List of poster presentations

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INNOVATIVE APPROACH FOR THE PRIMARY TREATMENT OF SOAK LIQUOR FROM TANNERIES THROUGH SEQUENTIAL OXIC ANOXIC BIO REACTOR USING FILAMENTOUS BACTERIA AND HALOPHILES

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The present research study focuses on the effective primary treatment of tannery saline soak liquor through the digestion of suspended solids and dissolved organics, using sequential oxic anoxic bio-reactor. The presence of high concentration of dissolved inorganic salts (NaCl) retards the biological degradation of dissolved organics present in the soak liquor. The aim of this study is to grow halophilic organisms using soak liquor nutrient by means of sewage culture, which will assist in removal of these organics in wastewater, which is performed by this reactor. The organisms were screened to synthesize all the three enzymes by utilizing the components in soak liquor as the substrate, with enzyme activity for protease, lipase and amylase. The hydraulic retention time of the reactor 12h was optimized on the basis of maximum removal of proteins, carbohydrates and lipids in this reactor. The noticeable amount of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) removal were observed. Moreover, the suspended solids removal was achieved up to a maximum level in the presence of Total dissolved solids (TDS) at a range of 3-7%. Instrumental analysis such as UV-Visible, Fluorescence spectroscopic studies also confirmed the degradation of dissolved and suspended organic matter present in soak liquor. And also, the morphology of the biofilm on the plastic baffle material was characterized by SEM analysis. Hence, this combined treatment system promises to be a more beneficial primary treatment option for tannery saline soak liquor by using halophilic organisms and filamentous bacteria in future.

Key words: Sequential Oxic-Anoxic Bioreactor, removal of organics, soak liquor, suspended solids removal

1. Introduction

Many industrial sectors such as agro-food industries, gelatine producing industries that use animal bones as raw materials, industries that are involved in leather production from animal skins /hides and petroleum industries discharge large amount of wastewater with high concentration of Total Dissolved Solids (TDS). Apart from these industries, tanning industry is the one which generates large quantity of saline wastewater. Major problem associated with the treatment of tannery wastewater may be due to presence of heavy metals, toxic chemicals, chloride, lime , suspended solids and other by-products formed during tanning processes (Uberoi, 2003; Sreeram and Ramasami, 2003). The tanning process was wholly a wet process which generates a large volume of waste water. This could be further classified into four main categories, storage and beam house operations, tanyard operations, post-tanning operations and finishing operations. The hyper saline wastewater generated in pickling and soaking of hides/skins contain as about 80g/L of NaCl (Lefebvre and

Moletta, 2006). Soaking process is being carried out in tannery to remove salts, any foreign materials such as dirt for leather production. The moisture content (MC) of the natural wet raw skin collected from slaughter house contains 60-65% in order to prevent microbial attack during the transporting operations sodium chloride is being used as a preservative. The dissolved salts, especially chlorides were serious concern when the effluent is discharged into lands/ponds (Lefebvre et al., 2006). The discharge of untreated wastewater containing high Total Dissolved Solids (interms of Sodium chloride/Calcium Chloride) and high organic content was to adversely affect the aquatic life, water potability and agriculture. At present, these soak waste water are being collected and evaporated in solar evaporation pans/thermal evaporators to get dry residue in India. The evaporated residue lacks its reusability characteristics due to the presence of organic pollutants. Hence residues are being stored under shelter as like hazardous solid waste to prevent ground water contamination by leachate. If, these organic pollutants are removed from the soak liquor, then there is a scope for reusability of the evaporated residue and thus avoid the burden of disposal of evaporated residue. Various treatments, such as physico-chemical processes, solar evaporation, mechanical evaporation, thermal evaporation and biological processes were applied to treat saline effluents (Sivaprakasam et al., 2011; Sekaran et al., 2014). However, the physico-chemical techniques are more energy-consuming, and their start-up and running costs are high. Therefore, the saline wastewater often being treated by biological processes after dilution by employing large amounts of microorganisms. But the activities of microorganisms, e.g. bacteria are usually affected due to high salt concentration, which can lead to low COD removal efficiency and bulking of the activated sludge. Conventionally available cultures cannot have efficiency to treat saline wastewaters beyond with the salt contents above 3%. Therefore, saline wastewaters should be treated at lower F/M ratios at low salt concentration. Because high saline (> 1%) concentration cause plasmolysis of bacterial cells and loss in activity are the main challenge for the traditional biological treatment (Ugyur, 2006; Kargi and Dincer, 2000) To overcome this above issue, a more salt-tolerant microorganisms are to be discovered for the wastewater treatment.Soak liquor contains approximately 2500-3500mg/L of suspended solids in the form of proteins, carbohydrates, and lipids. For the treatment of any kind of wastewater suspended solids has to be removed before being taken for other treatment steps (Boopathy et al., 2014).Conventionally, the removal of suspended solids in soak liquor are being removed various coagulating agents, flocculating agents. The addition of chemical agents as flocculants and coagulants may inhibit the treatment efficiency in biological treatment and also adds up additional cost on treatment process (Kumar and Mani, 2007). The coagulants that are usually employed in the treatment of industrial wastewaters are $Al_2(SO_4)_3 \cdot 18\ H_2O$ or $FeCl_3$. However, aluminium and iron in coagulated wastewater effluents considered a human and environmental health. Further, the presence of residual concentrations of Al and Fe may result in phenomena of negatively affecting the subsequent treatment of coagulated wastewater, for example, the scaling of ultra- filtration membranes in advanced filtration systems (Di Bella et al., 2014).Many researchers involved on the development of treatment of wastewater with high saline conditions. There are reports on the development of integrated biological, chemical treatment techniques for the effective removal of saline wastewater (Dincer and Kargi, 2001; Kubo et al., 2001; Sekaran et al., 1996; Dan et al., 2003; Ugyur and Kargi, 2004). At the same time, the concentration of suspended solids is being increased due to cell lysis during biological treatment processes. Biologically, filamentous bacteria may serve as a coagulation/flocculation for the removal of suspended solids in the wastewater. Various approaches have been attempted to cultivate microbial mats including using glass wool, coconut mesh, polyester fiber, silica particles and grass silage as a growth scaffold for the treatment

of saline wastewater (Akyon et al., 2015). In this proposed SOAR process, a regular packing plastic material for packed bed column was used for the growth of biofilm. Apart from removal of organic handling and disposal of sludge also a major task on wastewater treatment. The method of oxic/anoxic/anaerobic process helps in for wastewater treatment with less sludge production(Chen et al., 2003;Saby et al, 2003) Hence, this study focused on the development of oxic/anoxic process in SOAR system for the primary clarification of tannery saline soak liquor.

2. Materials and methods

2.1. Materials

All the chemicals used in this study for the determination of process parameters were procured from Merck (India) and other biological grade chemicals purchased from Himedia, India.

2.1.1. Design and fabrication of Sequential oxic-anoxic bio reactor (SOAR)

A rectangular shaped SOAR reactor was fabricated using acrylic sheet with a dimension of 25.5cmx15cmx15cm as shown in Fig.1. The SOAR comprised of three chambers connected with one another for the continuous flow and treatment of waste water. The total reactor volume comprising of 3.6L (compartment I-1.4L; compartment II-1.2 L and compartment III-1.0L) There are six oxic zone outlets and five anoxic zone outlets are positioned in the reactor. The compartments were packed with commercially available round shaped plastic packing medium (diameter 21mm) used for the adsorption/stripper column for the active surface area to grow bio film for the degradation of suspended and dissolved organic compounds present in soak liquor. Each compartment has an outlet port through which outlet sample was collected at aerobic and anaerobic region of the compartments for the characterization. A provision has been made to for alternating oxic and anoxic conditions to aid the native organisms on the bio film and to acclimatize for maximum removal of organic compounds in wastewater.

2.1.2. Preparation and characteristics of tannery saline waste water (soak liquor)

The saline wastewater used for the present investigation was prepared by taking 1 kg of salted goat skin collected from tannery (CLRI) and soaked in 3 L of distilled water for overnight for the saline wastewater for the experimental work. The soak liquor was allowed to settle for 2 h and cloth filtered to remove floating solids and its subsequent solids. The above solution characterized and presented in Table 1. For the investigation of the presence of suspended solids in different forms such as coarse, free and colloidal state, the initial soak liquor was filtered using three kinds of filtration: normal filtration using Whattman filter paper (NF), GF/A filtration (WF) and by centrifuge (CENT) at 10000 rpm for 20 min. At each stage of the SOAR process, all the parameters were analysed to study the contribution of suspended solids on organic loading rate of wastewater before and after the treatment using SOAR process.

2.2. Methods

2.2.1. Isolation and identification of microorganisms for protease, lipase and amylase activity at saline medium

The biofilm formed from extremophile was collected using phosphate buffer (pH=7) and it was serially diluted with sterile distilled water and the organisms were isolated using Nutrient Agar medium by pour plate method followed by incubated at 40 °C for 24–48 h for the growth of halophilic microorganisms. Microbial colonies, which appeared on the agar plates, were then pure cultured and subjected to qualitative screening for the identification of protease, amylase and lipase producing microorganisms on Skim Milk Agar (SMA) medium, Starch Casein Agar (SCA) medium and

Tri-Butyrin Agar Medium (TBA). Extracellular enzymes producing halophilic microorganisms produced a clear zone of hydrolysis when their appropriate dilutions were spread on the respective agar plates (SMA, SCA and TBA at 3 % NaCl) were incubated at 40°C. Based on the size of the clear zone on the agar plates, the proteolytic, amylolytic and lipolytic organisms were selected and maintained in nutrient agar slants and stored at 4°C.

2.2.2. Analytical methods

The COD, BOD_5, TOC, TDS, TSS, and TS were measured by the methods summarized in standard methods of analysis of wastewater (APHA, 1998).The quantification of protein in soak liquor and degradation studies were measured as per Lowry's method using bovine serum albumin BSA (Himedia) as the standard at λ650 nm using Cary100 UV – visible spectrophotometer. Standard curves for concentration calculations were plotted from 0, 10, 25, and 50 mg/L bovine serum albumin (BSA) diluted from a concentrated stock of BSA. The lipid estimation was determined by phosphovanilin method and the OD was taken at 533nm. For the determination of mucopolysaccharides 0.5 ml of sample solution was taken to which 0.5% aqueous solution of phenol, 2.5 ml of sulphuric acid was added and incubated for 20 min. The absorbance was measured at 490 nm. The protease activity was done by Anson method.The lipase activity was find out by taking Olive Oil as the substrate followed by acid base titration using Phenolphthalein indicator.The amylase activity was done by DNS method.

The estimation of amino acid was determined by Ninhydrin method.The estimation of fatty acids was determined by acid base titration using phenolphthalein as indicator. The estimation of glycerol was determined by the sodium periodate method.The estimation of glucosamine was carried out by Ethrlichs reagent method.The estimation of glucuronicacid acid was carried out by using carbazole reagent.

2.2.3. Instrumental analysis

The 16 r-DNA analysis was carried for the identification of organism strain-3 has protease, lipase and amylase activity. The SEM analysis of the bio film of plastic material in SOAR was done by scanning device attached to a JEOL JM 5600 electron microscope at 20 kV (JEOL, Japan) accelerating voltage with a 5–6-nm electron beam to confirm the presence of filamentous bacteria (FB). The degradation of soak liquor was studied by UV visible absorption spectra using CARY 5E UV–VIS-NIR Spectrophotometer, USA. The fluorescence spectrophotometer study was carried out to determine the excitation and emission characteristics of both soak liquor and the degraded products of SOAR, in range of λ 200-800nm (Cary Eclipse, USA). For the determination of Total organic carbon and Total nitrogen were analysed by TOC-TN analyser (SHIMADZU Model no: SHIMADZU CORP 00291, India).

3. Results and discussion

3.1. Characteristics of Tannery saline wastewater (soak liquor)

The initial characteristics of soak liquor implies the presence of organic bio molecules such as proteins, fats and mucopolysaccharides with 6-7% (w/v) of NaCl. The other constituents such as amino acids, fatty acids, glycerol, glucuronicacid and glucosamine were present in trace concentration. The presence of suspended solids in different sizes such as coarse suspended solids, normal settable suspended solids and colloidal suspended solids in soak liquor was evaluated by subjected to normal filtration (NF) using normal Whattman filter paper, filtration using GF/A paper and centrifugation at 10000 rpm for 20 min. The detailed characteristics of soak liquor were calculated and presented in Table 1. These results imply the presence of a high organic load of carbonaceous and nitrogenous species present in the soak liquor and which varies with each type of

filtration. Though the BOD:COD ratio was in an appreciable level (0.37), thus clearly indicates that the conventional biological treatment processes still pertain due to high TDS of soak liquor (6-7%). Then the inlet was passed through the reactor at different retention time. The samples were collected from the SOAR outlet and the analysis of all parameters were carried out according to standard methods of water analysis. In order to find a suitable route for the treatment of wastewater an anaerobic, anoxic and aerobic reactor system has been studied by inclusion of an anaerobic Side-Stream Reactor (SSR) in the sludge recirculation line. There are reports on such inclusion of an anaerobic SSR in the sludge recirculation line of an aerobic Sequencing Batch Reactor (SBR) and anoxic, oxic reactor (Li et al., 2014; Coma et al., 2013; Yagci et al., 2015; Zhou et al., 2015).

3.2. SOAR reactor

SOAR has been used to digest and degrade suspended and dissolved matter present in SOAK LIQUOR, by alternating the oxic and anoxic environment associated with the bio film formation on the plastic material. The inoculums for the SOAR were initially enriched by the addition of tannery soil acclimatized sewage culture to 10% of soak liquor and the percentage of the culture continuously increased each day up to 5 days to facilitate the acclimation of culture with the organisms of soak liquor.

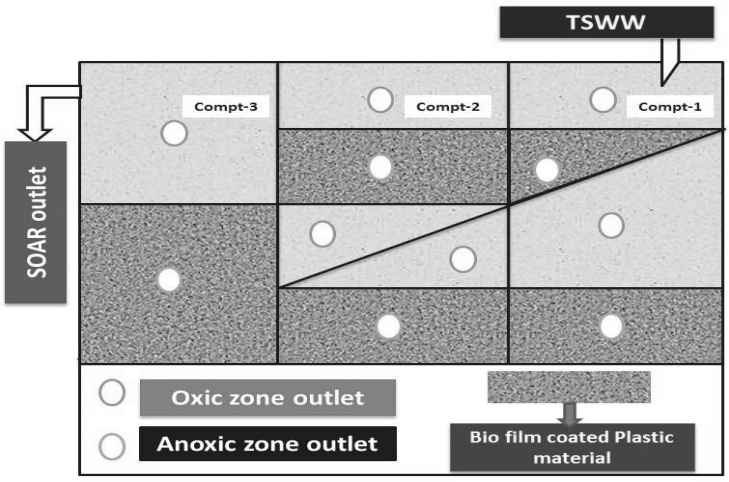

Fig.1 Treatment of soak liquor by SOAR reactor

The maximum removal efficiency was observed for the HRT operated at 12 h and illustrated that the reduction of proteins, lipids and mucopolysaccharides in soak liquor was found to be 47.4%, 70.4 % and 44.8% respectively. Although the reduction appeared to be normal for a SOAR outlet, it was highly important that the nature and the difficulty involved with the treatment of biomolecules was minimized as a result of change in the structure of these molecules by the organisms present in the biofilm of SOAR and these were confirmed through instrumental analysis. This may enhance the further removal of organics from soak liquor using biological treatment after SOAR process. The characterization of SOAR outlet indicates that the formation of smaller units of biomolecules of soak liquor after degradation by the halophilic organisms as shown in Table 2. The smaller units are amino acids formation after protein degradation; fatty acids and glycerol formation after Lipid degradation and glucosamine, glucuronicacid formation after MP's degradation. The protein molecules of soak liquor may be converted as the hydrolysates (oligo, deca and dodeca peptides) with different molecular weight. Hence, the amino acid content of SOAR outlet not exceed to higher in value compare with protein degradation. The removal of suspended solids was found to be about 72.6% as shown in Table 1. The removal of suspended solids and dissolved organics with respect to different sizes such as coarse, normal settable and colloidal solids were evaluated by subjected to normal

filtration (NF), filtration using GF/A paper and centrifugation and the results were shown in Table.1. This results mentioned that the fragmentation/removal of biomolecules was increased for SOAR outlet rather than for initial soak liquor upon different filtration systems. Also, SOAR outlet showed the removal of COD and BOD in the level of 36.8% and 31.2% respectively by microbial degradation using halophilic organisms as shown in Table.1. The increase in values of ORP (-302.2mV) in SOAR outlet indicates the degradation of organics of soak liquor.

Table. 1 Characteristics of soak liquor and SOAR outlet at different stages of filtration

Soak liquor				
Parameters	TSWW	NF	WF	CENT
pH	6.72	6.34	6.87	6.54
COD	5766	4987	4363	4051
BOD	2160	1820	1560	1440
BOD:COD	0.374	0.364	0.357	0.355
NH_3	294	279	255	241
TOC	924	757	664.5	567
TN	388	345	310	288
Protein	734	614	489	410
Amino acid	15.88	13.7	13.3	7.8
Lipids	138	98	76	53
Fatty acid	14.8	14.4	8.8	5.4
Carbohydrates	113.6	87.29	74.8	67.94
Glucosamine	26.81	14.12	13.8	11.78
Glucuronic acid	31.93	14.22	18.2	10.94
Sulphate	541	537	528	522
Chloride	58981	58450	57976	57452
ORP, mV	-526.7	-527.1	-526.9	-528.3
Total solids	69210	65431	64722	630936
Suspended solids	-	3779	4488	5274

SOAR outlet				
Parameters	SOAR	NF	WF	CENT
pH	7.09	7.14	7.03	7.23
COD	3644	3073	2750	2415
BOD	1486	1257	1092	967
BOD:COD	0.407	0.409	0.397	0.400
NH_3	276	254	248	240
TOC	483	449.9	418.4	378
TN	344	326	302	284
Proteins	386	346.4	270	242.22
Amino acids	29.03	17.13	14.96	14.061
Lipids	40.84	26.63	25.25	23.46
Fatty acids	24.4	22.8	22	21.2
Carbohydrates	62.70	55.43	52.02	47.93
Glucosamine	85.49	51.16	58.73	40.71
Glucuronic acid	50.03	40.15	39.94	33.32
Sulphate	521	502	498	496
Chloride	54677	54302	54288	54242
ORP, mV	-302.2	-301.4	-308.7	-304.4
Total solids	63288	62256	60272	57950
Suspended solids	-	1032	1984	2322

All the parameters except pH, BOD: COD and ORP, were expressed in mg/L

3.3. Isolation of microorganisms for thedigestion of suspended and dissolved solids present in soak liquor

The biofilm formed around the round shaped plastic packing material from the SOAR was collected for the isolation of microorganisms in phosphate buffer (pH=7) and it was serially diluted to calculate the colonies. Based on the serial dilution, the colonies were pour plated using Starch Casein Agar, Tributyrin Agar and Calcium Caseinate Agar medium with 3% of NaCl saline concentration. Then the plates were incubated at 37^0C for 24 h for growth of organisms as a response to different kinds of substrate with varying levels of saline condition. Totally five different microbial colonies were isolated from the biofilm collected from SOAR. Among which Strain-3 showed a positive response for

all three activities and hence it was considered for further experimental studies. Other four microorganisms exhibited different activity towards the substrate as depicted in Fig. 2.

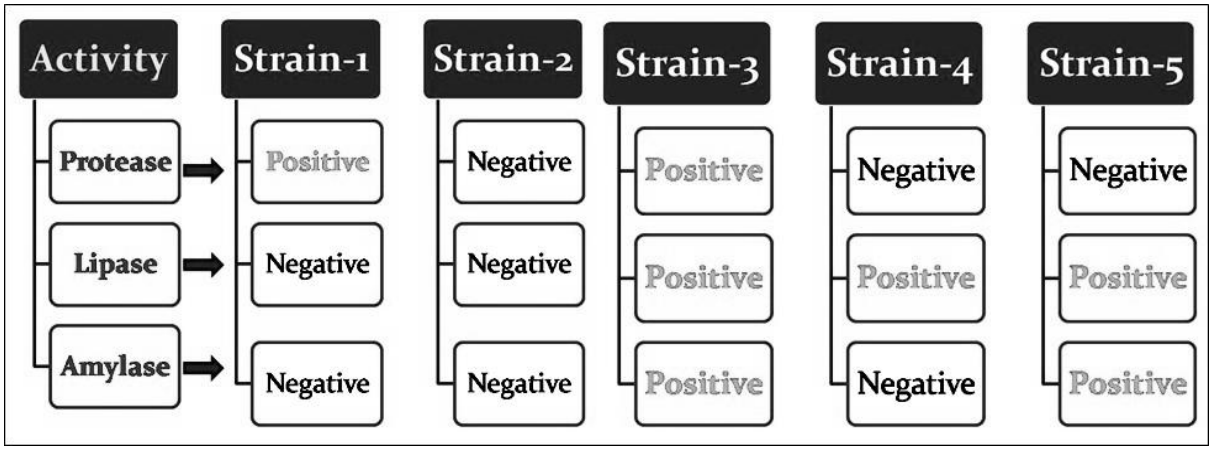

Fig. 2 Organisms having different activities isolated from bio film of the material was taken from SOAR

The production of amylase enzyme from Strain-3 was evaluated by zone of clearance i.e. blue colour disappearance was observed on Starch Casein Agar (SCA) in presence of 0.1N iodine solution onto the SCA plate. The zone of clearance on SCA indicated that these microorganisms utilized the starch as substrate in saline medium (3% (w/v) for their growth. The production of protease was determined by zone of clearance observed on Calcium Caseinate Agar (CCA) and for the ability to synthesize lipase was observed using Tri-Butyrin Agar (TBA) as a selective media. From these analyses confirmed that the selected Strain-3 has ability to synthesize all three enzymes (Amylase, Protease and Lipase).The microorganisms isolated from the plastic packing material of SOAR showed degrading performance on protein, carbohydrate and lipid, which were cultured and its optimum conditions were determined for the maximum production of enzyme. The optimised conditions were found to be time, 48 h; pH, 7; and temperature, 40^{o}C. The 16S-rDNA sequencing analysis confirmed that the isolated strain-3 is *Bacillus cereus*. The quantity and activity of enzymes extracted using acetone were found to be 110 (protease), 1320 (lipase), 1386 (amylase) U/ml respectively. The results confirmed that the presence of halophilic organisms was responsible for the degradation of organics present in soak liquor.

3.4. *Instrumental evidences*

3.4.1. *UV-Visible and fluorescence studies*

UV-Visible spectro photometer and fluorescence studies were carried out to confirm the organic degradation in soak liquor by SOAR process, and the results were shown in Fig. 3 (a) and (b). The absorption intensity was observed to be decreased with HRT which denoted the degradation of carbonaceous matter (proteins, lipids and mucopolysaccharides) present in soak liquor. The absorption peaks observed at 200-230nm may be attributed to presence of polypeptide backbone of protein presence and the peaks observed between 260-300nm may be due to the presence of aromatic amino acids of proteins in soak liquor (Ni et al., 2008)

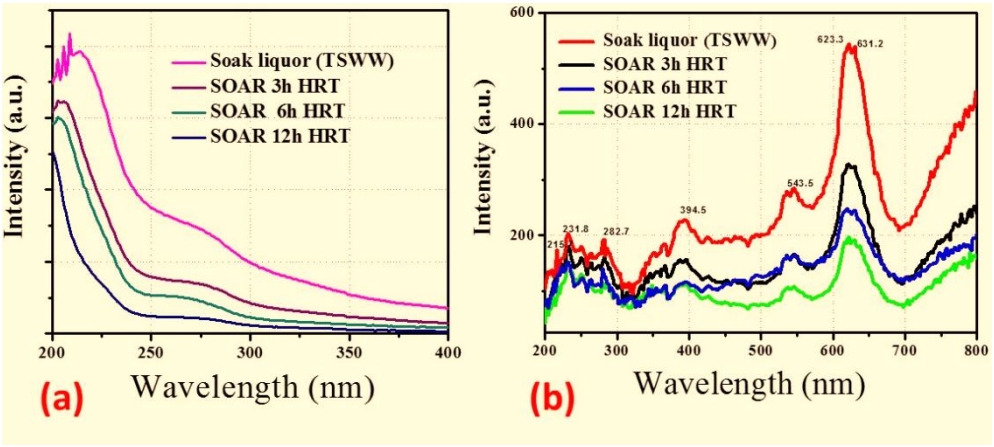

Fig. 3 (a) UV-Visible and (b) fluorescence spectrum of soak liquor and SOAR processed samples

A clear evident on decrease in absorption intensity for treated soak liquor than initial wastewater as shown in Fig**. 3**. Similarly the fluorescence spectrum showed that the peaks observed at 623.2, 631.2, 543.5, 394.5, 282.7, 231.8 and 215.7 for initial soak liquor denoted the presence of organic pollutants. The excitation peaks observed at 282.7 and 231.8 denoted the presence of polypeptide and amino acid components in the initial soak liquor (Wang et al., 2009). The fluorescence peaks where found to be decreased significantly after SOAR collected at different HRT such as 3h, 6 h and 12 h, and thus confirming the degradation of the organic by SOAR process. The characteristic fluorescence peaks of proteins vary for their active and denatured state (Flora et al., 1998). Hence, the microbial degradation of suspended particles and the dissolved organics by SOAR has proved to be an effective process for the primary treatment of soak liquor.

3.4.2. **SEM analysis**

The surface morphology of the microorganisms present in the plastic packing material was characterized by SEM analysis and it was found that they belong to the group of filamentous bacteria as shown in Fig. 4(a)-4(d).

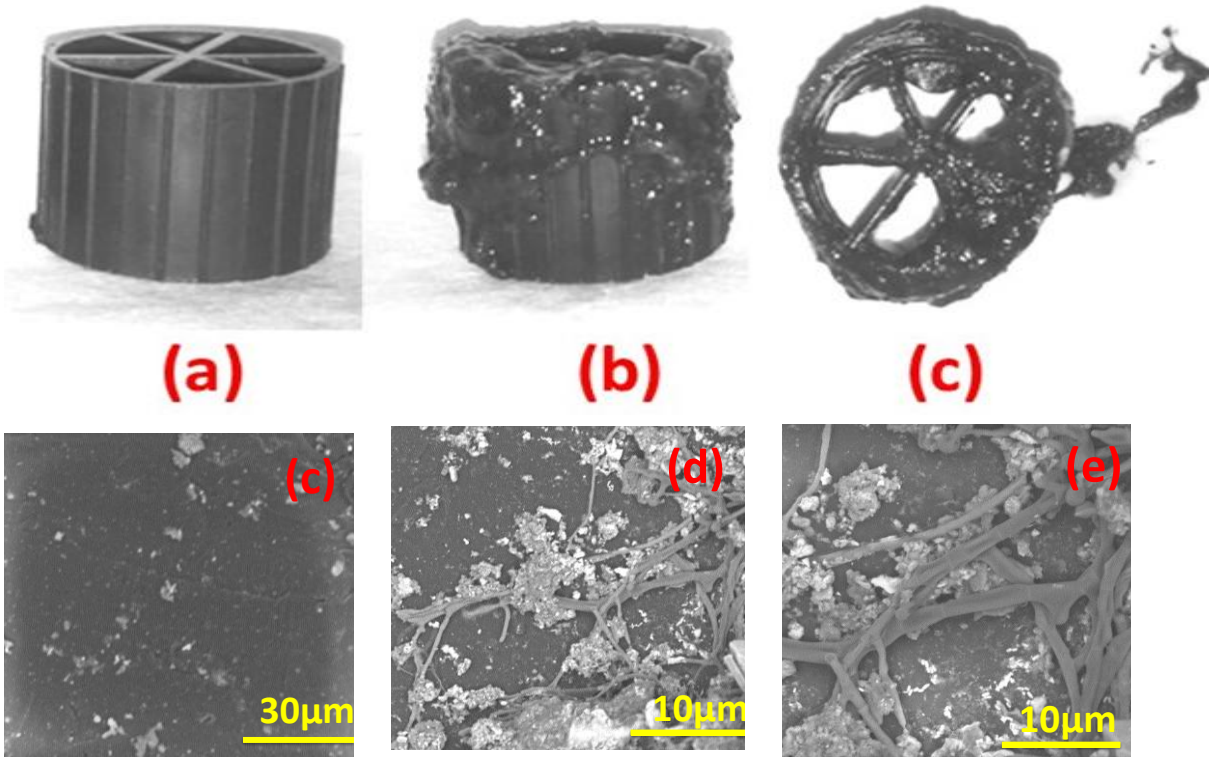

Fig. 4 Normal and SEM images of (a, c) the round shape plastic packing material (b, d) and (c, e) after the growth of bio film over on packing material reason for the digestion of suspended and dissolved organics of soak liquor in SOAR

The initial stage of the bio-film formation on the plastic material has been shown at 30 µm resolution in Fig 4 (a) which indicated that there were more the empty spaces available for the growth of the microorganisms. The growth of the microorganisms in clusters leading to the formation of the bio film lead to the occupation of these spaces on the plastic packing material depicted at 10 µm resolution in Fig. 4 (b) which is attributed to the digestion of the dissolved organic compounds in the soak liquor due to microbial metabolization (Akyon et al., 2015; Motten et al., 2013)

4. Conclusions

This study concludes that the tannery saline soak liquor was primary treated using a sequential oxic anoxic bioreactor by using the mixture of halophilic organisms and FB for the removal of suspended and dissolved organic compounds at high TDS environment (6-7%). The removal of suspended solids was achieved upto 72.6% at 12 h HRT. Totally five bacterial strains were isolated from the bio film formed on the plastic packing material and they displayed different characteristics such as ability to synthesize enzymes like protease, lipase and amylase at saline condition. The Strain-3 (Bacillus cereus) was found to synthesize all the three enzymes by utilizing the components in the soak liquor as the substrate, with enzyme activity for protease, lipase and amylase calculated to be 110, 1366, and 1305 U/ml respectively. Instrumental analysis such as UV-Visible, Fluorescence spectroscopic analysis also confirmed the degradation of dissolved and suspended organic matter present in the soak liquor. The morphology of the micro-organisms constituting the bio film on the packing material of the SOAR before and after the treatment process was observed and the digestion of the excess suspended matter in the sludge was attributed to the presence of filamentous bacteria in the bio film. Hence, the combined sequential oxic anoxic bio reactor system promises to be a more beneficial primary treatment option for soak liquor in future.

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SFS P-27

HEXAVALENT CHROMIUM REDUCTION BY CHROMIUM TOLERANT *BACILLUS* FROM TANNERY WASTE

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Cr (VI) designated as a priority pollutant or Class A pollutant by the United States Environmental Protection Agency (USEPA), cause mutations and cancer in humans. Tanneries are the major source of chromium pollution, releasing about 40 - 25,000 mg/L of Cr in their effluents. In addition to this, leakage due to improper handling and faulty storage containers also adds to the accumulation of chromium in the environment. Therefore treatment of tannery effluent containing hazardous compounds becomes necessary prior to their final discharge into the environment. Biological treatments arouse great interest because of their cost effective, safe and lower impact on the environment. Certain species of bacteria are capable of transforming much toxic and highly mobile Cr (VI), into less toxic and less mobile Cr (III) and thus chromate bioremediation is of considerable interest. In view of the potential applications of Cr (VI) reduction, the present study was aimed to isolate and enrich the Cr (VI) resistant strains from the tannery effluents and to mediate biosorption and detoxification of hexavalent chromium into non-toxic compound. An indigenous chromium-reducing bacterial strain wasisolated from the tannery solid waste located at Pallavaram and was identified as *BacillusSp*. based on its morphology, physiology and bio-chemical characteristics. This particular strain when grown in media containing $K_2Cr_2O_7$, could resist concentrations as high as 300mg/L of Cr (VI) and was able to reduce the entire chromate when cultured in as low as 10 mg/L after 48 h exposure of incubation.

Scanning electron microscopy (SEM) revealed the distribution of chromium on bacterial cell surfaces. Cr (VI) treatment brought several changes in the FTIR spectrum of bacteria treated with Chromium. This isolated organism can therefore be successfully used for reduction of significant amount of Cr (VI) in the natural environment as well.

Key words: Chromium, tanneries, bioremediation, *Bacillus*, SEM, FT-IR.

1. Introduction

Leather making is an environmentally challenging process. Tanning is the key processes that renders stability to the skin matrix against microbial degradation, heat, sweat, etc. (Rida et al., 2012). Chromium has found extensive use in tanning industry mainly because of the good quality of leather obtained. When the wastewaters containing chromium are discharged into the environment, they pose a serious problem to the quality of the latter (Onyancha et al., 2008). Cr(VI) causes severe carcinogenic, systemic, immunological, and developmental effects (Manahan, 2003) due to its rapid permeability through biological membranes and subsequent interaction with intracellular proteins and nucleic acids (Horitsu *et al.* 1978). Conventional techniques for removing dissolved heavy metals including chemical precipitation, chemical reduction and carbon adsorption ion exchange, solvent

extraction, reverse osmosis, membrane process, evaporation and other electrolytic and chemical methods (Abraham and Bai, 2003, Rengaraj et al., 2003)are ineffective when applied to low strength heavy metal ion concentration and have certain disadvantages which include production of secondary waste products, oxidation of Cr(VI)that makes it unstable (Park et al., 2005), high operating and maintenance cost, low efficiency, operational complexity, high energy requirements and incomplete metal removal (Ucun et al., 2002). Phytoremediation is another method which although is cost effective, is extremely time consuming. Hence there is a dire need to search for other new methodologies that would be efficient and cost effective at low concentrations of this pollutant. The methods using sorbents of biological origin (Babel et al., 2003) for removal of heavy metals are gaining interest among researchers due to several advantages that include possibility of metal recovery, good performance and low cost of the process. Biosorption employs inexhaustible, inexpensive and nonhazardous materials and natural affinity of biological compounds for metallic elements (Kratochvil and Volesky, 1998) and it does not produce toxic sludge and does not create any problem to ecosystem. The most frequently studied biosorbents for chromium by bacteria include *Pseudomonas aeruginosa* (Ganguli and Tripati, 2012), Bacillus sp. (Guojntun and Xiaohua, 2009) andfungi include *Ganoderm lucidum* (Krishna and Philip, 2005) and*Aspergillus niger* MTCC 2594 (Sandana mala et al., 2006). A recent examination on the accumulation of different metals in the water, soil and vegetables grown around the SIPCOT industrial area of Ranipet, India has reported the exceeding mean level of metals beyond the safe limits (Sujatha et al., 2013).

