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Characteristics of wastewater from various tanning processes: A comparative approach

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ABSTRACT

The article presents a characterization of two tannery plants located in Poland in the context of processes related to leather tanning and wastewater management. It highlights the difficulties associated with the large volume of wastewater generated as a result of various technological operations using diverse chemical agents. A particular challenge is posed by chromium-containing wastewater, which requires separate collection and specialized treatment due to its high chromium content. Such streams should not be combined with general facility wastewater. The article also presents the results of wastewater studies from different tannery plants, showing differences in the composition of general wastewater as well as wastewater generated directly after soaking, liming, deliming, and tanning processes. Chromium concentration in post-tanning baths exceeded 2000 mg/dm^3 in both plants, far above legal emission limits, highlighting the need for chromium recovery solutions.

Keywords: tannery, chrome, industrial wastewater.

INTRODUCTION

Tannery plants constitute the foundational stage of the leather industry. Their operations are based on the processing of raw animal hides. Tanned leather and raw hides differ substantially in their resistance to degrading factors. Improper storage conditions promote the rapid decomposition of hides as a result of microbial growth. The essence of the tanning process lies in the penetration of tanning agent particles between collagen chains and the formation of cross-links (network-forming bonds) between the collagen chains and the tanning agent [1]. As a result, leather fibers become resistant to the activity of microorganisms, do not shrink, and do not harden after drying. Putrefactive processes may lead to permanent damage to the grain layer. Currently, basic chromium sulfates are used in nearly 90% of tanneries worldwide [2–4]. Trivalent chromium salts, Cr(III), which are stable and exhibit low toxicity, are commonly employed. However, they must be clearly distinguished from hexavalent chromium, Cr(VI), which has been proven to have mutagenic and carcinogenic effects. Chromium(VI) does not occur intentionally in wastewater but appears as a result of undesirable oxidation of the trivalent form. This may occur at various stages of the product life cycle, including in wastewater – where it is promoted by high pH and the presence of oxidizing agents, and even in finished products, such as footwear. This process is often slow and associated with leather aging or exposure to UV radiation. It is also frequently a consequence of the use of low-quality chemical agents which, through the release of free radicals, lead to the conversion of the relatively safe Cr(III) into toxic Cr(VI) [5].

The operations carried out in tanneries are associated with a significant environmental impact. Leather processing encompasses numerous technological procedures performed in dry, wet, and finishing workshops [6–8]. The vast majority of these operations require an aqueous environment, in which hides undergo soaking and subsequent rinsing. Consequently, wet operations are the most water-consuming among all stages of production, consuming between 30 and 60 m³ per ton of raw hides [8–11]. The final volume of water used depends not only on the specific tanning method but also on the technological capabilities of the plant, its level of development, and the implementation of closed water circulation systems [12]. It is estimated that wastewater may contain up to 85% of the chemicals used in the tanning process [13]. Wastewater parameters are highly variable and depend on the specific operation, resulting in considerable fluctuations in composition. The effluents contain a wide spectrum of pollutants, including organic and inorganic compounds, mineral salts, tanning agents, acids, bases, dyes, solvents, proteins, hair, and solid particles, which is reflected in high values of COD and BOD_5 indicators, as well as in their strong odor [14–16].

In waste management, it is essential to distinguish between two wastewater streams. Particular attention must be given to chromium-containing effluents generated during the tanning process. Due to their specific composition and high content of heavy metals, these effluents require a tailored approach, including separate collection and specialized treatment methods. However, an advantage of this wastewater type is its considerably smaller volume compared to general wastewater, which translates into less frequent disposal and lower transportation costs.

The remaining effluents (excluding chromium-containing streams) are treated as general wastewater. Their combined collection leads to the averaging of pollutants, which is beneficial given the differences in composition among individual partial discharges. In the case of general wastewater, it may be discharged into the municipal sewer system (subject to obtaining the necessary permit) or require on-site pre-treatment. Consequently, the high volume of general wastewater is a primary argument for investing in water-saving technologies and loss minimization, although financial barriers often hinder such implementations [17]. More advanced plants may implement solutions for chromium recovery and its reuse. By recycling spent tanning baths, only a significantly smaller amount of fresh chromium tanning agent needs to be added, resulting in dual benefits: a reduced actual volume of wastewater generated during the tanning process and a decreased consumption of tanning chemicals.

