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Tannery: Environmental Impacts and Sustainable Technologies

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Abstract

The tannery is an old industrial sector well-developed, plays an important role in the global economy, and has been heavily industrialized over the years in all countries. In developed countries, the legislation forces the tannery sector to develop clean and sustainable production. Due to the strict legislation policies, there was a continuous change in the distribution of the processing sites. There are two main reasons for this shift of the distribution, namely: 1) lower labour costs in some countries than in others; 2) fewer environmental restrictions in some countries than in others.

The current tanning process is still mainly based on the traditional one, making use of chromium salts and being able to give leather of very high quality, despite its severe environmental drawbacks. Since its industrialization, the tannery has shown its heavy environmental impacts, caused by the operations and the processes done in the productive/supply chain, from the raw hides and skins to the final leather. Especially, this sector consumes a huge amount of water, which generates wastewater with high concentrations of pollutants (mainly, chromium(III), sodium sulfide, ammonium chloride, biocides, aldehydes, dyes, etc.). Emissions to the air and solid waste production are worth of consideration, too. At last, the health effects on the workers can give problems in the short as well as long term.

Looking at the current distribution of the processing sites, most are in developing countries, where the legislation is still weak.

Little amounts of leather derive from the green tannery, where the use of chromium is limited or completely avoided. The reason is the lower quality of the leather produced by the so-called "green technologies".

This paper analyzes the impacts deriving from the tannery industry due to the conventional chromium process. The reduced-chrome processes and green technologies are discussed, too, considering the role of nanotechnologies.

Keywords: Tannery; environmental impacts; green technologies; natural resource consumption.

1. Introduction

The tannery is an old industrial sector well-developed on all the continents. However, in the last years, there was a continuous change in the distribution of the processing sites. There are two main reasons, namely: 1) lower labour costs in some countries than in others; 2) fewer environmental restrictions in some countries than in others. Thus, this has entailed a migration of the environmental drawbacks.

The tanning process is still mainly based on the traditional one, making use of chromium salts and being able to give leather of very high quality, despite its severe environmental drawbacks.

Since its industrialization, the tannery has shown its heavy environmental impacts, caused by the operations and the processes done in the productive/supply chain, from the raw hides and skins to the final leather. Especially, this sector consumes a huge amount of water, which becomes wastewater with high concentrations of pollutants (mainly, chromium(III), calcium hydroxide, sodium sulfide, ammonium chloride, biocides, aldehydes, dyes, formic acid, etc.). Moreover, emissions to the air and waste production must be considered, too. Last, but not least, the health effects on the workers are worthy of attention due to the problems in the short as well as long term.

In 2020, the main leather production was distributed in China, Brazil, Russia, India, Italy, South Korea, Argentina, and the USA [1], where different legislations are in force.

As for all the industrial activities, in developed countries, the legislation into force pushes for the development of cleaner and sustainable production, whereas in developing countries, very often the legislations are still weak or lacking. This means a different world distribution of the severe environmental impacts due to this industrial sector.

Limited amounts of leather are derived from green tanning, where the use of chromium is limited or avoided at all. Unfortunately, at present, the leather produced by green technologies shows lower quality, especially for the shrinkage temperature, which does not reach the minimum value required by International Standards (100 °C).

As for many industrial sectors, these impacts are not compatible with the challenges defined by the 2030 Agenda for Sustainable Development adopted by the United Nations Member States in 2015.

The heaviest impacts, namely the high chromium concentration released in the wastewater and the huge water consumption, must be reduced more and more with improvement or changes to the production process, to get the Sustainable Development Goal 12 – Responsible Consumption and Production, and as a further goal, Sustainable Development Goal 6 – Clean water and sanitation.

The current paper wants to be an excursus on the impacts deriving from the tannery industry when the conventional chromium process is adopted. Among these impacts, chromium emission to wastewater and water consumption is particularly critical. For this purpose, the paper highlights the reduced-chromium processes and green technologies available to decrease chromium losses to the environment and water consumption. This is done by highlighting the findings available from the most updated studies.

