Environmental Science and Pollution Research (2021) 28:55905–55914
https://doi.org/10.1007/s11356-021-16216-z

REVIEW ARTICLE

Nanomaterials to help eco-friendly leather processing

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Received: 23 April 2021 / Accepted: 24 August 2021 / Published online: 7 September 2021

Abstract
The leather industry converts the hide, a byproduct of slaughterhouses, into leather, a value-added product. This old industry generates wastes, causing environmental pollution. However, nanomaterials can help to decrease this problem. These tiny particles (1–100 nm) can replace chemicals in various steps of leather processing. This paper aims at giving an overview of the fundamentals of classical leather process and how nanomaterials can be applied in each step to obtain a more sustainable manufacturing. After a comprehensive literature review of journal articles, six steps were identified for potential for application of nanomaterials: unhairing, tanning, retanning, dyeing, fatliquoring, and finishing. With nano-oxides, polymers, and metals, it is feasible to reduce the amount of chemical products and also improve the properties of leather. Thus, it is possible to reach a more eco-friendly and effective process with the use of nanomaterials to turn hide/skins into finished leather.

Keywords Leather industry; · Nanomaterials; · Eco-friendly; · Sustainability; · Clean technology

Introduction

The leather industry converts hides or skin, sub-products of the slaughterhouse industry, into leather, a product with high commercial value. It is a perfect example of circular economy industry (Omoloso et al. 2020). The importance of this industry relies in its high economic influence in many developing countries. But the generation of wastewater with potentially toxic and hazardous pollutants is a problem (Hansen et al. 2020). Leather processing is a source of solid wastes, gaseous emissions and wastewater with harmful chemicals (China et al. 2020). Eco-friendly technologies aim to minimize the environmental impact avoiding harmful chemicals (Dixit et al. 2015). Some examples are the salt-free preservation of raw skins and hides (Sivakumar et al. 2019), alternative tanning technologies (China et al. 2020) and water reuse (de Aquim et al. 2019). The environmental sustainability is an effort for this industry.

The classical processing of leather production may cause amounts of pollutants such as nitrogen, metals, salts, and sulfur, to be discharged into the wastewater. In post-tanning, the largest inorganic pollution load (due mainly to chlorides and sulfates) of wastewater comes from retanning agents (natural and synthetic tannins) (Hansen et al. 2020). This industry faces two main challenges: minimize environmental pollution and maintain the performance of leather products (Yorgancioglu et al. 2019). For this reason, and for upgrading leather performance, it requires new production techniques that are more eco-friendly, easier to apply, and more effective (Açikel et al. 2019).

Nanoparticles have drawn extensive enthusiasm from both academics and industrialists because of the functionalities inaccessible to the micron organized materials (Yorgancioglu et al. 2019). The growing concern of the leather market for the newest technological fields of application, added to the growing environmental awareness, compete to improve the knowledge of the leather scientists on this topic (Florio et al. 2019). More and more attention has been paid to

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nanomaterials in the improvement of traditional leather manufacturing (Pan et al. 2020). Increasing interests have been directed towards incorporating nanomaterials into leather processing (Kaygusuz 2017). In the leather industry, nanomaterials have been used for tanning operations due to its size and high surface area and they can penetrate into fibers to improve the properties of leather (Kothandam et al. 2016). Nanomaterials in leather manufacturing can lead to sustainable leather and cost-effective improvements to the quality of finished leather with the use of nanoparticles and nanocapsules (Kopp et al. 2019).

It seems to be appropriate to review the nanomaterials literature on leather production, focusing on eco-friendly production and identify which steps have potential to nanomaterials application. We identify that six steps of the leather processing have potential for application of nanomaterials: Unhairing, tanning, retanning, dyeing, fatliquoring, and finishing. This review shows that it is possible to achieve a more sustainable leather processing using nanomaterials instead of toxic chemicals.