Description of the study objects

The study covered two production facilities located in Poland, both processing bovine hides intended for footwear, but differing in scale and infrastructure. Facility A, located in the north-eastern part of the country, represents a model of a small-scale artisanal tannery. Its average monthly processing capacity is approximately 4 tons of raw hides. Due to its smaller scale and specific equipment, the average water consumption per ton is about 29 m³, generating a wastewater stream of approximately 120 m³ per month. Facility B, located in central Poland, is characterized by a higher production capacity (up to 10 tons of raw hides per month) and more modern technological infrastructure. Nevertheless, a higher unit water consumption of approximately 34 m³/t was recorded, resulting in a total monthly wastewater volume of around 340 m³. This higher unit water consumption may be attributed to insufficient optimization of the loading of tanning drums, which, as large-capacity devices, require maintaining a minimum bath volume when operated below full capacity, consequently increasing water usage per ton of hides. The differences may also stem from internal factors within the facility, including water used for sanitary purposes, workplace hygiene, and cleaning of machinery and floors, which constitute a significant component of the overall wastewater balance. However, apart from differences in the weight of processed hides and the resulting volume of wastewater, the processes in the analysed plants are carried out according to the same production cycle. In very similar way it is illustrated schematically for a typical tannery in Figure 1.

In both tanneries production cycle begins with sorting and, if necessary, preservation of the hides. Salt is commonly used for this purpose, its aim to inhibit microbial growth, which would otherwise trigger irreversible putrefactive processes. Additionally, preservation allows the start of the production cycle to be delayed in order to adjust it to the processing capacity of the tannery. First process is soaking, which aims to restore the hides' proper moisture content, soften them, and remove surface contaminants. The subsequent operation is fleshing, which involves the mechanical removal of subcutaneous tissue and remaining meat residues. As a result of this process, the hides become lighter, which directly reduces the amount of chemicals required in

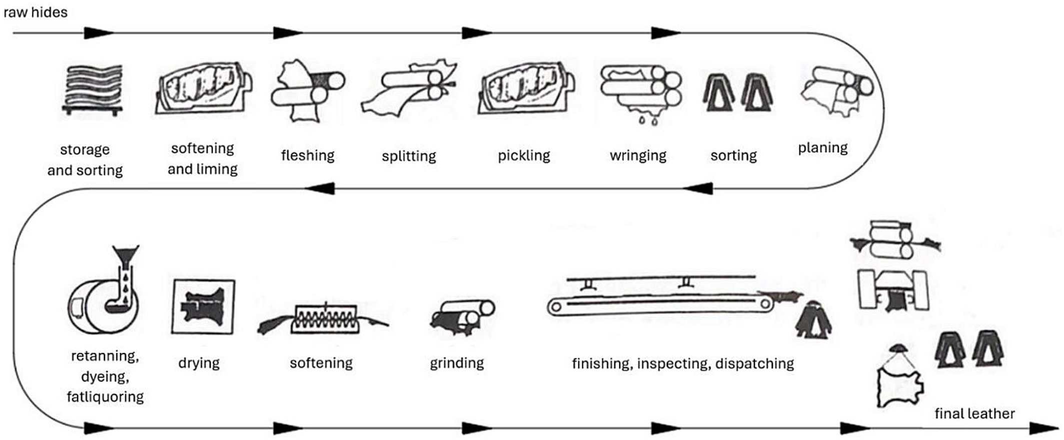

Figure 1. Schematic of the production processes in a tannery [12]

subsequent processing stages. The next stage is liming, leading to the hydrolysis of keratin. Concurrently, hair removal takes place, facilitated by the alkaline swelling of the hides. This process aids in opening the hair follicles and simplifies the removal of hair from the grain surface. The operation is carried out in a continuously rotating drum, additionally equipped with internal paddles that agitate the bath, while the hides rub against each other, further promoting efficient hair removal. The high pH of the liming bath affects the hides, often necessitating even two subsequent rinsing baths to more effectively neutralize the impact of the liming process. The swelling of the hides is an undesired effect and is reversed during deliming. By applying a bath of lower pH, the hides are deswelled, and their thickness is reduced to the level prior to liming. This process aims to regulate the condition of the hides following liming by lowering the pH of both the bath and the hides themselves. The next stage is pickling, purpose of this process is to further reduce the pH of the bath and the hides, which facilitates tanning and also allows the hides to be stored for a longer period prior to the main tanning process. The bath is highly acidic, with a pH of approximately 3.5. When tanning is carried out immediately afterward, it can be performed in the same bath by simply adding the tanning agent. Chromium-based tanning agents are most commonly used due to their rapid binding time and the considerably higher reliability of the process, which is intended to permanently protect the hides from degradation. The processes involved in the first wet workshop of leather production, the chemicals used and wastewater pollutants are described in Table 1. Next, mechanical operations are performed to impart the hides with the desired thickness through splitting and shaving, remove excess water during pressing, and eliminate damaged sections unsuitable for further processing during trimming. Such preparation of hides can be considered the standard tanning procedure in many tanneries. Subsequent processes are associated with the final form of leather. Their characteristics may vary, for example, in terms of coloration or water resistance during wet operations, and further in the final color, grain surface, and softness during finishing operations [18,19].

