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WATER AND WASTEWATER MANAGEMENT IN A SMALL TANNING FACILITY

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ABSTRACT: This paper presents a tannery industry's water and wastewater management problem. Information has been collected on the volume of water demand and, consequently, wastewater generation in these plants. This made it possible to relate them to the values generated by one of the smaller tanning plants located in Poland. The concentration of the pollutants contained in this wastewater, mainly chromium, was also determined from the study. Management of wastewater is a financial nuisance for small plants. The need to conclude contracts with specialized treatment plants, storage and long-distance transport of sewage, also by the respective companies, generates considerable costs, which may be a limiting factor of the willingness to invest in production. Wort reuse reduces the cost of purchasing chromium as a bath ingredient, reduces the frequency of waste disposal and significantly reduces company costs.

KEYWORDS: tannery, industrial effluent, chrome, industrial production

Introduction

Tanning is one of the oldest industries yet is an important element in the global industrial sector. Production is related to the direct handling of raw materials, which are animal skins – a by-product of animal origin – obtained as one of the products after the slaughtering process. The skins used may be from cattle, horses, sheep or pigs, and their uses may vary. Tanneries are also involved in the tanning of fur skins. Ultimately, a finished product comes out of a production facility which is further processed into finished products by the respective companies specialising in a given industry. There are many possible applications, from shoes to clothing, leather goods and various types of bags to more exclusive products such as furniture, car interiors, boats and many others.

Processed leather consists of three layers: epidermis, dermis and subcutaneous tissue. The dermis makes up about 80% of its total thickness and accounts for the largest proportion of its mass (Szalińska, 2002). The structure of the dermis includes fibrous tissue. This tissue is composed of collagen fibres. The processing of this layer of the skin through the penetration and cross-linking of tannin molecules is the essence of tanning proper (Chmielowski, 2019), while tanning proper itself is part of the overall process known as tanning. The tanning industry has been named after this process. The overall processes – in other words, leather tanning – consist of the stages of processing hides in wet workshop processes, including proper tanning and finishing operations (Bartkiewicz & Umiejewska, 2010; Bień et al., 2019; Lenort et al., 2017). Mechanical operations usually take place on hides that have already been tanned. Wet operations are the largest source of large pollutant loads in the resulting effluent (Aguilar-Ascón et al., 2019) resulting from the required processes carried out.

The tanning industry in statistical data

Based on knowledge of the PKD symbol – 15.11.Z – dressing of leather, tanning, dressing and dyeing of fur, it is possible to read data related to this industry on the scale of a province or a whole country. Figure 1 presents the number of national economy entities registered in the REGON register declaring their activity by voivodship and PKD 2007 and national economy entities newly registered in the REGON register declaring their activity by voivodship and PKD 2007.

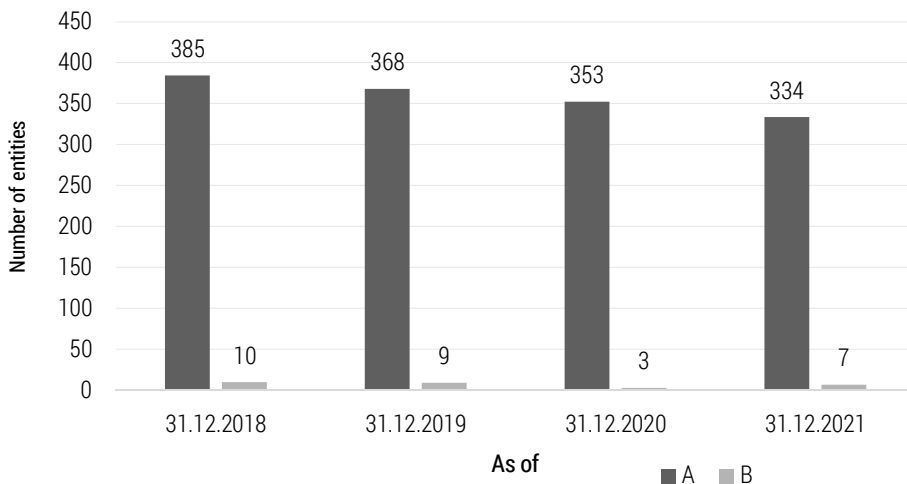


Figure 1. Number of entities registered (A) and newly registered (B) in REGON in the years 2018-2021 for PKD 15.11.Z

Source: author’s work based on GUS (2022).

