Chemical composition and toxicity of effluents from unhairing baths: case study of the Batna Unit, Algeria

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Abstract:

Introduction/Purpose: The leather industry in Algeria contributes significantly to the economy, but its unhairing process generates highly polluted wastewater. This study aimed to characterize the chemical composition of unhairing bath effluents and assess their environmental toxicity.

Methods: The study focused on wastewater samples from the Batna tannery unit, where sheep and goat skins were processed. Thirteen samples were collected manually over 35 days (April 5–May 10, 2022), and

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standard chemical analyses were conducted to evaluate parameters such as pH, conductivity, total suspended solids (TSS), sulfides, ammonia ions, and proteins.

Results: The results showed that the wastewater had a high pH (12.47 on average), high conductivity (13.38 mS/cm), and significant levels of pollutants: sulfides (1120–1650 mg/L), TSS (862–2220 mg/L), and chemical oxygen demand (10.422–43.747 mg/L). Additionally, the wastewater contained free amino acids and proteins, products of partially hydrolyzed skin proteins, increasing its toxicity.

Conclusions:The study highlighted the severe environmental risks of untreated unhairing wastewater, underscoring the need for effective treatment solutions to mitigate pollution. The findings provide important insights into the environmental challenges of the leather industry and stress the importance of sustainable wastewater management.

Key words: leather industry, pollution, unhairing effluent, characterization, wastewater, toxicity

Introduction

In Algeria, the leather industry has a significant contribution to the economy and is represented by 6 units specializing in "wet blue" leather tanning operations. Tanning activities involve transforming animal skin into leather by removing lipids and hair. Several processes are used in this transformation, including unhairing, deliming, and tanning (Tamersit and Bouhidel, 2020). As a result, tanning industries consume a large amount of water (30 to 40 liters per kilogram of treated skin) and produce significant amounts of wastewater and solid waste (Benhadji et al., 2018). The unhairing process is the first and most pollutant-intensive operation (Hasan et al., 2024) which results in a partial hydrolysis of the animal skin (Morera et al., 2016). Consequently, the produced wastewater is dark brownish, malodorous, and characterized by very high pH, conductivity, and COD. It is also loaded with sulfides, total suspended solids, and by-products of hydrolyzed skin proteins (keratin) (Tamersit et al., 2018).

In leather production, only approximately 20% of the chemicals used are retained within the final leather product, while the remaining 80% are discharged into the resulting wastewater. Notably, around 40% of the sulphide applied in industrial liming processes is released into wastewater effluents. According to literature, tannery wastewater ranks among the most hazardous forms of industrial effluents, posing serious environmental and health risks.

Tannery wastewater constitutes a serious threat to the environment due to the high concentration and non-biodegradability of the majority of pollutants present (Durai and Rajasimman, 2011). In addition, the final quality of unhairing effluent depends mainly on the nature and number of raw materials as well as the production operations applied (Mendoza-Roca et al., 2010). Thus, it is judicious to treat the tannery wastewater and in particular, the unhairing bath effluent before its discharge into the receiving medium (Hashem et al., 2021). In this context, wastewaters from unhairing baths should be evaluated and characterized in order to highlight their toxicity and to propose an adequate treatment technique according to the studied case (Zhao et al., 2022).

The objective of this study is to characterize the wastewater generated by the unhairing bath of an industrial tannery unit located in Batna, Algeria and to assess the impact of these discharges on the surrounding environment. This tannery discharges its wastewater into the nearby Oued El Gourzi River, which flows through the city and passes by the villages of FISDIS and EL-MADHER, areas known for their agricultural lands. As a result, the unhairing wastewater is either directly or indirectly used by local farmers for irrigation purposes.

The characterization and evaluation of unhairing tannery wastewater are conducted through a comprehensive analysis of 10 samples. Additionally, the number and type of animal skins processed, whether cattle, goat, or sheep, are clearly specified. The results obtained from this analysis are thoroughly interpreted, providing insights into the toxicity profile of these effluents.

Materials and methods

Industrial unhairing wastewater

In this study, the samples were collected from unhairing wastewater discharged by the Batna Unit, an industrial tannery unit located in the city of Batna.

