JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2024, 25(1), 320–326
https://doi.org/10.12911/22998993/174833
ISSN 2299–8993, License CC-BY 4.0

Received: 2023.10.18
Accepted: 2023.11.20
Published: 2023.12.04

Determination of the Composition of Wastewater from Individual Processes of Leather Tanning Production in a Small Plant

Katarzyna Ignatowicz[1*], Maciej Dziadel[1]

[1] Bialystok University of Technology, ul. Wiejska 45A, 15-351, Białystok, Poland

* Corresponding author's e-mail: k.ignatowicz@pb.edu.pl

ABSTRACT

The article introduces one of the leather industries, the tanning industry, which is responsible for some of the most critical processes that leather undergoes before it is used in subsequent parts of the industry. Since the processes carried out require significant amounts of water, they generate equally large amounts of wastewater, which, as industrial wastewater, requires appropriate treatment. Additionally, due to the quantities and complexity of the processes carried out, the chemicals used become demanding in terms of how they are treated and managed. The parameters of wastewater subjected to a collection in a typical tank are changed. In contrast, wastewater from chromium tanning processes, which should be discharged into a separate tank, is a source of chromium pollution with its high content, thus posing a significant danger to the environment. The study made it possible to assess the biodegradability of wastewater generated during production and the concentration of chromium compounds and other pollutants. Based on the results, it was found that the wastewater generated during the production process is biodegradable (except for mixed wastewater), and the concentration of chromium is 2.81–3.11 g/dm^3.

Keywords: industrial effluent, chrome, tannery.

INTRODUCTION

One of the many industries that rely on chemical compounds to function is the tanning industry. The processes use acids and alkaline compounds, and as a result, the reaction environment changes, improving the processes. The treated leather itself is also changed. The name of the tanning industry has its connection to one of the processes carried out, which is tanning proper. It is a short process, but the most important one. Tannins are then used, usually chromium-inorganic tannins but also organic plant tannins, which are compounds capable of transforming raw leather into leather with usable properties [Michalak 2021, Karanam Sai Bhavya et al. 2019, Hassan et al. 2020, Bharadwaj et al., 2020]. It has a place in the processes of wet workshops. It is the last of the processes before the upcoming machining, which prepares the leathers for the final form of finishing [Bartkiewicz et al. 2010, Bien et al. 2019]. Chemical compounds, used in significant amounts and at almost every stage of production, affect the accumulation of pollutant loads in the resulting wastewater, especially after wet workshop processes [Ascón-Aguilar et al. 2019]. 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].

METHODOLOGY

The most general division of processes is their separation into wet and dry workshops consisting of a series of chemical reactions and mechanical processes [Chmielowski, 2019]. The first of these is the wet workshop, in which hides are subjected to numerous processes using water baths.

Furthermore, in the dry workshop, the operations carried out are mainly based on mechanical processing affecting the shape, thickness, or smoothness of the hide. Hides processed in tanning facilities are classified as a byproduct of the slaughter of cattle, pigs, or sheep, from which face hide or fur hide is obtained. Depending on its final destination, the hide is subjected to further processes that improve its aesthetic or functional qualities. Hide processing can be divided into [Ayele et al. 2021, Santos et al. 2006, Drioli et al. 2023]:

- preliminary operations: cleaning, trimming, sorting, storage;
- wet workshop: soaking, demeating, liming, defuring, decalcification, etching;
- tanning proper: pickling, tanning;
- post-tanning operations: wringing, splitting, and scraping;
- wet finishing: neutralizing, additional tanning, dyeing, greasing, wringing, drying;
- dry finishing: softening, pressing, painting, mechanical finishing.

