**REVIEW**

# Nanotechnology for cleaner leather production: a review

**Lakshmipathy Muthukrishnan**[1]

## Abstract

The leather industry holds a significant place in the global economy, yet the scarcity of raw hides and skins, growing ethical concern, competitive leather substitutes and regulation of manufacturing processes with adverse environmental effects restrict the expansion of the leather industry. These issues may be partly solved by nanotechnology to add innovative products and to treat tannery effluents. This article reviews research gaps of conventional leather manufacturing processes including curing, tanning, and effluent treatment using nanotannage, photocatalysts and filtration. Nanomaterials have been applied at various stages of leather manufacturing to achieve better performances.

**Keywords** Leather production · Environment-friendly · Nanopreservation · Nanotannage · Nanofinishing · Nanofiltration

## Introduction

Leather, the most sophisticated form of hides and skins, constitutes an important and valuable resource of national and international significance. Although we live in the age of materials such as plastics, metals and synthetics, leather has been sustained for its aesthetics and superior quality. According to the FAO global statistical compendium for 1999–2015, nearly 1659.6 million bovine and 1163.7 million sheep from the overall livestock population were utilized by leather industry. Apart from the edible parts, the hides and skins flayed accounted for nearly 6531.1 and 414.2 thousand tonnes. The hides were processed to 558.4 thousand tonnes of heavy leather and 14,298.7 million sq. ft of light leathers relative to 5335.2 million sq. ft of leather processed from the skins (FAO 2016).

As leather and leather-based products are the most widely traded products across globe, it is predicted that the international trade has exceeded 80 billion US$ annually to keep pace with the increasing population and urbanization. The international trade statistics for the global import–export of raw hides, skins and leather for 2019 were valued to 20,351,371 and 19,535,920 thousand US$, respectively (ITC 2019). In accordance, the statistics for the world manufacturing production of leather and related products with an estimated growth rate of 0.2% output were reported (UNIDO 2019).

In the Indian context, leather industry holds a pivotal position in the Indian economy for its consistent export earnings in the international trade. According to the Council for Leather Exports (CLE), the revenue generated from exporting leather and leather based products was valued at 5.69 billion US$ during 2018–2019. Being self-reliant and by utilizing indigenous raw materials, about 3 billion sq. ft. of leather (13% of the global production) is produced annually employing intensive skilled and trained labor force (Das and Rangarajan 2020). According to Industrial Information system (IIS) portal of the National Investment Promotion and Facilitation Agency, India stands the second-largest producer (12.93%) of world's leather production of hides and skins. India has in abundance of accessing raw materials close to 20% of world's cattle and buffalo and 11% of world's goat and sheep population. This had seen a major transformation in exporting leather and leather products stood at US$ 5.07 billion in the fiscal year 2019–2020. Indian leather products have major markets in the USA (17.22%), Germany (11.98%), the UK (10.43%), Italy (6.33%) and France (5.94%). It is only because of the quality that India could export leather and leather products for US$ 1.06 billion during April

✉ Lakshmipathy Muthukrishnan
   mlakshmipathy@gmail.com;
   lakshmipathym.sdc@saveetha.com

1  Department of Conservative Dentistry and Endodontics,
   Saveetha Dental College and Hospitals, Saveetha Institute
   of Medical and Technical Sciences, Poonamallee High Road,
   Chennai, Tamil Nadu 600 077, India

to August 2020 and US$ 356.15 million in the month of August 2020 (IBEF).

## Brief history

Leather is probably one of the modern discoveries and an innovative fabric used by ancient humans for their survival. Its history dates back to Paleolithic period in which primitive man practiced hunting for want of food. With the beginning of Neolithic culture, animal husbandry superseded hunting by food production and supply; the skins and hides from dead animal carcasses were used for clothing, footwear and to build crude tents to protect themselves. This was one such *'waste to worth'* approach practiced by cavemen to utilize all the animal parts letting them not to go waste. Prehistoric people have noticed the putrefaction of raw skins and hide when kept wet, but turned hard and rough when dried out. This dried form was certainly inconvenient for wrapping up their body which made them attempt optimum drying to soften the fur and to render the skin soft and convenient. The foundation for *'art of tanning'* was laid down by rubbing some greasy substances onto the hides to last longer. Moreover, brain tanning and smoking of the besmeared skins over wood fire helped to preserve by penetrating through the skin. This made the skins more flexible and prevented against putrefaction. Later, tanning was performed using bark and leaf infusions of mimosa, chestnut, etc. The use of alum in tanning (*aluta*) came to be known and that of the salts of chromium of quite recent date. Although tanning was practiced, the process was kept secret and handed down from father to son and their succeeding generations.

The art had developed to a considerable extent and started spreading in the East. A high degree of proficiency in leather making was acquired by the Egyptians, the Chinese, the Babylonians and the Indians. A 4000-year-old granite stone carving located in Berlin museum showcased the operation of tiger skins dressing and people working on the skins (Bruce and Davis 1934). Notably, leather was also unearthed from Egyptian mummies. In the process of refining, Hebrews practiced tanning using oak barks; Romans and Egyptians used lime water to loosen the hair on hides and skins, a process which is being used today. Later in ancient Europe, Greeks and Romans mastered the art of leather manufacture and succeeded in tanning by using gall nuts, bark and sumac. Then, with the fall of the Roman Empire, the art of tanning had been lost to Europe and centuries later the invaded Moors brought back the art to Spain and revived artistic leather, the Cordovan leather in Europe (Watt 1934).

In India, leather processing was practiced by a group of people called *Chamars* and whose inscription in Rig-Veda marked its antiquity (Waterer 1946). Similarly, *Madiga* in medieval Andhra practiced tanning which served as a precursor process of the modern East India (EI) tanning. It was in 1857, the first modern tannery of India was established in Kanpur under the leadership of Captain John Stewart of British EI Company. In 1895, chrome tanning was introduced in India by Alfred Chatterton. The commercial-scale practice of chrome tanning was started in 1903 in Chennai and Mumbai. There was a rapid industrial development where 56 tanneries, 23 footwear units and 25 leather good units were established in India by 1941 (Duraivalan 1973; Thygarajan and Amudeswari 1994). This laid the foundation stone for the evolution of leather science and technology providing scientific support for the holistic growth and development of leather industry.

## Challenges in leather processing

Despite the global use of leather since ancient times, preservation of this collagen-based material remains a challenge for conservators. The conventional chemical methods and chilling although practiced for preserving skins and hides during transit and storage, the high cost and environmental hazard posed a great threat to ecological imbalance. In addition, chilling of skins at 4 °C or freezing at −20 °C affected the cellular arrangement leading to damage in tissue (Kanagaraj and Chandrababu 2002). Secondly, preservation of skins by salting method although effective, the lipolytic activity of extremely halophilic microorganisms found in the salt reduced the quality and commercial viability of hide (Birbir and Bailey 2000). This vulnerable attack by microorganisms served to be the most important factor for putrefaction of raw hides and skins making them unsuitable for leather manufacture.

## The advent of nanotechnology

During the last decades of the twentieth century, the world has witnessed innumerous scientific developments in almost all domains. Nanotechnology is one among them that has emerged with user-driven technology for manipulating and simulating matter at an atomic scale (Zsigmondy 1914; Bharat 2010). Although nanotechnology is considered as a new field, the phenomenon of nanoscience has been deeply impregnated in our cellular processes, e.g., the structure of DNA, replication and protein synthesis. But the nanotechnological concept has gained momentum with Richard Feynman's provocative talk "*There's Plenty of Room at the Bottom*" in 1959 (Feynman 1960) at Caltech. From then on, interest in "engineered nanoparticles" has significantly increased in recent years. Such materials were tailored to have at least one dimension of 1–100 nm with exorbitant properties compared to its bulk counterpart of the same composition. The understanding and maneuvering of the properties of engineered nanomaterials (nanoparticles, -fibers,

-tubes, -islands, -cones, -dots) have shown a paradigm shift and promising results in biomedicine, health care, energy, electronics, agronomy, food, environmental remediation and many other applications (Ramos et al. 2017; Gholizadeh et al. 2018; Serrano et al. 2009; Hu 2012).

Recent advances in the field of nanotechnology, particularly the ability to prepare highly ordered nanoparticulates of any size and shape, have led to the development of new era of nanobiotics. Although metal nanoparticles are synthesized by physical, chemical and biological methods, eco-friendly green synthesis has been the most preferred method. A variety of metal nanoparticles such as Ag, Au, ZnO, Pd, Se, Cu and Pt have been synthesized using biological catalyst. For instance, microalga *Chlorella sp*. has been harnessed for the synthesis of ZnO NPs under ambient conditions. The photocatalytic effect of the biomediated ZnO NPs was determined to degrade 97% of the organosulfur pollutant, dibenzothiophene (DBT) (Khalafi et al. 2019). Similar approach in the synthesis of ceramic alpha aluminum oxide nanoparticles with an optical band of 5.46 eV using the extract of an algae *Sargassum ilicifolium* was also reported (Koopi and Buazar 2018). Furthermore, a bacterial pigment extracted from *Pseudomonas aeruginosa* has been harnessed in fabricating AgNPs and its cytotoxicity was evaluated. The presence of aromatic compound present in the pigment, pyocyanin hastened the formation of AgNPs thereby acting as reducing and capping agent as well through intermolecular hydrogen bonding (Muthukrishnan et al. 2019a).

Biomolecules present in the plants such as proteins/enzymes, polysaccharides, alkaloids, flavonoids, terpenoids, phenolic compounds and vitamins were found to be involved in the reduction, formation and stabilization of metal nanoparticles (Gebregeorgis et al. 2013) such as silver, gold, copper and silica (Sepahvand et al. 2020; Buazar 2019; Suresh et al. 2020). For instance, CuO was bioreduced to CuO NPs ($22 \pm 1.5$ nm) by the seed extract of the plant, *Triticum aestivum* (wheat) and their catalytic activity in removing 4-nitrophenol was determined. The synthesized CuO NPs exhibited good stability for 90 days without any aggregation or sedimentation (Buazar et al. 2019). Deciphering the mechanism involved in green synthesis of inorganic nanoparticles is of prime importance for optimizing the parameters. Biomediated synthesis of ZnO NPs had been demonstrated using starch-rich potato extract. Starch with extensive hydroxyl groups facilitates easy complexation of Zn ions in its molecular matrix and the aldehyde terminals accomplish the reduction of $Zn^{2+}$ to $Zn^0$, thereby conferring stability by acting as a capping agent (Buazar et al. 2016a). The same group have synthesized $Fe_3O_4$ NPs using starch but proposed a different mechanism involved in the synthesis process. The presence of starch has initiated oxidation of $Fe_3O_4$ in alkaline conditions, and the electrons yielded reduced $Fe^+$ ions to $Fe^0$ NPs. The primary hydroxyl groups present in starch molecule get oxidized to carboxyl group thereby encapsulating the nanoparticle formed (Buazar et al. 2016b). Such economically viable approaches demand proper fine-tuning on the optimization parameters for controlling the size which in turn decides the effectiveness of the protocol adopted. On the contrary, chemical approach requires obnoxious chemicals (expensive) although capable of precisely controlling the size of the particle pose major threat to the environment and health challenging the evicting possibilities from the ecosystem.

