

WASTE FROM THE LEATHER INDUSTRY – A RESEARCH IN CURRENT CONTEXT

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ABSTRACT: The „take-make-trash" economic model of today increases the generation of waste and the consumption of raw materials, both of which have a negative impact on the environment when handled improperly. One of the most provided by the natural and contamination businesses is the leather manufacturing. The leather industry produces a lot of trash, which should be handled according to the circular economy's guidelines. Each leather manufacturing facility produces a sizeable amount of effluent with high pollutants that, if discharged into the environment without being properly treated, have a negative effect on the ecosystem. According to estimates, waste generated during the manufacturing of leather outweighs output of all products by 200 times. This article provides some insight regarding the types of waste and the water pollution due to the leather industry. Many secondary wastes can be recovered through these some processes and used in other industrial processes. Also, the article presents aspects related to the recovery and recirculation of industrial water from the leather industry.

KEYWORDS: leather industry, wastes, pollution, recovery, environment

1. INTRODUCTION

The leather business, just a really old branch of production, creates a wide range of products, including shoes, apparel, and purses made from leather. The food industry's leftovers, notably from the preparation of meat, are the source of the raw resources utilized in the leather business. These surplus materials are transformed into fashionable and practical leather goods [1]. One of the most traded commodities worldwide is leather and its derivatives. They were made from easily accessible, renewable resources. Due to the countries' expanding populations, and because it is becoming more urbanized, the trade in leather, which presently exceeds US\$ 80 billion yearly, is anticipated to increase [2].

Humans frequently utilize and consume leather; this occurs virtually daily. Any industry that makes leather requires waste from the meat industry and slaughterhouses as its main raw material. This raw material is turned into functional leather in tanneries. Therefore, the leather business is one of the primary elements for producing leather throughout the entire leather industry [3].

Several compounds are also used to turn the raw material into the end product, even though the waste from the meat sector is mostly employed in the tanning process. As a result, the leather sector uses up resources and creates toxins that are harmful to the environment [4].

Even though the leather sector is not specifically covered by EU law, it is still subject to several regulations regarding the environment, chemical use, advertising, and use of some harmful products, including the use of animal by-products.

2. LARGE LEATHER INDUSTRY AND WASTE

Given that the leather sector is one of the most polluted, there seem to be worries that the process of making leather may have a harmful effect on the environment. We can estimate that India produces roughly 2 billion square meters of processed skinning for leather, and the industry has set a target to double that amount over time [5]. There is greater waste as a result of increased meat demand and leather textile and footwear production. Cow, sheep, and pigskin are the three animal species from which leather is most frequently made. These raw materials are utilized to produce commodities in a number of industries, including the ones that make footwear, purses, clothes, furnishings, and ornaments. Chemical processes are used to extract and preserve a large number of raw materials before they are turned into final goods of the high standard.

One of the ancient industries around the globe is the leather industry. To fulfil the need for shoes, percussion, and percussion equipment in the past, specific activities were developed. Large commercial tanneries were built as a result of the overpopulation and the growing preference for leather and leather

goods. Vegetable tan and tanning using chrome are the two techniques used to tan hides and skins. Four broad categories of production line can be identified in a tannery:

- storage processes for skins and leather, as well as soaking and tanning techniques;
- courtship practices;
- post-tanning techniques;
- finalization processes [6].

Fine skin particles, reagents from numerous chemical releases, huge parts of skin cutting and residual skin, leftovers, solid hairline scraps, and garbage bag scraps are just a few of the waste material that emerge from the skin at all stages of manufacturing. Nearly 850 kg of the 1000 kg of basic leather that is produced during the processing of hides is solid waste. There are only 150 kg of basic materials used to make leather. As reported by the bioenergy consult website [7], a standard tannery produces enormous volumes of waste:

- Meat represents 56–60%
- Chrome splitting and polish dust make up 35–40%
- Skin removal: 5-7%
- Hair: 2-5%.

Given the dangers associated with some of the chemicals used throughout skin manufacturing, the industry faces a significant problem in producing leather on a regular schedule [8]. Tannery discharges are distinguished by their high concentrations of suspended, soluble organic and inorganic particles, which result in a significant requirement for oxygen, highly unsafe salts, and chrome trace elements. Additionally connected to tanning activities is the foul smell that results from the breakdown of protein waste as well as the existence of sulphur, ammonia, as well as other volatile organic compounds.