The main process of leather making

In leather making, changes in the structure of collagen occur. It is important to know its structure, to understand how the substances that are added in the production will work. The hide is formed by epidermis, dermis and hypodermis. The dermis is the layer of interest for tanneries and has in turn two other layers: the papillary layer and the reticular layer. In leather industry, the top papillary layer is called "grain" or "top split" (considered to be the noblest part, which contains the grain or thermostatic layer and part of the reticular layer) and the bottom reticular layer is called "flesh" or "bottom split" (only sub-reticular layer). In the thin structure of the skin, the fiber bundles are primarily visible, which in reality are made up of small structural elements, the elementary fibers. Elementary fibers are formed of fibrils which hold together and delimit one another. Type I collagen fibril is made up of around 7000 collagen molecules parallel to each other. Fibrils are composed of microfibrils, formed, in turn, by 5 units of collagen molecules. Each collagen molecule is formed by three α-chains (polypeptides), associated in a triple helix (Mancopes et al. 2008).

Figure 1a shows first the cross section of the hide with hair, epidermis, hypodermis, interfibrous material, and dirt and the other following illustrations show the hide/leather after the respective operations. In the beamhouse steps, first the raw hide is preserved (Fig. 1b) to dehydrate and so interrupt the attack by microorganism (bacteria) that would deteriorate and damage the grain layer. Thereafter, the hide is soaked (hydrate) to restore the original water content and start to clean up (Fig. 1c). In unhairing/liming, the hair is removed along with the epidermis both based of keratinous materials, the fibers are loosen and the hide structure swells up (Fig. 1d). At fleshing, the subcutaneous layer (hypodermis) is taken away (Fig. 1e). At splitting, the hide is divided into two layers, the top layer (Fig. 1f) ("grain" or "top split" and the bottom reticular layer (split leather, excluded in the figure). At deliming, alkaline substances introduced into the hide in the liming are removed and it reverses the swelling of the hide (Fig. 1g). The hide is finally deep cleaned with enzymes during bating (Fig. 1h).

The hide is pickled for preparing the fibers for penetration of tanning agents by acidification in the presence of salt to prevent acid swelling (Fig. 1i). In tanning (Fig. 1j), the hide is transformed into leather by reaction with tanning agents (mostly chrome). In the case of chrome tanning, wet-blue leather is produced. Thereafter, an adjustment is made to reduce and standardize the leather thickness in the shaving operation (Fig. 1k). In the wet-finishing operations (Fig. 1l), the leather is first treated to deacidify; in retanning, the physical–mechanical, texture, and surface characteristics of the leather are defined; the dyeing step gives color to the leather through the use of dyes; and fatliquoring uses oil to lubricate the fibers. Afterwards, the leather is dried and called crust leather, then the leather is milled to soften and follows to the mechanical pre-finishing operations (Fig. 1m). In finishing (Fig. 1n), the upper leather surface is covered by means of application of pigmented form film polymers and is given definitive leather resistance and aspect.

The major problems in making leather-pollution

Many steps are involved in the fabrication of leather in a complex process due to the parameters and various chemicals required (Kanagaraj et al. 2020). The major problems of leather manufacturing are the hazardous and restricted chemical substances, huge diversity and high quantity of chemicals in a great volume water, and generation of solid wastes.

Hazardous chemical substances are restricted and controlled in leather products, due the possibility of toxic effect when leather is in direct contact with human skin, as in clothing and footwear. Examples of these substances are: azo dyes; formaldehyde; pentachlorophenol; and other heavy metals. Each country has its own regulations and laws regarding chemicals. The non-conformity of the products export to European Union will prevent their entry and free commercialization. Also eco-labels signal to the consumer when the leathers have been manufactured with the aim of minimizing their impact on health and environment during manufacture, the entire useful life as well as during recycling and disposal (Fuck and Gutterres 2008).