At the end of the paper, the role of nanotechnologies is shown, too, both in the process chain and emission treatment, particularly, wastewater treatment. It is worthy of note the still limited use of this application at the industrial level due to the difficulties linked to the transferability of the findings from the laboratory scale to the production level.

2. Conventional process

Fig.1 shows the conventional tanning process, also called "chrome tanning".

The process is based on 4 steps, namely:

1) pretanning, to prepare the raw hide for the tanning process, removing improper materials;
2) tanning, to fix and stabilize the collagen;
3) post-tanning, to improve some leather characteristics;
4) finishing, to coat the leather for protection and aesthetic reasons.

In turn, each of them is composed of a series of operations, mainly chemical, while some are mechanical. Fig. 1 shows this, evidencing the impacts produced by each operation in terms of the production of wastewater, solid wastes and air emissions.

Fig. 2 shows the average quantities of wastewater, air emissions, and wastes produced in a conventional tannery. They represent impacts to be reduced, modifying, or substituting techniques and/or equipment.

To reduce and limit the environmental impacts, two approaches can be used, namely:

- the prevention, by downstream processes, to say changing and/or improving the tanning operations (prevention mode)
- the treatment, by end-of-pipe processes, which are the actions undertaken to solve the environmental problems generated by the tanning supply chain (treatment).

In each approach, the adoption of the Best Available Techniques (BATs) constitutes the most effective effort to produce sustainably. BATs represent the most modern and efficient techniques applicable at the industrial level to limit and prevent environmental impacts and take into account continuous technological improvements, and on the base of this definition, they must be updated through time. In the European Union, their adoption is compulsory [2,3]. The long experience done by the European Union in this field will be beneficial to the countries aiming to establish a similar approach to reduce and avoid the environmental impacts given by the industry.

In technological terms, nowadays huge efforts are done worldwide to prevent and minimize waste production, aiming to adopt the approach of the circular economy, where the waste is valorized by reuse, recovery, or recycling. In other words, reuse, recovery, and recycling must be applied to the maximum extent to make sustainable the industry.

As in other fields, for this purpose, nanotechnologies can play a relevant role.

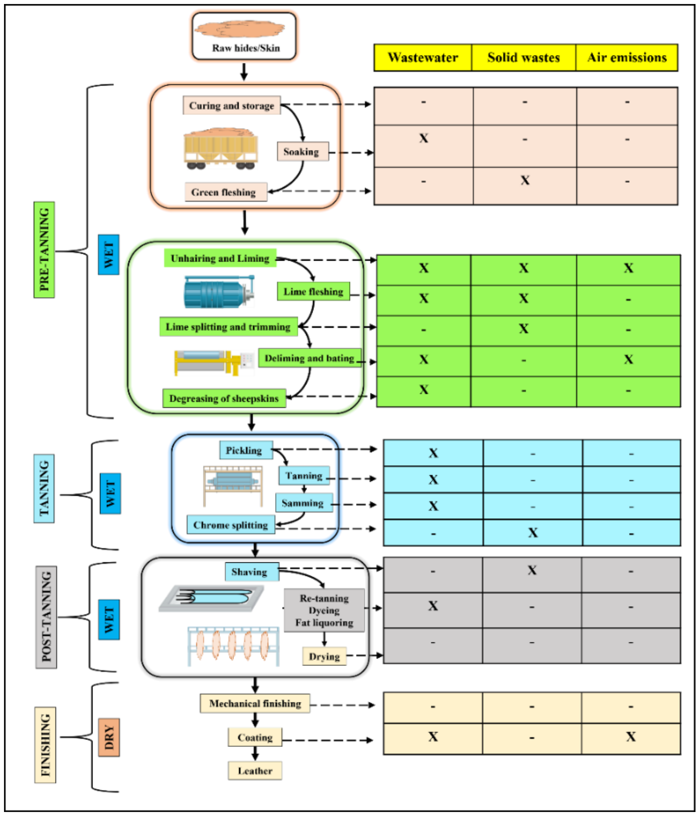

Fig. 1. Tanning process chain and its derived impacts.