The raw material delivered to the plant is subjected to cleaning and removal of fragments that will not be suitable for further processing. Depending on production and storage capacity, hides can be subjected directly to tanning processes or preserved with salt for later use. Hides that undergo leaching start their processes with soaking. It is a process designed to clean them of dirt, blood, and salt, as well as any free dirt on their surface. Soaking also promotes the hydration of the hides and restores their elasticity. The cleansed and soaked hides are then subjected to demeating. It is a mechanical process. As a result of the rotary movement of the knife roller, excess subcutaneous tissue is removed so that the hide loses unnecessary thickness and becomes much lighter. It carries dual advantages, both in terms of easier processing and the reduced amount of chemistry that will have to be used in the processes, especially when selecting the weight of the raw material entering the stage. The demeated hides return to the bath, where the first treatment - liming - is designed to alkalinize them. Increasing their thickness expands the hair follicles, which allows the fur to be released from the surface of the hide. Once they are removed, the reverse process, known as decalcification, is carried out. It is aimed at sliming – that is, reducing the thickness of the hides to their preprocess state. Alkaline compounds are then washed out, the pH of the hides is lowered, and they are prepared for tanning. The etching that follows successively promotes an increase in the properties of the hides in terms of elasticity and softness [Santos *et al.* 2006]. Enzymatic proteolytic compounds are used for this purpose.

These processes are followed by the part related to tanning proper. First, during pickling, using salt and acids, the pH of the bath solution, and thus the hides, is lowered to prepare them for tanning. Tanning involves the infliction of a tannin, usually chromium, whose action is much faster than in vegetable tanning. Chromium tannins are used in the vast majority of plants around the world. Through this process, hides become resistant to biological decomposition, are protected from rotting, and, unlike their raw state, will not spoil. A well-executed process contributes to the good quality of the final product.

After tanning, hides left to cure for one day are subjected to mechanical operations. First, due to wringing, excess water accumulated in them is removed, making them much lighter. Then, they can be subjected to splitting. This process affects the separation of one piece into two halves: the face, on the bristle side, and the flesh, on the inside. Each of them can be a separate product and participate further in other production lines depending on the desired effect. Their thickness can be uneven across the surface, which is leveled by scraping. Similar to deskinning, this machine aims to remove the excess thickness of the hide to its preset value, leveling its surfaces.

Hide prepared in this way goes back to water baths and wet finishing in processes including dyeing and greasing, where it obtains the desired final color or the suitable base, for example, spray painting. The use of suitable hydrophobic fats makes it possible to provide water repellency to hides, which affects their value and gives them an additional feature. Tanned hides are similarly wrung after tanning, removing excess water. Further drying is carried out in dryers and with the use of vacuum machines to extract the water accumulated inside. The dried hides are subjected to softening and pressing, followed by the appropriate finishing processes for the final product through all the steps related to the effect to be obtained. Many of the processes here can be intertwined and repeated.

This series of all the steps to which raw hides are subjected at the outset allows them to be given various characteristics, colors, but above all, strength and resistance. Despite the chemicals used, these are still natural products.

Of the chemical compounds used in the processes, many are not used in their entirety, and as a result, they end up in wastewater [Kubala and Przywara, 2015]. All of these factors consequently affect the degree of wastewater pollution and the content of individual substances. Flushing waters are also included in the total volume of wastewater. Although they affect the dilution of the concentration of wastewater contaminants, they increase the volume of wastewater significantly since, in some processes, the volume of rinse water is more significant than that used in the process. Estimates state that of the total volume of chemicals used, as much as 85% ends up in waste or wastewater [Rydin et al. 2013]. General wastewater is characterized by a considerable variation in parameters relative to each process [Dymaczewski, 2011].

Wastewater is characterized by the presence of pollutants such as COD, BOD_5, chlorides, sulfides, tannins, acids, alkalis and salts, dyes and solvents, proteins, hair, solid waste, and odors [Famielec 2015, Zhao et al. 2022].