During the leather processing, close to 130 different types of chemicals are used in a lot of water (Hansen et al. 2020), between 25 L and 80 L of water is used to process 1 kg of hide (Buljan and Kráľ 2019). Biocides used in the leather industry

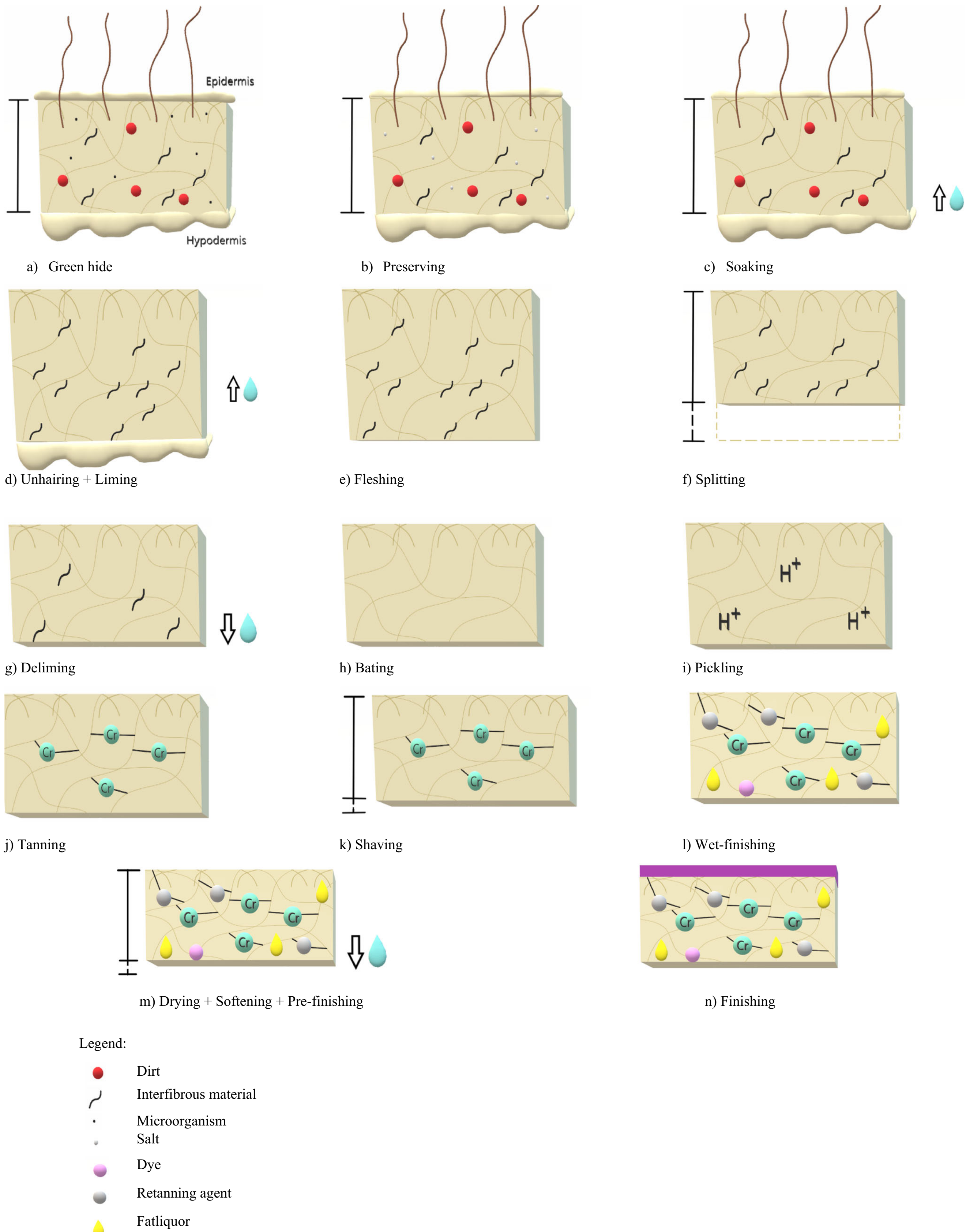

Fig. 1 Schematic of leather processing, a) Green hide, b) Preservin, c) Soaking, d) Unhairing + Liming, e) Fleshing, f) Splitting, g) Deliming, h) Bating, i) Pickling, j) Tanning, k) Shaving, l) Wet-finishing, m) Drying + Softening + Pre-finishing, n) Finishing

