2021

Best Practices for Sustainable Leather Manufacturing

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Submitted to

IUE Commission

International Union of Leather Technologists and Chemists Societies (IULTCS)

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PREFACE

1. CONVENTIONAL LEATHER MANUFACTURING – AN OVERVIEW

Leather manufacturing is one of the earliest activities of mankind. Animal skins and hides had served as a major raw material for personal protection, carrier, weaponry etc. Today leather is one of the essential commodities and leather/leather product industry plays an important role in the World's economy. The trade value of Global leather sectors is approximately 160 billion US$ per year. Global leather and allied sector occupies predominant role in employment generation and also to improve the life style of economically weaker population. It is estimated that the global leather industry processes around 7-8 million tons of raw hides/skins for every annum. Generally, leather manufacturing is the process of converting meat industry by-product such as hides/skins into fashionable material. Leather manufacturing is broadly divided into four segments viz. a) Pre-tanning, b) Tanning, c) Post-tanning and d) Finishing. The journey of hides/skin in conventional leather manufacturing is shown in Figure 1.

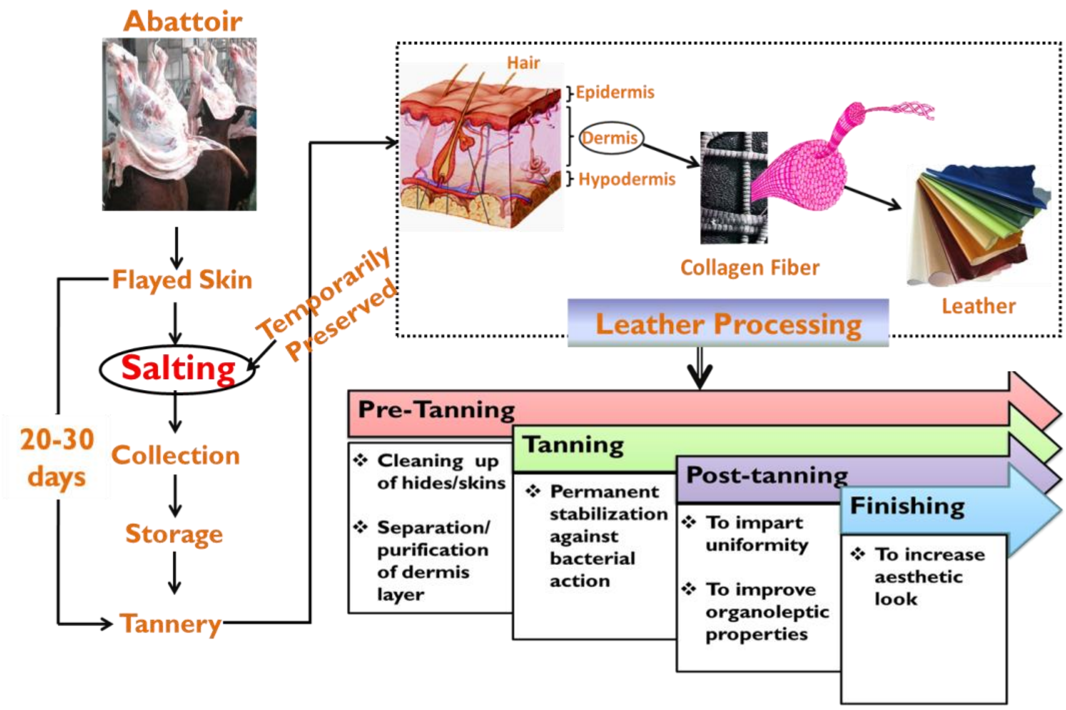


Figure 1 Journey of hides/skins in conventional practice

Collagen is the major fibrous component of hides/skins matrix, which is converted into leather. The other non-leather making materials such as hair, flesh, fat and other non-structural proteins are removed in pre-tanning process. Resistivity against bacterial and thermal degradation is greatly improved in tanning process where chromium(III) is widely used as a tanning agent. Today, 80-90% of World's leather production is based on chromium tanning process. Apart from chromium, various tanning systems based on vegetable tannins, Aldehydes, phosphonium salts, etc. are also in vogue.

In post-tanning, functional properties of the leather such as softness, colour and uniformity are fine-tuned with respect to the end-use. The surface feel and appearance of final leather are improved in finishing process. The material flow diagram of conventional leather manufacturing is shown in Figure 2.

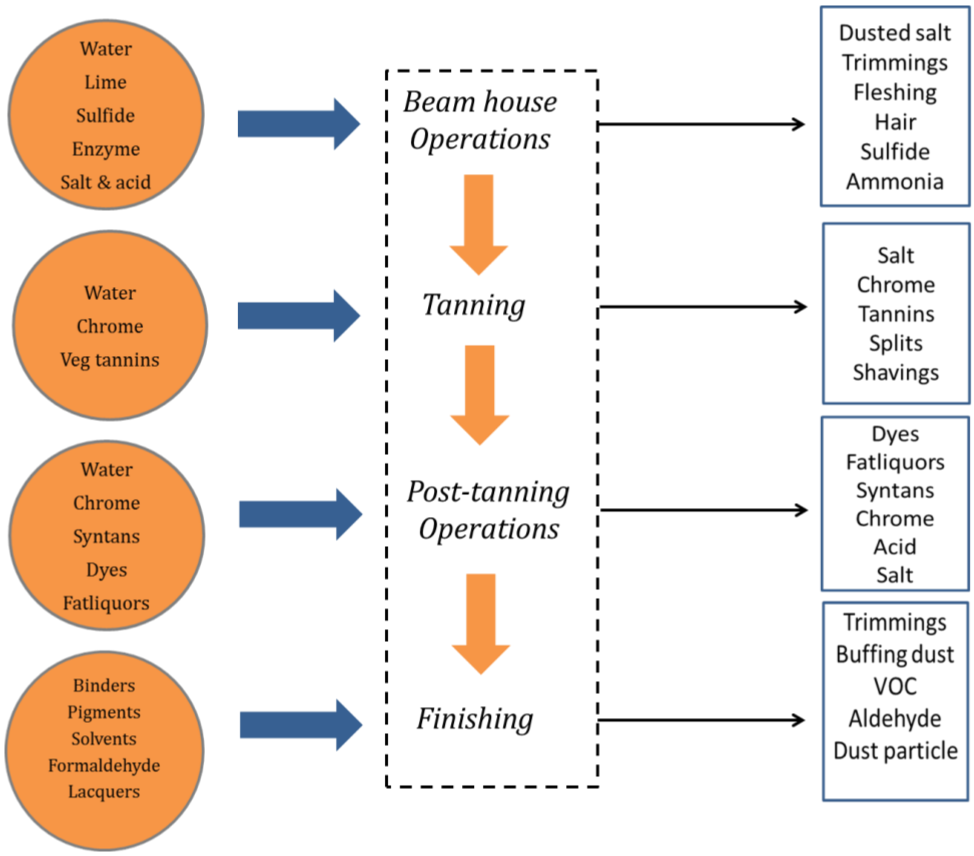


Figure 2 Material flow diagram of conventional leather manufacturing

1.1 Strategy of Conventional Leather Manufacturing

Conventional leather manufacturing is mainly based on do-undo process logic like, curing (dehydration) – soaking (rehydration), liming (swelling) – Deliming (deswelling), pickling (acidification) – depickling (basification), neutralization – fixing. Further, the hides/skins are subjected to wide variations in pH 2.8-12.5 (Figure 3). The change in pH demands the use of acids and alkali, which leads to the generation of large amount of neutral salts. This results in a net increase in total dissolved solids (TDS) comprising chlorides, sulfates and other minerals in tannery wastewater. In addition, toxic gases like hydrogen sulfide, ammonia are also evolved during the process.