Figure 2 shows the number of persons employed and the average employment in the section manufacturing of leather and leather products in 2017-2020 based on data collected by the Central Statistical Office (GUS).

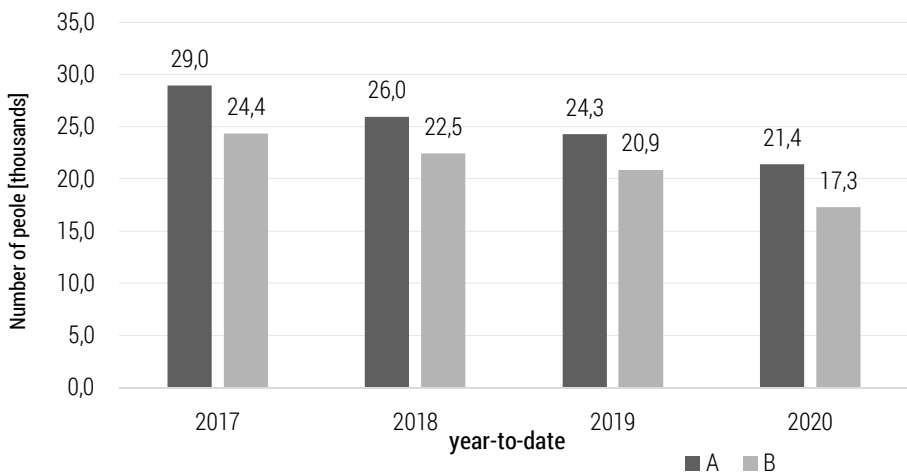


Figure 2. Number of employed persons (A) and average paid employment (B) in industry in the years 2017-2020

Source: author’s work based on GUS (2019, 2021).

Figure 3 shows the change in leather production volume, and Figure 4 shows the change in the number of pairs of shoes produced from 2017 to 2020.

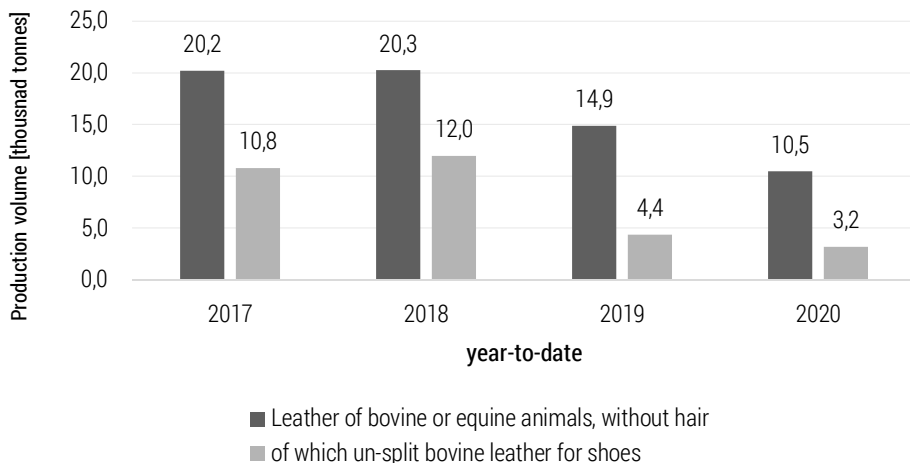


Figure 3. The volume of leather production in the years 2017-2020

Source: author’s work based on GUS (2019, 2021).