Although nanotechnology, its venture into leather industry and applicability to industrial scale is at infancy, there are certain limitations that restrict their wide application. For instance, the large-scale production and downstream processing of nanomaterials used in different processes involved in leather production. Secondly, the toxicity concern due to reduced size and altered physicochemical properties needs regular check for cleanup and remediation processes. On the other hand, 'green synthesis' approach avoids the production of unwanted or harmful by-products employing ideal solvent system and natural system attributing for reliable, sustainable and environment-friendly approach (Singh et al. 2018). There are certain advantages in using the nanomaterials in processes involved in leather production. Metal oxide nanoparticles ($Fe_3O_4$) possessing magnetic properties have been conjugated to enzymes and used for unhairing and fiber opening of skin without employing brutal osmotic forces (Murugappan et al. 2016). Secondly, the broad-spectrum antimicrobial activity of Ag, ZnO, CuO, etc. (Wang et al. 2017; Muthukrishnan et al. 2019b), would be used to get rid of microbes responsible for skin putrefaction. Nanomaterials and their role are greatly reflected on the finished products bestowed with self-cleaning properties, etc. The application of the same sequentially at all stages might enhance the durability, quality and the stability of the desired leather product. This approach might reduce the chemical load exposed to the finished leather product (Dixit et al. 2015).

Based on these considerations, this review highlights the nanotechnological intervention to resolve some of the commonly encountered issues pertaining to leather processing and environmental impacts for a cleaner production of leather in the forthcoming years.

## Methodology

A literature review on the conventional leather processing and nanotechnology-enabled leather manufacture was conducted. The review included the scope for alternative strategies for cleaner leather manufacture with the following research question: *How do the leather industry*

*work and the extent of environmental impact it creates. What are the alternate strategies in reducing the pollution load by a newer and a novel technologies and its global reach?* The Web of Science research engine was chosen for accessing multiple databases and for retrieving comprehensive citation data as a standard form of academic referencing. In addition, PubMed.gov has been accessed to retrieve leather-related articles and esp@cenet for accessing the patents published in the relevant field. The search string used for relevance included 'preservation of skins and hides', 'nanotechnology for leather', 'dehairing using nanotechnology', 'nanocomposite based tanning', 'effluent treatment by nanomaterials' and 'nanoleather finished products.' The references were recorded and processed by Mendeley citation manager. The populated articles published in the past two decades starting 2000 till 2020 were shortlisted and checked for relevance, critical evaluation and data extraction.

## Evolution of leather science

Leather science evolved at a tremendous pace since its inception with innovations related to new processes, devices and chemical feeds in leather manufacturing. The publication and patent portfolios of the leather sector generated in two decades from 2000 to 2020 have seen an exorbitant growth in leather technology which is depicted in Fig. 1. The publications and patents were classified based on the processing techniques, chemical modifications and product development. When the global publication data were compared to patents, a fluctuation trend reflecting a decline in technology transformation from the data published is well appreciated from Fig. 1. This demands a noticeable change in the trend where the technological inputs should rightly be nurtured and groomed to transform the cumulative data into a commercial product for the societal cause (Chakrabarti et al. 2006).

The emergence of nanotechnology has shown a ray of hope for leather producers to make leather of high quality.
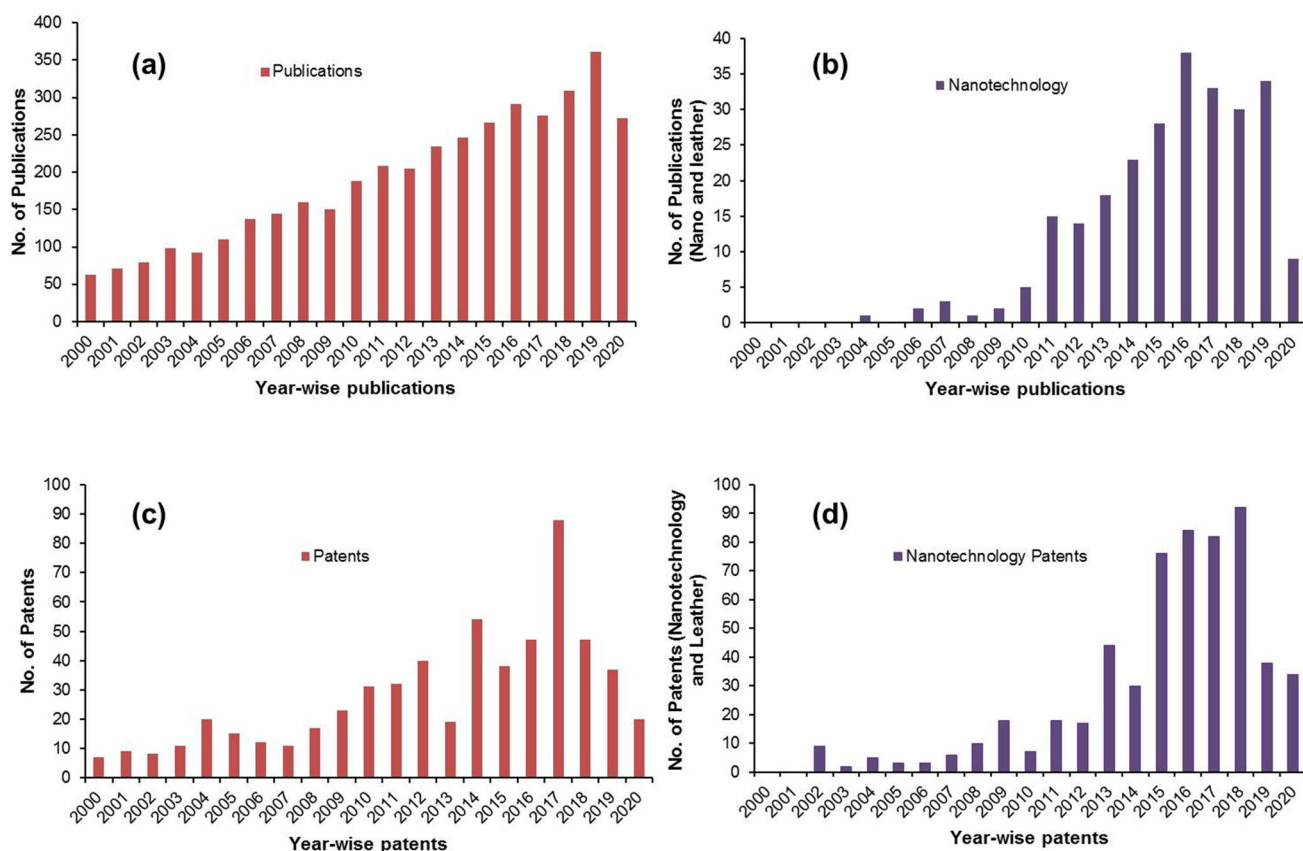


**Fig. 1** Scientific evolution of leather technology in the past two decades. Number of leather-related publications (the authors declare that they have no conflict of interest) and nanotechnology-integrated leather applications (**b**) were sourced from PubMed.gov. Patents filed globally related to leather (**c**) and nanotechnology-integrated leather applications (**d**) were sourced from the European Patent Office (esp@cenet)

This has been well established by the fabrication of nano-materials and their application in leather production sequentially at all stages in particular tanning stage in order to improve the functional characteristics of the product. In the search for nanotechnological implication in leather industry, a total of 256 articles related to nanotechnology were found, whereas 3967 articles concerned with leather and leather products have been published. Similarly, a total of 586 patents were filed in relation to leather processes and products. There were 578 patents filed with nanotechnology-driven leather processes and products during the years 2000–2020. Almost 98% of the patents filed in leather science integrated with nanotechnology show a positive trend in the development of nanobased leather applications (Fig. 1).

## Leather processing—a bird eye's view

In the process of leather making, there are four main stages involved, namely (1) pretanning or beamhouse process, (2) tanning, (3) dyeing, retanning, fat liquoring and (4) leather finishing. Schematics of the entire leather process are shown in Fig. 2, and the purpose of each step/stage is elaborated in Table 1. The most important step in the beamhouse operations is curing or preservation of skins and hides. Once flayed, they are prone to bacterial damage (Tancous and Jayasimhulu 1973) or putrefaction or autolysis if left untreated (Bailey 2003). Subsequently, there are innumerous

factors influencing the degradation, viz. temperature, pH, humidity, oxygen and various contaminants attracted toward dirt, blood stains and dung. Apart from microbial attack, involvement of an intracellular enzyme cathepsin in autolysis was also reported (Bienkiewiez 1983). To get rid of bacterial damage and to delay the process of putrefaction till the commencement of leather processes, curing method is followed.

## Curing

Curing is a critical preparative step in which the skins and hides are preserved temporarily by preventing putrefaction of the collagenous matrix from microbial attack during the time lag from flaying to processing (Kanagaraj et al. 2000, 2001). An ideal curing procedure must not interfere or damage the interfibrillar collagen structure and should reverse it to the original form during wetback or soaking. There are different methods of curing that have been adopted for the preservation of skins and hides. They are classified into (a) drying, (b) salting, (c) pickling, (d) chilling and (e) Irradiation. Among the following methods, salting is the most common method practiced in many countries. Notably, salt (40–50% of the green weight of skin) is applied on the flesh side of the skin or hide and the moisture content reduced to 40–50% from its original moisture content of 65–70%.