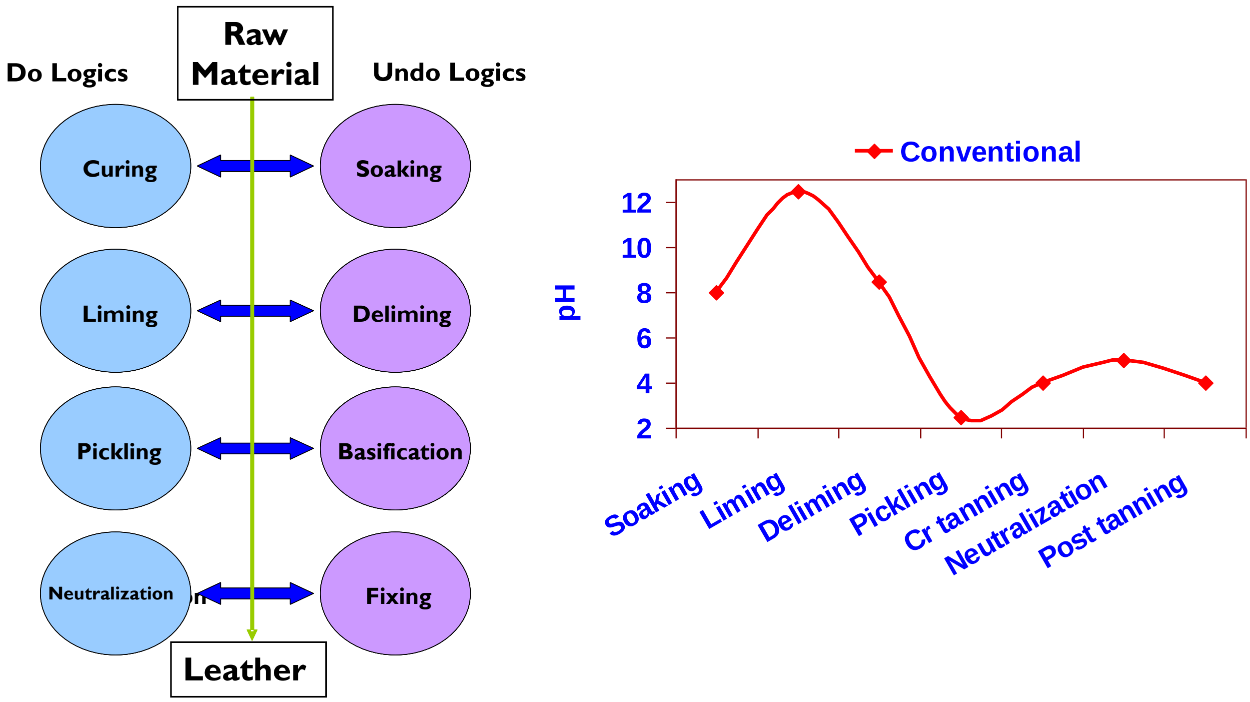


Figure 3 Strategy of conventional leather manufacturing

1.2 Major Concerns of Conventional Leather Manufacturing

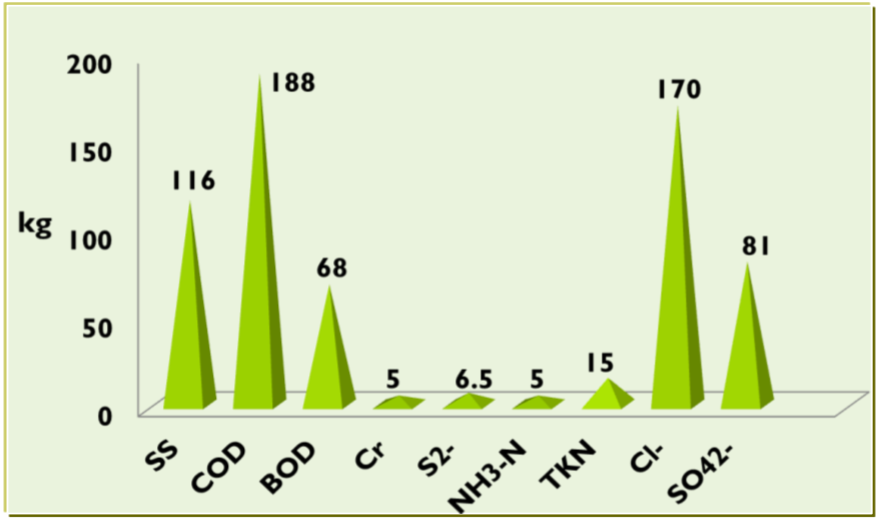
Though leather sector contributes to social development through significant amount of employment generation, it is also identified as one of the major polluting industries. The causative factors for pollution from the tanneries are a) emissions from hides/skins and b) discharge of residual chemicals in huge volume of wastewater. The waste generation from the conventional leather manufacturing can be categorized as follows:

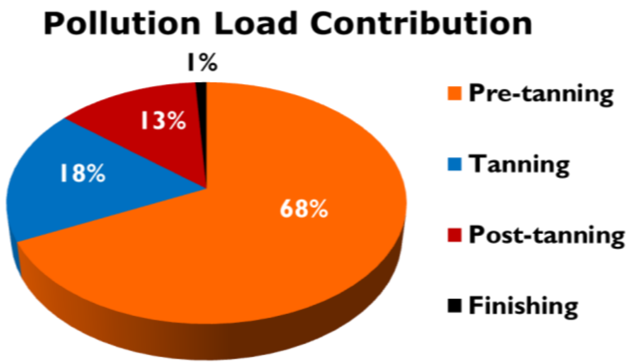
1. Liquid waste
2. Solid waste
3. Air emission

1.2.1 Liquid waste

Water is the largest input in leather manufacturing and its consumption is necessitated because all the unit operations in leather processing are water mediated. In addition, water is needed for cleaning, energy generation, wastewater treatment and sanitary purpose. Generally, to process 1 ton of raw hides/skins into leather about 30-50 cubic meter of water is used. The amount of water used for leather manufacturing is discharged as wastewater with high pollution load. The liquid waste emission scenario of conventional leather manufacturing is shown in Figure 4.

Pollution load kg/ton of raw hides/skins





Wastewater distribution profile

Process	Wastewater (m^3/t)
Pre-tanning	23-35
Tanning	3-5
Post-tanning	7-13
Finishing	1-3
Total	34-56

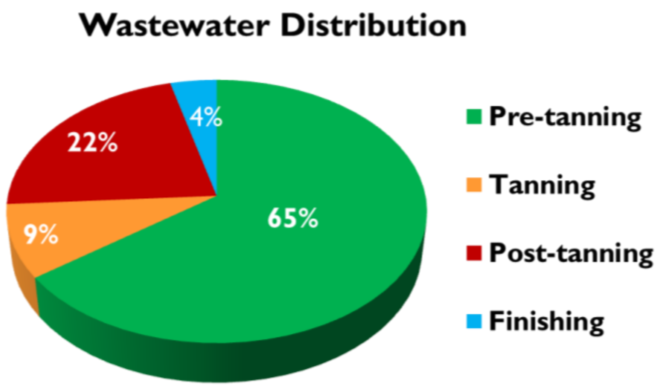


Figure 4 Conventional leather manufacturing: Current emission scenario (Source: UNIDO, 2015)

1.2.2 Solid waste

Statistical data from FAO (Food and Agriculture Organization) revel that globally, 5.84 million tons of solid waste is generated by processing 7.3 million tons of rawhide/skin. The intrinsic nature of the hide/skin, leather processing steps, wastewater treatment and the nature of chemicals employed are responsible for the generation of solid wastes. The nature and quantum of solid wastes generated during the processing of 1 ton of raw material are given in Table 1.

Table 1 Solid waste generation from leather manufacturing

Solid waste	Quantity (kg/ton of raw material)
Fleshings	300
Trimmings	100
Unusable chrome splits	107
Chrome shavings	99
Chrome off-cuts	20
Crust leather waste	5
Buffing dust	1
Finished leather trimmings	5
Total	637

(Source: UNIDO. 2019)

1.2.3 Air emission

Odour emanates from leather processing owing to various reasons such as decomposition of incorrectly cured or stored hides/skins, accumulated wastes, beam-house processes and wastewater treatment plants that are poorly controlled and maintained. Odour is not necessarily harmful or toxic, but constitutes a nuisance to affected neighbours, which in turn gives rise to complaints. Apart from a natural, distinct smell of raw hides, bacteria degrading the organic matter can cause pungent ammoniacal odour.

Volatile Organic Constituents (VOC): Organic solvents are used in leather predominantly during finishing of leather and sometimes during degreasing of the leathers. During both the above processes, owing to the low boiling point of the solvents used, it tends to evaporate at ambient room temperature and would result in distinct odour. emitted from finishing and degreasing processes of leather manufacturing.

Ammonia is liberated from improperly cured hides or skins and also from liming process. However, significant quantity of ammonia, both in the form of gaseous emission and in liquid form gets emanated from deliming process, owing to the use of ammonium based salts for deliming process.

Hydrogen sulfide gas gets emanated when the used lime liquor containing sodium sulphide come in contact with the acidic environment.

Dusts and Other Particulates: Airborne particulate matter can arise during mechanical operations such as milling, buffing and staking. The dust may also be emanated due to improper handling of powdery process chemicals

2. TECHNOLOGICAL SOLUTIONS FOR CONVENTIONAL LEATHER MANUFACTURING

PROCESS	TECHNOLOGY NEED	AVAILABLE TECHNOLOGIES
Preservation	▪ To avoid storage of contaminated salt ▪ To reduce the TDS/salinity	✓ Chilling ✓ Crushed ice + Preservative/Dry ice ✓ Salt + Alkali ✓ Silica gel/polyol as an alternative dehydrant ✓ Organic formulation as preservation-cum-unhairing (PCU) agent ✓ Application of various plant extracts
Soaking	▪ To reduce TDS load in soak liquor ▪ To avoid nonylphenol ethoxylate based wetting agent ▪ Reduction in wastewater volume	✓ Mechanical desalting ✓ Use of liner alcohol ethoxylates based wetting agent ✓ Counter current soaking ✓ RO/EO treatment and reuse in pickling
Unhairing/Fiber opening	▪ To eliminate/reduce lime & sulfide ▪ Avoidance of dissolved hair in wastewater and its volume ▪ To prevent H_2S gas liberation	✓ Enzymatic products ✓ Reuse of lime liquor ✓ Amine/oxidative unhairing agent ✓ Hair save unhairing/Online hair filtration

Deliming/Bating	▪ To prevent NH_3 liberation ▪ To reduce TKN in wastewater ▪ Reduction in wastewater volume	✓ Ammonia free deliming agent (weak organic acid) ✓ Gaseous CO_2 /Dry ice deliming ✓ Ester based deliming agents ✓ Ammoina free bating enzyme
Degreasing	▪ Avoidance of halogenated organic compound	✓ Use of linear alkyl polyglycol ether based degreasing agent
Pickling/Chrome tanning	▪ To reduce TDS/Cr load in spent liquor ▪ Reduction in wastewater volume ▪ Reduction in chromium containing leather solid waste	✓ Low salt/salt free pickling (Non-swelling acids) ✓ High exhaust chrome tanning ✓ Chrome liquor recycling ✓ Chrome recovery and reuse ✓ Zero water chrome tanning technologies ✓ Inverse chrome tanning
Retanning	▪ To improve the bio-degradability of retan liquor ▪ To reduce TDS load ▪ To avoid restricted substances	✓ Formaldehyde free re-tanning agent ✓ Use of low salt re-tanning agents ✓ Use of biomass-derived re-tanning agent ✓ Use of multifunctional re-tanning agents
Dyeing	▪ To dye exhaustion/ improve the biodegradability of wastewater	✓ Use of vegetable tannin based mordant dyes ✓ Natural dyes

Fatliquoring	▪ Avoidance of halogenated organic compound in water, soil and oil repellent fatliquours ▪ To avoid Cr(VI) formation	✓ Use of poly siloxanes based fatliquor ✓ Use of polymer based methacrylates or silicone oil or modified silicone oil based fatliquors ✓ Use of surfmers based fatliquor
Finishing	▪ To improve the coating efficiency ▪ To avoid/reduce VOC	✓ Control airborne particles/dust ✓ Use of water based finishing systems ✓ Avoidance of harmful crosslinkers ✓ Coating by advanced spraying equipment (airless, HVLP guns, scrubbers); curtain and roller coater
Solid waste	▪ Innovative approach in utilization and safe disposal	✓ High grade gelatin ✓ Compost preparation ✓ Activated carbon preparation ✓ Leather board preparation ✓ Leather auxiliaries preparation ✓ Fabric from leather waste
End-of-pipe treatment	▪ End-of-pipe treatment	✓ Electrochemical/Wet-air oxidation

3. CONCEPT OF BEST AVAILABLE TECHNOLOGIES (BATs)

Importance of BAT:

The concept of "Best Available technology (BAT)" can support industries, decision-makers, and regulators in addressing environmental and economic concerns in industries with regard to the application of abatement strategies.