Despite numerous studies on tannery wastewater, comparative analysis between small-scale and medium-scale Polish facilities remains limited. The primary objective of this research was to determine the composition of wastewater from individual tanning stages and to compare the pollutant loads between two facilities differing in production scale and technological equipment. Comparing plants with identical production cycles allowed for a clear assessment of how technological conditions impact wastewater parameters, with particular emphasis on the environmental burden of chromium following the main tanning process.

MATERIALS AND METHODOLOGY

To ensure the reliability and representativeness of the results in both plants (A and B), sampling was carried out in the same manner. For each technological stage (soaking, liming, deliming, and tanning), instantaneous grab samples were taken directly from the tanning drums immediately after the end of the process, just before

Table 1. Leather production processes, reagents and pollutants based on BAT [13]

Technological stage	Main chemical agents used	Characteristics wastewater pollutants
Soaking	Detergents, biocides, enzymes	High chlorides (salts), blood, dirt, high suspended solids (tss), organic nitrogen, COD, BOD
Liming and unhairing	Hydrated lime, sodium sulfide	Organic nitrogen, ammoniacal nitrogen, COD, BOD, TSS, very high pH>12
Deliming and bating	Ammonium salts, enzymes	Ammonium nitrogen, dissolved proteins, decreased ph, COD, BOD
Pickling and tanning	Sulfuric acid, sodium chloride, basic chromium sulfates	High chlorides, high total chromium contents, very low ph (~3.5), tannins
Post-tanning (retanning, dyeing, fatliquoring)	Synthetic or vegetable tannins, dyes, fatliquoring agents (oils, fats)	Strong color, suspended solids, fats, oils, COD, BOD
Finishing	Pigments, binders, polyurethane dispersions, solvents	Low volume of wastewater (mostly from equipment cleaning), polymeric residues, trace solvents

emptying the used baths. This approach made it possible to capture the final, actual pollution load generated at each specific stage. General (mixed) wastewater was collected directly from the main retention tanks, which – thanks to the cooperation of the plant management – were emptied prior to the studied cycles to prevent contamination from previous operations and accurately reflected only the specific processes covered by the study.

To account for long-term variability in wastewater composition, the monitoring was conducted over a five-month period (June-October 2025). Although both facilities operate regular, multiple production cycles weekly, sampling was conducted once per month, capturing one complete, representative tanning cycle during each monthly sampling event. During each of these five sampled cycles, wastewater was collected directly after individual unit processes (soaking, liming, deliming and tanning). Every collected sample was analyzed in triplicate (three analytical repetitions) to ensure measurement accuracy. The arithmetic mean of these three repetitions was treated as a single, independent data point (n=1). Consequently, the final results are presented as the overall mean of the five independent monthly cycles (n=5) along with the standard deviations.

They were obtained and analyzed in accordance with established methodology, using the equipment and laboratory facilities of the Department of Environmental Engineering at Bialystok University of Technology [20, 21]:

- Suspended solids – determined by filtering samples through medium quantitative filters, which were previously weighed and dried, and then reweighed.
- pH – measured according to PN-EN ISO 1053:2012 using the potentiometric method with an HQD probe equipped with INTELLICAL sensors.
- Conductivity – determined according to PN-EN 27888:1999 using the conductometric method with an HQD probe and INTELLICAL sensors.
- BOD_5 – measured according to PN-EN 1899-2:2002 using a manometric (electrochemical) method with the OxiTop Standard system and a WTW TS 606/2 thermostatic chamber.
- COD – measured according to PN-ISO 15705:2005 using the dichromate spectrophotometric method with a Hach thermoreactor, Merck Pharo 300 spectrophotometer, and Merck cuvette tests.
- Ammonium nitrogen – determined using a spectrophotometric method with a Merck Pharo 300 spectrophotometer, in accordance with PN-ISO 7150-1:2002.
- Chlorides – measured by argentometric titration using a standardized $AgNO_3$ solution in the presence of K_2CrO_4 as an indicator.
- Chromium – determined using flame atomic absorption spectrometry on a Thermo Scientific™ iCE™ 3500, following wastewater mineralization in a BUCHI K-425 block digester using a mixture of concentrated nitric acid and hydrogen peroxide.

RESULTS AND DISCUSSION

The complexity of the chemical processes described in the introductory section is directly reflected in the characteristics of wastewater discharged from tanneries. The actual impact of the production technology on pollutant parameters is illustrated in Tables 2 and 3, which summarize the results of analyses of samples collected immediately after the soaking, liming, deliming, and tanning processes, as well as from mixed wastewater. Additionally, Table 4 shows the pollutant loads per 1 tonne of raw hides processed in plants A and B.

