A Review of Bio-tanning Materials for Processing of Fish Skin into Leather

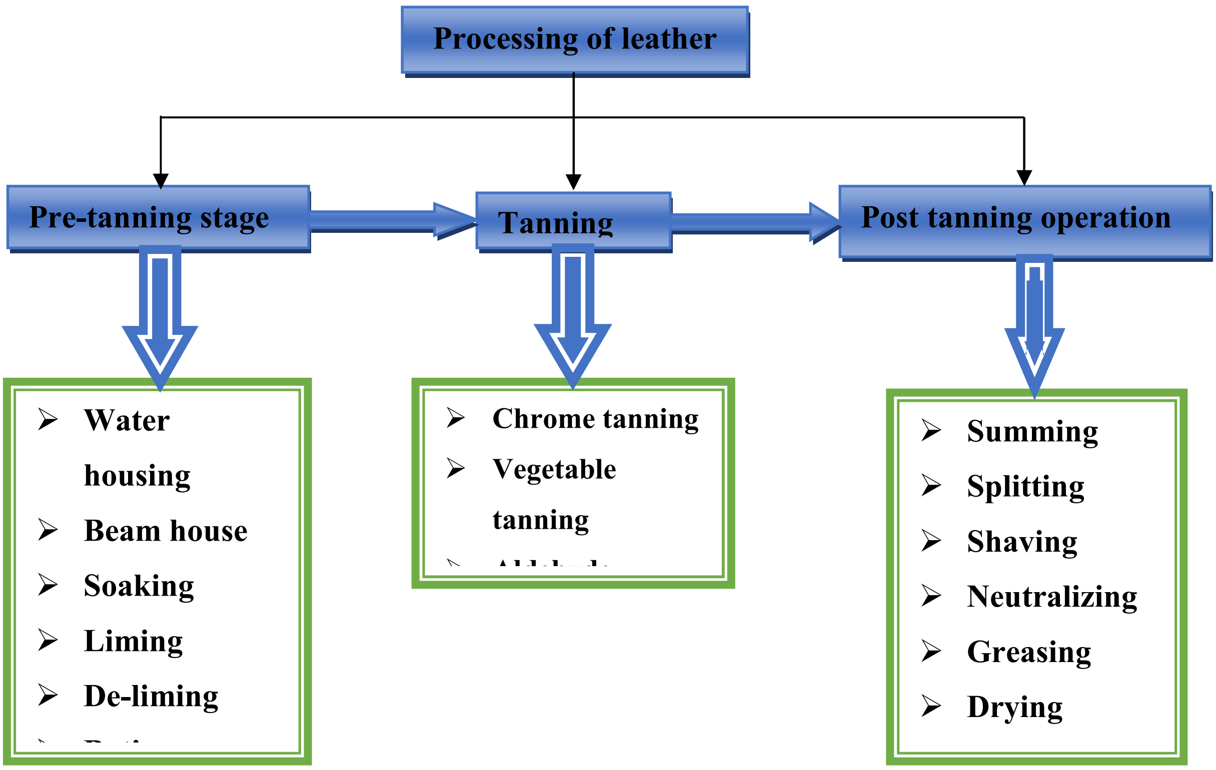
Ramesh Duraisamy Seguye Shamena
Department of Chemistry, College of Natural Science, Arbaminch University, Arbaminch, Ethiopia

Abstract
Leather is a durable and flexible material created by the tanning of animal raw hide and skin, primarily cattle hide and natural grain, variation in the grains, good breathability and other natural features are all signs that the material is genuine. The most commonly used tanning methods are chrome and vegetable tanning. The bio-tanning of hide/skin refers to tanning of hide or skin by employing vegetables, animals especially brain and microorganism (enzyme) to produce leather as it is considered as the "green tanning agent" because of its biodegradation and environmental friendly as well as can easily be applied for various sorts of leather. The vegetable tannins are extracted by using a suitable solvent, usually water followed by concentration and spray drying to get powder or solid. The production of fish skin leather is based on taking waste and turning it into a useful product and due to similarity in strength to tough cow hide, can be used for anything from handbags, belts, clothing, small accessories and shoes, furniture, interior decoration, etc.
Keywords: leather, bio-tanning, tannins, fish skin, spray drying, vacuum drying, tilapia fish