**Fig. 2** Steps involved in leather processing starting beamhouse operations till finished crust leather and the possible nanotechnological intervention for improved leather production in connection with environmental impact (Thorstensen 1976)
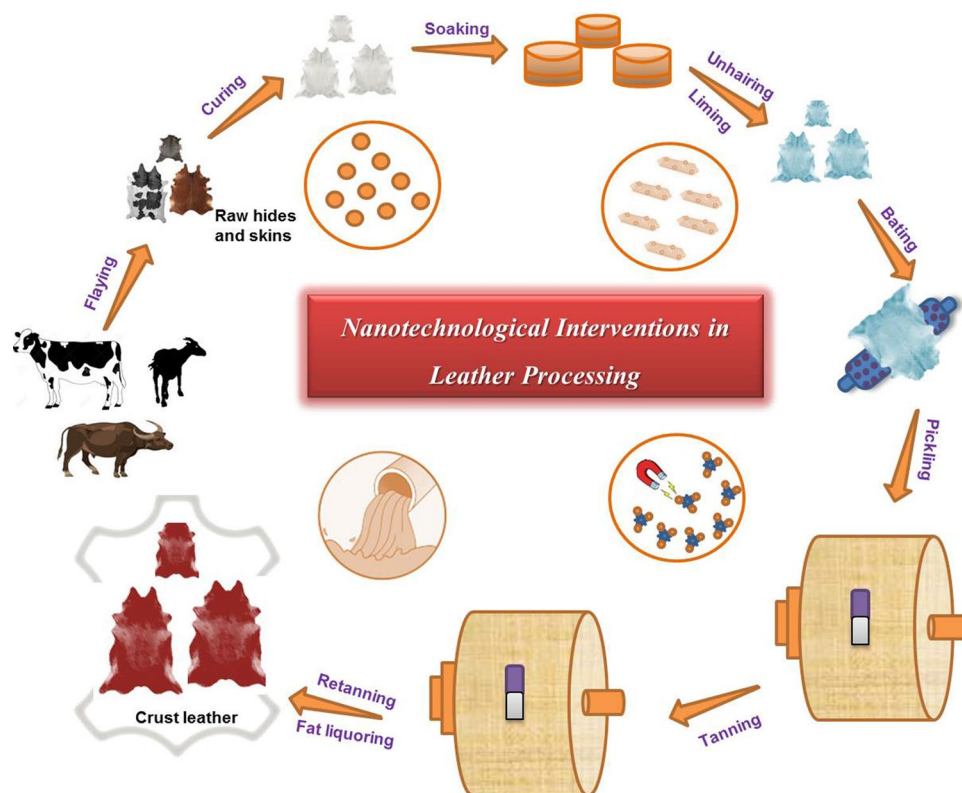
**Table 1** Steps involved in processing of skins and hides to leather

| Process | Agents used | Mechanism |
|---|---|---|
| Beamhouse operations (Sharphouse 1983; Dutta 1985) | | |
| Soaking | Water | Removal of salt left over from curing |
| | | Increase the moisture |
| Liming (unhairing and scudding) | Lime (Ca(OH)$_2$), sodium sulfide, sodium hydroxide, sodium hydrosulfide, dimethyl amine | Removal of hair and keratinous matter |
| | | Removal of interfibrillary proteins and extraneous flesh |
| | | Swelling up of the fibers |
| | | Splitting of collagen fiber bundle |
| De-liming bating | Ammonium sulfates and ammonium chlorides | Removal of alkali from the pelt |
| | | Deswelling of the fibers |
| | | Removal of scuds and clean, flat and scud-free surface is obtained |
| Pickling | Sulfuric acid, hydrochloric acid and salt | Facilitate even penetration of tanning agents |
| De-greasing | Lipases, detergents or solvents | Removal of fats and grease from the interfibrillary space |
| | | Makes leather soft and pliable |
| Tanning (Covington 1997) | | |
| Vegetable tanning | Chestnut, oak, tanoak, hemlock, quebracho, mangrove, wattle and myrobalan | Binding of tannins to collagen proteins |
| | | Decreasing the water solubility |
| | | Increasing the resistance to bacterial attack |
| Mineral tanning | Chromium sulfate | Formation of poly chromium (III) compounds and cross-links collagen subunits |
| | | Hydrothermal stability and shrinkage temperature is increased |
| | | Wet blue leather offers more durability |
| Post-tanning operations (Heidemann 1993) | Water, tanning agents, fats/oils, waxes, dyes, filling agents etc. | Thinning, retanning and lubricating the skin and hide converting them into crust leather |

## Chemistry behind curing

Curing using salt (NaCl) removes excess water from the hides and skins by means of difference in osmotic pressure. As a result, the moisture content in hides and skins is greatly reduced to 40% with the increase in osmotic pressure thereby rendering the environment unsuitable for bacterial growth. This dehydrating and bacteriostatic effect imparted by salt treatment remains the crux in long-term preservation of skins. The wet salting method adopted for curing hides demands heavy salting and pressing for a span of 30 days, whereas in brine curing, hides are submerged and agitated in a saltwater bath for about 12–24 h. These brine-cured hides were used for the production of heavier and high-quality leathers. Curing accompanied by low temperature has also been found effective in the preservation of skins and hides (Berber and Birbir 2010).

Although the salt curing method is simple and economical, it suffers heavily from the environmental perspective attributing high TDS (> 2100 mg/L) accounting to 40% and chloride content 55% in the effluents (Kanagaraj et al. 2005a). Alongside, removal of TDS in the soak liquor discharge is quite difficult and requires huge investment. In view of it, the tanning industries have been forced to install

reverse osmosis (RO) plants for recovering and reusing the water spent for leather processing (Ranganathan and Kabadgi 2011). Moreover, the salt sourced from marine areas contains impurities such as sulfates and chlorides of calcium and magnesium which leaves a salt stain on the skin. Notably, the large number of halophilic bacteria present in the salt adheres to the skins and hides causing 'red heat' (Anderson 1954; Ghosh et al. 2010) that interferes at large with the leather quality.

## Alternatives to salt curing

As an alternative, potassium chloride was used in the preservation process by which steer-hide could effectively be preserved using brine curing. Besides, it could effectively prevent red heat and used as a nutrient source for plants. The high cost and temperature-dependent solubility limited its use in long-term preservation. Thereafter, a combination of powder-biocide formulation termed Liricure was applied over the green skins. The biocides used were para-chloro meta-cresol (PCMC) and ethylenediamine tetra acetic acid (EDTA). This approach could effectively preserve the sheep skins and cattle hides for 12 months, and the finished leather products processed from them were comparable to

those derived from salted skins and hides. This approach faced a major setback where more amount of chromium was precipitated by EDTA during effluent treatment (Russel and Tandt 1997).

Along this line, benzalkonium chloride, an organic salt classified under quaternary ammonium compound, was used in the preservation of skins and hides. With no difficulty in handling and with no adverse effects, it was best suited to preserve fresh calf skin at 0.1–0.4% (Cordon et al. 1964; Kanagaraj et al. 2005b). Following the similar trend, boric acid and silica gel were used for short-term preservation of skins and hides. Saturated solutions of boric acid (~4.5%) alone and in combination with sodium chloride could effectively preserve skins for 5 days. Boric acid combined with naphthalene at 0.5% was found effective in eliminating bad odors, flies and other pests in the stored hides. Despite the merits, the use of boric acid has been called off owing to effluent restriction (Hughes 1974). Similarly, silica gel at 15% and 10% in combination with the biocide para-chloro meta-cresol (PCMC) aided effective preservation of skins. This had beneficial effects in reducing the pollution load by 75% and 85% in terms of TDS and chlorides, respectively (Munz 2007).

### Greener approach

Greener approaches in the curing process have been studied by various groups considering the environmental impact of the effluent. Plant extracts possessing antimicrobial properties have been harnessed for preservation of skins and hides. Studies on neem oil used for the preservation of hides were reported (Venkatachalam et al. 1981). The studies were extended further by employing *Acalypha indica (A. indica)*-based formulations in preserving goat skins for up to 2 weeks without any observable sign of putrefaction. Later, combinatorial approach in preservation was demonstrated using 15% *A. indica*, neem leaf, neem seed paste and 0.25% 2-bromo-2-nitro-1,3-propanediol (BNPD) with 10–20% varied concentrations of KCl. This approach could extend the shelf life of skins from minimum 10 to maximum 77 days with significant reduction in TDS levels (Vijayalakshmi et al. 2009). An eco-friendly method was developed using *Semecarpus anacardium* nut extract for the short-term preservation. This method was effective due to its antibacterial and dehydrating properties as investigated from organoleptic characteristics (Iyappan et al. 2013). The same group has worked on developing a saltless method of preservation using *Aegle marmelos* extract. They could achieve remarkable reduction in pollution load in terms of BOD (46%) and manifold decrease in COD and TDS (Iyappan et al. 2020).

With the growing concern over reducing salinity in tanneries, de-oiled neem cake was used as a potential bio-additive in preserving skins for 21 days utilizing its broad-spectrum antibacterial potential. This low-salt preservation method showed ideal strength properties of leather processed from salt-cured leathers (Vedaraman et al. 2013). Apart from indigenous plant, the preservation efficacy of an Ethiopian plant *Rumex abyssinicus* root extract combined with salt (1:1.5) was also investigated. This formulation could effectively preserve the skins for 30 days, and the processed leather showed characteristic physical and organoleptic properties as salt-cured leather. The pollution load was significantly reduced in the soaked liquor demonstrating 55% TDS and 70% chloride highlighting cleaner approach in leather manufacturing (Mohammed et al. 2016). Hashem et al. (2018) have proposed a preservation method using *Moringa oleifera* leaf paste with lower salt additive on goat skins. After 28 days of effective preservation, the leather processed from the preserved skins fulfilled typical characteristics of crust leather. Further, there was a significant reduction in TDS (39%), chlorides (46%), BOD (46%) and COD (48%) attributing a sustained approach in preservation.

## Nanopreservation

The advent of nanotechnology and its recognition in recent years has provided unlimited opportunities in almost all domains of science and technology. It is noteworthy to mention that leather industry has also adopted nanotechnological nuances for developing innovative products using nanostructured materials. This technological implication has conferred antibacterial (Giannossa et al. 2013), flame resistance (Jiang et al. 2015) and self-cleaning properties (Petica et al. 2015) to finished leather product. Nanomaterials (metals, polymers, bimetals, graphene oxide) employed not only imparted antimicrobial properties but also can act as carriers for natural antimicrobial compounds and chemicals (Gholizadeh et al. 2018). The most commonly used nanomaterials with their antimicrobial mechanism are shown in Table 2.

