

**OGÓLNOPOLSKA IZBA BRANŻY SKÓRZANEJ**

**Z SIEDZIBĄ W RADOMIU**

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**Investigations on utilisation chromium tanned leather residues by chrome recovery and biogas production**

The production of tanned leather is very harmful for the environment. A lot of chemicals are used. The global volume of waste from the leather industry amounted to more than 800 million t per year, of which about 200 million t was generated in Europe. Approximately 210 million square meters of leather are produced per year in the European Union. About 3.5 million t of various chemical reagents and 8.4 million m3 of water are used for the production of such skins.

These figures only include waste whose chemical composition is comparable to that of finished leather. Most of these residues, as well as used leather and leather-based consumer products, are disposed of with conventional residual waste and, depending on the country, either landfilled or incinerated. The chromium and heavy metal components contained are returned to the environment either directly or via the ashes, while new chromium has to be provided for the tanning of new leathers.

For centuries leather tanning has been one of the most important industries for mankind. It is also the one producing the most polluted wastes. In general, the industry is based on the production of hides as a by-product of the meat industry. Tanneries generate plenty of wastes during all stages of their production. In the first phase, when the hide is prepared for tanning, the wastes consist mainly of untanned scraps from flashing and splitting, wastes from unhairing and pulp from degreasing. Hides are very often preserved with salts (sodium chloride). The amount of this preservative is sometimes very high - up to 300 kg per 1000 kg of hides skins. Before the production process starts, these preserved hides skins are soaked with water, and this treatment generates large amounts of wastewater with partially extremely high salt contents. The treatment of this highly polluted waste water is very demanding and cost-intensive. The next process is tanning while the protein chains in the leather form stable complexes with chromium in case of Cr-tanning. This process is executed in water-containing chromium (III)-salts producing wastewater up to 250 kg per 1000 kg of hides. The third and last operation is finishing, which includes various process steps including glazing, polishing and coloring. It can also generate wastes containing leather dust and also chemical reagents. It can reach 100 kg per 1000 kg of hides. Generally, processing of 1000 kg of hides in tannery enables to obtain 200 kg of tanned leather, 350 kg of non-tanned solid wastes, 250 kg of tanned solid wastes and 200 kg of wastes in 45 m3of wastewater. As chromium tanning is the most common tanning process at present, chrome is one of the chemical reagents that remains in the wastewater as well as the solid waste. Chromium is usually used and present as Cr(III), which is relatively stable, poorly soluble in water and does not generally condemn health problems. But Cr(III) can be oxidized to Cr(VI) which can also occur partially through improper tanning. Cr(VI) is toxic and carcinogen, has a greater solubility compared to Cr(III) and easily penetrates biological membranes leading to a high ecological risk.

Besides high Chromium concentrations, tannery wastewaters also contain high concentrations of both organic (proteins, fats) and inorganic (salts) components. The combined wastewater usually is pretreated onsite and then transferred to local treatment plants. As chromium is a problem for sewage treatment plants, it often is precipitated previously .

Among all tanneries in Poland, 80-90% using chromium (III) as a main chemical agent. The Chromium (III) is not mentioned in 2000/60/WE Directive also after revision made in 2008/105/WE directive, but the problem is in possibility to change it in Chromium (VI) by oxidizing Most of tannery process are made in water solution. So the wastewater are the main problem in this industry.

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The method consists in adding chemical reagents such as sodium carbonate, sodium hydroxide or calcium carbonate. As a result, a precipitate of chromium (III) hydroxide is formed . The recovered chromium regenerate can be re-used in the chromium tanning process. Whereas the obtained supernatant due to the reduced chromium content can be subjected to biological treatment. The advantage of using the precipitation method is the reduction of chromium content in wastewater. On the other hand, the disadvantages are: the addition of additional chemical reagents to the wastewaters, the duration of the process depends on the alkaline agents used, the need for special filtering devices and sludge containing small amounts of chromium, as well as proteins and fats. In addition, if the chromium regenerate is not re-used, it goes to a landfill site where it is stored in a suitably protected way.

Currently, there are a lot of researches on the use of membrane techniques for the treatment of chromium tannery wastewaters. In the literature can be found information about on the use a low pressure membrane processes such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). However, the practical application in the separation of chromium has found the nanofiltration process (NF). By using nanofiltration processes for the treatment of chromium tannery wastewater, two streams can be obtained: permeate containing high concentration of monovalent ions salt (e.g. chlorides) and retentate containing a high concentration of chromium multivalent

ions salts (e.g. sulfates). The permeate can be used as a pickling bath, whereas the retentate can be used in the tanning process . The use of pressure membrane techniques has certain advantages, including low energy demand, the possibility of enlarging the process on a larger scale (modular construction), separation processes are carried out continuously, no need for additional chemical reagents . Inconveniences appearing during the use of pressure membrane processes for wastewater treatment are: Flux decrease associated with the occurrence of concentration polarization and fouling, as well as the resistance of the membranes used.