Skin tanning, keratin, meat, chromium, and cleaning waste are the main types of solid waste produced by the leather industries. Protein is the major constituent of it. The environment will face a serious pollution issue if these proteins and the other chemicals present in the chemically altered protein aren't really utilised properly.

Raw hides are the raw material for the leather production. Salts used to protect skin release colossal load of toxic waste in charge of total dissolved solids (TDS) and chlorine. Other important toxic chemicals used in the tanning production [9, 10] are lime, sodium sulphide, ammonium salts, sulfuric acid, chromium salts and green tanning agents. Today, higher than 6.5 million tonnes of moist and salty hides are handled each year worldwide. About 3.5 million tons of different chemicals are used to treat the skin.

A significant portion of this volume ends up in wastewater. The leather industry consumes an average of 45-50 m³ of liquid effluent and 800 kg of substantial waste per tonne of rawhide. The content of smooth and solid waste arising by tanneries worldwide is COD, 1470. BOD, 619; suspended solids, 920; chromium, 30; sulphur, 60; and solid waste (haircuts, shaving and crunching powders), 3 million tons [11].

Leather industry pollution

Pollution of the soil: Tannery waste that has not been handled has been dumped on the ground. Directly owned soils that receive irrigation from tainted groundwater become less productive. Heavy metals like Cd, Zn, Cr, Ni, Pb, and Mn found in tannery sludges have the potential to build up on ground and absorb nutrients in plants, livestock, and other living things. Due to irrigation using wastewater that contains a high percentage of chromium-rich tannery pollutants, the amount of chromium in the soil is substantial [12]. Because tanneries employ a considerable portion of NaCl as a raw material when tanning skin, a sizable quantity of chloride is released into the ground [13]. The soil's pH rises as a result of the alkalization brought on by sodium carbonate, bicarbonate, and chloride during the tanning process [14].

Aerosol pollution -Due to the foul smell they produce, tanneries are infamous in proverb. Salted hides and skins that have been rehydrated typically release an smell of volatile lipids and amino acids as a result of biological degradation occurring in the presence of humidity. Additionally, tanneries are predominately affected by the toxicity of hydrogen sulphide combined with acids, lipids, carbohydrates, etc. in the processes of limestone and tannery. Air pollution is caused by the dispersion of undesirable compounds into the surrounding atmosphere and subsequent long-distance transportation. Humans are fatally affected by hydrogen sulphide in ambient air at 20 ppm (30 mg/m³). Demineralisation produces pungent and prickly ammonia that goes into the surroundings. Ammonia in the atmosphere is only permitted in quantities up to 50 mg/m³. Phenolic substances (monohydric, dihydric, and trihydric) are released into the atmosphere during the post-tanning and final processes for hides and skins. 10,2 mg/l is the maximum allowed number of phenolic compounds as phenol (C₆H₅OH) in water. In drinkable water, the content must not be higher than 0,3 mg/l. To be able to control toxicity, its value was reported at tannery level. Our healthy existence depends on the oxygen that is present in the atmosphere. Nevertheless, since the 1960s, poor air quality was a major problem in both wealthy and developing nations alike. Because

of the particles, toxic metals, monoxide and dioxide, benzene, N₂O, PAH, NH₃, and other waste products manufactured by tanning techniques, particularly after post-tanning and completing procedures, polluted air poses a major risk to human wellbeing [15].

Water toxicity - Tannery pollutants are a significant ecological disaster since they contribute significantly to the decline of the water device's quality by releasing hazardous compounds into it. Proteins and carbohydrates found in tannery residue are biodegradable organic materials that contribute to the liquid oxygen depletion in waterways that is brought on by the breakdown of microorganisms [16]. Low levels of dissolved oxygen have a detrimental impact on marine life, promote anaerobic activity and the production of toxic gases, alter the nutritional makeup of aquatic life, and ultimately pose a serious health threat to humans by increasing the risk of water-borne illnesses like cholera, parasitic infections, scarlet fever, dysentery, and stomach flu [17, 18].