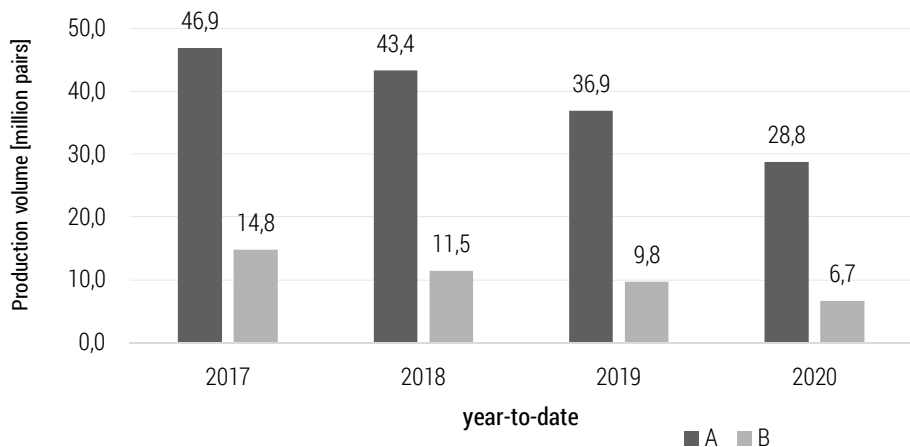


Figure 4. Production volume of footwear (A), including footwear with leather uppers (B), from 2017 to 2020

Source: author’s work based on GUS (2019, 2021).

The total industrial output detailing the share of manufacturing and the production of leather and leather products is presented in Table 1.

Table 1. Total industry output sold, of which manufacturing, including production of leather and leather products

Specification	Sections and divisions	2017	2018	2019	2020
Sold production of industry [mln PLN]	Total industry	1,417,247.1	1,520,836.1	1,615,202.7	1,579,859.6
	Section C – industrial processing	1,220,552.6	1,318,404.8	1,398,652.0	1,356,747.8
	Division 15 – Manufacture of leather and related products	5,549.5	5,377.8	5,009.4	4,327.0

Source: author's work based on GUS (2022).

A review and analysis of the statistics presents an industry that is difficult to sustain. This is evidenced by the downward trend in almost every aspect of the approach to this topic. The number of entities that were registered in the REGON register between 2018 and 2021 decreased from year to year by about the same amount, and the situation was similar for newly registered entities during this same time period (Figure 1). The biggest change occurred in 2020 when, compared to 2019, most of the entities deregistered their activities, and the least were newly registered. Data from the Central Statistical Office also shows a downward trend (Figure 2). The numbers of employed persons and average employment in the industry leather and leather products manufacturing section decreased year by year between 2017 and 2020. Together with the reduction in activity and employment, a decrease in the volume of leather and leather products production can be observed. The volume of leathers processed remained flat from 2017 to 2018, with soft cowhides and footwear accounting for the bulk of the share. In 2019, there was a decrease of more than 25% in the volume of production, followed by a decrease of 50% in 2020 relative to 2018.

Along with this, the share of soft leathers to total production decreased significantly from more than 50% in 2017-2018 to less than 30% in 2019-2020. The decrease in the volume of leather produced was accompanied by decreases in the volume of footwear produced. The share of footwear with uppers made of leather to the total volume of footwear production fell from over 30% to about 23% between 2017 and 2020.

Any decline is reflected in the industry's sales production (Table 1). Despite the year-on-year increase in the value of sales production from 2017 to 2019 of the total industry and the industrial processing section, the production of leather and leather products, which is one of its divisions, had

a continuous decline in these years. In the comparison of 2019-2020, each of the analysed parts of the industry achieved a decrease in value, with the total industry and the industrial processing section not being lower than the year before (2018), and division 15 production of leather and leather products achieved a decline even more severe than the 2017-2019 total.

The industry suffered the largest declines in 2020, a consequence of the global problem of the COVID-19 pandemic, the effects of which continue to this day. The situation of the leather industry deteriorated significantly in the first quarter of 2020 and improved only in the third quarter (Monitoring Branżowy [Industry Monitoring], 2020;2021), thanks to the loosening of the restrictions imposed on the market. The aforementioned restrictions on the operations of some companies suspended trade and production, which contributed to a reduction in the profitability of the operations of many factories and this encouraged their closure, suspension and non-opening of new operations.

Characteristics of the production process

The technological processes in a tanning facility can be divided into a dry department and wet department processing. The dry department includes the use of appropriate machinery to bring the leather to a given state, while the wet department includes elements related to soaking the leather in baths with specific properties. These stages intertwine with each other during processing. Depending on the size of the plant, the processing capacity and the applied technologies, the methods of leather processing as well as the sequence of the processes used may differ.