Definition of BAT:

According to the Integrated Pollution Prevention and Control (IPPC) directive, BATs are defined as "*the most effective and advanced stage in the development of activities and their methods of operation, which indicates the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and where that is not practicable, to reduce emissions and the impact on the environment as whole.*

- ***"Best"*** means most effective in achieving a high level of production of the environment as a whole
- ***"Available"*** technologies mean those developments on a scale, which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages.
- ***"Technologies"*** includes both the usage and the way in which the installation is designed, built, maintained, operated and decommissioned.

Factors to be considered for any BAT:

- Technological advances and changes in scientific knowledge and understanding
- The economic feasibility of such techniques
- Time limits for installation in both new and existing plants
- The nature and volume of the discharge and emissions concerned

3.1 Best Available Technologies (BATs) for Leather Manufacturing Sector: Global Scenario

Consumer awareness and statutory stipulation norms on waste discharged from leather industry call for environmentally sustainable leather manufacturing. In addition, water is the major input of conventional leather manufacturing and today it is a scarce resource. It is projected that by 2025 about 1800 million people are expected to be living in countries or regions with absolute water scarcity (<500 m^3 per year capita). Two-thirds of the World's population could be living under water-stressed conditions (between 500 -1000 m^3 per year per capita). Therefore, water consumption is one of main criteria to be considered for BAT. The criteria to be considered for the selection of BAT for leather manufacturing are shown in Figure 5.

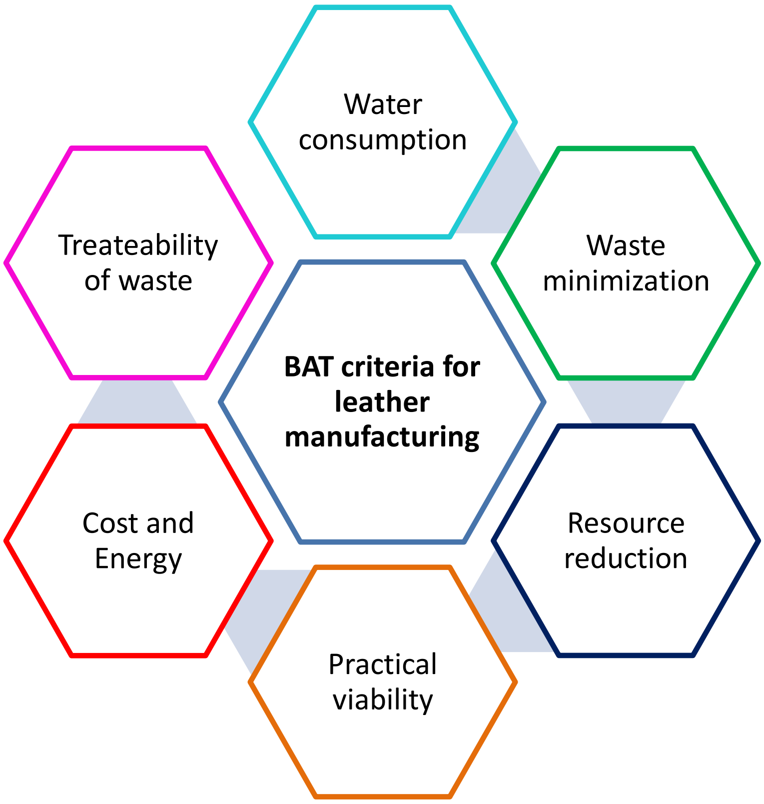


Figure 5 Criteria for selection of BAT in leather manufacturing

The currently available technologies are analysed through BAT selection criteria. Based on this, some of the technologies are selected as BAT and their sequence in leather manufacturing is shown in Figure 6.

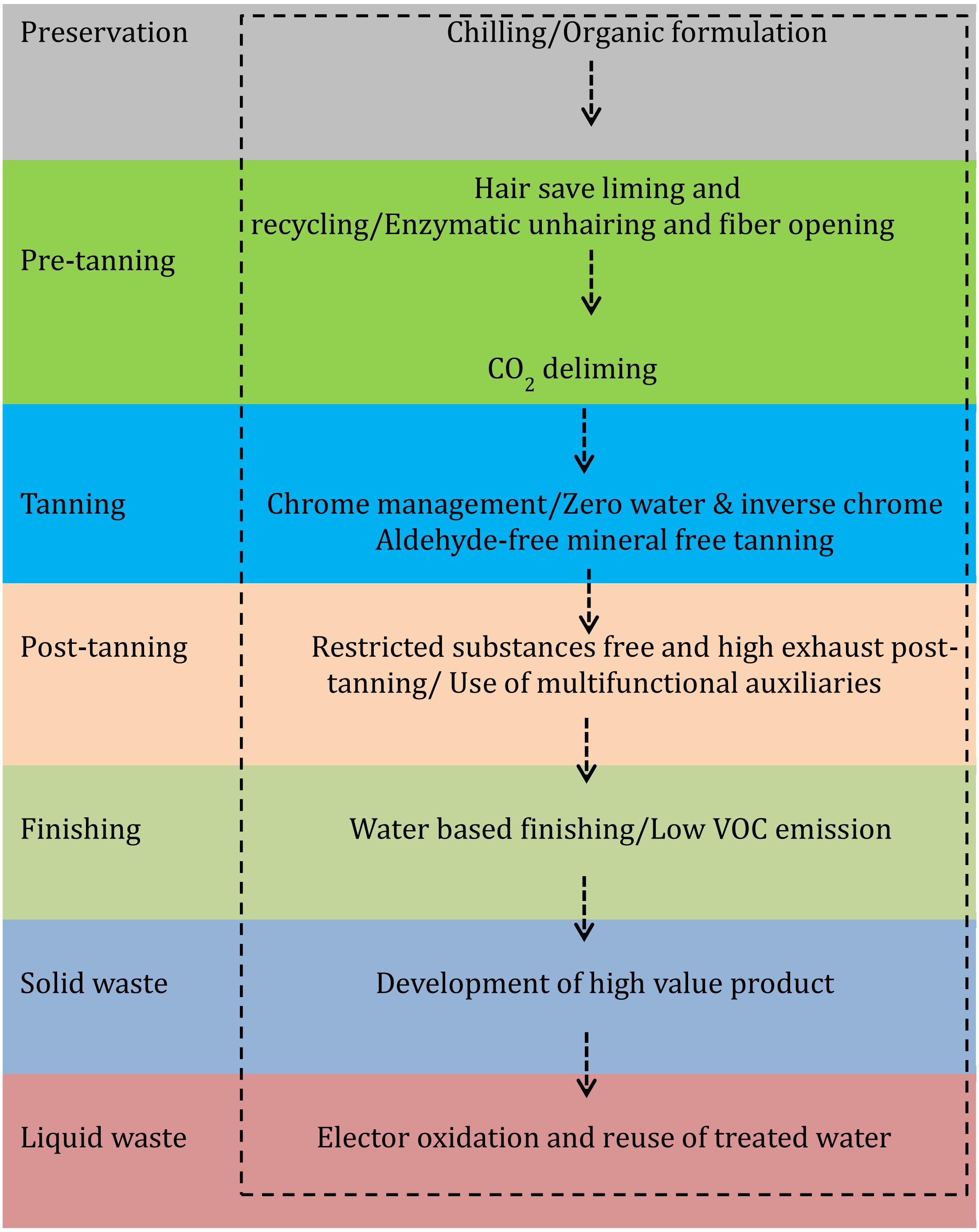


Figure 6 BATs for cleaner leather manufacturing

3.2 Preservation

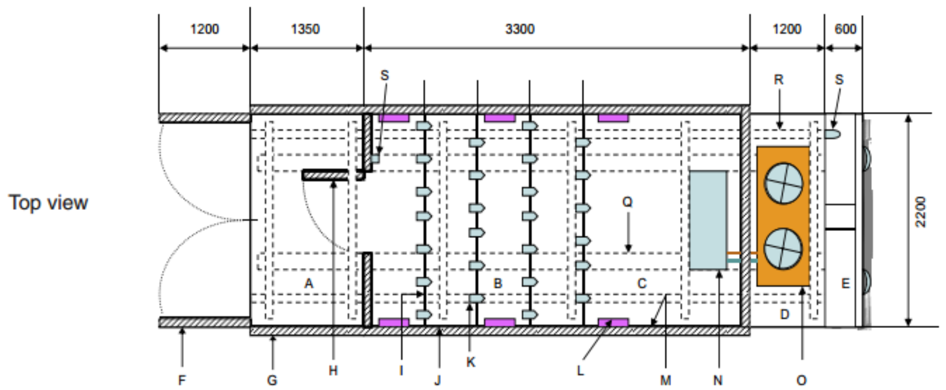
Challenge: Avoidance of salt and reduction of TDS

BAT: Chilling
Use of Organic Formulation

Technical description:

3.2.1 Chilling

Chilling the hides/skins is a short term preservation method and it's based on reducing the hides/skins temperature to 10-15 ^{o}C. The temperature to which hides/skins to be chilled is depend on the required duration of preservation. If the refrigeration temperature is reduced to 2 ^{o}C hides/skins can be stored for three weeks without any damage. Chilling technology was successfully implemented in Australia. In India CSIR-CLRI developed a mobile chilling model for effective preservation (Figure 7).