3. TYPES OF WASTE GENERATED FROM THE LEATHER INDUSTRY

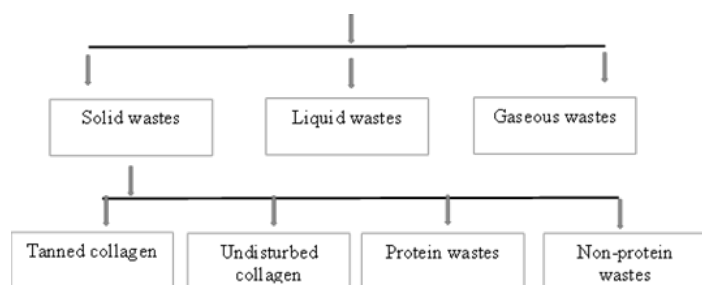


Figure 1. Types of trash produced by the leather sector

Skin-related collagen - Proteins (90–95% of solids, 35% by weight), lipids, carbs, mineral salts, and water make up animal skin. Collagen is the most abundant protein and, when mixed with tanning chemicals, helps to build the skin. Other kinds of proteins include elastin, keratin, glycoproteins, albumins, and globulins. At ordinary temperature, collagen fibres contained in the sarcolemma, a soft tissue, are not soluble in water, weak solutions of alkaline solutions, and organic solvents. In the lack of salt solution, collagen has more swelling behaviour in aqueous, acidic, and alkaline conditions. Collagen has three strands with a repeating Gly-X-Y pattern that is staggered by one residue from one chain to the next. Collagen is distinguished by having a high glycine concentration (33%), with a glycine present across every third residue. Proline and hydroxyproline, which make up 22% of all amino acids, have an annular shape that resists rotation around the N-C bond in peptide chains. In particular, spin all around C-C=O connection is constrained, according to procedure and energy calculations. Therefore, proline

and hydroxyproline play a key role in stabilizing verification. Each amino acid can go before or after glycine in the X and Y locations of collagen. Several tendencies have been seen in practice. Position X typically contains glutamic acid, histidine, leucine, and phenylalanine, while position Y typically has threonine, lysine, and arginine. When proline comes before glycine and is typically converted to 4-hydroxyproline post translation, proline would be spread uniformly. Different methods can be used to incorporate water molecules into the structure. It has been proposed that there are two hydrogen-bound water connections per triplet from the hydroxy group in hydroxyproline to a carbonyl oxygen column [19].

Solid waste During the processing of 1000 kg of unprocessed leather, over 850 kg of solid waste is generated. The amount of primary material used to make 150 kg of leather. Tanneries produce vast quantities of solid waste, with the following breakdown: flesh, 50–60%; chrome, split chrome, and cleaning powder; balance the skins, 5-7%; and hair, 2-5%.

The tanning process produces 20% of the solid waste from the manufacturing of hides, whereas finishing produces 1% [20].

There are numerous techniques to hydrolyse waste products and use the by-product in productive ways. (Figure 2):

- Keratin waste - Keratin is challenging to hydrolyse and highly immune for many chemicals and enzymes. Cysteine is abundant in it. Keratin was hydrolysed with NaOH or HCl levels. Chromium has been tanned and retained at various amounts using hydrolysis made from keratinous substance. The depletion of chromium in the tanner solution and the retention solution is facilitated by hydrolysis [21].
- Meat waste – The possibility of using offloading (50–60% of the waste produced by the leather industry) in functional end goods has been investigated. The redesigned meat hydrolysate, made using meat and acrylic acid, demonstrated better chromium retention in tanning and reuse at a level of 2%. Compared to normally produced skin, the strength and organoleptic qualities of this skin are superior. Lime fabrics were used to stabilize decalcified skin, which was called Reactive Protein (RP). It was created using a particular chemical process that used the reduction and oxidation approach to partially transform the amino acids to aldehyde, which may be used as a tanning product to preserve the skin [22, 23].
- Chrome finishing waste - It was possible to obtain adhesive, gelatine, protein flavours, including

regenerated collagen by using chrome-tanned leather, clefts, and textiles. The aforementioned items can be produced by using hydrogen peroxide to achieve a significant amount of maceration, followed by grinding and extracting to generate the by-product (95%). The effectiveness of solubilization is increased and the quantity of enzyme required is decreased when employing magnesium oxide by itself or in conjunction using calcium hydroxide, sodium hydroxide, and sodium carbonate to finish with hydrolysed chromium. This results in a greater cost-effective treatment [24,25].