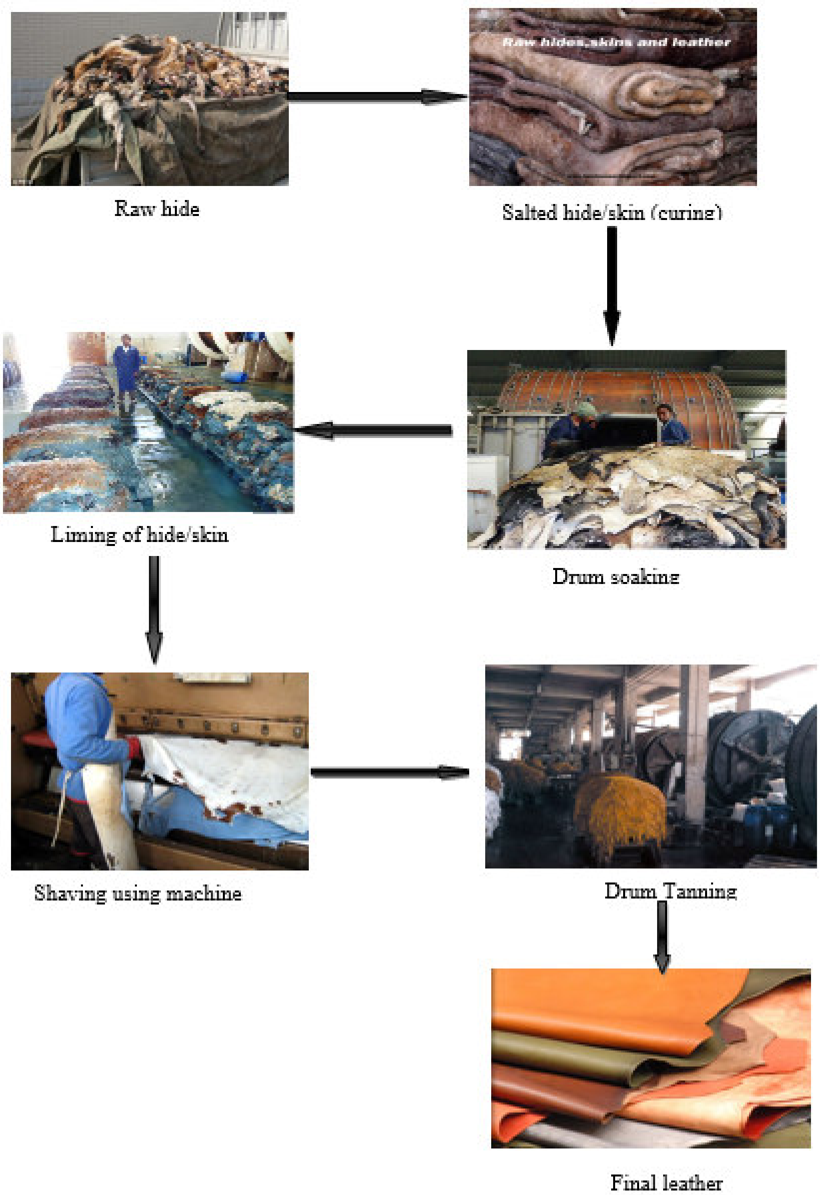
I. Introduction

1.1 Leather

Leather is a durable and flexible material created by the tanning of animal raw hide and skin, primarily cattle hide. It was extensively used from the primitive times and is widely used now-a-days. Natural grain, variation in the grains, good breathability and other natural features are all signs that the material is genuine [1]. The processing of leather upon hide or skin is in different stages such as preparation of skin/hide, tanning and post-tanning is shown in schemes.1 and 2.



Scheme.1 Processing of leather [2]



Scheme.2 Processing of Leather [2]

Among these processing of leather, tanning is an essential phase in one of the civilization's oldest processes about the transformation of hides/ skins into leather [2]. Tanning is a process in which the leather-making protein is completely stimulating against heat, enzymatic biodegradation, and thermo mechanical stress. In commercial practice, vegetable and chrome tanning methods are widely used [3]. The objective is to convert the fibrous protein of raw hide or skin (structure of the skin, see figure.1) into a stable material, to prevent hide or skin from putrification and making the leather that is suitable for a wide variety of end applications [4].

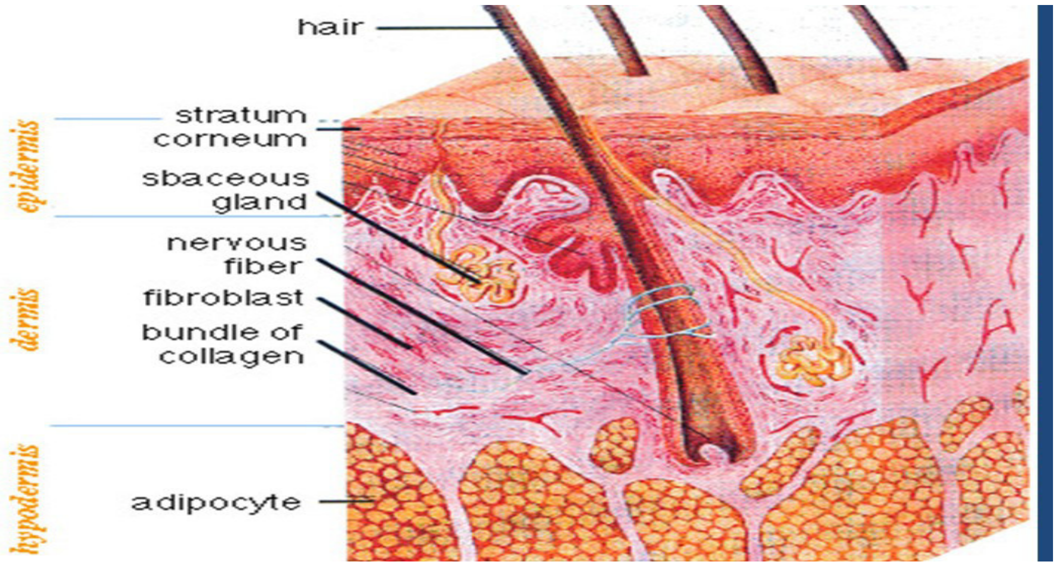


Figure.1 Structure of the Skin/hide [5]

In tanning processes tanning materials are able to crosslink with reactive site of fibrous protein, shown in figures.2 and 3 [5]. It also involves conversion of putrefiable skin or hides to a non-putrefiable material [6] by employing various techniques over time to preserve and make conditioning of hides and skins. These included the use of animal fat, brain and other substances which were used purposely for softening and arresting putrefaction [7].

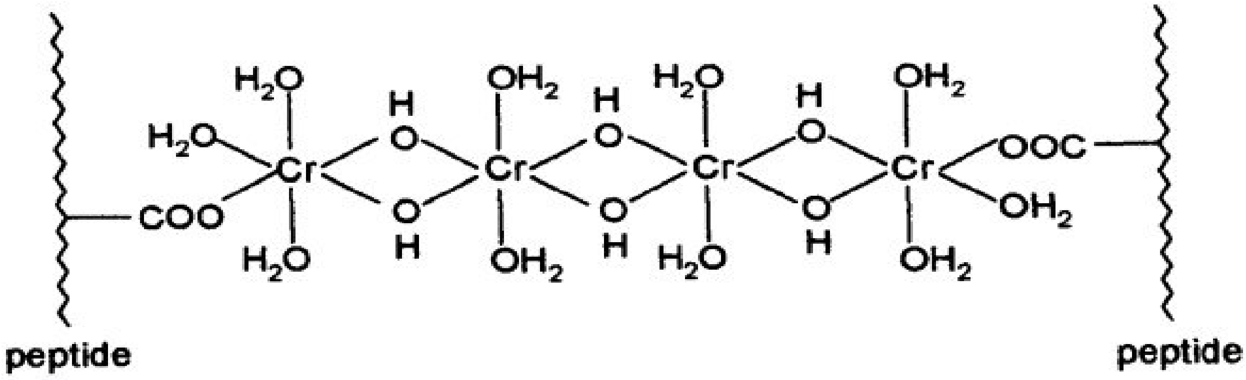


Figure.2 Chrome tanned cross-linkages with collagen (protein) of the hide/skin [8]

