

## Assessment of the Quality of Wastewater Generated During Production at a Tannery Plant

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### ABSTRACT

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. Since the plant uses chromium salts for the actual tanning process and the resulting wastewater is separated into two streams, it was possible to determine the content of chromium and other pollutants in the wastewater at different stages of the production processes. This allowed us to evaluate the biodegradability of the wastewater produced during production, the concentration of chromium compounds and other contaminants. Based on the results obtained, the wastewater generated during the production process was found to be non-biodegradable (except for the mixed wastewater) with chromium concentrations of 2.0–2.46 g/dm<sup>3</sup>.

**Keywords:** industrial wastewater, tannery, chrome.

### INTRODUCTION

Leather processed in a tannery leaves the factory as a clean, high-quality product, representing a class, which is in contrast to a number of processes associated with leather tanning. These involve the use of technological processes, a considerable amount of water, chemicals both artificial and of natural origin as well as fixatives and finishing agents. This consequently gives the leather new properties, durability and aesthetics. It generates, however, a significant amount of wastewater which poses problems related to its storage and the need to separate it into two streams in order to separate chromium compounds from the rest of the wastewater, as well as its treatment. Basic chromium sulphates are the basic tanning agents used in more than 90% of tanneries worldwide. Methods for their synthesis were developed in the 19th century, when modern tanning started on chromium tannins [Famielec 2014]. In addition to chromium(III) salt solutions, chromium worts are often used [Kubala and Przywara 2015]. In general, the processes implemented in tanning plants related

to leather tanning consist of a series of complex chemical reactions and mechanical processes [Chmielowski 2019, Lenort et al. 2017]. A typical scheme of the processes occurring in a tannery plant is shown in Figure 1. It takes into account the reagents used at each stage and the effluents generated during the process. The effluent generated during the leather outfitting has its origin primarily in the wet stages. In addition to the actual baths containing the appropriate agents, multiple rinses are used in between, generating further amounts of wastewater. It is assumed that water consumption per ton of raw hides is in the range of 40–60 m<sup>3</sup>, which is also influenced by the size of the tanning facility [Mendrycka and Stawarz 2012]. The volume and composition of the resulting wastewater is characterized by a high variability of parameters depending on the plant, the scale of production and the way of conducting water and wastewater management in it. [Dymaczewski 2011] An example of wastewater discharge is shown in Figure 2.