Soaking is the basic and first step. Both raw hides and hides previously preserved, e.g., with salt, undergo this process. Salted leathers which have been stored for a long time become dry and stiff. Soaking is mainly aimed at restoring the original water content in hides. It also makes it possible to clean them of impurities, blood residues, salt residues and loose fibres.

The next step involves the use of mechanical processing elements referred to as de-muscling or fleshing of hides. This is a process in which hides are subjected to mechanical removal of excess subcutaneous tissue, residual fat, meat and structural fragments contained within this thickness of skin (Śmiechowski et al., 2009). The effect of the process significantly reduces the weight of a single piece, and this translates directly into further proportioning the amount of water and chemicals in the processes carried out. The placement of this process in the processing sequence of individual plants may vary, as fozing can be carried out either before or after soaking, after liming or after pickling (BAT, 2013).

The de-muscled hides are returned to the wet department to drums, where they are limed. Using solutions of calcium hydroxides and sulphides, the hides swell. The swollen hides increase in volume and are loosened, which affects the opening of hair follicles resulting in the removal of hair from the surface of the hide, its hydrolysis or dehairing of the hides (BAT, 2013; Śmiechowski et al., 2009).

Afterwards, the skins in this condition are subjected to the opposite process, the purpose of which is to restore them to their previous state. The alkaline characteristic of the skins is neutralised, and compounds are washed out, which lowers the pH of the skins and the bath itself. This contributes to the removal of alkaline swelling, and the skins lose volume (Śmiechowski et al., 2009).

After decalcification, the leather is subjected to pickling, which may take place in the same bath. At the end of the pickling process, rinsing takes place, followed by the process which precedes tanning itself – pickling. Its purpose is to create an acidic bath environment. The substances include water, sulphuric acid and table salt. This form of bath acidifies the hides, which can additionally be used as a form of preservation and storage of the hides for a long period of time due to the low pH of the medium at about 3.5 (BAT, 2013).

The last of the series of processes in the wet workshop, the first stage of animal leather tanning, is tanning proper. It is of key importance in the processes carried out, as it imparts the most changes to the structure of the leather, changing its properties completely. Tanning is necessary to protect raw hides from microbiological degradation, moisture and heat (Wiczorek-Ciurowa et al., 2011). The application of a tanning bath using the most widely used chromium tannins leads to their penetration into the subcutaneous tissue, where binding reactions with skin collagen occur. The tanned leather requires some time to stabilise, after which further processes associated with its tanning are carried out but no longer associated with such processes in the wet workshop.

The following mechanical operations start with annealing of tanned hides, in which considerable volumes of water are accumulated, the removal of which will facilitate the processing of hides both mechanically and logistically, obtaining much lighter semi-finished products. The raised skins are then subjected to splitting. Introduced between two rollers, the leather is cut into two flaps: a face split and a flesh split. At this point, the leather reaches a certain thickness, which is adjusted using planers, which scrape off the excess thickness to the expected value.

The skins are then returned to the wet department for rinsing to remove loose impurities and substances not rinsed from the skin. They are then neutralised by increasing their pH using alkaline compounds. This process is followed by tanning, or filling, to improve and even out the quality of the