It is quite obvious from Table 2 that most of the nanomaterials showcase a similar trend in inhibiting the bacterial growth. Initially, the nanomaterials establish contact with the microbial cell wall through electrostatic interaction resulting in cell surface depression. With the successful contact, membrane permeability permits the internalization and accumulation in bacterial cell membrane. Most of the nanomaterials show high degree of binding affinity toward thiol (-SH-)-containing groups and inactivate the enzymatic processes. The ions released by the nanoparticles induce a massive proton leakage disrupting the cellular membrane. The nanomaterial undergoes oxidation on its surface and starts destructing the cell by increasing the oxidative stress. Alongside, the ROS ($H_2O_2$, $\cdot OH$, $O^{2-}$) generated from the oxidative stress-induced nanomaterials damages proteins

**Table 2** Nanomaterials and their antimicrobial mechanism of action

| Nanomaterials | Antimicrobial mechanism | References |
|---|---|---|
| Silica nanoparticles | Inducing an unfavorable condition for bacterial growth<br>Reducing the adhesion and proliferation of bacteria | Cousins et al. (2007) |
| Calcium oxide nanoparticles (CaO NPs) | High alkalinity<br>Generation of reactive oxygen species (ROS)<br>Damage to cell membrane, leakage of cellular contents | Yamamoto et al. (2010) |
| Silver nanoparticles (AgNPs) | Oligodynamic effect<br>Disruption of cell membrane<br>Interfering with disulfide linkages in proteins<br>Catalyzing formation of free radicals<br>Genotoxic effect damaging DNA | Duran et al. (2010) |
| Magnesium oxide nanoparticles (MgO NPs) | High-alkaline nature<br>Presence of oxygen gaps<br>Cell membrane damage<br>Lipid peroxidation | Jin and He (2011) |
| Aluminum oxide nanoparticles ($Al_2O_3$ NPs) | Bacterial cell wall disruption<br>ROS generation<br>Intrusion and accumulation in the cell wall | Ansari et al. (2013) |
| Copper oxide nanoparticles (CuO NPs) | Easy penetration across the cell membrane<br>Impairment of bacterial enzyme machinery | Ingle et al. (2014) |
| Gold nanoparticles (AuNPs) | Photothermal effect with ROS generation<br>Disruption of bacterial cell wall and DNA damage<br>Osmotic imbalance and disruption of cell wall integrity. | Shah et al. (2014) |
| Iron oxide nanoparticles ($Fe_3O_4$ NPs) | Penetration of cell membrane<br>Interference with electron transfer | El-Zowalaty et al. (2015) |
| Titanium dioxide nanoparticles ($TiO_2$ NPs) | Generation of ROS in the presence of UV (Photocatalytic effect)<br>Lipid peroxidation<br>Disruption of cell membrane<br>Damage to DNA | Yadav et al. (2016) |
| Zinc oxide nanoparticles (ZnO NPs) | Reduction in microbial viability<br>Formation of $H_2O_2$<br>Electrostatic attraction and accumulation on bacterial membrane<br>ROS generation | Moghaddam et al. (2017) |

and DNA accounting for effective antibacterial activity (Wahab et al. 2012; You et al. 2012).

## Nanocharacterization

The dimensions of materials when reduced to nanoscale demonstrate unique properties entirely different from that of their bulk counterparts. Such properties are harnessed for different applications. Despite fabrication of nanomaterials with attractive electronic/optical properties and mechanical/structural stability, there are challenges in characterizing them at nanoscale for desired applications emphasizing the need for nanocharacterization (Raza 2019). For characterizing any nanomaterial, spectroscopic and electron microscopic analysis would be the most sought-after techniques. Spectroscopy involves the precise identification and quantification of materials based on changes in the electronic energy, vibrational and rotational relaxations, intersystem crossings and internal conversions as well. The techniques involving electromagnetic

spectrum for identification of nanomaterials are as follows: ultraviolet–visible spectroscopy, photoluminescence spectroscopy and infrared spectroscopy (Coates 2000).

Ultraviolet–visible (UV–Vis) spectroscopy is the most commonly employed technique to quantitatively characterize organic and inorganic sized materials based on *Beer-Lambert* law. It is also utilized to identify the constituents of a substance, determine the concentration and to decipher the functional groups (Onubogu et al. 2011). Different-sized materials ranging from transition metal ions and small molecular weight substances with diameters to several Ångstroms (Å), polymers, nanoparticles and bulk materials can be characterized. Size-dependent properties such as peak broadening and absorption shifts at nano- and atomic scales can also be observed. Electronic properties such as band gap of the material are also determined using this technique.

Photoluminescence (PL) spectroscopy is a technique employed to monitor the light emitted from atoms or molecules prior to absorption of photons by the photoluminescent

material. By considering these four parameters, viz. intensity, emission wavelength, bandwidth of the emission peak and the emission stability, PL emission properties can be characterized. As with the reduction in size to nanoscale, the emission properties may change in such cases and a size-dependent shift in the emission wavelength could be determined using PL spectroscopy. For instance, semiconductor nanocrystals produce narrow emission peaks that differ from that produced by luminescent organic molecules with bandwidth of around 30–40 nm. Such smaller bandwidth makes it easier to discriminate individual wavelengths emanating from multiple sources (nanocrystals) (Tokida and Adachi 2012; Zhang et al. 2016).

Nuclear magnetic resonance (NMR) spectroscopy remains one of the complex techniques employed to study the chemical structure of organic and inorganic compounds at nanoscale. Nuclei containing odd numbers of protons or neutrons have an intrinsic magnetic moment is made to align with a very powerful external magnetic field. The alignment is further disturbed by the radio-frequency electromagnetic field, and that response to the disturbed field is used in NMR spectroscopy. Novel nanocompounds can be fabricated by determining the chemical structure using NMR studies (Agarwal et al. 2018).

X-ray photoelectron spectroscopy (XPS) is another characterization technique used to quantify the chemical and electronic states of the elements within the atomic layers of a surface. In addition, this technique could identify chemical bonds, chemical compositions that ease deriving the empirical formulae. The XPS is based on the photoelectric effect in which photoelectrons are ejected from the surface by the action of X-rays. XPS experiments are limited to just few Å beneath the surface as the ejected electrons must travel through the sample retaining the energy to reach and excite the detector. As XPS is surface sensitive, it is an ideal technique to characterize sensing layers where the interaction between the analyte and sensing layer occurs. For instance, CdSe semiconducting nanocrystals coated with trioctylphosphine oxide (TOPO) were subjected to XPS spectroscopy to confirm the presence of the coating (Aziz and Ismail 2017).

X-ray diffraction (XRD) is one of the crystallographic techniques used to identify and quantify various crystalline phases present in the nanomaterials and powders. The crystalline nature and size of the grains and nanoparticles are determined. Upon directing the X-rays on the sample, a proportion diffracted from the crystalline sample produces a pattern which is then compared with the internationally recognized databases such as International Center of Diffraction Data—ICDD and the phases identified. The inherent limitation of XRD is that the mixtures of phases having low symmetry are difficult to differentiate owing to the large number of diffraction peaks. As from the XRD data,

the widths of the diffraction peaks allow the determination of crystalline size using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where $D$ is the crystallite size, $K$ is a constant, $\lambda$ wavelength of the X-rays, $\beta$ is the full width at half maximum of the broadened peak and $\theta$ corresponds to Bragg's angle (Ingham 2015).

Dynamic light scattering (DLS) is one among the light scattering techniques that involve analyzing the light scattered from materials. Based on the frequency of light and the type of scattering, this technique provides information regarding the size of the particles, composition and structure of nanomaterials. Moreover, this technique is applied to study the system dynamics of nanomaterials in real time. Notably, determination of monodispersity of prepared nanoparticles and any small changes associated with the hydrodynamic diameter of the particles upon adsorption or encapsulation could be determined at a relatively rapid and straightforward fashion. DLS is suitable for particles that exhibit Rayleigh scattering, i.e., the particles' size must be larger than about a tenth of the illuminating wavelength (Carvalho et al. 2018a, b).

Raman spectroscopy is another spectroscopic technique that monitors the intensity and wavelength of light that is scattered inelastically from crystals or materials. It is a powerful tool to qualitatively and quantitatively defining the composition of materials. In Raman spectrum, Raman shifts are plotted against their respective intensities originated from the interacting photons with molecular vibrations (phonons). Upon irradiation, there would be an exchange of energy between them in which the phonons may gain or lose energy. Thus, the information provided by the spectra attributes for the 'fingerprint' of that particular molecular and identified (Kumar 2012). The main limitation of Raman spectroscopy is that the interpretation of weak inelastically scattered light from the intense Raleigh scattered light. Secondly, the photoluminescence due to the incident light may hinder the Raman spectrum. To overcome such limitations, surface-enhanced Raman spectroscopy (SERS) was employed in which the Raman signal could be enhanced when the molecules are adsorbed onto roughened metal surfaces such as silver or gold. By bringing about changes in analyte polarizability scattering could be enhanced by more than a million-fold. For successful SERS, the particles' features need to be small on a par with the wavelength of the incident light and the system must possess structures typically in the size range of 5–100 nm (Lindquist et al. 2019).

Microscopy has played a vital role in the rapid developments in nanotechnology and nanoscience. Besides, other

**Table 3** Techniques used for the characterization of materials at nanoscale

| Techniques | Type of materials | Characterization environment | Resolution/ quantitative/ qualitative |
|---|---|---|---|
| Imaging techniques | | | |
| SEM | Solid | Vacuum | Nanometer |
| TEM | Solid | Vacuum | Å |
| AFM | Solid/liquid | Room temperature | Å |
| STM | Solid/liquid | Room temperature | Å |
| Particle size determination | | | |
| DLS | Liquid | Liquid | Nanometer |
| XRD | Solid | NA | Å |
| TEM | Solid | Vacuum | Å |
| Crystalline nature | | | |
| XRD | Solid | NA | Quantitative |
| TEM | Solid | Vacuum | Quantitative |
| DLS | Solid/liquid | NA | Qualitative |
| Chemical composition | | | |
| RBS (Rutherford Back-scattering Spectrometry) | Solid | Vacuum | |
| XPS | Solid | Vacuum | |
| Chemical bonding | | | |
| XPS | Solid | Vacuum | |
| IR | Solid/liquid/gas | NA | |
| Raman | Solid/liquid/gas | NA | |
| NMR | Solid/liquid | NA | |
| Compound identification | | | |
| Mass spec | Solid/liquid | Vacuum | Qualitative |
| UV–Vis | Solid/liquid | NA | Quantitative |
| PL | Solid/liquid | NA | Quantitative |
| IR | Solid/liquid/gas | NA | Quantitative |
| Raman | Solid/liquid/gas | NA | Quantitative |

characterization technique, this tool is concerned with the interaction between the electrons and material. The high-energy electron beam upon interacting with the surface of the material could reveal details about topography, chemical composition, morphology and crystallographic structure at nanoscale and with a better resolution. Scanning electron microscope (SEM) is the most routinely used instruments for characterizing both organic and inorganic materials. It typically highlights the topographical and morphological features of the desired material. SEM could also be used to monitor the formation and growth of thin films and nanostructures. Transmission electron microscope (TEM) reveals information about the morphology, crystallography, particle size distribution and its elemental composition when a high energy beam of electrons is transmitted through the sample. Furthermore, TEM could provide atomic-resolution lattice images and give chemical information at a spatial resolution of 1 nm. It also has the capability to create both electron microscopic images and diffraction patterns for the same region by adjusting the strength of the magnetic lenses.

On the other hand, high-resolution transmission electron microscope (HRTEM) could be used to dissect the crystal structure and the images formed due to difference in phase of diffracted electron are captured (Smith 2015; Su 2017).

In a step further, atomic force microscope (AFM) tends to be one of the most reliable characterization techniques that measures attractive or repulsive forces acting between the scanning probe tip and the surface of sample and provides atomic-scale images of surfaces. The deflection caused by the forces (Van der Waals, electrostatic, magnetic, capillary, Casimir and solvation) acting between the tip and the sample surface is measured and correlated. AFM not only provides the topographical information but also acts as a chemical, physical and biosensor. Imaging to the order of several micrometers, scan area and deformation of tip's shape upon encountering shear force are some of the challenges that this technique need to overcome (Zhong and Yan 2016). In addition to the above-mentioned techniques, there are other techniques which are enlisted in Table 3.