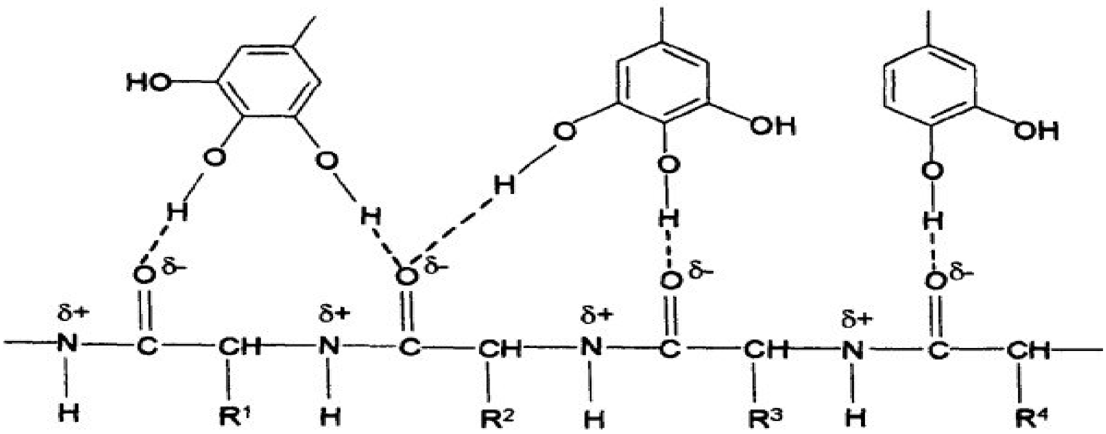


Figure.3 Model of hydrogen bonding between plant polyphenols and collagen [7]

1.2 Chrome tanning

Leather making is a lengthy process and consists of many different chemical and mechanical processes. The chrome tanning method is widely used in leather industries which accounts approximately 85% of the world's heavy leather making [8]**.** Chrome tannage has proven to be an effective method of tanning and is done in tanneries worldwide. It is used for the production of the great majority of leathers such as upper, garments and other light leathers. Chrome tan gained the leather with better characters such as high thermal stability, light weight and high strength properties [9].

1.3 Bio-tanning materials and tannins

Vegetable or plant or animal or microorganism tannins are called bio-tannins that are probably the earliest used reagents [10] for tanning of skin/hide and convert into useful end product called leather. Tannins are polyphenolic secondary metabolites of higher plants water soluble high molecular weight (500 - 20,000) polyphenolic compounds [10] and ability to precipitate the proteins and alkaloids. Tannin is an acid, and occurring naturally in the roots, wood, bark, leaves and fruit of many plants. Tannins bind (shown in figure.3) to the collagen proteins in the hide and causing them to become less water-soluble, and more resistant to bacterial decomposition [11]**.** Tannins are used in industries for the production of leather, adhesive, dye stuff and ink. Also, based on their bitter taste properties tannins are used as medicines in pharmaceutical industry, which promote rapid curing and formation of new tissues on wound and inflamed mucosa [10, 12].

Tannins are classified as condensed and hydrolysable tannins and they have ability to crosslink with collagen to form a non- putrefiable and hydrothermal stable product called leather inorganic [8, 13&14]. According to Matt Richards [14] the bark material that contain hydrolysable tannins are liable to decomposition by hydrolysis. They include gallotannins, derivatives of gallic acid and ellagitannins are derivatives of ellagic acid. The phenolics of these compounds are formed by interaction of their oxygen atom with glucose molecule by ester bonds. They make leathers become pink, red or dark brown shades that are more 'solid'. Further, these tannins also create greenish-black spots on contact with iron. Mimosa, birch, hemlock, quebracho, alder and fir bark contain catechols. Oak bark contains both types of tannins that are used for the tanning of hides/skin [14].

Hydrolysable tannins are categorized in three sub-groups are depsides, gallotannins and ellagitannins. Myrobalan, chestnut, valonia, sumac, tara and divi-divi are examples of hydrolysable tannins containing plants [14]. Condensed tannins are not decomposed by hydrolysis but liable to oxidation and polymerization to form insoluble products. Condensed (catechols) tannins have more stable composition than hydrolysable tannins, which cause phenolic aromatic compounds to combine with carbon atoms. Mimosa, quebracho, hemlock, willow and gambir are few examples of condensed tannins containing plants. These are preferable for leathers intended for book binding, upholstery and other purposes where longevity is essential. The resultant leather is of pale color varying from creamy or yellowish to light brown. Pyrogallols make bluish-black spots on contact with iron and resist changes in pH value. Sumac, chestnut, oak galls and oak-wood contain pyrogallols [14]. This type of tannin produces “tannin reds “while boiling with acid [13, 14].

Brain tissue contains a fairly high fat and oil content that helps explain why it softens leather, keeps it flexible and protects it from water. Another of the active ingredients relevant to brain tanning is a compound called “lecithin,” which probably helps the fats and oils in the thick gravy derived from cooking and mashing brain tissue interact with the non - oily components of the leather [13].