Due to the contamination and use of chromium in plants, postprocess wastewater is managed in such a way that leads to its separation into general and chromium wastewater. This form of accumulation makes it possible to approach them individually and use separate methods of treatment. In the case of accumulated mixed wastewater, free of chromium, it can be treated together with municipal wastewater in its on-site treatment plants or pretreated before entering municipal treatment plants [Rydin et al. 2013]. Due to the toxic nature of chromium, chromium wastewater requires treatment before entering the environment [Malovanyy et al. 2020]. Its concentration in wastewater can reach 4950 mg/dm^3 [Lofrano et al. 2013]. According to the current regulation of the Minister of Maritime Affairs and Inland Navigation dated July 12, 2019. (Dz.U. 2019 poz.1311), maximum chromium concentrations are specified, which cannot exceed 0.05 mgCr/dm^3 for chromium Cr(VI) and 1.0 mgCr/dm^3 for total chromium. These are values for the tanning industry only. Comparing these data with the obtained values in wastewater, the concentration of total chromium is several thousand times higher than the permissible limit. This requires an absolute individual approach for this type of wastewater. However, there are cases that require these concentrations. An example is the Lesiow treatment plant, which had requirements for incoming wastewater, and in which the chromium concentration could not be lower than 2 gCr/dm^3 [Bartkiewicz et al. 2010]. For this type of wastewater, some technologies allow the recovery of chromium. This element is used in excess in the processes, and thus, its volume in the wastewater is significant, which is equal to the fact that its secondary use is also possible in the form of chromium wort discharged after the previous process. A bath prepared in this way may require only a small portion of fresh chromium, limiting its consumption. The used wort can be used for the pickling or tanning process. In the case of recycling for tanning, it is possible to reduce the fresh chromium dose by 25%, for cattle hides, and the chromium content of the effluent can be reduced by 60% [Rydin et al. 2013]. The development of gutting technology and water and wastewater management in plants should be one of the priority activities and goals of such plants striving for the best possible development and protection of the environment [Rüffer H. et al. 1998]. Technological limitations are responsible for the significant increase in the time needed for proper development and investment [Bień et al. 2017].

RESULTS

The results of the study in Table 1 were based on the analysis of wastewater generated during technological processes at a small tanning plant. Five samples, each from the processes, were taken periodically:

- wetting,
- liming,
- decalcification,
- tanning,
- mixed.

Wastewater was sampled directly after the processes during the bath drainage and, in the case of mixing, directly from the general wastewater tank. Samples were filtered before determination, and determinations were made using the methodology of [Łozowicka *et al.* 2016, Ignatowicz 2009, 2011, Manjushree 2015]:

- suspension – a method of filtration through quantitative medium sieves, previously weighed, dried and weighed again;

- pH – potentiometric method, HQD probe with INTELLICAL sensors, according to PN-EN ISO 1053:2012;
- conductivity – conductivity method, HQD probe with INTELLICAL sensors, according to PN-EN 27888:1999 standard;
- COD – bichromate spectrophotometric method, Hach thermoreactor, Merck Pharo 300 spectrophotometer, Merck cuvette tests, according to PN-ISO 15705:2005;
- BOD_5 – manometric (electrochemical) method, OxiTop Standard system, WTW TS 606/2 thermostatic cabinet, according to PN-EN 1899-2:2002 standard;
- ammonium nitrogen – spectrophotometric method, Merck Pharo 300 spectrophotometer, according to PN-ISO 7150-1:2002 standard;
- chromium – by flame atomic absorption spectrometry on a Thermo Scientific™ iCE™ 3500 apparatus, after digestion of wastewater with a BUCHI K-425 block digester in a mixture of concentrated nitric acid and hydrogen peroxide.

The chromium concentration was determined in chromium wastewater, the average value of which was 2.95 g Cr/dm^3. The tanning process and the use of chromium tannins directly influence this amount. Compared to Kavitha (2015), the chromium concentration varied between 1.5 and 4.0 g Cr/dm^3. A similar value was presented by Dziadel (2022) for another plant, where an average of 2.2 g/dm^3 was obtained after tanning processes.