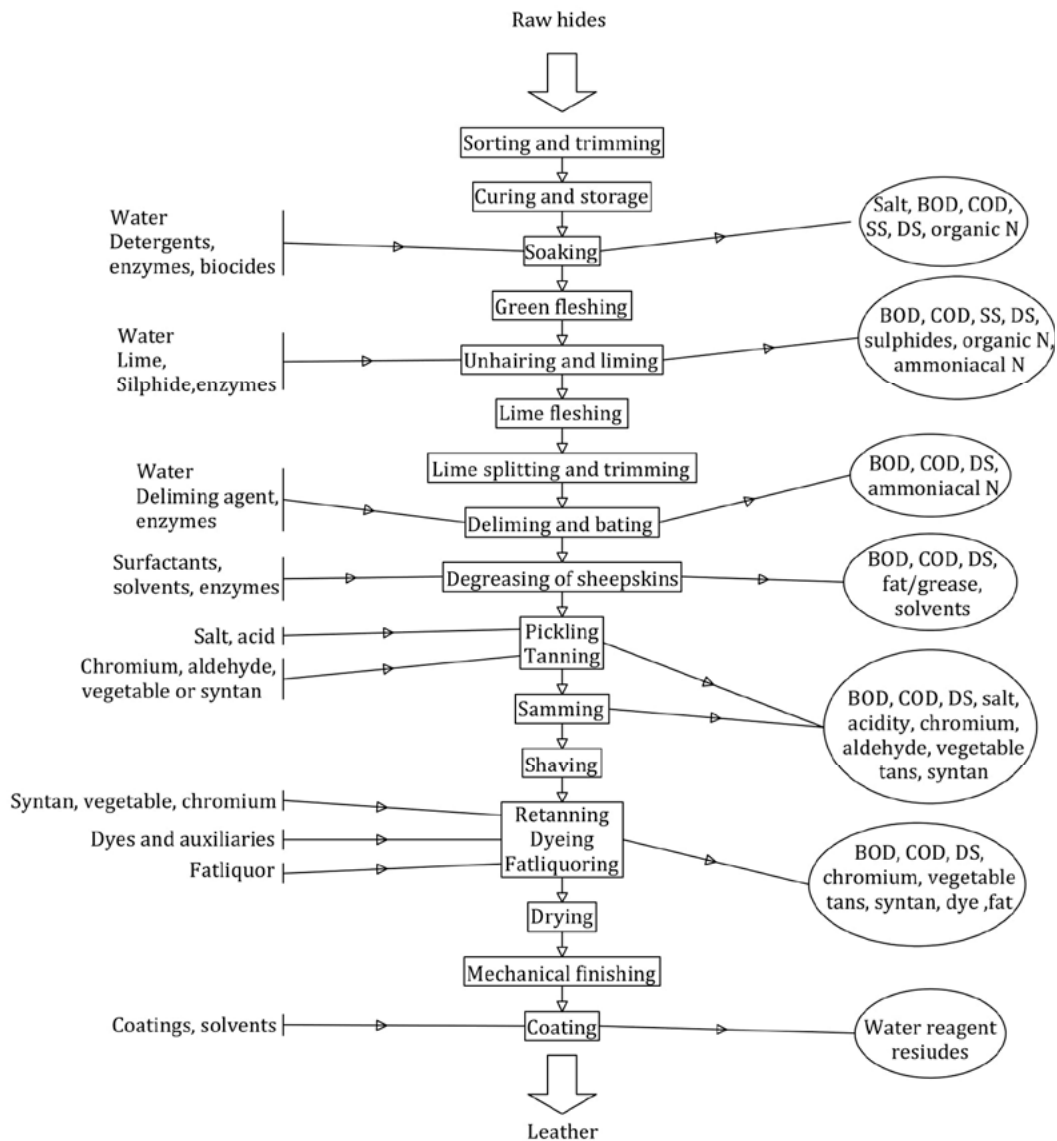


Figure 5. Processes, substances used, wastewater generated during leather tanning processes

Source: author's work based on Joint Research Center (2013).

leather over its entire surface (Śmiechowski et al., 2009). Re-tanning also uses chromic, vegetable or synthetic tanning agents, depending on the techniques used. The subsequent process is very important to the whole process, as it gives the leather its initial or final colour depending on what is expected

from the final product. Greasing is a complementary process, i.e. treatment of leather in a bath with greasing agents, which affects the permeability of water vapour and air or water absorption, and the application of appropriate types of greases makes it possible to obtain water-resistant leathers. Processes carried out in such a way, starting from a raw product, through tanning, mechanical processing and bath finishing, give leather which is already partially finished, another semi-finished product in the process called "crust". The operations described above are found in many tanneries.

Further processes can be divided and start with drying using machines or special rooms. Completely dried leathers require mechanical softening and pressing to level their surface. Thus, prepared leathers may be subject to applying finishing coats on their face. This may be done with the use of spraying units or rollers. Another form of leather finishing is the grinding of dyed leather, after which the application of additional surface coatings is not necessary in every case.

Figure 5 shows the flow of activities performed from the beginning to the final output. Some of the activities are duplicated and have a different place in the order in which they are performed, which is reflected in the variability in the nature of the production sequence between different plants.