## Nanomaterials versus skin

In the preliminary study conducted at CLRI, gallic acid-fabricated nanosilver sized 30 nm was fabricated for the preservation of goat skins prior to optimization studies. The antimicrobial susceptibility testing was performed against the skin flora. There was a significant antibacterial effect exerted by these nanoparticles at a final concentration of 0.156 mg/mL (Table 4). Compared to Gram-positives, Gram-negative strains sustained extensive membrane damage attributing to 'pits' which might have been resulted due

to the release of silver ions on the surface of the membrane (Fig. 3). These results were found consistent with the SEM micrograph showing the typical 'pitting effect' in the cultures exposed to AgNPs. Control cells remained unaffected retaining their smooth surface and original rod shape. The internalization of AgNPs was evidenced from the EDAX profile where the atomic concentration of silver accounted to 8.47% of total elements (Unpublished data). The skins remained in good condition for 15 days upon examining the physical characteristics, odor and fullness. It was understood that these nanoparticles get internalized exhibiting its

**Table 4** Antimicrobial susceptibility testing of AgNPs against a panel of bacteria inhabiting goat skins

| Test organisms | Concentration of AgNPs (mg/mL) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 5 | 2.5 | 1.25 | 0.625 | 0.312 | 0.156 | Control |
| *Ps. aeruginosa* | 0 | 0 | 0 | 0 | $4.2 \pm 0.07$ | $7.1 \pm 0.21$ | $10.5 \pm 2.12$ |
| *Bacillus* sp. | $2.1 \pm 0.14$ | $2.25 \pm 0.35$ | $2.5 \pm 0.71$ | $3.5 \pm 0.51$ | $4.5 \pm 0.71$ | $4.8 \pm 0.35$ | $5.5 \pm 0.71$ |
| *S. aureus* | 2 | 2 | 2 | 2 | 2 | 2 | $4.8 \pm 0.35$ |
| *Proteus* sp. | 0 | 0 | 0 | 0 | $1.1 \pm 0.14$ | $2.0 \pm 2.83$ | $5.5 \pm 0.71$ |
| *E. coli* | 0 | 0 | 0 | 0 | $2.5 \pm 0.71$ | $3.7 \pm 0.49$ | 6 |
| *Citrobacter* sp. | 0 | 0 | 0 | 0 | 2 | $3.3 \pm 0.35$ | $4.2 \pm 0.21$ |
| *Acinetobacter* sp. | 0 | 0 | $0.5 \pm 0.71$ | $1.75 \pm 1.06$ | $2.0 \pm 0.71$ | $2.8 \pm 0.35$ | $4.5 \pm 0.71$ |
| *GPS* | 0 | 0 | $1.1 \pm 0.14$ | $1.6 \pm 0.07$ | $1.8 \pm 0.28$ | $2.2 \pm 0.21$ | $4.9 \pm 0.18$ |
| *K. pneumoniae* | 0 | 0 | 0 | 0 | $1.6 \pm 0.57$ | $3.7 \pm 0.49$ | $4.75 \pm 0.35$ |
| *Enterococcus* sp. | $2.15 \pm 0.07$ | $2.4 \pm 0.21$ | $2.5 \pm 0.21$ | $2.5 \pm 0.23$ | $3.5 \pm 0.71$ | $4.5 \pm 0.71$ | $5.8 \pm 0.28$ |
| *S. typhi* | 0 | 0 | 0 | $2.5 \pm 0.64$ | $4.2 \pm 0.21$ | $4.8 \pm 0.42$ | $6.4 \pm 0.21$ |
| *Candida* sp. | 0 | 0 | 0 | $1.3 \pm 0.21$ | $1.3 \pm 0.35$ | $1.4 \pm 0.07$ | $3 \pm 0.28$ |
| *V. cholera* | 0 | 0 | 0 | 0 | $2.6 \pm 0.14$ | $3.6 \pm 0.57$ | $5.5 \pm 0.71$ |
| *Coagulase Negative Staphylococcus* | 2 | $2.1 \pm 0.07$ | $2.4 \pm 0.21$ | $2.4 \pm 0.14$ | $2.6 \pm 0.07$ | $2.7 \pm 0.28$ | $4.9 \pm 0.14$ |
| *S. paratyphi* | 0 | 0 | 0 | $2.9 \pm 0.49$ | $4.6 \pm 0.35$ | $5 \pm 0.21$ | $6.8 \pm 0.49$ |
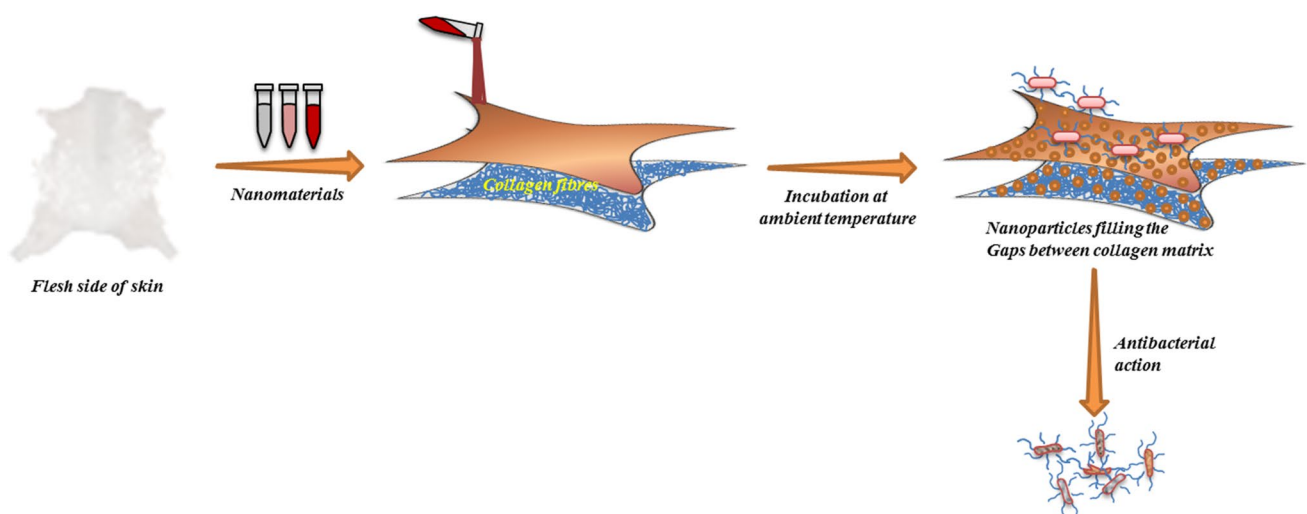


**Fig. 3** Schematic representation of application of metal nanocolloids (Ag/Au/TiO$_2$, ZnO, etc.) and their preservation efficacy demonstrated through antibacterial mechanism (Gaidau et al. 2010)

antimicrobial effect by releasing silver ions. Putrefaction by microbial action came to a halt, and the mechanism behind the collagen interaction needs further research.

Gaidau et al. (2010) have investigated on the interaction of silver nanoparticle with leather under simulated conditions to explore the conformational changes influencing collagen. The interaction was analyzed using Fourier transform infrared spectroscopy (FTIR), atomic absorption and fluorescence spectroscopy. FTIR analysis revealed a modification at amide I band corroborating an altered secondary structure of collagen through hydrogen bonds in carbonyl group. Fluorescence spectroscopic analysis of treated leather recorded tyrosine spectrum at 306 nm clearly elucidating the interaction of AgNPs and collagen through reticulation links. A compatible interaction between AgNPs deposited on $TiO_2$ and collagen was observed with no deformation in collagen structure during nanoparticle treatment and/or chromium salt treatment.

Collagen–nanoparticle interaction was also studied using circular dichroism (CD) spectrometry on modeled medical leather and fur skins. The dichroic spectra of the various nanomaterial combinations were subjected to dichroic spectral studies to determine the possible modifications pertaining to conformational changes. From the interaction studies using various nanomaterials and combinations, the dichroic spectra of $Ag/TiO_2$ combination showed maximum positive ellipticity at 220 nm. It signified that the triple helical structure and integrity of the collagen remained unmodified and unaltered. The internalization of $Ag/TiO_2$ was determined using atomic absorption spectroscopy as 3450 ppm and 10 ppm without and with chromium, respectively. This combinatorial approach imparted microbial resistance to leather and fur skins to keep fungi and bacteria at bay (Gaidau et al. 2009). This possible interaction between nanosilver (doped and stand-alone) and collagen studied using simulated collagen models shows the possibility of designing artificial leather with durability and quality as original animal produced leather.

Castaneda et al. (2008) have proposed Tiopronin (N-(2-mercaptopropionyl)glycine)-protected gold nanoparticles (TAuNPs) for the cross-linking of collagen fibers via EDC (1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide) coupling. The carboxyl group present on the surface of AuNPs facilitated the formation of multiple cross-links with lysine moieties of collagen, thus reducing the pore size from 140 to 1 μm. This nanoparticulate cross-linking of collagen fibers showed improved stability and biocompatibility (Fig. 4).

Stabilization study on nanoparticulate interaction with collagen was proposed by Sangeetha et al. (2012). Metal oxide nanoparticles, preferably chromium (III) oxide nanoparticles, encapsulated in a polymeric matrix sized 50–70 nm were treated against collagen solution. The intactness of nanoparticle-treated triple helix structure of collagen showed a positive CD spectrum at peak around 220 nm with Rpn (ratio of positive to negative peak intensity) close to 0.1, which confirmed the unaltered and stable three-dimensional conformation of collagen. The involvement of amino acids present in the collagen was found to enhance the cross-linking of the core–shell nanostructures through hydrophilic poly(acrylic acid) (PAA) surface groups conferring thermomechanical stability. Further, FTIR studies confirmed the intact native structure of the collagen upon treatment with chromium (III) oxide encapsulated polymeric nanostructures. Investigations on iron oxide nanoparticles (FNPs) functionalized with gum Arabic and its possible interactions with collagen have been reported (Kandamchira et al. 2013). CD spectral studies on collagen–nanoparticle interaction revealed significant peak at 220 nm and the ratio of the positive to the negative peak (Rpn) of native collagen close to 0.1 determining the stability of collagen prior to nanoparticle treatment. FTIR studies revealed the finger print amide I, II, III peaks of collagen remained unchanged even after the interaction with GA functionalized iron oxide nanoparticles but with slight changes from that of the native collagen.