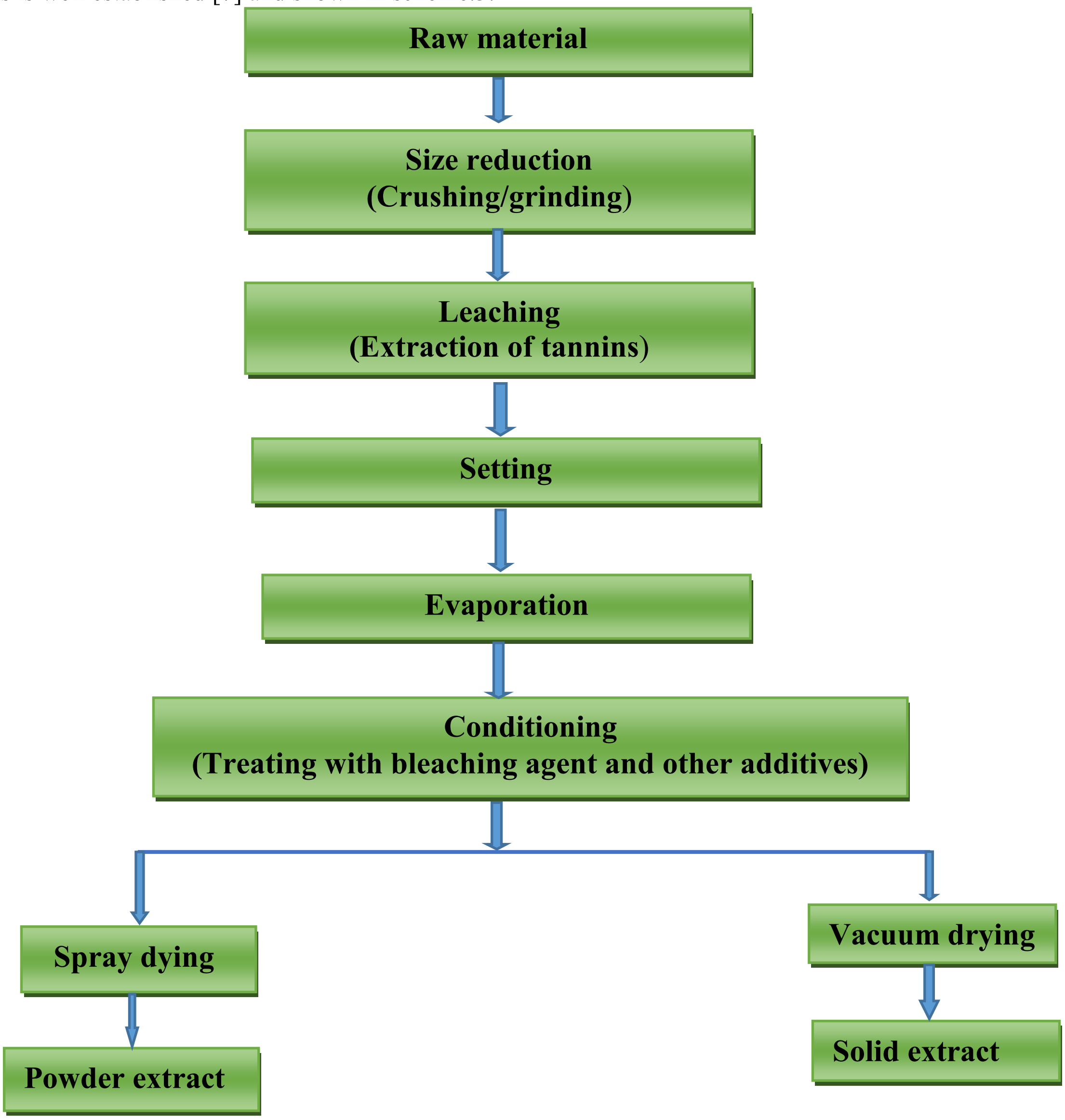
1.3.1. Vegetable tanning materials

Vegetable tanning, which is also referred as bark tanning and it is the time-tested method of using vegetable materials to process animal hides and skins into water resistant, non- putrefiable, soft, flexible, heat resistant material [15]. Bark tanning is an ancient method of creating durable, water repellent leather with a lot of body. It can be done to virtually any skin, but it is generally reserved for tanning grain on leathers from large thick hides such as cattle, horse, buffalo and pig. It has been commonly used for saddles, canteens, stiff shoes, belts, wallets, holsters, harnesses, helmets, pouches, trunks, shields and gun cases.

Vegetable tanning involve treating the hides/skins with leaves, root and barks containing tannins [5] and it is considered as the "green tanning agent" because of its biodegradation and environmental friendly than that of inorganic tanning. Vegetable tanned leather has excellent fullness, moldering properties, wear resistance, air permeability and solidness; hence, it is of greater significance to reduce chrome pollution in leather making process. Vegetable tanned leather is used in making heavy leather such as furniture leather, garment leather and shoe upper leather [15]. The vegetable tanning method does not require the prior preparation of pickling and therefore the contributions to pollution load from sulfate salts are lower. In addition with vegetable tannins have several advantages such as it make leather to be hard to biodegrade, and hence wastes bearing vegetable tannins degrade slowly [16], ingredients (no harmful chemicals) are used when dying the hides are lighter in color and can be converted into pastel shade leathers, high softness, good lightness, natural sensation, pleasant touch, beauty over the time environmental friendly and can be recycled, each leather product that is dyed using vegetable tanning is completely unique, rich, warm-tone colors which look completely natural and high performance leather can be obtained, often better than chrome tanning.

1.4 Extraction of tannins from vegetables/plants

Plant tannins are polyphenols that are distributed as condensed and hydrolysable tannins with an immense structural variability and reaches high degree of polymerization. Extracts of tannin-rich plants are analyzed and being an important part of leather manufacturing. The manufacturing of vegetable tannin extract is essentially based on the extraction of tannins by using a suitable solvent usually water followed by concentration and spray drying to get powder or solidification to get solid (block) extract [7]. The extraction procedure of tannins from plants is well established [7] and shown in scheme.3.



Sheme.3 Extraction process of vegetable tannins from plants

1.5 Significance of the study

Generally, leather's are produced from hides and skins of different animals including fish, using basic chromium sulphate as tanning agent. Chrome tanning produces a leather with better suited for certain applications, particularly for the upper parts of boots and shoes, and requires less processing time than traditional vegetable tanning but this chrome tanning is not environmentally friendly and cause the environment and to human. Also, now-a-days worldwide all the nations are posing the environmental legislation to control the use of pollution causing chemicals/methods for any industrial processing. Therefore, the use of bio-tanning is more advantageous than that of chrome tanning due its environmental friendly approach. Most of the researchers are also interested to processing the fish leather from its skin by chrome tanning, and so still there is a gap (no literature found) for tanning of fish skin using bio-tanning materials. Hence, this review will emphasize to apply the bio-tanning material into fish skin to produce fish leather without harm of their physical properties to produce leather with eco-friendly approach.

II. Review of Literature

2.1 Bio-tanning

Bio-tanning materials have tannins that kept their importance for thousands of years in processing of leather. Even now-a-days, many researchers reported by employing vegetable tannins like bio-tanning materials on both single and combined use with other bio tannins, aldehydes, syntans and various metal salts [17]. Since long back, they are important as retanning agent in leather production and have been recognized as important tanning agent in non-chrome tanning methods [18]. Bio/vegetable tanned leather has excellent fullness, moldering properties, wear resistance, air permeability and solidness; hence, it is of greater significance to reduce chrome pollution in leather making process [18]. It is a better alternative method of tanning to chrome tannage because of environmental friendly mean eco-friendly than chromium tanning, cheaper and also can easily be applied for various sorts of leather [19].

Bio-tanning is a common tanning procedure which renders, elasticity to leather through a complex interaction of skin/hide proteins (collagen) with phenolic molecules present in tanning agents. Vegetable tannins, falling into the categories of condensed and hydrolysable tannins, interact with collagen basically via two possible modes such as hydrogen bonding at the collagen peptide links, and "fixing" to amino and carboxylic acid groups on side chains, which is a pH dependent process [20]. Several companies providing industrially produced tannin extracts of plants such as extracts of Schinopsislorentzii (quebracho), Acacia mearnsii (mimosa), Caesalpiniaspinosa (tara), and Uncariagambir (gambier) were chosen, and reported that the different approaches of evaluation for the tannin content and its structure of selected plant extracts, and application of its for tanning of leather by M.Kardell et.al., [21].