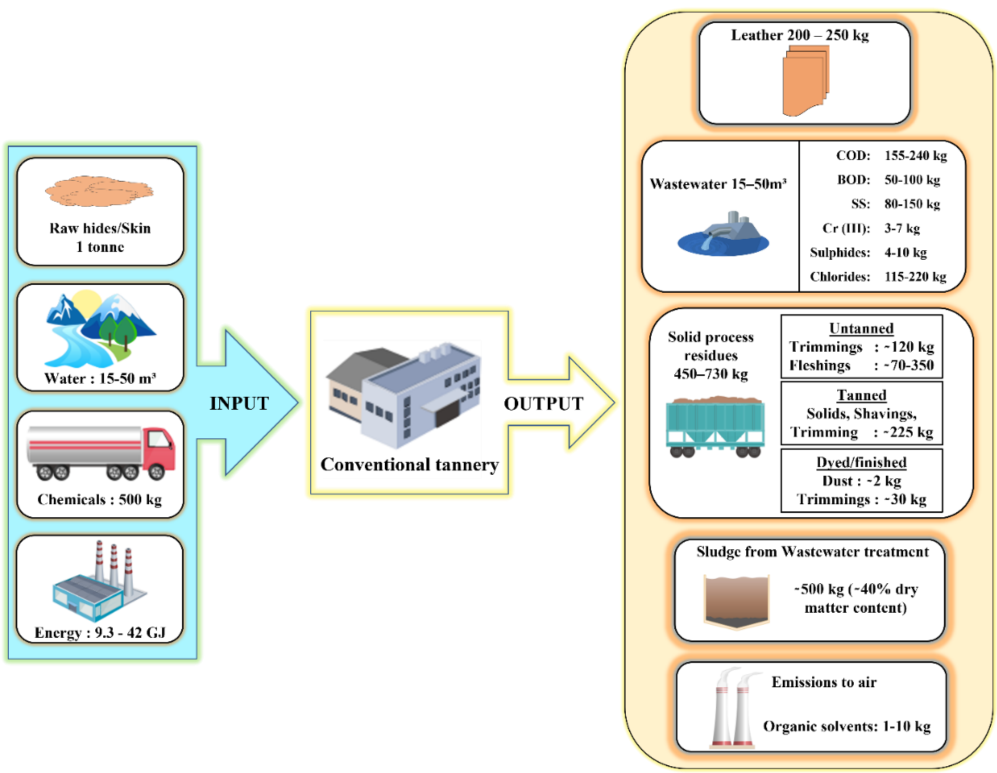

Fig. 2. Mass and energy input and output of the tanning process.

2.1. Wastewater characteristics

The tanning wastewater has always pollution concentrations over the limits imposed by the national legislation for the discharge into surface- and groundwater. This imposes an efficient treatment, on-site, or at a consortial plant, to reduce the pollutant quantity.

Table 1 shows the average pollution production for each tanning step.

Table 1. Water consumption and pollution production in the main steps of the tannery.

	Wastewater and pollutant production (kg/tonne hide)				
	Pre-tanning	Tanning	Post-tanning	Finishing	TOTAL
Wastewater (m^3)	8-30	2-5	4-10	1-5	15-50
Suspended Solids (SS)	70-126	5-10	5-11	0-3	80-150
COD	120-170	10-20	25-40	0-10	155-240
BOD5	40-70	2-7	8-20	0-3	50-100
Chromium(III)	-	2-5	1-2	-	3-7
Sulfides	4-10	-	-	-	4-10
N-NH4+	3.2-4.5	0.5-1.0	0.3-0.5	-	4-6
Total Kjeldalh nitrogen	9.5-15.0	0.5-1.0	1-2	-	11-18
Chlorides	90-150	20-60	5-10	-	115-220
Sulfates	5-30	30-55	10-40	-	45-125

The main pollutants are chromium(III), sulfides, chlorides, and suspended solids. The high concentration of COD and BOD_5 is especially due to the chemicals used for the pre-tanning process, and hide/skin residues, respectively.