Highly soluble Cr(VI) in bacteria, is transported rapidly across the cell membranes via the sulfate pathway and reduced in the cytoplasm to trivalent Cr(III). Trivalent chromium, which interacts with proteins and nucleic acids, however, is far less soluble than hexavalent chromate and does not pass through biological membranes. Sludge deposition from tanning industry with “chrome liquor” provides a natural environment for enrichment of chromium-resistant bacteria. Chromium-resistant microorganisms from such chromium contaminated sediments have been isolated by several investigators (Horitsu *et* al. 1978; Luli *et al.* 1983). The reduction of Cr(VI)to the less toxic Cr(III), either extracellularly or intracellularly, could find useful application in the treatment of industrial waste.

The present study was an attempt to evaluate potential of the bio reduction of toxic hexavalent chromium to less toxic trivalent chromium by chromium-resistant bacteria isolated from the tannery effluent sediments of tanning industries located at Pallavaram Town, Chennai.

2. Materials and methods

Collection, Isolation, identification and characterization of chromium reducing bacterial strains

Tannery effluent sediment samples were collected in sterilized screw capped plastic containers from the outlets of tannery near Pallavaram town in Chennai District of TamilNadu, India. The effluents were stored at 4ºC to avoid changes in its characteristics.

Hexavalent chromium tolerant bacterial isolate was isolated using Nutrient Agar plates amended with potassium dichromate ($K_2Cr_2O_7$) and incubated at 37ºC for 24 h. The isolate used for the Cr(VI) biosorption was enriched by a series of transfers by gradually increasing the Cr(VI) concentration from 10 to 300 mg/L. The selected bacterial isolate were characterized morphologically under microscope after Gram staining and biochemically for the activities of Indole production, MR-VP test,

Catalase, Nitrate and Citrate utilization and identified upto generic level by employing the standard methods as described in Bergey's manual of Systemic bacteriology (Holt et al., 1994).

Metal analysis

The total Cr content and other heavy metals present in dried tannery solid waste sample were determined using Atomic Absorption Spectroscopy (AAS) (Perkin Elmer, USA, model Analyst 300) in a digestion mixture of HNO_3:$HClO_4$ (6:1) (NIOSH, 1987).

Antibiotic resistance

Antibiotic resistance of the isolate was tested by the standard agar diffusion method using commercial discs (Dia-Himedia) impregnated with antibiotics such as bacitracin (10 units), Chloramphenicol (30 mcg), Penicillin (10 mcg), Polymixcin B (300 mcg), gentamycin (10 mcg) and Neomycin (30 mcg). Inhibition zones in diameters were measured in cm using a caliper and classified as Resistant (R), Intermediate (I) and Susceptible (S) according to the standard antibiotic disk sensitivity testing method (DIFCO Manual 10^{th} ed. DIFCO Laboratories Inc).

Cr biosorption

The reduction of Cr(VI) with the selected isolate P1 was carried out under varying conditions such as initial Cr(VI) concentration (10-160mg/l), pH (3-9), temperature (25-40^{o}C) to optimize the parameters in nutrient broth medium. Flasks containing 50 mL of NB medium supplemented with 80 mg/l Cr(VI) were inoculated with exponential phase inoculum and incubated at 37°C. Control experiment without the isolates was also maintained to ensure that removal was due to microorganisms and not due to any other abiotic reason or precipitation. The amount of Cr was estimated by Diphenyl carbazide method at an OD of 540nm at time intervals of 24, 48, 72 and 96 h respectively (Snell and Snell 1959). The reduction in the concentration of Cr(VI) was taken as the reducing ability of the isolates. As the bio-reduction of Cr(VI) by bacterial isolate was good up to 80mg/l concentration, the characterization of reduced product associated with bacterial cells was carried out with this concentration by SEM and FTIR.

High Resolution Scanning Electron Microscope (SEM)

The bacterial cells associated with Cr reduction, after 48h incubation was filtered, washed with buffer (pH-8.0), fixed in 3% glutaraldehyde and again washed with Tris-HCl buffer followed by de-ionized water several times. The ethanol dried sample with unloaded and Cr(VI) loaded biomass were mounted on gold coated aluminium stab under vacuum and micro-photographed by HRSEM at 200kv (Quanta 200 FEG).

FT-IR analysis

A qualitative and preliminary characterization of the main functional chemical groups present on the bacterial biomass responsible for heavy metal biosorption was studied through FT-IR. A raw sample of bacterial biomass and biomass loaded with Cr(VI) were analyzed using an Infrared spectrophotometer (IR) (Model; ABB MB3000) following KBr disk technique. Absorbance/transmittance of FT-IR was analyzed with reference to standard values (Silverstein et al., 1991).

3. Results and Discussion

Identification and characterization

A Cr resistant bacterial colony showing maximum tolerance towards Cr(VI) was isolated based on its growth observation in $K_2Cr_2O_7$. The morphology and biochemical tests assigned the isolate to the genus *Bacillus* and named as P1. Table 1 present the biochemical nature of the isolate. The sludge from the tannery waste disposal site used for isolation of Cr(VI) reducing bacteria contained 71.6 mg/kg and the pH was 7.8. Despite the high concentrations of Cr in contaminated soils and sediments, occurrence of a substantial quantity of bacterial populations has been reported. The count of bacteria on Nutrient agar containing Cr(VI) decreased with increasing concentrations of Cr(VI). This may have been due to the inability of sensitive organisms to grow on Cr-supplemented plates. Similar declines in bacterial populations of the Cr-contaminated sediments were also reported by Luli et al.(1983) and Losi and Frankenberger (1993). For chromate-resistance, the isolate was screened primarily on chromate supplemented solid media and was found resistant to 300 mg/L of Cr(VI).

The present study revealed that the Cr(VI) resistant *Bacillus sp* P1was capable of removing significant concentration of Cr (VI). However, the highest Cr uptake of P1 was observed with 10mg/L at 48 h incubation time. Microorganisms can be used for the removal of Cr(VI) from the environment owing to their ability of Cr(VI) tolerance and reduction (Camargo et al., 2003). Chromium- resistant bacteria isolated from industrial waste materials had been studied to be used for remediation purposes of metal-polluted environments (Faisal et al., 2004). The isolate P1 was studied for its temperature, pH dependence of the Cr(VI)-reducing ability at different initial Cr(VI) concentrations (data not shown). The optimal temperature was found to be 37^{o}C and pH was 9 for maximum Cr(VI) reduction. It is in agreement with Sultan and Hasnain (2007) who also found the optimal temperature as 37^{o}C for maximum Cr (VI) reduction by *Ochrobactrum intermedium* SDCr-5.

Metal analysis

The total chromium content of tannery effluent was found to be 70.75mg/kg. The other heavy metals like Cd, Pb, Cu, Ni and Zn were found to be 1.00, 1.69, 3.00, 5.45 and 4.97mg/kg respectively (Table 2).

Antibiotic resistance

As heavy metal resistance is linked with antibiotic resistance, the chromate resistant isolate P1 was tested for its sensitivity to antibiotics and results shown in Table.3 and Fig 1. The isolate was highly resistant (HR) to Bacitracin and penicillin, intermediate to Neomycin and Polymyxin and sensitive to Gentamycin and Chloramphenicol. This multiple antibiotic resistance of this isolate is also correlated with high degree of resistance to different heavy metals (Basu et al., 1997).

Cr biosorption

SEM

The biosorption of Cr by P1isolate was analyzed by scanning electron microscopy to understand its surface morphological characterization of bacteria. The bacterial cells without Cr treatment are elongated in shape and appeared to be plump having smooth surfaces in a loosely-bound form (Fig.3). After incubating in 80 mg/l of Cr(VI) for 48 h, the bacterial cells were coated with either the precipitate of reduced Cr(III) or adsorbed Cr(III) (Dhal et al., 2010-139).SEM showed occurrence of flakes like morphology with inscribed cluster formation after usage of metal ion. Konstantinidis et al., stated that the outer envelope of the bacterium cells may change when grown in the presence of

heavy metals. It has been reported that, with progressive increase in chromium concentration, the cell becomes both longer and wider. However, further increase in chromate led to decreased cell size (Srivastava and Thakur 2007). In fact, this change in cell shape due to the exposure of heavy metals is an adopted mechanism to resist the toxicity of the heavy metals. Here, the stress-induced morphological changes might have important role to keep up metabolic activity and survival and hence the absorption of chromium from the medium/effluent. The first mechanism for removal of heavy metals from the environment involves extracellular binding. Cationic heavy metals attach to some anionic compounds on the bacteria surface. So, binding of heavy metals to the surface of bacterium cells changes the shape of the bacterium (Fig 3). The results of the present study showed that the binding of Cr(VI) by P1 altered the shape of bacterium cells compared to the control.

FT-IR analysis

The functional groups present on the bacterial cell wall responsible for the adsorption of Cr(VI) and other heavy metals due to non-specific binding of metal ions with them and FTIR spectra are shown in Fig 4. Analysis of absorption of chromium untreated and chromium treated bacteria samples showed significant functional group interaction by means of shifting the absorption frequencies as seen in the spectra. The shifts at 2924cm^{-1} to 2942cm^{-1} denotes C-H. Alkane stretches and shifts are denoted by 1052cm^{-1} to 1087cm^{-1}. Higher frequency bands are more intense in anhydrides and the lower frequency band is more intense in cyclic hydrides. New bands corresponding to cro_4^{-2} also appeared at 905cm^{-1} and 957cm^{-1}. Generally, heavy metals affect its bio-specific interaction with the expression and suppression of certain functional groups on bacterial cell wall which might help the bacterial strain to tolerate the toxicity of the heavy metals (Kamnev 2008).

4. Conclusion

From this study, it is therefore concluded that the highly toxic Cr(VI) has bio-remediated by the bacterial isolate of this study to produce less toxic trivalent chromium. This isolate could be used for the reduction of Cr(VI) which is likely to be formed from tannery effluent or for the treatment of the effluent generated from Cr discharging units.

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Table 1- Biochemical Test for the identification of Bacteria

Characteristics	Gram stain	Indole	MR	VP	Citrate	Catalase	Nitrate
Result	-	-	+	-	+	+	-

Table 2. Heavy metals in Tannery Sludge

Metal	Chromium	Cadmium	Copper	Nickel	Lead	Zinc
Concentration (mg/Kg)	70.75	1.00	3.00	5.45	1.69	4.97

Table 3. Antibiotic resistance in terms of diameter of inhibition zone in cm

Antibiotics	Zone of inhibition (cm)
Bacitracin (10units)	-
Chloramphenicol (30mcg)	2.1
Penicillin (10mcg)	-
Polymyxin (300mcg)	1.6
Gentamycin (10mcg)	2.4
Neomycin(30mcg)	1.7

Figure 1.Antibiotic resistance disk Figure 2.Reduction of Cr(VI) by bacillus Sp.

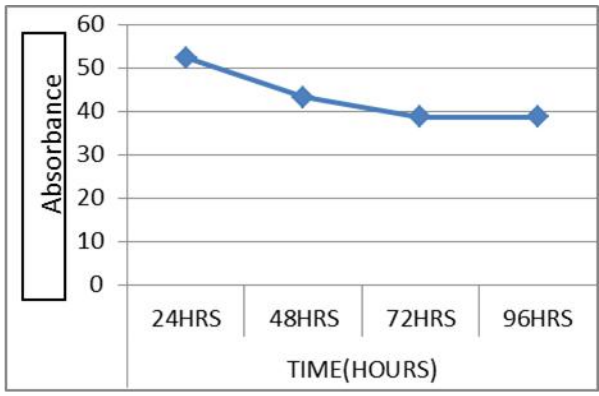


Figure 3. SEM micrographs of Bacillus sp. P1. [A] In the absence of Cr (control) and [B] exposed to Cr (VI) indicating modification in bacterial shape and chromium aggregation

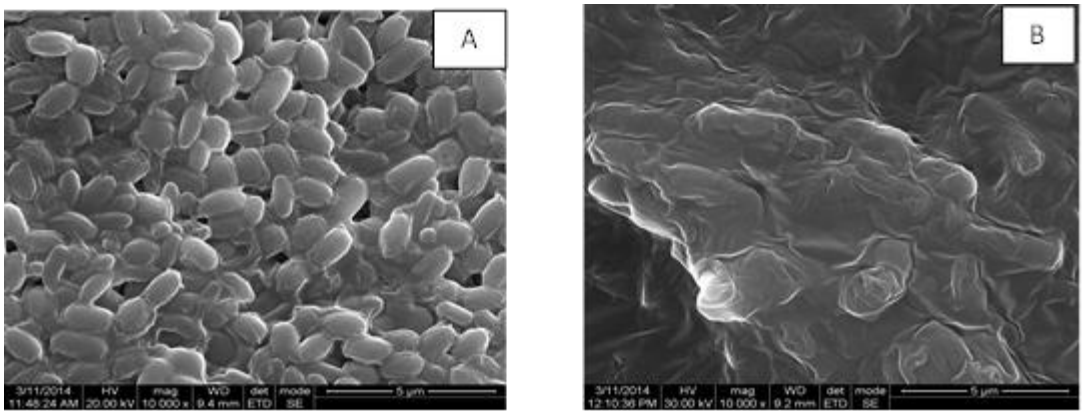
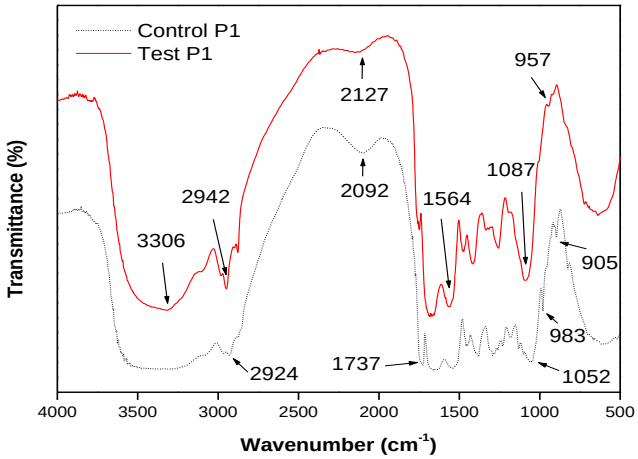


Figure 4. FTIR spectra of the *Bacillus sp*. P1 untreated (control) and treated with 80 mg/l of Cr(VI) in nutrient broth medium after 48 hrs.



ECT P-25

CHROMIUM REMOVAL FROM THE TANNERY WASTEWATER USING BIOSORBENT

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Disposal of wastewater from the tannery causes a serious environmental pollution. In tanning process, most of the tanneries use basic chromium sulphate as tanning agent where only 60% is taken up by the pickle pelt and the remaining 40% chromium reminded as the solid or liquid phases especially in spent chrome liquor. Discharging of chromium after chrome tanning operation is the most common pollutants in tannery. Removal or recovery of chromium from the tannery wastewater is an important issue. In this study, an investigation was made to remove the chromium from wastewater using the prepared low cost charcoal of plant bark on the removal of high concentrated chromium tanning wastewater. The effectiveness of chromium removal was examined by investigating different parameters e.g., charcoal dose, contact time.The chromium removal efficiency was obtained at optimized conditions 99.9%. This approach will enable a substantial reduction of environmental pollution. The use of low cost indigenous biosorbent could be better option for the removal of chromium from tanning wastewater.

Keywords: Tannery, Chrome tanning wastewater, biosorbent

1. Introduction

Chromium is discharged into the aquatic systems from the anthropogenic activities e.g. tanning industries, electroplating, metal finishing, textile industries and chromate preparation. Contamination of water, soil or sediment by the chromium is a significant concern for the environment. It could enter into human food chain from the water, soil or sediment.

Many works have been studied on the toxicological effects of chromium presence into various food items on the human health (Cubadda et al. 2003; Bratakos et al. 2002; Uluozlu et al. 2009). Chromium has several oxidation states e.g. di-, tri-, penta-, hexa-; among them, thetrivalent and hexavalent state of chromium can be mainly existing in the aquatic environment (Evangelou 1998). Although chromium (III) is considered as an essential trace element for some metabolic function in the human body (Kalidhasan et al. 2009), a long-term exposure to Cr(III) is recognized to cause allergic skin reactions and cancer (Eisler 1986). On the other hand, chromium (VI) can be toxic and carcinogenic (Matos et al. 2009; Yalçin and Apak 2004).

In tanning process, 90% tanning industry use basic chromium sulphate as tanning agent (Aravindha et al. 2004) where 60% chromium is taken up by the pickle pelt and the remaining 40% chromium remained as the solid and liquid wastes especially in spent chrome liquor (Fabibi et al. 1997). It is reported that chromium content in the wet blue spent chrome liquor ranges from 2656-5420 mg/L (Hashem et al. 2015). Therefore, the level of chromium in the spent chrome liquor is strictly regulated in many countries.
Removal of chromium from the various industrial wastewaters, especially tannery wastewater is an important issue.

Good numbers of methods have been developed to remove chromium from the wastewater. Chemical precipitation and electrochemical precipitation are widely used for the removal of heavy metals. Both the techniques have a significant problem in terms of disposal the precipitated wastes (Ozdemir et al. 2005; Meunier et al. 2006); the ion exchange technique does appear to be economical (Pehlivan and Altun 2006). Many attempts have been carried out for the removal of heavy metals with low-cost adsorbent e.g., wood materials (Shukla et al. 2006), agricultural by-product (Chuah et al. 2005), natural zeolite (Erdem et al. 2004), clay (Marquez et al. 2004) and eggshell and powered marble (Elabbas et al. 2015).
In this study, an investigation was made to remove the chromium from the wastewater using the prepared low cost charcoal of *Syzygium cumini* bark on the removal of high concentrated chrome tanning wastewater. The effectiveness of chromium removal was examined by investigating different parameters e.g., charcoal dose, contact time, pH effect.

2. Material and Methods

2.1Adsorbent preparation

The bark of *Syzygium cumini*was collected from a local Saw mill, Khulna, Bangladesh. The bark was cut into small pieces and sun-dried. Then, the sun-dried bark was burnt at 450-550°C, cooled and grinded to make a powder using a mortar. The grinded charcoal was sieved on 80-mesh and preserved for the experiment.

2.2 Sample collection

Chromium containing wastewater was collected from the SAF Leather Industries Ltd., Jessore, Bangladesh. The wastewater containing chromium sample was collected in a polyethylene container, pre-washed with diluted nitric acid, and immediately transported to the laboratory for experimentation.

2.3 Reagents

The reagents: nitric acid (Merck KGaA, Germany), sulphuric acid (Merck KGaA, Germany), perchloric acid (Merck, India), *N*-phenyl anthranilic acid (Merck, India), ferrous ammonium sulphate (Merck, India) and glass beads (Loba Chemie, India) were purchased from a local scientific store, Khulna, Bangladesh.

2.4 Treatment of chromium-containing wastewater

Batch-wise chromium removal examination was performed with the prepared charcoal. The scheme for the treatment of wastewater is shown in Fig. 1.

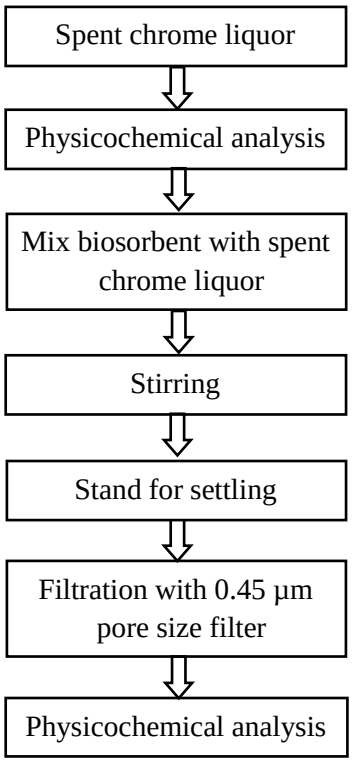

Fig. 1 Scheme for the chromium removal treatment process

Firstly, physicochemical parameters of the untreated chromium-containing wastewater were analyzed and filtered through 0.45 µm pore size filter. Secondly, 75 mL filtrate wastewater was mixed the prepared charcoal. The charcoal mixed wastewater was stirred over a fixed time period and the mixture was allowed settling for a fixed time period. After settling, the mixture was filtered through 0.45 µm pore size filter. Chromium and physicochemical parameters of the supernatant were analyzed.

2.5 Physicochemical analysis

Physicochemical parameters of the untreated and treated spent chrome liquors: total dissolved solids (TDS) and total suspended solids (TSS) were determined gravimetrically following the standard methods of APHA (APHA 2012). pH of the spent chrome liquor was measured by using the pH (UPH-314, UNILAB, USA) meter. Electrical conductivity (EC) and salinity were measured by using the conductivity meter (CT-676, BOECO, Germany) meter. The dissolved oxygen (DO) was measured by the DO meter (DO-580, BOECO, Germany). Before measuring, all the meters were calibrated with the standard solutions.

2.6 Determination of chromium

Chromium content in the untreated spent chrome liquor and after treatment in the filtrate was performed by the titrimetric method by following the official methods of analysis of Society of Leather Technologist and Chemists (1996) official method of analysis (SLC 208). A 50 mL sample volume was taken in 500 mL conical flask. 20 mL concentrated nitric acid was added followed by 20 mL perchloric acid/sulphuric acid mixture; the flask was gently heated and boiled until the mixture had become a pure orange-red color and continue boiling for one minute. The flask was removed from the heating source and as soon as ebullition has ceased; rapidly the flask was cooled by swirling in cold water bath. Carefully, 100 mL distilled water was added with a few glass beads and boiled for 10 minutes to remove free chlorine. Then, 10 mL 30% (v/v) sulphuric acid was added and cooled to room temperature. The mixture was titrated with freshly prepared 0.1N ferrous ammonium sulphate solution with six drops of *N*-phenyl anthranilic acid as an indicator. The end color was indicated by a color change from the violet to green.

2.7 FT-IR Analysis

The Fourier transform infrared spectroscopy (FTIR) study was carried out to obtain adsorption spectrum of pure and chromium-loaded bisorbent. The FTIR spectra were recorded using Fourier transform infrared spectrometer (FTIR 1600, Perkin-Elmer) between 400 and 4000 cm^{-1}.

2.8 Process optimization

Tests were carried out to optimize the chromium removal parameters: charcoal dose, contact time and settling time. The optimized conditions were established by investigating the removal efficiency of chromium.

3. Results and Discussion

3.1 Characteristics of the spent chrome liquor

Characteristics of wastewater are shown in **Table 1**. Results indicate that wastewater had strong pollution loads because it contained higher quantities of pollutants e. g. high chromium content, suspended solids, total dissolved solids (TDS), strongly acidic (4.0<pH). Wastewater containing chromium is threatening to the environment, it is very important to treat the liming wastewater properly to reduce its polluting potency.

Table 1 Data comparison with Bangladesh standard (MoEF 1997)

Parameters	Raw sample	Treated sample	Bangladesh Standard
Cr (mg/L)	2920.24±0.73	3.46±0.31	2.0
pH	3.85±0.1	8.9±0.3	6–9
TDS (mg/L)	42.2±0.05	47.95±0.2	2100
EC (mS)	71.85±0.1	80.5±0.42	1.20
Salinity (ppt)	43.8±0.14	50.8±0.14	–

3.2 Optimization of adsorbent

The dose of adsorbent is the most important parameter that has a significant effect on the chromium removal. Chromium removal efficiency on adsorbent dose and respective pH changes are depicted in Fig. 2. It is clear from the figure that chromium removal efficiency was increased with the increasing of adsorbent dose.

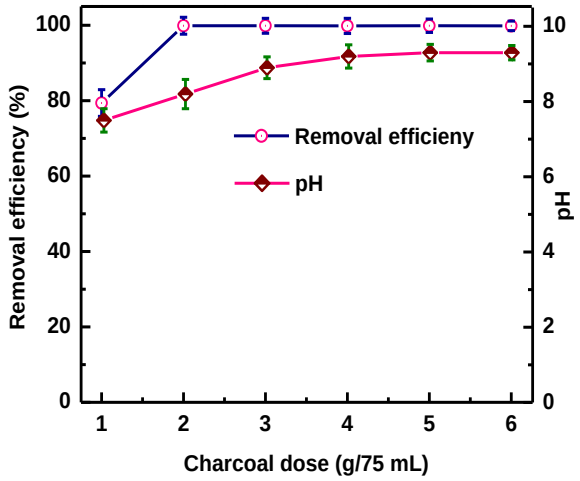

Fig. 2 Chromium removal efficiency on adsorbent dose

At adsorbent dose 3 g for 75 mL, chromium removal efficiency was 99.88% and after that there was no significant change occurred. It was also perceived that with increasing the adsorbent doses increasing the mixture pH; gradual increase the pH simultaneously increases the chromium removal efficiency. Therefore, it was anticipated that the maximum removal of chromium occurred with 3 g adsorbent dose for every 75 mL wastewater where pH was 8.9.

3.3 Optimal contact time

Contact is one of the important for the removal of chromium in the spent chrome liquor. In Fig. 3 shows the chromium efficiency on contact time.

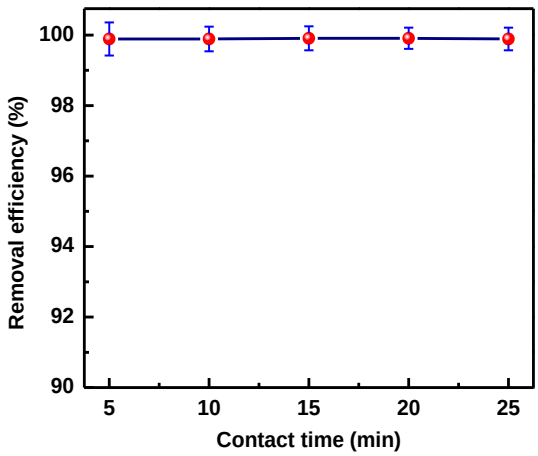

Fig. 3 Chromium removal efficiency on contact time

It is clear from the above figure that chromium removal efficiency was gradually increased with increasing the contact time. The chromium removal efficiency for 5 min, 10 min, and 15 min was 99.89%, 99.89%, and 99.91%, respectively and after that removal efficiency was unchanged. Thus, it was assumed that extreme removal of chromium happened at 15 min contact time.

3.4 FTIR Analysis

FTIR spectrum of pure and chromium-loaded bisorbent is inserted in Fig. 4. The figures show a shift in the peak intensity. This gives an indication of the various functional groups which are responsible for the removal of chromium by bisorbent.

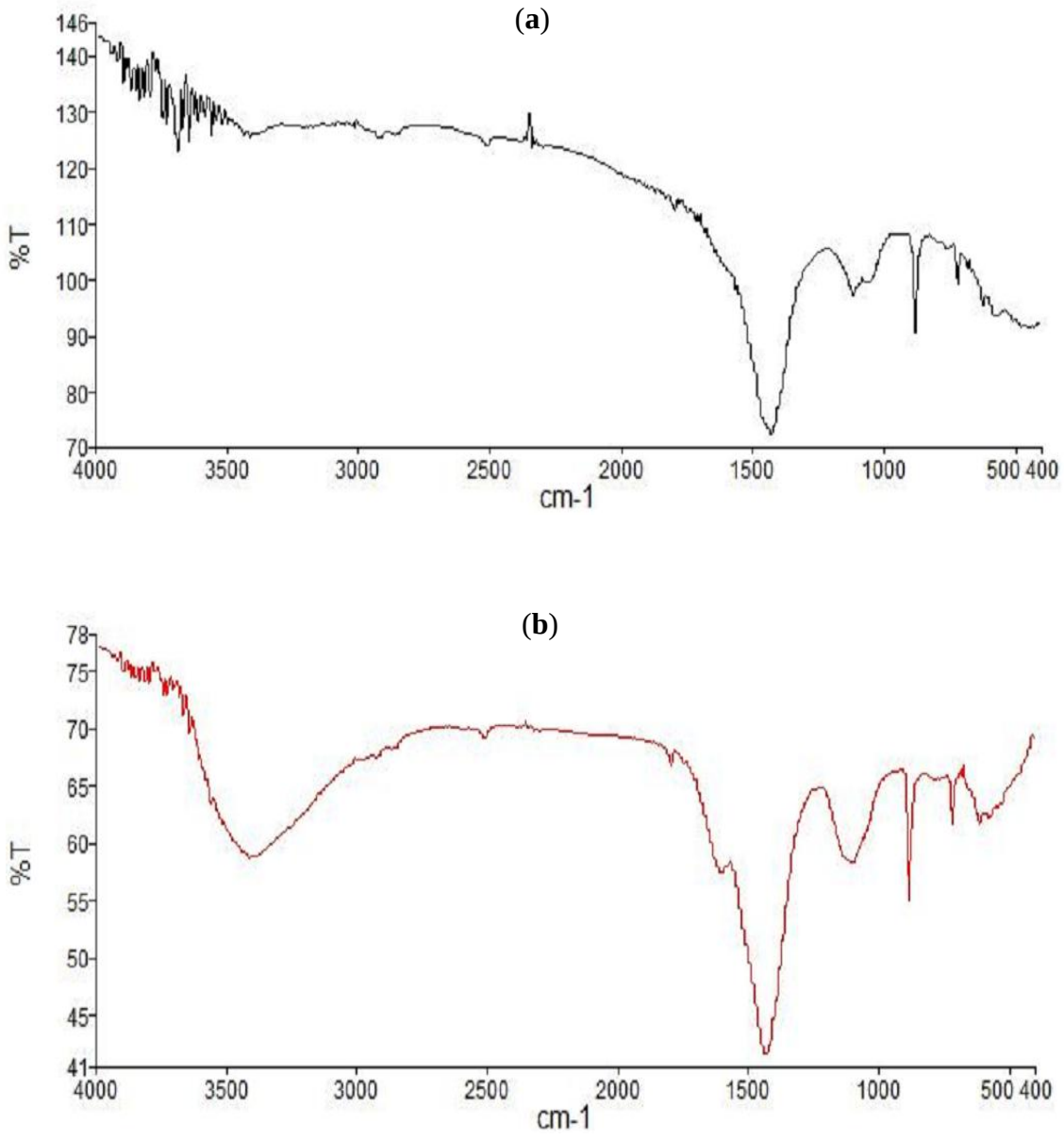

Fig. 4 FT-IR spectrum of pure biosorbent (**a**) and chromium-loaded bisorbent (**b**)

3.5 Treatment process efficiency

The results of the treatment process with optimum conditions are represented in Table 1. The physicochemical parameters were obtained after all stages of treatments were: chromium 3.46 mg/L, pH 8.9±0.3, TDS 48.51±0.2 mg/L, EC 69.35±0.21 mS, and salinity 48.42±0.21 ppt. The highest percentage of chromium removal of chromium was 99.9%. It seems that after treatment pH was within the discharged level although other parameters e.g. TDS, EC and salinity were slightly increased. In batch-wise experiment higher percentage of chromium was removed from the tannery wastewater by *Syzygium cumini*bark charcoal as bisorbent.

4. Conclusion

Batch-wise spent chrome liquor was treated to remove chromium. The removal efficiency of chromium at optimized condition was obtained 99.9% although others parameters were slightly increased. The investigation indicates that it was an effective technique to reduce toxic substances that will minimize pollution load from the spent chrome liquor. The study could be helpful to design the treatment of spent chrome liquor in house prior to discharge and the adsorbed chromium could be recovered by desorption.

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ECT P-27

AN ECO-FRIENDLY SHORT TERM PRESERVATION OF GOAT SKIN USING INDIGENOUS PLANT LEAF PASTE

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Hide/skin is the basic raw materials for the leather production, which is the by-product of meat industry. The degradation of hide/skin starts within several hours after the death of the animal if it is left untreated. Application of common salt (sodium chloride) is the most popular preservation method of hide/skin; it preserves the skin by its dehydrating ability and bacteriostatic effect. The hostile effect of sodium chloride is that it generates a huge amount of pollution in the form of total dissolved solids (TDS) and chlorides during leather processing. In the present study, an investigation was made to preserve goatskin using indigenous plant leaf paste. The preservation process was assessed by monitoring different parameters e.g. shrinkage temperature, hair slip, putrefaction odor, moisture content, nitrogen content, and bacterial count in comparison to the conventional salting method. Results indicate that the leaf paste could be used as curing agents to preserve goat skin. Preparation with 10% leaf paste + 10% NaCl could preserve the goat skin for a period of 28 days. This less-salt preservation method reduces pollution load e.g., chlorides and TDS in soaking operation by 51% and 41.6, respectively.

Key words: Skin, Preservation, Pollution, TDS, Plant leaf paste

1. Introduction

Animal skin is the basic raw materials for the leather industry. About 60-70% (w/w) moisture and nearly 25-30% (w/w) protein are the main constituents of skin makes the materials susceptible to bacterial attack. The degradation of skin starts within 5-6 h after the death of the animal if it is left untreated (Kanagaraj et al. 2005). The bacteria on raw skin may penetrate the most important part of the skins (corium) from the flesh surface in 8-12 h; the bacteria may also form serious grain peeling and voids in the skin in 15-24 h (Emel and Meral, 2011). Quality of leather depends on the presence of intact protein materials. Therefore, proper curing process is an important to prevent the proteins degradation of the skin from putrefaction due to bacterial attack before being processed into leather.

