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WASTE FROM LEATHER INDUSTRY. THREATS TO THE ENVIRONMENT

ODPADY PRZEMYSŁU GARBARSKIEGO. ZAGROŻENIA ŚRODOWISKOWE

Abstract

Leather industry generates significant amounts of solid waste and industrial sewage. They originate from various technological steps of leather production – 1 Mg of raw hides yields altogether about 700 kg of waste. Moreover, tannery waste contains chromium compounds, commonly used as tanning agents. This poses a further threat to the environment. In the article, the amounts of tannery waste generated in recent years in Poland and in the EU are presented. The general qualitative characteristics and physicochemical properties of tannery waste are described. The article discusses environmental threats resulting from chromium content in the waste as well as the methods of tannery waste utilization. Moreover, the authors present new technological solutions for the leather industry, which may contribute to environmental threats reduction, i.e. the concept of thermal waste treatment including chromium accumulation in ashes, which can be recovered in other industrial processes.

Keywords: tannery waste, leather industry, environmental protection, thermal waste treatment

Streszczenie

Przemysł garbarski generuje znaczne ilości odpadów stałych oraz ścieków poprodukcyjnych. Odpady powstają na różnych etapach technologicznych produkcji, łącznie w ilości ok. 700 kg z 1 mg skór surowych. Ponadto zagrożeniem dla środowiska jest obecność w odpadach związków chromu, które używane są powszechnie jako garbniki. W artykule przedstawiono skalę problemu, tj. ilości odpadów generowane w Polsce oraz w Unii Europejskiej w ostatnich latach. Zaprezentowano również ogólną charakterystykę jakościową oraz właściwości fizykochemiczne odpadów garbarskich. Opisano zagrożenia dla środowiska związane z obecnością chromu w odpadach, a także sposoby utylizacji tych odpadów. Ukazano nowe rozwiązania technologiczne dla garbarstwa, które mogą przyczynić się do zmniejszenia zagrożeń środowiskowych, m.in. koncepcję termicznej utylizacji odpadów garbarskich z akumulacją związków chromu w popiołach, z których chrom w dalszych procesach można odzyskiwać.

Słowa kluczowe: odpady garbarskie, przemysł skórzany, ochrona środowiska, termiczna utylizacja odpadów

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1. Introduction

Production of leather from raw hides has been one of the most important industrial processes since ancient times. For centuries, leather was one of few available materials for the production of high durability garments and footwear. Nowadays despite the variety of synthetics leather is still one of the leading materials for clothing and footwear production due to its unique properties.

1.1. The tanning process

The tanning process consists of many mechanical and chemical stages, which can be divided into three fundamental sub-processes: preparatory stages, tanning and crusting. The first sub-process includes preservation, soaking, liming, unhairing, fleshing, splitting, bating, degreasing and pickling. Next, the pre-treated raw material is tanned. Tanning is the process, which converts the protein of the raw hide or skin into a stable unputrefiable material. Chromium(III) compounds are used most often as tanning agents (in 90% tanneries worldwide). Crusting consist of such stages as thinning, retanning, lubricating and often colouring. Subsequently the tanned leather needs a finishing step, which gives it the required pattern, gloss or waterproof qualities. Finishing operations may include oiling, brushing, impregnation, polishing, embossing, glazing and tumbling [1, 2].

1.2. Amounts of tannery waste

Modern leather industry is based on hides which are a by-product of meat industry. In this aspect tanneries reuse waste from other industries. But on the other hand, the tanning processes generate even greater quantities of by-products and waste than those of finished leather. 1 Mg of wet salted hides yields only about 200 kg of leather. The rest – about 800 kg – becomes waste, including tanned solid waste (about 250 kg), non-tanned waste (about 350 kg) and waste lost in wastewater (about 200 kg). Water required for the processing of 1 Mg of hides amounts to 45–50 m^3 [3]. The chemical reagents consumption is also high – for 1 Mg of hides about 400 kg of chemicals is needed, including sodium chloride, lime, sodium sulphide, sulphuric acid, basic chromium sulphate and others [2]. Thus, the impact of tanning industry on the environment is significant and the proper waste and wastewater management by tanneries is of great importance.

Due to FAO statistics, the worldwide annual production of bovine hides and skins amounts to about 6 million Mg (wet salted weight) – see Table 1. Sheepskins, lambskins, goatskins and kidskins are processed for 600 thousand Mg (dry weight) [4]. Rough calculations reveal that the world leather production generates about 3–3.5 million Mg of solid waste, which requires appropriate treatment in respect of the environmental protection standards. The production of leather has increased in recent years, mostly in developing countries.

The UE-countries process about 11% of world bovine hides production and about 12% of sheep- and goatskins production (mostly Italy, Spain and Germany). The amounts of bovine hides processed in Poland have decreased in recent years, yet the values are still significant – 22.7 thousand Mg in 2009 [4]. Other sources give information about the leather production

in Poland – about 9.5 thousand Mg of leather from bovine hides was produced in 2008 [5]. The leading voivodeships in leather production are Małopolskie, Śląskie and Mazowieckie (especially the Radom area) [6].

Table 1

Production of bovine hides and skins (wet salted weight, thousand Mg) [4]

	2000	2003	2007	2008	2009
World	5860.0	6065.7	6025.8	6056.7	6042.4
EU (27)	-	-	701.6	701.5	708.7
EU (15)	679.0	666.4	626.0	625.9	633.5
Poland	31.6	31.2	23.0	22.9	22.7

Roughly calculating, about 10–15 thousand Mg of solid tannery waste is generated in Poland annually. Leather waste from footwear and garment production as well as tannery wastewater and sludge from wastewater treatment plants must also be taken into consideration. The total amount of waste described by the code 04 01 (wastes from the leather and fur industry, including also tanning liquor, sludge and other) only in Małopolskie Voivodeship in 2009 reached the level of 24 thousand Mg [7].