The effect of sago starch mediated silver nanoparticles and their interaction with collagen have been spectroscopically investigated by Mandal et al. (2015). The interaction took place in such a manner that sago starch acted as a bride in connecting the silver nanoparticles through hydrophilic moiety leaving behind free hydrophobic end for collagen



**Fig. 4** Schematic representation of AuNPs-interlinked collagen fibers (Castaneda et al. 2008)
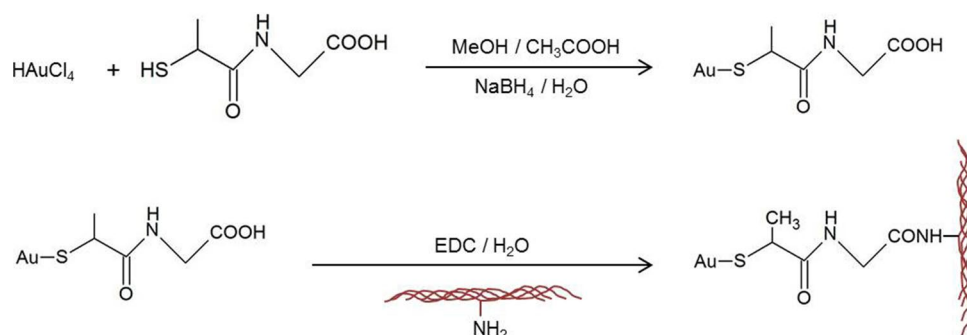
interaction. This was evidenced from the shift in the finger print regions from 950 to 1075 and 1425 to 1420 cm$^{-1}$ confirming the interaction between –NH$_2$ group of collagen and –OH group of starch. Alongside, the FT Raman spectra showing a peak at 235 cm$^{-1}$ ascribed stretching vibrations of Ag–N and Ag–O bonds formation with collagen conferring stability was also deduced. Similarly, curcumin-loaded silver nanoparticles were fabricated and their interaction with collagen was proposed (Srivatsan et al. 2015). The inter- and intrahelical cross-links achieved through Cur@AgNPs significantly enhanced the thermal stability and enzymatic resistance in the triple helical collagen. The CD spectra of Cur@AgNPs-treated collagen showed a positive peak at 220 nm with no conformational change in the collagen attributing to successful cross-linking. Further, Kishen et al. (2016) opined on the collagenase resistance acquired by the cross-linking between chitosan nanoparticles and type I collagen. Collagen and collagenase formed complexes with chitosan nanoparticles, thus reducing the collagen degradation up to 54 h attributing a successful cross-linking conferring stability.

## Alternatives to liming and unhairing

Liming is considered to be one of the most important steps in leather manufacture involved in the removal of interfibrillar proteins, noncollagenous materials such as hairs, flesh, etc. This step contributes to about 35% of the overall pollution load of beamhouse operations. Lime and sodium sulfide are the vital chemicals used for liming process. Unhairing of skins and hides is facilitated by the action of these chemicals. The brutal osmotic forces of –OH and –SH present in the chemicals break the disulfide bond in cysteine and thereby disintegrate the keratin present in hair. As a result, hair is either pulped or removed and opens up the fiber for the diffusion of chemicals during subsequent processes. The use of chemicals at large contributes for 50–60% of TDS, COD and BOD in the effluent (Thanikaivelan et al. 2004). This demanded a paradigm shift toward the use of enzymes replacing lime and sodium sulfide for dehairing process (George et al. 2014).

A step further, cocktail of enzymes comprising protease and amylase has been immobilized onto metal oxide nanoparticles for unhairing and fiber opening applications. Nanozyme (iron oxide nanoparticles tagged with cocktail of enzymes) at 3% concentration was found efficient in achieving desirable unhairing within 7 h and fiber opening in skins without any adverse effects as evidenced from the organoleptic and histological studies. This immobilization of enzymes in the nanoparticulate matrix attributed for enhanced enzymatic activity with their high membrane permeability (Murugappan et al. 2016).

Similarly, copper oxide nanoparticles (CuO NPs) were used to immobilize protease–amylase enzyme system for dehairing and fiber opening process. The antagonistic activity of protease against amylase was prevented by the buffering action of CuO NPs (Murugappan and Sreeram 2019). Recently, immobilization of proteases on the surface of zinc oxide nanoparticles for unhairing process has been reported. The robustness and the catalytic activity of the enzyme at 1% concentration were improved when compared with conventional sulfide method. These zinc nanoparticles prevented putrefaction of skins by its antimicrobial property and extended thermal stability. The pollution load was significantly reduced and comparable to enzymatic treatment in terms of COD, BOD and chromium content in spent liquor (Murugappan et al. 2020).

## Nanotannage

Tanning is an irreversible process that involves permanent alteration in the collagen structure by the introduction of cross-links for more durable leather (Nair BU 2005). Besides innumerous tanning methods, chrome tannage remains to be the most predominant method used across the globe (Eid and Al-Ashkara 2007) transforming 90% of skins and hides into leather. In recent years, the leather industry is in need of alternative sound eco-benign approach besides retaining the versatility of chrome tanning challenging the environmental impacts. Secondly, the considerable absorption of chemicals (60% of chromium) and release of hexavalent chromium in the effluent despite end up in environmental hazard. To cut pollution levels to considerable extent, there is a paradigm shift toward nanotechnological implications for cleaner production of leather. Nanomaterials are finding their way in leather industries to improve chromium uptake by reducing their use. Along these lines, an acrylic retanning emulsion was successfully synthesized from methyl methacrylate, n-butyl acrylate and methacrylic acid via microemulsion polymerization. These nanosized polymers measuring 100 nm were capable of penetrating the skins and thus filling the interfibrillar spaces. The increased surface area to volume ratio enabled proton transfer to form complex with either collagen or chromium conferring stability. This nanobased approach could increase the shrinkage temperature to 118 °C in wet blue goat skins (Mallikarjun et al. 2002). As with the excessive aggregation of the emulsifiers, there was an increased possibility of denaturation of the retanned leather. This was tackled by adopting semi-continuous microemulsion copolymerization subsequently reducing the size in the range of 16–64 nm. Upon treatment with 2% dosage, there were 68% and 44% improvements in tensile and tear strength, respectively, in retanned pig bottom splits (Wang et al. 2005).

Further, in situ polymerization of aldehyde–acid copolymer-mediated montmorillonite nanocomposite was fabricated and applied in leather tanning process. They exhibited excellent dispersion property along the collagen fibers. It was inferred that the carboxyl and aldehyde groups present in the nanocomposite bind to the amino groups of collagen side chains by electrovalent and covalent bonds, respectively. This combinatorial approach along with tanning agents (2% chrome) forms close knitted network in the interior of chrome complex eventually cross-linking with the collagen fibers conferring stability. There was a significant increase in shrinkage temperature of the tanned sheep skin up to 90 °C (Ma et al. 2003; Bao and Ma 2010). On the other hand, cross-linking between bi-/polynuclear chromium ions and carboxylate side chains of collagen fibers in chrome tanning is established by coordinate covalent bonds (Usha and Ramasami 2000; Rýglová et al. 2017a, b). A schematic representation of mechanism involved in chrome and nanocomposite-based tanning is shown in Fig. 5.

Similarly, vinyl polymer-based nanocomposite of mean size 10 nm was fabricated using $SiO_2$ nanoparticles and used as tanning agent. They act at the interface separating organic from inorganic phase with a suitable coupling agent onto $SiO_2$ nanoparticles. The pivotal role of these nanostructures was to fill the interfibrillar space facilitated by hydrogen bonds formed between surface hydroxyl groups and carboxylate/amino groups of collagen. Such interactions have conferred hydrothermal stability by way of intense cross-linking with the collagen fibers (Pan et al. 2005).

Moreover, in situ nanohybridization using tetraethoxysilane or tetrabutyl titanate precursor has been proposed for effective tanning. Initially, these precursor molecules are dispersed into a polymer or oil-based supporter for easy penetration into the skins/hides. Under specific triggering conditions (radiation, pH, heat etc.), the precursors subsequently undergo reduction resulting in the formation of inorganic particles such as $SiO_2$ and $TiO_2$ in situ. The criticality

in triggering decides the homogeneity and size reduction (~ 90 nm) enabling easier penetration into skins and hides. Such highly reactive nanoparticles generated exhibit high degree of specificity toward cross-linking of collagen fibers (Liu et al. 2010). It was presumed that hydrolyzed and condensed tetraethoxysilane reacts with pendant groups of arginine, histidine, tryptophane and hydroxyl groups of collagen forming –Si–C– bonds and hydrogen bonds (with C=O and N–H) conferring stability thereby increasing the shrinkage temperature up to 95 °C (Fan et al. 2005).

Gao et al. (2010) have investigated on diallyldimethyl ammonium chloride copolymer-mediated synthesis of $SiO_2$ nanoparticles for tanning operations. The usage of chromium was reduced to 2% when combined with polymer/nanocomposite for leather tanning. Spectroscopic studies revealed the intramolecular bonding between the free $–NH_3$ group of nano-$SiO_2$ and –COOH of polymer conferring stability. The leather tanned using polymer diallyldimethyl ammonium chloride-acrylamide-acrylic acid with nanosilicon dioxide containing hydrogen bonds (PDM-AM-AA/RNS-H) nanocomposite imparted high hydrothermal stability, tensile and tensile strength.

Li et al. (2011) have proposed a vinyl polymer mediated fabrication of ZnO nanocomposite for application in leather industry as a tanning agent. Free radical polymerization was employed to prepare polymer matrix and polymer–ZnO nanocomposite formulated using ultrasonic treatment. Upon combining polymer–nanocomposite conjugate with 2% tanning agent preferably chromate, a synergistic effect was evidenced attributing for improved tensile strength (11.90%), tearing strength (23.72%) and thermal stability. In 2014, the same group have investigated the chromium uptake efficacy in the tanning process of suede leather by combining polymer/ZnO nanocomposite with a commercial grade tanning agent, chromate B (33% basicity). Studies revealed significant chromium uptake during tanning and retanning process, thereby reducing the chromium content in the effluent with



**Fig. 5** Tanning mechanism involved in chrome tanning (**a**) and aldehyde-acid copolymer/montmorillonite nanocomposite (**b**) (Bao and Ma 2010)
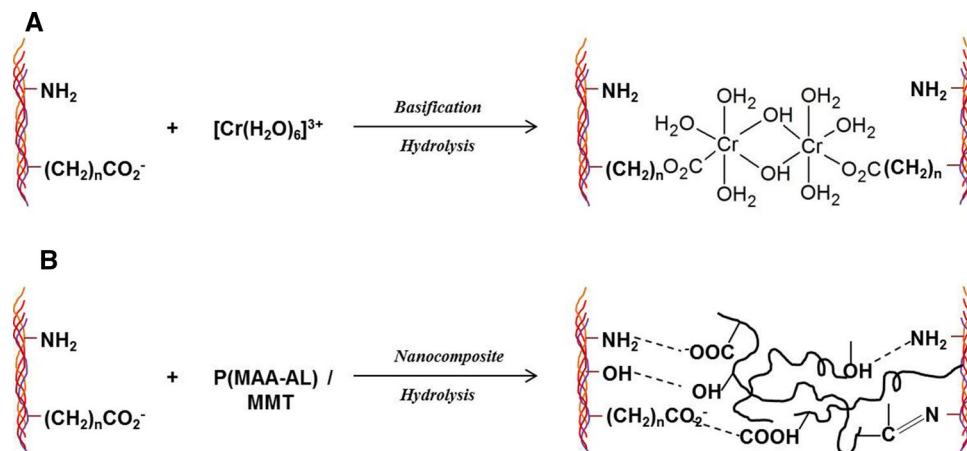
BOD: COD equaling to 0.37. Alongside, the leather thus processed showed high hydrothermal stability, biodegradability, softness and improved properties pertaining to cleaner approach (Ma et al. 2014).