Looking at the data for the tanning step, the chromium(III) concentration in the wastewater is in the range of 0.06-0.47 g/L (60-470 mg/L). The lowest concentration limit is higher than the value given by most legislations for emissions in the sewer. As an example, in Italy, the maximum emission limit of total chromium in the sewer is 4 mg/L [4], whereas in India it is more stringent and equal to 2 mg/L [5]. The need for a drastic reduction of concentration is evident. A paper on the legislation for chromium emission to aquatic systems was published by Vaiopoulou and Gikas [5].

2.2. Sludge and solid wastes

As noticeable from Fig. 2, each tonne of processed raw hide produces at least one tonne of solid residues/sludge, with different compositions and characteristics.

They can be defined as:

- Solid waste, if it has no future use, and it must be sent to disposal;
- Sludge, one of the outputs of the wastewater treatment plant, usually with a water content over 50%;
- By-product, when it can be used in other industrial sectors (for example, low-quality leather).

Based on their hazardousness, solid wastes and sludge can be defined as non-hazardous or hazardous, for example, due to the chromium or chlorinated solvent content. This status means different cost levels for their management and disposal, and it is ruled by different legislation.

Vice versa, by-products are not ruled by the waste legislation and their trade is easier than the waste one.

Altogether, most residues are not hazardous, even if their management can pose problems for the treatment or disposal, in particular, the putrescible material deriving from the pre-tanning operations.

2.3. Air emissions

As shown in Fig. 2, the tanning process is also responsible for pollution emissions into the air, mainly composed of organic solvents, used in the finishing, namely in the coating. Some of these compounds are particularly toxic and harmful, and their abatement is mandatory. The most common treatment is the adsorption on activated carbon. Unfortunately, only one part of the emission can be collected and removed, the residue being fugitive emissions and not collectable. This constitutes a serious drawback to the workers' health.

Liming and deliming can give origin to emissions of hydrogen sulfide and ammonia, respectively.

As a whole, the tannery does not suffer from heavy problems of air emissions, compared to the impacts due to the use of chromium.

3. Cleaner processes

As aforesaid, the conventional tannery has high consumptions of chromium, usually in form of sulfate: they are in the order of 15-16 kg/tonne of raw hide, with uptake by the hide around 50-60%. The residual part, 40-50% of the consumption, is lost into the wastewater is around 3-7 kg/tonne of raw hide, but this is not sustainable anymore. To overcome this, several technological alternatives have been studied, and some of them are considered BATs.

3.1. Low chromium emission

A low chromium emission in wastewater can be achieved with different systems, that give similar results and are described here following.

3.1.1. Increase in the chromium uptake

The chromium uptake depends mainly on the processing parameters, in particular pH and temperature, that must be optimized.

The first system to improve it consists of changing pH from 3.5 to 4.5 and increasing the temperature to 50 °C (the process cannot start at a temperature over 30 °C). Operatively, this means a slow temperature growth during the tanning operation.

In this way, the chromium uptake can reach 80% of the applied quantity, decreasing its concentration in the wastewater, which will be never over 500 mg/L, and reducing the impact on the wastewater.

A second technique involves the use of chemicals to improve chromium uptake:

- Adding chemicals (dicarboxilic acids) reacting with chromium to give origin to complexes able for cross-linking with collagen;
- Adding chemicals (phtalic acid, glyoxylic acid) reacting with collagen to increase its number of sites able for cross-linking with chromium.

The main result is the decrease in chromium content in the wastewater. However, the presence of chemicals in wastewater makes difficult the precipitation of chromium as chromium hydroxide. Moreover, the final product can have a lower quality compared to the traditional one, and the use of certain chemicals (for example, epoxydic resins) can cause dermatitis. Therefore, at the moment this technique is not considered BAT (in the European Union it is not used anymore).

3.1.2. Recycling of the chromium solution

A direct recirculation of the spent chromium solution to the tanning itself can be carried out, after the process end and hide discharge from the reactor. Chromium must be added to substitute the uptaken amount. Moreover, the spent solution basicity must be raised to the initial value (around 33%), to have many hydroxyl groups useful to enhance the interactions between collagen-chromium. Recycling can be done up to 10 times.