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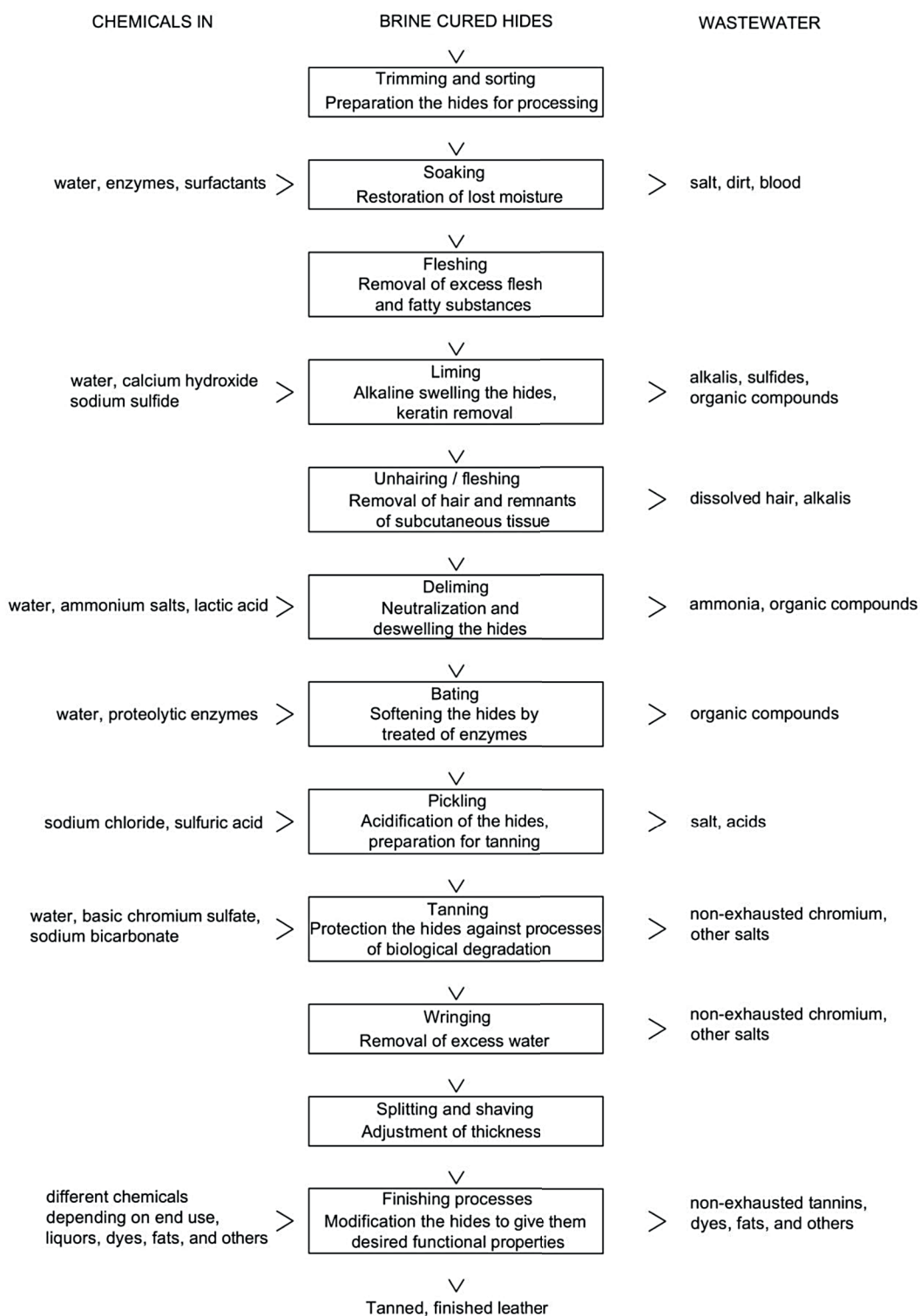


Figure 1. Schematic diagram of the tanning processes in a typical leather tanning operation [Famielec 2014]

different stages of the technological process. This will allow the evaluation of the biodegradability of wastewater generated during production, the concentration of chromium compounds in them and also to slowly propose a concept of their pre-treatment and conduct preliminary experiments.

## MATERIALS AND METHODS

The study was conducted in a small tanning plant in the Podlaskie Province. Based on the leather tanning methodology used in the plant, the total volume of wastewater per 55 pieces



**Figure 2.** Bath discharge from a tannery drum in a small plant in the Podlaskie Province.  
From left: bath after liming process; water discharge from rinsing stage

weighing 1400 kg was determined, which is about 22 m<sup>3</sup> after tanning processes and about 4.8 m<sup>3</sup> after bath finishing processes. The total volume of wastewater for this batch is 26.8 m<sup>3</sup>. To this value, we should add the volume of wastewater used for domestic needs, wringing, washing machines, containers and floors, as the used water from these processes also goes to the wastewater tank. Assuming the total volume of produced wastewater to be 30 m<sup>3</sup> for a batch of 1400 kg of hides, the volume of wastewater per one ton of hides is 21.43 m<sup>3</sup>. 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 m<sup>3</sup> of wastewater per month. 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,
- BOD<sub>5</sub> – 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 AgNO<sub>3</sub> in the presence of K<sub>2</sub>CrO<sub>4</sub> as an indicator,
- NH<sub>4</sub><sup>+</sup> – 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 mineralization with BUCHI K-425 block mineralizer in a mixture of concentrated nitric acid and hydrogen peroxide.