Common salt (sodium chloride) is widely used for the short term preservation of skins. Application of 40-50% salt preserves the skin by its dehydration ability and bacteriostatic effect. It reduces the moisture content of skin from 70 to 30% which makes the skin non-conducive for bacterial growth while bacteriostatic effect check the bacterial growth on animal skin (Kanagaraj et al. 2001, 2005). The hostile effect of sodium chloride (NaCl) is that it generates a huge amount of pollution in the

form of total dissolved solids (TDS) and chloride during leather processing. The wet salting method pays more than 40% of TDS and 55% chlorides in the tannery effluent (Covington, 2011). Till to date there is no available technology for treating the effluent containing a high concentration of neutral salt especially sodium chloride (Kanagaraj et al. 2005). The significant level of chlorides renders the ground water saline and reduce the fertility of soil.

To reduce pollution during tanning or cleaner tanning, numerous researchers are continuously trying in developing the alternative preservation methods with salt-free or less salt. Several alternative preservation methods are being developed. Physical preservation methods are energy intensive and economically unviable, alternative chemicals methods are either not practicable or have other environmental impacts. The attempts reveal several chemical preservation methods e.g. potassium chloride (Bailey and Gosselin 1996), boric acid (Hughes 1974), soda ash (Rao and Henrickson 1983), benzalkonium chloride (Cordon et al. 1964), antibiotics (Berwick et al. 1996), bacteriocin (Kanagaraj et al. 2014), formaldehyde (Sharphouse and Kinweri 1978), silica gel (Kanagaraj et al. 2001), Vantocil IB (Haines 1973), chlorites and hypochlorites (Margold and Heidemann 1977), sulphates (Vankar and Dwivedi 2009), and bisulphite-acetic acid (Hopkins et al. 1981). These approaches are good but in some cases they are potentially hazardous or are not virtually possible or are not cost-effective. Solution of this problem lies in developing green technologies to keep a check on pollution levels. The present study was attempted with the use of *Ficus carica*leaf paste formulation in combination with the less amount of common salt.

In this present study, an attempt was made more ecofriendly preservation method for goat skin with *Ficus carica*leaf paste with or without sodium chloride. The curing process was monitored for a month and evaluated by examining different parameters e.g., moisture content, hair slip, bacterial count, extractable nitrogen, and shrinkage temperature in comparison to the conventional salt curing method.

2. Material and Methods

2.1 Materials

To examine the possibility of *Ficus carica* for the preservation of skin, freshly flayed goat skins of average weight 1 kg per skin were purchased from a nearby local slaughter house at Khulna, Bangladesh. The *Ficus carica*plant leaf was used for this study which was collected from near university Campus, Khulna University of Engineering & Technology, Khulna, Bangladesh. The leaf was paste using laboratory mortar and used for the experiments.

2.2 Chemicals

Analytical grade chemicals were used for the determination of biochemical and pollution parameters. Commercial sodium chloride was used for the preservation experiments and commercial auxiliaries were used for pre-tanning and post-tanning processes to make shoe upper leathers.

2.3 Experimental systems for preservation

Primary experiments were conducted to define the minimum quantity of salt required for the preservation. Four (04) samples of size 30 cm × 30 cm was cut from the freshly flayed goat skin. The different percentages (w/w) of preserving materials were offered with different combinations based on the raw weight as shown in Table 1 and assessed periodically (1^{st}, 2^{nd}, 4^{th}, 7^{th}, 14^{th}, 21^{st} day of preservation) for the physical changes e.g., odor, hair slip, and moisture content. Based on primary experimental results, the optimum concentration of salt for preservation was found to be 10% (w/w) with the leaf paste. After assuming the amount of salt in the proposed preservation method; the method was compared with the conventional wet salting preservation method. Freshly flayed two (02) goat skin was collected from the local slaughter house; one piece was taken for the control (50% NaCl) and ii) another piece was used as experimental sample (10% NaCl + 10% leaf paste). After applying preserving materials, the skins were piled up flesh to flesh and kept for preservation at surroundings temperature (28±2°C) for 28 days. The preservation approaches was critically assessed by determining moisture content (%), shrinkage temperature, hair slip, odor, bacterial count and total extractable nitrogen at different intervals. To carry out these analyses, a small piece of goat skin samples were collected on the 1^{st}, 2^{nd}, 4^{th}, 7^{th}, 14^{th}, 21^{st}, and 28^{th} day of preservation time.

Table 1 Leaf paste optimized in preservation method

No.	% of curing agents
01	10% leaf paste
02	5% NaCl + 10% leaf paste
03	10% NaCl + 10% leaf paste
04	15% NaCl + 10% leaf paste

2.4 Monitoring the preservation method

2.4.1 Determination of moisture content

The moisture content (%) of the goat skins were determined by taking about 5 g of the preserved skin pieces from the experimental and control samples at different periods of curing storage according to the standard procedures (Bureau of Indian Standards, BIS, 1971). The samples were weighed in a suitable silica crucible and placed it for 3 h in an oven at 105±1°C. The samples cooled in a desiccator and weighed. The procedures were repeated for extra 1 h or more until the samples mass remains constant (within 0.1 mg difference). Each experiment was conducted in triplicate.

2.4.2 Determination of extractable nitrogen content

The cured samples of known weight (5 g) were kept in distilled water ten times its weight, shaken well in a conical flask at 200 rpm for 30 min to extract the soluble nitrogenous compounds. The extract was then filtered through a filter paper, digested, and the amount of nitrogen was determined by Kjeldahl method (APHA, 2012). Each experiment was conducted in triplicate.

2.4.3 Determination of extractable nitrogen content

The cured samples of known weight (5 g) were kept in distilled water ten times its weight, shaken well in a conical flask at 200 rpm for 30 min. A volume of 1 ml extract liquor was taken in 9 ml of

sterile water in a vial and shaken well to make uniform suspension of bacteria. After that, 0.1 ml of the corresponding diluted solution was poured in a sterile Petri plate and molten nutrient agar at 40°C was poured. The Petri plate was shaken gently to get uniform distribution of the bacteria. The Petri plate was incubated at 37°C for 48 h. The number of colonies on the agar media was counted using colony counter. Each experiment was conducted in triplicate.

2.4.4 Hydrothermal stability determination

The SATRA shrinkage meter was used to determine the shrinkage temperature of the preserved goat skins. The temperature at which the specimen starts shrinking was noted as shrinkage temperature of the particular skin. All the experiments were performed in triplicates.

2.4.5 Leather processing

Conventional leather processing method was performed for the present approach preserved goat skins. After 28 days of preservation, both the control and experimental goat skins were processed to manufacture shoe upper crust leathers following the conventional leather making procedures.

2.4.6 Pollution load generated during leather making

Pollution load in soaking operation of leather processing was determined. The wastewater in soaking operation both from the control and experimental was collected and analyzed for chlorides (Cl^-), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and total suspended solids (TSS) following the standard methods of APHA (2012). All the experiments were analyzed in triplicates.

2.4.7 Physical strength of leather

The produced crust leathers were conditioned at temperature 20 ± 2°C and relative humidity 65 ± 2 % over a period of 48 h; samples were taken from the specified sampling location. The properties such as tensile strength, elongation at break, and bursting strength were assessed following ISO 3376:2011 and ISO 3379:2015.

3. Results and Discussion

3.1 Optimization of leaf paste

The percentage leaf paste combination with NaCl for preservation of goat skin is shown in Table 2. It seems that with the all conditions preserved goat skin was intact. But the physical feel (hand feel) was different. Preservation without salt the skin was very hard and it will be difficult to process in drum or in paddle. Preservation with 10% leaf paste and 5% NaCl, skin was medium hard that will be hindrance to process in drum or paddle. Therefore, in this approach preservation with 10% leaf paste and 10% NaCl was considered to carry out the experiment.

Table 2: Leaf paste optimized in preservation method (21days)

No.	% of curing agents	Hair slip	Odor	Physical feel
01	10% leaf paste	No	No	Hard
02	5% NaCl + 10% leaf paste	No	No	Medium hard
03	10% NaCl + 10% leaf paste	No	No	Flexible
04	15% NaCl + 10% leaf paste	No	No	Soft and flexible

In Table 3 and Table 4 show the moisture consents and shrinkage temperature of the new approach preservation method. The shrinkage temperatures of the preserved goat skins with the various conditions were unchanged. It seems that based on shrinkage temperatures of the conditions of preserved goat skins were in good. It is clear from Table 4 that moisture contents of the preserved goat skins were gradually decreased. In case of goat skin preservation with 10% leaf paste and 5% NaCl + 10% leaf paste, on 21st day moisture contents was 23.2% and 29.6% respectively. On the other, on 21st day, moisture contents in the preserved goat skins with 10% NaCl +10% leaf paste and 15%NaCl + 10% leaf paste were 39.3% and 41.6%, respectively. It is obvious that preservation using only leaf paste goat skin was flint like feel and it was difficult to rehydrate. It is also noticeable that with increasing NaCl moisture content in preservation method moisture content was increased due to NaCl having the hygroscopic property. The moisture content in the preserved goat skin with 10% NaCl + 10% leaf paste 39.3% which value was close to the moisture content (43.1%) in the control method (50% NaCl).

Table 3: Shrinkage temperature of the preliminary experiment (21 days)

Duration	10% leaf paste	5% NaCl + 10% leaf paste	10% NaCl + 10% leaf paste	15% NaCl + 10% leaf paste
Fresh	64.1	64.3	65.1	64.3
1st day	65.1	65.8	65.1	66.2
4th day	65.8	66.1	65.3	66.4
7th day	65.4	66.3	65.4	66.4
14th day	65.5	66.4	65.6	66.3
21st day	65.4	66.5	65.7	66.4

Table 4: Moisture content of preliminary experiment (21 days)

Duration	10% leaf paste	5% NaCl + 10% leaf paste	10% NaCl+ 10% leaf paste	15% NaCl + 10% leaf paste
Fresh	77.54	58.3	66.7	70.1
1st day	60.16	50.12	50.5	58.7
4th day	44.6	41.9	48.4	49.0
7th day	27.7	32.2	44.1	44.1
14th day	25.4	30.7	40.5	43.2
21st day	23.2	29.6	39.3	41.6

3.2 Effectiveness of the preservation method

3.2.1 Total extractable nitrogen

The extractable nitrogen content in experiment and control is depicted in Figure 1. The extractable nitrogen was calculated by the amount of nitrogen extracted in aqueous phase. Total extractable nitrogen is the best indicator whether bacteria degrades in the animal skins or not. The putrefaction of skin proteins result the release of nitrogenous components, which lead the emission of putrefaction odor and hair slip.

In this study, physical assessments e.g., hair slip and odor of the preserved goat skin by control and experiment were observed; there were no hair slip and odor during preservation period up to 28 days. In fresh goat skin, extractable nitrogen contents were 1.5 g/kg and 3.4 g/kg for control and experimental respectively. On 1st day, 4th day and 7th day extractable contents were in goat skins significantly different but there were no hair ship or odor of the preserved skins by control and experiment. On 14th day, 21st day and 28th day, extractable nitrogen contents in both goat skins were almost same. It is noticeable that combination of 10% NaCl and 10% leaf paste preserves the goat skin for 28 days.

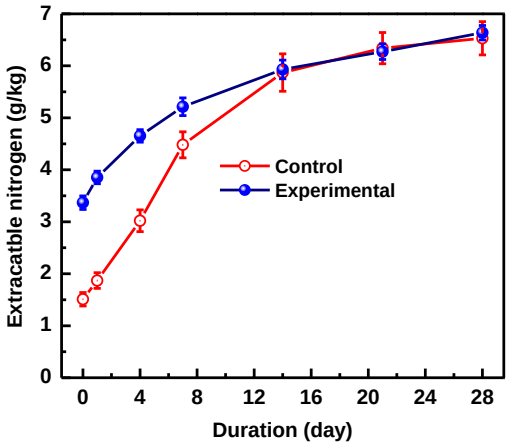

Figure 1: Extractable nitrogen content in preserved goat skin by control and experimental methods

3.2.2 Bacterial count

Bacteria count of the control and experiment preservation of the goat skins is shown in Table 5. On 4th day, the bacterial count was for control and experimental 1.74×10^{5}/gand 3.9×10^{9}/g respectively. On day 7th, 14th and 21st, bacterial count of the experimental preserved goat skin was less in comparison of the control preserved goat skin; preservation in the present approach (10% NaCl and 10% leaf paste) has biocidal effects which inhibit the bacterial population. Although on day 28th, bacterial count was higher in the experimental preserved goat skin than in control preserved goat skin. However, there were no hair slip, odor in the present approach preservation method by using 10% NaCl and 10% leaf paste.

Table 5 Bacterial count (CFU/g) in the preserved goat skins

Duration	10% NaCl + 10% leaf paste	50% NaCl
Fresh	1.23×10^{5}	3.2×10^{3}
1st Day	1.64×10^{4}	8.4×10^{9}
4th Day	1.74×10^{5}	3.9×10^{9}

7th Day	2.72×10^5	2.1×10^7
14th Day	2.06×10^5	4.6×10^6
21st day	13.8×10^5	1.7×10^6
28th day	16.4×10^5	5.1×10^5

3.2.3 Moisture content

Raw skin contains about 60-70% moisture which is favorable condition for bacterial growth. The moisture content (%) of preserved skin is considered an important indicator that can be used to evaluate preservation method. The moisture content in the experimental (preservation with 10%leaf paste + 10% NaCl) goat skin in comparison with the conventional method is shown in FigURE 2 during the period of 28 days. There is no significant variation in moisture content between the experimental and control.

It can be seen from Figure 2, moisture content was same both in experimental and control methods within the first 24 h. On 4th day, moisture content was little higher (5.7%) in experimental but there was no sign putrefaction which may be due to the potential antibacterial aids of the *Ficus carica*leaf paste against degrading microorganisms.On 7th day, moisture content was 3.8% higher than the conventional preservation method. Subsequently, in the both preservation methods, moisture content was gradually decreased and it was lower than the critical moisture content (50%). Moisture content was almost constant from the 14th day to 28th day and the percentages of moisture content in experimental was 1.2% to 3.7% higher than the control methods. It is obvious that there was no skin degradation e.g., hair slip, odor etc.

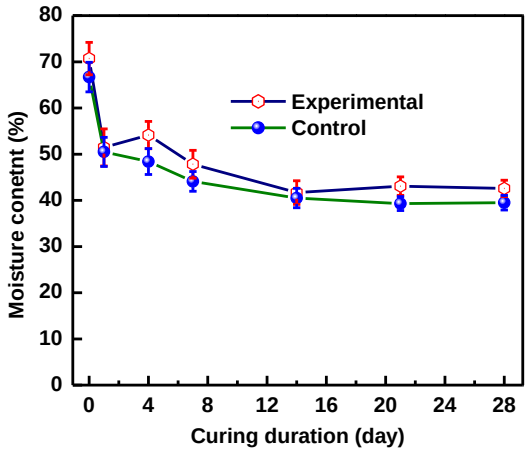

Figure 2: Moisture content of preserved goat skin in control (50% salt) and experimental method (leaf paste 10+ 10% salt)

3.2.4 Hydrothermal stability

The hydrothermal stability (shrinkage temperature) of collagen is considered as a significant property for the assessment of the animal skin quality because it indicates indirectly any structural deterioration of the skin protein. The shrinkage temperature is the measurement of the breakdown

of stabilizing linkages and the bases for the type of interactions existing in the collagen matrix (Babu et al., 2012). The purpose of this parameter of the study was to know whether the proposed preservation method had any effect on the deterioration of collagen matrix. The hydrothermal stability of the experimental (preservation with 10% leaf paste + 10% NaCl) goat skin in comparison with the conventional method is shown in Figure 3 during the period of 28 days.

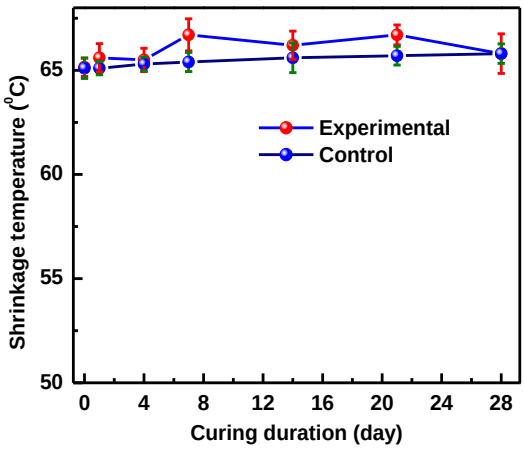

Figure 3: Shrinkage temperature of preserved goat skin in control (50% NaCl) and experimental method (10% leaf paste + 10% NaCl)

The shrinkage temperature of experimental skin shows marginal differences in comparison with control preserved skin. In Figure 3 shows that up to 4th day (fresh, 1st day and 4th day) there is no significant difference in shrinkage temperature for experimental and control methods. On 7th, 14th and 21st day, shrinkage temperatures were little higher in experimental (66.7°C, 66.2°C and 66.7°C) than conventional (65.4°C, 65.6°C and 65.7°C) preserved skins. However, on 28th day, the shrinkage temperature was for experimental and control was same (65.8°C). Therefore, it can be decided that *Ficus carica* leaf paste based preserving does not modify the stability of the collagen protein matrix in skin.

3.2.5 Pollution load in soaking operation

Pollution load generated in soaking operation of the preserved goat skins for both control and experimental samples were depicted in Table 6. It seems that the chloride and TDS load were greatly reduced when the 10% NaCl + 10% leaf paste was used in preservation in place of the control salt. Even though there was little decrease in the BOD and COD levels in the experimental soaking wastewater compared to the control. The main pollution problem of the leather manufacturing: chloride and TDS were reduced 51% and 41.6% respectively in the experimental soaking wastewater.

Table 6: Pollution load generated in soaking of preserved goat skins

Sample	Cl^- (mg/L)	TDS (mg/L)	BOD (mg/L)	COD (mg/L)
Control	18224 ± 203	42260 ± 517	1260 ± 36	5250 ± 63
Experimental	8925 ± 09	24660 ± 143	1142 ± 13	4484 ± 41

3.2.6 Physical properties of leather

In Table 7 shows the organoleptic properties and physical strength of the crust upper leather of experimental in comparison with the control. The crust leathers were assessed for softness, grain tightness, fullness and smoothness. The tabulated physical properties in Table 7 indicate that the physical strengths e.g., tensile strength, grain crack of the experimental skin preserved with 10% leaf paste and 10% NaCl are comparable with that of the corresponding control sample. The elongation at break (%) and load at grain crack (kg) values were fulfilled required values. It could be concluded that the present approach for preservation the goat skin in combination with 10% leaf paste and 10% NaCl reduce the salinity in soaking operation.

Table 7: Physical properties of processed control and experimental leather

Parameters	Experimental	Control	Requirements (Kanagaraj et al. 2001)
Tensile strength (kg/cm^2)	226.14	244.2	200
Elongation at break (%)	44.6	39.6	40-65
Bursting strength:			
Distension at grain crack (mm)	8.0	8.3	7
Load at grain crack(kg)	32.0	43.0	20

4. Conclusion

The novel preservation system based on *Ficus carica* leaf paste in combination with less salt formulation could be a cleaner preservation choice to the conventional wet salting preservation methods. Preparation with 10% leaf paste + 10% NaCl could preserve the skin for a period of 28 days. The physical properties of the produced leather were fulfilled the requirement of shoe upper. This less-salt preservation method reduces pollution load e.g., chlorides and TDS in soaking operation by 51% and 41.6, respectively. The method could be a viable option to preserve goatskin which could reduce the pollution load during leather processing.

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IVL P-17

FABRICATION OF COMPOSITE FROM DECHROMED LEATHER SHAVINGS FOR INSOLE

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The processing of conversion of putrescible hide/skin into imputrescible leather generates huge amount of solid waste. One of the potential solid wastes generated from leather industry is chrome shavings, and its disposal is increasingly becoming a huge challenge on disposal to tanners due to presence of chromium. The present study aims to develop sustainable technology for management and valorization of chrome shavings by the process of dechroming and preparing composite from the dechromed fibre. Investigations were carried out to remove chromium from chrome shavings by treating with organic acids. Oxalic acid yields best dechroming among diammonium oxalate, oxalic acid, and citric acid. Then delimed shavings was incorporated with various chemicals to obtain define properties and finally coagulant was used for sheet forming. The mixture was then poured on nylon net into aluminum sieve. The fabricated composite sheet was dried and pressed. The fabricated composite sheets were inspected and characterized for their physical properties. The chromium removal efficiency from shavings was obtained 85%. The tensile strength and elongation at break of the finished composite were 222.7 ± 2.5 kg/cm^2, 24.2 ± 0.15%, respectively. The results indicate that the fabricated composite could be used in the footwear and leather products industry. The present approach has dual benefits for the tanner: i) it allows the production of new valuable product for the commercial use and ii) it could reduce the environmental impact from the tannery.

Keywords: Chromium, Leather shavings, Dechroming, Organic acid, Composite, Insole

1. Introduction

Leather industry plays a significant role in the economy of country in terms of its contribution to domestic market and export which consumes by-product of meat industry as raw material. Now leather production is advancing due to the increase in meat consumption. These leathers are used as raw material in many sectors such as footwear industry, bag industry, clothing industry, and furnishing and decoration.

In Bangladesh there are 220 tanneries; 85% of them are located at Hazaribagh, western part of Dhaka and others are scattered all over the country (PKF 2013). Leather and its allied industries are one of the biggest export earners of Bangladesh. One of the main problems associated with the activity of tanneries is the great amount of environmental pollutants. Due to environmental pollution tanneries of Bangladesh has gained a negative image thus facing a stringent challenge to survive. Tanneries are considered as the major sources of environmental pollution in Bangladesh.

Environmental pollution parameters can be classified as solid, liquid and gas. It is a matter of distress that every chemical and mechanical operation of leather processing generates substantial amounts of solid, liquid and gaseous pollutants. Whatever the forms of waste in quality and quantity; it has the adverse impact on the environment.
Tannery solid waste problem ascends in both leather processing and wastewater treatment plant. Solid wastes in tanneries from leather processing are raw trimmings, hair, fleshings, limed trimmings, splittings, shavings, tanned trimmings, buffing dust, and sludge. It is reported that more than 60 kg solid waste is generated from the conversion of 100 kg raw hide/skin into leather (Boopathy et al. 2013). The solid wastes in tanneries have been recognized as a real problem for many years. It is not possible to minimize the solid waste because of removing unwanted portions of the hide/skin is essential to produce quality leather. The most common way to manage these solid wastes is by disposing of them on controlled land sites (Fernhdez-Sempere et al. 1997).

Chrome shavings are obtained as waste material when chrome-tanned leather undergoes the process of shaving operation. Chrome shavings in fibrous shredded form are available as 1%–2% on the weight of the raw hide. The chromium present in chrome shavings is in trivalent state. Worldwide, about 0.8 million tons of chrome shavings is generated per year (Fathima et al. 2012). The generation of solid wastes during leather manufacturing is unavoidable. The generated huge amount of shavings is not well managed in Bangladesh. These wastes are partly utilized, but mainly they are deposited in storage yards, posing a hazard to the environment (Przepiorkowska et al. 2007). The deposition of huge quantity of tanned collagen–chromium complex wastes in land is a potential danger to public health due to the possibility of oxidation of chromium(III) into toxic chromium(VI). Chromium(VI) has been shown to cause serious toxic and carcinogenic effect leading to respiratory, lung, skin and bladder cancer. Proper recycling of these wastes would certainly save the energy and conserve the resources. However, only limited eco-friendly processes were developed from leather wastes because of the presence of hazardous chemicals or ingredients. Hence, there is a need to develop cleaner processes in order to find a practical solution to the disposal of this potentially toxic waste (Ashokkumar et al. 2010).

It is possible to minimize the pollution during the treatment process by applying environment-friendly technologies and methods as an alternative to these treatment levels. Approaching more new information would be able to offer widespread answer for tannery waste management.

In the present study, chrome shavings were dechromed with organic acid and used it to fabricate composite sheet for the footwear and leather products making. The feasibility tests of the composite were performed by monitoring physical properties.

2. Material and Methods

2.1 Sample collection

Chrome shavings was collected from the SAF Leather Industry Ltd., Jessore, Bangladesh and transported to the laboratory for experimentation.

2.2 Materials

Chemicals used for dechroming of shavings were surfactant (Eusapon OC, BASF, Germany), lime (commercial grade), diammonium oxalate, oxalic acid, and citric acid (Merck, India) were purchased from local scientific store. Chemicals used for fabrication of composite from dechromed shavings are generally used in leather and footwear industry. Fungicide (BUSAN 30L, Buckman, USA), vegetable extract (Quebracho, Unitan, Argentina), latex (Thai Rubber Latex Corp., Thailand), glycerin, fat (Synthol AC, Smith & Zoon, Holland), sulphuric acid (Qingdao Lasheng, China), aluminum sulphate (Sanfeng, China) were also purchased from local scientific store. In addition, during experimentation always distilled water was used.

2.3Dechroming of shavings by organic acids

Inorderto facilitatesubsequentmechanicalandchemicaleffects,itisnecessaryto makethespaceincreasedamongshavingsfibers.Waterimmersion canincreasethefiberspace,and thehydrogenbondbetweenfiberand fibercanbedamagedsocanmakeshavingsfillwater.Insoaking,theshavingsto water ratiowas1:10.After 12 h, the weight of shavings is no longer a big change; therefore, water immersion time was limited to 12 h.

After that, theshavingswasimmersedinalimeliquor forfurtherprocessingofloosefiber,replenishitsexpansiontoincrease fiberspacing. Consideringthesolubilityof$Ca(OH)_2$inwater,takeshavingsas reference,theconcentrationof$Ca(OH)_2$was takenas0.4 g/L.The limed shavings were washed repeatedly with warm water (60°C) to remove lime from shavings structure.

Different organic dechroming agents such as oxalic acid, diammonium oxalate, and citric acid were investigated to obtain maximum removal efficiency. The shavings was mixed with water (1000%) and dechroming agents (50%). The mixture was stirred hourly for 5 minutes. The dechroming time was 24 h. The pH of dechromed shavings was adjusted to 7-8 by using sodium carbonate. The duration of neutralization was 2 h. Finally the dechromed shavings were washed with water repeatedly.

2.4Process optimization for dechroming

Assays were carried out to optimize the treatment parameters: oxalic acid dose and reaction time. The optimized conditions were established by investigating the chromium removal efficiency and fiber structure. To optimize oxalic acid dose, varying doses were used for each batch 10%, 20%, 30%, 40%, 50%, and 60% where other parameters were left unchanged, such as reaction time (24 h) and water used. To optimize reaction time, shavings fiber structure was monitored physically after every hour time period; water and oxalic acid dose used were left unchanged.

2.5 Characterization of shavings

2.5.1 Determinationofchromiumcontent

For determination of chromiumcontent, each sample (2 g) was digested with nitric acid (65% HNO_3, Merck KgaA, Germany). The acid-mixed samples were heated and refluxed on hot plate for several hours; occasionally nitric acid was added until no brown fumes were given off. Then, the mixture was cooled and hydrogen peroxide (30% H_2O_2, Merck, India) was added. The mixtures were heated and refluxed on hot plate and hydrogen peroxide was added to it in gradual doses until the fizziness became minimal or the mixture appearance was unchanged. The mixtures were continually heated until the volume had decreased to 5 mL. Then, 50 mL deionized water was added and the mixtures were again heated for another one hour. The mixtures were then cooled and filtrated through filter paper (Whatman No.1) and solution volume was increased to 100 mL with the addition of deionized water. The samples were preserved in high-density polyethylene (HDPE) bottles at 4°C until to complete the analysis.

The chromium content in the aliquot was determined by following Society of Leather Technologists and Chemists (1996) official method of analysis (SLC 208). A 50 mL sample was taken in 500 mL conical flask, 20 mL concentrated nitric acid was added followed by 20 mL perchloric acid/sulphuric acid mixture; heated the flask gently at the boil until the mixture had become a pure orange-red-color. After reaching this point, heat was continued boiling for one minute. The flask was removed from the heating source and as soon as ebullition has ceased; rapidly cool by swirling the flask in cold-water bath. Carefully, 100 mL distilled water was added with a few glass beads and boiled for 10minutes to remove free chlorine. Then, 10 mL 30% (v/v) sulphuric acid was added and cooled at room temperature. The mixture was then titrated with freshly prepared 0.1N ferrous ammonium sulphate solution using six drops of N-phenylanthranilic acid as an indicator. The end color was indicated by a color change from violet to green. The analysis was done in triplicates and the mean value was used for calculations.

2.5.2 Chromiumremoval efficiency

Theremoval efficiencyofchromiumfrom chrome shavingswascalculated by following Eq. 1.

$$\text{Chromium removal efficiency } (\%) = \frac{W_1 - W_2}{W_1} \times 100 \qquad (1)$$

Where,
W_1 = Chromiumcontent beforeremoval, W_2 = Chromiumcontentafterremoval

2.6 Fabrication of composite

Batch wise composite was fabricated by using buffing dust with different chemicals. Firstly dechromed shavings was mixed with water, preservative and stirred for 5 min. After that, 6% vegetable extract was added and stirred for 10 min. Then 3% fat was added with stirring for 10 min. Latex 40% (optimized) and few drops of glycerin were added and stirred for 15 min. Finally, 10% aluminum sulphate (optimized) was gradually added; pH was adjusted 4.5-5.0 (optimized) with dilute sulphuric acid then stirred for 15 min. The mixture was then poured on nylon net into 210 × 297 mm aluminum sieve. The fabricated composite was dried under sunlight and finally pressed.

2.7 Properties of fabricated composite

The surface of fabricated composite was inspected. Softness, flexibility, elasticity etc. were checked. Dumb-bell shaped 1 cm × 11 cm specimens were prepared from fabricated composite. Tensile strength (kg/cm^2) and elongation at break (%) was measured using SATRA STD 172 simple tensile tester (Eq. 2 and Eq. 3) following ISO 3376:2002.

$$\text{Tensile strength (kg/cm}^2) = \frac{\text{Breaking load (kg)}}{\text{Thickness (cm)} \times \text{Width (cm)}} \quad (2)$$

$$\text{Elongation at break (\%)} = \frac{\text{Length at break (cm) - Initial length (cm)}}{\text{Initial lenghth (cm)}} \times 100 \quad (3)$$

Crack resistance was determined by bending the test sample around a mandrel of diameter not more than three times the thickness of the board. The test sample was examined for any visible crack.

2.8 Leaching test

Solubilisation test of fabricated composite sheet was determined following Brazilian norm NBR10006 (Associacao Brasileira de Normas Tecnicas 1987a). The solubilisation test is a tank leaching test used to classify a material on a scale between non-inert and inert. The fabricated composite was grounded to particle size of less than 9.5 mm were mixed with 10 times of distilled water. After mixing for 5 min the mixture was left in beaker for 7 days. After this period the liquid constituents were separated from the solid by filtration. The liquid constituents were analysed for chromium content by following Society of Leather Technologists and Chemists (1996) official method of analysis (SLC 208).

3. Results and Discussion

3.1 Dechroming of shavings by organic acids and salt

The results drawn from the investigation of dechroming by different dechroming agents is represented in Table 1. Chromium content of the collected chrome shavings was 23.74 ± 0.18 mg/g. Chromium content in the chrome shavings dechromed with oxalic acid, diammonium oxalate, and citric acid were 3.57 ± 0.05 mg/g, 18.48 ± 0.11 mg/g, and 10.62 ± 0.09 mg/g respectively.

Table 1: Chromium content (mg/g) in chrome shavings before and after dechroming

Sample	**Shavings**	**Shavings + oxalic acid**	**Shavings + diammonium oxalate**	**Shavings + citric acid**
Chromium (mg/g)	23.74 ± 0.18	03.57 ± 0.05	18.48 ± 0.11	10.62 ± 0.09

It is clear from Fig. 2 that oxalic acid yields better chromium removal from the chrome shavings. The chromium removal efficiency for oxalic acid, diammonium oxalate, and citric acid were 85%, 22%, and 55%, respectively.

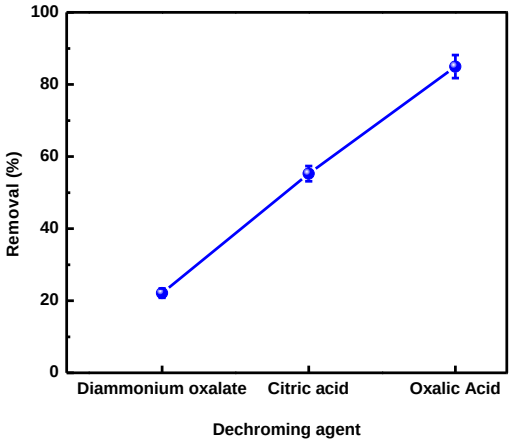

Figure 2: Effect of different dechroming agents

3.2 Process optimization for dechroming

The effect of oxalic acid dose on removal percentage of chromium from shavings is represented in Fig 3. The figure clearly indicates that the concentration of oxalic acid has a significant effect on the removal of chromium. It was perceived that with increasing oxalic acid dose, the removal percentage of chromium was increased gradually to 40 g per 100 g shavings and subsequently with increasing oxalic acid dose; removal percentage of chromium was almost constant. The removal percentage of chromium for an oxalic acid dose of 40 g/100 g shavings was 84.7%, for a dose of 50 g/100 g shavings, removal was 84.9%, for a dose of 60 g/100 g shavings, removal was 85.0%. Therefore, it was assumed that maximum removal of chromium occurred with 40 g dose of oxalic acid for every 100 g shavings.

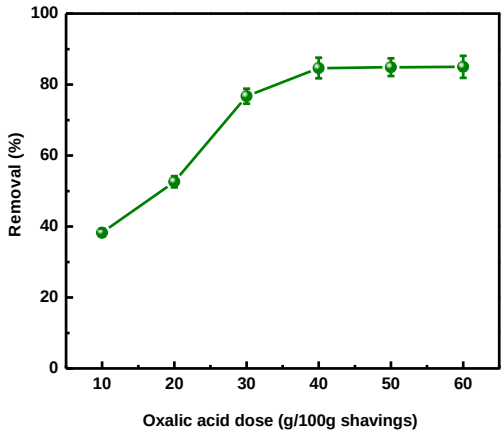

Figure 3: Effect of different oxalic acid dose on dechroming

Structure of shavings was observed at regular time intervals to determine the optimal reaction time. With the lapse of time, there was a gradual damage of the shavings. After 12 h, the structure was good as well as chromium removal efficiency was at its maximum.