This technique is easy to apply. However, it needs careful monitoring of the quality of the final product due to possible build-up of impurities and process chemicals in the bath, entailing a lower leather quality.

This means that the technique can be used to produce cheap leather.

3.1.3. Chromium recovery by precipitation

Precipitation can be used to recover chromium in form of chromium hydroxide from the spent solution, adding a strong basic compound to speed up the operation. Commonly, sodium hydroxide is used, or, as an alternative, sodium carbonate. The value of pH cannot be over 10, to avoid the precipitate being again dissolved. The use of flocculants can help the separation from the exhausted solution. Then, the precipitate is removed from the supernatant and dissolved in sulphuric acid.

As for the previous technique, impurities and other chemicals can build up, and they must be removed before the separated chromium is solubilized.

In general, this technique has a removal efficiency of 95-98%, arriving at 99% in some tanneries with efficient recovery processes. This amount represents about 35% of the chromium required in the tanning process.

In Europe, several companies adopt this technique, in consortium or individually.

3.1.4. Tanning pretreatment without chrome tanning chemicals

Pretanning can be done with chemicals such as aluminium salts, glutaraldehyde compounds, titanium salts or colloidal silica, to improve the chromium uptake in tanning, changing some chemical and physical properties of the raw hide. In this way, chromium is used only in the tanning step, reducing its whole consumption.

Moreover, splitting and shaving give origin to chromium-free wastes, that can become by-products instead of wastes.

In the European Union, some installations have adopted this technique.

3.1.5. Pretanning with aldehydes

As seen in the previous paragraph, aldehydes, in particular, glutaraldehyde and its compounds, can be used as a tanning agent. As aforesaid, the most evident result is the production of chromium-free waste instead of chromium-polluted ones.

Aldehydes allow to get leather with very low dry-shrinking, and this property is highly appreciated in some uses, for example when the final product is used as upholstery. However, this technique has the severe drawback to need higher quantities of retanning agents, giving a higher cost than in the conventional process.

3.2. No chromium emission

Many studies have been carried out on metals different from chromium as tanning agents, for example, aluminium, zirconium, iron, and titanium.

Unfortunately, the final leather shows poor quality, not competitive as the production achieved with the conventional tannery. The worst characteristic is the shrinkage temperature, usually lower compared to that achieved in the conventional process: it is 85 °C at most, against a minimum of 100 °C, as required by International Standards. The limit of 100 °C is compulsory for leather used in footwear manufacturing, where high temperatures are applied during their manufacturing. Therefore, these metals do not represent substitutes for chromium, yet.

Other tanning agents are organics, namely:

- Vegetables, traditionally used in tanning, such as woods, leaves or bark extracts: The tanning agents are extracts from woods, leaves or bark. Their action is due to their chemical composition, namely as a) hydrolysable tannins (pyrogallol type), or b) condensed tannins (catechol type). To carry out the vegetable tanning, the hide must be treated with pretanning agents (polyphosphates and/or syntans) to ease and speed up the uptake of vegetable tanning compounds. This system is already applied on an industrial scale. However, from an environmental point of view, vegetable tanning is responsible for the production of wastewater with a high COD concentration, dark colour and toxicity for aquatic life. This cannot be disregarded when the system adoption is decided. Currently, many studies at the laboratory scale are focusing on the use of natural compounds as substitutes for chromium and are under development to optimize the operative parameters. Several reviews on this topic are already available [7-9], and the aim of this paper is not to add another review to the list. However, some studies deserve to be named. Sundar and Muralidharan [10] tested some vegetable extracts rich in polyphenols, derived from tara and esterified jatropha seed oil, that can link to collagen in substitution of chromium. The final leather showed good comfort, thermal stability, and compatibility with human skin. Using these natural chemicals, the wastewater contained a lower concentration of BOD_5, COD, TDS, and chlorides, even if the main result is the absence of chromium. Wu et al. [11] used amino acids as tanning agents. The final leather satisfied the standard values for tensile strength, tear strength, and elongation at 10 N of shoe upper leather. Also in this study, the concentration of BOD_5, COD, TDS, and SS was lower than in the conventional tanning one. The study of Ding et al. [12] showed a positive effect due to the addition of low-molecular chitosan to leather tanned with dialdehyde carboxymethylcellulose. The main result was the enhancement of the thermal stability and the increase of the tensile and tear strength. Recently, Shi et al. [13] proposed the use of a mixture composed of hydrolysable tara tannins mixed with synthetic clay nanoplatelets and active aluminium salts. The tanned leather showed good hydrothermal stability and facilitate the exhaustion of anionic post-tanning chemicals.