2.2 Vegetable tanning materials

Vegetable tannins are natural products of relatively high molecular weight which have the ability to complex strongly with carbohydrates and proteins. In this context, they are the most important natural products used industrially, specifically in leather tanning processes and the extracted commercial pod of tara (extracted at 1 hour with water (1:40 w/v) at 65^0C) was spray-dried to obtain tara tannins then the quantity of the components are analyzed after and before hydrolysis and these result in obtaining the concentration of gallotannins (gallic acid) in the extract reached 53 % reported in literature [22]. V. Sivakumar et al. [23] studied the use of power ultrasound in solid- liquid extraction of biotanning materials. This vegetable tanning extracts is essentially based on the extraction of tannins from the tannin-bearing material using a suitable solvent, usually water, followed by concentration and spray drying to get powder or vacuum dried material of solid [23]. Tannins are defined as phenolic compounds of high molecular weight ranging 500 - 3000 Da, which they found in plants leaves, bark, fruit, wood and roots located basically in the tissues of vacuoles [24, 25]. Vegetable tannins from four indigenous and exotic woody plant species were studied by different methods such as gelatin salt

Different methods are conducted for extraction of tannin from vegetables. According to the literature [26] the influence of particle size, temperature, methanol content and time on the extraction of tannins from caesapiniacoriaria (divi-divi pods) determined by pressure autoclave method and tannins are determined by NMR spectroscopy, resulted in degradation of the compound is less at low temperature (40^0C), the effect of time and substrate concentration on the extraction and evaluation of tannins were studied. The process of stabilizing the skin collagen against denaturation under heat, enzymes, stress etc., popularly described as tanning is carried out by vegetable tannins derived from plant sources rich in polyphenols extracted with ethanol as the green solvent and highlights the significance of the developed method, in not only enhancing tannin to non-tannin ratio (T/NT), but also improving thermal stability of the tanned collagen. Extracts of tannin-rich plants is an important unit during leather manufacturing, there are several companies providing industrially produced tannin extracts of plants such as, extracts of Schinopsislorentzii (Quebracho), Acacia mearnsii (Mimosa), Uncariagambir (Gambier) and Caesalpiniaspinosa (Tara) has 164.3, 108.2, and 169.3 g kg^{-1} of tannin respectively and Tare reached 647.5 g/kg of tannins, which is extracted as based on photometrical methods as well as HPLC-ESI-MS [21].

2.3 Animal tanning materials

Brain tanned leathers are made by a labor-intensive process that uses emulsified oils, often those of animal brains such as deer, cattle, and buffaloes are used as tanning materials. They are known for their exceptional softness and washability [27]. The purpose of brain tanning is to let the hides soaked in oils of the brain to lubricate the fibers to make the soft hide, pliable, and has elasticity and hide being soaked in a brain and water solution for 15 to 20 minutes (at minimum), then squeezed and stretched for approximately 45 minutes to one hour, then the resulting hides are differed greatly from one another in softness and texture [28].

2.4 Tanning by microorganism: Enzyme

Enzymes have found uses in various pre-tanning processes of leather manufacture such as soaking, unhairing, bating, dyeing and degreasing (see table.1). According to literature reported [29] an eco-friendly vegetable tanning process combining pickle-free tanning and application of proteolytic enzymes to improve the exhaustion of vegetable tannins and resulted in more than 95% tannin exhaustion in the case of the experimental process, an increase of 10% compared with the conventional vegetable tanning process. Furthermore, the enzymes are successfully employed to make the better quality leather production with less pollution impact [23].

Table: 1 Enzyme function and it involvement in different leather processing

Stage	Enzyme evolved	Function of enzyme
Curing	Enzyme are directly not involved	To preserve hide and skin
Soaking	Alkaline and pancreatic protease	To remove non fibrillary protein
Dehairing	Alkaline and neutral protease	To improve the waste water quality
Degreasing	Lipase and protease	To remove fat
Bating	Trypsin and alkaline protease	To make soft, supple and pliable
Tanning	Enzyme are directly not involved	To influence the quality of tanning
Waste processing	Trypsin and proteolytic enzyme	Chrome tanned waste processing

Source [24]

Enzymes like proteases (most commonly used enzymes in leather production), lipases (used in degreasing operation to hydrolyze fat particles embedded in the skin), and amylases (used to soften skin, to bring out the grain, to impart strength and flexibility to the skin) have an important role in the soaking, Dehairing, degreasing, and bating operations of leather manufacturing. By using enzymes for tanning that should not damage or dissolve collagen or keratin, but should be able to hydrolyze casein, elastin, albumin, and globulin-like proteins, as well as non-structured proteins which are not essential for leather making [30].

2.5 Fish skin tanning

The production of fish skin leather is based on taking waste from the food industry and turning it into a useful and desirable material for the fashion and textile industries. Similar in strength to tough cow hide, fish skin leather can be used for anything from handbags, belts, clothing, small accessories and shoes, to furniture and interior decoration [31, 32]. Fish skins have gaining interest among tanners as an additional source of raw material for making leathers due to their attractive and unique grain structure possessing high market value reported by R.Karthikeyan et al., [33]. The authors suggest that the thickness of the raw skin after green fleshing ranges from 2-5 mm with beautiful grain structure, and it is traditionally used for the production of decorative leather for ornamental goods. Stingray skins have dentils instead of scales, it imparts attractive appearance to the finished leather [32]. The tanning process completely removes all odors and transforms what was once trash into treasure. The result is richly-colored leather with an exotic scale pattern unique to each species [33]. The skin (shown in figure.3) of fishes is composed largely of a system of collagen fibers that form alternating layers of right and left helices wrapped about the long axis of the animal.