These values in Table 4 refer to average water consumption for the processes mentioned, which is approximately 29 m^3 for plant A, of which 27 m^3 is used for pre-tanning processes and 2 m^3 for tanning, and 34 m^3 for plant B, of which 2.7 m^3 is used for tanning, and 31.3 m^3 for other processes. A higher pollutant load in mixed wastewater per 1 tonne of processed hides is observed for plant A. It is 6% higher for total suspended solids, 9% for ammonium nitrogen, 1.6% for COD, 2% for BOD$_5$, and the largest difference is observed for chlorides which are 20% higher. In the case of tanning wastewater, the pollutant load is higher in plant B by approximately 12.7% for total suspended solids, 12.3% for ammonium nitrogen, 15% for COD, 17% for BOD$_5$, 3% for chlorides and 2% for chromium.

This indicates that while the overall mixed wastewater in both plants carries comparable pollutant loads (with the exception of chlorides), the specific stream from the tanning process in plant B is more heavily polluted. Notably, plant B generates a higher pollutant load per tonne of hides during tanning despite its higher water consumption for this specific stage (2.7 m^3 vs 2.0 m^3). This suggests a less efficient chemical uptake by the hides, or a higher initial dosing of tanning agents compared to plant A, which directly translates into a greater environmental burden per unit of production.

The laboratory results presented in Tables 2 and 3 illustrate a significant variability in pollutant parameters depending on the stage of leather processing, as well as differences arising from the operational characteristics of the two facilities. In both plants, a marked increase in pH is observed in wastewater following the liming process (pH ranging from 12.30 to 12.40). This reflects the actual course of this stage of tanning and the comparable quantities of chemicals used. A similar pattern is observed when analyzing the pH of wastewater after the tanning process; in both cases, due to the action of acids, the effluents exhibit a low pH (ranging from 3.84 to 3.96). These values further indicate the considerable variability of parameters that each bath must meet to ensure proper process performance and the effective treatment of raw hides. The discharge of wastewater from pre-tanning processes into a single tank promotes the averaging of these parameters. In Facility A, general raw wastewater exhibits a more alkaline pH of 9.19, compared to 8.56 in Facility B. This further confirms the proper separation of chromium-containing effluents from those of other processes. The amount of suspended solids in the wastewater is primarily influenced by the soaking and liming processes, during which free contaminants are washed from the hide surface after the initial processing, and hair and epidermal residues are removed and dissolved during liming, with their solid remnants entering the wastewater. Liming is carried out after mechanical fleshing, so fragments of subcutaneous tissue remaining on the hide surface also contribute

Table 2. Parameters of raw wastewater after selected processes in facility A

Parameter [unit]	Wastewater collected after crocess				
	Soaking	Liming	Deliming	Tanning	Mixed
pH [-]	7.69 (± 0.11)	12.40 (± 0.09)	8.43 (± 0.10)	3.84 (± 0.09)	9.19 (± 0.09)
Total suspended solids [mg/dm^3]	2279 (± 141.66)	7043 (± 415.20)	848 (± 64.38)	588 (± 63.60)	3616 (± 379.38)
Conductivity [mS/cm]	47.62 (± 1.97)	16.36 (± 0.84)	10.48 (± 0.63)	56.92 (± 2.73)	21.96 (± 1.29)
Ammonium nitrogen [mg N-NH$_4^-$/dm^3]	82 (± 6.83)	200 (± 22.30)	649 (± 64.30)	103 (± 16.94)	204 (± 23.02)
COD [mg O$_2$/dm^3]	3593 (± 162.41)	19617 (± 1196.35)	4226 (± 247.37)	4053 (± 359.40)	10350 (± 740.37)
BOD$_5$ [mg O$_2$/dm^3]	1244 (± 86.72)	8361 (± 566.53)	1814 (± 130.07)	684 (± 86.78)	4488 (± 325.22)
Chlorides [mg Cl$^-$/dm^3]	27725 (± 2118.37)	4390 (± 385.44)	2090 (± 214.74)	20428 (± 1496.28)	10121 (± 963.58)
Total chromium [mg Cr/dm^3]	-	-	-	2759 (± 333.85)	-

Note: Mean value (± standard deviation).