Pan et al. (2017) have developed surface modified spherical silica nanoparticles using tetraethyl silicate via a simple method. The modifiers used were methacryloxy(propyl) trimethoxysilane, dimethyl diallyl ammonium chloride and poly(methacrylic acid) known for their hydrophobic, amphiphilic and hydrophilic properties. The tanning suitability of surface-modified $SiO_2$ nanoparticles showed enhanced tanning efficacy compared to pure polymer mediated process. It was inferred from the study that $SiO_2$ NPs with their small size could penetrate easily through the pores of the sheep skin facilitated by agitation in the rotating drum. Once into the skin, the NPs–polymer conjugate forms a complex with the tanning agent and establishing cross-links with the network structure of collagen fibers. This dense cross-link improved the thermal stability and increased the shrinkage temperature of the wet white sheep skin to 76 °C. This surface modification approach offered $SiO_2$ NPs with excellent dispersibility to intrude and fill effectively among collagen fibers, thereby improving the physical and mechanical properties of leather.

Furthermore, nanocomposites were used as pre-tanning agents to reduce the chromium release and increase its uptake in cowhide shoe upper leather. Lyu et al. (2018) have proposed an efficient chromium reduction approach via synthesis of polymer–ZnO nanocomposites. As a pretanning agent, there was a considerable reduction in chromium from 6 to 4%. In addition, the chromium content in the leather increased significantly from 13,489 to 15,030 mg kg$^{-1}$ subsequently reducing the concentration in the effluent attributing for efficient reuptake by these nanostructures. The shrinkage temperature ($T_s$) was greatly enhanced to 99.8 °C when 2% of polymer/nanocomposites were combined with 4% basic chromium sulfate (BCS) and slightly different from $T_s$ (99.9 °C) of the sample processed from conventional method by using 6% of BCS.

A step further, self-assembled chromium-loaded mineralized nanoparticles triggered by pH were developed for in situ delivery of chromium. The nanocomposites were stable at high salt concentration and pH > 3. The chromium is delivered effectively into pickled pelt without interfering with collagen bundles during penetration. Once into the pelt and upon lowering the pH to 2.5, chromium core $[Cr(OH)_3]$ disintegrates from the nanocomposite complex releasing $Cr^{3+}$ ions leading to uniform distribution. During basification process, the released $Cr^{3+}$ ions cross-links with the –COOH groups on collagen fibers and copolymers conferring higher thermal stability and durability (Li et al. 2019).

Laponite, synthetic smectite clay beyond having potential technological and biological applications in tissue engineering and drug delivery, has now been applied in leather industry as a tanning agent. A novel wet-white tanning agent was developed using tetrakis(hydroxymethyl)phosphonium sulfate (THPS) and laponite clay nanoparticles. This approach has relatively reduced the risk of formaldehyde, thereby improving the performance of leather. Notably, this system comprising THPS (2.5%–laponite (3%) at pH 4.5 conferred $T_s$ above 85 °C. More interestingly, these laponite nanoparticles were found equally dispersed and bound between the collagen fibers without altering the original conformation of collagen. This novel combination was reported to improve yellowing resistance, lightfastness and strength properties (Shi et al. 2019).

Recently, high-exhaustion chrome tanning and chrome-less tanning technology has been proposed. In brief, pH-driven chrome (III)-loaded nanoparticles were fabricated by self-assembly of poly(ethylene glycol) methyl ether acrylate-co-acrylic acid-co-glycidyl methacrylate (PEGMA-co-AA-co-GMA) polymers for utilization as chrome-less tanning agents. This core–shell strategy prevents $Cr^{3+}$ from reacting with the pelt during penetration but delivering $Cr^{3+}$ effectively in the interior of pelt. Upon basification, the released $Cr^{3+}$ establishes cross-linking with the collagen fibrils and the polymer via –COOH group resulting in high exhaustion chrome tanning effect. Moreover, this synergistic effect resulting from chrome and organic tanning reduced the use of chromium to considerable extent (Zhu et al. 2020).

## Nanofinishing

Application of nanotechnology in finished products helps to develop and improvise existing performance making intelligent leathers with unique characteristics and properties. Nanoparticles preferably silver, $TiO_2$, ZnO, $SiO_2$, etc., have been used to develop finishes to impart heat and chemical resistance and to block UV rays. The leather products with nanofinish help protect them from UV rays and increase the longevity of the product. The peculiarity of most of the nanoparticles is the antimicrobial effect which prevents the growth of bacteria and fungi coming in contact with leather. Alongside, the antibacterial effect of nanosilver hinders the spread of infection and prevents odor, itchiness and sores. Novel nanotechnological implications in the development of self-cleaning leathers have been fabricated using $TiO_2$ and $SiO_2$ exhibiting hydrophobicity (Li et al. 2019; Gurera and Bhushan 2018). Some of the nanofinished patented products for leather application are shown in Table 5.

**Table 5** Nanotechnology-based patents filed in leather applications

| Product | Specifications | Country | Patent ID/year |
|---|---|---|---|
| Leather nanosilver | A high concentration of colloidal silver (Ag) is uniformly deposited on the natural leather. Both the surface and the inner side of the fabric retain the antibacterial properties for long. Silicon dioxide nanocolloids of diameter 2 nm confer permanent protection such as scratch resistance, superhydrophobic effect, weather-, UV- and thermal-resistance (withstanding 750 °C) | South Korea | KR100750196B1/2006 |
| Leather nanopigment paste | Nanopigment paste comprises of nanoforms of $TiO_2$, $ZnO$ and $SiO_2$. This nanometer based paste shows antibacterial, mildewproof, UV-irradiation resistant, flame retardant performance which are used in coating leather for its longevity | China | CN101412869B/2008 |
| Polyacrylate/nanometer ZnO composite finishing agent | This finishing agent is suitable for base coating of clothing leathers, instep leathers and corrected leathers. The advantages include water tolerance, and increase in elongation at break, air permeability and water vapor permeability | China | CN102304316B/2011 |
| Nanoparticle-coated genuine leather | This genuine leather includes leather pigment and a nanopowder comprising a mixture of nanosilver and sub-nanometer $SiO_2$. This offers antibacterial activity and high degree of resistance to wear and tear and moisture | United States | US20130078451A1/2013 |
| Polyacrylate/nano-ZnO composite leather finishing agent | This method of preparation overcomes the deficiency of poor polymerization stability of polyacrylate/nano-ZnO composite emulsion prepared by in situ method. Tensile strength and water resistance are improved | China | CN103113804B/2013 |
| Antibacterial casein-based nano-ZnO composite leather finishing agent | Nano-ZnO is introduced into casein system for the preparation of leather finishing agent. This inorganic/casein leather finishing agent exhibit excellent antibacterial properties | China | CN104830231A/2015 |
| Graphene/aluminum oxide nanocomposite tanni0 agent | Graphene/aluminum oxide nanocomposite based tanning agent at 5% increases the shrinkage temperature to 112 °C with 95% absorption. Softness, elasticity, fullness are comparable to that of chrome tanned leather | China | CN104745736A/2015 |
| Leather product cleaning agent | A self-cleaning leather product comprising anatase-type nanotitanium dioxide, lemon juice, sodium silicate, acrylic resin etc. An effective antibacterial and a crack filling agent | China | CN106367233A/2017 |
| Semiconductor-oxides nanotubes-based composite for dye-removal | This innovative method involves an ion-exchange mechanism operating at dark condition and in aqueous solution. Nanotubes of semiconductor-oxides (hydrogen titanate, anatase $TiO_2$ and Ag- doped anatase $TiO_2$) are deposited on the surface of fly ash and metal oxide nanoparticles. This system removes the organic synthetic dye from the effluent via surface-adsorption | United States | US20180290135 A1/2018 |
| Poly-octavinyl polyhedral oligomeric silsesquioxane–acrylic acid nanocomposite auxiliary agent | Cocktail of octavinyl silsesquioxane, organic solvent, ammonium persulfate, distilled water and surfactant. Help easy penetration and fills the gaps in the collagen fibers. Best suited for improved filling and reduces the release of chromium content in water bodies | United States | US 20190284650 A1/2019 |

## Nanotechnology in effluent treatment

Leather industry despite generating revenue also generates huge amount of solid and liquid wastes causing adverse effects to the environment. It is estimated that around 60–70% of the pollution load is contributed by the effluent released during beamhouse operations. Environmental hazards start from the initial cleaning up of skins/hides through curing, soaking, tanning constituting the beamhouse operations till the addition of aesthetics during finishing of leather and leather products. A variety of chemicals used such as acids, alkalies, lime, sodium and ammonium salts, chromium, tannins, antifungals, fatliquors, dyes, auxiliaries during each process and their partial utilization and absorption in leather release considerable amount of unabsorbed chemicals as effluents. To avoid ecological disturbance and prevent human health hazard, effluent treatment remains a mandate. Conventional treatment strategies comprise physicochemical and biological processes (Doble and Kumar 2005). Notably, exhaust gases like mercaptans (2-mercaptobenzoxazole–MBO) unlike effluents require immediate removal from the environment through photocatalysis (Buazar et al. 2015). While this treatment system could effectively remove pollutants, suspended solids, chromium, etc. removal of total dissolved solids (TDS) having the potential of deteriorating pedological components and reducing crop yields needs alternate strategy to relieve environmental stresses (Chowdhury et al. 2015).