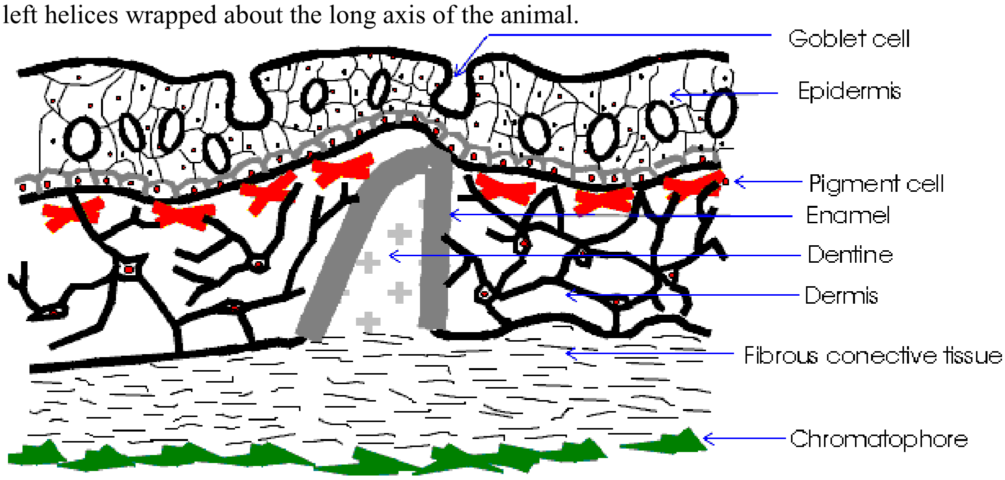


Figure.4 Structure of fish skin

2.6. Processing fish leather [32, 33]

2.6.1. Process - 1

Raw Material: Green Fleshing: The fresh skins were green fleshed and rinsed with water for 15 minutes with clean water.

Depigmentation: Dark brown colored pigment adhered to the entire dorsal portion of the fish skin may not be removed by using lime. A sulphide rich paste is applied to remove the adhered pigments. The sulphide paste is to be prepared by 4% (based on green fleshed weight) of sodium sulphide flakes with water to make slurry and applied on fish skin. It is left for 12 h or overnight and on next day, the skins were rubbed with gunny bag or brush to remove the pigments.

Fiber Opening: Introduce the depigmented fish skin into the mixture of 10% lime in 250% water and kept for 3 days in a pit. This is to be handled twice a day, the skins were fleshed and the weight was noted. After weighing, the skins were piled grain to grain and secured with staples or stitched along the outside edge to protect the dentils of stingray from the mechanical action of drum during processing. This method of processing also avoids the folding of the skin and protects the beautiful grain structure from damage.

Deliming and Bating: About 1% ammonium chloride was prepared in 100 ml of water and drummed for 30 minutes. The drummed liming material is mixed with 2% Microbate about on 45 minutes. Then continued the process through fleshing and washing,

Pickling: The pickling process is continued by using 10% salt placed in 100 ml water about about on 10 minutes, then further pickling proceeded with 1% hydrochloric acid for 100 minutes, and the pickling was continued in bath through overnight. Next day, 1% of hydrochloric acid was and kept for 100 minute, and the pH was maintained about 2.0, then again pickling bath was left overnight. Next day the pelts were taken and piled for 10 days.

Re-pickling: About on ten days pickled skin were taken into a bath containing 80% Water and 8% of salt for about 10 minutes, then 1% of hydrochloric acid solution was added and the bath is left for another 90 minutes.

Chrome Tanning: The repickled skin is tanned in a drum containing 50% pickle water, 4% BCS powder, 1% Cationic fatliquor, 1% nonionic fatliquor, is ran for 60 minute. Then 4% BCS powder, 1%Cationic fatliquor, 1% Nonionic fatliquor was placed in tanning drum, and the drum is runned for 60 minute. Afterwards, the drum pH maintained as 3.8 followed by addition of 50% Water about 30 minute 30', 1% sodium formate (in 10% water), and 1% Sodium bicarbonate is about on 90 minutes (thin was done in 10% water). The skin was rinsed and piled through overnight. The corresponding fish leather processing is shown in scheme.4, which was reported by R. Karthikeyan et al. and others [38-40].