In this way, we've:

- Utilization of by-products all through conservation - Maintaining meat may be necessary in the factory to stop putrefaction (left to rot), preserve the skin, and enable successful transportation (as well as storage) inside the tannery. Salts are typically used in the preservation process to inhibit bacterial development, even though this causes significant amounts of total dissolved solids (TDS) inside the softening solid and liquid industrial effluents. The search for a different, greener approach has therefore received a lot of study attention. Coffee peel has demonstrated its promise as a salt replacement for skin conservation. The dried skin of coffee beans known as the coffee peel is a by-product created during the preparation of coffee seed pulp. When allowed to rest for 30 minutes, the substance chlorogenic acid, which is recognized for its capacity to inhibit the growth of germs, successfully inhibited microbial growth on goat skin, permitting for 15 days of conservation. Moreover, there was no discernible change in the skin's characteristics and the wastewater produced had a substantially reduced TDS level. Potential uses for the biowaste the Bael tree produces include skin conservation. An extract can be created by combining the dried leaves of a Bael tree, a tree with strong antibacterial properties, with ethanol. Raw goat skins were treated with a 5% concentration, and the skin was effectively kept on for just a month. Compared to production lines, the final skin was equivalent to that produced using traditional methods, although water usage and pollution levels were significantly lower. These two instances show how combining waste streams from several industries can reduce input costs while increasing waste.
- Liming and softening processes that utilise by-products - Softening as well as liming are the steps in the production of hides for tanning. Since the traditional methods of liming and farrowing involve chemicals that produce a lot of contamination, like sodium sulphide and lime, enzyme-assisted removal has also been embraced as a more sustainable

substitute procedure. Goat skin removal using enzymes obtained from fish waste has been successful. Scanning electron microscopy evidence shows that the fish waste extract was responsible for completely removing the hair from goat skin. Furthermore, the skin's physical strength after shrinking at that temperature was comparable to control levels. The pollutant loads in the waste stream have significantly decreased thanks to the enzymatic decomposition of fish faces. The hides or skins are decoupled, then they are incarnated, decalcified, crushed, and processed to get them ready before tanning. Chromium salt tanning is the most common technique, although worries about environmental degradation are encouraging the development of more ecological and environmentally tanning techniques. It has been discovered that using kraft fibre, a by-product of papermaking procedures, could take the place of tanning with more ecologically responsible chromium. When applied to sheepskin, the phenolic compound created by the breakdown of lignin kraft gives tanned skin characteristics similar to those of traditional chromium-tanned flesh. If the leather is of poor quality, additives may be necessitated to enhance the final feel and appearance. Traditional petroleum-based fillers have been completely replaced by whey protein, a by-product of the dairy sector. Whey-filled leather displayed good physical characteristics, including a noticeably better strength properties and more youthful pattern than did traditional fillers.

- Using leftovers from post-tanning procedures – Painting happens next for tanning. Fungi have been grown from agricultural residues to create bio-pigment. When employed as a colouring agent on moist skin, liquid bio-dyes derived by fungi have shown efficacy. When tested for dyeing potential using both dry and wet friction, a yellow bio-dye resulted in positive results. Additionally, the yellow leather displayed good light resistance and strong heat stability.

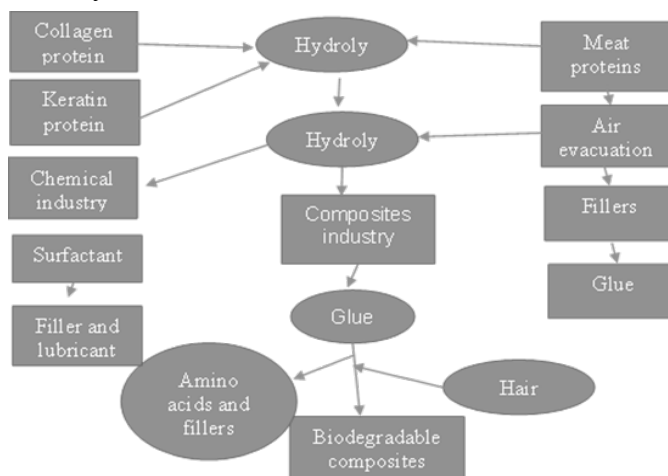


Figure 2. Use of solid waste [20]