A – Air lock; B – Chilling area; C – Storage area; D – Gen Set / Power pack; E – Driver cabin; F – Airlock doors; G – CRCA sheet; H – Blast chiller door; I – SS rod for SS hooks; J – PUF insulation; K – SS hooks; L – Air agitator; J, N, M – S S 306 sheet; N – Cooling coil; O – Condensing unit; P – Refrigerant piping; Q. Chassis; R – M.S. channel frame work; S – Safety alarm.

Figure 7 Design features of mobile chiller *(*Source: Chandrababu et al., 2012)

Benefits:

- Complete elimination of salt from soak liquor
- Time and water reduction
- Lower stock holding and lower working capital needed

3.2.2 Use of organic formulation as preservation-cum-unhairing (PCU) agent

Recently, Sathish et al developed an organic formulation which is capable of preserving the hides/skins at ambient conditions without dehydration and subsequently hair gets loosened during the transport /storage period. Low level of sulphide was used during alkaline fiber opening for removal of traces of hair. The strength and organoleptic properties are on par with salted skins/hides. The developed process completely eliminates the use of salt and 75% sulphide and also reduces the time and water required for soaking process. The developed system reduces 85% of pollution load discharged from soaking and unhairing processes.

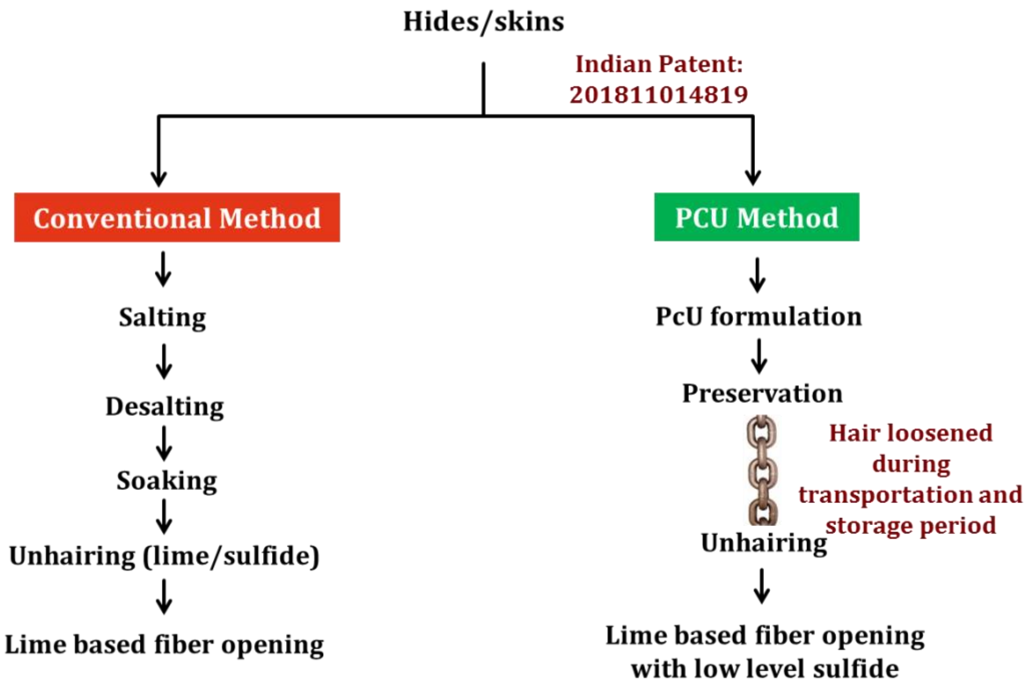


Figure 8 Process flow diagram of conventional and PCU process

Benefits:

- Complete elimination of salt from soak liquor
- Reduction in sulfide usage
- Considerable amount of water/time reduction

3.3 Pre-tanning

3.3.1 Unhairing and fiber opening

Challenge: Avoidance of dissolved hair in wastewater
Reduction lime/sulfide

BAT: Hair save techniques
Recycling of spent lime/sulfide liquor
Enzymatic unhairing and fiber opening

Technical description:

Though several unhairing agents were developed for hair depilation, combination of lime and sulfide based agents find a prominence place in leather manufacturing, because of its versatility. It is well suitable for all kind of hides/skins. However, in this method hair gets digested and discharged with spent unhairing liquor, which increases the BOD/COD. Apart from that, presence of dissolved hair in spent liquor limits the reuse of liming liquor for subsequent batches. If the pH of sulfide containing spent liquor is allowed to fall acidic condition in wastewater treatment, hydrogen sulfide gas will evolve.

Hair filtration equipment is available, for recirculating the float and separating the hair from the spent liquor, before it is sent out for treatment plant. Hair separation is preferably carried out at the same time as hair loosening, so as to minimize the degradation of hair. After hair separation, the spent liquor is used again for fiber splitting. The process can be continued up to 20 cycles without affecting the quality of leather. Recycling system also helps to reduce the high level of water consumption in unhairing/fiber splitting process. Block diagram of hair filtration system is shown in Figure 9. The emission reductions achieved using hair filtration system is shown in Table 2.

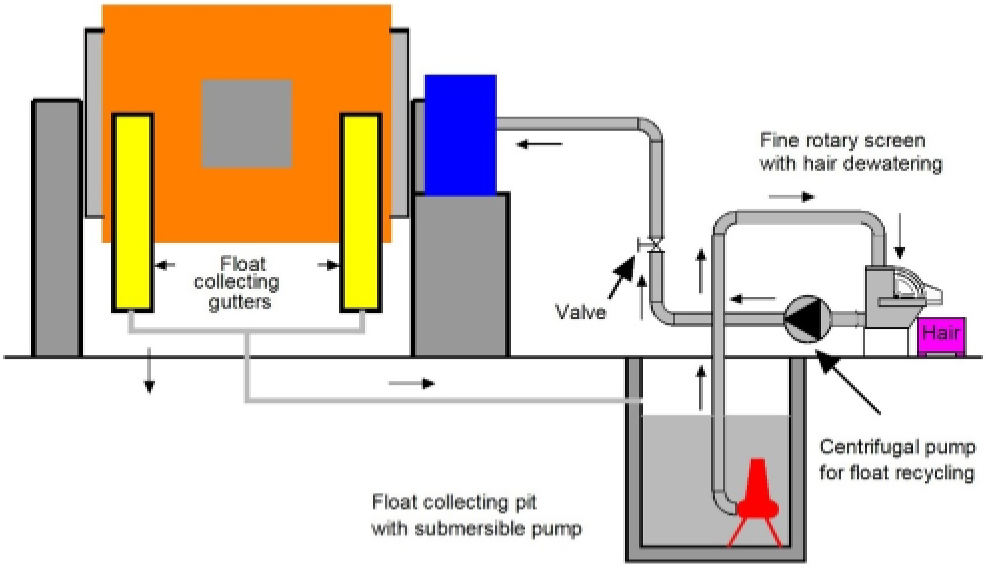


Figure 9 Block diagram of hair filtration system (Source: UNIDO, 2015)

Table 2 Reduction of emissions from hair-save unhairing compared to hair-destroying techniques

Discharge from hair-save unhairing		% reduction compared to hair destroying unhairing	
Emission Parameter	kg/ton of raw hides	In unhairing liquor	In total tannery wastewater
Total solids	60	30	8
Suspended solids	15	70	43
BOD_5	20	50	28
COD	50	50	28
TKN	2.5	55	22
Ammonical nitrogen	0.2	25	2
Sulfide (S^{2-})	0.9	55	55
Source: UNIDO, 2015			

Benefits:

- Reduction in BOD and COD
- Lower suspended solids
- Reduction in sulfide and lime input

Enzymatic unhairing and fiber opening

Protease and amylase based enzymes are used for unhairing and fiber opening respectively. Therefore, usage of lime and sulfide can be completely avoided.

Benefits:

- Complete elimination of lime
- Reduction in water consumption
- Time reduction
- Flesh is free from lime and it can be used for high value application

3.3.2 Deliming

Challenge: Avoidance of ammonia gas generation
Reduction of ammonical nitrogen

BAT: CO_2 deliming

Technical description:

CO_2 deliming is an environment friendly process, which could replace the ammonium salts from leather manufacturing. In carbon dioxide deliming, CO_2 gas is passed into a well-equipped vessel or drum containing water to produce carbonic acid, which has the ability to neutralize the alkali present in the hides/skins matrix. Solid carbon dioxide (dry ice) can also be used for deliming application, which avoids the risk of pressure valves failure.

Emission load of conventional ammonium based deliming and CO_2 deliming process are shown in Table 3.