3.3 Properties of fabricated composite

Different concentration of chemicals, especially latex provides different properties of composites. Lower percentage of latex did not show good quality composite and higher percentage enhanced higher physical properties but it reduced buffing property and increased chemical cost. The fabricated composite at optimized conditions is shown in Fig. 4.

Figure 4: Fabricated composite from dechromed shavings

The composite surface was smooth. It was light in weight, flexible and elastic in nature. The tensile strength and elongation at break of the finished composite were 222.7 ± 2.5 kg/cm^2, 24.2 ± 0.15%, respectively. The results indicate that the fabricated composite could be used in the footwear and leather products making. The comparative physical properties of the fabricated composite with the Indian standard values for leather boards are inserted in Table 2. It seems that tensile strength of the fabricated composite was higher than the minimum value and elongation at break (%) was below the maximum value. The obtained results indicate that the fabricated composite is suitable as insole material.

Table 2: Properties of fabricated composite compared with Indian standard for leather board (1970)

Parameters	**Fabricated composite**	**Requirements**
Tensile strength (kg/cm^2)	222.7 ± 2.5	60 (min)
Elongation at break (%)	24.2 ± 0.15	25 (max)
Crack resistance	Did not crack	Shall not crack

3.4 Leaching test

The chromium concentration in the liquid phase was 0.02 mg/L. The result from solubilisation test clarifies that chromium was not solubilised from the fabricated composite sheet. According to the Brazilian Regulation NBR10004, Maximal concentration of chromium to consider a material inert is 0.05 mg/L (Associacao Brasileira de Normas Tecnicas 1987b). So that it could be assumed the fabricated composite sheet is inert.

4. Conclusion

This study is an approach to utilize the solid waste generated during shaving operation in tannery. Chrome shavings were dechromed by treating with oxalic acid. The composite sheet was fabricated from the dechromed shavings incorporating with different chemicals which are generally used in leather and leather products industries. Chromium removal efficiency could be obtained 85%. The fabricated composite was showed good tensile strength and elongation at break as well as gave pleasant surface which could be used in the footwear and leather products industry. This will enable a substantial reduction of environmental pollution consecutively will produce valuable product.

5. Acknowledgements

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IVL P-18

A NOVEL METHOD TO PRESERVE GOAT SKIN WITH INDIGENOUS PLANT EXTRACT TO REDUCE SALINITY IN THE EFFLUENT

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Hides/skins, the outer coverings of animals are used as the basic raw material for the leather industry. Proper curing is essential to save the hides/skins before to start the tanning process. In the tropical countries like Bangladesh and India, conventionally fresh hides/skins are preserved by the wet-salting method using sodium chloride. Although sodium chloride is cost effective, available, and easy to apply, the method suffers heavily from the environmental point of view. In the last few decades, numerous works have been carried out with various curing agents efficiently to preserve the hides/skins to reduce pollution load from the effluent. Unfortunately, they are not commercially viable because of their limitations. In the present study, an attempt has been made to preserve the goat skins with the extracted oil from the seed of *Aphanamixis polystachya.*The oil was applied on the flesh side of the skin in different concentrations. The efficacy of the curing method was periodically assessed by analysis of the preserved goat skin for hair slip, odor, moisture content, bacterial count, total extractable nitrogen, and shrinkage temperature which compared with control method. Results indicate that the system is effective in preserving goat skins for more than a month. The production of preserved goat skins revealed that the pollution loads from soaking are significantly reduced. The main pollution problem of the leather manufacturing: chloride and TDS were reduced 97.8% and 82.3% respectively in the experimental soaking wastewater. The leather produced from experimental skins show comparable strength properties with that of control skins. The developed oil based method is proven to be an auspicious alternative to the traditional wet-salting by reducing pollution from leather processing.

Keywords: Hides/skins curing, Wet-salting, Pollution, Environment, Indigenous plant extract

1. Introduction

Hides/skins, the outer coverings of animals, are used as basic raw material for the tanning industry. After flaying hides/skins are susceptible to bacterial attack which starts within 5-6 hours after the animal death (Balada et al. 2008). Bacteria either in native or derive from the air or soil, putrefy the proteins and makes hides/skins inapt for the production of quality leather (Vijayalakshmi et al. 2009).

Animal death causes a dramatic metabolic change in hides/skins due to not supplying oxygen and nutritional components. As a result, accumulation of toxic substance leads to cause inactivation of some coenzymes; autolysis starts to decompose the protein to peptide and finally amino acids. Autolysis products are further broken down through the secondary process by the action of putrefactive bacteria (Bienkiewickz 1983).

To stop the decomposition of hides/skins protein after flaying two possible options are available i) instantly start tanning process and ii) properly curing. The first option is not possible and even in some cases impossible because a lot of hide/skin are slaughtered in the remote where there is no tanning facility as well as a large number of hide/skin is collected in the especial occasion for example during Eid-Ul-Azha (Muslim festival) period, which cannot be processed at the collection time. Therefore proper curing is the best option to save the hide/skin before transport to the tanning industry.

In tropical countries like Bangladesh and India, conventionally fresh hides/skins are preserved by wet-salting method where 40-50% common salt (sodium chloride) is applied immediately after flaying (Vankar and Dwivedi 2009). The dual actions of sodium chloride: i) dehydrating and ii) bacteriostatic properties are being exploited in this curing method (Babu et al. 2009).

Although sodium chloride is cost effective, available, and easy to practice hide/skin, the method suffers heavily from the environmental perspective. It is reported that only after soaking 70% TDS of the entire leather processing is released in the effluent as chloride ion (Selvi et al. 2015). Processing of one ton conventional wet-salted hides/skins contributes about 350-450 kg of salt as total dissolved solids in the wastewater. Chlorides remain a burden to the environment as it is not affected by the effluent treatment because of its high solubility. The high amount of salt contained in the effluent will increase surface salinity, thus reducing the fertility of soil resulting in the poor yield of crops (Preethi et al. 2006). An eco-friendly preservation of raw hides/skins has become a great challenge for the researchers and scientists.

In the last few decades, numerous works have been carried out with various curing agents efficiently to preserve the hides/skins to reduce salinity load from the final effluent. A great deal of research has done to cure hides/skins chemically which is likely to generate secondary pollutants which need to be treated. Some physical curing approaches were developed. But the proposed techniques is facing challenge because of high establishing cost, high operating cost, as well as low curing efficiency. To overcome these problems some plant based curing have been investigated to preserve hides/skins (Preethi et al. 2006; Rashid et al. 2008; Vedaraman et al. 2009; Vijayalakshmi et al. 2009; Iyappan et al. 2013; Selvi et al. 2015). Unfortunately, they are not commercially accepted because of limitations.

An investigation was carried out to use indigenous plant extract which has the curing potentiality and also available even in remote area of Bangladesh. One of the most common negative images for Bangladesh is not to cure the hides/skins properly after flaying in the remote area. In the long run many hides/skins are putrefied causing lots of materials are downgraded or even rejected due their defects.

In the present study, goat skins were preserved with the extracted oil from the seed of the indigenous plant. The outcome of this research will be very effective in the economy as well as environment friendly.

2. Material and Methods

2.1. Goat skin sample collection

Freshly flayed goat skins of average weight 1.4 kg per skin were collected from a local slaughterhouse located at Khulna, Bangladesh and immediately transported to the laboratory for experimentation. The collected skins were firstly washed with water to remove adhering blood, dung, and dirt. The washed skins were hanged for 30 min to drain extra water.

2.2. Plant extract

The seeds of *Aphanamixis polystachya* were collected from a local area of Sirajganj, Bangladesh which isabundantly available. The collected seeds were washed with water and dried well under shade at room temperature. The dried seeds were grounded to fine powder. The powders were subjected to heating with water at water bath for several hours. After clearly separated oil from seed, the mixture was then transferred to the separating funnel and finally, oil was separated from the aqueous phase. The residual water in oil was then distilled off.

2.3. Materials

Sodium chloride (commercial grade) used for the preservation experiments was purchased from local market. Surfactant, bactericide, sodium sulphate, lime, sodium sulphide, ammonium chloride, ammonium sulphate, formic acid, sulphuric acid, sodium bicarbonate, sodium formate, basic chromium sulphate, vegetable tannin, syntan and fungicide all were procured from a tannery which were used for pre-tanning and post-tanning processes to manufacture crust upper leathers. Analytical grade chemicals were used for determination of total extractable nitrogen, bacterial count, chloride (Cl^-), biological oxygen demand (BOD), and chemical oxygen demand (COD).

2.4. Curing experiments

Preliminary experiments were conducted with 5%, 10%, 15%, and 20% oil only to know the minimum quantity of salt required for skin preservation. Four (04) samples of size 5 cm × 5 cm was cut from the butt portion of the freshly flayed goat skin. The different percentages (w/w) of oil were applied on the flesh side of the skins. Skins were assessed periodically for physical changes like odor, hair slip, and moisture content for confirmation of good preservation. The obtained results indicate that the optimum concentration of oil for preservation was found to be 15% (w/w). After assuming the required amount of oil in the proposed preservation method; it was compared with the conventional wet salting preservation method. A freshly flayed goat skin was cut into halves along the backbone to avoid skin to skin variation. The left half was taken for the control sample (50% sodium chloride) and the right half was used as experimental sample (15% oil). Each experiment was repeated for three times. The efficacy of the preservation method was periodically (after 1^{st}, 4^{th}, 7^{th}, 14^{th}, 21^{st}, and

30^{th}days of preservation) assessed by analysis of the cured skin for total extractable nitrogen, bacterial count, hydrothermal stability, as well as moisture content.

2.5. Observing the effectiveness of proposed curing method

2.5.1. Preparation of skin extract

The preserved skin pieces of known mass were kept in sterile water (ten times by volume of its mass), shaken well in an orbital shaker at 200 rpm for 30 min. The extract liquor was then filtered through a filter paper (Whatman No.1); the filtrate and further used for nitrogenous and bacteriological analysis.

2.5.2. Determination of total extractable nitrogen content

The extract liquor was digested using sulpuric acid (H_2SO_4), potassium sulphate (K_2SO_4), and copper sulphate ($CuSO_4$) in a Kjeldahl flask providing the temperature 375-385°C for effective digestion. The nitrogen content was determined by Micro-Kjeldahl method according to the standard method of APHA (2012). Each experiment was conducted in triplicate.

2.5.3. Determination of bacterial count

A volume of 1 ml extract liquor was taken in 9 ml of sterile water in a vial and shaken well to make uniform suspension of bacteria. After that, 0.1 ml of the corresponding diluted solution was poured in a sterile Petri plate and molten nutrient agar at 40°C was poured. The Petri plate was shaken gently to get uniform distribution of the bacteria. The Petri plate was incubated at 37°C for 48 h. The number of colonies on the agar media was counted using colony counter. Each experiment was conducted in triplicate.

2.5.4. Determination of hydrothermal stability of the skin

The hydrothermal stability of the skin is typically evaluated by shrinkage temperature. The shrinkage temperature (°C) of the preserved skin was determined using a shrinkage tester (SATRA STD 114, UK) according to the standard method (ISO 3380:2015). Each experiment was conducted in triplicate.

2.5.5. Determination of moisture content

The moisture content of the skins was determined by following Bureau of Indian Standards (1971). About 5 g persevered skin samples were cut and weighed. The samples were dried in a drying oven at 50-60°C temperature for 5-6 h. The dried samples were cooled in a desiccator and weighed. The weight loss was calculated. Each experiment was conducted in triplicate.

2.6. Leather making

After 30 days of curing, both the control and experimental goat skin were processed to manufacture upper crust leathers as per conventional leather making procedures.

2.7. Pollution load generated in leather making

Pollution load generated in the soaking operation of leather processing was determined. The wastewater generated from the control and experimental soaking operation was collected and analyzed for chlorides (Cl^-), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and total suspended solids (TSS) following the standard methods of APHA (2012). Each experiment was conducted in triplicate.

2.8. Physical properties of leather

The leather samples were tested for their physical characteristics to compare proposed oil cured leather with conventional wet-salted cured leather. After conditioning the crust leather at 20 ± 2 °C and 65 ± 2 % of relative humidity over a period of 48 h according to ISO 2419:2012 standard, samples was taken from specified sampling location as per ISO 2418:2002. The properties such as tensile strength, elongation at break, and bursting strength were assessed following ISO 3376:2011 and ISO 3379:2015. Each experiment was conducted in triplicate.

3. Results and Discussion

3.1. Optimization of oil concentration for curing

The hide/skin is composed of proteinaceous substances which are susceptible to microbial attract. Proteinaceous substances are hydrolysed to amino acids by proteolytic enzymes produced from bacteria; bacteria further hydrolyse the amino acids and liberate ammonia gas. Therefore, odour of ammonia gas is considered as the initiation of putrefaction. Hair follicles on the skin and hide are fairly appropriate structures for many species of bacteria to easily colonize. Hence, hair slip is the first indication of putrefaction as the protein present in the bulb of the hair is degraded by the bacteria during the commencement of putrefaction. Hence, putrefaction odor and hair slip is monitored as physical evaluation to determine effectiveness of curing method.

The standardization of optimum concentration of oil for curing of goat skin is depicted in Table 1. It seems from results that 15% was found to be effective in curing the skin for more than 2 months. There was no putrefactive odor or hair slip observed indicating no putrefaction of the goat skin.

Table 1: Optimization of oil concentration

S.N.	**Oil applied**	**Effectiveness of curing method**	
		Putrefaction odour	**Hair slip**
01	5%	Light odour	Light hair slip
02	10%	Light odour	No hair slip
03	15%	No odour	No hair slip
04	20%	No odour	No hair slip

3.2. Effectiveness of the curing method

3.2.1. Total extractable nitrogen content

Total extractable nitrogen content is a vital factor for assessment the effectiveness of curing skins. The putrefaction of skin proteins result the release of nitrogenous components which leads the emission of putrefaction odour and hair slip. The putrefaction was measured by the amount of nitrogen extracted in water. Figure 1 shows the total extractable nitrogen content in the preserved goat skin. It is clearly seen that the putrefaction contributes extractable nitrogen in the extract liquor. The release of total extractable nitrogen content in the experimental skin showed lower values. The control experiment showed slightly higher total extractable nitrogen content after 7 days of curing. The results confirm that the decrease in total extractable nitrogen content in the experimental skin is due to the oil strongly responsible for impeding the bacteria from putrefaction.

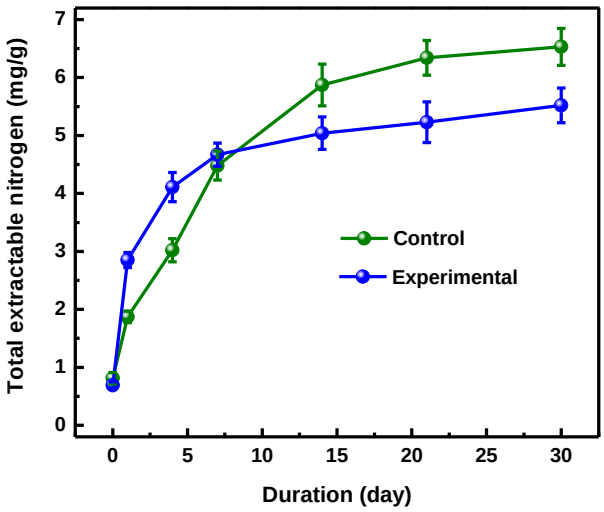

Figure 1: Total extractable nitrogen content of cured goat skin by control and experimental methods

3.2.2. Bacterial count

The bacterial count in preserved skins was performed to determine number of bacteria present in the skins. The effectiveness of preservation principally depends on the development of inhibitory properties for bacteria on the skin. The bacterial count reveals the degradation of skin i.e. the presence of bacteria on the skin during preservation. The bacterial count of the control skin and experimental skin at different intervals are represented in Table 2. The experimental skin exhibited relatively lower bacterial count in comparison to the control skin. This clearly validates the antibacterial property of oil. The results disclose that the oil starts preservation skin not only at initial stage but also at later stages.

Table 2: Bacterial count of control (50% NaCl) and experimental (15% oil) skin

Duration	Bacterial count (CFU/g)	
	Control	Experimental
Fresh	3.2×10^{3}	2.5×10^{3}
1st day	8.4×10^{9}	6.1×10^{7}
4th day	3.9×10^{9}	1.7×10^{7}
7th day	2.1×10^{7}	5.3×10^{6}
14th day	4.6×10^{6}	2.9×10^{5}
21st day	1.7×10^{6}	4.0×10^{4}
30th day	5.1×10^{5}	1.9×10^{4}

3.2.3. Hydrothermal stability

The hydrothermal stability of collagen is considered as a significant property for the assessment of the hide/skin quality because it shows indirectly any structural deterioration of the hide/skin protein. The purpose of this parameter of the study was to know whether the proposed curing method had any effect on the deterioration of collagen matrix. The shrinkage temperature of preserved skins in different time periods in represented in Figure 2. No remarkable change in the shrinkage temperature of control and experimental skins was observed. It could be concluded that the preserved skins were not deteriorated during curing.

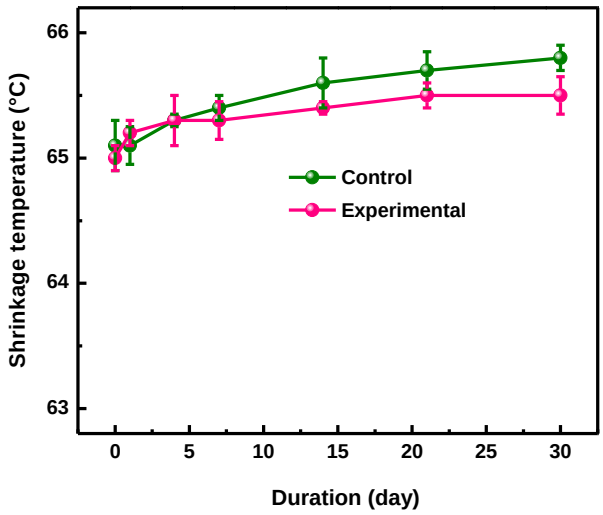

Figure 2: Shrinkage temperature of cured goat skin by control and experimental methods

3.2.4. Moisture content

The moisture content (%) of preserved skin is an important to assess the effectiveness of preservation method. The moisture content of the preserved control and experimental skins at different time intervals are depicted in Figure 3. The moisture content of control and experimental skins were reduced 19.3% and 50.0% respectively after 4 days. The moisture content was reduced to

34.5% and 13.2% respectively for control and experimental skins at the end of 30 days. The greater reduction in moisture content in experimental skin could be due to the hygroscopic properties of oil.

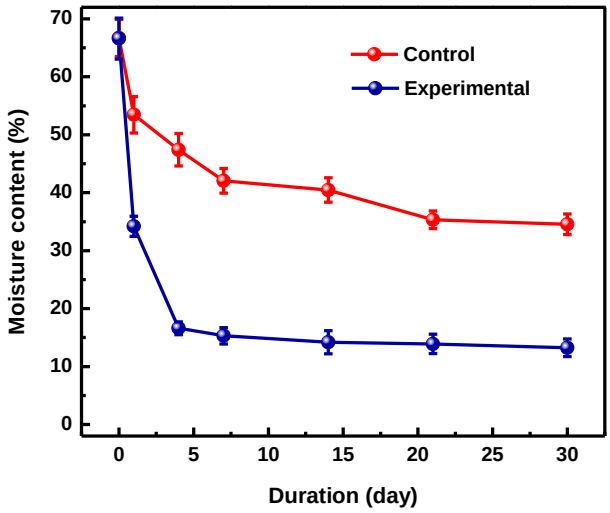

Figure 3: Moisture content of cured goat skin by control and experimental methods.

3.3. Pollution load generated from leather making

The analysis of pollution load generated in soaking operation of preserved goat skins for both control and experimental samples were represented in Table 3. The table depicts that the chloride and TDS load were greatly reduced when the oil was used in preservation in place of the control salt. Even though there was little increase in the BOD and COD levels in the experimental soaking wastewater compared to the control. The main pollution problem of the leather manufacturing: chloride and TDS were reduced 97.8% and 82.3% respectively in the experimental soaking wastewater.

Table 3: Pollution load generated in soaking of preserved goat skins

Sample	**Cl^- (mg/L)**	**TDS (mg/L)**	**BOD (mg/L)**	**COD (mg/L)**
Control	18232 ± 203	42260 ± 517	1260 ± 36	5250 ± 63
Experimental	398 ± 12	7470 ± 143	1440 ± 29	6048 ± 71

3.4. Physical properties of leather

The physical properties e.g., tensile strength, elongation at break, distension at grain crack, and load at grain crack of crust leathers which were obtained by processing of preserved cured skins are represented in Table 4. The results disclose that there is no significant variation in physical properties between control and experimental leather samples. The values fulfilled minimum physical properties. The physical properties results clear the effective preservation by oil.

Table 4: Physical properties of control (50% NaCl) and experimental (15% oil) leather

Parameters	Control	Experimental	Minimum requirements (Kanagaraj et al. 2001)
Tensile strength, kg/cm^2	245.1 ± 1.18	259.8 ± 1.13	200
Elongation at break, %	39.8 ± 0.45	39.4 ± 0.51	40-65
Bursting strength:			
Distension at grain crack, mm	7.9 ± 0.14	7.8 ± 0.16	7
Load at grain crack, kg	43.3 ± 0.64	40.0 ± 0.59	20

4. Conclusion

Commercially feasible salt-free curing development has become a great challenge in recent years to save environment from pollution. To response, an investigation was made to preserve goatskin using indigenous plant oil. The oil is capable to preserve goat skins for more than a month because of the antimicrobial property present in it. The results from experiments indicate that the oil is an effective and ecofriendly curing agent. The present study averts the limitations: cost, and no availability in remote areas. The novel preservation method based on plant oil could be a cleaner preservation choice to the conventional wet salting preservation methods.

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IVL P-19

PHYSICAL PROPERTIES APPRAISAL OF THE FABRICATED COMPOSITE FROM FAT EXTRACTED LIMED FLESHING

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In beamhouse, just after liming pelt has to pass through an operation known as 'Fleshing.' It is one of the most indispensable mechanical operations in leather processing where substantial amounts of inevitable solid waste (fleshings) are produced. Here an attempt was made to fabricate composite from fat extracted limed fleshing and assessment of physical properties. The collected fleshing was delimed with boric acid and pH was adjusted 6-7 by the diluted hydrochloric acid and further washed with water. The delimedfleshing was subjected to heating at water bath in a beaker with water for several hours. After clearly separated fat from fleshing, the mixture was then transferred to the separating funnel; finally fat was separated from the aqueous phase. The fat extracted fleshing was sun-dried and grinded to make 0.5-1.0 cm sizes. Then, grinded fleshing was mixed with epoxy resin and hardener. The mixture was then poured into aluminum sieve. The physical properties of fabricated composite were investigated and it shows good young's modulus and tensile strength. This approach will enable a substantial reduction of environmental pollution consecutively will produce valuable product.

Keywords: Fleshing, Fat, Composite, Young modulus, Tensile strength

1. Introduction

Recycle-reuse-reduce (3R) are three great ways to eliminate waste and protect our environment. An industry only could survive if the industry maintains the 3R ways. Now-a-days leather industry has become great challenge to survive due to generating inevitable solid wastes. Due to environmental regulations many countries are going to stop leather processing because of generating high pollutants. Leather processing involves the conversion of putrescible hide/skin into imputrescible leather and consequently huge amount of solid waste. In tannery at beam house, fleshing is one of the most indispensable mechanical operations in leather processing where substantial amounts of inevitable solid waste (fleshings) are produced. The other solid wastes consist of curing salt, raw trimmings, keratins (hair, wool, nail etc.), shavings and buffing dust etc. The quality and quantity of solid waste generation depend on many features such as animal species, breeding conditions, slaughterhouse practices, conservation conditions, leather process stages, mechanical operations, qualification of the personnel, and chemicals used in processes (Ozgunayet al. 2007).

In leather processing, from every 1000 kg raw hide/skin only 150 kg of the raw material is converted into leather and nearly 850 kg is generated as solid wastes (Kanagarajet al. 2006). Skipping the fleshing operation would inhibit diffusion of tanning agents as well as other chemicals into hide/skin

from the flesh side. Consequently, chemicals will be wasted and quality leather will not be produced. Fleshing contains proteinaceous substances that are hydrolyzed to amino acids through proteolytic bacteria; further amino acids are hydrolyzed by bacteria, which liberate gaseous ammonia (NH_3), hydrogen (H_2), carbon dioxide (CO_2), volatile fatty acids (VFAs) etc., that are directly merged to the air (Shanmugam and Horan 2009). Fleshing contains protein 5-7%, fat 4-18%, lime 2-6%, sulphide 2-4% etc. (Lupo 2006).

In the last decades, numerous steps have been taken to minimize solid wastes generated in tanneries. Many efforts have made to utilize the fleshing in various techniques e.g. production of feed ingredients (Rai et al. 2010), compost (Rvindran and Sekaran 2010), biogas (Ravindranath et al. 2010), biodiesel (Šanek et al. 2015), and soap production (Hashem and Nur-A-Tomal 2016).

In this study, an approach was made to fabricate composite material from the fat extracted limed fleshing to reduce the disposal load. The feasibility studies of the composite were performed to ensure the quality. The novel approach would be able to offer more widespread answer for tannery waste management.

2. Material and Methods

2.1 Sample collection

Cowhide fleshings was collected into polyethylene from a tannery at Khulna, Bangladesh and brought back to the laboratory immediately for experiment.

2.2 Chemical and reagents

Commercial boric acid and commercial hydrochloric acid were used as deliming agent and were collected from a local scientific store at Khulna, Bangladesh. The standard epoxy resin (Araldite AW106, India) and hardener (Araldite HV 953 IN, India) were procured from the Khulna, Bangladesh.

2.3 Deliming of fleshing

The collected fleshing was washed with water to remove the free lime and cut into small pieces to facilitate the next operation. The fleshing was delimed with 2% (w/w) boric acid and 60% water for about 5-6 hours to remove lime. The pH of the delimed fleshing was adjusted at 6-7 by treating with hydrochloric acid. The delimed fleshing was further washed with water.

2.4 Fat extraction

The delimedfleshings was subjected to heating at water bath in a beaker with water (water: fleshings = 1:1) for several hours. After clearly separated fat from fleshings, the mixture was then transferred to the separating funnel and finally fat was separated from the aqueous phase. The residual water in fat was then distilled off. At optimized conditions 6.2% (dry weight) fat is extractable (Hashem and Nur-A-Tomal 2016).

2.5 Drying of fat extracted fleshing

The fat extracted fleshing was sundried and finally at oven at 105°C. Then, the dried fleshing was grinded with mortar to make granules.

2.6 Fabrication of composite

The granule of fleshing was mixed with the epoxy resin and hardener at different ratios; mixture was then poured into aluminum sieve and kept for overnight for curing.

2.7 Fabrication process optimization

Experiments were carried out to optimize the fabrication process e.g., fixed amount of fleshing granules with the ratio of epoxy resin and hardener (epoxy resin: hardener = 2:1). The epoxy resin and hardener ratio was fixed because of the manufacturer guide. Fabrication ratio for the composite is shown in Table 1.

Table 1 Composite fabrication combination

Sample ID	Fleshing granules (g)	Ratio (Resin: Hardener)
A	60	20:10
B	60	30:15
C	60	40:20
D	60	50:25
E	60	60:30

2.8 Physical properties of composite

The fabricated composite sheet was inspected: tensile strength, elongation at break (%) and Young's modulus were measured by the standard method of ASTM: D225 using Universal Testing Machine (UTW, WAW-2000E, India). The tested data were used finally to calculate value with the Eq. (i), Eq. (ii) and Eq. (iii).

$$\text{Tensile strength } (\text{N/mm}^2) = \frac{\text{Breaking load (N)}}{\text{Thickness (mm)} \times \text{Width (mm)}} \quad \text{.....(i)}$$

$$\text{Elongation at break} = \frac{L_1 - L_0}{L_0} \times 100 \quad \text{.....(ii)}$$

L_1 is the separation of jaws or sensors at break; L_0 is the initial separation of jaws or sensors.

$$\text{Young's modulus} = \frac{\text{Sress}}{\text{Strain}} \quad \text{.....(iii)}$$

3. Results and Discussion

3.1 Fabricated composite

The fabricated composite is shown in Figure 1. The fabricated composite was rigid in nature, gray in color with dry feel. The average thickness of the composite was 14.3 ± 0.16 mm.

Figure 1: Fabricated composite from fleshing granule

3.2 Physical and mechanical properties of composite

The fabricated composite was investigated for tensile strength, elongation at break (%) and Young's modulus. Tests were done to verify the usability of the composite.

3.2.1 Tensile strength of composite

The tensile strength of the composite with various combinations is depicted in Figure 2. Results indicate that for a fixed amount of fleshing (dried fleshing granule wt. 60 g) with increasing the amount of mixture (resin: hardener=2:1) gradually tensile strength was increased. For the combination of composite sample D (fleshing granule: resin: hardener=60:50:25) tensile strength was maximum 10.80±0.34 N/mm^2. In combination of composite sample E (fleshing granule: resin: hardener=60:60:30) the tensile strength 9.4 ± 0.3 N/mm^2. It seems that with the increasing amount of mixture (resin and hardener) for a fixed amount of fleshing tensile strength was decreased. It may be the reason; the ratio of fleshing granules and resin should not more than 1. However, the ratio of fleshing granule: resin: hardener= 60:50:25 was decided the optimum ratio.

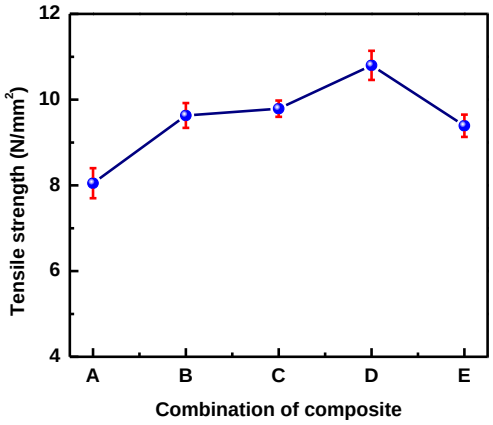

Figure 2: Tensile strength of the fabricated composite

3.2.2 Elongation at break (%)

In Figure 3 shows the elongation at break (%) of the fabricated composite at varying combination. The elongation at break (%) of the composite sample B was the highest 10.2 ± 0.2%. After that elongation at break (%) was gradually decreased; for composite sample D (6.0 ± 0.2) was minimum. As composite is going to be used as rigid body with less elongation, therefore, combination of the composite sample D selected for the fabrication of composite.

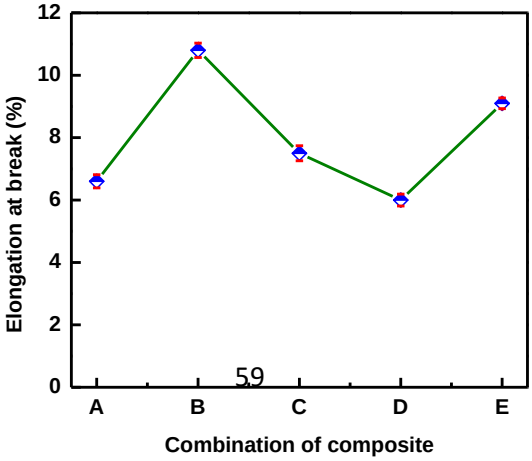

Figure 3: Elongation at break (%) of the fabricated composite

3.2.3 Young's modulus

Young's modulus or elastic modulus is the measure of the stiffness of solid material. The mechanical property, Young's modulus of the fabricated composites is shown in Figure 4.

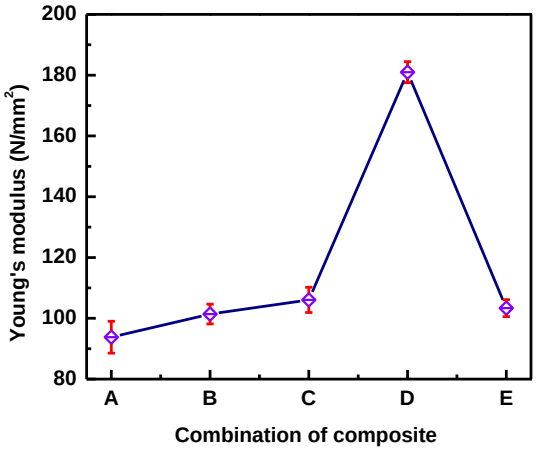

Figure 4: Fabricated composite' Young's modulus

It could be seen that Young's modulus of the fabricated composite was gradually increased; Young's modulus for the composite samples A, B, and C were 93.8, 101.4, 106.1 N/mm^2 respectively. In case of fabricated composite sample D, Young's modulus was the highest 181.0 N/mm^2. After that the value of Young's modulus was drastically deceased; composite sample D has the highest Young's modulus which will show more rigidity under pressure during real life application.

4. Conclusion

This study was an approach to utilize the limed fleshing in a dual ways **i**) fat extraction and **ii**) fabrication of composite from the fat extracted fleshing. The fabricated composite was showed good tensile strength, elongation at break and Young's modulus which could be used in hard board, leather products reinforcement, etc. The developed fabrication composites could provide a solution to the environmental problems associated with the waste management of the leather industry.

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THE DEVELOPMENT OF GRAPHENE FOR POLYURETHANE COMPOSITE FUNCTIONAL MATERIALS

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Graphene has a unique two-dimensional structure and excellent thermal conductivity and electrical conductivity. It can be used to modify the performance of other materials for broader application. Synthesis of composite material with polyurethane is a kind of new functional polymer material research direction and the composite material has wide application prospect. This paper reviews the preparation methods of graphene and polyurethane composite materials, as well as the application of the self-healing, UV curing, shape memory, conductive, electromagnetic shielding, and biocompatibility properties of the composite material. Finally, we made certain outlook of the application of graphene in polyurethane.