4. RECOVERY AND RE-ENTRY INTO THE CIRCUIT OF INDUSTRIAL WATERS FROM THE LEATHER INDUSTRY

Water serves as a working environment for the basic phases of the skins processing process, for example, tanning and painting, is carried out in barrels and other equipment that uses fleets in which chemicals are dissolved. Water is also used to clean the skin, machines, and workplace. The tannery's permitted and controlled wells, along with corporate and public water mains, constitute the most significant water supplies. The two environmental factors of the leather business that are particularly crucial are source of freshwater and wastewater reuse.

European tanneries obtain the water from municipal, commercial, and perhaps even regional wells that are regulated and approved by the municipal government. Wastewater from tanning procedures includes toxic particles and organic debris and needs to be properly processed until being released back into the environment, usually on-site or in shared treatment facilities.

The leather business uses a technique to transform unfinished leather into a sturdy substance which uses a lot of water and other chemical agents and generates a lot of waste. Because the skin generated has good physical and chemical qualities and is affordable, chromium tanning is currently the most used method. Chromium salt is added to the skin as a result of the process, but 20–30% of the salts are not fixed and, after chemical precipitation, are retained as sludge in wastewater treatment facilities. The saltiness of the wastewater is significantly increased by the salt needed to conserve the skins, pickles (chlorides), and tanning treatments (sulphates).

With substantial concentrations of organic, mineral, and nitrogenous chemicals, chromium, sulphides, suspended solids, and dissolved solids, the effluent from the leather sector is extremely complicated. Tannery wastewater is cleaned physically, chemically, biologically, or by integrating multiple processes. Big corporate tanneries were built as a result of the overpopulation and the increasing preference for leather products and leather goods. Tanneries are typically thought of as highly polluting large factories that produce a wide variety of highly concentrated effluent. The filling and pulling activities related to the tanning procedures, as well as the various methods employed for the prepping, tanning, and completion of hides, all contribute to the heterogeneity of tannery effluent. The kind of skins that are utilized and the qualities needed for the final product govern these processes. Metals, hazardous

compounds, chloride, lime with high soluble and suspended salts, and other toxins in drainage cause serious issues [26].

Inside the leather business, the properties of wastewater vary greatly between tannery to tannery based on factors including scale, the solvents used during a given operation, the volume of water consumed, and the kind of finished product created. Tannery wastewater is primarily identified by studies of chromium and sulphides, suspended solids (SS), dissolved total solids (TDS), chemical oxygen demand (DOC), biochemical oxygen demand (BOD), and other parameters. In generally, tannery wastewater typically basic, dark brown in colour, and contains a lot of different organic compounds, according on the agents employed. Because of its large number of chemicals and basic composition, the effluent from tanning can seriously harm the environment [27]. Multiple traditional procedures, including biological systems, the oxidation reactions, and the chemical reaction, are used to dispose of effluent from the leather sector.

Wastewaters can be effectively treated via biological treatment, according to research. In order to stabilize waste for bacterial treatment, it must first be converted into safe inorganic materials either using an aerobic or anaerobic method. The pace of degradation in the aerobic is quicker than the anaerobic treatment and is not associated by foul odours, whereas the anaerobic system takes an extra duration of retention and produces foul odours.

It has recently been demonstrated that oxidative therapy is most effective within a certain ozone usage range and noticeably enhances the aerobic recyclability of resistant molecules. Additionally, full nitrification may be achieved through later aerobic decomposition, and any leftover ammonia is eliminated.

But compared to nylon, cotton, or numerous synthetic leathers, goods often exhibit increased resistance to wear and tear. The leather processing manufacturing, for its size, is one of the largest water-consuming in the entire planet, from of the water used in animal farming to the water used during tanning and completing operations. However, the total water footprint of the leather industry does not compare in real terms with a sector like hydroelectric. The quantity of sewage the sector produces, often with a heavy load of contaminants, also sets it apart. Even though the process of making leather utilizes a lot of water, it is important to remembered that the skins utilized in the process are merely a result that would normally be wasted by the leather sector.