2. General characteristics of tannery waste

The chemical composition of untreated hide or skin waste (fleshings, trimmings, splits) depends mainly on a kind and quality of the raw material, treatment type and process conditions. The main components are proteins and fat, up to 10.5% (w/w) for both groups. Water content is high, moisture amounts up to 60%. These wastes contain small amounts of mineral substances, 2–6% (w/w). Chromium compounds are not present in the material.

The tanned leather wastes are mainly useless splits, shavings and trimmings. These waste groups differ mostly in size and shape, the chemical composition is comparable for each. They contain 3–6% (w/w) of fat and about 15% (w/w) of mineral components, including 3.5–4.5% (w/w) of chromium as Cr_2O_3 [8].

Another type of tannery waste is wastewater and sludge. Wastewater contains pollutants, such as unused chemicals, leached proteins and products of hide and skin degradation. BOD_5 and COD for 1 Mg of hides processed amount to 35–105 and 88–280 kg, respectively [3]. Sludge form wastewater treatment plants contains mostly water (up to 65% (w/w)), organic substances (30% (w/w)) and chromium(III) compounds (about 2.5% (w/w)).

Moreover, tanneries emit odours and other volatile compounds from the tanning processes as well as from biological decomposition processes that take place in stored raw hides, wastewater, etc. Such pollutants as ammonia, hydrogen sulphide, volatile hydrocarbons, amines and aldehydes are present in air at tannery plants. Currently, all these gaseous pollutants are emitted to the atmosphere [8].

3. Tannery waste treatment methods

3.1. Tannery waste treatment nowadays

Tannery waste brings about multiple problems for tanneries. Its treatment is difficult and there are no methods of its comprehensive utilization. Non-tanned waste was used as a raw material for glue, gelatine, technical fats, protein sheaths and even feed and fertilizers. This waste is also suitable as a substrate for biogas production. The tanned leather waste can be used for secondary leather production. Nevertheless, for economic reasons waste remains mostly unutilized and goes to landfills. Of importance are the BSE-related restrictions which treat non-tanned waste similarly to slaughterhouse waste. It cannot be therefore processed to feed anymore [3, 8, 9].

Due to the European Waste Hierarchy, landfilling is the least favoured waste treatment method. Landfilling of tannery waste poses serious threats to the environment. The non-tanned waste undergoes biological degradation, which may be the source of pathogenic bacteria and volatile organic compounds emission. The tanned waste contains up to 4.5% (w/w) of chromium, mostly as relatively non-toxic to living organisms chromium(III). It can, however, undergo oxidation to chromium(VI) which is known for its carcinogenic properties. The disposal of chromium in tannery waste is significant – about 30 thousand Mg per year worldwide [3]. The environmental effects of such proceedings go far beyond the potential contamination of the environment. The reuse of chromium from tannery waste could help save energy and financial expenditure for chromium ore output and processing.

3.2. Combustion of tannery waste as a comprehensive method of its utilization

Tannery waste contains organic substances and the energy values of different types of waste are relatively high. That is why they can be used as fuel in the combustion process. The problem is the high content of moisture – up to 60% (w/w) for some groups of waste. Amounts of ash are relatively low, 4–8% (w/w). Analyses show that the ash containing chromium compounds may be used as a substitute for chromium ore in chromate(VI) production [10]. A brief characteristic of tannery waste in aspect of its combustion is shown in Table 2.

The combustion should be processed in such a system, which in the first step enables water to evaporate. After the release of water, the temperature should increase gradually, and the ignition should take place. The temperature of combustion should be high enough to meet the appropriate standards (850–900^{o}C). It is important that combustion is complete and no unburned material remains in the ash.

All the types of solid tannery waste may be treated in this way. Sludge due to its low heating value could be mixed with other types in moderate proportions. The combustion process can therefore be a solution for tanneries as a comprehensive tannery waste utilization method. Moreover, the heat energy produced in the process may be recovered and used.

Table 2

Characteristics of tannery waste [10]

Kind of waste	Total organic substances content in dry matter [% (w/w)]	Moisture [% (w/w)]	Combustion residue (ash) [% (w/w)]	Lower heating value [kJ/kg]
Shavings	87.5	53.6	7.8	6663
Sludge	65.5	54.7	24.3	716
Buffing dust	87.4	14.3	6.2	16953
Leather trimmings	87.7	10.2	4.7	19772
Hide trimmings	86.9	59.9	4.7	7753
Fleshings	91.4	59.5	4.6	8952

The practical implementation of the system described above is a tunnel furnace. Waste will be put on special shallow containers, and then the containers will be shoved into the tunnel of the furnace. By regulating temperature in individual zones of the furnace as well as time of waste remaining in each zone the whole process can be controlled. At present, the prototype of such a system is being developed at the Faculty of Chemical Engineering and Technology, Cracow University of Technology. In the near future it will be tested and optimized.

4. Conclusions

Due to its significant amounts and specific properties, tannery waste is a serious environmental burden. Landfilling does not solve the problem in an environmental friendly way; moreover, it brings about threats like potential contamination and generates energetic and financial costs. The proper utilization of this waste not only eliminates the negative environmental impact of its landfilling, but also brings benefits such as energy and material recovery. The combustion process permits to utilize all types of solid tannery waste. Since the waste contains mostly organic matter (apart from moisture), significant amounts of energy may be recovered in this process. Moreover, ash containing chromium compounds may be used for chromate(VI) production. The tunnel furnace is supposed to be the appropriate implementation of the tannery waste combustion system. The further research aiming at developing and optimizing the described technology will be carried out in near future.

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