Table 3. Parameters of raw wastewater after selected processes in facility B

Parameter [unit]	Wastewater collected after crocess				
	Soaking	Liming	Deliming	Tanning	Mixed
pH [-]	7.59 (± 0.10)	12.30 (± 0.09)	8.34 (± 0.11)	3.96 (± 0.09)	8.56 (± 0.11)
Total suspended solids [mg/dm^3]	2034 (± 150.56)	5664 (± 356.13)	650 (± 60.21)	499 (± 42.78)	2930 (± 325.19)
Conductivity [mS/cm]	42.54 (± 1.73)	14.50 (± 0.75)	8.48 (± 0.63)	50.52 (± 1.73)	17.96 (± 1.29)
Ammonium nitrogen [mg N-NH_4^-/dm^3]	68 (± 8.38)	168 (± 15.37)	549 (± 57.63)	87 (± 9.80)	159.60 (± 17.34)
COD [mg O_2/dm^3]	3094 (± 167.31)	16712 (± 922.43)	3628 (± 249.34)	3528 (± 256.26)	8784 (± 636.66)
BOD$_5$ [mg O_2/dm^3]	1043 (± 78.31)	7036 (± 394.50)	1503 (± 125.81)	610 (± 55.00)	3794 (± 264.92)
Chlorides [mg Cl$^-$/dm^3]	22372 (± 1644.02)	3238 (± 452.36)	1445 (± 167.41)	15642 (± 1375.67)	6941 (± 634.59)
Total chromium [mg Cr/dm^3]	-	-	-	2084 (± 84.02)	-

Note: Mean value (± standard deviation).

Table 4. Analysis of pollutant loads in mixed wastewater and wastewater after the tanning process

Parameter in kg/tonne of raw hides	Wastewater type, plant			
	Mixed		After tanning	
	A	B	A	B
Total suspended solids	97.63	91.71	1.18	1.35
Ammonium nitrogen	5.51	5.00	0.21	0.23
COD	279.45	274.94	8.11	9.53
BOD$_5$	121.18	118.75	1.37	1.65
Chlorides	273.27	217.25	40.86	42.23
Total chromium	-	-	5.52	5.63

to the suspended solids in the effluent. In Facility A, the measured suspended solids after these processes were 2279 and 7043 mg/dm^3, respectively, while slightly lower values were recorded in Facility B: 2034 and 5664 mg/dm^3.

The concentration of ammonium nitrogen in the wastewater reaches its highest level after the deliming process, during which ammonium salts are applied. After this stage, the average concentration was 649 mg N-NH_4^+/dm^3 in Facility A and 549 mg N-NH_4^+/dm^3 in Facility B. The lowest concentrations were recorded after the soaking process, with values of 82 mg N-NH_4^+/dm^3 for Facility A and 68 mg N-NH_4^+/dm^3 for Facility B. The wastewater is characterized by high salinity, with the highest chloride concentrations observed after the soaking process: 27 725 mg Cl$^-$/dm^3 in Facility A and 22 372 mg Cl$^-$/dm^3 in Facility B. Following the tanning process, chloride concentrations were 20.428 mg Cl$^-$/dm^3 and 15.642 mg Cl$^-$/dm^3 in Facilities A and B, respectively. Similar values were reported by Bhardwaj et al. [22], who found chloride concentrations of 22 500 mg Cl$^-$/dm^3 after soaking and 20 000 mg Cl$^-$/dm^3 after tanning. The electrical conductivity of the wastewater correlates with its high salinity (from hide preservation before soaking and the presence of sodium chloride in the tanning bath), but it is also enhanced by the use of acids, such as sulfuric and formic acid, which are applied to acidify the bath for the tanning process. This indicates that, in addition to salt, the presence of acids also influences wastewater conductivity. The highest conductivity values were recorded after the tanning process, reaching 56.92 mS/cm in Facility A and 50.52 mS/cm in Facility B, and after soaking, with 47.62 mS/cm (A) and 42.54 mS/cm (B). This relationship is illustrated in Figure 2, showing conductivity values relative to chloride content in the wastewater.

The most significant concern is the chromium content in the wastewater, which was measured only in effluents from the tanning process. In both facilities, the chromium concentration was substantial, but highest in Facility A, where it reached approximately 2759 mg Cr/dm³ – over 30% higher than in Facility B, which had an average value of 2084 mg Cr/dm³. This primarily reflects the high saturation of the tanning bath with chromium and its incomplete utilization. The values obtained for Facility B are comparable to those reported by Manjushree et al. [23], who recorded 2075 mg Cr/dm³, and by Bhardwaj et al. [22], who reported 2250 mg Cr/dm³ in wastewater following tanning. From a technological perspective, the excess tanning agent ensures greater reliability and guarantees the appropriate duration and quality of leather tanning, which is crucial for the final protection of the hides against degradative factors. However, from an environmental standpoint, this represents a highly hazardous source of pollution. These findings suggest the potential for implementing chromium bath recycling, which would allow the unused chromium to be returned to the process and reduce the consumption of fresh raw materials.