## RESULTS AND DISCUSSION

Acids, alkalis, chromium (III) salts, sulfides and many other substances that are used during firing are not completely exhausted and become components of wastewater [Kubala and Przywara 2015]. This affects their degree of pollution and the content of individual substances. Additionally they undergo numerous dilutions, therefore the occurrence of pollution will be variable after each process. It is generally estimated that the effectiveness of specialty process chemicals leads to their 15% contribution to the final product, suggesting that 85% ends up in waste or wastewater [Rydin et al. 2013]. Wastewater from tanning plants contains the highest total chromium concentration (up to 4950 mg/dm<sup>3</sup>) [Lofrano et al. 2013]. The vast majority of all tanning plants use this tanning method which consequently results in 40% of the global chromium pollution being attributed to this industry. [Celary and Sobik-Szołtysek 2014]. As a result, an important element of water and wastewater management in tannery plants is the segregation of wastewater flows allowing their separation into liquids containing and not containing chromium compounds. Such management is carried out in the analyzed plant, which makes it possible to take separate samples of wastewater from different streams.

The results of the tests carried out to determine the composition of the wastewater generated in the selected tannery are presented in Table 1. Ways of treating wastewater from the

tanning industry are mainly associated with the problem of the presence of chromium in them. Considering its toxicity, such wastewater must be neutralized before entering natural reservoirs [Malovanyy et al. 2020]. Advanced technologies are used at specialized wastewater treatment plants where this element is recovered. This allows its reuse, since the amount of tannin applied at the tanning stage is not fully utilized. It has been established that chemical coagulation and flocculation applied as a first treatment step is required to remove not only solids and other contaminants, but also chromium (VI), which inhibit biological treatment [Lofrano et al. 2013]. The main disadvantage of the classical chromium wastewater treatment method is the obtaining of a volumetric chromium hydroxide sludge, which must be further processed. For dilute wastewater, ion exchange or solvent extraction with a selective and hydrophobic extractant is an effective treatment method [Kopczyńska et al. 2011]. Different environment and substances with which chromium can react cause the possibility of the formation of chromium compounds with different degrees of oxidation. There are two types of its stable forms - cationic - chromium (III) and anionic - chromium (VI) [Wojtal 2017]. Chromium at the sixth oxidation state is highly toxic and easily passes through biological membranes [Ascón-Aguilar et al. 2019]. In organisms, it is usually found in the trivalent form because they do not have the capacity to oxidize chromium (III) but are capable of reducing chromium (VI) in many tissues. [Mahmudi et al. 2020, Wojtal 2017]. In

**Tabela 1.** The results of the tests carried out to determine the composition of the wastewater generated in the selected tannery

Wastewater	Parameter							
	Suspension	pH	Conductivity	NH <sub>4</sub> <sup>+</sup>	COD	BOD <sub>5</sub>	Cl <sup>-</sup>	Cr
	g/dm <sup>3</sup>	-	μSm/cm	mgN <sub>NH4</sub> /dm <sup>3</sup>	mgO <sub>2</sub> /dm <sup>3</sup>	mgO <sub>2</sub> /dm <sup>3</sup>	mgCl/dm <sup>3</sup>	gCr/dm <sup>3</sup>
Mixed With Soak	2.97–3.39	6.50–6.83	60.91–70.63	102.46–118.81	13920–15080	1880–2180	24843–30576	-
	3.23±0.16	-	64.80±4.30	109.00±6.17	14500±458.53	2000±132.66	27300±2300.34	
Mixed With Soak And Liming Process	1.09–1.27	8.81–9.35	43.30–45.50	14.30–15.50	13442–15587	1843–1957	1746–1854	-
	1.16±0.08	-	44.60±0.86	14.90±0.47	14300±948.55	1900±42.49	1800±40.25	
From The Decalcification Drum	1.41–1.63	8.64–9.09	25.85–29.98	31.21–36.19	6223–7216	1128–1308	1128–1308	-
	1.49±0.08	-	27.504±1.56	33.20±1.88	6620±374.55	1200±67.88	1200±79.60	
Mixed With Soak, Liming, Decalcification And Pickling Processes	3.17–3.43	8.12–8.80	33.12–35.88	269.70–283.60	9659–11000	2328–2448	3290–3815	-
	3.30±0.10	-	34.50±1.09	278.02±5.56	10180±626.79	2400±48.00	3500±197.99	
Mixed From Pickling And Tanning Processes	1.53–1.74	3.56–3.74	57.90–67.14	-	7793–9036	-	16815–19116	2.00–2.46
	1.61±0.09	-	61.60±4.09		8290±468.86		17700±1009.06	2.20±0.18

Min-max/mean ± st. dev.