An effective strategy for managing water management is achieved by determining the optimal amount required for each stage of the process and introducing the correct quantity with the help of simple measuring equipment. Batch washing involves washing the skins during processing by introducing the necessary amount of clean water into the processing vessel and using the action of the pot to achieve the necessary agitation. The first step towards streamlining process water involves optimizing water consumption and decreasing the consumption of chemicals used in the process. Thus, both the size required to treat the wastewater in the plant and the energy consumption will be reduced. While cleaning focused sewage water is more successful, decreasing water use doesn't always significantly decrease the impact of several physico-chemical contaminants. The amount of water used for rinse procedures differs widely amongst leather industry. A significant main causes of water waste is selecting water treatments.

For many years, European tanneries have prioritized environmental preservation by lowering water use per product unit. Planning ahead for continual development with a focus on creating sustainable water procedures and water reuse technology has generally created this achievable. The remainder, which is primarily water that dries while production or the moisture levels of trash transported for reuse and/or disposal, makes up over 95% of a water used throughout tanneries. The wastewater that has been released then goes for processing. 100% of European leather industry treated their wastewater with comprehensive and intricate cleaning techniques, in contrast to some of their non-European rivals in which environmental law is either non-existent or badly applied.

Most of the leather is produced in the regions inside the southern European nations. Integrated treating wastewater facilities were constructed here and throughout time, they underwent constant improvement. At the international scale, district consortia-managed consolidated wastewater treatment plants are a great illustration of corporate increase. The European tanning sector has made significant progress in lowering the amount of water needed in manufacturing and the number of pollutants in the wastewater that results. The effectiveness of the technique and the capabilities of manufacturable substances and processes will eventually hit their

partnership for ecological responsibility. In this situation, tanneries typically only perform basic processes; the other physically, chemically, and biologically procedures are left to the consolidated effluent treatment systems. A same wastewater treatment facility that was initially constructed to support the tanning sector have continuously developed in the areas in which the tanning areas are situated, and they now considerably serve to the cleaning of civic wastewater. Beyond the larger firms, tanneries handle their own treatment process and primarily release cleaned effluents into sanitary drainage systems. With the exception of soluble salts, that remain an unsolved technological issue on a global scale, the several wastewater treatment technologies used in European tanneries obviously ensure outstanding filtration efficiency for practically all criteria. By creating and applying strategies that are part of the procedure that aim to lower the level of chemicals in effluent either by reducing the number of chemicals dosed or by favouring a greater saturation of fleets, water contamination was reduced in European tanneries.

The European leather sector has also always made an effort to use less water. Through the application of effective watery ecosystem procedures and water reuse technology, this development, which started long years back, is still continuing to grow. To create one square meter of leather in Europe from 2016 through 2018, facilities used an average of 0.121 cubic meters of water, which is roughly 7% lower than what was recorded for both the period 2010 to 2011. It is indeed crucial to remember that this was accomplished despite the fact that there were more entire businesses, which consume more freshwater. As a result, the industry may have improved more than initially thought.

The following image on the effectiveness of water treatment about other contaminants for tanneries illustrates how fighting contaminants in wastewaters is more difficult if there is a need to minimize the quantity of wastewaters. If the wastewater quantity is decreased without the contaminating load being reduced, the contaminating charge will essentially

limits, though. To combat this, the European leather sector is collaborating with companies in the chemicals industry to create procedures that are more effective and new substances that will raise the sector's sustainability performance.