Materials and methods

Just as the order of the processes performed differs, the quality of the wastewater generated in different plants may differ (Chmielowski, 2019). The volume of wastewater generated during leather tanning per 1 ton of raw hides also differs in literature data. According to Chmielowski (2019), water consumption for the production of leather for footwear is about 15 m³. According to Bartkiewicz and Umiejewska (2010), the average water consumption in tanning plants by specialisation is:

- min. 33 m³/t of bovine hides,
- 200-400 m³/1000 sheep skins,
- 12,5 m³ / 1000 rabbit skins,
- 8,5 m³/1000 furskins of aquatic animals.

In turn, Mendrycka and Stawarz (2012) report that water consumption in plants can be as high as 40-60 m³ per tonne of raw hides. The level of pollution and volume of wastewater depends on the tannery's rhythm of operation, the type of leather processed, the technology and mainly the preparation and tanning processes (Malovanyy et al., 2020). The aim is to reduce water consumption and reuse baths in the cycle with the use of pro-ecological technologies (Rüffer & Rosenwinkel, 1998).

The aim of the study was to determine the composition of wastewater generated in a small tannery plant in the Podlaskie Province at different stages of the technological process. This will allow the evaluation of the biodegradability of wastewater generated during production and the concentration of chromium compounds in them and to slowly propose a concept of their pretreatment and conduct preliminary experiments.

In one tannery in the Podlaskie Province, the water consumption was 21.43 m³/t, with 39 pieces per ton of raw hides (Dziadel & Ignatowicz, 2022). Assuming an average skin size of 4 m², the mentioned volume of wastewater per square meter of finished skin is about 137.4 dm³. The weight of one square meter of leather of average thickness being about 1 kilogram makes it possible to conclude that one ton of readily marketable leather absorbs more than 137 m³ of water in the production processes. This total volume represents mainly wastewater from pre-tanning and tanning operations, wet-finishing operations and all activities related to the use of water for non-production purposes, such as the washing of machines, floors and sanitary needs. Assuming the total volume of produced wastewater to be 30 m³ for a batch of 1400 kg of hides, the volume of wastewater per one ton of hides is 21.43 m³. Since the production capacity of the plant is variable, depending on the period, 3 or 4 full production cycles were carried out per month. Therefore, assuming that each cycle was identical, the plant generates between 90 and 120 m³ of wastewater per month.

In many tanneries, methods are used to separate wastewater streams, especially the separation of chromium wastewater. The separation of wastewater allows to management it in different ways, e.g. in the case of chromium wastewater after the tanning process, chromium recovery technologies are used since it is not completely used in the process, and even in excess to ensure the proper tanning of hides. In addition to chromium recovery, techniques are used to reuse chromium wort with a small addition of fresh chromium. This reduces the amount of nuisance wastewater generated after processes that cannot be disposed of by primary treatment plants and from which the chromium content can be further utilised. Management of wastewater is a financial nuisance for small plants. The need to conclude contracts with specialised treatment plants, storage and long-distance transport of sewage, also by the respective companies, generates considerable costs, which may be a limiting factor of the willingness to invest in production. Wort reuse reduces the cost of purchasing chromium as a bath ingredient, reduces the frequency of waste disposal and significantly reduces company costs. Separating chromium from the general or otherwise residual wastewater stream also allows the wastewater to be managed in a different way. Pre-treatment plants in, the plant reduces effluent contamination parameters to levels that allow the effluent to be discharged to the local sewer if possible and then

treated at the local sewage treatment plant. For plants that can afford the investment both financially and in terms of land, a hydrophytic treatment plant may be applicable, where the wastewater could be disposed of after preliminary treatment. Treatment of wastewater in its own area, even a part of the total outflow, contributes to the reduction of costs of its disposal. If the outflow of treated wastewater is suitable for reuse in processes, it would also reduce the amount of water taken from waterworks, further lowering costs with the additional pro-environmental effect of saving water. However, this requires separation of chromium compounds whose concentrations are significant.

Wastewater samples were collected in 2021 during processes of leather production. The following samples were collected from the constituting processes:

- 1) mixed drains from presoak and soak,
- 2) mixed effluent from the initial steeping, the actual steeping and the liming process,
- 3) drain from decalcification taken directly from the drum,
- 4) mixed effluent from the preliminary steeping, proper steeping, liming, decalcification and pickling processes,
- 5) mixed effluent from pickling and tanning processes.