Keywords: Polyurethane; graphene; functional materials; review

1. Introduction

Graphene (GNS) is a two-dimensional honeycomb material from a single layer of carbon atoms connected together sp^2 hybrid, with a huge surface area (2600 m^2/g) and excellent electric properties of high-speed electron mobility (at room temperature rate 15000 cm^2/VS and thermal conductivity (5300 W/mK). Polyurethane (PU) is composed of isocyanate and polyol polymerization of polymer materials. It has outstanding properties, such as the adhesion, abrasion resistance, cold resistance, elasticity, etc. It is widely used in adhesives, leather finishing, textile, construction, light industry and other fields (Virendra Singh et al, 2011). Composite material can be formed by the nanometer materials with polyurethane matrix to endow them with more features. The composite materialsprepared with graphene and polyurethane are new type of functional polymer materials with excellent electrochemical properties, thermodynamics and mechanical performance (Karima Benhamou et al, 2015). The composite materials have good application prospects in many fields such as the electrode materials, solar energy materials, electromagnetic shielding.

2. Preparation of graphene/polyurethane composites

Graphene possesses high surface energy. But it's easy to reunite and has poor compatibility with polymer and it's difficult to evenly disperse in the polyurethane system. Finally, it will affect the performance of the polyurethane composite material and limit its application scope. Currently, the main methods of graphene dispersing in polyurethane systems are blending, graft copolymer and in situ polymerization.

2.1 blending method

The graphene/polyurethane composite material can be prepared by blending method without damage the structure of graphene. The physical performance of graphene and polyurethane can be mixed in the composite material. It is relatively a simple and commonly used method by solution blending, melt blending, and other methods to carry out the sol blending. The blending can be prepared by mechanical stirring with ultrasonic agitation and then dispersed in the polyurethane system. The surface modification of graphene before blending can improve its compatibility in the polyurethane system.

Xin Wang used the KH-550 to modify the graphene oxide (GO) and waterborne polyurethane (WPU) complex by sol-gel method. It was found that the mechanical and thermal properties of the composites were significantly improved. The tensile strength and Young's modulus of the composites were increased by 71% and 86% when the dosage of KH-550 was 2.0 wt% (Xin Wang et al, 2012). Nariman Yousefi used the solution blending method to prepare the GO and PU composite. A small amount of hydrazine was added by heat treatment. With the reduction of oxygen containing functional groups of graphene oxide (rGO), the hydrogen bonding was formed between the amide groups of PU chains. Finally, the rGO can be well dispersed in the PU system. The results showed that 3 wt% of rGO made the elastic modulus and tensile strength of the composites increased by 21 times and 9 times. At the same time, the confirmed rGO achieved the molecular level of dispersion in polyurethane system. With the increase of the content of rGO, the water vapor permeability of polyurethane systems declined (Nariman Yousefi et al, 2013). Jian-ning ding used the polyvinylpyrrolidone to improve the dispersibility and stability of an aqueous solution with a higher concentration of graphene. The graphene / waterborne polyurethane conductive composites were prepared by solution methods. The research also used γ- aminopropyl triethoxysilane (KH-550) to modify the surface property of the graphene oxide (functionalized graphene oxide). The hydrophilic of the graphene oxide sheets was reduced. Furthermore, the dispersibility in organic solvents and intermiscibility with polymer were improved. Finally, the graphene oxide/aqueous polyurethane nanocomposites was prepared (Jian-ning ding et al, 2011). Zhao Jian et al prepared the thermoplastic polyurethane/graphene composites by solution blending method and studied relationship between the structure and properties. The results showed that the high temperature reduction of graphene could greatly improve the storage modulus of thermoplastic graphene/polyurethane composite material. The electrical properties of the composite appeared mutant in the mass fraction of 1% to 3% of the amount of filler range resulted in 6 orders of magnitude decreasing of the volume resistivity (Zhao Jian, et al, 2013). Mingkai Liu, et al. studied the prevention of graphene reunion by the carbon nanotubes and graphene hybrid to form three-dimensional structure. The thermoplastic polyurethane/graphene composites were prepared by solution blending method. The results found that the conductivity of the composites was significantly increased. Carbon nanotubes played a

supporting roleon on the layer of graphene and avoided the overlap between layer and reunion (Mingkai Liu, et al, 2013).

2.2 Graft copolymer method

Graft copolymerization method is a common method for producing a polyurethane nanocomposite. This means that a chemical bond was formed between the polyurethane molecular and surface graphene in the polymerization process to prepare the composite material. This method makes the grapheme dispersed in the system more evenly and stable performance.

Santosh Kumar adav et al used the diazotization reaction to functionalize the graphene oxide and then seal the pre-polymers with isocyanate to copolymerize (shown in figure 1). Finally, the F-GNP/PU nanocomposite was synthesized. The results showed that the addition of graphene significantly improved the mechanical, thermal and shape memory properties of the composites. With the increasing of f-GNP dosage, the elongation at break and shape memory of the composites were improved. The elastic modulus increased by 10 times when the dosage of f-GNP was 2 wt%, while the thermal stability upgrade by 30℃ (Santosh Kumar adav et al, 2013).

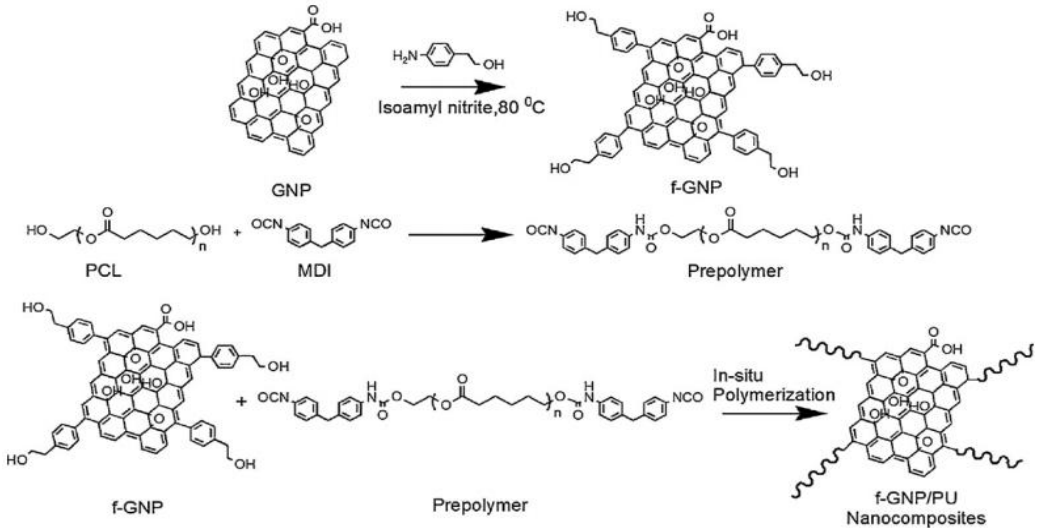

Fig. 1.Synthesis of f-GNP/PU nanocomposites by in situ polymerization

2.3 In situ polymerization

In addition to the physical blend and graft copolymer, in situ polymerization is also one of the important methods for the preparation of graphene/PU composite material.

Yuqi Li et alused MDI to modify GO before synthesizing GO/polyurethane composites by in-situ polymerization. Furthermore, the composites were compared with (PU/GO/EP) composites which were synthesized by blending with epoxy resin (EP). It was found that the mechanical performance and thermal stability performance were improved significantly (Yuqi Li et al, 2013). Mukesh Kumar et al synthesized the graphene/polyurethane nanocomposites with the graphene oxide as a kind of "pseudo-crosslinking agent". The results showed that the compound materials were synthesized by the reaction between the hydroxyl on the surface of graphene oxide and the -NCO sealing side polyurethane without any chain extender. Compared with pure polyurethane, the thermal stability of the complexes was significantly enhanced (Mukesh Kumar et al, 2013). Zhongxin Chen et al

synthesized graphene/waterborne polyurethane (WPU) composite material using in situ polymerization by 1-pyrene methanol modified graphene oxide reduction, and then reacted with the isocyanate and polyethylene glycol under certain conditions (shown in figure 2). The results showed that the thermal stability, mechanical properties and the elongation at break of the composite material were significantly enhanced. Compared with pure polyurethane, the tensile strength, tensile modulus and toughness of composites increased by 50.7%, 50.7% and 104.8% when the adding quantity is 2 wt % of modification of graphene (Zhongxin Chen et al, 2012).

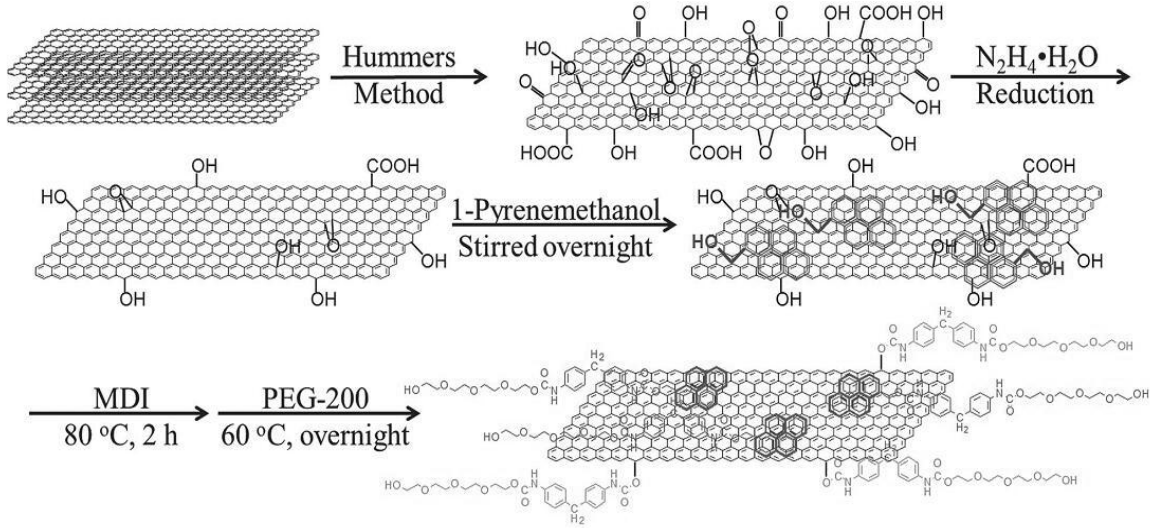

Fig. 2. Synthesis route for covalently and non-covalently functionalized GNs (HO-GNs).

The above method can be seen in contrast, blending method is simple to operate, but because of the graphene surface area is larger, so it's easy to reunite. The evenly spreading out and dispersing in the polyurethane matrix is the most difficult part in the present study. The graft copolymer and in situ polymerization method can ensure the branched chain of polyurethane to be fully connected with the edges of functional groups of modified graphene, and there is certain interface interaction between them which is advantageous for the graphene dispersion in polyurethane. The difficulty is, however, the experimental condition is stricter, and then makes the large-scale applications to be more difficult. However, the above methods are commonly used in water-based polyurethane with graphene composite, since the composite materials research is not mature, and the basic research is in the experimental stage now, most researchers are still exploring, so the composite materials have more extensive application prospect. Therefore, we can learn from other methods of graphene composite polymeric materials, such as graphene and polycarbonate (PC), polypropylene (PP), polystyrene (PS), polyethylene alcohol (PVA), polymethyl methacrylate (PMMA) and other materials, which provides a more experimental scheme for the preparation of graphene/polyurethane composite material, and also provides a powerful theoretical basis.

3. The functionalization application of grapheme/polyurethane composite material

In recent years, graphene materials become more popular because of its excellent physical, chemical and mechanical properties which have made great progress in the field of polymer materials. The research shows that grapheme/polyurethane composite material exhibits excellent electrical mechanical, electromagnetic shielding, UV and biocompatibility.

3.1 Self-Healing Material

Self-healing material is a new functional material to repair it by itself when it was damaged. Its wide range of applications, including the field of military equipment, electronic products, automobiles, aircraft, construction materials, etc. (Lewis R. Hart, et al, 2014), where its application in the smartphone and tablet screens have attracted the most attention. Research and development of this kind of material can not only improve the service life of the product but also can reduce the waste of resources.

Jin Tae Kim et alused phenyl isocyanate and a small amount of hydrazine as modification to the GO compound with hydroxyl polyurethane sealing side by solution blending method. Under conditions of infrared radiation, the infrared heat generated induced polymer chains healed. The study found that when the dosage of modified graphene was 0.75 wt%, the self-healing effect of the composite was the most obvious shown in figure 3(Jin Tae Kim et al, 2013).

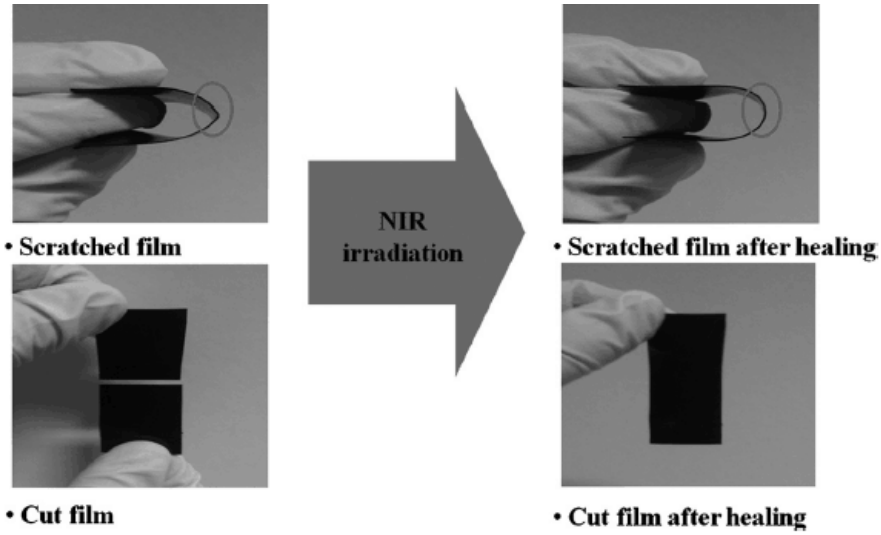

Fig. 3. Photographs showing NIR induced healing of PU/MG nanocomposite films

3.2 The UV curing material

Photocurable material is a polymeric substance shows the physical and chemical changes rapidly within a short period of time when exposure to light, commonly used in the coatings. Compared with the traditional natural drying or heat-curable coating, this material has high energy utilization, suitable heat sensitive substrate, nonpolluting and thin film deposition speed properties. Furthermore, the quality of coating film is high which is suitable for continuous mass production and conform to the requirements of environmental protection in countries around the world today.

S H Yoon et al used allyl isocyanate modified graphene oxide (iGO) to synthesize waterborne polyurethane hydroxyethyl acrylate terminated prepolymer. iGO was added to prepare UV curing of WPU/iGO nanocomposites when emulsified. The research showed that iGO in the WPU molecular chain by chemically combine, played a dual role of a crosslinking agent and an inorganic filler. The mechanical properties and thermal performance of composite materials improved significantly when the iGO adding amount was 1 wt % (S H Yoon, et al, 2011). Xin Wang et al, prepared nanocomposites using the modified graphene KH-570 (F-GNS) and acrylic-based polyurethane under the conditions of

UV radiation. The study found that the thermal decomposition temperature of the composites increased by 16℃, the energy storage modulus and glass transition temperature was significantly enhanced when the F-GNS dosage was 1wt% (Xin Wang et al, 2013).

3.3 Shape memory material

Shape memory material can be deformed and fixed under certain conditions. What's more, it can be quickly restored to its original shapeunder suitable ambient conditions (e.g. heat, light, electricity, chemical treatment, etc.).

Samsook Han et al used sodium dodecyl benzene sulfonate, sodium borohydride and amino benzene ethanol to modified graphene oxide surface. It was found that the graphene modified by carbamate with polyurethane formed a crosslinked structure, and the role of hydrogen bonding exhibited excellent shape memory properties and mechanical properties. Within the four times cycles, the material exhibited as much as 98% of the shape fixability and 94% of the shape recovery ratio, the hysteresis loss was as low as 0.5% to 2% (Samsook Han et al, 2014). Hye Jin Yoo et al.prepared shape memory polyurethane (PU) nanofibers based on the polycaprolactone (PCL), graphite alkylene oxide (GO), PCL- functionalized graphene (PCL-fGO) and reduction of graphene oxide (rGO) complex, and explored their mechanical and shape memory properties (show in Figure 4). Modulus and fracture stress of graphene/polyurethane nanofiber increased when compared with pure polyurethane nanofiber. Especially the PCL-GO polyurethane nanofiber showed the maximum mechanical properties due to the increased interaction between the polyurethane and PCL-GO. Measurement of the shape memory, the speed of recovery of PCL-GO/polyurethane nanofiber and rGO/polyurethane nanofiber was much faster than pure polyurethane nanofibers. The shapes of the PCL-GO and r-GO polyurethane nanofiber recovery time were 8 seconds when the addition amount was 1 wt%, while the pure polyurethane nanofibers and GO-polyurethane nanofibers were 25 seconds and 13 seconds. This study showed that PCL-GO integrated into the shape memory polyurethane nanofibers can effectively achieve high speed recovery and high mechanical strength (Hye Jin Yoo et al, 2014).

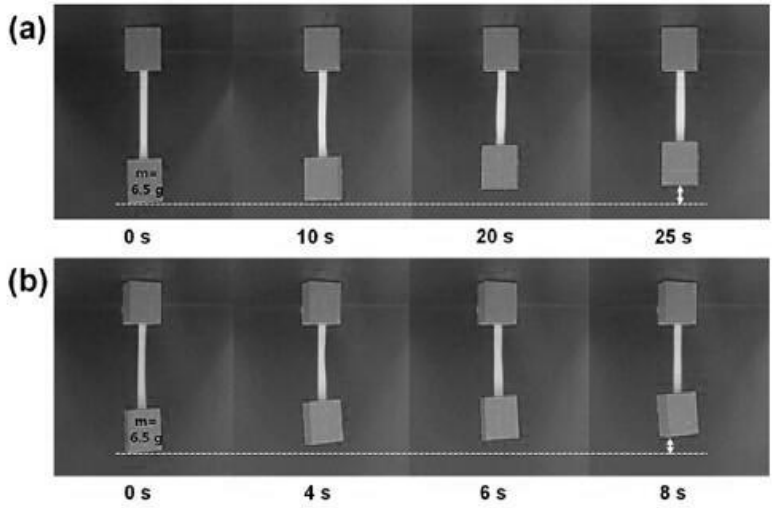

Fig. 4. Shape recovery images of (a) PU and (b) PU/GO05 nanofibers

3.4 Conductive Composites

Conductive composite materials are mainly prepared by polymerizing with a variety of conductive materials. With the emergence of graphene, it is applied to the conductive polymer composites direction, and used in the electronics, electrical, petrochemical, machinery, and other aspects of integrated application prospects because of its excellent electrical conductivity.

Anjanapura V et al used the thermal reduction method to prepare the graphene. And then they prepared grapheme/waterborne polyurethane nanocomposite by in situ polymerization and solution blending methods, respectively. The results showed that the addition amount of the graphene was 2wt% can improve the five orders of magnitude of conductivity, while the glass transition temperature of the material can also be reduced significantly (Anjanapura V et al, 2012). RM Hodlur et alprepared a kind of active material with flexible polyurethane foam and graphene oxide, and prepared pressure-sensitive conductive composite material by the reduction using hydrazine hydrate. The conductivity of the material was pressure-sensitive. Under weak pressure (0.5 atm), the conductivity of composites increased more than 5 orders of magnitude; the graphene was linked by a chemical bond with polyurethane and distributed uniformly in the matrix through infrared, scanning electron microscopy and thermogravimetric analysis confirmations shown in figure 5 (RM Hodlur et al, 2014).

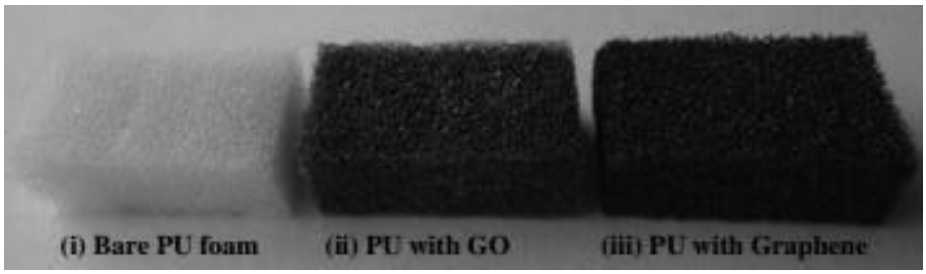

Fig. 5. Photographs of (i) bare PU foam, (ii) PU with GO and (iii) PU with graphene.

Ken-Hsuan Liao et al prepared graphene with acrylic polyurethane composite and the tetrahydrofuran was used as solvent. They got the low percolation threshold of the composite conductive material. The results showed that when the dosage of graphene was 0.15 wt%, the composite material can form a conductive network and its thermal stability improved significantly (Ken-Hsuan Liao et al, 2013). Yuan-Li Huang et al prepared the silver nanoparticles load on the graphene sheets by chemical methods. Polyurethane nanocomposite fibers with high light transmittance and high electrical conductivity were prepared by self-assembly. The study found that graphene as a "bridge" between silver particles and polyurethane, had good compatibility. When the addition ratio of grapheme/silver nanoparticles was 0.05 wt%, the composite materials had 150Ω/sq surface resistivity and 85% transmittance. What's more, the mechanical performance was significantly improved at the same time (Yuan-Li Huang et al, 2012). Hsi-Wen Tien used silver nanowires with cysteamine, graphene with high conductivity and surface area to composite AgNW by self-assembly method. This material in the land of NH^{3+} alkaline environments can combined with sulfonate functional groups on the surface of the waterborne polyurethane, generated high transmittance and low surface resistance of transparent conductive films (Hsi-Wen Tienet al, 2013).

3.5 Electromagnetic shielding materials

Electromagnetic shielding material is, when the electromagnetic wave reaches the surface of the material, the impedance of air and material at the interface is discontinuous, and the incident wave

will be reflected. Wave without being reflected will get into shielding material, the process of the forward propagating within the material, the shielding material will be attenuated, so-called absorption. In summary, electromagnetic shielding materials absorb electromagnetic waves are mainly based on the reflection and attenuation of electromagnetic waves. It is a threat to people's health that a variety of radiation in current life, so the electromagnetic shielding materials become popular research materials now.

Sheng-Tsung Hsiao prepared aqueous polyurethane fibers by electrospinning method, using L-B-L self-assembly method to support nGO with pGO on the polyurethane fiber, then treated it by hydroiodic acid to give the graphene/aqueous polyurethane composite fibers. The results showed that, the electrically conductivity of conjugate fiber was significantly enhanced (about 16.8 S/m), the electromagnetic shielding performance was increased by about 34 db, and the frequency range of the electromagnetic shielding was in 8.2-12.4 GHz (Sheng-Tsung Hsiao et al, 2013). Chen-Chi M. Mareduced and adsorbed graphene oxide of cationic surfactants (octadecyl trimethyl ammonium chloride) and graphene oxide without any modification by sodium borohydride to obtain P-GNS and S-GNS, then two kinds of graphene and polyurethane physical blending composite material were prepared. The results showed that, sulphonated graphene due to good interface effect can be uniformly dispersed in the aqueous polyurethane, and also exhibited lower conductivity percolation threshold and good electrical conductivity, electrical conductivity increased by about 5.1 S/m. When the S-GNS dosage was 7.7 wt%, the electromagnetic interference (EMI) shielding efficiency would be increased to 32dB (Chen-Chi M. Ma et al, 2014).

3.6 Biocompatible material

Graphene can be used as a drug carrier and applied in the modification of biomaterials because of its unique large specific surface area and a single atomic layer structure.
Jin Su-xing et al usedthe phosphorylcholine supported on the surface of graphene oxide, and then it was physically blended with polyurethane to prepare polyurethane/graphene load polymer phosphorylcholine composite materials. Protein adsorption tests and platelet adhesion test assessment showed that the composite may improve non-specific protein adsorption and platelet adhesion. These studies showed that, graphene/polyurethane composite material could be used for drug delivery, for application in the biomedical fieldin (Jin Su-xing et al, 2013).

4. Conclusions

In summary, the graphene/polyurethane composite materials have excellent performances on UV curing, conductive, electromagnetic shielding, the shape memory, enhanced material aspects, self-healing, electromagnetic shielding and UV. In the drug carrier’s aspect, it can also show potential applications. Overall, the current graphene/polyurethane composite material scope of the study is still narrow and faces many problems and challenges, such as the compatibility between graphene and polyurethane, the nature of the interaction of themselves and the development of composite material performance, etc. The further in-depth study is still needed. But the presence of graphene/PU composite material offers a variety of research object. Perhaps in the near future, graphene/polyurethane composite material will be significant application in different areas and change our lives.

5. Acknowledgement

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FLS P-08

STUDIES ON EFFECT OF DIFFERENT PIGMENT AND BINDER COMBINATIONS ON SURFACE PROPERTY OF FINISHED LEATHER

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The present work attempts to analyze the surface and physical properties of leathers finished with various combinations of binders and pigments by keeping other auxiliaries constant. The contact angles of liquid drops resting on the leather surface have been used to evaluate surface energy, acidity, basicity components of the surface energy, polarity and work of adhesion. Contact angle values have been measured for chrome tanned and conventionally retanned crust and finished leather made by varying pigment and binder combinations. The wettability of finished leather has been correlated with the contact angle values: the higher the contact angle value the lesser is the wetting observed. Complete wetting can be obtained when the contact angle value is zero i.e. the drop of liquid spreads spontaneously on the surface and partial wetting is obtained when the contact angle value is in between 0and 90^0. Acrylic binders with different film forming properties, protein, polyurethane and butadiene binders have been combined to prepare different finish formulations. Pigment to binder ratio for acrylic system and acrylic with polyurethane binder system have been optimized from the information obtained from contact angle values, which have direct relation to degree of wetting. And the results have been correlated with wet and dry rub fastness, finish adhesion, vamp flexing value, water vapour permeability and water proofness. It has been observed that when the surface of leather is coated with acrylic binder the contact angle value due to polar solvents(water) , non polar solvents(hexadecane) and moderately polar(DMSO) and methyl iodide show that as the thickness of coating increases, the contact angle value decreases for the base coat and sharply increases when top coat is applied. Top coats have the ability to increase the contact angle and they improve the performance properties of leather such as water resistance, fastness, finish adhesion etc. Cationic and anionic finishing formulations have been compared to study their effect in modifying the surface of finished leather based on contact angle values, wet and dry fastness to circular rubbing and water resistance. It has been observed that leathers finished using anionic finishing technique shows better wet rub fastness and water resistance effect compared to cationic finishing technique.

Key words: contact angle; surface energy; cationic finishing; anionic finishing; work of adhesion; acidity; basicity

1. Introduction

The object of finishing is to give a treatment of coatings to the grain surface to protect it against dirt, staining, wetting, mechanical stresses like rubbing, scuffing, flexing etc., levelling or evening out the colour of the grain surface, hiding grain blemishes and upgrading its quality, improving the aesthetic appeal and the sales value of the product. By the finishing process, the grain surface of the leather is coated with various substances and is then submitted to different mechanical operations, depending upon the purpose intended whereby the appearance of leather can be highly influenced to make it more useful, attractive and appealing to users. Finishing may be employed to impart colours, a uniform shade, special patterns, a smooth or grained or printed/embossed surface, lustre (Matt or glossy) as well as opaque (covered) or transparent (aniline/semi-aniline) appearance to the leather surface. Finishing operation is the most vital part of the processing of leather as the final product is judged by its appearance, evenness of colour and surface, feel, handle, break, gloss etc. Hence it is usually the finishers who have to face the complaints or blames, if anything goes wrong. They are also expected to correct whatever faults that have occurred during the earlier operations [1].

In this work, the overall objective has been to understand the surface energy parameters of different finishing of leather and relate these properties to the quality of finishing. Further, the work has attempted to optimize the quantity, nature and the combination of different finishing chemicals to obtain optimal finishing properties for different types of leathers.

2. Materials and methods

Materials used for this study were finishing chemicals from Stahl India, glass plates for preparation of finish films, glassware, contact angle measuring instrument, universal physical testing machine, goat crust leather.

Several finish formulations were prepared to study the surface property of finished leather by varying binders and pigments alternatively and keeping other auxiliaries constant. Contact angle value for different solvents such as water, methyl iodide, DMSO and hexadecane were determined for the respective finish formulations by the help of optical microscope having digital camera mounted perpendicular to the test sample where the drop of solvents going to be applied. The detail procedure for preparation of sample in order to determine contact angle, and the design of the whole experiments were described. The experiments were also conducted to study the advantage and disadvantage of anionic and cationic finishing technique, the effect of pigment to binder ratio on the surface and physical properties of finished leather, film forming properties of different binders, effect of commonly used top coats on the surface of the leather and etc

Surface energy calculation for two liquid systems

$$\gamma_{lv}(1+\cos\theta) = 2[\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} + \sqrt{\gamma_{sv}^{p}\gamma_{lv}^{p}}] \quad \text{---------- (1)}$$

Where θ= contact angle

γ_{lv}=liquid- vapour surface energy

γ_{sv}^{d}=solid- vapour interfacial energy of non polar component

γ_{lv}^{d}=liquid- vapour interfacial tension of non polar solvent

γ_{sv}^{p}=solid- vapour interfacial energy of polar component

γ_{lv}^{p} =Liquid- vapour interfacial energy of polar component

Surface energy calculation for three liquid systems

$$\gamma L(1+\cos\theta) = 2\sqrt{\gamma s^{LW}\gamma L^{LW}} + 2\sqrt{\gamma s^{+}\gamma l^{-}} + 2\sqrt{\gamma s^{-}\gamma l^{+}} \quad \text{---------- (2)}$$

Where,

γs^{LW} = the Lifshitz–van der Waals (non-polar) component of the surface free energy

γs^{+} And γs^{-} = the Lewis acid parameter and the Lewis base parameter, respectively.

From the contact angles of at least three liquids of known surface tension parameters($\gamma L, \gamma s^{LW}$ / $\gamma sv^{d}, \gamma l^{+} and \gamma l^{-}$) equation (2) can be used to determine the van Oss, Chaudhury and Good parameters for the surface free energy of the solid.

3. Results and Discussion

Contact angle and surface energy value for dyed crust and different finish formulations.

The crust sample was cut into appropriate rectangular shape with size similar to microscopic slide i.e. 3cm by 1cm. The contact angle for the dyed crust was measured with the help of contact angle measuring instrument which is microscope where digital camera is mounted on it to take the droplet pictures on the test specimen. Three different solvents highly polar (water), less polar (methyl iodide) and completely non-polar (hexadecane) have chosen and the values were described as follows:-

Table 1. Contact angle values for crust leather for shoe upper (black)

Sample no.	contact angle values			Remarks
	WCA	MICA	HDCA	In each cases one drop of the solvents (approximately **5µl**)were applied
B1	69.01	ND	ND	
B2	80.69	ND	ND	
B3	80.66	ND	ND	
B4	66.02	ND	ND	
B5	85.61	ND	ND	
B6	73.47	ND	ND	
B7	78.12	ND	ND	
B8	83.59	ND	ND	
B9	62.43	ND	ND	
Average	75.51	-	-	

ND=not detectable

From above table one can conclude that the surface contact angle with less polar solvent (methyl-iodide) and non polar solvent (hexadecane) for the crust leather is negligible i.e. the drop of the liquid was spontaneously dispersed on the surface of the leather this might be due to the imbalance between the solid – liquid interfacial energy and the cohesive force of the molecules of the solvents. But in the case of water the contact angle is approximately more than 75^{0}C which is indication of hydrophobic nature of the given leather. The cohesive force which is due to the interaction of the molecules of water /surface tension of water is more than the solid- liquid (leather surface /water) interaction. Therefore the molecule of water tends to form droplets rather than spontaneously spreading as it was observed in the case of methyl iodide and hexadecane. The higher value of the contact angle indicates the slower wettability of the surface by respective liquids in contact with the surface.

By using young's equation, the surface energy of any solids can be calculated from the contact angle value.

$$\gamma lv(1 + cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}} + \sqrt{\gamma sv^{p}\gamma lv^{p}}] \quad \text{---------- (3)}$$

Where θ= contact angle

γlv=liquid- vapour surface energy
γsv^d=solid- vapour interfacial energy of non polar component
γlv^d=liquid- vapour interfacial tension of non polar solvent
γsv^p=solid- vapour interfacial energy of polar component
γlv^p =Liquid- vapour interfacial energy of polar component

By using equation [1], it is possible to determine the surface energy of crust leather and finished leather finished with different finish formulations as follows. As it has described in table-17 above, the average value of contact angle for the crust leather is 75.51 in degrees. By using equation [1], it is possible to calculate polar and non polar components of surface energy and hence total surface energy. For the surface energy calculation, contact angle for water and hexadecane were used.

Surface energy calculation for two liquid systems.

Consider the contact angle for hexadecane to be zero and for water to be 75.51^o
Θ of water=75.51^0
Θ of hexadecane=0^0
γlv for water=72.8mN/m
γlv for hexadecane= 27.47mN/m
It is possible to calculate the total surface energy by using equation (1) as follows:

$$\gamma lv(1+cos\theta) = 2[\sqrt{\gamma sv^d \gamma lv^d} + \sqrt{\gamma sv^p \gamma lv^p}]$$

In the case of hexadecane, the polar component will be vanished because it is highly non- polar substance, therefore;
The above equation becomes:

$$\gamma lv(1+cos\theta) = 2[\sqrt{\gamma sv^d \gamma lv^d}$$

27.47mN/m (1+cos0)=2[$\sqrt{\gamma sv^d * 27.47 mN/m}$
By rearranging the values

γsv^d=27.47m N/m

In similar way, the polar component of surface energy(Υsv^p)can be calculated, by considering the contact angle value of water and its polar and non polar component of surface tension values as follows:-

$$\gamma lv(1+cos\theta) = 2[\sqrt{\gamma sv^d \gamma lv^d} + \sqrt{\gamma sv^p \gamma lv^p}$$

By substituting the values

$$72.8 mN/m(1+cos 75.81) = 2[\sqrt{\frac{27.47 mN}{m} * \frac{21.8 mN}{m}} + \sqrt{\gamma sv^p * \ 51 mN/m}]$$

By rearranging terms, the polar component of surface energy will be:-
γsv^p=8.53m N/m
From the polar(γsv^p)and non polar(γsv^d) component of surface energy values one can see that there is inverse relationship between surface energy and contact angle i.e. the higher contact angle the smaller the surface energy and vice versa.
The total surface energy of the solid material (crust leather) is the sum of polar and non polar components.
γsv= γsv^p+γsv^d=8.53m N/m+27.47m N/m=36m N/m

The above surface energy value is the specific for the particular crust leather taken for the control. The magnitude will vary based on the type of re-tanning and fat-liqouring chemicals used. Any surface treatments like coating and

different mechanical operations have significant influence on the surface energy value.