Table 3 Emissions from conventional ammonium and CO_2 deliming process

Emissions kg/ton of raw hide	Conventional Ammonium deliming	CO_2 deliming
BOD	3	3
COD	6	6
TS	45	30
TKN	5	1.5
NH_4-N	4.1	0.1-0.2

(Source: Sathish M et al., 2013)

Benefits:

- No ammonia gas generation
- Reduction in nitrogen content of wastewater
- Significant reduction in total solids

3.4 Chrome Tanning

Challenge: Reduction of TDS and chromium from spent chrome liquor
Avoidance of chromium containing solid waste generation

BAT: Chrome liquor recycling
Chrome recovery/reuse
Zero water chrome tanning technologies
Invers chrome tanning technology

Technical description:

3.4.1 Chrome liquor recycling

Tanning is an important process of leather manufacturing which permanently stabilize the hides/skins matrix against putrefaction. Today, 80-90% of World's leather production is based on chromium tanning. But, the uptake of chromium in conventional tanning process is about 50-60% and the remaining is discharged into wastewater streams. The uptake of chromium can be increased by modifying the tanning agent and increasing the reactivity of hides/skins matrix. Generally, dicarboxylic acids/etholamine is used to modify the chromium tanning agent. The uptake of chromium in high-exhaustion tanning is about 80-85% and then the spent tannin liquor can be recycled for subsequent batches of tanning. The process flow diagram of chrome liquor recycle for chrome tanning is shown in Figure 10.

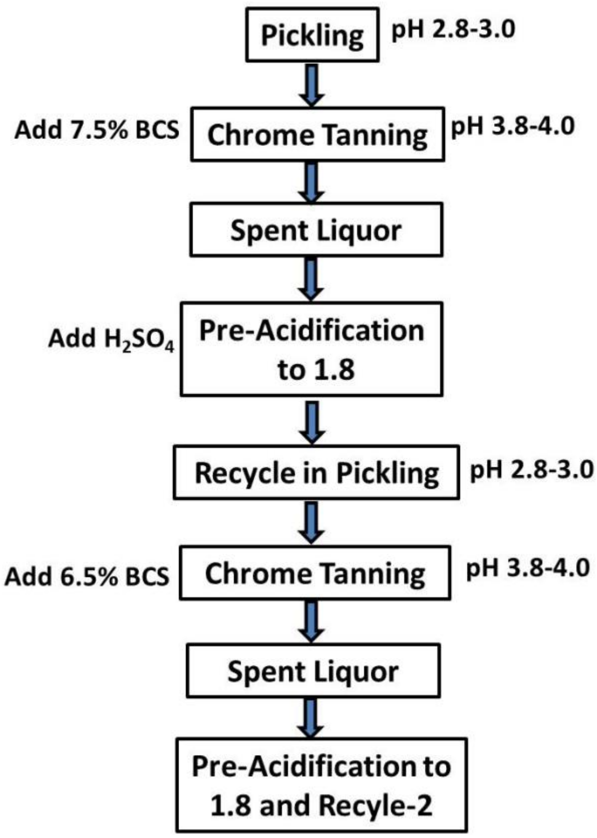


Figure 10 Cr liquor recycling

Benefits:

- Significant reduction in salt input
- Reduction in discharge of chromium containing wastewater
- Reduction in water consumption
- Simplest form of reuse
- Low capital cost
- No additional chemicals needed
- Suitable for all kind of raw material
- Suitable for new and existing tannery
- Leather quality is not affected

3.4.2 Chrome recovery and reuse

It is a commercially proven technology and around 98% of chromium can be recovered by using this technology. This technology has been widely accepted by many global tanners.

Process chemistry of Cr recovery:

The process involves two steps namely precipitation and acidification.

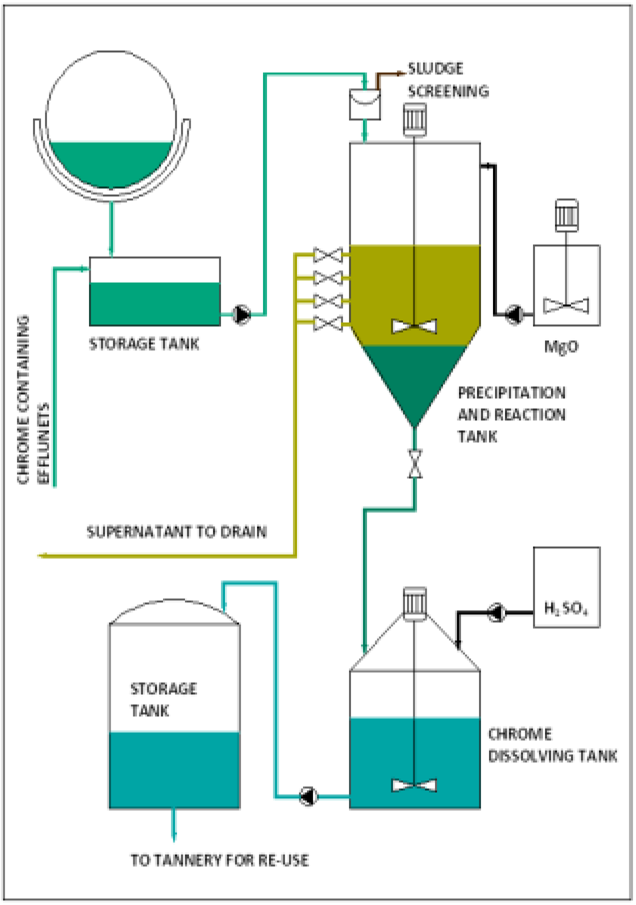
(i) ***Precipitation:*** The spent chrome liquor is precipitated using MgO as an alkali by raising the pH to 8.0-8.5.

$$Cr(OH)SO_4 + MgO + H_2O \text{ ---------> } Cr(OH)_3 \downarrow + MgSO_4$$

(ii) ***Acidification:*** The chromium hydroxide precipitate is acidified using sulphuric acid to the pH of 2.5-2.8 to produce basic chromium sulphate which can be used for tanning.

$$Cr(OH)_3 + H_2SO_4 \text{ ---------> } Cr(OH)SO_4 + H_2O$$

The process flow diagram of chrome recovery system is shown in Figure 11. After the precipitation process the supernatant can be used for pickling of subsequent tanning process.



(Source: UNIDO, 2015)

Figure 11 Process flow diagram of chromium recovery

Salient features:

- ✓ Simple and easy to adopt
- ✓ Ensure complete recovery of Chromium
- ✓ Commercial acceptance established
- ✓ Suitable for small, medium and large scale units
- ✓ Economically viable

3.4.3 *Zero water chrome tanning technologies*

Now-a-days pickle/basification free zero water chrome tanning technologies based on process/product are emerging. In the case of process technology, the delimed pelts are subjected to pre-treatment without using any speciality chemicals and subsequently treated with BCS (% offer is reduced than conventional process). During chrome tanning, no process water is added and inherent water presents in pre-treated pelts is effectively utilised for chrome tanning. CSIR-Central Leather Research Institute developed a Waterless Chrome Tanning Technology (WCTT) and the technology was implemented in several tanneries in India. On the other hand, several chemicals houses including CSIR-Central Leather Research Institute developed a speciality product for zero water chrome tanning process. In this technology the delimed pelts are treated with developed product followed by BCS without water.

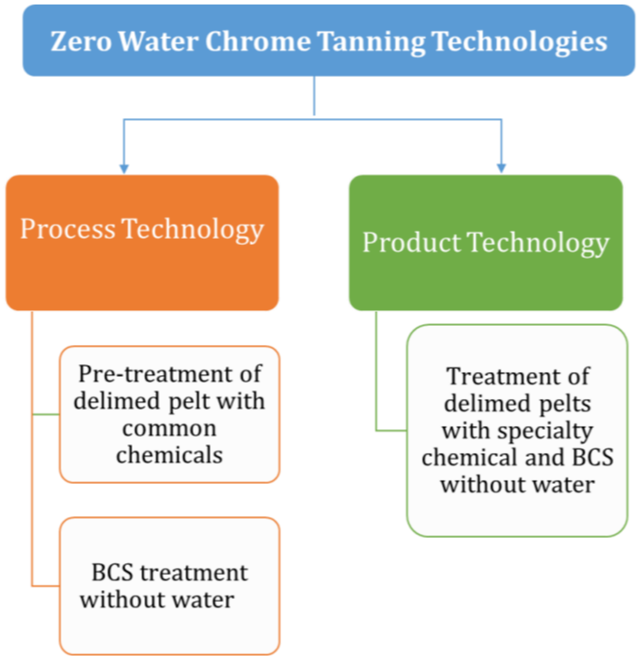


Figure 12 Process flow diagram of zero water chrome tanning

Salient features:

- ✓ No discharge of wastewater from chrome tanning
- ✓ Total elimination of pickling and basification
- ✓ Reduction in BCS offer and high chrome content in leather
- ✓ Simple process and does not demand additional infrastructure or new chemical
- ✓ Suitable for both hides and skins

3.4.4 Inverse chrome tanning

None of the metals present in periodic table stabilize the collagen matrix and improve its thermal stability as like chromium(III). In conventional approach (Figure13a), mechanical, enzymatic and thermal stability of the leather is improved together by using chromium. Therefore, the generation of chromium containing solid waste is inevitable during the subsequent mechanical operations. In the case of inversion tanning method (Figure 13b), the organic pre-tanning is adopted which predominantly targets the improvement of mechanical and enzymatic stability. Further, the leathers are subjected to mechanical operations and the generated solid waste is completely free from chromium which may be utilised for high value product preparation. Subsequently, the thermal stability of the leather may be improved in post-tanning process by using chromium.