The effluent pH was lowest for chromium effluent, ranging from 4.07 to 4.15, and the highest value of 12.26 was obtained with liming effluent. In mixed wastewater, the pH ranged from 5.48 to 5.67. Similarly, data presented by Manjushree (2015) show the highest pH after the liming process at 12.5 and the lowest after tanning at 3.8. Similarly, Kavitha (2015) reported the highest pH after the liming process, ranging from 10 to 12.8, and the lowest for tanning, with values ranging from 2.5 to 4.0. The extreme pH ranges are a requirement and a result of the processes carried out and the chemicals used. Liming requires alkaline baths, while tanning requires acid baths. This is evidenced by the repeatability of test results. As a consequence, however, the general wastewater is mixed together with the liming wastewater, and thus the overall pH is altered. This pH and wet environment, affects the life of especially metal parts that can corrode.

The highest conductivity value, averaging 78.06 ± 2.95 mS/cm, was reported for chromium wastewater, and the lowest in mixed wastewater was 27.8 ± 1.97 mS/cm. In the data presented by Manjushree (2015), the highest conductivity was also shown in chromium wastewater, but it was almost four times higher than their own results, at 295 ± 15 mS/cm. The lowest, on the other hand, was determined for decalcification wastewater, amounting to 12 ± 1 mS/cm.

Ammonium nitrogen in the highest amount was shown in the wastewater after tanning, averaging 111.8 ± 5.02 mg $N\text{-}NH_4/dm^3$. A slightly lower concentration was determined for mixed wastewater, for which it was 98.0 ± 4.23 mg $N\text{-}NH_4/dm^3$. The last, on the other hand, was shown in the sample from liming, obtaining 0.8 ± 0.07 mg $N\text{-}NH_4/dm^3$. For the decalcification

Table 1. Composition of wastewater from individual leather tanning production processes in a small plant

Wastewater from the process	Parameter						
	Suspension	pH	Conductivity	Ammonium nitrogen	COD	BOD_5	Chromium
	g/dm^3	–	mS/cm	mg $N\text{–}NH_4/dm^3$	mg O_2/dm^3	mg O_2/dm^3	g Cr/dm^3
Wetting	1.52 – 2.01	8.21 – 8.24	69.1 – 71.7	5.1 – 5.7	7057 – 7854	4708 – 5017	–
	1.83 ± 0.197		70.3 ± 0.93	5.4 ± 0.22	7471.2 ± 316.40	4856.2 ± 134.1	
Liming	2.28 – 2.78	12.25 – 12.26	38.1 – 42.2	0.7 – 0.9	10548 – 11673	2517 – 2948	–
	2.60 ± 0.208		40.6 ± 1.50	0.8 ± 0.07	10899.20 ± 466.39	2753.0 ± 158.86	
Decalcification	0.19 – 0.26	7.17 – 7.21	40.1 – 43.0	0.8 – 1.0	5139 – 5711	4790 – 5150	–
	0.24 ± 0.029		41.62 ± 1.21	0.9 ±0.10	5423.4 ± 214.08	4932 ± 134.98	
Tanning	0.47 – 0.57	4.07 – 4.15	74.1 – 81.3	107 – 117	4228 – 4513	37 – 48	2.81 – 3.11
	0.52 ± 0.046		78.06 ± 2.95	111.8 ± 5.02	4348.4 ± 118.06	40.6 ± 4.34	2.95 ± 0.12
Mixed	0.77 – 0.83	5.48 – 5.67	25.0 – 30.2	93.8 – 105	4136 – 4299	2310 – 2515	–
	0.79 ± 0.025		27.8 ± 1.97	98.0 ± 4.23	4215.0 ± 57.71	2400 ± 94.67	

Note: Min-max/mean ± standard deviation.

process, an equally low value equal to an average of 0.9 ± 0.1 mg $N\text{-}NH_4/dm^3$ was obtained, while Dziadel (2022) determined an ammonium nitrogen content of 33.20 ± 1.88 mg $N\text{-}NH_4/dm^3$ for a sample from the same process. The significant difference may be due to the different production methods or alternative agents used in the process according to the expedition methodology.