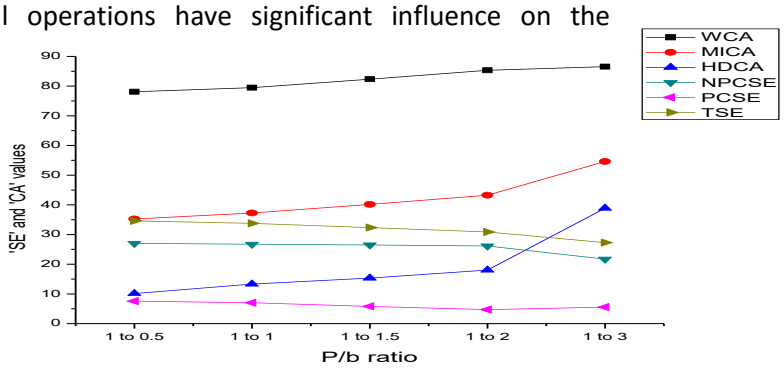

Figure-1. Contact angle (CA) and surface energy (SE) values for p/b ratios for acrylic binder (RA-17, RA-27006 and RA-2354) **combinations.**

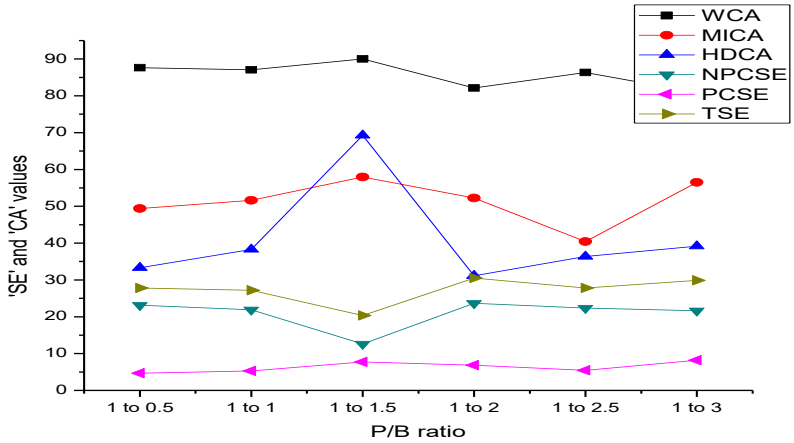

Fig. 1 contact angle and surface energies for very soft resin binder (RA-17)

From the fig 2 it is evident that maximum contact angle value and minimum total surface energy was observed at p/b ratio of 1:1.5 and the PCSE does not show significant change as the ratio of p/b ratio varies. At p/b ratio of 1 to 0.5 and 1 to 1 higher NPCSE was observed**.**

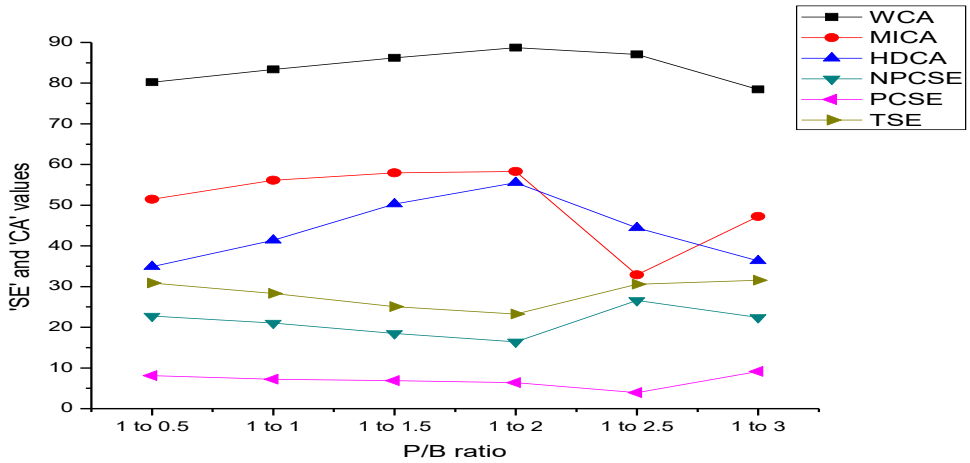

Figure 2 contact angle and surface energies for soft resin binder (RA-27006)

From the graph 3 it is clear that as the contact angle value increases the surface energy value decreases. Smaller surface energy values and higher contact angle (WCA, MICA and HDCA) values were observed at P/B ratio of 1 to 2. These values indicate that the surface of the finished leather is less wettable at this ratio because the higher the contact angle the surface of the solid is difficult to be wetted. And the graph shows that when the binder concentration increases beyond the limit the water contact angle value was observed to be decreased because the hydrophilic nature of the binder this in turn affect surface of finished leather i.e. the surface was appeared to be plastic, tacky and has poor fastness value.

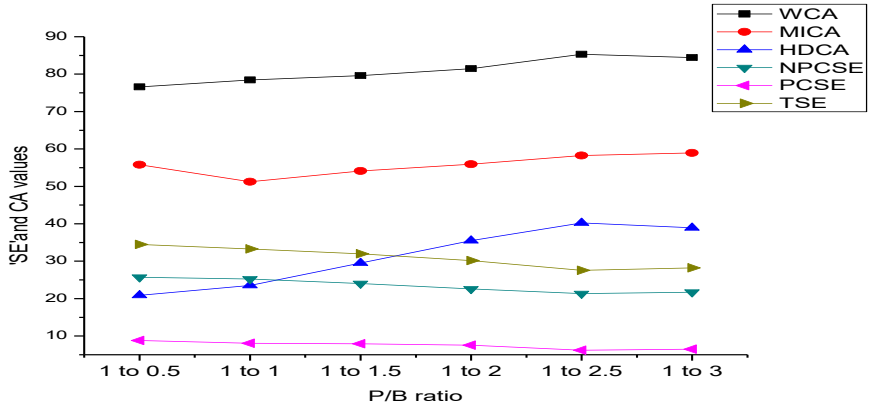

Figure 3 plot of contact angle and surface energy values versus P/B ratios for medium soft resin binder. (RA-2354).

From the graph in fig 4 higher contact angles and lower surface energy values were observed at P/B ratio of 1 to 2.5.This is the optimum value to get better finishing effect. That means at this ratio better fastness, flexing endurance and other surface properties were observed. It was also shown in the above graph that the contact angle value increases as the ratio of p/b increases up to ratio of 1 to 2.5 and beyond this value it starts to decrease gradually. But the total surface energy value was high at lower concentration of binder up to certain limit and then starts increasing. This result is better indication for a finishing technician in deciding the quantity of soft binder to be used.

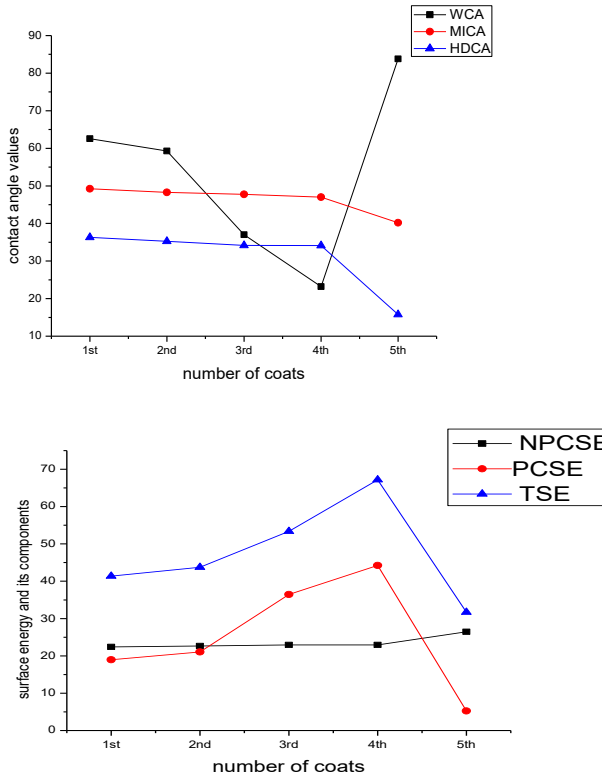

Fig-5. Effect of number of base coats and use of CAB top coat on surface energy and contact angle value

In fig 5, the contact angle value and surface energy showed inverse relationship that means the higher contact angle the lower surface free energy and as the number of coat increases the surface energy also increased initially and decreased sharply when the top coat was sprayed and the water contact angle value also start slowly decreasing and then showed sharp increase after the forth coat but the change in contact angle value for methyl iodide and hexadecane was not as high as compared to water contact angle. Because all the finishing chemicals used are water based and have polar groups, the change in water contact angle value is high during the coating process.

Table 2 contact angles for p-b combinations (1:2 ratios) by varying the type of binders.

Type of binders used	Contact angle value		
	water	DMSO	Hexadecane
B_1 27154	67.050	ND	ND
combination VS,S,MS(1:1:1)without filler	79.747	62.389	ND
Resin binder combination with filler	87.65	70.36	38.17
CRUST for control	75.829	ND	ND
RA-2354	87.094	60.347	ND
RA-27006	91.431	58.609	ND
RA-17	88.536	59.807	ND
B_1 27047	65.871	ND	ND

Note: - Vs= RA-17,S= RA-27006, MS=RA-2354, ND= not detected

Surface energy calculation for three liquid systems

By using the contact angle value of the three liquids it is possible to calculate the Lewis acid parameter (cationic nature) and Lewis base parameter (anionic nature of the surface of the resin finished shoe upper leather using equation [2].

Let's consider the contact angle values determined in the case of resin binder combination with filler in the table 2,

For hexadecane, since it has no polar component of surface tension value, equation [2] is reduced to:

$$\gamma \boldsymbol{L}(\mathbf{1}+\boldsymbol{cos\theta}) = \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{\boldsymbol{LW}}\gamma \boldsymbol{L}^{\boldsymbol{LW}}}$$

Where, θ=37.17, $\gamma \boldsymbol{l}^{\boldsymbol{LW}} = \gamma \boldsymbol{L}$**=27.47mN/m**

By substituting the given values,:$27.47(\mathbf{1}+\boldsymbol{cos}\mathbf{37.17}) = \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{\boldsymbol{LW}}27.47}$

By rearranging terms; $\gamma \boldsymbol{s}^{\boldsymbol{LW}} = 23.84 mN/m$, non- polar component of surface energy

To calculate the Lewis acid parameter or the cationic nature of the surface, one can use water and DMSO contact angle and surface tension values.

Since DMSO has very small γl^{+} value compared to $\Upsilon \boldsymbol{l}^{-}$ value, it is logical to neglect the last term in equation [2] and the equation is reduced to:

$$\gamma \boldsymbol{L}(\mathbf{1}+\boldsymbol{cos\theta}) = \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{\boldsymbol{LW}}\gamma \boldsymbol{L}^{\boldsymbol{LW}}} + \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{+}\gamma \boldsymbol{l}^{-}}$$

From literature, for DMSO we can get

$\gamma \boldsymbol{L} = \mathbf{44}\boldsymbol{mN/m}$

$\gamma \boldsymbol{L}^{\boldsymbol{LW}} = 36m\ N/m$

$\gamma \boldsymbol{l}^{-}$ =32m N/m, Θ = 70.36

By substituting the above values

$$44(\mathbf{1}+\boldsymbol{cos}\mathbf{70.36}) = \mathbf{2}\sqrt{23.84 * 36} + \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{+}32}$$

$$22(\mathbf{1.336}) = 29.30 + \sqrt{\gamma \boldsymbol{s}^{+}32}$$

$$0.092 = \sqrt{\gamma \boldsymbol{s}^{+}32}$$

Squaring both sides and rearranging terms

$\gamma \boldsymbol{s}^{+}$=0.003mN/m, the Lewis acid parameter which signifies the cationic nature of the surface.

To calculate the Lewis base parameter ($\gamma \boldsymbol{s}^{-}$), one can use surface tension of water and the above surface energy components obtained in the case of hexadecane and DMSO.

For water

$$\gamma \boldsymbol{l} = \mathbf{72.8}\boldsymbol{mN/m}$$

WCA= 87.65^0

$$\gamma \mathbf{l}^{-} = \gamma \mathbf{l}^{+} = 25.5\mathrm{mN/m}$$

$\gamma \boldsymbol{L}^{\boldsymbol{LW}}$=21.8mN/m

By using equation [2] and substituting the known values:-

$$72.8(\mathbf{1} + cos87.65) = \mathbf{2}\sqrt{23.84 * 21.8} + \mathbf{2}\sqrt{0.003 * 25.5} + \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{-} * 25.5}$$

$$37.89 = 23.08 + \sqrt{\gamma \boldsymbol{s}^{-} * 25.5}$$

Solving for the unknown value and rearranging terms

$\gamma \boldsymbol{s}^{-}$=8.6mN/m, Lewis base parameter which signifies the anionic nature of the surface of the leather finished with the above formulation indicated in table 26

The polar component of the surface energy can be estimated by using equation as follows:-

$$\gamma \boldsymbol{s}^{\boldsymbol{p}} = \mathbf{2}\sqrt{\gamma \boldsymbol{s}^{+} \gamma \boldsymbol{s}^{-}}$$

By substituting the values

$\gamma \boldsymbol{s}^{\boldsymbol{p}} = \mathbf{2}\sqrt{0.003 * 8.6}$ =0.32 mN/m

The total surface energy is the sum of polar and non polar components

$$\gamma \boldsymbol{s}^{\boldsymbol{total}} = \gamma \boldsymbol{s}^{\boldsymbol{LW}} + \gamma \boldsymbol{s}^{\boldsymbol{p}}$$

$\gamma \boldsymbol{s}^{\boldsymbol{total}} = 23.84 mN/m$ +0.32 mN/m=24.16mN/m

From the surface energy and its component values one can deduce that the coated surface of leather have more of non polar nature and the charge characteristics is mostly anionic in nature even though there is residual cationic charges.

4. Conclusion

The current research presents different finish formulations were prepared by using commercially available finishing chemicals to study the effect of pigment and binder combinations on the surface property of shoe upper leather. Contact angle was used as a parameter to study the effect of each finish formulations on the surface property of the leather. Water, methyl iodide, hexadecane and DMSO were used to measure the liquid-solid contact angle. The experimental result from contact angle value showed that coating with pigments and binders have increased the contact angle value compared to the control crust. And the corresponding value of surface energy were calculated by using Thomas young equation and the results showed that there is decrease in surface energy when the contact angle increases. It was observed that when the contact angle increases the degree of adhesion and the wettability of the surface of the leather were decreased. In addition to this the

effect of top coats and other finishing auxiliaries other than pigments and binders on contact angle value were investigated. Fillers have the ability to increase the contact angle.CAB top coated leather showed more contact angle than PU and acrylic top coats. This value clearly showed that wettability is more in the case of PU and acrylic top coated leathers than CAB top coated leathers. The effect of number of top coats on water contact angle value were determined ,and the experiment showed that the value were decreased gradually at the beginning of the coat because the top coats are water based so during the coating process the hydrophobic nature of the surface of chrome tanned leather have decreased. And finally the contact angle value were increased and the corresponding surface energy were reduced when CAB top coat were sprayed. In general when the coating chemicals have more polar groups the contact angle values were observed to be increased.

Physical tests like rub fastness, finish adhesion, water vapour permeability and flexing endurance were conducted for leather samples finished with different acrylic binder pigment combination, cationic finish formulations and PU binders with and without incorporation of performance chemicals. The physical test results showed that pigment binder ratio and the property of the given binder have significantly affected the above mentioned physical test parameters. In the case of acrylic binder- pigment combination better result were obtained when we use combination of soft, medium soft and very soft binders at 1 to 3 p/b ratios but very soft binder has to be used in smaller proportion to minimize the tackiness effect. And better wet rub fastness and water resistance effects were observed in the case of acrylic resin finish and PU based finishing technique compared to cationic finishing technique.

Film forming property of different acrylic binders and protein binders were studied and the result showed that soft, medium soft and very soft acrylic binders form flexible, softer films and hard acrylic binders do not form film at room temperature where as protein binders form discontinuous and brittle film.

The wettability of the surface of leather has to be good before applying the top coat otherwise the top coat cannot adhere to the surface of the leather whenever such hard binder is used at the base coat in larger proportion. Resin binders having lower water contact angle are ideal for base coat since they can easily spread on the surface of the leather this in turn facilitates degree of adhesion.

Stahl finishing binders such as RA-2354, RA-27006 and RA-17 can be used in base coat since they have lower contact angle value compared to RA-1216. And hence the surface of the leather before applying the top coat is easily wettable. But if they are used at the top coat the surface of the leather can be easily affected by different soiling agents such as dust, dirt, fats and oils because of their tackiness.

When RA-17, RA-27006 and RA-2354 are used independently with other finishing chemicals in base coat, optimum finish effect is observed at p/b ratio of 1 to 1.5,1 to 2 and 1 to 2.5 respectively. And when these binders are combined the optimum value is observed at p/b ratio of 1 to 3. The percentage elongation of the films prepared by soft, very soft and medium soft resin binders showed maximum value where as when the hard resin binder (RA-1216) the value has reduced. The Young's modulus which indicates the stiffness of the finish film were increased when hard binder is incorporated

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IVL P-20

COLLAGEN HYDROLYSATE SYNTAN: A PRODUCT OF HIGH VALUE FROM LIMED TRIMMINGS

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Ethiopian tanneries processing from hides result in the generation of significant amount of limed trimming wastes. Annually about 2000 tons of limed trimming are generated from Ethiopian tanneries. Most of these trimming wastes go unutilized and utmost find use in industrial glue, a product of low value. This study reports a methodology for making syntan from these limed trimming waste thus not only internalizing the trimming waste problem but also generating high value product from waste. In addition, such a syntan would be an ecofriendly alternative to syntans based on phenol-formaldehyde or other resin syntans. In order to meet the property requirements brought about by the combination of other syntans, preparation of the collagen hydrolysate composite with varied molecular weight fractions is required. Collagen hydrolysate syntans with varied amount of alkali of hydrolysis has been prepared and characterization of the collagen hydrolysate syntan has been carried out. Further, the application of these syntan in retanning for the manufacture of various types of leathers and characterization of the leathers has been carried out to determine the effectiveness of the collagen hydrolysate syntan for retanning purpose. Thus, this study will solve not only solid waste disposal problem but will also generate high value returns from waste.

Keywords: collagen hydrolysate; trimming waste; syntan; retanning

INTRODUCTION

Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. These tannery solid wastes have different characteristics. Some tannery solid wastes made of organic collagen protein will rot away after being placed for a period of time in nature environment. And the others contain substances, such as chrome.

However tannery solid wastes contain collagen protein, which is a valuable resource. Collagen proteins have application for making gelatin, additive component for cosmetics, biomaterial for medical products[1], for animal feed staff, nutrition component for health care products, and as raw material for protein based industrial products. Moreover some of tannery solid wastes contain chrome, which is a valuable material for tanning.

Trimmings of about 5-10% of hides are trimmed in beam house operation mainly for the ease of handling hides/skin in leather making. It may be noted that these trimmings contain a very high proportion of collagenous protein. The practice of trimming the offal and other undesired portions of hides and skin is carried out before soaking process. In Ethiopia in addition to trimming in raw, the practice of trimming after liming is very common especially in the case of bovine. About 50-100 kg of limed trimmings is generated per ton of wet salted raw hide processed. The limed trimmings are done to facilitation of the limed splitting operation which is a common practice in Ethiopia tanneries.

Annually about 2000 tonns of limed trimming are generated from Ethiopian tanneries. These trimmings which are rich in collagen are utilized for making glue. There is a great opportunity available for making valuable products using collagenous wastes. In our approach to internalize this waste within the tanning industry, we explored the preparation of collagen hydrolysate syntan, a greener option to amidst of wide variety of non-biodegradable to so hard to biodegradable syntans in retanning. This is first of its kind approach for making collagen hydrolysates from limed trimmings. Early reports on collagen hydrolysates were based on raw trimmings or chrome shavings.

Collagen hydrolysis can be brought about through several approaches. Vera Kasparkova Etal have reported the preparation of collagen hydrolysate using chemical hydrolysis.[2] Brown etal have separate the protein from chrome shavings and the collagen hydrolysis was carried out using enzyme.[3,4] These protein hydrolysates were targeted for agricultural application.

Collagen is a unique protein which provides structural integrity to connective tissues. Type I collagen present in hides and skin are about 3000^{o}A long and 15^{o}A in diameter. These collagen molecules are highly organized in fibrillary form in skin. In general collagen molecules are resistance to wide range of proteases such as trypsin, pepsin. Only enzymes such as collagenases, chymotrypsin, has the ability to breakdown collagen in native form.

In this paper, we present a simple approach for the preparation of collagen hydrolysates from limed trimming waste using alkaline hydrolysis method. We have also demonstrated the effectiveness of these collagen hydrolysate compositions as a retanning auxiliary in leather manufacture.

MATERIALS AND METHODS

Materials

Hide limed pelt trimmings. Chemicals used for the analysis were of analytical grade. Chemicals used for processing of skins were of commercial grade.

Preparation of collagen hydrolysate

Limed pelt trimmings were collected. 100 g of it was weighed and delimed completely with 100% water and 1% ammonium chloride based on its weight. Then the delimed pelts were cut into small pieces. They are weighed and transferred in to 500 ml conical flask. Then 150% (v/w based on the wet weight) of water was added. 2%, 4%. 6% and 8% of sodium hydroxide pellets were added. The trimmings are then digested by heating at 80^{o}C for 4 hours in autoclave. After that the hot melted dispersion is cooled to room temperature. The extracted collagen hydrolysate was then filtered off with Whatman filter paper. Then it was neutralized to a pH of 6.2 with 0.1N HCl. Finally it was concentrated with rotary evaporator at a temperature of 40^{o}C.

Characterization of the collagen hydrolysate

Matrix Assisted Laser Desorption/Ionization (MALDI-TOF)

In analyzing our collagen hydrolysate with MALDI-TOF, sinapinic matrix was used. Both positive and negative ions were collected and the spectrum of the hydrolysate m/z over a wide mass range versus intensity was plotted.

Application of collagen hydrolysate to wet blue leathers

The prepared collagen hydrolysate products (four) prepared at different concentrations were used for retanning trials to see the efficacy of the products for its effectiveness for the intended purpose. Five pieces of wet blue goat leathers with a dimension of 10 cm x 10 cm was prepared by cutting them around butt area. The four pieces were used for experimental trials (CH-1 (2% NaOH), CH-2 (4% NaOH), CH-3 (6% NaOH), and CH-4 (8% NaOH)) and one pieces was used for control process using commercially available syntan. The offer of the syntans in both the control and experiment were 10% based the shaved wet blue leather weight. No other syntans were used in both the control and experiment. Acrylic drums of the same size were used for processing control and experimental leathers, and the same post tanning process formulation was used except for the use of retanning agents.

Organoleptic evaluations of crust leathers

The experimental and control leathers were evaluated by a group of experienced technologists for their organoleptic properties. The organoleptic properties such as softness, fullness, roundness, grain smoothness, grain tightness, and intensity of the shade of the color and overall appearance of the crust leathers treated with collagen hydrolysate samples (CHs) and control were evaluated. The values were rated from 1 to 10; higher value represents better functional property.

Physical Strength characteristics of crust leathers

The five pieces of crust leathers were tested for physical strength properties. Sampling and conditioning was done as per standards ISO 2418:2005 and ISO 2419:2005. Physical strength properties tensile strength and elongation at break, and double edge tear strength were measured as per standard procedure .

RESULTS AND DISCUSSION

Matrix Assisted Laser Desorption/Ionization (MALDI-TOF) of Collagen Hydrolysate

MALDI-TOF spectrum of the collagen hydrolysates sample prepared are presented in Figure 1. You can note that there are no differences in the molecular weight of the fractions between the four samples. However if you observe closely, the ratio between fractions there are minor differences, in the case of CH-4 the degree of hydrolysis is higher because the proportion of 440 Daltons is lower compared to 200's. Generally it was observed that the molecular weight of the fractions varied from 200 to 450 Daltons for all the collagen hydrolysates prepared.

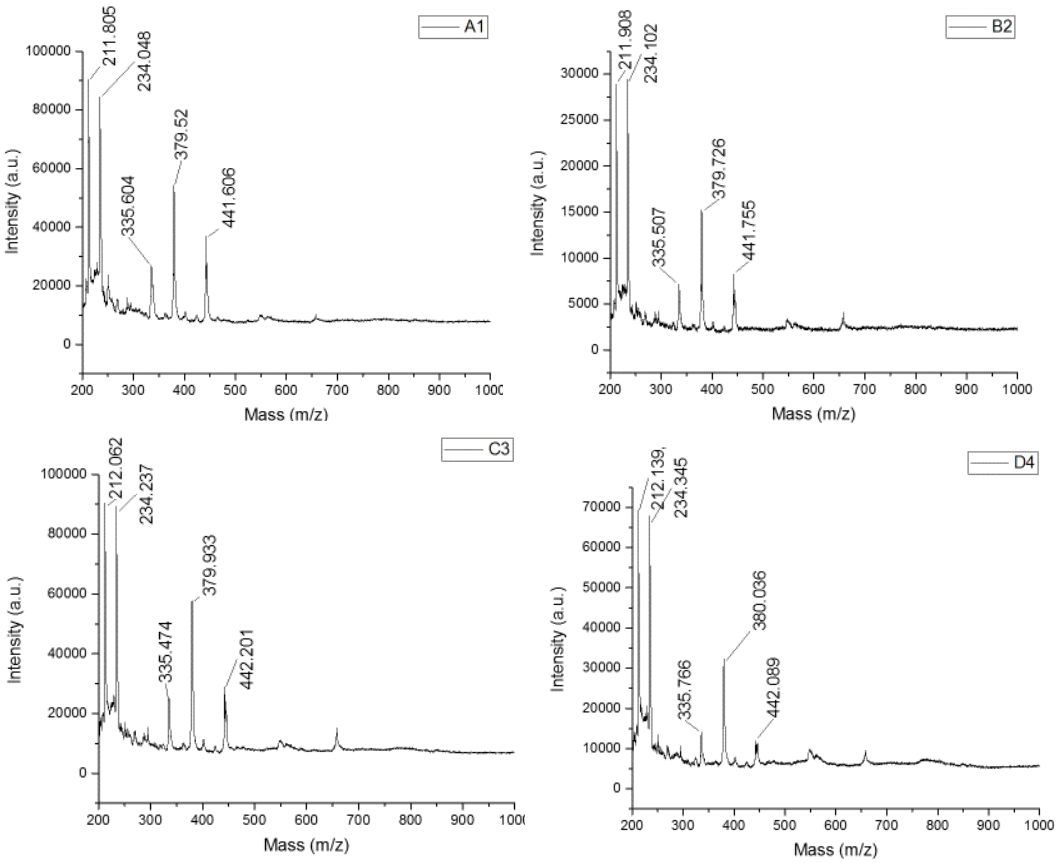

Figure 1: MALDI-TOF spectrum of collagen hdyrolyzate, CH-1 (top left), CH-2 (top right), CH-3 (lower left) and CH-4 (lower right)

Organoleptic properties

The organoleptic properties of the experimental and corresponding control leathers are presented in Figure 2. The fullness and roundness properties of collagen hydrolysate treated samples are comparable with that of the control, whereas the grain tightness, grain smoothness, intensity of the shade/uniformity of samples which has been treated with CH, are better than control leathers.

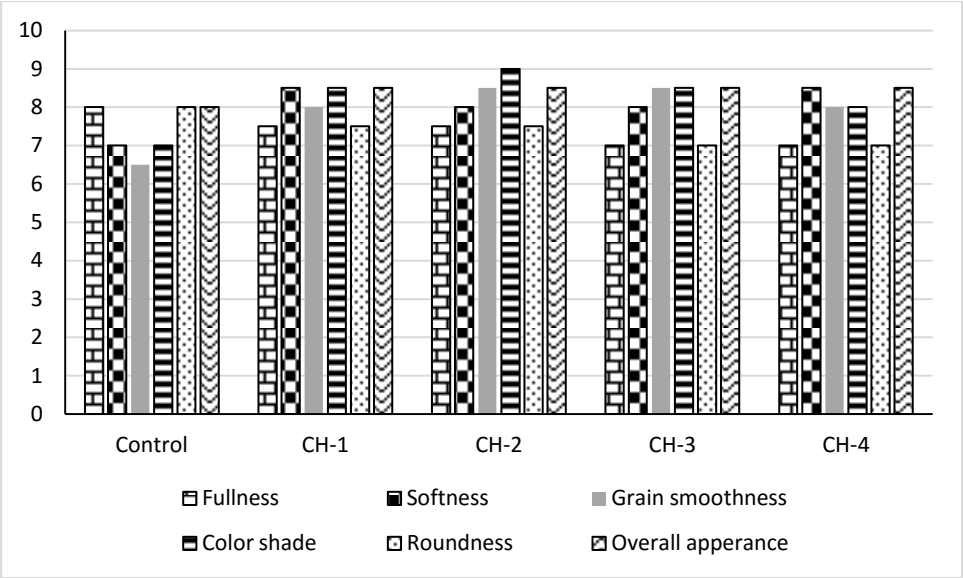

Figure 2:- Organoleptic properties of control and experimental leathers

Physical Strength properties

The tensile strength, percent elongation and double edge tear strength had been presented in Table 1. Experimental leathers had been observed to have better tensile strength, tear strength and elongation than the control. But there were minor differences among the samples that have been treated with collagen hydrolysates.

TABLE 1

Tensile and tear strength of control and CH treated leathers

Retanning Treatment	***Tensile Strength (N/mm^2)***	***Elongation (%)***	***Tear Load (N/mm)***
Commercial syntan	22.45±1.65	62.81±1.21	51.32±1.08
CH-1	30.40±1.75	66.10±1.64	62.41±1.19
CH-2	35.30±1.62	65.12±1.35	66.10±1.26
CH-3	33.48±1.56	66.26±1.08	64.37±1.15
CH-4	34.89±1.41	64.16±1.46	62.87±1.34

CONCLUSIONS

Collagen hydrolysates from limed trimming wastes were successfully prepared by a simple procedure using sodium hydroxide. The molecular weight fractions of the collagen hydrolysates prepared by alkaline hydrolysis were observed in the range of 200 to 450 daltons.

The data of tensile and tear strength indicate that collagen hydrolysate increases the strength properties of the leathers. Furthermore, comparable fullness and better softness, grain smoothness and color shade of the grain are achieved by treating leathers with collagen hydrolysate.

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ECT P-29

PRACTICAL ACHIEVEMENTS OF VARIOUS TECHNOLOGIES FOR SUSTAINABLE LEATHER MANUFACTURE IN KANPUR LEATHER CLUSTERS

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Super Tannery Ltd, Jajmau, Kanpur
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With the overall objective to enable local leather-based industry to sustain conversion of locally available raw hides and skins into exportable products without jeopardizing the livelihood of the human settlements and supplementing various ongoing activities to achieve total environmental security, the UNIDO Kanpur Leather Development Project has been demonstrating various cleaner tanning technologies in volunteer tanneries. These units have been developed as pilot demonstration units (PDUs) as "Show-How" models. The flow of events in these demonstrations is as follows: Implementation on pilot but commercial scale → Fine tuning the process → Closely monitoring the operational parameters and analysis of results → Preparation of technology packages → Dissemination widely among the industry (through on-site demonstrations, workshops and seminars).

The following six cleaner technologies have been demonstrated within the first year of the project:

PDU1: Hair save unhairing/liming,

PDU2: Water mixing and measurement,

PDU3: Solar water heating and its effect on leather quality and waste reduction,

PDU4: Solar air heating,

PDU5: Processing fresh chilled hides,

PDU6: Desalting,

PDU7: Lime water recycling system

Key words: Cleaner technology, Kanpur, Hair save unhairing, solar water heating, solar air heating, Core group on Cleaner technology

PDU1: Hair save unhairing/liming

Hair-save unhairing method in leather processing, accompanied using cleaner technologies in all other stages of the processing, contributes to substantial improvements in the waste water discharge. Dissolving the hair results in high organic pollution in the waste water. With increasingly stringent environment requirements, it has become necessary to reduce the pollution load in wastewater as much as possible. This may be done by treating the wastewater biologically: an expensive undertaking. Moreover, wastewater treatment generates a large amount of sludge posing disposal problems. For this reason, hair-save unhairing has taken on renewed importance. Today, it is a well-established practice, especially in industrialised countries.

The hair save unhairing is achieved using a screw type filter for recovering hair from the liming-unhairing float. A special arrangement was made in a tannery by connecting one hair filtering equipment to serve four liming drums. The unhairing-liming liquor after immunization of hair is collected from drums through drain valve-banana channels-conveyance drain-transfer pit-filtering and pumped sent back to drum. The filtered hair is collected and disposed separately and liming continued. A series of characterization tests were made on waste lime liquors in the conventional process and after installation of hair save system. This system helps reduce pollution parameters of the liming bath, namely Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), sulphides and total suspended solids by 32 to 42%, 37 to 49%, 55 to 66% and 40 to 61% respectively. Duration of hair filtration, duration of hair immunization and float levels were varied and arrived at optimum values as 40 minutes, 60 minutes and 80 to100% respectively.