The Batna Unit factory, the subject of this study, consumes enormous quantities of water, exceeding 500 m^3/d; 28.8 m^3/d is the volume of concentrated wastewater from the unhairing operation. This consumption varies depending on the quality and quantity of the raw material.

In all countries, these effluents must meet discharge standards.

Unhairing bath wastewater sampling was carried out manually in the morning after the first discharges from 6 AM. to 8 AM. The samples were collected according to the collection and storage standards and processes. The samples were stored in polyethylene containers of two-liter volume and carefully labeled. The collection of 13 samples of unhairing wastewater was spread over a period of 35 days (April 5 – May 10, 2022).

The volumes of daily discharges are not regular, rather peaks are observed. During the early hours of the morning, there is usually a peak of 250% compared to the hourly average. At this time of the day, different wastewaters present extreme analytical characteristics. During the other hours of the day, wastewater production represents 50% of the hourly average.

Analysis methods

Temperature, pH and conductivity measurements were carried out in situ. For other analyses (COD and BOD5), the samples were stored at 4 °C until the time of analysis to avoid any modification. Various analyses were carried out after decanting the samples. For certain analyses, dilution and/or filtration had to be carried out beforehand.

The pH and conductivity of the samples were determined by using a pH meter, Model 720 WTW and a Hanna Instruments conductivity meter, Model EC 215, respectively.

Tha analyses of chemical oxygen demand (COD), biological oxygen demand (BOD5) , total suspended solids (TSS), ammonia ($N\text{-}NH_3$), sulfide (S^{2-}), chloride (Cl^-), and phosphate ($P\text{-}PO_4^{3-}$) were carried out in accordance with the standard methods (Rodier et al., 1996).

Results and discussion

Number of treated skins

In the tannery, the consumption of both water and chemicals as well as the final quality of the wastewater from each stage depend on the quality and quantity of the treated hides. In this work, each sample was characterized previously by their number and type of treated skins.

According to the information provided by the workers, sheep skins have been the most used ones in recent years. Through the following histogram in Figure 1, which represents the number of skins treated in the bath of each sample, it is clear that the number of skins treated is between 600 to 900. However, the number and type of skins used vary depending on availability.

In comparison with the nineties, there is a drop in the number of skins treated (more than 1000 skins per bath) as well as a relative decrease in the availability of goatskins.

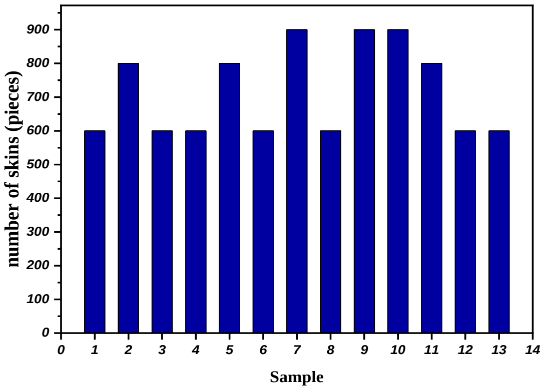

Figure 1 – Histogram of the number of treated skins from different samples, the Batna Unit

Using the results obtained, we can subsequently see whether the number and nature of the treated skins influence the quality of the final wastewater or not.

Analysis of the physicochemical parameters

The physicochemical quality of wastewater can be evaluated based on the values of several parameters:

• The pH is a pollution indicator with excellence; it varies depending on the nature of the basic or acidic effluents.

• Temperature is a parameter that influences the kinetics of metabolism, the distribution of species, and the dissolution of gases dissolved in water.

• Conductivity makes it possible to quickly and approximately assess the mineralization of wastewater and to monitor its evolution.

The pH, temperature, and conductivity significantly influence the fate of various contaminants in the receiving environment. These parameters play a crucial role in controlling the behavior and mobility of contaminants across different environmental compartments.

Determination of temperature

Temperature is one of the most important parameters determining the efficiency of the process.Figure 2 shows the evolution of the temperature values of the wastewater from the unhairing bath. These values ranged between 11-18 °C, so these values were *below* the discharge limit values (40 °C)(Sawadogo et al., 2012).