are synthetic and generate environmental risks (Kopp et al. 2019). The unhairing step led to the discharge of sulfur compounds that affected the air, soil as well as water in the proximity of tanneries (Murugappan et al. 2020). In tanning step, not all chromium salt is fixed in the leather, and the remaining gets its way to the effluent. Also, chrome tanning produces solid wastes in the form of chrome-tanned leather shavings, trimmings and buffing powder (China et al. 2020). At dyeing, 1 to 5% of the dye applied in the leather dyeing remains in the effluent (Fuck et al. 2018) and the effluents from dyeing are difficult to treat by conventional methods (Ortiz-Monsalve et al. 2019). Fatliquoring agents are applied to the leather as oil emulsions, obtained by dispersing the oil in water using surfactants. They are the chemical group that presented the highest toxicity of post-tanning process (Hansen et al. 2020).

The main method to solve the problem

Several sustainable technologies have been developed to solve the problem of pollution from leather industry (Kanagaraj et al. 2020). It is possible to use more eco-friendly chemical products to avoid the use of hazardous substances. The use of essential oils instead salt and biocides, to achieve a sustainable preservation of hides (Kopp et al. 2019; Kanagaraj et al. 2020); avoid sulphide in dehairing, using enzymes (Dettmer et al. 2013; Andrioli et al. 2015); tanning without chrome, using vegetable tannins (Auad et al. 2019) and tannins with aluminium sulphate (China et al. 2020); as an alternative to synthetic dyes (mainly azo dyes), natural biodyes from filamentous fungi can be used (Fuck et al. 2018). Instead the traditional finishing systems containing solvents, the use of aqueous systems aim to reduce atmospheric emissions (Winter et al. 2015). The problem of using a huge amount of water can be solved with the reuse of the floats from tanning step, even containing chromium. The reuse of wastewater minimizes the disposal of the wastewater with chromium and uses the residual chromium float (de Aquim et al. 2019). Tannery solid wastes as chromium tanned leather (Piccin et al. 2016), leather shaving (Gomes et al. 2015) and activated carbon produced from tannery solid waste (Mella et al. 2019) can be used an adsorbent for color removal from leather dyeing effluent. Also, it is possible to produce biogas from tannery solid wastes (Agustini et al. 2018).

Novel method of solve the problem

The focus of leather industry should be the prevention of waste generation containing dangerous chemicals. Nanomaterials are an alternative to prevent this kind of wastes. These tiny particles (1–100 nm) can replace chemicals in various steps of leather processing to achieve an eco-friendly leather manufacturing. In tanning with nanomaterials, it was possible to reduce the pollution indexes of TN (total nitrogen), TOC (total organic carbon), COD (chemical oxygen demand), BOD (bio-chemical oxygen demand), protein, oil, and salts and eliminate the chrome of wastewater (Lv et al. 2016).

From all steps of the leather processing, six appear to have potential for application of nanomaterials to obtain an eco-friendly process, as shown in Table 1. In this table, each step and its purpose are summarized. All interactions are molecular and between the agent and the proteins (collagen or keratin).

The application of nanomaterials in leather processing

Unhairing processing

The unhairing step has the purpose of removing the epidermis together with hair and other keratinous materials from the hide (Gutterres and Mella 2015). This process can destroy the hair (hair-burning processes) and uses sodium sulfide and lime. Hair-saving is an alternative process that preserve the hair and uses enzymes (de Souza et al. 2020). In enzymatic unhairing, the proteolytic enzymes attack the hair roots and the epidermis. The hair-saving technique has not found a broad industrial impact due to the instability of enzymes due to even slight changes in temperature, pH, and ionic strength of the medium. There is an emerging need to ensure the robustness of this process for large scale applicability. This way, enzyme can be immobilized into nanoparticles, which also increases their activity.