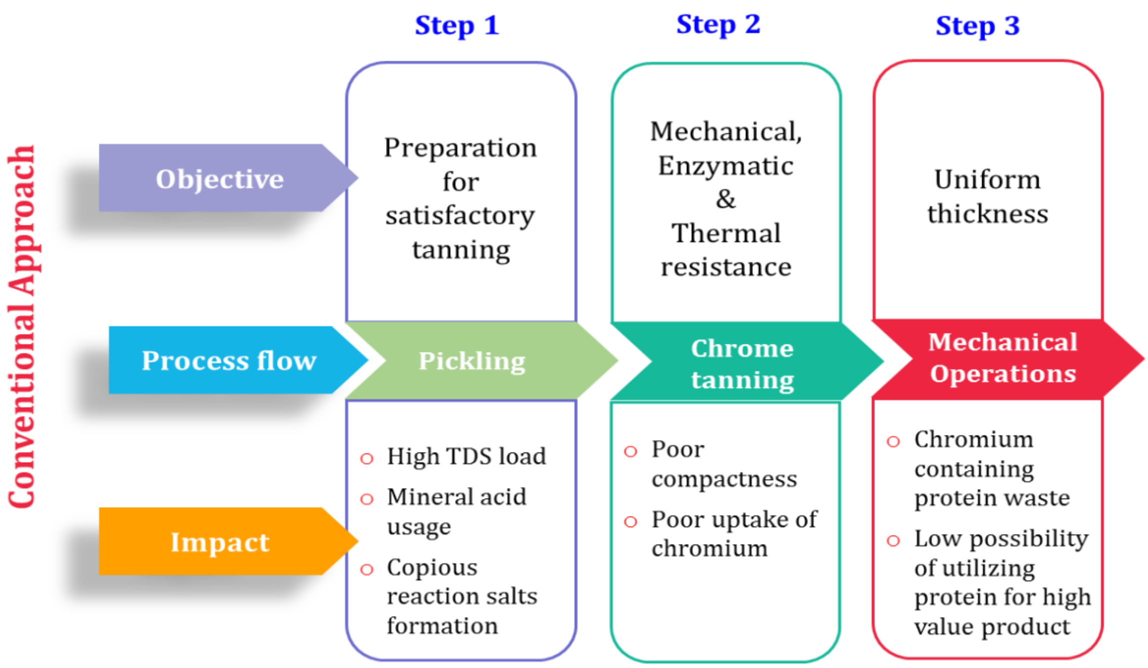


Figure 13a Process flow diagram of conventional chrome tanning

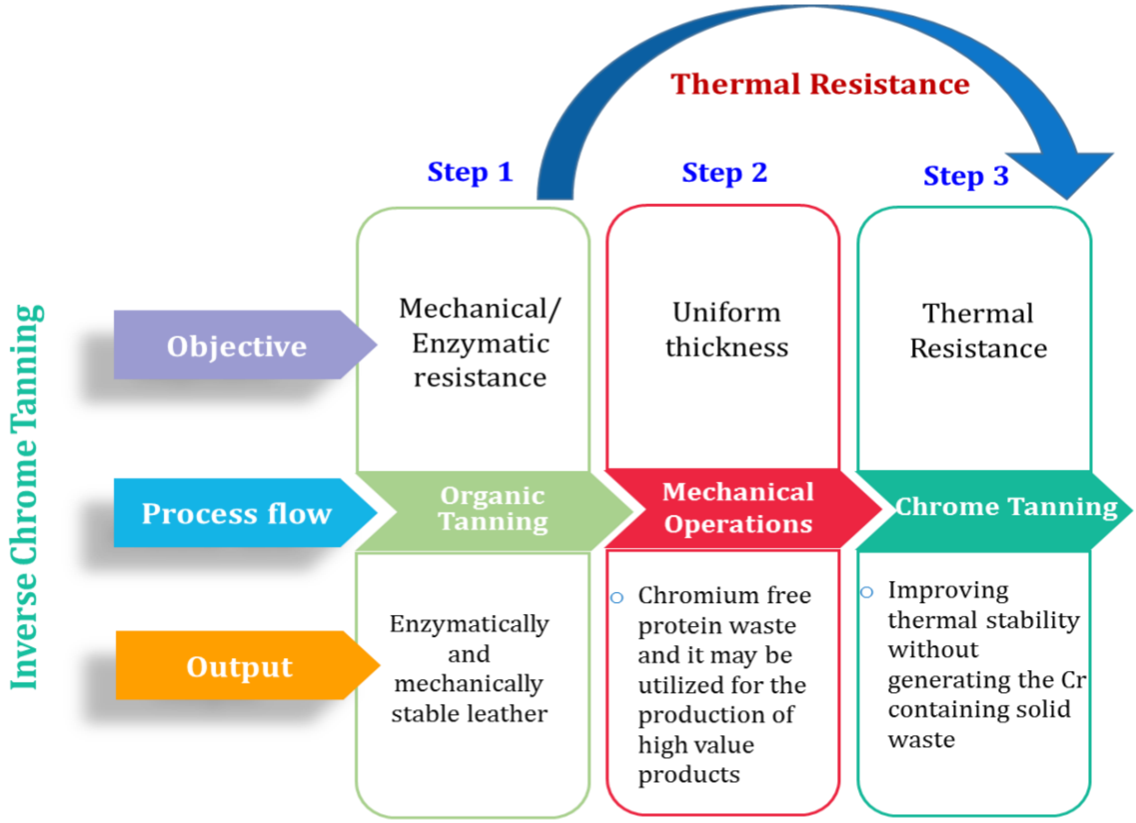


Figure 13b Process flow diagram of inverse chrome tanning

Salient features:

- ✓ Tanned solid waste is free from chrome and it may be used for high value application
- ✓ Reduction in chromium input
- ✓ Thermal stability of the final leather is on-par conventional chrome tanned leather

3.5 Metal-Free Tanning

Challenge: Aldehyde free tanning agent

BAT: Diazine based tanning agent
Sulfone based tanning agent
Wet-green Tanning

Technical description:

Recently, aldehyde-free tanning agents are derived from the knowledge of reactive dye chemistry. Generally, reactive dye is containing two units such as chromogen and anchoring group. The chromogen unit provide desirable hue value and subsequently anchoring group covalently attached with the fibrous matrix. Predominantly, cyanuric chloride and sulfone ester is used as an anchoring unit in reactive dye preparation. The process and mechanism of diazine and sulfone based tanning system is shown below.