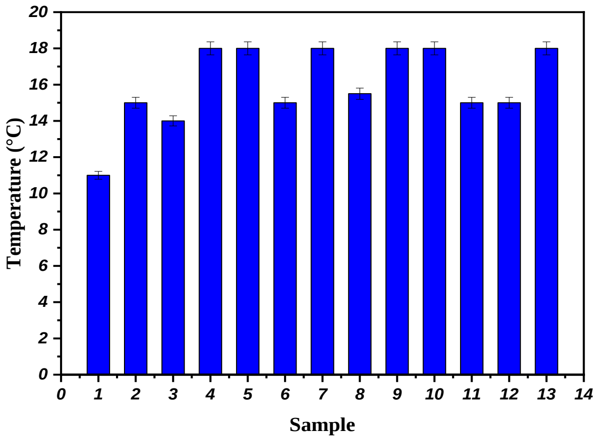

Figure 2 – Histogram of the temperature monitoring of the unhairing wastewater from the tannery, the Batna Unit

Determination of the pH

The evolution of the pH of different samples from the unhairing bath showed that these wastewaters are relatively alkaline with an average value of 12.47 and extreme values of 12.04 to 13 (Figure 3).

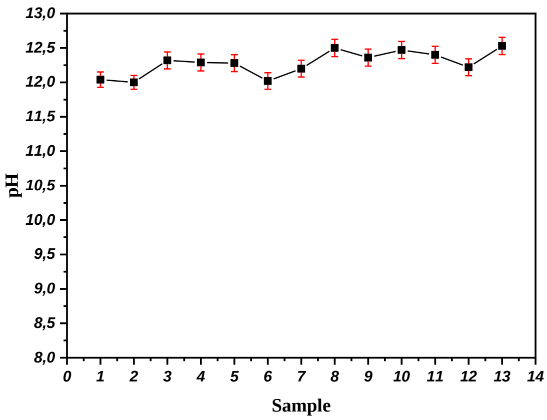

Figure 3 – Curve of the pH monitoring of the unhairing wastewater from the tannery at 20°C, the Batna Unit

This high pH is due to the presence of alkaline substances, S^{2-}, HS^{-} and $Ca(OH)_2$. The pH of the obtained results does not meet the general standards recommended for wastewater disposal (Islam, B.I. et al., 2014). In this case, neutralization of these wastewaters is necessary before their discharge into the receiving environment. However, there is the risk of emission of H_2S gas release at pH 7.

Electrical conductivity (EC)

The salinity level, expressed in average electrical conductivity, is 13.38 mS/cm (Figure 4). The conductivity varies depending on the quantity of chemicals used during the operation (or the conservation stage). The dominant salt in these effluents is sodium chloride due to the high concentration of sodium and chloride in the studied environment. Salty skins release large amounts of NaCl.

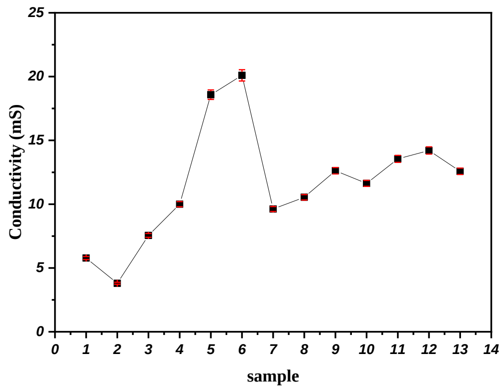

Figure 4 – Curve of the conductivity monitoring of the unhairing wastewater from the tannery at 20 °C, the Batna Unit

Above 2500 µS, salinity inhibits the proliferation of microorganisms and therefore reduces its purifying power; this is the major problem encountered with biological treatment. On the other hand, the presence of a high level of some ions such as chlorides and sulfates can cause the solubilization of a metal slurry through complexation reactions.

Determination of total suspended solids (TSS)

Suspended matter (TSS) represents the suspended mineral and organic particles contained in the effluent. These values are from 862.5 to 2220.8 mg/L with an average of 1804.22 mg/L (see Figure 5).