The results obtained indicate a serious environmental challenge in the context of current legal standards. According to the European reference document on best available techniques (BAT-AEL) for the tanning industry, the permissible levels of total chromium emissions in direct wastewater discharges range from 0.3 to 1.0 mg Cr/dm³ [13]. Similarly, Polish national regulations – the Regulation of the Minister of Maritime Economy and Inland Navigation of 12 July 2019 – classify chromium as a substance particularly harmful to the aquatic environment, the release of which should be limited. In the case of the tanning industry, a strict limit has been introduced for wastewater discharged into the environment, where the permissible value for total chromium is a maximum of 1 mg Cr/dm³ [24]. A limit for chromium (VI) has also been set at 0.05 mg Cr/dm³. In turn, restrictions on direct discharge into the sewage system are specified in the Announcement of the Minister of Infrastructure and Construction of 29 September 2016, which sets the limit for total chromium at the same level of 1 mg Cr/dm³ for industrial wastewater, and for chromium (VI) at 0.2 mg Cr/dm³ [25]. Polish regulations impose a very high limit for chromium (VI), although it is not used in tanning, does not act as a tanning agent, and its trace amounts may arise as a result of the oxidation of chromium (III), which means that its detected levels are usually minimal or below the detection limit. When comparing the values obtained for plants A and B, they exceed the permissible standards, indicating a very high need and, therefore, the likely potential for the need to introduce solutions to retain chromium in circulation, for example by recycling the tanning bath or other possible forms of chromium recovery from the used bath. The standard and commonly used industrial method for such recovery is alkaline precipitation (e.g., using MgO or NaOH), followed by redissolution in sulfuric acid. However, a prerequisite for the economic

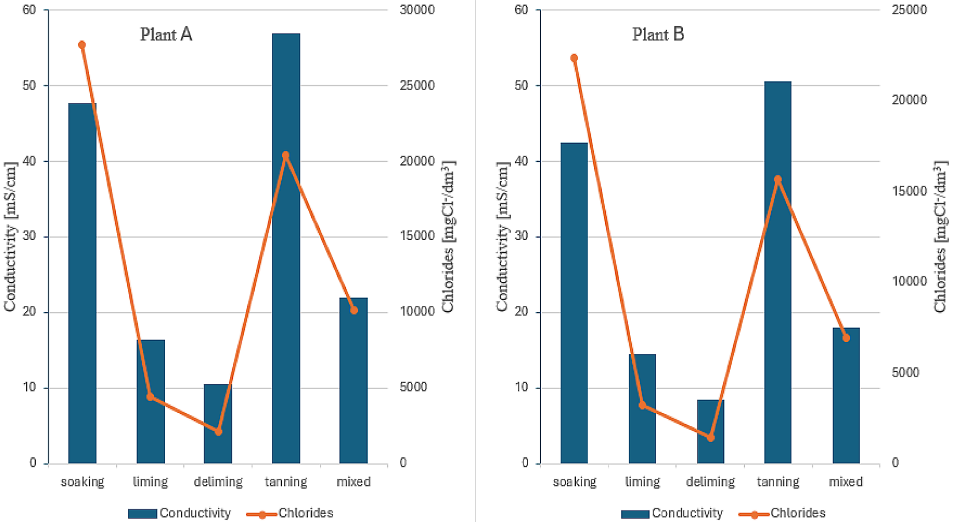

Figure 2. Variations in salinity (chloride concentration) and conductivity during the technological cycle in Plant A and Plant B

and technological feasibility of this method is the complete separation of the chromium stream from other alkaline wastewaters to prevent premature precipitation and contamination of the recovered chromium sludge. Despite its widespread use in industry, this technique currently receives limited attention in the latest scientific literature and reviews [13,16]. Therefore, it may only be available to larger plants that can conduct additional research into the practical application of the method. Another solution that is easier to implement and brings measurable benefits is the recycling of used tanning liquor, which contains significant amounts of chromium from the previous process, to which only a small amount of fresh chromium needs to be added, thus reducing the amount of tannin added and limiting the total amount of wastewater and pollutant load.

The wastewater was also analyzed for oxygen demand parameters, COD and BOD_5, in effluents from selected technological stages. The highest chemical oxygen demand was observed after the liming process, resulting from the drastic increase in pH and the hydrolysis of protein structures in the hides, reaching 19 617 mg O_2/dm^3 in Facility A and 16 712 mg O_2/dm^3 in Facility B. The soaking, deliming, and tanning processes exhibited similar COD values, with the next significant increase observed in the general raw wastewater, where concentrations were 10 350 mg O_2/dm^3 in Facility A and 8784 mg O_2/dm^3 in Facility B. A similar pattern was observed for biochemical oxygen demand. The highest values were again recorded after liming, reaching 8361 mg O_2/dm^3 and 7036 mg O_2/dm^3 in Facilities A and B, respectively. The mean BOD_5 values in general raw wastewater were 4488 mg O_2/dm^3 for Facility A and 3794 mg O_2/dm^3 for Facility B. After the other processes, BOD_5 values were more comparable, although they exhibited greater variability than COD. These values and their comparison are illustrated in Figure 3.