Figure 1 & 2: Hair saving screen installed within existing tannery

Figure 3 below provides the environmental benefits obtained so far in terms of reduction of pollution load in liming wastewater while adopting the hair sae unhairing:

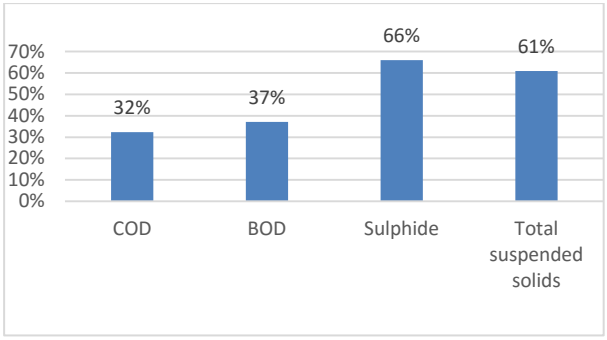

Fig. 3. Reduction of pollution load in liming wastewater while adopting hair save unhairing

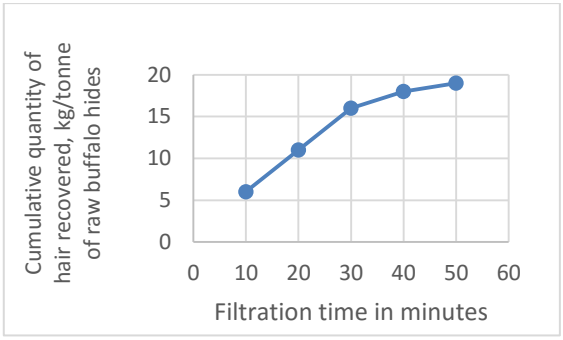

Fig. 4. Quantity of hair recovered during filtration

PDU2: Water mixing and measurement

In many tanneries in Kanpur, the float levels in processing vessels are not measured but judged visually. Calculations and observations on float levels used in processing vessels revealed that the water consumption is higher by 50 to 200 percentage points over the actual requirement. The following Table 1 shows the estimated levels in water consumption based on 64 measurements, ranging from soaking to post tanning in tanneries.

Table 1: Estimated water consumption levels in different process vessels

Process stage	Process vessel	Requirement (as per recipe)	Actual usage	Excess percentage points
Beamhouse	Paddles	150 to 200%	200 to 216%	+50 to +66%
Tanning	Drums	70 to 150%	120 to 200%	+50 to +130%
Post tanning	Drums	100 to 150%	220 to 300%	+70 to +200%

Three different methods of measuring water were demonstrated, namely, woltman type water flow meters, electro-magnetic flow meter with solenoid valve and automated water mixing cum addition systems.

Measuring water levels itself has reduced the water consumption by 20 to 30% in these tanneries. This has also resulted in reduction of quantum of pollutants like COD and TDS by 15% and 10% in the dyeing/fatliquoring bath contributed by increased uptake of chemicals.

Figure 5 & 6: Water mixing unit; control panel of the water mixing unit

PDU3: Solar water heating

The tanning industry uses a considerable amount of hot water in its processing, mainly during the beamhouse, tanning and dyeing. Up to now, the industry has been heating water with fossil fuels, gas oil and natural gas, either with a conventional boiler or, in certain locations, with cogeneration.

New technologies are available for the industry to produce hot water. Thermal solar energy can be an option to produce hot water in tanneries and reduce costs for energy but in same time also reduce carbon emissions, greenhouse gases and minimise reliance on fossil fuels. Indian tanneries are favourable located for application of the solar water heating systems.

The solar insolation data for Kanpur was obtained from NASA Surface meteorology and Solar Energy - Available Tables. The same is provided in the following Table 2.

Table 2: Monthly averaged insolation incident on a horizontal surface (kWh/m^2/day) for Kanpur

Lat 26.5 Lon 80.3	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual average
22 year average	3.72	4.67	5.75	6.32	6.57	5.91	4.8	4.48	4.51	4.87	4.26	3.6	4.95

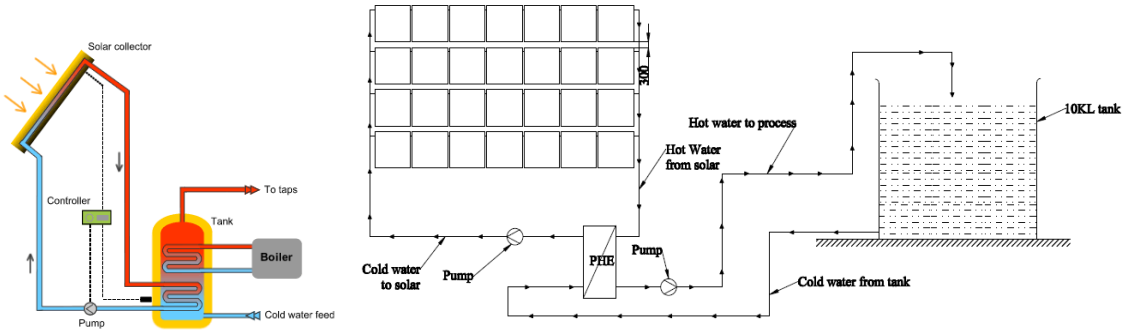

Figure 7 & 8: Active solar water heating

Installation of solar water heating system reduced the demand for steam thereby reducing the coal consumption in boiler. The solar water heating system of solar field area of 192 m^2 provides hot water of about 7000 litres per day on annual average. The use of hot water in leather processing increased uptake of chemicals thereby reducing the chemical consumption. The environmental savings are reduction in COD 17-30% and TDS 6-13% in post tanning operations contributed by increased uptake of chemicals. Fuel savings is about 155 kg of coal per day.

Benefits:

- Reduced costs for energy (coal, gas, oil), reduction of Rs. 400,000 per annum for this capacity

- Lower CO_2emissions, 108 to 109 tonnes of CO_2 reduction per annum for next 15 years (life of the system)
- Approx. 130 litres of 75°C produced by 1 m^2 of panel

Fig 9 & 10: Solar water heating system

PDU4: Solar air heating

In autospray and roller coating, the leather is dried in tunnel driers using hot air at about 80 to 90^0C. Hot air is produced from steam or hot thermic oils. Hot air is generated using solar energy over the roof top and applied directly to the tunnel driers to dry the leathers. Installation a 270 m^2 of solar air heating provides heat energy to one autospray drier with five compartments and of working width 3m.

The solar collectors consist of the following materials starting from bottom: roof sheet, insulation for 100 mm thickness, corrugated black painted aluminium base material, space for air flow and glass cover on top. The air is circulated between the black painted material and glass, during which it gets heated. The air is collected through insulated ducts and applied to the tunnel drier.

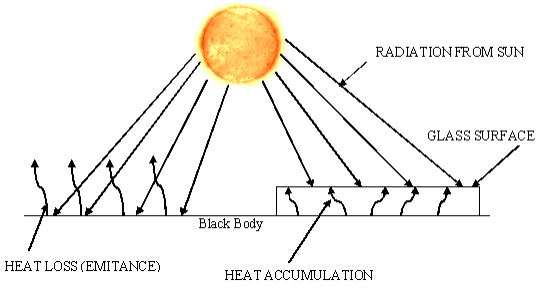

Fig. 11. Conceptual diagram of solar hot air generation

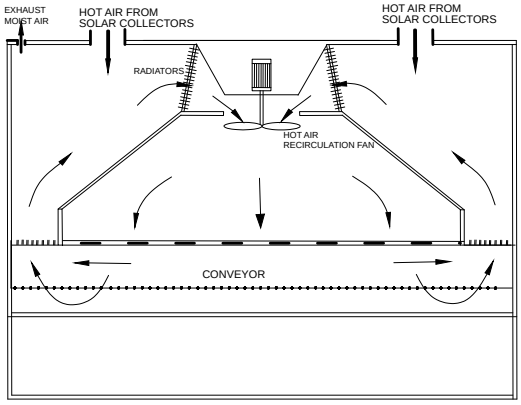

Fig.12. Cross section view of autospray drier introduction of solar hot air introduction

The solar panel is formed by 45 m^2 x 6 solar modular units installed on the support frame over the factory building. The solar collector is formed using aluminium extrusions, high sensitive special absorber, 4mm thick toughened glass (partial double), mineral wool insulation, and polyurethane sealant and EPDM rubber. The short-wave length radiation from sun transmits through glass up to 92%. When it falls on the black absorber radiant energy is converted into thermal energy. As glass blocks re-radiation [long wave length] from the absorber, temperature raises in the absorber. Fresh air will be zig – zagged below the absorber sheet so that the collector will deliver hot air in the range of 70 – 100^0C depending upon solar radiation. Air makes three passes and finally exits at the insulated outlets which are connected to a metal box which is again insulated. A solar blower of 2.2 kW, 7000 m^3/h, and 1420 rpm draws the hot air from the panel and pushes it through the auto sprayer through the insulated duct.

Fig. 13. A view of solar hot air collectors

Fig.14: Ducting arrangement to introduce hot air in autospray drier

The savings are 35 tonnes of coal per year and CO_2 emission reduction by about 88 t CO_2 per annum in one autospray.

PDU5: Processing chilled hides

Process steps for chilled buffalo hides to wetblue were arrived at. The reduction of 300 kg of salt per tonne of raw material is estimated. This corresponds to reduction of about 50% of salt discharge from conventional salted hide processing.

A commercial scale trial was conducted on fresh chilled hides without salt preservation to produced wetblue. About 350 buffalo hides were obtained from a slaughterhouse in Unnao by a tannery located in Unnao. The weight of the material was 10 tonnes. The wetblue produced were like regular production. This trial alone has saved release of about 3000 kg of salt into environment. Now, a group of tanners have expressed their interest to process fresh chilled hides. The effluent streams were analysed in a private laboratory. Table 3 below provides a comparison of TDS and chlorides in soak liquor from wet-salted and chilled hides processing. Preliminary observations have revealed that about 10000 hides per day could be available for tanneries in this region as fresh chilled hides, if proper chilling and transportation facilities are arranged. This could lead to saving release of about 90 tonnes of salts per day into environment.

Fig.15: Loading fresh chilled hides for processing

Fig16. Wetblue produced from chilled hide processing

Table 3: Comparison of TDS and chlorides in soak liquor from wet-salted and chilled hides processing

TDS in soak liquor discharged from chilled hide processing	15,652 mg/l
TDS in soak liquor discharged from wet-salted hides	53,780 mg/l
Chloride content in soak liquor discharged from chilled hide processing	387 mg/l
Chloride content in soak liquor discharged from wet-salted hides	15,000 to 30,000 mg/l (Sources of pollution in leather processing, *Dr. S Rajamani,* UNIDO, 1998)

PDU6: Desalting

Desalting of raw hides prior to soaking in salt shaker provides dusted salt 60 to 90 kg per tonne of raw material. In the case of salted hides processing, desalting reduces the fixed dissolved solids content by 15% in combined effluent.

The desalting drum (cage) is primarily made of stainless steel 316 and is rotated by a motor of 15 kW. The rpm of the drum is kept at 6.

The raw material is loaded with even folded condition through a belt conveyor. The hides get unfolded in the desalting cage and the salt sticking on the hides fall off. The inclination of drum is possible to adjust the timing of the desalting. The salted hides come out of the drum at the rear end of the drum. The diameter of the drum is 2.7 m and the overall length is 7.7 meters, in which the length of the drum (cage) is about 5 m. While the transfer time for one hide through the drum varies depending on the inclination, it is generally takes about 3 to 6 minutes. The duration for the desalting of 10 tonnes takes about 2 hours.

Figure 17: Desalting drumFigure 18: Raw hides after desalting

The TDS of soak liquor was tested after desalting. The following Table 4 shows the TDS in soak liquor before and after desalting:

Table 4: TDS in soak liquor after desalting

TDS emission in soak	First soak	Second soak
Average TDS of soak liquor without desalting (300% water for soaking)	53,780 mg/l	27,580 mg/l
Average TDS of soak liquor after desalting (300% water for soaking)	33,250 mg/l	15,000 mg/l

The overall reduction in TDS in the combined effluent stream due to desalting of raw hides / skins has been found to be about 15%.

PDU7: Lime liquor recycling system

The waste relime liquor is rich in dissolved lime content, which gives an opportunity to recycle back to reliming. The dissolved lime is more useful for reaction of lime with pelts. In this pilot demonstration unit, the relime liquor is collected separately from the drum through bath segregation channels. This liquor is sent in a separate channel which is protected against ingression other waste streams to a collection sump. This liquor is pumped to two hopper bottom settling tanks operating serially. The

unwanted solid particles if any from the liquor are settled in these settling tanks and clear liquor is collected in lime water storage tank. This liquor is recycled back to reliming drums for subsequent batches.

Fig. 19: A view of lime liquor recycling system

The relime liquor recycling has reduced the fresh water demand up to 64% in relime. The float requirement is 125% for reliming in drums. About 80% of float is used from recycled liquor and only 45% of water is added as freshwater. Per this tannery's capacity of 2.5 tonnes a day, it is possible to reduce the volume by 600 m^3 per annum and equal amount of freshwater exploitation.

The CaO content in the recycled lime liquor is about 3 g/l, hence this liquor of 80% volume per tonne material corresponds to 2.4 kg CaO, which is equivalent to 3 kg lime of 80% CaO content. There is reduction of 0.3% lime for reliming, i.e., from 1% lime it is reduced to 0.7%.

Rainwater harvesting

Roof top rainwater harvesting has been implemented. The rainwater from the roof top is collected in gutters. Pipelines and filters are arranged in such that the debris can be easily removed and the filtered rainwater is sent through pipe into borewell. Thus, the ground water gets recharged. The system is patented by the supplier.

Rain water catchment area is approximately 3500 m^2 and per season about 7564 thousand gallons of rain water filtered from 47 different points is estimated to be deposited to the under-ground water streams by connecting them with bore-well through pipe conveyance system after filtration process.

Fig 20: Pipeline and filter arrangement in rainwater harvesting in Kings International

Dissemination of the results and Sustainability of project activities

The results are being accumulated and on-site demonstration programmes are being organised for the local tanners to get familiarised on the new technologies. In addition, the propagating programmes includes, workshops, seminars and audio visual print versions of the installations.

Further a Core Group on Cleaner Technology (CGCT) has been established consisting of all leading tannery associations, Government agencies like CLE and research institutions like CLRI and leading tanners. The Cleaner Technology Core Group is useful in bringing synergy among the various stakeholders involved in promotion and implementation of cleaner technologies in tanneries and share the knowledge on the results of implementation of cleaner technologies under the UNIDO project among the stakeholders.

Brief about Kanpur Leather Cluster

Kanpur is located on the banks of Ganga River in Northern part of India and it is an important industrial city in the state of Uttar Pradesh. Textiles and leather are the major industrial activities besides several ordnance factories, chemical industries, etc.

Kanpur leather cluster is one of the important tannery clusters in India. The Kanpur leather is also well known for saddlery and harness leather, safety footwear, army shoes, sole leather and upholstery leather besides footwear production. The annual export value of leather and leather products from this cluster is about Rs.7160 crores in which Rs.3136 crores being the export of finished leather during 2015-16. This corresponds to about 44% of export basket of leather and leather products.

The tannery sector in Kanpur is in five different pockets around the Kanpur city, namely Jajmau, Banthar, Unnao, Magarwara and Jainpur areas. Jajmau is one of the major cluster located on the banks of river Ganga. Majority of tanneries, about 402 tanneries, are in Jajmau, processing about 1000 tonnes of raw material per day.

Jajmau cluster of tanneries is also located just on the banks of Ganga River. During the 1992-93, under a project funded by The Netherlands, a large common effluent treatment plant (CETP) of capacity 36 mld was commissioned for the Kanpur city's domestic waste and industrial effluent based on UASB technology. Later several modifications were carried out in this CETP but at present the performance is not as expected is the general opinion from several quarters. The main issues faced are the capacity of the CETP, while the CETP was established for 9 mld of wastewater, currently it appears that the volume of waste water discharge has increased many times. Nevertheless, the volume of effluent is reported up to 50 mld, the consensus among the stakeholders appears to be of 25 mld.

At 35 km from the city of Kanpur, there is a tannery estate in Unnao. There are 21 tanneries in this Uttar Pradesh Industrial Development Corporation (UPSIDC)-developed estate. There is a CETP, Unnao CETP, established only for the tanneries of capacity 2.15 mld functional from around 1995.

During 2000, UPSIDC has created another tannery estate in Banthar over 600 acres and 42 tanneries and 150 leather product units have been planned. But presently the estate covers about 300 acres, and 20 tanneries and 1 product unit are functional. Banthar is located half way between Kanpur and Unnao. A CETP is functional for these tanneries with a capacity of 4.5 mld but presently operational with 3 mld of effluent.

Brief about the UNIDO Kanpur Leather Development Project

Kanpur Leather Development Project is funded by Department of Industrial Policy and Promotion, Government of India with overall financial budget of about US$ 1 million with scheduled implementation of 2 years from November 2015. The following are the specific objectives of the project:

- Environment sustainability & improved efficiency and best practices in leather processing
- Waste Management

The counterpart organizations of the project are Uttar Pradesh Leather Industries Association, Kanpur Unnao Leather Cluster Development Company, Central Leather Research Institute, Council for Leather Exports, UNIDO International Centre for Inclusive and Sustainable Industrial Development, New Delhi.

Conclusions

Adoption of cleaner technologies in leather processing such as hair save unhairing, desalting, use of optimum process parameters like volume of water and temperature of float in leather processing vessels, processing chilled hides without preservation by common salt, reduces the pollution level has been proven yet again.

- Hair save unhairing reduces the pollution load in terms of sulphides, total suspended solids and COD by about 66%, 61% and 32% in liming effluent.
- Hair recovery is about 2% on weight of raw hides
- Measurement of water itself reduces the water consumption by 20% to 30%

- Use of hot water at about 60^0C in post tanning operations increases the chemical fixing and thus reduces the pollution load by 17-30% in terms of COD in the post tanning streams
- Solar water heating and solar air heating systems reduces consumption of coal, there is reduction of coal by 0.8 kg/d.m^2 (for every 1 m^2 of solar collector)
- For every solar hot water collector area, the hot water generation is up to 130 litres
- CO_2 emission reduction is about 8 tonnes per sq.m of solar collector totalling in its life time.
- CO_2 emission reduction 8 tonnes per sq.m of solar field in its life time.
- While the TDS reduction in chilled hides processing is about 50%, the desalting reduces the overall TDS by 15%
- Desalting prior to soaking help recover salt by 60 to 90 kg per tonne of raw hide otherwise would have entered effluent drains
- Recycling of relime liquor reduces fresh water demand by 60% and lime reduction by 30%

Acknowledgements

The authors gratefully acknowledge Department of Industrial Policy and Promotion (DIPP), Government of India, Central Leather Research Institute, Council for Leather Exports, Uttar Pradesh Leather Industries Association, Kanpur Unnao Leather Cluster Development Company, Small Tanners Association, Jajmau Tanners Association, and the tanneries who participated in the pilot demonstration units, particularly the participating tanneries' willingness to contribute financially in their respective demonstration units.

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ECT P-30

DEVELOPMENT OF NOVEL MULTIENZYME SYSTEM FROM A MICROBIAL SOURCE FOR ENVIRONMENTAL FRIENDLY BEAM HOUSE OPERATIONS

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Production and development of novel multienzyme system containing protease, amylase and lipase was studied for leather processing particularly in beamhouse operations for unhairing, fiber opening and degreasing operations. *Aspergillus tamarii* MTCC5152 has been identified as a single microbial source for the production of this multienzyme system in the same culture medium. The various parameters for maximal production of these enzymes have been optimized by solid state fermentation method (SSF).
The unhairing, fiber opening and degreasing potential of this multienzyme product has been studied using cow hides and goat skins. The bioprocessed hides and skins were assessed by biochemical, microscopic methods and subjective analysis. Experimental and control hide/skin samples after beam house operations were processed to chrome tanned crust leathers and assessed for softness, fullness, grain smoothness, grain tightness and general appearance by hand and visual examination. The results indicate that the multienzyme product has the potential to be used for bioprocessing of hides and skins in beam house operation and the results are comparable with the chemically processed hides and skins. The net benefits envisaged from this approach are: Elimination of several processes, viz., liming, reliming and deliming is possible with subsequent reduction in process time, TDS, COD and total elimination of lime sludge; better exhaustion of chromium in tanning and reduction in the use of chemicals and cost with a reduction in utilities like water.
Keywords: Multienzyme, *Aspergillus tamarii*, unhairing, fiber opening and degreasing.

Introduction

The growing global concern of environmental pollution is forcing all the processing industries to adopt greener and cleaner manufacturing practices. Thus, the leather industry is being pressurized to look for cleaner leather processing. Leather processing involves a number of unit operations. The dehairing process with sodium sulfide and lime is responsible for 84% of BOD, 75% of the COD, 92% of suspended TDS.[15] Besides, the lime based swelling removes interfibrillary materials through osmotic forces leading to the formation of a large amount of lime sludge apart from the pollution load to the effluent and subsequently in the soil. The use of ammonium salt for deliming of hides/skins leads to emission of noxious gas (ammonia). On the other hand substrate specific enzymes including protease and α-amylase disintegrate the proteoglycans making the fiber matrix open thereby inducing swelling.

This approach obtains a clean pelt with the desired fiber opening and a significance reduction in lime sludge.

In bioprocessing of leather, enzymes are involved mainly in processes such as unhairing (depilation) bating (fiber opening) and degreasing operations. In leather industry these processes are called as beam house operation. Proteases, interestingly microbial proteases are finding increasing application in enzymatic unhairing and in bating operations. The enzyme α-amylases are involved in the opening up of the collagen fiber bundles. Lipases are used in the degreasing operation to remove fat from hides/skins to make leather soft and supple.

Typically, a single enzyme catalyzes a reaction from a substrate to a product. Thus, it is limiting to find many one step reactions to produce higher value products using one enzyme. Multienzyme systems have successfully been used for various applications when single enzyme catalysis was not effective (Gill, 1998; Lee *et al*., 2003). The present work employs lime-sulfide free enzymatic unhairing and fiber opening and degreasing processes using the multienzyme. The fungus *Aspergillus tamarii*MTCC5152 has been identified to produce all the three enzymes in good yield in the same cultivation medium. These enzyme consortium has been used along with the preservative (Busan-30) in beam house processing in two consecutive steps for unhairing, fiber opening and degreasing processes. The results are discussed and comparable with chemical methods of beam house processing of hides/skins.

Materials and methods

Production of protease, α-amylase and lipase by solid state fermentation by *A.tamarii* MTCC5152

The enzymes protease, α - amylase and lipase have been produced by solid-state fermentation (SSF) at pilot scale level using wheat bran as the substrate in Koji room based on conditions standardized at lab scale studies. SSF was conducted using 2 Kg capacity aluminium trays (20 nos). The trays containing the substrates were sterilized and the moisture content of the substrate was maintained at 70% moisture level. Fungal spores of *A.tamarii* MTCC5152obtained from a fully fermented wheat bran substrate containing 1X 10^6 spores/mlwere added as inoculum to each tray and mixed well and incubated at 26-28^{0}C for a period of 72-96 h at 90-95% humidity. Sampling was done at 24 h intervals to ascertain fungal growth and enzyme activity. Salted cow hides and goat skins were obtained from a commercial processing unit. The enzyme consortium is obtained from *A.tamarii* MTCC5152 isolated from soil. The multienzyme (protease, α-amylase and lipase)prepared from the fungus by solid state fermentation using wheat bran as substrate. The fungus have 140 u/g protease activity,680 u/g α- amylase activity and 954 u/g lipase activity. All other chemicals used were of commercial grade.

Enzyme extraction and ultra concentration

The fermented wheat bran substrate was mixed with Borate buffer (pH 9.5) in the ratio of 1:10 and soaked for 30 min at 4^o C and kept in the shaker for another 30 min. After mixing the crude enzyme extract was filtered through nylon mesh, centrifuged at 10,000 rpm for 20 min at 4ºC. The supernatant was collected and stored at 4ºC and used as a crude enzyme. The crude enzyme was loaded in to the ultra concentrator and the nitrogen gas was applied to give the pressure. The ten fold concentrated enzyme was collected and stored at 4 ºC.

Assay for protease, α - amylase and lipase activity

Protease activity was determined according to the method of Anson[6] (1938) with slight modification using casein as the substrate followed by Berla Thangam & Suseela Rajakumar[7] (2000). The concentrated enzyme was dissolved in different concentration in 20 mM borate buffer (pH 9.0)

containing 2 mM $CaCl_2$. The amount of protease activity was determined using a standard graph prepared from tyrosine. One unit of protease activity (U) was defined as the amount of enzyme required to produce 1 mg of tyrosine per ml of enzyme in 30 min at 55 °C.

The enzyme α- amylase activity was assayed by the Dinitrosalicylate (DNSA) method of Miller[8] (1959) using 0.3 % starch as the substrate. The α - amylaseactivity was determined using a standard graph prepared from maltose. One unit of α - amylase activity (U) was defined as the amount of enzyme required to liberate 1 mg of maltose/ml/min at 55^{o}C.

Two methods were adopted to assay the lipase activity. Enzyme activity was assayed through alkali titration with olive oil emulsion as the substrate, using a modified version of the procedure described by Saxena et al. (2003). In brief, the assay mixture consisting 5 ml of olive oil emulsion, 4 ml 0.1 M phosphate buffer (pH 7.0) and 1 ml crude enzyme extract was mixed well and incubated for 20 min at 37^{o}C. The reaction was stopped by the addition 20 ml acetone. The mixture was then titrated with 0.05M NaOH in the presence of phenolphthalein (0.1ml) as indicator. The titre values were calculated for lipase activity. One unit of lipase activity is defined as the amount of enzyme required to release 1µmol of fatty acid per minute under the standard assay conditions. To confirm the lipase activity spectrophotometric method was also performed (Kwon and Rhee, 1986), a good agreement has been noted between the results obtained using the two methods. Protein content of the crude enzyme extract was analysed by the method of Lowry et al. (1951).

Enzyme based dehairing process

Salted cow hides (2ft X 2ft size) / goat skins (1/2 size) were soaked to remove the salt following conventional procedure, drained and used for bioprocessing studies. The concentrated enzyme was mixed with borate buffer (20 mM, pH 9.0). The multienzyme paste was prepared by mixing the liquid enzyme with 10% W/V of Kaolin or Diatomaceous earth based on the weight of the hide/skin and applied on the flesh side of the hides/ skins. The hides/ skins were folded flesh to flesh and piled at room temperature and assessed for their unhairing property after 18-24 h following traditional method using a blunt knife for hair removal. Soak method was also studied by soaking the hides/ skins in various concentrations of enzyme using 20% V/W water.

The degreasing effect of multienzyme product was assessed by estimating the free fatty acid liberated during drumming by the method of Saxena et al (2003).

Enzyme based fiber opening and degreasing

An enzymatic pathway without lime forms a 'green' route for and fiber opening. Using enzyme formulation without sodium sulfide has been designed for hides/skins at an operational pH of 6-6.5. The unhaired hides/skins were treated with different concentrations of liquid enzyme along with 20% water and subjected to drumming for 6 h with intermittent drumming with breaks for 30 min and every 30 min run for fiber opening and degreasing actions. The hides/skins were processed to crust leather and the leather quality was assessed by testing the strength properties. The hides/ skins after bioprocessing were also evaluated by microscopical analysis after staining.

Estimation of hexosamine from hides

The hexosamine content of hide/ skin pieces an indication of fiber opening of hides/skins were determined by estimating the amount of pyrrole condensation product formed by the reaction between hexosamine and alkaline solution of acetyl acetone. The pyrrole that is formed gives a purple red colour with an alcoholic acid solution PDAB (Para- dimethyl amino benzaldehyde) which is read at 530 nm.

About 0.2 g of hide samples were washed with physiological saline and cut into small pieces, defatted with chloroform: methanol (2:1V/V) and dried. 0.1 g of dried hide pieces were hydrolyzed with 5 ml of 6N HCl at 110 ^{o}C for 18-20 h in sealed glass tubes. After hydrolysis the samples were evaporated to dryness and the residue was dissolved in water and made up to a known volume. The hexosamine content was estimated by the method of Elson and Morgan[6] (1933).

Histological studies of processed hides/skins

Hide pieces obtained after dehairing and fiber opening process were preserved in 10 % formalin for histological studies[17]. Formalin preserved hide/skin samples were processed and the dried slides were viewed through microscope (Nikon) at 4x100X magnification following usual procedure.

Results and discussion

The crude extracellular enzyme extract obtained from *A.tamarii* MTCC5152 was assessed to have protease, α-amylase and lipase activities and in good concentrations. To ascertain the suitability of these three enzymes for leather processing their activities and stabilities were estimated at different pH levels. The crude protease has an optimal activity at pH 9.0 (Fig.1a). The enzyme is active over a broad pH range of 8- 10. Similar studies were conducted with α-amylase for the purpose of fiber opening studies. The results show that α-amylase has maximal activity at pH 6.5 (Fig.1b) and the enzyme showed good pH stability in the pH range of 5.0- 7.0 with moderate activity at pH 8.0-9.5. The lipase also showed the highest activity at pH 7.0. The pH activity and stability relationship shows that α-amylase and lipase can be used in the fiber opening and degreasing processes without any change in the process operation.

Table.1 shows the effect of enzyme concentration on dehairing of cow hides/ goat skins in both paste and soak method. In both the methods cow hides were completely dehaired by applying 3% V/W of the enzyme and complete dehairing was observed in the case of goat skins at 2% V/W concentration. Fiber opening and degreasing of cow hides were conducted using multienzyme obtained from *A.tamarii* MTCC5152. The hides after drumming for 6 h were assessed for hexosamine content. Data on hexosamine content of the hide/ skin samples after treatment with enzymes shows (Table-2a) that by using 3% V/W and 3% V/W multienzyme maximum degradation of preteoglycan was removed from the cow hides and goat skin, respectively. The results also show that hexosamine removal from hides were better in enzyme treated hides than that of lime and sulphide treated hides (Control III) indicating the potential of this enzyme for beam house operation for bioprocessing. The results also show that the enzyme treated hides/leathers were comparable to control samples processed with lime – sulfide and in certain properties better than the control leathers as evidenced from microscopical analysis of hides/skins (Table-2a) and from physical properties of tanned leathers.

Microscopic analysis of hide/ skin samples after dehairing and fiber opening process using enzyme consortium from *A.tamarii* MTCC5152 is given in (Fig.3a-3f.). It's clear from the results that the enzyme treated hides/skins were dehaired without any trace of hair and the fiber opening was good comparable to the leather prepared by traditional methods. This could be due to the combined actions

of the presence of both protease and α- amylase in the enzyme preparation used for these processes. The enzyme acted very efficiently on the hides/skins and removed the interfibrillary materials by degrading the carbohydrate moieties present in the glycoprotein through enzymatic actions. The presence of protease in the enzyme consortium also helps in the removal of any root hair and scuds present in the hides/skins. The degreasing effect of the lipase in the multienzyme product was increased in comparison with a commercial degreasing agent. The results are comparable with the commercial degreasing agent used traditionally (Fig-2).

The subjective assessment of leathers by hand evaluation for both control and experimental leathers are presented in a 0-10 point scale. It is apparent that the experimental leathers exhibited comparable properties to that of control leathers (Fig. 4 and Fig. 5). Properties like softness, fullness, grain tightness are improved in enzyme treated leathers compared to control leathers. Thanikaivelan et al. (2006)[16] reported similar trends in integrated hair removal and fiber opening process using commercial mixed enzymes containing protease and α-amylase.

Conclusions

Enzyme-based bioprocessing including dehairing, fiber opening and degreasing is a paradigm shift away from conventional chemical-based leather processing. The multienzyme product developed in this investigation from *A.tamarii* 5152 has the potential to be used in bioprocessing in beam house operations with clear advantages of quality leather and significant reduction in pollution load and increase in the area of yield. The hair can be saved without any degradation.

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Table-1. Effect of *A .tamarii* 5152 enzyme consortium for dehairing and fiber opening

Process details	**Enzyme concentration (%**V/W**) dehairing and fiber opening index after 24 h**			
	1%	2%	3%	5%
Paste method (cow hide)	-	XX	XXXX	XXXX
Soak method (cow hide)	-	XX	XXXX	XXXX
Paste method (goat skin)	XX	XX	XXXX	XXXX
Soak method (goat skin)	XX	XX	XXXX	XXXX
Fiber opening (cow hide)	+++	++++	++++	++++
Fiber opening (goat skin)	+++	++++	++++	----

XX- Slight dehairing; XXX –Moderate dehairing; XXXX-- complete dehairing**;**
+++- Moderate fiber opening; ++++- complete fibre opening ; ---Not done.