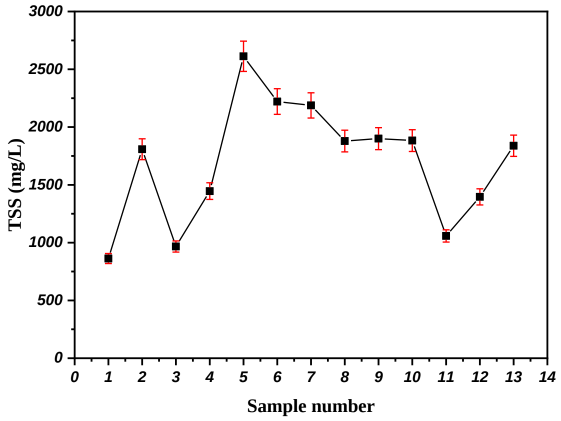

Figure 5 – Curve of the TSS monitoring of the unhairing wastewater from the tannery at 20 °C, the Batna Unit

High MES values are higher than the norm; they are directly linked to the nature and quality of the raw material processed in this industry (animal skins) in relation to the quantities of water used. These MES values come from hair, debris, skin fibers and any material attached to the used skin.

Analysis of cations and anions

Cations

Several cations were analyzed in the unhairing wastewater bath, such as those of calcium, magnesium, sodium, and potassium.

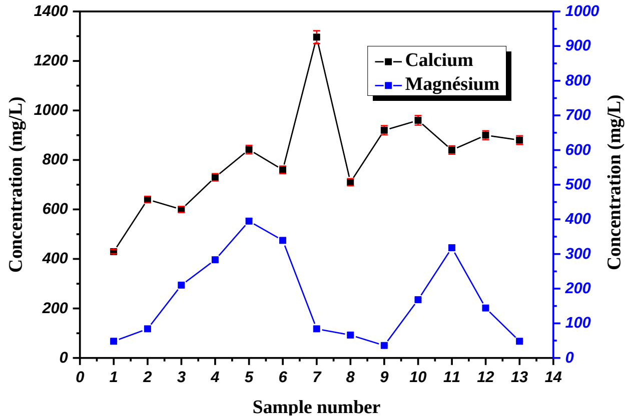

Figure 6 – Curve of the calcium and magnesium ions content monitoring in the unhairing wastewater from the tannery, the Batna Unit

Figure 6 represents the evolution of calcium and magnesium; the average magnesium content is around 171 mg/L. Calcium reaches an average value of 808.27 mg/L; this high value is essentially due to the use of lime ($Ca(OH)_2$) during this unhairing operation.

Sodium (Figure 7) is present in the effluents at an average content of around 4659.92 mg/L. This relatively high value is due both to the use of sodium chloride for the preservation of raw hides and to its presence in Na2S, the main reagent for hair removal.

For potassium, its concentration varies between 184.89 and 1393 mg/L; the average value is around 561.55 mg/L.

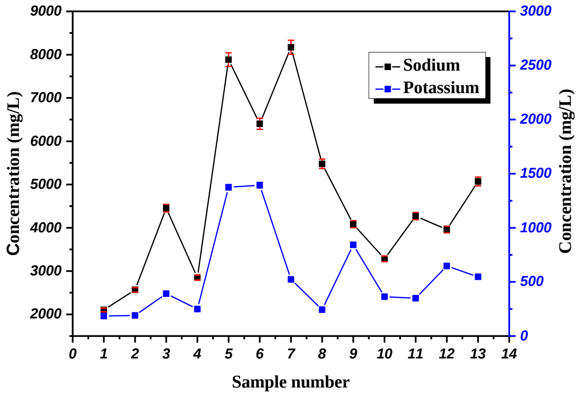

Figure 7 – Curve of the sodium and potassium ion content monitoring in the unhairing wastewater from the tannery, the Batna Unit

Anions

The anions analyzed in the unhairing wastewater bath were chlorides and sulfides.

The chloride ion content (Figure 8) was in the range of 720 and 1212 mg/L with an average value of around 906.91 mg/L.