Enzyme protease was immobilized in ZnO nanoparticles (Murugappan et al. 2020). The goat skins treated with enzymes during the course of dehairing, started to putrefy, unlike those treated with immobilized enzymes, behavior which may be assigned to the antimicrobial properties of nano-ZnO. After immobilization of enzymes, an increase in activity has been observed, detected by the higher removal of intrafibrillary material from the skin as compared to the control. In addition, the leather has improved tensile tear strength, possibly due to the crosslinking of ZnO through PEG to collagen. Compared to the conventional unhairing method using sodium sulfide, the emission loads from the process were reduced. Protease and amylase enzymes were immobilized in iron oxide (Fe_3O_4) nanoparticles (Murugappan et al. 2016). The nanozyme-treated leather revealed faster dehairing and fiber opening. The nanozyme-treated matrix confirms that there was good ordering and opening of fiber bundles due to the enzyme effect. The general parameters like grain smoothness, color, and general appearance remains better in the nanozyme as compared to the fibrozyme-treated pelts.

Tanning

The use of nanomaterials comes as an alternative to classical tanning, due to the concerns about the environment. Nano-

Table 1 Potential application of nanomaterials in leather processing

Step	Purpose	Mechanism/process	Molecular interaction
Unhairing	Removal of the epidermis together with hair and other keratinous materials from the hide	Chemical or enzymatic process	Molecular at keratin substrate
Tanning	Giving the skin resistance to microbial attack, provide chemical, thermal, and physical stability, transforming it into leather	Bonding process	Molecular due to crosslinking of tannin agents with collagen
Retanning	Defining chemical, physical-mechanical, and textural properties	Bonding/fixation process	Molecular at collagen or interstices deposition
Dyeing	Giving color	Bonding process. Dye is soluble in water to diffuse	Molecular at collagen, mainly ionic interactions
Fatliquoring	Lubricating the fibers, soften the leather	Bonding/ fixation process and lubrification of the fibers and soften the fibrils	Molecular at collagen: micrometric level (fibers) and nanometric level (fibrils and microfibrils)
Finishing	Treating the surface to give properties and appearance of the final product	Binder material forming continuous film on the leather surface	Physico-chemical with leather surface and molecular in polymer crosslinkages of the coating

tanning agents should be able to form chemical bonds with the collagen fibers and have nano-effects of the agent (Lv et al. 2016). The challenge of a nano-tanning agent is its dispersion in aqueous solution, to be able to penetrate into collagen fibers, and reach the appropriate shrinkage temperature (Ts). At nanoscopic level, the collagen proteins parallelly bunch together by a quarter of the molecule length to form collagen nanofibers (50–200 nm) (Wang et al. 2019).

Most of the nano-tanning agents usually used are inorganic. The use of graphene oxide (1 - 60 nm) leads to the highest shrinkage temperature (96.8°C), compared to the other nanoagents, and met the quality requirements for commercial leather products. This way it is possible to achieve a clean leather tanning. Even so, the mechanical properties are not similar to chrome tanning possibly due the mechanism in the leather tanning process, that is via chemical bonding and nanoeffects (Lv et al. 2016).

Tetrakis(hydroxymethyl) phosphonium sulfate (THPS) and commercial laponite clay lead to a Ts of 79°C due to the covalent cross-linking formation between active hydroxymethyl groups of THP molecules and functional amino groups of collagen side chains. An eco-friendly and sustainable alternative to conventional chrome (Shi et al. 2019).

The addition of poly (methacrylic acid) (PMAAS) copolymer increased the Ts to 76°C due to the firm combination of nanoparticles with the collagen fiber through chemical bonds (Pan et al. 2017). The tanning with silica nanoparticles reached a Ts of 55°C, so the hide was not considered tanned (Benvenuti et al. 2019).

In pre-tanning, it was possible to reduce the chrome tanning agents using a nanocomposite of nano-ZnO and dimethyl diallyl ammonium chloride (DMDAAC) polymer (Lyu et al. 2018). Pre-tanning nano-emulsion, based on acrylic acid ester co-PMMA and butyl acrylate (BA), improved the physical properties, shrinkage temperature, and the mechanical properties of the tanned leather, and also enhanced the texture (El-Monem et al. 2017).

Retanning

A biodegradable nanocomposite of hydroxyapatite nanoparticles and poly (lactide co-glycolide) (PLGA) co-polymer showed high mechanical properties and improved filling. The softness, fiber compactness, and thermal resistivity showed significant improvement. Also, the chemical load in the wastewater was minimized (Selvaraju et al. 2017).