In recent years, a major problem is the utilization of chromium solid waste coming from the various stages of the processing of skin. These wastes are classified as particularly dangerous for the natural environment. Therefore, they cannot be stored, because after some time the chromium compounds get into the soil. Currently, technologies are being developed that allow the utilization of tannery waste by incineration while recovering chromium (III) from them. However, due to the cost of purchasing the right furnaces for this, such solutions are used to a lesser extent. During the combustion of tanning waste in conventional furnaces, chromium (III) transforms into chromium (VI), which is then released into the atmosphere. Therefore, it is necessary to search for innovative solutions enabling the recovery of chromium compounds from solid tannery wastes, which can be reused in industrial practice, among others during the processing of raw skins. Taking up such actions will contribute to the limitation of the possibility of chromium (III) compounds entering the natural environment and its transformation into carcinogenic forms of chromium (VI).

New valorization pathway for chromium tanned leather residues by a combination of protein extraction, chrome recovery and biogas production), acronym LeatherProBio

Research will be performed by the PFI (Prüf – und Forschungsinstitut Pirmasens.V.) from Germany, and the Lukasiewicz - Institute for Sustainable Technologies (L-ITEE) and the Countrywide Polish Chamber of Leather Industry (OIBS), from Poland, both situated in Radom. The OIBS representing a large number of SME’s , the PFI and Ł-ITEE have experienced research laboratories to perform the research.. OIBS will represent the leather industry and will provide extensive sample material. The SME´s will be informed on a regular basis on the progress of this precompetitive research and will have the opportunity to guide the research according to their needs.

Within the project, the goal is the development of new pathways for the recycling of chromium tanned leather residues, to re-use the contained chromium for the tanning of new leather, to minimize the release of chromium into the environment and to use the biotechnological potential of the contained biomass to safe energy costs. The primary objective is the removal of chromium from tanned leather residues and subsequent combined material and energy utilization of the remaining organic content.

In order to achieve this goal, the chromium must be extracted from the leather waste and the organic material contained in the waste has to be made available to the microorganisms. This can be realized by a special physicochemical treatment process, the thermal pressure hydrolysis (TPH). After the process, the treated material can be divided into two fractions: Liquid phase and solid phase. By adapting and optimizing of the treatment conditions, the chromium content can be selectively enriched in one fraction. Chromium dissolved in the liquid phase can be made available for tanning by special processes, developed by the ITEE. The recycled chromium will be tested by the ITEE and the OIBS by performing extensive tanning tests on various leather materials to define weather the chromium can be reused. The leathers from that tanning-tests are subjected to all necessary material testing to demonstrate their recyclability and to specify the content of recycled chromium in future tanning processes. The chromium-free organic residues will be tested for their biogas potential and as additives for biotechnological applications. Based on the results from the tests energy balances for different scenarios can be established. It will be shown how much of the required energy can be recovered via biogas production from the remaining organic residues. The results are incorporated into the economic and ecological considerations.

The economic potential of the project is based on combined energy and material recovery of by-products and production waste from leather production. Currently, the solid waste is collected from the tanneries by specialized disposal companies and usually incinerated or land filled. The costs for this disposal increase from year to year and have doubled in recent years alone to around € 150 per ton. The costs for waste water treatment are also rising continuously. The technologies developed within the framework of the project can significantly reduce the disposal costs for the tanneries. By using the solid waste for biogas production, energy costs can be significantly reduced and recovery of the chromium content from the production residues reduces the procurement costs for tanning chemicals

In the first activities in the frame of this project the actual situation with waste utilization in Polish tannery industry was investigated. The analyze was made after answers got from 53 tanneries, based in different regions in Poland.

The results are showed below:

The amount of water used in this process, reported by inquired tanneries was different, and vary from 1,5 m3 up to 8 m3 per 1000 kg of hides. The average value was 2,7 m3.

So big differences are because of two reason:

first - different kinds of processed leathers, so it means also different amount of salt in them

and, second - the different technical condition of installations. The older, used and worm out installations are not suitable for water sawing.

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The actual way of waste water treatment

Most of the examined tanneries have not their own installation for waste water treatment.

But not all tanneries gave the feedback. Only 2 tanneries reported, that they have own installation for waste water collection and clarifier at the mechanical treatment plant. All others use the other, specialized firm for waste water collection. The costs of it is also very different. The feedback information showed the value from 25 up to 80 Euro. m3 of waste water. The differences are because of the regions in Poland have the differences in local price lists and from special conditions in agreements.

Fig 1. The actual ways of waste water treatment.

Only 6 from examined tanneries declare the water recycling. The amount of recycled water is no more then 30% of fresh water, used for operations. The main problem in increasing this amount is contaminations from salt.

The solid waste generates during tanning process.

The amounts of solid waste, reported by inquiring tanneries were different, in range 200 kg up to 600 kg of wastes for 1000 kg of hides. The average amount was 350 kg.

 Ilość odpadów stałych powstających podczas przerobu 1 tony skór

The differences are because of kinds of leather and their quality are usually different in tanneries. Also technical equipment in tanneries has the influence on solid waste amount.

Fig 2. The percentage of solid wastes contents

Trimmings 34

Splits 36

Shaving 18

Dust 12

Fig 3. Actual ways of solid waste treatment

 Most of the examined tanneries have not their own installation for solid waste treatment.

Generally, the solid wastes are collecting by outer firm, after preparing by pressing and baling for volume reducing. Only 3 middle size tanneries have their own installation for solid waste treatment..

The costs of solid waste collecting is similar in all tanneries and vary from 90 up to 120 Euro / 1000kg of waste.