- Reactive organic chemicals, especially syntans, combined with vegetable or organic agents: The technique makes use of reactive organics and vegetable or organic tanning chemicals. Syntans are frequently used, after pretanning, due to their limited impact on air emissions. However, they are scarcely biodegradable, and their removal takes a long time in the biological processes of a wastewater treatment plant. This system is especially applied to produce leather for the automotive sector.
- Oil: It constitutes a niche technique, adopted to produce leather for hunting parts, gloves and coats. Originally, it was based on cod oil, whose oxidation inside the hide gave the tanning action. Later, the oxidation has been improved by warm air injection into the tank where the tanning occurs.

4. Reduction of water consumption

As shown in Table 1, the usage of waste is very high, namely, 15-50 m^3/tonne raw hide.

It should be noted that there is a minimum consumption required to process the raw hide and, at the same time, avoid damage to the hide itself. This volume has been calculated equal to 12 m^3/tonne raw hide [3].

Water saving can be done along the whole production chain, through a series of actions, starting to monitor the quantities used in each process operation. In this way, the mass balance of water is feasible, and it will be useful for better management of wastewater treatment plants.

Very often, leakages, losses, and waste are present. These drawbacks can be solved with efficient maintenance and staff training, linked to the automated dosage at least for the main tanks/reactors where the water consumption is relevant.

These actions can be adopted as preventive but also as determined. They are not very expensive compared to the achieved results and are rather easy to apply. Altogether, they are considered fundamental for a modern tannery.

Another action is the reuse of the wastewater from a given operation in another. This needs to consider the kind and level of pollution of the wastewater itself compared to the acceptable pollution in the receiving operation, for the operation itself as well as to avoid damages to the leather. If it is not acceptable, the wastewater must be treated to reduce or remove the pollutant(s), and in this case, the total treatment cost (investment + management) must be balanced by the advantages, in terms of both environmental and economic ones (water saving). Recycling of the chromium solution, described in Section 3.1.2, is one example, which joins the saving of water and chromium.

Water management and wastewater reuse in other operations are considered BATs.

Currently, a well-known solution is the Zero Liquid Discharge (ZLD) system, already widely adopted in many tanneries. It consists of a closed water cycle, to avoid wastewater discharges, except for the additions to balance the natural losses. The wastewater is treated by removing its pollutants, in particular the suspended solids, to recycle and reuse the water inside the tannery process. The output consists of a highly concentrated brine, that can be exploited as a byproduct to recover salts or disposed as waste. The main drawback is represented by the high cost, both for investment and management, balanced by environmental sustainability.

The technique is based on physical operations, namely: reverse osmosis, forward osmosis, thermal evaporation, electrodialysis, and membrane distillation. Usually, a combination of these operations is used, also based on the local needs and opportunities where the ZLD system will be installed.

Some recent reviews describe this technique, giving updated information on its technical features, costs, and environmental impacts [14-19]. The tangible evidence of the beneficial use of ZLD is represented by the continuous growth of its market around the world, also due to the more stringent legislation on the environmental impacts produced by industrial activities.

5. Nanotechnologies for tannery

In the last years, nanotechnologies are applied to many sectors, and the tannery is one of them. In particular, nanomaterials were and are studied and developed both to limit and decrease the process impacts and treat the emissions, especially the wastewater.

Table 2 reports recent studies on nanomaterials used in the operations of the tannery to increase the sustainability of the process, without worsening the final leather quality. More details can be found in the review by Muthukrishnan [20], which also reports some of the patents for nanomaterials developed for the finishing step.