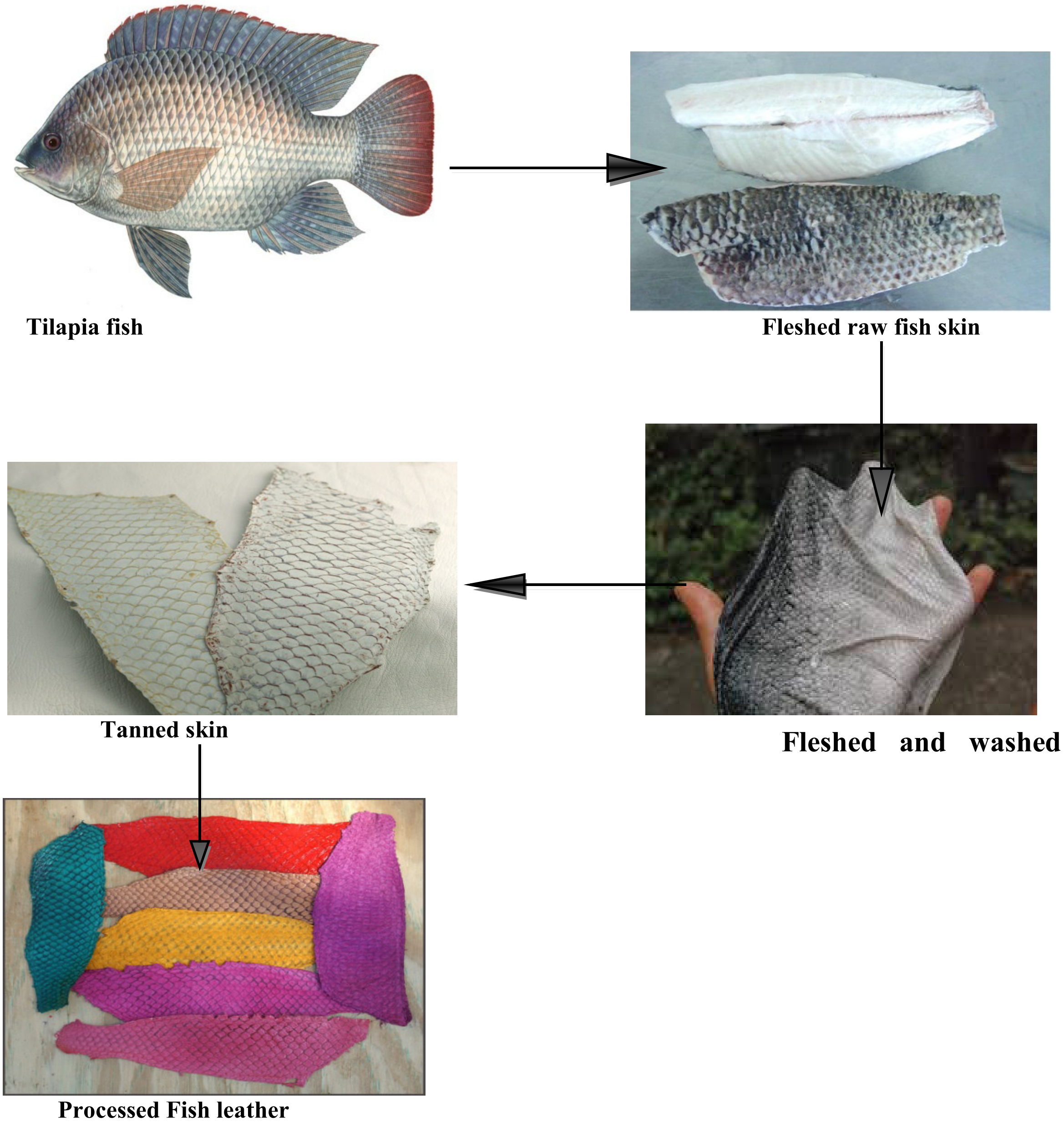
2.6.2. Process - 2

Raw Material: Fresh stingray skins. **Green fleshing:** The fresh skins were green fleshed and rinsed with water for 15 minutes.

Depigmentation & Fiber Opening: The fresh skin is de-pigmented in a drum containing 4 % Xylanase enzyme (percentage based on green fleshed weight), and 30 % water for about 5 hours. The skins were rubbed with brush to remove the pigments, fleshed and the weight was noted.

Pickling: The de-pigmented skin was pickled in a bath contains 10 % salt solution for 10 minutes, then the bath is kept overnight after added of 1% sulphuric acid (in water) about on 100 minutes. Next day adjust the pH become 2.8 and 50% pickled water was drained.

Chrome Tanning: The repickled skin ws tanned in a drum containing 50% pickle water, 4% BCS powder, 1% Cationic fatliquor, 1% nonionic fatliquor is ran for 60 minutes. Followed by this process 4% of BCS powder, 1% cationic fatliquor, 1% nonionic fatliquor was used and tanning is proceeds in tanning drum for 60 minutes. Afterwards, the drum pH is maintained about 3.8 followed by addition of water around 30 minutes; followed by addition of 1% Sodium formate (in water), and 1% sodium bicarbonate for about 90 minutes, then the skin is rinsed and piled through overnight. The corresponding fish leather processing is shown in scheme.4, which was reported the literatures [31-33].



Scheme: 4 Processing of fish skin in to leather

Conclusion

Leather processing involves three principal steps, first for purification of the multi-component skin/hide into a single protein, collagen, (b) stabilization of purified collagen matrix and (c) addition of aesthetic values for applications by employing either chrome tanning method or bio- tanning method.

Bio-tanning refers to tanning of skin/hide using chrome free tannins such as vegetable (plant), animal (brain) and enzyme. Vegetable tanning are extracted in different method and are applied for various types of hide/skin in order to produce leather that can be degraded at their end uses and being environmental friendly. Among various types of skin now-a-days researchers are also produces leather from fish skin. Fish skins have gaining interest among tanners as an additional alternative source of raw material for making leathers due to their attractive and unique grain structure possessing high market value.

Scope for the future work

Fish leather has surprised into the leather industry and global designer fashion industry. The skins from fish are now considered the principal residual by-product of this aquaculture business. The skin can be processed and transformed into quality raw material of unique and peculiar aspect after tanning, due to its resistance and drawing on its surface, mainly skin of fish with scales. The skin of fish is considered exotic and innovative leather, being accepted in different clothing industry segments. The high-end market also aligns itself with the current politically correct marketing strategy as "environmentally friendly alternative exotic leather" because they use an otherwise wasted product.

Arba Minch is well known in the production and exporting of fish meat for marketing. The fishers are collecting the fish from the two lake (Abaya & Chamo), they purchase the meat after slaughtering the skin and the skin part is disposed away as a waste due to lack of knowledge for production of fish skin to leather. The skin can be processed and transformed into quality raw material of unique aspect after tanning, due to its resistance and drawing on its surface, mainly skin of fish with scales, this review will create the awareness to the local fishers to have knowledge for the important of fish skin for the production of leather. This is also generate job opportunity for the fishers to export fish skin to the tanners and keeps the environment safely.

Tanning of fish skin also gives additional income for Ethiopian leather industries, because fish leather is one of value added materials due to availability of fish.

The main future scope provide by this review is to create the opportunity in Arbaminch town to export pickled skin and other processed items such as clothing and small items such as belts, purses, wallets, and bikinis using biotanning methods.