A leather product with durable antibacterial property was developed using gallic acid modified with silver nanoparticles. Silver nanoparticles were used due to their antibacterial and fungicide effect, being eco-friendly. They were used as multifunctional retanning agents instead of traditional acrylic resin to be filled into the leather matrix, due to the high carboxyl group density on its surface. These particles were chemically immobilized onto the collagen fibers through crosslinking by chrome (Liu et al. 2018).

There is a scarcity of reports on the preparation of multifunctional retanning agents with improved leather shrinkage temperature, thickening rate, mechanical properties and assisting dyeing performance (Liu et al. 2020). This way, the main develop should be a nano-retanning agent able to complex with Cr^{3+}, with carboxyl groups on the particle surface.

Dyeing processing

Currently in the leather industry, more than 90% of leathers are dyed with azo dyes and many of these synthetic dyes, used extensively all over the world, have a negative impact on human health and the environment. To avoid that the dye remains in the effluent, it is possible to increase the exhaustion of dyes, using a nano-polymer with the dye (Kanagaraj and Panda 2011). This polymer with carboxyl groups forms hydrogen bonding at multi-points with the substrate, giving rise to additional stability with the collagen. To address this issue, nanomaterials can be applied to promote stability and surface properties of free dyes in nanoscale dimensions, allowing uniform penetration as well as a surface fixation. Instead of ionic bonding, with nanostructured dyes it is possible to have stronger bonds, such as hydrogen bonding (Ramalingam and Jonnalagadda 2017). The dye molecules diffuse through pores of leathers and get fixed with the functional groups of collagen (Kanagaraj et al. 2016). This way, the smaller the particles are, the easier they are to diffuse.

Free dyes can be stabilized when encapsulated into nanoscale dimensions. Silica is used due to its biocompatibility, easy surface functionalization, and low cost. The interaction of skin protein (pure collagen), triple helical unit, with silica-functionalized colorant may be by hydrogen bonding. Dye encapsulated into silica nanoparticles showed benefits such as the use of less dye. Such an approach may also avoid auxiliaries, like high polymeric syntans, self-emulsified fatliquors, and acid−base fixing auxiliaries with incremental pollution load, and it does not require any pre-treatment like acidification for fixing the colorant (Ramalingam et al. 2016). This step was economically and environmentally beneficial as compared to traditional dyeing (Ramalingam and Jonnalagadda 2017).

Fatliquoring processing

The addition of nano-agents is an efficient way to improve different properties, such as light fastness or antimicrobial property. Besides, nano-agents can penetrate even more deeply into the leather. Moreover, the nano-agent can replace the usual emulsifying chemical agents used to increase the stability of emulsions and avoiding many chemicals.

A multi-functional fatliquoring agent was developed using paraffin with nano-ZnO due to its antimicrobial action. The leather showed better light fastness properties as compared to conventional process (Yorgancioglu et al. 2019). Castor oil is a renewable low-cost feedstock for fatliquor production. However, it can cause white or light-colored leather to yellow under UV irradiation, and thus largely affects the appearance and the use of the leather. The addition of nano-ZnO improved the UV resistance, stability, and anti-yellowing (Duan et al. 2015). When TiO_2 was added to castor oil, the presence of nano-TiO_2 resulted in a stable emulsion which leads to a reduction of many chemicals utilized to get the lightfastness of leather (Lyu et al. 2016).

Most fatliquors present among the fibers are those with a linear structure, or linear fatliquors with fewer branches. Because of this relatively simple structure, it is hard to produce fatliquors with high efficiency. Wang et al. (2017) developed a nano-polymer in which the ester compound (HPAE) of 3-(bis(2-hydroxyethyl)amino)propionic acid and pentaerythritol were treated with undecylenic acid to obtain novel hyperbranched multi-terminal alkenyl polymers (HPAE-UAs). HPAE-UAs used in leather could improve the thermal performance, and the physical and mechanical properties.