The highest values for suspended solids were obtained after soaking processes of 1.83 ± 0.197 g/dm^3 and liming of 2.60 ± 0.208 g/dm^3. This is due to the washing of impurities from the skins in the first process, during which they are cleaned. In the second, bristles are removed, which, due to insufficient dissolution, are discharged as suspended solids. Suspended solids are not separated from the general wastewater before being sent for treatment, and the simplest way to separate them is by sedimentation. The lowest value was obtained in the effluent from decalcification, averaging 0.24 ± 0.029 g/dm^3. According to data reported by Manjushree (2015), the highest amount of suspended solids occurred in the liming processes of 11.0 ± 0.0045 g/dm^3 and decalcification at 11.0 ± 0.001 $g/dm^{3,}$ and the lowest occurred after the tanning process, averaging 1.0 ± 0.002 g/dm^3. Kavitha (2015), on the other hand, reports the smallest amount of suspended solids after the pickling process of 1 to 3 g/dm^3 – similar after the tanning process of 1 to 2.5 g/dm^3, while the highest value was determined for liming ranging from 6 to 18 g/dm^3.

Determined as COD, chemical oxygen demand was determined in all of the samples. Average values ranging from 4215.0 ± 57.71 mg O_2/dm^3 to 10899.20 ± 466.39 mg O_2/dm^3 were obtained, the lowest for mixed wastewater and the highest for wastewater after the liming process. Kavitha (2015) reported the COD parameter highest for the liming process in the range of 10000 to 25000 mg O_2/dm^3 and the lowest for the tanning process between 1000 and 2500 mg O_2/dm^3. Manjushree (2015), on the other hand, obtained the lowest value for the decalcification process, equal to 4200 ± 10.5 mg O_2/dm^3, and the highest value for the tanning process amounting to 49000 ± 40 mg O_2/dm^3.

Another of the parameters is $BOD_{5,}$ which determines the biological oxygen demand. The lowest value was obtained for the tanning process, with a mean value of 40.6 ± 4.34 mg O_2/dm^3. The highest occurred for the effluent after the decalcification process and was 4932 ± 134.98 mg O_2/dm^3. Kavitha (2015) reported a BOD_5 value of 350 to 800 mg O_2/dm^3 after tanning processes, which was the lowest value, and the highest value was determined for wastewater from the liming process, amounting to 5000 to 10000 mg O_2/dm^3. The trends presented by Manjushree (2015) are the opposite. The highest value was obtained for the wastewater after the tanning process, where it was 2000 ± 0.1 mg O_2/dm^3, and the lowest for the liming process, 700 ± 7.5 mg O_2/dm^3 and decalcification 700 ± 10 mg O_2/dm^3. Low BOD_5 parameters after tanning, are typical of these processes.

The discrepancies that exist between the in-house and comparative results are directly related to the production technology and method of gutting at each plant. The source of the samples referenced by Kavitha (2015), Manjushree (2015) and Dziadel (2022) is the Vellore district area in India, the Hazaribagh industrial zone in Bangladesh and tanneries from central and northeastern Poland. Despite such distant locations between the sites studied, some of the results are similar which, in addition to the differences, indicates similarity in processes.

The ratio of BOD_5 and COD parameters compared to each other provides the possibility to determine the susceptibility of wastewater in terms of biological decomposition, as shown in Table 2. As the ratio decreases, the susceptibility to biological decomposition decreases, and there are more substances in the wastewater that are undegradable by activated sludge microorganisms. The unfavorable ratio of these parameters is strongly influenced by industrial wastewater [Karamus, 2017]. Based on this and the results obtained for the mixed wastewater, since these final wastewaters with averaged parameters

Table 2. Evaluation of the biological degradation of chemical compounds [Karamus, 2017]