Samples were collected from the general wastewater tank, the chromium wastewater tank and directly from the bathing sink. Each time wastewater samples were filtered, and each of the following parameters were being determined in accordance with the applicable methodology (Lozowicka et al., 2016; Ignatowicz, 2009, 2011; Manjushree et al., 2015):

- Suspension – filtration method through a quantitative medium filter, previously weighed, dried and reweighed,
- pH – potentiometric method, HQD probe with INTELLICAL sensors, according to PN-EN ISO 1053:2012 standard,
- Conductivity – conductometric method, HQD probe with INTELLICAL sensors, according to PN-EN 27888:1999 standard,
- COD – dichromate spectrophotometric method, Hach thermoreactor, Merck Pharo 300 spectrophotometer, Merck cuvette tests, according to PN-ISO 15705:2005 standard,
- BOD₅ – manometric method, OxiTop Standard system, WTW TS 606/2 thermostatic cabinet, according to PN-EN 1899-2:2002 standard,
- Chlorides – Argentometric method by titration with a standard solution of AgNO₃ in the presence of K₂CrO₄ as an indicator,
- NH₄⁺ – spectrophotometric method, Merck Pharo 300 spectrophotometer, according to PN-ISO 7150-1:2002 standard,
- Chromium – Atomic Absorption Spectrometry method on Thermo Scientific™ iCE™ 3500 apparatus, after wastewater mineralisation with BUCHI

K-425 block mineraliser in a mixture of concentrated nitric acid and hydrogen peroxide.

Results and discussion

The characteristic features of tannery wastewater are odor, turbidity and colouration. They contain large amounts of organic compounds (such as proteins and fats) and inorganic compounds, including chromium and nitrogen sulfide. The acids, bases, chromium (III) salts, sulfides and many other substances used in the processes remain in the wastewater (Przywara, 2017). Table 2 shows the average pollutant values contained in the wastewater at one of the tanneries.

Table 2. Average effluent contamination rates at different stages of the skin treatment

Wastewater	Parameter							
	Suspension	pH	Conductivity	NH ₄ ⁺	COD	BOD ₅	Cl ⁻	Cr
	g/dm ³	–	μSm/cm	mgN _{NH4} /dm ³	mgO ₂ /dm ³	mgO ₂ /dm ³	mgCl/dm ³	mgCr/dm ³
Mixed with soak	3.23	6.70	64.80	109.00	14,500	2,000	27,300	–
Mixed with soak and liming process	1.16	9.08	44.60	14.90	14,300	1,900	1,800	–
From decalcification drum	1.496	8.91	27.504	33.20	6,620	1,200	1,200	–
Mixed with soak, liming, decalcification and pickling processes	3.30	8.46	34.50	278.02	10,180	2,400	3,500	–
Mixed from pickling and tanning processes	1.61	3.67	61.60	–	8,290	–	17,700	2,200

Source: author's work based on Dziadel & Ignatowicz, 2022.

The suspended solids content of the tested wastewater varied between 1.09 and 3.39 g/dm³. Its amount depends mainly on the moment of sampling and the degree of mixing of the wastewater in the general tank where it is collected. The suspended solids in the effluent consisted of fragments of solids, detached remains of skins or undissolved hair. Since the different baths

required the use of different substances, the environment in which the hides were housed was variable, resulting in changes in its pH from 3.67 to 9.08. In most of the processes, the reaction is alkaline, only in the pickling process, the sulfuric acid used acidifies the volume of the bath in order to prepare the hides for the proper conduct of chromium tanning, a better binding of the tannin. According to Manjushree (2015), the pH of the effluent at different stages of leather tanning ranged from 3.8 to 12.5. Ammonium nitrogen ranging from 14.90 to 278.02 $\text{mgN}_{\text{NH}_4}/\text{dm}^3$ was present in the effluent in higher amounts after the soaking process, which washes away the impurities from the hides, including nitrogen-rich faeces.