Finishing

During leather finishing processes, nanomaterials showed a cost-effective improvement to the quality of the finished leather, because as particles get smaller, the surface area to the volume ratio increases effectively. The improved chemical bonding between the nanoparticles and leather surface provides a more durable and high-quality leather (Yasothai et al. 2019). Also, nanoparticles could provide enough surface roughness to form a superhydrophobic leather surface which provides extraordinary properties, such as self-cleaning, anti-corrosion, and water repellency (Ma et al. 2015).

Table 2 shows some examples of the use of nanomaterials in the finishing steps. Most of the nanomaterials used are oxides, polymers, and metals. The size of nanoparticles used in the finishing step ranged from 5 to 250 nm. Nanocapsules and nanocomposites reached up to 480 nm. Different properties are achieved depending on the used nanoparticle. Various researchers have looked to increase leather hydrophobicity. For finishing stage, the property of water resistance is important, and this was achieved by using the carbon nanomaterials/PMMA-PMAA methacrylic polymer/nanocomposites, obtaining a sustainable hydrophobic leather (Ayyappan et al. 2020). TiO_2 nanoparticles doped with SiO_2, F, Fe or silver enhanced the properties of leather, like photocatalytic properties, thermal resistance, and self-cleaning properties (Petica et al. 2015; Gaidau et al. 2017). In addition, characteristics for flame and heat tests were improved for silica-doped nanoparticles embedded in finishing composites for bovine leathers. Low environmental impact is reached with formulations with embedded nanoparticles in base coat or top coat allow getting a wide range of properties, as compared to the use of nano materials in powder state (Gaidau et al. 2015).

Table 2 Nanomaterials and properties in leather finishing

Nanomaterial	Size	Properties in leather	Author(s)
Oleic acid coated iron oxide	5 nm	Effective stabilization of collagen fibers so as to elevate the shrinkage temperature up to 90°C	Alliraja et al. (2015)
TiO_2 doped with SiO_2	15−18.1 nm	Photocatalytic properties and thermal resistance	Gaidau et al. (2017)
TiO_2 doped with SiO_2 or Ag	TiO_2-SiO_2: 51.4 nm; TiO_2-Ag: 46.3 nm	Resistance to dermatophytes attack, self-cleaning photocatalytic properties, improved characteristics for flame and heat	Gaidau et al. (2015)
Nano ZnO on nitrocellulose emulsion	Nano-ZnO: 50-150 nm	Elimination of Cr(VI) formation by providing high UV protection	Yilmaz et al. (2015)
TiO_2 doped with N and Fe	20 nm TiO_2 15.7 and 24.7 nm crystal sizes	Photocatalytic activity in visible light region; self-cleaning properties (TiO_2)	Petica et al. (2015)
Ag-TiO_2	< 8 nm	Antimicrobial properties and photocatalytic potential	Gaidau et al. (2019)
Ag–TiO_2	10 nm	Antimicrobial activity and a low toxicity of nanoparticles	Carvalho et al. (2018)
Cu	25–50 nm	Improved wet and rub fastness, color fastness to water, and adhesion strength	Kothandam et al. (2016)
Ag	1–250 nm	Antibacterial and fungicide effect	Bacardit et al. (2016)
Nano Ag coatings	Particles: 20–45 nm	Effective antimicrobial properties	Lkhagvajav et al. (2015)
Nano Ag-TiO_2 coating	Particles: 3–15 nm	Effective antimicrobial properties	Kaygusuz et al. (2016)
Casein-based SiO_2	136 nm	Tensile strength and water resistance	Xu et al. (2015)
Carbon nanomaterials (carbon nanotubes and fullerenes)/PMMA- PMAA polymer	0.771−4.20 nm	Super-hydrophobicity	Ayyappan et al. (2020)
Nano encapsulated phase change materials (octadecane) in polystyrene	450 nm	Temperature control performance and comfort of leather products	Jie et al. (2017)
Polyaldehyde	80–110 nm	Hydrophobicity and wet, rub fastness, color fastness and adhesion strength	Yasothai et al. (2019)