A more detailed analysis of wastewater with respect to these parameters, specifically the BOD_5/COD ratio, makes it possible to determine the biodegradability of wastewater and its susceptibility to biological degradation. Generally, biological treatment is considered feasible when the BOD_5/COD ratio exceeds 0.3–0.4. Therefore, in the case of general wastewater which is directed to the wastewater treatment plant, a BOD_5/COD ratio of approximately 0.43 is obtained, indicating normal to good biodegradability and allowing for the application of methods such as, for example, hydrophytic treatment. Achieving such an index is facilitated by the collection of partial effluents from individual processes into a single common tank, where the wastewater undergoes averaging and its parameters become equalized, resulting in the homogenization of concentrations and the elimination of extreme values. A completely different situation is observed for chromium-containing wastewater; in both plants the BOD_5/COD ratio is below 0.2, which indicates a lack of biodegradability of these effluents [26]. This is consistent with the obtained parameters of this wastewater, including very low acidic pH and a high chromium content, which is a toxic factor, with concentrations in both cases exceeding 2000 mg Cr/dm^3.

Table 5 presents the average values of pollution indicators for raw general wastewater originating from various tannery plants (designated Z1–Z6). These are mixed wastewaters generated throughout the entire production line and equalized in retention tanks. The analysis included key parameters such as total suspended solids, pH, BOD_5, COD, and chromium concentration. The highest concentration of suspended solids was recorded in plant Z4 (27 600 mg/dm^3). This value is ten times higher than that observed in plant Z2 (2750 mg/dm^3) and more than 27 times higher than in the remaining plants. Such a pronounced difference may indicate specific technological characteristics of this plant or the collection of samples during a temporary discharge of accumulated solids. The amount of suspended solids in plants A and B reached slightly higher but comparable levels in general wastewater to those observed in plant Z2.

The wastewater pH in all analyzed plants exhibited an alkaline character. In plants Z1, Z2, Z3, and Z6, pH values ranged from 7.2 to 7.8, whereas distinctly higher values were recorded in plants Z4 (8.35) and Z5 (8.50). The pH of raw wastewater from plant B (8.56) was very close to that observed in plant Z5, while wastewater from plant A was the most alkaline (pH = 9.19). These results are consistent with the data reported by Tanko et al. [33], who observed pH values in the range of 8.80–9.10 for raw tannery wastewater. However, differences in suspended solids content should be noted. The values reported by Tanko et al. [33] ranged from 489 to 567 mg/dm^3 and are comparable to the results obtained for plants Z5 and Z6, but significantly lower than those observed in plants Z4, A, and B.

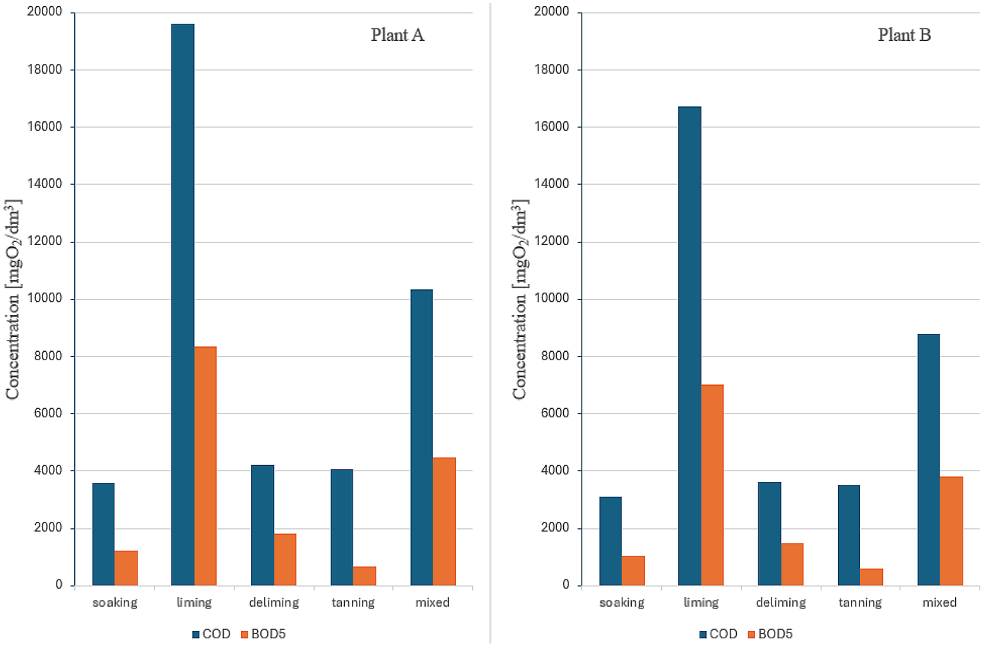

Figure 3. Comparison of COD and BOD_5 concentrations during the technological cycle in Plant A and Plant B