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  $2200 \pm 180$  mgCr/dm<sup>3</sup>, with a minimum value of 2000 and a maximum value of 2460 mgCr/dm<sup>3</sup>. This chromium comes from the tanning process using chromium tannins, specifically alkaline chromium sulfate. According to Manjushree (2015) Cr concentration in pickling and chrome-tanning effluents in located at Hazaribagh leather industrial zone in Bangladesh was the highest ( $2075 \pm 200$  mg/dm<sup>3</sup>) among the selected toxic elements. According to Jayakumar Gladstone Christopher (2016), the concentration of chromium in tanning effluents was only 500 mgCr/dm<sup>3</sup>.

The amount of organic compounds measured as COD and BOD<sub>5</sub> were determined in the collected samples. The lowest amounts of organic compounds determined as COD were obtained in the wastewater from the decalcification drum and mixed with the pickling and tanning processes ( $6620$ – $8290$  mgO<sub>2</sub>/dm<sup>3</sup>), while the highest amounts were obtained in the wastewater mixed from the steeping process ( $14500$  mgO<sub>2</sub>/dm<sup>3</sup>) and mixed from the steeping and liming processes ( $14300$  mgO<sub>2</sub>/dm<sup>3</sup>). The concentration then decreased during subsequent production stages due to mixing of successive batches of wastewater with each other. The amount of organic compounds defined as BOD<sub>5</sub> averaged between  $1200$  and  $2400$  mgO<sub>2</sub>/dm<sup>3</sup>, with no biologically degradable organic compounds found in the chrome wastewater mixed from the pickling and tanning process. According to Manjushree (2015) the mean BOD<sub>5</sub> and COD of the effluents at different manufacturing units of the selected industries in Bangladesh were in the range  $700 \pm 10$  to  $2400 \pm 70$  mgO<sub>2</sub>/dm<sup>3</sup> and  $7200 \pm 20$  to  $71040 \pm 40$  mgO<sub>2</sub>/dm<sup>3</sup>, respectively. According to Jayakumar Gladstone Christopher (2016) the amount of

organic compounds termed as BOD<sub>5</sub> was on average  $50,000$  and as COD was  $250,000$  mgO<sub>2</sub>/dm<sup>3</sup>.

A comparison of BOD<sub>5</sub> and COD can determine whether the wastewater is susceptible to biological degradation. The BOD<sub>5</sub>/COD ratio and the susceptibility to biological decomposition determined from it [Karamus 2017, Kogut et al., 2014] are shown in Table 2. Table 3 gives the average values of BOD<sub>5</sub> and COD in the wastewater samples, the calculated BOD<sub>5</sub>/COD ratio and the susceptibility of the wastewater to biological decomposition. The wastewater from the first three processes of the tannery industry was found to be not susceptible to biological degradation. However, the effluents after mixing from the mangrove, liming, decalcification and pickling processes have some potential for biological decomposition and can be classified as slowly decomposable effluents (average BOD<sub>5</sub>/COD is 0.24).

Suspended solids in tanning wastewater originate mainly from the first stages, where contaminants and hair are washed off the surface of the hides and skins as a result of the separation of frayed flesh fragments from the hide, e.g. after the dehairing process. The amount of suspended solids fluctuates considerably, and can also be affected by the time of sampling and the degree of mixing of the wastewater in the holding tank. The amount of suspended solids in the collected wastewater samples ranged from  $1.09$  to  $3.39$  g/dm<sup>3</sup>. In tanning wastewater, the pH of the bath environment is of great importance, because it directly affects the quality of the leather,

**Tabela 2.** Evaluation of biological degradation of organic compounds

BOD <sub>5</sub> /COD <sub>Cr</sub>	Decrease in COD <sub>Cr</sub> %	Susceptibility to biodegradation
>0.5	>90	Easily biodegradable
0.4–0.5	50–90	Normally biodegradable
0.2–0.4	10–50	Slowly biodegradable
<0.2	<10	Non-biodegradable