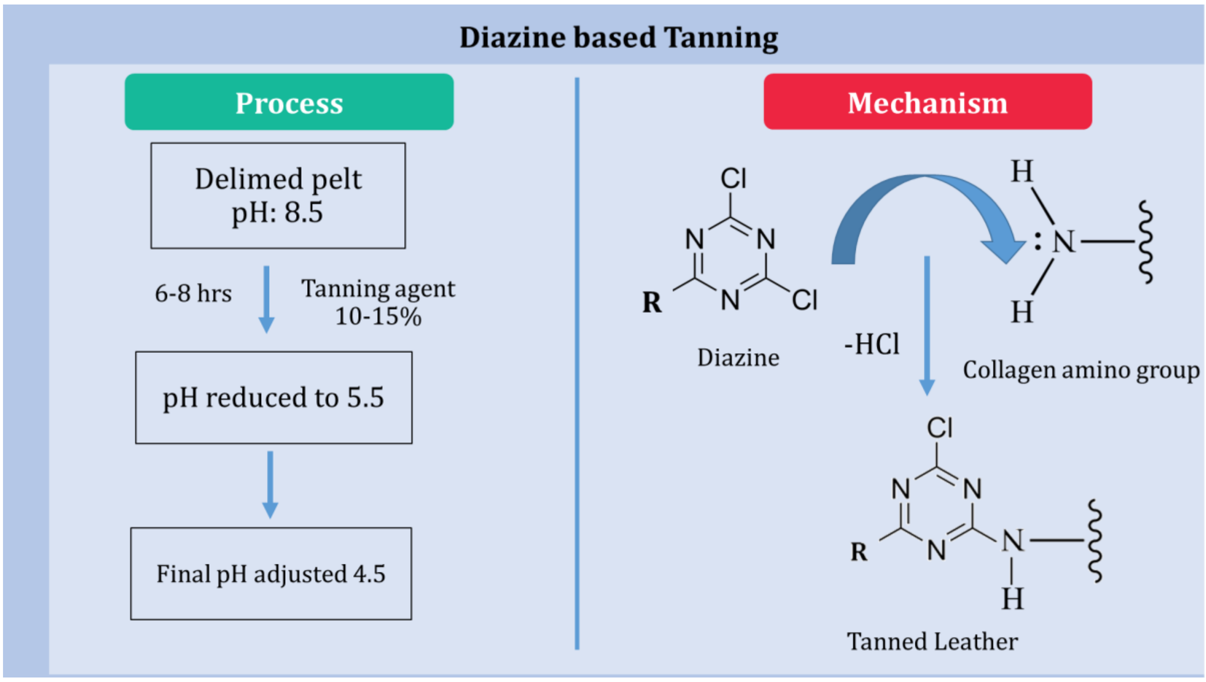


Figure 14a Process and mechanism of diaine based tanning system

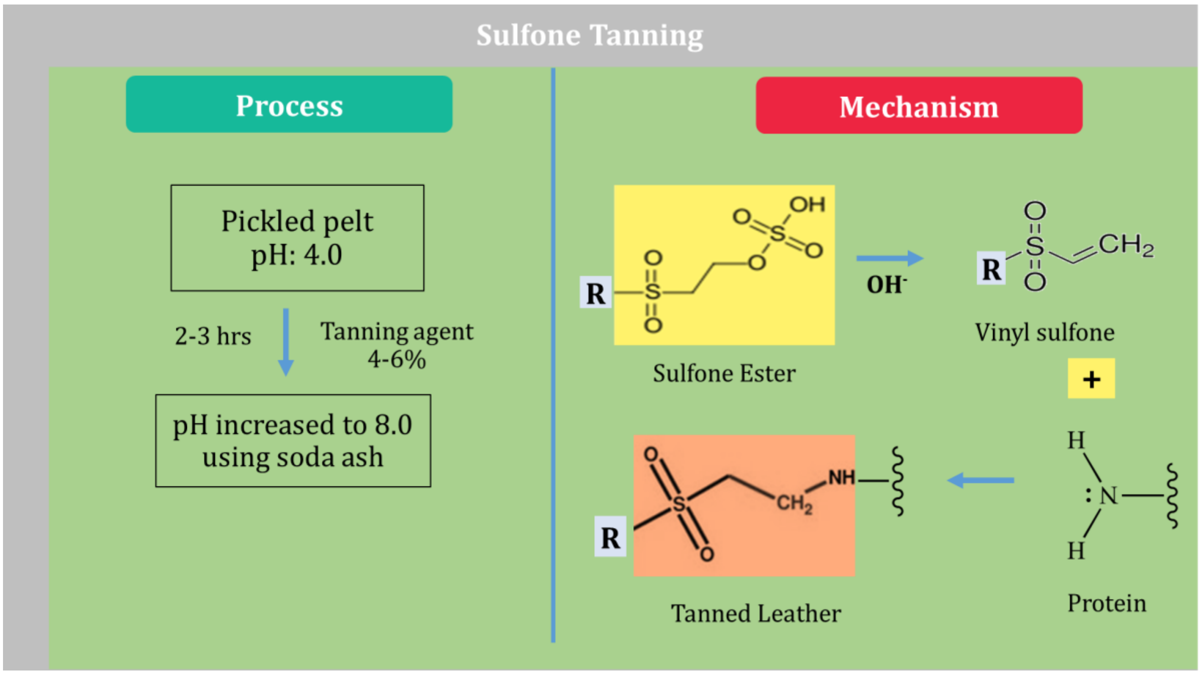


Figure 14b Process and mechanism of sulfone based tanning system

In addition, the use of olive tanning agent is emerging especially garment leather manufacturing. During olive harvests, leaves accounts for approximately 10% of the harvest weight and its rich in polyphenol. The wet-green tanning system uses polyphenol extracted from olive leaves.

Figure 14c Olive tanning

Salient features:

- ✓ Excellent grain firmness
- ✓ Dense fiber structure
- ✓ High dimensional stability
- ✓ Excellent shrinkage behavior
- ✓ Outstanding embossability
- ✓ Premium milling behaviour

3.6 Post-Tanning

Challenge: Reduction of BOD/COD and TDS
Avoidance of restricted substances
Discharge of non-biodegradable pollutant
Avoidance of fatliquor triggered Cr(VI) formation

BAT: High exhaust and restricted substances free post-tanning chemicals
Use of polymeric fatliquor
Electro oxidation of non-biodegradable pollutant and reuse of treated water

Technical description:

In post-tanning three types of leather auxiliaries such as synthetic tanning agents, dyes and fatliquors (emulsified oil) are used to fine tune the properties of tanned leather. The specific functions and the problems associated with post-tanning auxiliaries are discussed below.

3.6.1 Synthetic tanning agents:

Synthetic tanning agents (syntans) are predominantly based on condensation product of phenol (its derivatives) and amino compounds with formaldehyde. Syntans make the tanned leather uniform by filling the looser and empty parts, thus increasing the cutting value. In addition, it also helps to improve alkali/perspiration resistance and general feel/handle. Syntans are a major source of COD and TDS from post-tanning process which is mainly due to the following reasons.

- Incomplete exhaustion of syntans
- Residual monomers present in syntans
- Neutral salts present in syntans

Optimizing the process parameters and careful selection of post-tanning chemicals would help to reduce the negative environmental impact. Operating the post-tanning process at 50-60^{o}C with short float and addition of amphoteric polymers improve exhaustion of syntan. Replacing the synthetic polymers with natural polymers or protein hydrolysate prepared from leather solid waste would also increase the exhaustion and also improve the biodegradability.

Release of formaldehyde from conventional syntans is one of the main drawbacks as formaldehyde is being classified as a potential carcinogen. Recently, there are products available which do not have any free formaldehyde and products which are devoid of formaldehyde.

3.6.2 Dyes:

The dyeing process is carried out to produce leathers with a selected uniform shade of colour. The typical dyes for leather are either anionic or basic dyes. From the chemical point of view, the dye stuffs are predominantly azo dyes or anthraquinone dyes. Triphenylmethane dyes may also be used. Metal complex dyes consist of a central metal ion and one or more azo dyes ligands. The central metal ion can be iron, chromium, nickel, copper and cobalt.

Dyes in the effluent are difficult to remove and may result in a colouring of the receiving waters; even the presence of 10 ppm dye is visible to human eyes. This creates undesirable aesthetic pollution and may have a negative impact on the environment as it could influence the penetration of light in surface water. Apart from that, the used dyeing auxiliaries are not retained in leather and discharge into to wastewater. These chemicals not only increase the COD, but also result in the release of absorbable organic halogens (AOX).

The negative environmental impact of dyeing process can be resolved in the following ways.

- Increasing the dye bath temperature (60^{o}C)
- Usage of short float
- Usage of amphoteric polymers, which improve the dye intensity thereby reducing the dye consumption

- Employment of dye fixatives and proper adjustment of dye pH to be around 3.5
- Usage of salt free dyes
- Usage of liquid dyes
- Usage of natural polyphenol based mordant dyes
- Use of natural dyes

3.6.3 Fatliquors:

It is produced by emulsification of saturated or unsaturated hydrocarbons either from natural or synthetic source. Fatliquors are used to provide lubrication between fibers thereby increasing the softness. Fatliquors are significant cause of wastewater contamination which also increases the COD load. In addition to that toxic short/medium chain halogenated compounds and ethoxylate based surfactants are discharged from fatliquoring process.

The fatliquor exhaustion can be increased up to 90% by the following ways.

- Increasing the fatliquor bath temperature (60 ^{o}C)
- Usage of short float
- Usage of amphoteric polymers
- Employment of new class of fatliquors based on modified polyol

3.7 Finishing

Challenge: Reduction of VOC emission
Avoidance of harmful cross linkers
Improvement of coating efficiency

Technical description:

Aesthetic value of final leather is improved in finishing operations. The basic components of finishes and the problems associated with finishing system are given below.

(a) **Binders** are film forming material based on protein (casein) and resin emulsion like acrylics, butadienes, polyurethane and vinyl acetate. The presence of solvents, toxic catalyst used in binder preparation and usage of harmful cross-linkers for protein finishes are the major environmental concern.

(b) **Colouring agents** include dyes and pigments. Both organic and inorganic pigments are used in leather finishing. The inorganic pigments containing lead and chromate are classified as toxic substance.

(c) **Crosslinking agents** are predominantly based on polyisocyantes, carbodiimides, aziridines, formaldehyde, ethylamine and formaldehyde. Most of the crosslinking agents are potential carcinogen.

(d) **Carries** are used to produce suspensions/dispersions of binders used in finish formulations. The organic solvents used to dissolve the binders (PU) and to dilute the binders for desired concentration (eg. Methoxyproponal and isoproponal). Organic solvents are main source for VOC or VOX.

(e) **Other auxiliaries** like dispersing agent, surface active agents, organic solvents, stabilizing agents, thickening agent, stabilizing agents and plasticizers (phthalates). Some of the phathalates used in leather finishing are potential carcinogen.

(f) Further, the coating efficiency of the conventional air spray technique is only about 35-45% which mainly due to the high operation pressure. In conventional air spray technique, the pressure is about 2 bar which results in bouncing back of coating materials from the leather surface.

BAT: Aqueous finishing and modified cross linkers like polyairidines
Controlling of VOC emissions

Approaches for Controlling of VOC emissions

(i) Pre-application control – Improvement of coating efficiency

(a) ***Use of roller coating machines***

Here, 30-40% in finishing materials is saved and transfer efficiency of the system is around 80-95%. Impregnation, base coats and top coats, application of hot oils and waxes, split finishing and foam finishing can be done by reverse roller coating.

(b) ***Use of high volume low-pressure systems***

These systems have high efficiencies, low bounce back/spray fog, high quality automization, simple to use, requires no external air supply, high application rate are possible. Disadvantage being slow application speed, requires bulky hose (turbine), high input pressure (venturi and operator adjustments). Transfer efficiency of this system is 50-75%.

(c) ***Use of foam finishing and airless spraying***

These systems have a very high application rates, rapid coverage of large areas, a high film build up, reduce a spray fog and handles high viscosity materials.

Disadvantages being high fluid flow, lack of fluid flow control, requires high pressure pump, low quality finish, difficult to use by an unskilled operator. Transfer efficiency is 55-80%.

(d) ***Use of air assisted airless spraying***

These systems have higher application rates, handle high viscosity materials give low bounce back/spray fog and results in lower fluid flows than airless spraying. The fluid easily blocks the small orifice and hence the system requires a high pressure pump. The other disadvantages are that it is difficult to be used by an unskilled operator and has restricted pattern versatility. Transfer efficiency of this system is 50-75%.

(ii) Post-application control – Advanced extraction ventilation and abatement systems

Post application control involves collection of exhaust from spray booth and dryer and treating the exhaust to reduce the VOC emission by

- Combustion by introducing the solvent containing exhaust vapour into combustion furnaces. Eg. Incineration and Combustion.
- Recovering the solvent in the adsorption plants especially designed for this purpose. Eg Carbon bed absorption.

3.8 Solid Waste Management

Challenge: Complete utilization
Avoidance of land disposal

BAT: High value product from waste

Technical description:

Preparation of high grade gelatine and protein hydrolysate is an economically profitable technology for converting waste in to valuable products. High grade gelatine is predominantly used in pharmaceutical industry to prepare capsule for drugs and food industry to make jelly candies, ice cream and as thickening agent in cakes. CSIR-CLRI developed a process for preparation of high grade gelatine and protein hydrolysate from raw trimmings. For every kilo gram (@ 30% moisture and 35% salt) of trimming waste, about 160-180 grams of high grade gelatine, 70 – 80 grams of protein hydrolysate and 30 – 40 grams of keratin hydrolysate are generated from this technology.