References

1. Priyanka Kesarwani, Shahnaz Jahan, Kirti Kesarwani, (2015) "A Review on Leather Processing", International Journal of Applied Research, Vol.1 (9) pp. 977-982.
2. Frederik H.Romer , Andrew P. Underwood , Nadine D. Senekal , Susan L. Bonnet, Melinda J.Duer, David G.Reid and Jan.H.van der Westhuizen (2011) "Tanni Fingerprinting in Vegetable Tanned Leather by Solid State NMR Spectroscopy and Comparison with Leathers Tanned by Other Processes", Molecules, Vol.16, pp.1240-1252.
3. A.E Musa1 and G.A Gasmelseed, (2013) "Eco-friendly Vegetable Combination Tanning System for Production of Hair-on Shoe Upper Leather" Journal of Forest Products & Industries, Vol.2 (1), pp.5-12.
4. Ebtesam El-Bestawy, Fahad Al-Fassi1 RanyaAmer, Reham Aburokba, (2013) "Biological Treatment of Leather-Tanning Industrial Wastewater Using Free Living Bacteria" Advances in Life Science and Technology, Vol.12, pp.46-65.
5. Alex Kuria1, Jackson Ombui, Arthur Onyuka, Alvin Sasia, Cheruiyot Kipyegon, Pennina Kaimenyi, Antony Ngugi, (2016) "Quality Evaluation of Leathers Produced By Selected Vegetable Tanning Materials from Laikipia County, Kenya" IOSR Journal of Agriculture and Veterinary Science (IOSR-JAVS) Vol. 9, Issue 4, Ver. I, pp.13-17.
6. Swarna V. Kanth, R. Venba, B. Madhan, N.K. Chandrababu, S. Sadulla, (2009), "Cleaner tanning practices for tannery pollution abatement: Role of enzymes in eco-friendly vegetable tanning" Journal of Cleaner Production, Vol.17, pp.507–515.
7. Koloka, O. and Moreki, J.C. (2011), "Tanning hides and skins using vegetable tanning agents in Hukuntsi sub-district, Botswana" Journal of Agricultural Technology, Vol.7 (4), pp.915-922.
8. Mahdi Haroun, Palmina Khirstova, Gurashi Abdallah Gasmelseed and Covington D, (2009) "Potential of vegetable tanning materials and basic aluminum sulphate in Sudanese leather industry", Journal of Engineering Science and Technology, Vol.4 (1) pp. 20-31.
9. Elshahat H.A. Nashya, Osama Osmanb, Abdel Aziz Mahmoudb, Medhat Ibrahim (2012), "Molecular spectroscopic study for suggested mechanism of chrome tanned leather", Spectrochimica Acta, Vol.88, pp.171-176.
10. Mahdi Haroun, Palmina Khirstova, Glavtch I (2006), "Characterization of Acacia Nilotica as an indigenous tanning material of Sudan", Journal of Tropical Forest Science, Vol.18 (3) pp.181–187.
11. Sathiyamoorthy M, Selvi V, Derese Mekonnen, Shewarega Habtamu, (2013) "Preparation of Eco-Friendly Leather by Process Modifications to Make Pollution Free Tanneries", Journal of Engineering, Computers & Applied Sciences (JEC&AS) Vol. 2 (5), pp.17-22
12. Mahdi Haroun, Palmina Khirstova, Tony Covington (2013), "Tannins Characterization of some Indigenous and Exotic Woody Plant Species and Two Agricultural Crops in Sudan", Journal of Forest Products & Industries, Vol. 2 (6) pp. 38-46.
13. Koloka, O. and Moreki, J. C. (2011),"Tanning hides and skins using vegetable tanning agents in Hukuntsi sub-district, Botswana", Journal of Agricultural Technology, Vol. 7 (4) pp.915-922.
14. Ramakrishnan, K. Krishnan, M.R.V. (1994), "Tannin: Classification, Analysis and Applications", Ancient Science of Life, Vol .XIII (3 & 4) pp.232 - 238.
15. Rolland Wemegah (2014), "Vegetable Tanning in Bolgatanga: Challenges and the Way Forward", Arts and Design Studies, Vol.16, pp.27-37.
16. A.E Musa and G.A Gasmelseed (2013), "Eco-friendly Vegetable Combination Tanning System for Production of Hair-on Shoe Upper Leather", Journal of Forest Products & Industries, Vol.2 (1) pp.5-12.

17. Altan Afsar and Ozgur Sekerogluan (2008) "Investigation about the effect of oxazolidine on modified valonia extract tanning", African Journal of Biotechnology, Vol. 7 (20) pp. 3737-3742.
18. A.E Musa and G.A Gasmelseed (2012), "Characterization of Lawsoniainermis (Henna) as Vegetable Tanning Material", Journal of Forest Products & Industries, Vol.1 (2), pp.35-40.
19. Alim AbdElgadir Haj Ali, Gurashi Abd Allah Gasm Elseed and Adil El Haj Ahmed (2016), "Utilization of Improved Indigenous Tannins of Grain Powder (Acacia Nilotica) in Eco Friendly Tannage", International Journal of Multidisciplinary and Current Research, Vol.4, pp.14-20.
20. Ekaterini Malea, Stamatis C. Boyatzis, T, Marina Kehagia, (2010) "Cleaning of Tanned Leather: Testing with Infra-Red Spectroscopy and SEM-EDAX", Joint interim meeting of five ICOM-CC working groups: Leather and Related materials, pp.1-12.
21. Kardell, M. Taube, F. Schulz, H. Schütze, W. Gierus, M. (2013) "Different approaches to evaluate tannin content and structure of selected plant extracts", Journal of Applied Botany and Food Quality, Vol.86, pp.154 - 166.
22. J.M. Garro Galvez, B. Riedl and AH. Conner (1997) "Analytical Studies on Tara Tannins", Holzforschung, Vol. 51 (3) pp.235-243.
23. Sivakumar, V. Ravi Verma, V. Rao, P.G. Swaminathan, G. (2007) "A Studies on the use of power ultrasound in solid-liquid myrobalan extraction process", Journal of Cleaner Production, Vol.15, pp.1813-1818.
24. Shahin Hassanpour, Naser Maheri-Sis, Behrad Eshratkhah and Farhad Baghbani Mehmandar (2011), "Plants and secondary metabolites (Tannins): A Review", International Journal of Forest, Soil and Erosion, Vol. 1 (1) pp.47-53.
25. Nallabilli Lokeswari, Peela Sujitha (2011), "Isolation of Tannins from Caesalpinia Criaria and the Effect of Physical Parameters", International Research Journal of Pharmacy, Vol.2 (2) pp.146-152.
26. Bhargavi Narayana Reddy Gari, Gladstone Christopher Jayakumar, Kalarical Janardhanan Sreeram, Jonnalagadda Raghavarao and Balachandran Unninair (2015) "Towards Sustainable Leather Production: Vegetable Tanning in Non-aqueous Medium", JALCA, Vol. 110, pp.98-102.
27. Matthew Richter and Darby Dettloff (1995) "Experiments in hide rain-tanning with a comparative analysis of stone and bone tools", pp.301-308.
28. Swarna V. Kanth, R. Venba, B. Madhan, N.K. Chandrababu, S. Sadulla (2009) "Cleaner tanning practices for tannery pollution abatement: Role of enzymes in eco-friendly vegetable tanning", Journal of Cleaner Production, Vol. 17, pp.507-515.
29. R.B.Choudhary, A.K.Janna and M.K. Jha, (2004) "Enzyme technology application in leather processing", Indian Journal of chemical technology, Vol.11, pp. 657-671.
30. Leena Oijala (2013), "Fiber Watch: A Different Kettle of Fish Leather", website: http://ecosalon.com/fiber-watch-a-different-kettle-of-fish leather.
31. N.K. ChandraBabu, A.B.Mandal and P .K. Sehgal (2009), "Studies on the Preparation of Soft Leathers from Himantura (Family Dasyatidae) Stingray Skins and their Applications in Foot and Hand Reflexology",
32. Songchotikunpan, P. Tattiyakul, J. Supaphol, P. (2008) "Extraction and electro-spinning of gelation from fish skin", International Journal of Biology Macromolecules, Vol.42, p.242.
33. Karthikeyan.R, Chandra Babu, NK. Mandal AB. (2011) "A new depigmentation and fibre opening method for the conversion of stingray skins into leathers", Journal of American Leather Chemical Association, Vol.105, p.25.