In fact, inorganic sulfides (NaHS or Na_2S) and lime treatment were used in the unhairing process. The determination of sulfide (Figure 9) in all samples shows that their values vary between 1120 and 1650 mg/L. These values are rather comparable to those reported by other works. The presence of high concentrations of sulphides in wastewater causes a serious problem of odor and corrosion in sanitation canals. Dissolved sulfide is found in the form of a mixture of hydrosulfide ions and hydrogen sulfide (H_2S). The high toxicity of sulfides comes from the H_2S released (Floqi, T. et al., 2007), the content of which depends on the pH value. After evacuation, the effluents were diluted and neutralized in the natural environment releasing H_2S gas into the atmosphere, thus causing serious olfactory nuisances (Floqi et al., 2007).

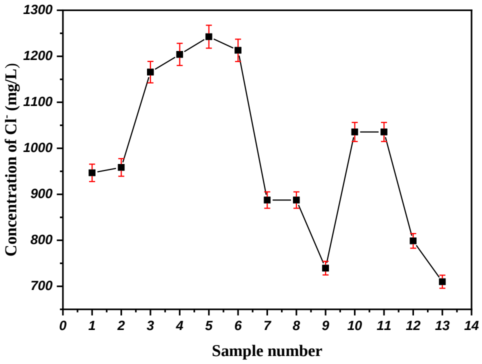

Figure 8 – Curve of the chloride ion content monitoring in the unhairing wastewater from the tannery, the Batna Unit

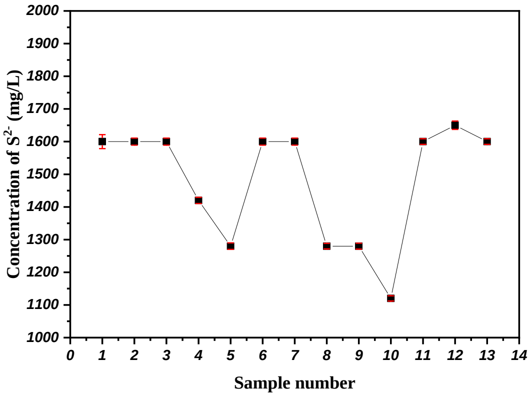

Figure 9 – Curve of the sulphide ion content monitoring in the unhairing wastewater from the tannery, the Batna Unit

Phosphorus analysis

Figure 10 shows the evolution of phosphates which vary between 44.66 and 736 mg/L with an average value of around 258.35 mg/L. These values are higher than the standard (1 mg/L); the presence of phosphates may be due to the use of detergents for rinsing the skin.

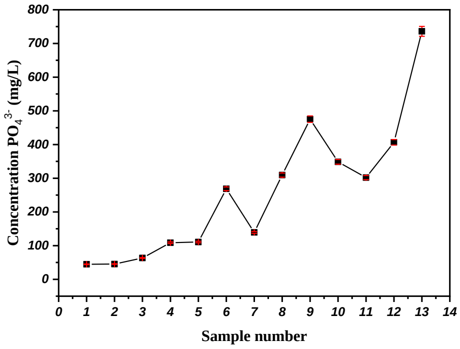

Figure 10 – Curve of the phosphate ion content monitoring in the unhairing wastewater from the tannery, the Batna Unit

Nitrogen analysis

From Figure 11, the ammonium ion concentration average was 16.3 mg/L with extreme values of 2 and 25 mg/L; these values are lower than the standard of the World Health Organization WHO (80 mg/L). As for the oxidized forms (nitrites and nitrates), the analyses indicate an average nitrite concentration of around 0.306 mg/L. However, for nitrates, the concentrations were more significant with an average value of around 28.8 mg/L (Figure 12) - this value is higher than the standard set by the WHO (1 mg/L). A high quantity of nitrate can contaminate underground water by infiltration, especially in cases where the soil is permeable.