Benefits:

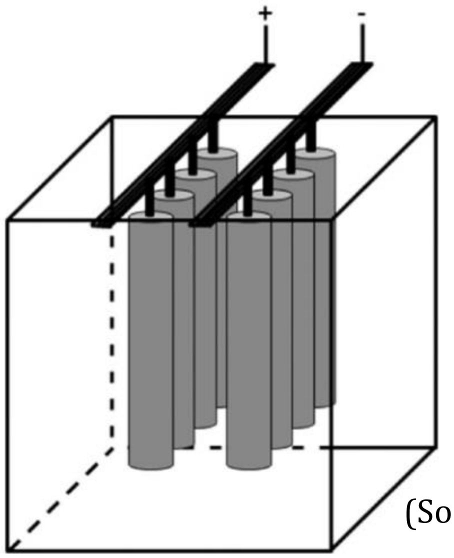
1. Complete utilization raw trimmings
2. High value product from waste (Cost of pharma grade gelatine: RS 700/kg)
3. Economically profitable

In addition to that some other technologies are available to convert the solid waste into valuable materials.

- ✓ Preparation of compost from hair
- ✓ Generation of bio-energy from fleshing waste
- ✓ Conversion of chrome shavings into lamp shades and leather like material

3.9 Liquid Waste Management

In this technique organic pollutants are removed by electro-generated oxidizing agents like chlorine and hypochlorite. In general, the following reaction takes place during electro-oxidation using graphite electrodes in the presence of sodium chloride. The schematic diagram of electro oxidation cell is shown in Figure 15.



(Source: Sundrapandiyan et al., 2010)

Figure 15 Schematic diagram of electro-oxidation cell

At the anode:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

In the undivided cell, chlorine formed at the anode and hydroxides formed at the cathode react to form chloride and hypochlorites. Both the hypochlorite and free chlorine are chemically reactive and oxidize the organic pollutants in the effluent to carbon dioxide and water.

HOCl formation

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$$

The HOCl further dissociates into OCl^- and H^+ ions

$$HOCl \leftrightharpoons H^+ + OCl^-$$

Hypochlorite ions act as a main oxidizing agent in the organic degradation. The overall desired reaction of electrolysis is:

$$\text{Organic matter} + OCl^- \rightarrow \text{intermediates} \rightarrow CO_2 + Cl^- + H_2O$$

Some of the salient features are

- ✓ No discharge of wastewater.
- ✓ The capital investment is not very high.
- ✓ Capital cost is much lesser than the cost of wastewater treatment plant for the same volume of wastewater. The capital cost for the ZWDT is around 40% of the wastewater treatment plant.
- ✓ The operating cost is comparatively lower than the conventional wastewater treatment system.
- ✓ This system provides scope for reduction in water input and reuse of salt.
- ✓ This is not associated with any harmful gaseous emissions and sludge generation.
- ✓ No primary and secondary sludge.
- ✓ Easy to control and maintain.

Benefits:

1. Economically viable
2. Complete removal of organics

4.0 BATS FOR SUSTAINABLE LEATHER MANUFACTURING

Leather industry is continuously forced to adopt environment friendly processes due to consumer awareness and statutory environmental norms. Several Best Available Technologies (BATs) have been implemented at a commercial scale and such initiatives, no doubt are effective in addressing the current issues associated with leather industry. However, the effectiveness of BATs for fulfilling the future demand of leather industry is under serious question. The future demand of leather industry may lie on

1. Water
2. Time
3. Energy

Water is recognized as one of an important and crucial resource, which is depleting exponentially. Saving water is imperative for the sustainable future. Whereas, it is evident that there is a huge demand and supply gap exists for water even for direct consumption, the industrial consumption of water warrants serious scrutiny. There is an urgent need to develop technologies that demand less water if not zero water for processing industries. Therefore, development of waterless leather manufacturing would be a future need for sustainable leather industry.

One of the other key concerns of a future leather manufacturing would be the time of processing. Current schedules of a minimum of one week for processing would need to be reduced to a day or so through appropriate adoption of technology and mechanization/automation.

Therefore, in order to make the future leather manufacturing sustainable the above points need to be considered.

4.1 Futuristic Technologies for Sustainable Leather Manufacturing (FTSL)

Concept of Sustainability

Sustainability is defined as the development that meets the needs of the present without compromising the ability of the future generation to meet their own needs. Unless the economic growth is driven to meet the needs of the present in an intelligent and equitable manner, the natural resources that are necessary for the future needs of the society cannot be met. Sustainability therefore does not encompass environmental protection alone.

Figure 16 Pillars of Sustainability

The comprehensive sustainability is built upon three pillars namely society (Figure 16), environment and economy. The comprehensive sustainability encompasses the environmental sustainability, economic sustainability and social sustainability. Environmental sustainability is the ability of maintaining the factors and practices that contribute to quality of environment on a long-term basis. Economic sustainability is the ability state of utilization of the resources in a responsible and efficient manner so as to reap a consistently the operational profit. Social sustainability is the ability of a social system to consistently achieve a good social well-being. Attainment of sustainability is the process of moving to the right point of intersection of the three aspects viz. society, environment and economy. Leather industry utilizes the co-product of the meat industry, the hides and skins. This itself is a perfect model of sustainability in the sense that the waste or co-product of one industrial activity is utilized better to create value and employment.

Sustainable Leather Manufacturing

In the view of sustainable leather manufacturing some of the BAT processes of different unit processes are sequenced and same is shown in Figure 17 as Futuristic Technologies for Sustainable Leather Manufacturing (FTSL). In FTSL process more than one BAT processes may be combined for a particular unit process and more the process sustainable.

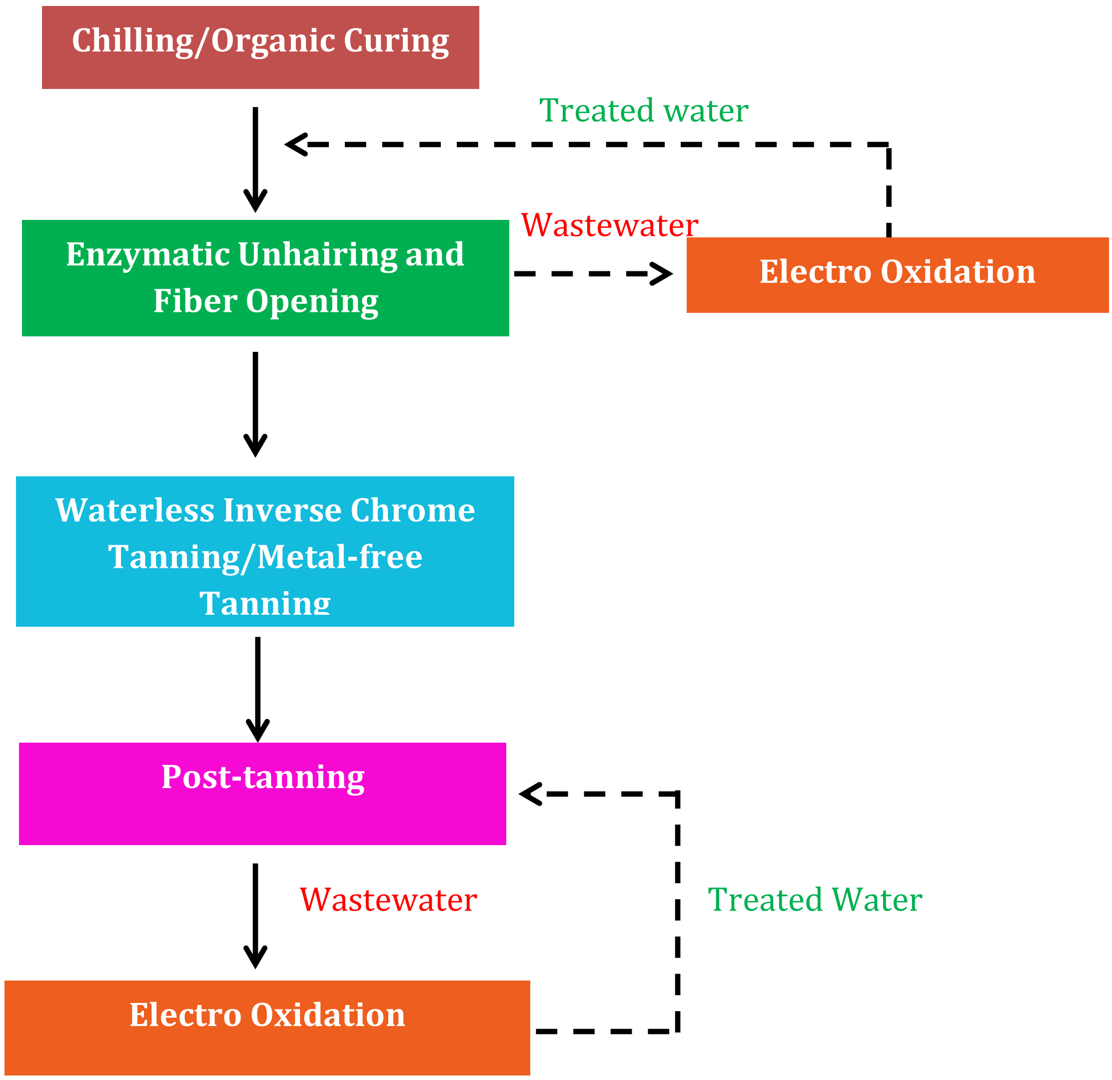


Figure 17 Futuristic technologies for sustainable leather manufacturing (FTSL)

In conclusion, FTSL process completely eliminates the salt, sulfide and lime from leather manufacturing and also reduces the water consumption up to 60-70%. The number of unit process and process duration involved in leather manufacturing can also be reduced, which in turn accelerates the leather production. Therefore, implementation of FTSL process would definitely lead to sustainable leather manufacturing.

Contributors

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