Table 5. Selected parameters of raw general wastewater generated after processing in various tannery plants: Z1 [27], Z2 [28], Z3 [29], Z4 [30], Z5 [31], Z6 [32]

Average values of pollution parameters	Origin of wastewater – production plants					
	Z1	Z2	Z3	Z4	Z5	Z6
Suspended solids [mg/dm^3]	980	2750	778	27600	391	428
pH [-]	7.28	7.40	7.8	8.35	8.5	7.2
BOD_5 [mg O_2/dm^3]	561	903	803	4200	1405	164
COD [mg O_2/dm^3]	2961	2200	5400	11500	2821	1186
Cr [mg Cr/dm^3]	89.52	235.0	-	-	28.0	11.73

Similarly to the analysis of individual processes presented in Tables 2 and 3, the BOD_5 values in general wastewater were consistently lower than the COD values. The BOD_5/COD ratio, which is an indicator of wastewater susceptibility to biodegradation, was below 0.20 for plants Z1, Z3, and Z6, suggesting potential difficulties in biological treatment. More favorable parameters were observed in plants Z2 (0.410) and Z4 (0.365), and particularly in plant Z5 (0.498), indicating a high content of biodegradable organic matter. It should be noted that both BOD_5 and COD exhibited substantial variability among the analyzed plants. COD values varied widely, ranging from approximately 1200 to 11 500 mg O_2/dm^3, which can be attributed to differences in production scale and the degree of wastewater dilution. In the case of plants A and B, BOD_5/COD ratios similar to those observed for plant Z2 were obtained.

The chromium concentration in general wastewater was lower than that observed in post-tanning baths (Tables 2 and 3) as a result of dilution with other wastewater streams. The highest value was recorded in plant Z2 (235.0 mg Cr/dm^3), an intermediate level in plant Z1 (89.52 mg Cr/dm^3), and the lowest concentrations in plants Z5 and Z6 (28.0 and 11.73 mg Cr/dm^3, respectively). Despite dilution, these values remain higher than those reported by Tanko et al. [33], where chromium concentrations did not exceed 9.80 mg Cr/dm^3. This indicates either the combined collection of chromium-containing and general wastewater or insufficient control over chromium ingress into other wastewater streams. However, regardless of how chromium wastewater is treated at plants Z1-Z6, its concentration is also many times too high compared to the limits set out in BAT.

CONCLUSIONS

The final product of a tannery occurs at the cost of a significant environmental burden on water resources, particularly during wet workshop operations. The complexity of individual unit processes and their diverse impact on wastewater composition present substantial technological challenges regarding the selection of collection and treatment methods. Detailed comparative analysis revealed varying dynamics depending on the wastewater stream. While Plant A generated higher overall unit pollutant loads in mixed wastewater (e.g., 20% higher chlorides and 6% higher total suspended solids), plant B exhibited significantly higher unit loads specifically during the tanning stage, including 15–17% higher COD and BOD_5 per tonne of raw hide. A key issue remains the high chromium concentration in post-tanning baths, which in this study exceeded 2000 mg Cr/dm^3 (2759 mg Cr/dm^3 and 2084 mg Cr/dm^3 in plants A and B, respectively). These values exceed the permissible concentrations by thousands of times in relation to BAT-AEL and Polish National Regulations. This reflects a considerable excess of tanning agent in the process, which should not be viewed solely as a wastewater treatment problem but also as a resource potential. This creates an opportunity for the implementation of recycling technologies and the recovery of chromium-containing baths (from which the simplest method seems to be the recycling of used tanning baths), enabling reductions in raw material consumption and providing tangible economic and environmental benefits. It should be emphasized, however, that due to the specificity of production, processing methodology, and the type of hides treated, each plant requires an individual assessment of the feasibility of such solutions. Which argues for the need for more detailed research in the context of the percentage use of baths. Furthermore, it is highly recommended to investigate the technological and economic feasibility of implementing pilot-scale chromium recovery and recycling systems tailored specifically for small and medium-sized enterprises in the region.

It is not only tanning wastewater that can benefit from new solutions. The cases analyzed present mixed wastewater with a BOD_5/COD ratio of approximately 0.43, which indicates its biodegradability. This gives the green light for the use of hydrophytic methods where the terrain allows, integrating "green" technologies into the production cycle and ultimately enhancing the overall environmental sustainability of the plant.

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