Table 2. Nanomaterials applicable to tannery operations.

Operation	Nanomaterial	Reference
Pretanning	Nano ZnO and polymer/ZnO nanocomposites	[21]
Dehairing	Enzymes on magnetite nanoparticles	[22]
Dehairing	Protease on nanoparticles	[23]
Tanning	Vinyl polymer/zinc oxide nanocomposite (PDM/ ZnO)	[24]
Tanning	Amphoteric vinyl polymer/montmorillonite nanocomposite	[25]
Tanning	Spherical silica nanoparticles/copolymer composites	[26]
Tanning	Nanoparticles Cr/poly[poly (ethylene glycol) methyl ether acrylate-co-acrylic acid-co-glycidyl methacrylate (PEGMA-co-AA-co-GMA)]	[27
Tanning	PVA(PEG)-SiO_2-GO nanocomposites based on polyvinyl alcohol (PVA) or polyethylene glycol (PEG) on SiO_2 nanoparticles loaded onto graphene oxide nanosheets (GO)	[28]
Retanning	Clay/polymer nanocomposites based on poly (methyl methacrylate-co-butyl acrylate-co-acrylic acid) and bentonite modified by cetyltrimethylammonium bromide	[29]
Finishing	TiO_2 nanoparticles (TiO_2-Ps) doped with N and Fe	[30]

Most operations with nanomaterials are still at the laboratory scale. It is beneficial that their applicability is demonstrated both for the final leather quality and process sustainability, to transfer soon these operations at the industrial scale.

Several nanomaterials were and are also studied and developed to treat wastewater, especially to remove chromium(III). Table 3 reports some examples of nanomaterials applicable to decreasing the pollution of tannery wastewater.

As for the nanomaterials for tanning operations reported in Table 2, most studies are still at the laboratory scale. This means that their applicability at a large scale is not demonstrated, yet.

In general, for the use of nanomaterials in the tannery, many efforts are still required, and many ways are open.

Last, but not of minor relevance, the production of nanomaterials efficient in some tannery operations will have to demonstrate its sustainability for environmental protection and workers' health.

Table 3. Nanomaterials applicable to tannery wastewater treatment.

Pollutant	Nanomaterial	Reference
COD, TDS, TSS, Cr, Co, Pb, Cd, Ni	Maghemite nanoparticles (γ-Fe_2O_3) biosynthesized by *Penicillium expansum*	[31]
Dye, COD, TDS, TSS, Cr, Co, Pb, Cd, Ni	MgO nanoparticles biosynthesized by *Aspergillum niger*	[32]
COD and Cr(VI)	TiO_2 nanoparticles synthesized from leaf extract of *Jatropha curcas L*	[33]
Cr(VI)	Diatomite-embedded nanopyroxene	[34]
Cr(VI)	Graphene oxide-magnetite nanocomposites	[35]
COD	$NaLi_{1.07}Co_{2.94}(MoO_4)_5$ nanoparticles	[36]
NaCl and Na_2SO_4	TiO_2 modified poly(vinylidene fluoride-*co*-hexafluoropropylene) nanocomposite membranes	[37]

6. Conclusions

As highlighted in this paper, many improvements were done to the tanning process to make it sustainable from an environmental point of view. However, many studies are still in the laboratory or small scale, and time will pass before their adoption at the industrial level. This means that must still be done to get fully sustainable tanning, or, in other terms, to Sustainable Development Goals before 2030, in particular, Goal 12 - Responsible Consumption and Production. In this challenge, cooperation among research, academy and industry will be essential to identify the process operations that can be modified to this scope (industry), study their feasibility at laboratory or small scale (research), transfer the knowledge to the educational programs for skills suitable to the challenges of the Third Millenium (academy).

Concerning the nanomaterials, the cost for their synthesis and the scalability of the application to the tannery needs to be assessed considering their environmental impacts.

At last, in developing countries, the Governments play a major role in encouraging and educating small-scale tannery companies to adopt newer technologies and monitor the impacts on the environment without compromising the economic development of their country.

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