n/a not available

Enhancement of the properties can be achieved by the combination of two nanoparticles, such as Ag-TiO_2 which replaces antimicrobial chemicals. Besides the antimicrobial activity of the metal particles, photocatalytic potential was achieved (Carvalho et al. 2018; Gaidau et al. 2019). Silver nanoparticles were used for antibacterial and fungicide effect (Bacardit et al. 2016). The use of TiO_2–SiO_2 nanocomposites, reducing the utilization of chemicals, obtained by the sol-gel method plus plasma treatment in the finishing step, increased the water contact angle, surface hydrophobicity, and improved fastness properties and water vapor permeability (Kaygusuz et al. 2018).

Nano ZnO in nitrocellulose emulsion was applied as a finishing agent. This emulsion provides high UV protection and substantially eliminated Cr(VI) formation, which could affect human health (Yilmaz et al. 2015). To add economic value to the leather, nanocapsules of different essential oils were applied to leather after tanning. For aroma enrichment, orange, lavender (Velmurugan et al. 2017) and lemongrass essential oils (Velmurugan et al. 2015) were encapsulated in chitosan. Besides the aroma enrichment, the nanocapsules possess antimicrobial activity against bacteria and fungi using natural oils.

Conclusion

Eco-friendly production and sustainability are key points for the future of leather industry. Nanomaterials can help to increase a more sustainable process, being used in different steps of leather manufacturing. This review described the classical leather processes and the nanomaterials applied to reach a cleaner process.

As shown in this paper, the steps of leather processing that explore nanomaterails are: Unhairing, tanning, retanning, dyeing, fatliquoring, and finishing. From these steps, tanning is the most explored due the concerns about the traditional chrome tanning. Besides the elimination of chrome pollution, nano-tanning agent graphene oxide showed a reduction of 77.9% of TOC. Retanning should be more investigate, as it is the main contributor to the post-tanning inorganic pollution load and there are few studies about nanomaterials and sustainability in this step, a possibility of a nanocomposite that would reduce pollution is hydroxyapatite nanoparticles and PLGA. COD was reduced in 23.4 % and total dissolved solids in 36.8 %. In the literature, liming, deliming and pickling do not have nanomaterials applied. In liming, the fibers are opened using lime but when enzymes are used in unhairing, there is no need of lime. So that step can be excluded from the process and the deliming step is unnecessary. In pickling, the used acids can be replaced by enzymes. In this way, enzymes could be immobilized in nanoparticles.

The application of nanomaterials can lead to reduction of many chemicals, thus the wastewater will be less polluted. The challenges of using nanomaterials in this industry are the costs to develop these materials on an industrial scale. Also, more studies need to be carried out about the nanomaterials and human health. Less steps in leather manufacturing means fewer chemical products and water used, which lead to an eco-friendly production. This study propose that the future of leather industry relies on nanoparticles use. Further studies with nanoparticles could decrease the number of leather processing steps, minimize the number of steps and use one material to achieve different goals. The future of the leather industry depends on the consumers, who, day by day, are becoming more conscious about the manufacturing processes of products.

Abbreviations DMDAAC, dimethyl diallyl ammonium chloride; GLYMO, (3-glycidyloxypropyltrimethoxysilane); HMDSO, hexamethyldisiloxane; PLGA, poly(lactide co-glycolide); PMMA, poly(methyl methacrylate); PMAA, poly(methacrylic acid); PMAAS, methacrylic acid-co-acrylamide-co-acrylonitrile-co-salicylic acid tetrabasic copolymer; TEOS, tetraethoxysilane

Author contribution Victória Kopp: investigation, writing—original draft. Caroline Agustini: writing—review and editing. Mariliz Gutterres: writing—review & editing, supervision. João dos Santos: conceptualization, writing—review & editing, supervision.

Funding V.V.K. thanks CAPES for the grant. J.H.Z.S. thanks FAPERGS (19/2551-0001869-0) for the financial support.

Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval Not applicable

Consent to participate Not applicable

Consent for publication All authors mutually agree that the manuscript can be submitted to Environmental Science and Pollution Research

Conflict of interest The authors declare no competing interests.

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