BOD_5/COD_{Cr}	Decrease in $COD_{Cr\%}$	Susceptibility to biological decomposition
>0.5	>90	readily decomposable
0.4 – 0.5	50 – 90	moderately decomposable
0.2 – 0.4	10 – 50	slow decomposable
<0.2	<10	undecomposable

will be subjected to treatment, it is possible to conclude that based on the accumulated values of BOD_5 = 2400 mg O_2/dm^3 and COD = 4215 mg O_2/dm^3, the ratio of BOD_5/COD is equal to 0.57. It means that mixed tannery wastewater is a readily biodegradable load. Analyzing the data presented by Kavitha (2015), in mixed wastewater for average values of BOD_5 = 2100 mg O_2/dm^3 and COD = 5250 mg O_2/dm^3, the BOD_5/COD ratio is 0.4. also demonstrates the biodegradability of tannery wastewater. And it is possible to treat it, for example, using plant treatment methods. This is also demonstrated by Zapan (2020) on a model hydrophytic treatment plant. Two-stage treatment was given to tannery wastewater pretreated with physicochemical treatment, introduced to the first treatment stage – a horizontal subsurface flow bed with the plant Isolepis cernua. The second treatment stage was a free-flow bed and the Nasturtium aquaticum plant. Despite the small scale, such a treatment method is a feasible alternative for treating tannery [Zapana, 2020].

CONCLUSIONS

Using water and wastewater management, involving the separation of two wastewater streams and making attempts to reduce the amount of water used, for example, by changing the characteristics of the processes, are already steps toward tangible pro-environmental benefits. Separate collection of chromium wastewater with appropriate technology allows its secondary use, and general wastewater without chromium can be treated at municipal treatment plants where local infrastructure allows. Since this wastewater has a high ratio of BOD_5 to COD in mixed wastewater, it is also possible to treat it using hydrophytic methods. It does not apply to wastewater after tanning processes since the high chromium content indicates its toxicity, and in this case, as in many tanneries, the concentration of chromium in the wastewater was 2.95 g Cr/dm^3.

Acknowledgments

The research was carried out as part of research work no. WZ/WB-IIŚ/2/2021 and WI/WB-IIŚ/10/2023 at the Bialystok University of Technology and financed from a subsidy provided by the Ministry of Education and Science.

REFERENCES

1. Ascón-Aguilar E., Marrufo-Saldaña L., Neyra-Ascón W. 2019. Reduction of total chromium levels from raw tannery wastewater via electrocoagulation using response surface methodology. Journael of Ecological Engineering, 20(11), 217-224.
2. Ayele M., Limeneh D.Y., Tesfaye T., Mengie W., Abuhay A., Haile A., Gebino G. 2021. A Review on utilization routes of the leather industry biomass. Advances in Materials Science and Engineering, Vol. 2021, Article ID 1503524.
3. Bartkiewicz B., Umiejewska K. 2010. Industrial wastewater treatment. PWN Scientific Publishers. Warsaw.
4. Bharadwaj M., Mondal B.C., Lata M. 2020. Scope of utilization of tannin & saponins to improve animal performance. Journal of Entomology and Zoology Studies, 9(1), 2168-2179.
5. Bień J., Celary P., Wystalska K. 2017. The problems in achieving sustainable development in the tannery industry in regard to sewage sludge management. Journal of Ecological Engineering, 18(6), 13-20.
6. Bień, J.B., Sobik-Szołtysek, J., Wystalska. K., Kowalczyk, M., Kamizela, T. 2019. Disposal of industrial wastewater. Publishing House of the Częstochowa University of Technology, Częstochowa, Poland.
7. Chmielowski K. 2019. Water and wastewater from the tanning industry. Municipal Review, 1, 28-31.
8. Drioli E., Cassano A. 2023. Membranes and integrated membrane operations as clean technologies in the leather industry. Clean Technologies. 2023, 5, 274-296.
9. Dymaczewski Z. (Ed.). 2011. wastewater treatment plant operator's handbook. Poznan.
10. Dziadel M., Ignatowicz K. 2022 Assessment of the quality of wastewater generated during production at a tannery plant. Journal of Ecological Engineering, 23(5), 109-115.
11. Famielec S. 2015. Environmental effects of tannery waste incineration in a tunnel furnance system. Proceedings of ECOpole'15 Conference (14-15.10.2015, Jarnoltowek, Poland).
12. Hassan Z. M., Manyelo T. G., Selaledi L., Mabelebele M. 2020. The effects of tannins in monogastric animals with special reference to alternative feed ingridients. Molecules, 25, 4680.
13. Ignatowicz K. 2009. Occurrence study of agrochemical pollutants in waters of Suprasl catchment. Archives of Environmental Protection, 35(4), 69-77.
14. Ignatowicz K; Puchlik M., Łozowicki J. 2020. Removal of pesticides from wastewater by the use of constructed wetlands. Journal of Ecological Engineering, 21(1), 219-223.
15. Kanagaraj J., Velappan K.C., Babu N.K., Sadulla

S. 2006. Solid wastes generation in leather industry and its utilization for cleaner environment - A review. Journal of Scientific & Industrial Research, 65(7), 541-548.