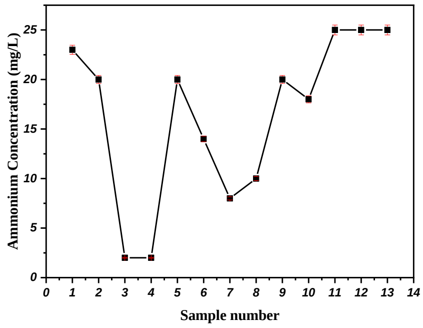

Figure 11 – Curve of the ammonium ion content monitoring in the unhairing wastewater from the tannery, the Batna Unit

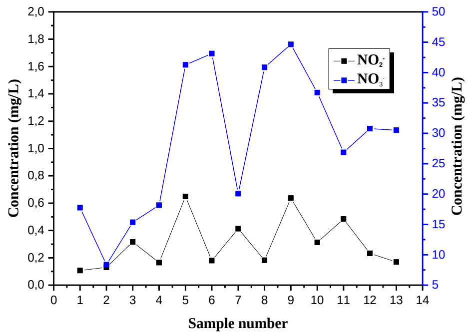

Figure 12 – Curve of the nitrite and nitrate ions content monitoring in the unhairing wastewater from the tannery, the Batna Unit

Analysis of organic pollution parameters (COD and BOD5)

For the studied samples, the COD values are between 23289 and 40000 mgO2/L with an average value of 30696 mg O_2/L (Figure 13); these values exceed the Algerian standard which is 1000 mg/L. As for BOD5, the values are 1150 to 2650 mg/l with an average of 1644.61 mg/L (Figure 14). In the tannery, around 75% of the organic load (measured as BOD5 or COD) is produced in the unhairing process. This high load of organic matter is mainly due to the biogenic material of hides and some used chemicals.

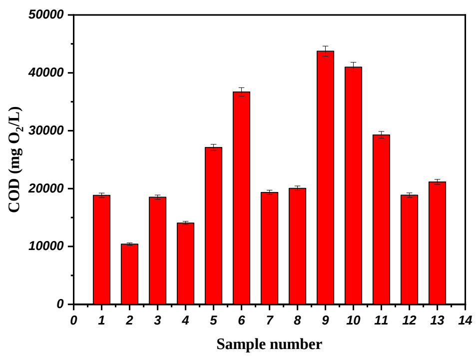

Figure 13 – Curve of the chemical oxygen demand monitoring in the unhairing wastewater from the tannery, the Batna Unit

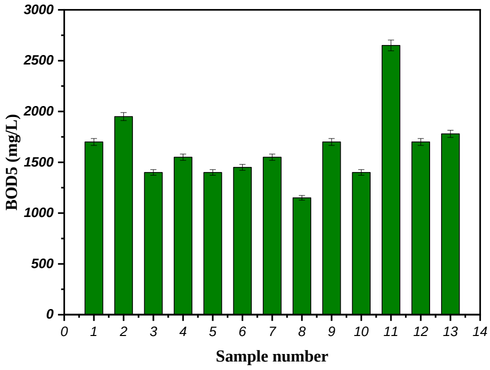

Figure 14 – Curve of the biochemical oxygen demand monitoring in the unhairing wastewater from the tannery, the Batna Unit

Calculation of the COD/BOD5 ratio

In this analysis, we calculated the COD/BOD5 ratio to assess the biodegradability (K coefficient) of the organic matter present in the unhairing wastewater from the tannery.

Table 1 – Values of the K coefficient for the studied samples

N° sample	1	2	3	4	5	6	7	8	9	10	11	12	13
K	6.6	3.2	7.9	5.4	11.6	15.1	7.4	10.4	15.4	17.5	6.6	6.62	7.1

The results shown in Table 1 indicate a high value of the K coefficient. These results suggest that the wastewater from the tannery's unhairing bath is not biodegradable. The primary cause of this is the presence of salts which inhibit bacterial growth. Therefore, biological treatment can be effective if combined with another treatment technique to reduce salinity.

Summary of the obtained results

The obtained results are summarized in Table 2.