A significant increase in ammonia nitrogen occurred in mixed effluent after processes including decalcification which is related to the use of ammonium sulfate for skin dehairing, removal and dissolution of fur. Christopher et.al. (2016) reported an average value of ammonia nitrogen in tannery wastewater of 10,000 $\text{mgN}_{\text{NH}_4}/\text{dm}^3$. In the case of chlorides, the first source of chlorides is the way the leather is preserved before tanning. Salt from salted leather is washed from it during the naming process, and its concentration in the wastewater is very high (27300 mgCl/dm^3). The second source is the pickling process, in which salt is one of the substances required in the process, hence its high content in chromium wastewater (17700 mgCl/dm^3). The lowest chloride content was found in the effluent after the decalcification process (1200 mgCl/dm^3). Referring to Manjushree (2015), the amount of chloride was 5005 mg/dm^3 . High chloride content ($>1000 \text{ mg}/\text{dm}^3$) in water, can lead to human diseases and affect plant growth. The main wastewater polluting processes in COD and BOD_5 parameters are the soaking and liming stages of the skins. COD contents ranged from 8290 mgO_2/dm^3 to 27300 mgO_2/dm^3 and BOD_5 from 1200 to 2400 mgO_2/dm^3 . These two parameters show a relationship towards each other indicating susceptibility to biological decomposition. Referring to Manjushree (2015), the mean value of COD and BOD_5 from the selected plants were 700 ± 10 to $2400 \pm 70 \text{ mgO}_2/\text{dm}^3$ and 7200 ± 20 to $71040 \pm 40 \text{ mgO}_2/\text{dm}^3$, respectively. Based on Christopher (2016), the mean value of COD was 250,000 mgO_2/dm^3 , and BOD_5 was 50,000 mgO_2/dm^3 .

Of the 4 effluent types, only the mixed effluent from all processes from naming to etching had a BOD_5/COD ratio of 0.24, defining these effluents as slowly degradable (Dziadel & Ignatowicz, 2022; Karamus, 2017). In the studied wastewater samples collected during the successive stages of production, chromium was only present in the wastewater mixed from the pickling and tanning process coming from a separate chromium wastewater tank. The average chromium concentration of $2200 \pm 180 \text{ mgCr}/\text{dm}^3$, with a minimum value of 2000 and a maximum value of 2460 mgCr/dm^3 . This chromium comes from the tanning process using chromium tannins, specifically alka-

line chromium sulfate. No biodegradable organic compounds (BOD_5) were found in this wastewater, and nitrogenous compounds are not used in this process. Based on Manjushree (2015), the chromium content, on average, in the wastewater was 2075 mgCr/dm^3 . On the other hand, Christopher et al. (2016) reported an average concentration of chromium in wastewater of only 500 mgCr/dm^3 . The significant concentrations of chromium in wastewater and the high use of these compounds by up to 90% of all tanning facilities boil down to the fact that the tanning industry is considered one of the most polluting in the world and responsible for about 40% of global chromium pollution (Bień et al., 2017; Celary & Sobik-Szołtysek, 2014; Chmielowski, 2019).

Conclusion

The tanning of hides and skins carried out by tanneries involves a number of different operations which change the properties of the hide so that it is best prepared for the next process and ultimately becomes high quality and a high value product. The most water consuming processes are the wet-shop processes from the beginning to tanning, where each stage requires a separate bath and numerous rinses. The overall water consumption depends greatly on the specific plant. According to different data, the volume of wastewater generated per ton of raw hides is about 15 m^3 (Chmielowski, 2019), 33 m^3 (Bartkiewicz & Umiejewska, 2010), and even $40\text{--}60 \text{ m}^3$ (Mendrycka & Stawarz, 2012). The literature data is corroborated by one of the smaller tanning facilities, where the tanning processes of a ton of raw hides consumed 21.43 m^3 (Dziadel & Ignatowicz, 2022). While the absorption of such large quantities of water, if available, may not be a problem in these plants, the resulting corresponding quantities of wastewater are already their nuisance. Due to the the variable nature of the wastewater, its quality requires appropriate approaches such as the separation of partial effluent streams to separate chromium compounds from the wastewater, providing appropriate treatment or an additional pre-treatment. The inconveniences faced by the plants make it a difficult business, and the leather industry has been witnessing declines year after year in recent times. The lower production of leather goods is indicative of a reduction in tannery production, which is confirmed by the data of the Central Statistical Office. The unfavourable image of the industry may, in time, lead to a situation where the tanning profession will be considered extinct.

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The contribution of the authors

The article was written in collaboration with all authors.

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