## Nanofiltration

A valid approach to recover the primary resources utilized in various industrial processes constitutes membrane process. Indeed, crossflow microfiltration, ultrafiltration, nanofiltration, reverse osmosis and supported liquid membranes were used for recovering chromium, reducing the pollution load in unhairing and for color removal from the effluents released from leather industry. As for the nanofiltration, the pore size of the semipermeable membrane is typically between 0.5 and several nanometers corresponding to a molecular weight cutoff of 200–1000 g/mol. The efficiency of filter is determined based on charge specificity, where monovalent ions will pass through retaining divalent and multivalent ions as shown in Fig. 4. Cassano et al. (2003) have proposed using nanofiltration process to recover tannins and non-tannins from the retentate solutions. With a mean permeate flux of 12.5 l/m$^2$h, the volume reduction factor was determined as 5.25 and the increase in tannin to non-tannin ratio were 1.1–2.3 achieving almost 75% reduction in COD of the effluent (Fig. 6).
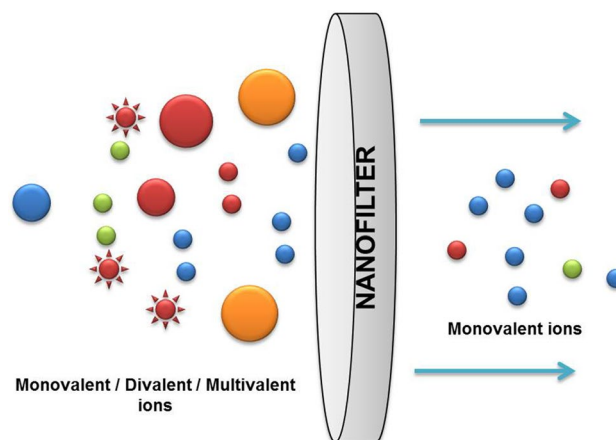


**Fig. 6** Typical nanofilter showing selective filtration of monovalent ions to pass through while retaining the divalent and multivalent ions (inspired from Abdel-Fatah 2018)

Nanofiltration combined with reverse osmosis (RO) has been applied in leather industries for the removal of total dissolved solids (TDS) from the tannery effluents. A spirally wound polyamide membrane with pore size of one hundred individual nanofiltration units and 2 nm in combination with reverse osmosis was devised. This combinatorial approach could effectively remove $Mg^{2+}$ (65%), $Ca^{2+}$ (55%), $SO_4^{2-}$ (98%) and $Na^+$ and $Cl^-$ by 94–98% from the tannery effluents. The overall performance of this system in removing the TDS accounted for 98% on a par with conventional membrane filtration systems (Suthantharajan et al. 2004). Similarly, Molinari et al. (2004) have investigated on the recyclability of tannin/non-tannin from vegetable tannage operations using different types of membranes from RO to nanofiltration. The permeate flux and retentate modules were compared considering flux reduction with time relative to osmotic pressure differences ($\Delta\pi$) and estimated by measuring electrical conductivity.

Ahmed et al. (2006) have proposed a nanofiltration process for application in tanneries using an organic membrane Nanomax50 (filtration area 0.37 m$^2$) with negative charge mechanically supported by a macroporous polyester and a microporous polysulfone for the removal of chromium and sulfides. An initial pretreatment was carried out during liming and tanning process using precipitation, coagulation and flocculation in order to prevent clogging of the membrane. Pretreatment was performed using $FeSO_4$–HCl–$Ca(OH)_2$ to reduce the complexity of liming and tanning baths and subjected to nanofiltration. Likewise, pretreatment followed by nanofiltration has been sequentially implied at each stage by adjusting the pH from basic to acidic, thereby refining the process of nanofiltration with a total ionic retention in the order of 40%.

The efficiency of nanofiltration relies on the membrane and feed characteristics in challenging the fouling phenomenon that was frequently encountered in membrane systems. A comparative antifouling study of three nanofiltration membranes, namely NF-270, NF-90 and BW30XLE, was investigated considering the crucial characteristics (hydrophobicity, surface charge and roughness) determining the filtration efficiency. Among them, NF-270 showed the lowest fouling owing to its hydrophilicity, negative charge and smooth surface when the organic compounds, NaCl, $Na_2SO_4$ and $CaCl_2$ were fed. Moreover, NF-90 and BW30XLE showed moderate antifouling characteristics attributing for its rough surface. It was also inferred from the investigation that colloidal fouling increased with increase in ionic strength and colloidal charge (Boussu et al. 2006).

An alternative method of re-using tannins from cork processed wastewater has been developed using nanofiltration. A spiral-wound NF200-2540 nanofilter comprising a polyadmide thin-film composite membrane with a cutoff of 200 Dalton and hydraulic permeability of $2.3 \times 10^{-11}$ m/s/Pa was employed. The rejection coefficients of the nanofilter showed 95% efficiency attributing for an improved tannin concentrate permeating the depleted stream of organic matter. A total yield of 34.8 g/L cork tannin concentrate was reported, and their use as tanning agent increased the hydrothermal stability of leathers (Geraldes et al. 2009).

Recently, an advanced oxidation-nanofiltration setup was developed for the effluent treatment in leather industry. Graphene-oxide nanocomposite was employed in the filtration unit to achieve maximum purification. Typical hydrophilic nature and high selectivity of the nanofiltration unit attributed for its high efficiency filtration of Cr (99.5%), COD (> 99%) and TDS (> 96%) retaining the quintessential $Ca^{2+}$ and $Mg^{2+}$ ions. A high permeability flux at around 200 L ($m^2$ h) at 16 lbs pressure for a long standing of 150 h characterizes it as a potential effluent treatment regimen (Pal et al. 2020).

## Nanoadsorption

Although tanning remains an important process in the leather manufacture, a grave concern over the release of chromium in the effluents poses serious environmental consequences and health hazards in human beings. Therefore, limiting its release or reabsorption/reuptake remains to be the viable option to reduce the trivalent chromium content in the effluent (Table 6). It was inferred from the various investigations that pH plays a pivotal role in adsorption of Cr(III) to the nanocomposite. The increased pH facilitated formation of chromium(III) oxo-hydroxide clusters via olation and oxalation. As a result of coordination in ligand, oxygen/hydroxyl bridge coordinates easy accessibility to chromium(III) center of the oxo-hydroxide clusters. With more phenoxide ligands and at increased pH, there is an increased absorption by nanocomposites (Guan et al. 2016). In this line, carbon nanotubes, more preferably multiwalled carbon nanotubes (MWCNTs), have shown excellent absorbing capabilities in combination with magnetite particles. The

**Table 6** Nanomaterials of various kinds used for effluent treatment

| Nanomaterials | Optimum adsorption parameters (Temp, pH) | Initial Cr concentration (μM) | Removal efficiency (%) | Final Cr Concentration (μM) | References |
|---|---|---|---|---|---|
| *Iron oxide-based nanomaterials* | | | | | |
| Maghemite (γ-$Fe_2O_3$) | 26 °C, 5 | 9.6 | 92.8 | 0.7 | Jiang et al. (2013) |
| GA@AMEO@$SiO_2$@$Fe_3O_4$ | 24.8 °C, 2.5–5.5 | 100 | 95.2 | 4.9 | Guan et al. (2016) |
| Magnetite ($Fe_3O_4$) | 25 °C | 192 | 99 | 1.9 | Ren et al. (2017) |
| Magnetite ($Fe_3O_4$) | 25 °C, 2 | 962 | 58.5 | 399 | Jain et al. (2018) |
| rGO-nZVI | 25 °C, 3 | 769 | 99 | 7.7 | Ren et al. (2018) |
| *Carbon based nanomaterials* | | | | | |
| MWCNTs | 25 °C, 6 | 1.9 | 98 | 0.04 | Pillay et al. (2009) |
| MWCNTs | 25 °C, 2.5 | 3.85 | 75 | 0.96 | Dehghani et al. (2015) |
| SWCNTs | 25 °C, 2.5 | 3.85 | 95 | 0.19 | Dehghani et al. (2015) |
| Magnetic-MWCNTs (MM) | 25 °C, 3 | 481 | 99.9 | 0.48 | Huang et al. (2015) |
| PPy/OMWCNTs | 25 °C, 2 | 6732 | 99.99 | 0.67 | Bhaumik et al. (2016) |
| *Graphene/graphene oxide-based nanomaterials* | | | | | |
| PPy-GO-NC | 25 °C, 2 | 3847 | 99.98 | 1 | Setshedi et al. (2015) |
| 8-HQ-GO-$Fe_3O_4$ | 34.85 °C, 6.55 | 19.2 | 95.8 | 0.8 | Sheikhmohammadi et al. (2017) |
| GO | 25 °C, 3 | 3847 | 66.2 | 1300 | Shaban et al. (2018) |
| GO-FH bionanocomposite | 25 °C, 2 | 1924 | 90 | 57.7 | Samuel et al. (2018) |
| CS-GO | 27 °C, 2 | 1924 | 90 | 192 | Samuel et al. (2019) |

activated carbon demonstrated an excellent absorption of Cr(III) relative to time, agitation speed and pH. Cr(III) once absorbed by these activated carbon meshes could easily be removed using magnetic field (Gupta et al. 2011).

## Conclusion

Leather although attractive and fascinating, the processes involved in the manufacture pose serious concern from the environmental perspective. It is high time to develop and propose alternative nanotechnological strategies to overcome challenges that the leather industry is currently facing. A detailed understanding on the conventional leather manufacturing process, their drawbacks and a challenging alternative technology has been highlighted in this review article. Application of nanotechnology (nanomaterials, nanocomposites, etc.) in general and not limited to the leather industry has paved way in either minimizing or totally replacing the obnoxious chemicals fed at different stages. A paradigm shift toward 'Green approach' moreover has limited the utilization of resources for sustainability and thereby reduces the adverse effects on the environment. Secondly, the internalization of nanomaterials takes over the role of chemicals and acts by themselves and/or in combination with the chemicals manifesting synergistic effect. Further, antimicrobial, hydrothermal, heat, chemical and UV-resistant properties have been imparted to the leather products, thereby increasing its functional characteristics. Notably, nanomaterials (SW/MWCNTs, magnetite nanoparticles) used in leather industry have shown promising results in the effluent treatment in particular the chromium reuptake or absorption by way of nanofiltration and nanoadsorption. The universal mantra for conservation of environment depends on 3R's, namely reduce, reuse and recycle. In order to achieve sustainability and environmental protection, extensive research studies on nanomaterial fabrication and application must aim 3R's mantra. Prior to industrial applications, there must be proper regulatory measures on the selection of appropriate method of synthesis of high-quality nanomaterials (either single or in combination) with desired properties, limited impurities and scalability. Further developing strategies in selecting appropriate nanomaterials having the capability to adsorb and dissociating specific reactants and handing over them to second metal nanocomposite system either to nullify the effect or exhibiting catalytic activity from poisoning the ecosystem. Yet another limitation that exists with nanomaterial fabrication is the high cost, a grand challenge that restricts their practical application of catalytic decomposition of chemical pollutants present in air and water.

There is no doubt that nanotechnology will be the most promising and intelligent cutting-edge technology in the near future possibly penetrating into almost all processes beyond the confines of what has been discussed in this review. This nanoconvergence would provide opportunities for an innovative and competitive products in turn leading the industries toward high-efficient, cost-effective and eco-friendly prospect. In an effort to make this nanotechnology compatible with leather manufacturing, huge investment is required which may lead to economic complexity. The above-mentioned challenging issues require the concentrated efforts of researchers from all domains of science and engineering, viz. material chemist, environmental chemist, microbiologist, biotechnologist and chemical engineers. Addressing the same would eventually pave way for nanomaterials-based catalysts toward their practical applications.

## Compliance with ethical standards

**Competing interest** The author(s) declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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