Table 2 – Extreme and average values of the studied parameters

Parameter	Range	Average value
Temperature, °C	11-18	16
pH	12.04 – 13	12.47
Conductivity, mS	3.8 – 20.1	13.38
Turbidity, NTU	42 - 1000	416.3
TSS, mg/L	862.5 - 2220.8	1804.22
Calcium, mg/L	429.6 - 1296	808.27
Magnesium, mg/L	36 – 394.8	171
Sodium, mg/L	2103.82 – 8168.51	4659.92
Potassium, mg/L	184.89 - 1393	561.55
Chloride, mg/L	710 - 1212	906.91
Sulfide, mg/L	1120 - 1650	1479.23
Ortho phosphate, mg/L	44.66 - 736	258.35
Nitrate, mg/L	8.37 – 44.65	28.8
Nitrite, mg/L	0.107 – 0.649	0.306
Ammonium, mg/L	2 – 25	16.30
COD, mg O_2/L	10422.32 – 43747.97	30696
BOD5, mg O_2/L	1150 – 2650	1644.61

Conclusion

The results obtained from the comprehensive analysis of the unhairing bath wastewater indicate that the majority of the measured parameters exceed both national and European discharge standards. These findings highlight the substantial environmental impact of untreated tannery wastewater, reinforcing its role as a major source of pollution. The data gathered in this study provide essential baseline information that is critical for evaluating and developing effective wastewater treatment strategies.

The wastewater from the unhairing process exhibited a highly alkaline pH (12), elevated conductivity (13 mS), and significant concentrations of suspended solids (1800 mg/L) and sulfides (1500 mg/L). Additionally, the effluent contained excessive organic matter and demonstrated a high Chemical Oxygen Demand (30000 mg/L). The hair removal process was found to generate highly toxic and alkaline wastewater, enriched with valuable organic compounds such as proteins, polypeptides, and free amino acids, resulting from the partial alkaline hydrolysis of skin proteins, including collagen and keratin.

While the leather industry plays a crucial role in utilizing slaughterhouse by-products to produce leather, its environmental impact remains considerable. The tanning process generates large volumes of contaminated wastewater, posing severe ecological risks. Despite its socio-economic contributions, such as job creation and income generation, the industry continues to face negative public perception due to its environmental footprint. Therefore, implementing sustainable wastewater management and treatment solutions is essential to mitigate pollution and enhance the industry's environmental sustainability.

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Хемијски састав и токсичност отпадних вода из каде за уклањање длака при обради сирове коже: студија случаја штавионице у Батни, Алжир

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ОБЛАСТ: хемија животне средине
КАТЕГОРИЈА (ТИП) ЧЛАНКА: оригинални научни рад

Сажетак:

Увод/циљ: Индустрија коже у Алжиру значајно доприноси њеној економији, али се током процеса штављења стварају отпадне воде високог степена загађености. Циљ студије јесте да утврди хемијски састав отпадних вода из када за уклањање длака при штављењу, као и да процени њихову токсичност на животну средину.

Методе: Анализирани су узорци отпадних вода из штавионице у Батни где су се прерађивале овчије и козје коже. Тринаест узорака је ручно прикупљено током 35 дана (од 5. априла до 10. маја 2022), а затим су извршене стандардне хемијске анализе за процену параметара попут pH вредности, проводљивости, укупних суспендованих материја (ТСС), сулфида, јона амонијака, као и протеина.

Резултати: Показано је да отпадне воде имају високу pH вредност (12,47 у просеку), високу проводљивост (13,38 mS/cm), као и знатно високе нивое загађивача: сулфида (1120–1650 mg/L), TSS (862–2220 mg/L) и хемијске потрошње кисеоника (10,422–43,747 mg/L). Отпадне воде су садржале и слободне аминокиселине и протеине, производе делимично хидролизованих протеина коже, што је повећавало њихову токсичност.

Закључак: Услед непречишћених отпадних вода пореклом из када за скидање длака при штављењу долази до великих ризика по животну средину. Стога се, ради смањења загађивања, наглашава потреба за ефикасним решењима за пречишћавање . Резултати пружају важан увид у еколошке изазове индустрије коже и истичу важност одрживог управљања отпадним водама.

Кључне речи: индустрија коже, загађивање, отпадне воде од скидања длака, карактеризација, отпадне воде, токсичност

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