16. Karamus Ł. 2017. wastewater treatment plants and their operation, KaBe Publishing House, Krosno, 2017.
17. Karanam S.B., Raji P., Selvarani J. A., Samrot A.V., Javad P.T.M., Appalaraju V.V.S.S. 2019. Greener approach for leather tanning using less chrome with plant tannins and tannins mediated nanoparticles. Journal of Cluster Science, 30(6), 1533-1543.
18. Kavitha P.R., and Ganapathy G.P. 2015. Tannery process and its environmental impacts a case study: Vellore District, Tamil Nadu, India. Journal of Chemical and Pharmaceutical Sciences, 8(4), 757-762.
19. Kubala A., Przywara L. 2015. Oxidation of sulfides in tannery wastewater. ECOpole'14 Conference (15-17.10.2014, Jarnoltowek, Poland), 9(1), 253-260.
20. Lofrano G., Meriç S., Zengin G.E., Orhon D. 2013. chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review. Science of the Total Environment, 461-462, 265-281.
21. Lozowicka B., Kaczynski P. Szabunko J., Ignatowicz K., Wawrentowicz D., Lozowicki J. 2016. New rapid analysis of two classes of pesticides in food wastewater by quechers-liquid chromatography/mass spectrometry. Journal of Ecological Engineering, 17(3), 97-105.
22. Malovanyy M., Palamarchuk O., Trach I., Petruk H., Sakalova H., Soloviy K., Vasylinych T., Tymchuk I., Vronksa N., 2020. Adsorption Extraciotn of Chromium Ions (III) with the Help of Bentonite Clays. Journal of Ecological Engineering, 21(7), 178-185.
23. Manjushree Ch., Mostafa M.G., Tapan Kumar Biswas, Mandal A., Kumar Saha A. 2015 Characterization of the effluents from leather processing industries environ. Processes, 2, 173-187.
24. Michalak A.M., 2021. In vitro and in vivo cultures of Iris pseudacorus plants as a source of biologically active compounds. Doctoral dissertation. University of Gdansk, Interuniversity Faculty of Biotechnology of the University of Gdansk and Gdansk Medical University. Gdansk.
25. Ordinance of the Minister of Maritime Affairs and Inland Navigation of July 12, 2019 on substances particularly harmful to the aquatic environment and conditions to be met when discharging wastewater into waters or into the ground, as well as when discharging rainwater or snowmelt into waters or into water facilities. Dz.U. 2019 poz. 1311.
26. Rüffer H., Rosenwinkel K.H., Treatment of industrial wastewater, Oficyna Wydawnicza Projprzem-EKO, Bydgoszcz 1998.
27. Rydin S., Black M., Scalet B.S., Canova M. 2013. Best Available Techniques (BAT) Reference Document for: Leather tanning.
28. Santos L., M., Gutterres M. 2006. Reusing of a hide waste for leather fat liquoring. Journal of Cleaner Production, 15, 2006, 12-16.
29. Zapana J.P.S., Arán D.S., Bocardo E.F., Harguinteguy C.A., 2020. Treatment of tannery wastewater in a pilot scale hybrid constructed wetland system in Arequipa, Peru. International Journal of Environmental Science and Technology, 17, 4419-4430.
30. Zhao J., Wu Q., Tang Y., Zhou J., Guo H. 2022. Tannery wastewater treatment: conventional and promising processes, an updated 20-year review. Journal of Leather Science and Engineering, 4(10), 1-22.