ammoniacal nitrogen, where the values diverge from each other. It is important to note that it may be a direct result of the method of gutting and the means and technology used by the plant. Since the data in the case of the reference document referred to the results obtained through good practices, the above values may diverge due to differences in the level of technological development of the plants. Actions that can be counted as good practices include appropriate decisions regarding facility and process management, water management, activities that increase the efficiency of flushing runs, and control of all processes carried out. Analyzing and selecting the appropriate optimal volumes of water is required to perform a given stage until the right quantities are obtained. In addition to water distribution, these measures should also be taken for the chemicals used by selecting the right amount and controlling during dosing. Consequently, by controlling and increasing efficiency, the entire leather tanning plant operation process can be improved, and tangible savings can be achieved regarding environmental, economic, and water management (Rydin et al., 2013). On the other hand, based on a general comparison of the results, it can be concluded that these converge and agree and, thus, are reproducible in many tanning plants. The parameter levels of the pollutants, in turn, indicates their substantial toxicity to the environment and the need for appropriate management.

Changes in the leather and leather products manufacturing sector

Table 4. Revenues, costs, and financial result of enterprises – industrial processing – production of leather and leather products

Year	Parameter				
	Total revenue	Total costs	Gross financial result	Mandatory charge to gross profit	Net financial result
	PLN million				
2010	2371	2232	139	19,5	119
2015	3908	3488	419	60,7	359
2019	3847	3588	259	48,7	210
2020	3412	3195	217	39,3	177
2021	3701	3338	363	54,3	309
2022	3791	3639	152	52	100

Source: authors' work based on CSO (2022b, 2023b).

Table 5. Business entities – for sections and divisions – manufacture of leather and leather products

Year	Number of business entities		
	Total	Public sector	Private sector
2005	4696	8	4688
2010	3210	3	3207
2020	2565	3	2562
2021	2325	2	2323
2022	2141	1	2140

Source: authors' work based on CSO (2021, 2022a, 2023a).

Over the years, changes in the leather and leather products manufacturing sector have been characterized by a downward trend, as shown in Table 4. Despite increasing revenues, the financial results of the enterprises are declining due to rising costs and fixed expenses related to taxes and other

financial obligations. The growth of revenues and costs occurred from 2010 to 2015, where it reached a maximum and, in that year, relative to the others, the highest revenues and the highest net financial result was achieved despite high overhead costs. In 2019 and then 2020, there was a significant decline in revenues. The following two years were very irregular. The year 2021 showed higher revenues and overhead costs did not increase as significantly, resulting in a net financial result almost double that of 2019 and 14% lower than that of 2015. The year 2022 reversed the trend of improvement; revenues relative to 2021 were higher, but overhead costs also increased significantly. As a result, the net financial result of enterprises was more than three times lower than that of the previous year. As reported in Industry Quarterly 4q22 (2022), cost dynamics exceeded revenue dynamics from the second quarter of 2022.

Increasing costs of doing business, higher fees and investments, and disproportionately increasing revenues also affect the number of active businesses, which are fewer and fewer each year, as indicated in Table 5. Both are in the public sector, where there is one less business entity each year from 2020, remaining at one in 2022, and the number of private businesses from 2020 to 2022 decreased by about 16.5%.

As described by Dziadel et al. (2022b) and according to information in the Statistical Yearbooks of the Republic of Poland (2022b, 2023b), there is a cyclical decline in the number of employees in this sector.

Conclusions

The tanning industry is definitely not one of the simplest to operate, which brings the need to adapt the plants to accommodate many complex processes and technological improvements, mainly based on reducing the amount of water used and the appropriate collection of wastewater. Such adaptations result in mutually correlated benefits, as the limited amount of water in turn reduces the volume of wastewater generated and reduces the costs associated with its management. However, the formation of wastewater is necessary because, without it, it would not be possible to carry out the complex processes that produce high-quality leather. The series of reactions makes it possible to obtain an extremely durable product from what was originally raw leather, which, if left in adverse conditions, would immediately biodegrade and become unusable. However – as is the case in any business – all investments entail costs, which can affect the companies' finances, whether related to investments in technology or environmental protection through proper water and wastewater management. The cost to the enterprise also includes the employees, their salaries, and the associated ancillary fees. Taken together, the expenses can be so high that the profitability of production will not be viable, resulting in reduction of employees, or the decision to eventually close production and shut down the plant. This trend can be clearly seen over the past few years as attested by the attached tables and statistical data. Unfortunately, tanning plants are placed at the very beginning of the leather industry. If the products do not find customers, especially at prices that allow earnings, running such a business is very difficult and requires an appropriate approach in terms of environmental protection, often making their existence economically unjustifiable.

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The contribution of the authors

The article was written in collaboration with all authors.

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Maciej DZIADEL • Katarzyna IGNATOWICZ • Piotr KOSZELNIK

CHARAKTERYSTYKA ZANIECZYSZCZEŃ I ZMIAN W PRZEMYSŁE GARBARSKIM

STRESZCZENIE: W artykule przedstawiono zakres procesów, które mają miejsce w specjalizujących się przerobem skóry zakładach garbarskich. Są one podstawą przemysłu skórzanego. Wskazane zostały trudności z jakimi zmagają się te zakłady, podano parametry ścieków i porównano je z danymi literaturowymi, potwierdzając, że są one problemem dla wielu zakładów. Opisano również dobre praktyki związane z gospodarką wodno-ściekową, mające na celu poprawę aspektów środowiskowych. Dane przemysłu skórzanego zostały przeanalizowane pod względem ekonomicznym względem ostatnich lat, co pokazało, że perspektywa tego przemysłu nie jest optymistyczna. Rosnące koszty wpływają na ograniczenie zysków, a to przekłada się na zamykanie działalności, zmniejsza się przez to ilość zatrudnionych pracowników. Sektor skórzany i występujące w nim garbarnie od wielu lat przechodzą trudny okres istnienia.

SŁOWA KLUCZOWE: garbarnia, ścieki przemysłowe, produkcja przemysłowa