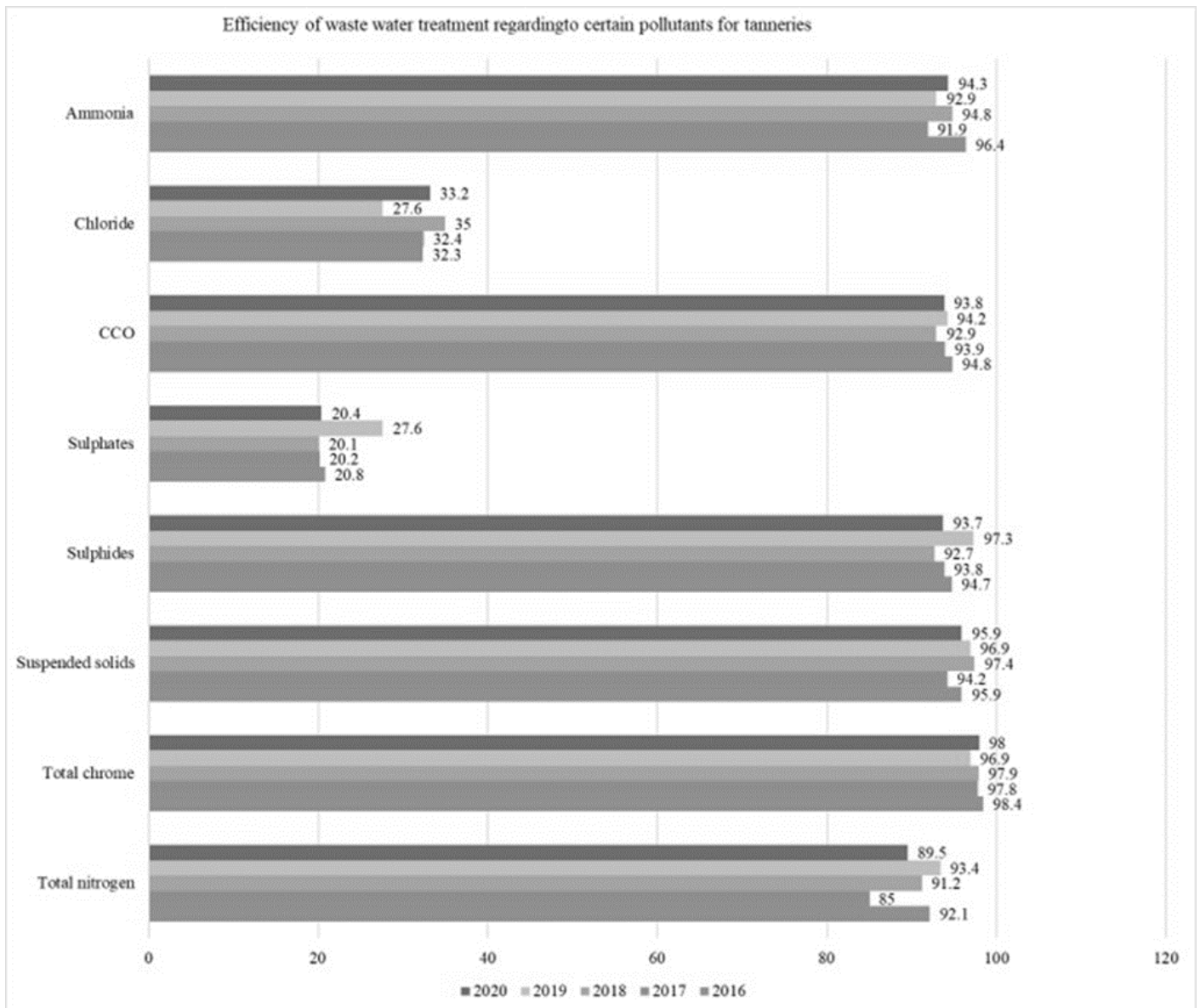


Figure 3. Efficiency of wastewater treatment regarding certain pollutants for tanneries

Today's tanneries consume less water, less energy and have replaced dangerous chemicals. It treats wastewater efficiently, recovers and recycles most of the organic waste. To ensure the long-term viability of tanneries in overall as well as the European area, cutting-edge advancements in technology must be linked with innovations in socio - ecological systems and the synchronization of global norms on the global impact of goods.

Natural resources provide the essential elements for manufacturing at the unit level of production. This is an asset used to craft items that are often discarded after use. After using them, waste is created without the possibility of reusing the components or perhaps the entire product for other purposes. Making more efficient use of ecological resources, reducing environmental pollution, and promoting economic growth are circular economy principles that can also be applied at the leather industry level [28].

5. CONCLUSIONS

Four million tons of garbage are generated yearly by the leather industrial alone. As the cost of garbage compactors and the use of fossil fuels to produce electricity increases, it is more crucial than ever to look for reasonable options to current waste categories and renewable energy sources. By implementing a full exploitation strategy for all categories of significant tannery trash and sludge, the current problem with the garbage heap can be resolved. Also, a decrease in air pollution and the negative effects of odours on the ecosystem might improve life for those who located nearby to tanneries.

6. ACKNOWLEDGEMENTS

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