**Tabela 3.** Evaluation of the biodegradability of wastewater from different stages of production

Wastewater	Average value		BOD <sub>5</sub> /COD ratio	Susceptibility to biodegradation
	BOD <sub>5</sub>	COD		
Mixed with soak	2000	14500	0.14	Non-biodegradable
Mixed with soak and decalcification processes	1900	14300	0.13	Non-biodegradable
From the decalcification drum	1200	6620	0.18	Non-biodegradable
Mixed with soak, liming, decalcification and pickling processes	2400	10180	0.24	Slowly biodegradable

as well as the substances dosed in the processes, which can only increase their activity at a certain pH. Acids, alkalis, hydroxides and salts are all used in the process and each of them influences the reaction. Most of the wastewater from the leather dressing stages mixed in one tank has an alkaline pH (8.12–9.35), while the wastewater from the soaking process has a pH below neutral (6.5–6.83). In the case of the wastewater mixed from the pickling and tanning processes, the significant decrease in pH (3.56–3.74) is due to the use of acid in the pickling process to prepare the hides and bath environment for the proper process of tanning the hides with chromium salts. In the effluent samples collected, the pH ranged from 3.56 to 9.35. According to Manjushree (2015) the pH values of the effluents at various leather manufacturing stages ranged from 3.8 to 12.5. The use of nitrogen containing agents such as soda ash or ammonium sulfate causes ammonium salts to be present in this wastewater. The process in which such compounds are used is the decalcification step. The concentration of ammonium nitrogen in the samples collected ranged from 14.3 mg/dm<sup>3</sup> in the effluent from the mixed with the soak and liming process to 283.60 mg/dm<sup>3</sup> in the effluent mixed with the soak, liming, decalcification and pickling processes. According to Christopher et al. (2016), the average concentration of ammonium nitrogen in tannery wastewater was 10,000 mg/dm<sup>3</sup>.

Chloride concentrations in tannery effluent increase as a result of the use of salt in baths in particular. Salt can also be introduced along with fresh hides into the drum, as its use is one way to store rawhide until the tanning process begins. Chloride concentrations in the samples collected ranged from 1128 mg/dm<sup>3</sup> in the drum effluent from decalcification (mean 1200 ± 79.60) to 30576 mg/dm<sup>3</sup> in the effluent from mixed with the soak (mean 27300 ± 2300.34). All the values are very high compared to the standard limits, indicating chloride pollution. Chloride is essential for cell functions in plant and animal life, but high levels of chloride (>1000 mg/dm<sup>3</sup>) in water can cause human illness and can affect plant growth. Similar amounts of chloride in tannery wastewater were found by Manjushree (2015) where the concentration was 5005 mg/dm<sup>3</sup>. The high values of chloride in the effluent might be due to the chloride salts used in hide and skin preservation and in the picking process.

## CONCLUSIONS

Tannery wastewater can be treated together with municipal wastewater after mixing (with the exception of chromium wastewater). The disadvantage is that some substances can be broken down more effectively in special wastewater treatment plants. Tanning wastewater can also be treated directly at the plants in their own wastewater treatment facilities [Rydin et al. 2013]. However, with the current state of technology, it is fair to say that sustainable tanning will not be achievable for a long time due to technological limitations. [Bień et al. 2017]. The pollutants present in tannery wastewater are characterized by different values, which are directly influenced by both the condition of the leather entering the process and the chemicals used in the process. In the tannery plant from which the wastewater was collected, tanning with chromium compounds is carried out and its concentration in the wastewater after the processes averages 2200 g Cr/dm<sup>3</sup>. This necessitates advanced wastewater treatment as well as processes to recover chromium. The ratio of BOD<sub>5</sub> to COD allows determining the susceptibility of wastewater to biological decomposition. In the tannery plant analysed, the mixed wastewater averaged from all the processes carried out before tanning hides can be considered as susceptible to biological decomposition and slowly degradable. This will allow future experiments on wastewater treatment from a small tannery using chemical methods supported by hydrophytic processes.

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