Table-2. Hexosamine content of the generated in cow hide after treatment with enzymes

No	Concent. of enzyme (%V/W)	Hexosamine content (mg/ml)
1	1	4.5
2	2	2.8
3	3	0.48
4	5	0.39
5	Control-I	6.8
6	Control- II	3
7	Control-III	1.6

Control-I Untreated hide
Control- II 10% lime
Control-III 10% lime+ 2.5% sodium sulfide

Table-2b. Pollution load beam house operation

Parameter	Cow hide		Goat skin	
	Experiment	Control	Experiment	Control
BOD (kg/ton)	13.7	32.7	22	45
COD (kg/ton)	61	160	46	110
TDS (kg/ton)	68	163	65	162
TSS (kg/ton)	49	58	40	53

Fig-1a. Effect of pH on protease activity

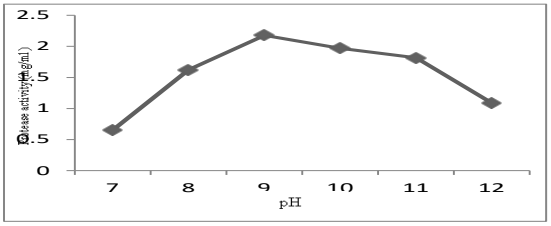


Fig-1b. Effect of pH on α-amylase activity

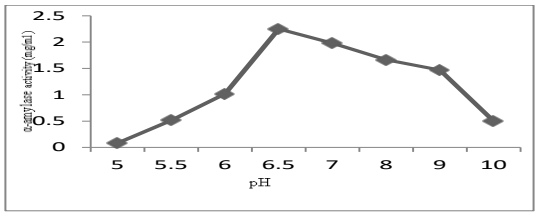


Fig-1c. Effect of pH on lipase activity

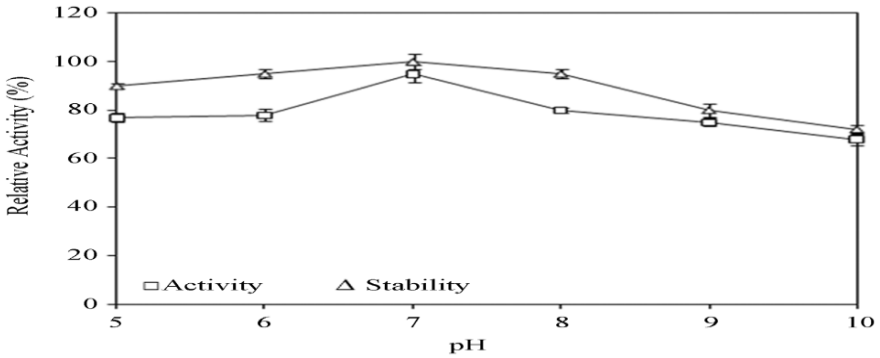


Fig-2. Degreasing effect of commercial enzymatic agents and *A. tamarii* 5152 multienzyme on hide

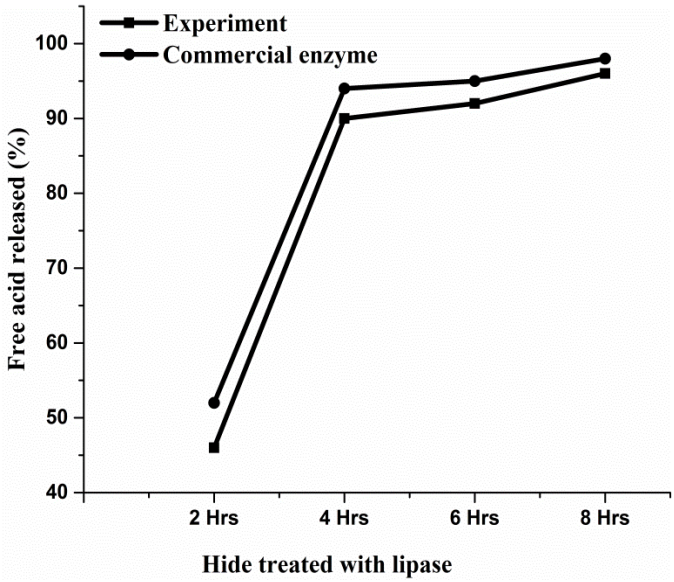


Fig- 3a. Photomicrograph of unhaired cow hide (control)

Fig-3b. Photomicrograph of unhaired cow hide (multienzyme 3%)

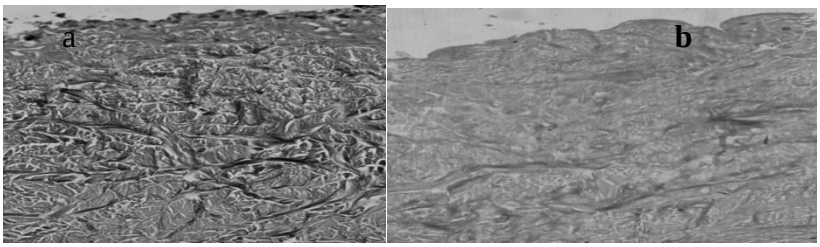


Fig- 3c. fiber opening (Control)

Fig- 3d. fiber opening (multienzyme 3%)

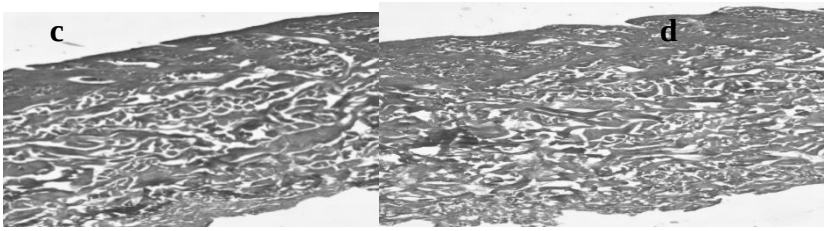


Fig-3e. fiber opening (control) goat skin

Fig- 3f. fiber opening (multienzyme 2%) goat skin

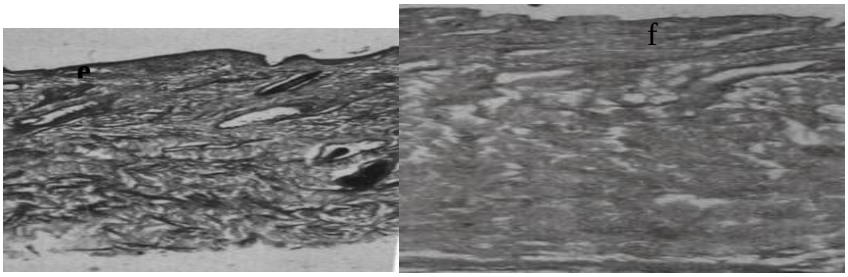


Fig.4. Hand and visual of wet blue leather

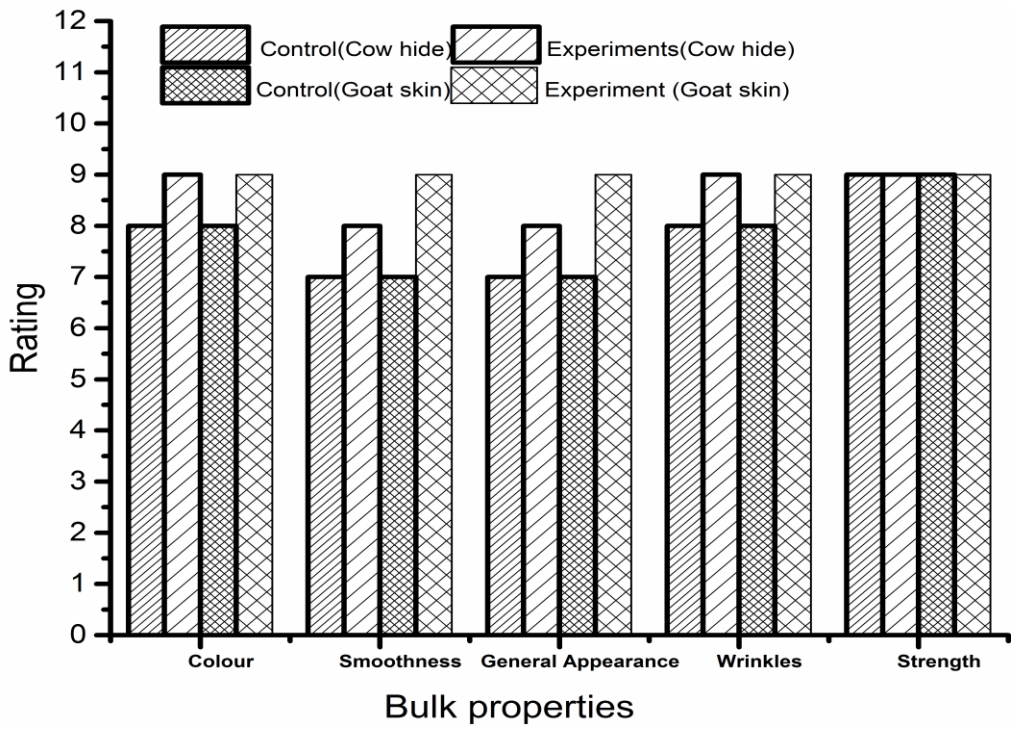
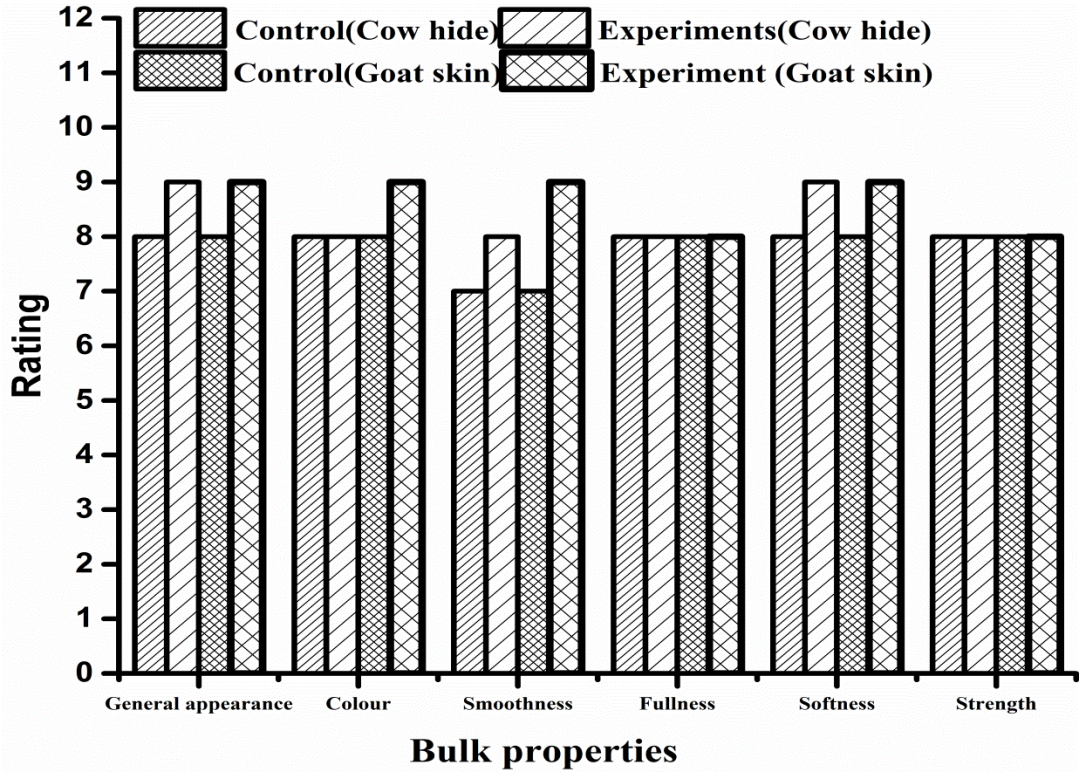


Fig.5. Hand and visual assessment of crust leather


Control(Cow hide)
Experiments(Cow hide)
Control(Goat skin)
Experiment (Goat skin)
Rating
0
1
2
3
4
5
6
7
8
9
10
11
12
General appearance
Colour
Smoothness
Fullness
Softness
Strength
Bulk properties

IVL P-22

The Mechanism of FabricationHigh Moisture Permeability Unfigured Sea-island Superfine Fiber Synthetic Leather Base Via Surface-modified Biomass materials

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Collagen and vegetable tannins are considered to be the largest renewable animal and plant biomass resources in the world. In this work, The present studied proposes a "two-steps" method of grafting collagen/chromium-vegetable tannin (C-CrT) on nylon fiber of unfigured sea-island superfine fiber synthetic leather base (USFSLB) for improving the moisture absorption and transfer abilities. The two-steps surface modification was developed, involving sulfuric acid hydrolysis and grafting of C-CrT on nylon fiber. Compared with that of pristine USFSLB, the moisture absorbption and permeability of modified USFSLB was improved greatly. And the self-assembly mechanism of grafting collagen/chromium-vegetable tannin (C-CrT) on the nylon fibers of USFSLB was analyzed and reported.

Keywords: collagen, vegetable tannins, unfigured sea-island superfine fiber synthetic leather base, surface modification

1. Introduction

Unfigured sea-island superfine fiber synthetic leather belongs to high-grade simulated leather. It has many characteristics and advantages of natural leather. And its mechanical strength, chemical resistance and homogeneity are better than that of leather. Compared with leather, the wearing comfort of superfine fiber synthetic leather is worse due to its poor moisture absorbption and permeability. Therefore, the study on moisture absorption and permeability of superfine fiber synthetic leather has become a hot topic.

The present researches on improving moisture permeability of USFSLB had been carried out. Such as formic acid[1,2], sulfuric acid[3], triethanolamine, protease, pancreatic hydrolysis, collagen material filling[4], soluble chitosan derivatives (CS-HCA)[5], glutaraldehyde and polyamidoamine dendrimers[6-8], phosphine and collagen[9,10] had been used to modify USFSLB and the moisture permeability of it had improved finitely. But the mechanism of modification was common sphysical adsorption and filling which made the modifier be unstable.

The sustainable developing and utilizing of biomass has been constantly studied by researchers. China is known as a country with leather mass production. Consequently, the production inevitably gives rise to leather solid wastes. It is estimated that more than 1.4 million tons of leather solid wastes are produced every year. But more than 80% collagen exists in the wastes.[11]. At the same time the natural

polyphenols, tannins, are extensively distributed in root, bark, stalk, and fruits of plants as metabolism products.[12-15]

In this work, we report the modification of USFSLB by chemical etching of the fiber surfaces and grafting of biomass materials, collagen and chromium-vegetable tannins, as shown in Figure 1. USFSLB modifed with collagen and chromium-vegetable tannins had excellent property, expesially the moisture absorption. And the self-assembly mechanism of grafting collagen/chromium-vegetable tannin (C-CrT) on the nylon fibers of USFSLB was analyzed and reported.

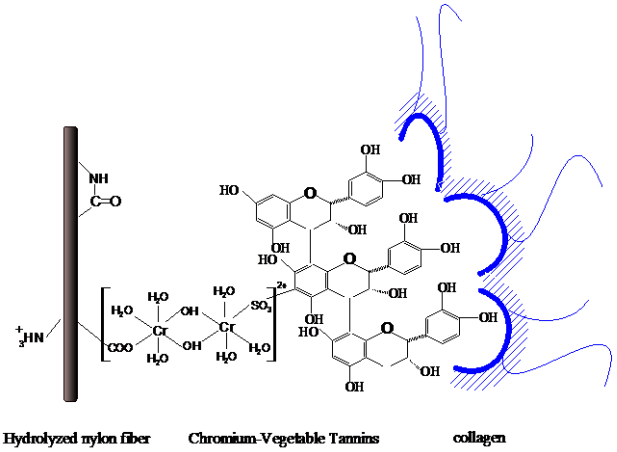

Figure 1 Schematic illustration of C-CrT modified nylon fiber of USFSLB

2. Material and methods

Materials. The materials and instruments used in the experiments are as follows: Collagen (G1) (Mw3690, Haining Debang CO., Ltd), chromium-vegetable tannins (with 5% chromium,Mw2374, Sichuan De Cai CO., Ltd), Unfigured sea-island superfine fiber synthetic leather base with 536.7g/m^2 and 1.4mm thickness (Yantai Wanhua Co., Ltd), Infrared heating device (Hua Gao automation equipment CO., Ltd), Constant temperature and humidity equipment (GT-7005, Gao Tie, Taiwan), Video based contact angle measuring device (OCA20, Dataphyscs, Germany), Scanning electron microscope (TM-1000, HITACHI, Japan), X-ray photoelectron spectrometry (XPS) (Thermo Fisher Scientific, US).

Modification Methods. Two steps are involved in the modification. Step 1: Samples were first made by cutting into 19×9cm with weight of 10.7±0.2g, They were then put into the cups of infrared heating device (Hua Gao automation equipment CO., Ltd) with 5000wt% water （the dosage percentage related to this experimental process was calculated by the mass of the dry USFSLB） and washed for 30min with 70°C . And then the samples were hydrolyzed for 4h with sulfuric acid at 15wt% with 5000wt% water (the percentage of the dry USFSLB mass). They were then washed in water for 30min by ultrasonic and hung dry.

Step 2 : After hydrolyzed, the samples were put into cups with 15wt% collagen and 1500wt% water (the percentage of the dry USFSLB mass). The cups were kept shaking for 3h at 45°C. The samples were then removed and the pH of collagen solution was adjusted to 4.0 with formic acid. Again they were put

into the cups after the 5wt% chromium-vegetable tannins were fed into. The cups were kept shaking for 3h at 60°C, and the samples were washed for 30min by ultrasonic and hung dry.

Determination of Moisture Permeability. Static water-vapour transmission rate (SWVT) [8] was detected. The brief was that samples were cut into circular pieces 55mm in diameter, and then put into constant temperature and humidity equipment for air conditioning. The modification condition was temperature 20 ± 2 °C and relative humidity 65 ± 2% for 24h. After air conditioning, 30ml of distilled water was poured in the test cup. The sample and rubber gasket were put onto it in turn. And the aluminum cover was tightened up. Then the total mass of the test cup with the sample was weighed and recorded as m_1. The test cup was then put in a desiccator with 98% sulfuric acid as dryer. And the desiccators were kept in the constant temperature and humidity equipment (GT-7005, Gao Tie, Taiwan) with temperature 20 ± 2 °C, relative humidity 65 ± 2% for 24h. After water-vapour transmission, the test cup was removed and weighed again, recorded as m_2. All the measurements were performed quartic in parallel.

$$SWVT=(m_1-m_2)\ /At \qquad (1)$$

Where m_1 and m_2 is the test cup mass before and after water-transmission respectively, A is valid test area (10 cm^2) and t is test time (24 h).

Liquid wicking rate(LWR)[16]was detected. Liquid wicking rate is the measurement of capillarity of the test material, i.e. the rate at which the liquid is transported into the fabric by capillary action. Namely,the liquid wicking height was achieved per unit time in the textile material by capillary action.It can assess the moisture absorption ability of fabric. The specific measurement is as follows: the sample was first cut into 30mm wide, 50mm long and then placed into an oven (105°C) drying to constant weight. The end of sample was immersed in water for about 15 mm, and then was timed until the liquid wicking height reached 30 mm, recorded as time (s) and calculated as the liquid wicking rate (mm/s). All the measurements were performed quartic in parallel.

Physical Property Testing. The tensile strength and elongation at break of USFSLB were tested (refer to QB/T 2710-2005)[17] via a tensile tester (PT-1171, Dongguan Baoda International Co., Ltd). All the measurements were performed quintic in parallel at least.

The softness of modified USFSLB was tested (refer to ISO 17235:2011, IULTCS IUP/36 TEST METHOD)[18] via a softness tester (GX-5039, Dongguan gaoxin Co., Ltd). The actual diameter of circular aperture was selected as 24.975 ± 0.025mm. All the measurements were performed thrice in parallel.

The antistatic property were detected according to GB/T 12703-91[19] via anti-static tester (FY403E, Wenzhou Fangyuan Co., Ltd). And the timing method was selected. The decay time was 10 seconds. The friction time was 60 seconds. And then the peak voltage (V) was recorded. All the measurements were performed thrice in parallel.

Characterization. The water contact angle of the surfaces was determined by using a static contact angle measuring device (OCA20, Dataphyscs, Germany). The water contact angle was measured by

sessile drop before and after modification, keeping water droplets for 2s. Each stated contact angle is the average of 11 measurements from various positions on the surface.In order to observe possible changes in material surface morphology, SEM was used. The samples were placed into an oven (105℃), kept drying to constant weight . After Au spraying, the micrographs of samples surface were taken using a field emission scanning electron microscope (FEI Q45+EDAX Octane Prime, USA). The EDS was used to determine elements of the surface of nylon before and after treatment.Attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) were acquired via a Fourier transform infrared spectrometer (VECTOR-22, Bruker, Germany). For each spectrum, a resolution of 4 cm^{-1} was applied and 32 scans were accumulated.X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical composition of the samples before and after different treatments. All XPS spectra were collected using a Al-Kα X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) using monochromatic X-rays focused to a 300 μm spot size. The collagen and collagen-chromium tannins solution was detected by TEM (FEI Tecnai G2 F20 S-TWIN, FEI, USA). Atomic force microscopy (AFM) were used for surface imaging.

3. Results and Discussion

Moisture Permeability. SWVT and LWR of the hydrolyzed USFSLB was 658 g/m^2•24h and 0.513mm/s respectively, and that of the C-CrT- grafted USFSLB were 986 g/m^2•24h and1.323mm/s (shown in Figure 2). So compared with pristine USFSLB the moisture permeability of hydrolyzed USFSLB was improved by 27% and 72%, and C-CrT- grafted USFSLB was improved by 90.35% and 344% respectively. The reason was that sulfuric acid hydrolyzed the nylon fiber of USFSLB to make the amide bonds （-CO-NH-） broken. As a result, carboxyl (-COOH) and amino ($-NH_2$) were exposed on the nylon fibers of USFSLB. These polar groups not only improved the moisture permeability but also provided available active groups for subsequent modification. That is, chromium vegetable tannins was reacted with these active groups through coordination bond (from chromium complexes) and hydrogen-bonding (from phenolic hydroxyl of tannins). Therefore, the collagen and chromium vegetable tannins with a lot of polar groups such as OH, NH_2, and COOH were grafted on the surface of nylon fiber of USFSLB and improved moisture permeability of USFSLB.

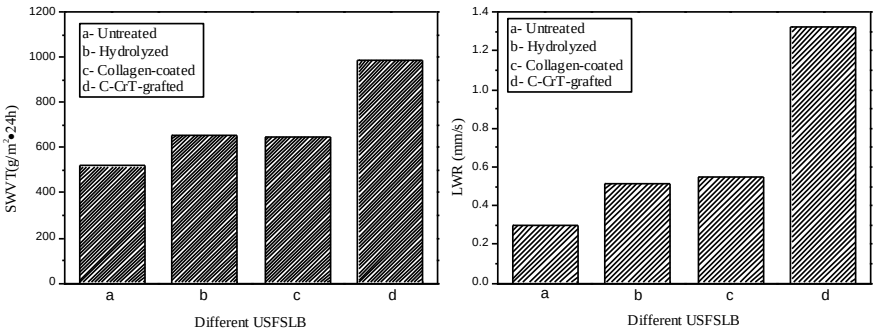

Figure 2 Moisture permeability of USFSLB before and after treatment

Physical property

Tensile strength and elongation at break of USFSLB was improved after modification (Table 1). It was because the cross-linking between nylon fibers occurred. The thickness and uniformity of C-CrT-grafted USFSLB were obviously increased(Table 1) owing to the good selective filling properties of collagen and tannins. The softness of hydrolyzed USFSLB was improved(Table 1), indicating that the sulfuric acid made the nonwoven loose which was confirmed by SEM (in Figure 4). But the softness of C-CrT-grafted USFSLB was declined obviously compared with that of pristine USFSLB. It was because that a lot of collagen was grafted on the surface of nylon fibers by chromium vegetable tannins. Polar functional groups such as OH, NH_2 and COOH of collagen would cross-link each other via hydrogen bonding in the process of USFSLB dehydration. So the molecules didn't slip relatively and the softness of C-CrT-grafted USFSLB declined. Furthermore, the chromium vegetable tannins was grafed on the nylon fibers of USFSLB which still resulted in declined the softness of C-CrT-grafted USFSLB .

Anti-static performance was improved after modification, especially the collagen-covered USFSLB . But anti-static performance of the C-CrT-grafted USFSLB was lower than that of collagen-covered USFSLB (Table 1). It was because that the collagen covered the nylon fiber and the polar functional group was exposed fully on the surface of nylon fiber. These polar functional groups adsorbed water molecules easily and the conductive water film would be formed on the surface of nylon fiber. As a result, the anti-static performance was improved. But on the fiber of C-CrT- grafted nonwoven there was a lot of different size of microspheres (as shown in Figure 4). The microspheres composed with collagen and chromium-vegetable tannins with a large number of polar groups. These polar groups still formed the conductive water film on the surface of microsphere but on the nylon surface. Therefore, the conductive water film was discontinuous on the surface of nylon fiber and the anti-static performance of the C-CrT-grafted USFLB was lower than that of collagen-covered USFSLB.

Table1 Performance of USFSLB before and after treatment

	Pristine	Hydrolyzed	Collagen-covered	C-CrT-grafted
Tensile strength （Mpa）	16.06	17.66	17.64	17.88
Elongation at break （%）	68.6	72.7	67.68	72.34
Thinkness （mm）	1.406	1.415	1.503	1.585
CV of thinkness(%)	2.60	1.98	1.09	1.63
Anti-static performance [a](V)	1035	986	488	588
Softness(mm)	5.4	5.8	5.5	4.8

[a]Anti-static performance was stated by the peak voltage (V) during the friction time (60s).

Characterization of Modified USFSLB. There was slight change between the contact angle of hydrolyzed USFSLB and that of pristine USFSLB(Figure 3ab). After collagen was coated on fiber of USFSLB, the contact angle decreased obviously(Figure 3c). It turned much lower after chromium-vegetable tannins grafted (Figure 3d). These changes suggested that the hydrophility of USFSLB was improved after C-CrT

grafted. And this point had been further confirmed by the contrast of digital images of dyed water droplet on pristine and C-CrT-grafted (Figure 3).

The SEM images of the top view of pristine, hydrolyzed, collagen-covered and C-CrT-grafted was shown (Figure 4), the nylon fibers of USFSLB became loose after sulfuric acid treatment, a lot of microspheres on the nylon fiber were observed. These microspheres were composed of collagen and chromium-vegetable tannins. It confirmed that the collagen was grafted on the nylon fibers by chromium-vegetable tannins successfully.

Compared with pristine and C-CrT- grafted, the additional peak 1038 cm^{-1}occurred (Figure 5 bc), attributed to cyclic ether from the vegetable tannins. The band intensity 3300 cm^{-1}, attributed to the N-H stretching vibration, was broadened (Figure 5 c) by increased number of N-H from collagen. Therefore, it was confirmed that collagen and chromium-vegetable tannins were grafted on the nylon fibers of USFSLB successfully.

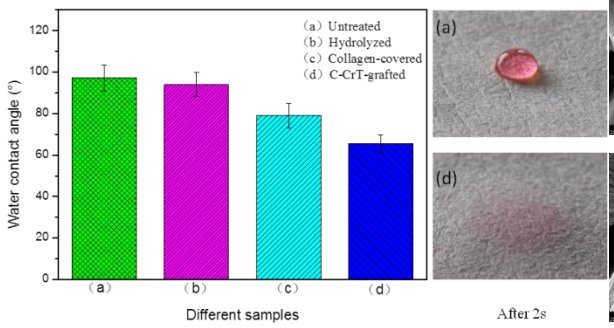

Figure 3.The water contact angle of untreated , hydrolyzed, Collagen-covered and C-CrT-grafted, Digital images of dyed water droplet on (a) pristine, (b) C-CrT-grafted after 2s

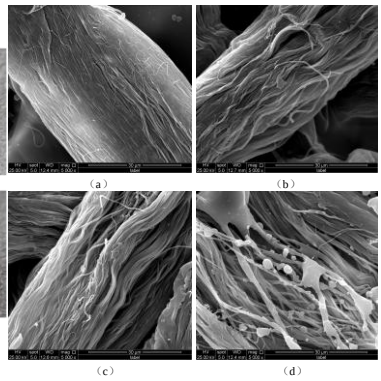

Figure 4 SEM images of the top view of (a) pristine (b)hydrolyzed(c) collagen-covered (d) C-CrT-grafted

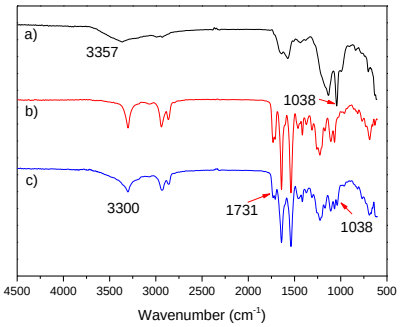

Figure 5 FTIR spectra of (a)chromium tannins (b) Pristine (c) C-CrT-grafted

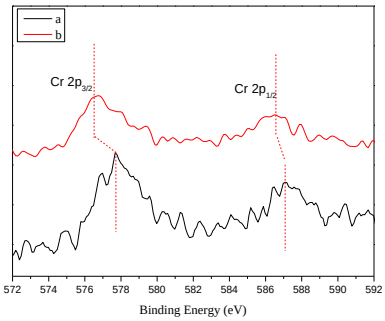

Figure 7 XPS narrow scanning spectra ofa Cr in the chromium-vegetable tannins and b the C-CrT-grafted USFSLB

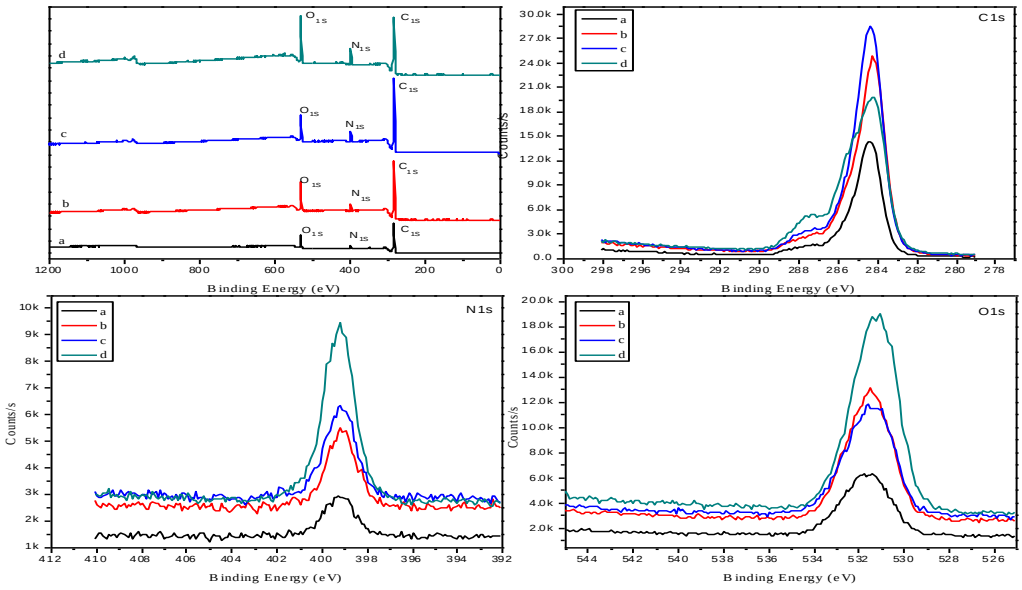

Figure 6 XPS survey and narrow scanning spectra of C1s, N1s, O1s on(a) pristine,(b)hydrolyzed, (c)collagen-covered, (d) C-CrT-grafted

Table 2 XPS elemental analysis of USFSLB before and after treatment

	Chemical composition (%)					Atomic ratio (%)	
Sample	C1s	O1s	N1s	Cr2p	S2p	C/O	N/O
(a) Pristine	78.62	16.16	5.22	0	0	4.87	0.32
(b) Hydrolyzed	80.22	14.91	4.47	0	0.4	5.38	0.30
(c) Collagen-covered	80.76	12.34	6.65	0.13	0.12	6.54	0.54
(d) C-CrT-grafted	70.76	18.29	9.26	0.45	1.25	3.87	0.51

Chemical composition of the sample surface was investigated by XPS with high sensitivity. According to XPS survey and narrow scanning spectra of N1s, O1s and C1s (Figure 6), in N1s and O1s spectra the peak intensity of C-CrT-grafted was increased significantly compared with pristine(a), hydrolyzed (b) and collagen-covered (c), attributed to increased amino nitrogen from collagen and phenolic oxygen from chromium-vegetable tannins. And in C1s spectra the peak of C-CrT-grafted had an asymmetrical tail (Figure 6 C1s), attributed to higher content of carbon with a binding energy of 287.2 and 288.7eV corresponded to the presence of functional groups (O=C-N, and O=C-O species) on the collagen

surface.[20] Furthermore, Compared with of pristine(a), hydrolyzed (b) and collagen-covered (c), the [C]/[O]ratio of the C-CrT-grafted decreased significantly (as shown in Table 2), attributed to the presence of phenolic hydroxyl groups from the vegetable tannins. Thus, it was confirmed that the C-CrT was grafted on the nylon fibers of USFSLB successfully.

Figure 7 showed results of the XPS Cr in the chromium-vegetable tannins and the C-CrT-grafted surface. The Cr in the chromium-vegetable tannins gave distinct peak: 577.6 eV (Cr 2p3/2) and 587 eV (Cr 2p1/2), and on the nylon fiber of C-CrT-grafted USFSLB gave distinct peak: 576.6 eV (Cr 2p3/2) and 586.5 eV (Cr 2p1/2). The oxo-functional groups(denoted by CxOH) including -OH and -COOH from the collagen, vegetable tannins and hydrolyzed nylon surface greatly influence the Cr valence states. The Cr ions of chromium-vegetable tannins with higher positive redox potential was unstable in the presence of electron donor functional groups (-OH and COOH). So the Cr species was bound to the phenolic hydroxy and carboxyl groups through complexation reaction.[21]

Self-assembly Mechanism of Collagen with Chromium-vegetable Tannins. The chromium-vegetable tannins consisted of hydrophilic and hydrophobic part.(Figure 8) In consideration of the diversity of molecular structures among the vegetable tannins and the many different functional groups in collagen, all of the following interaction types would take place in principle: hydrogen bonding, ionic bonding, hydrophobic bonding, and covalent bonding.[22] But the latter represented an irreversible change that required molecular oxygen and was favored by high pH or by the presence of polyphenol oxidases[23], and the charged groups was absent in the condensed tannins. Proanthocyanidins became charged only at high pH by dissociation of the phenolic hydroxyl groups with formation or phenoxide ions.[24,25] So the interaction types of ionic bonding and the covalent bonding between collagen and vegetable tannins was not considered. Thus, the presence of hydrogen donors in the form of phenolic hydroxyl groups in the vegetable tannins and of hydrogen acceptors in the form of carbonyl functions of the peptide linkages of the collagen would naturally lead to a possibility of formation of hydrogen bonds. The hydrophobic amino acid side chains on collagen such as aromatic ring, pyrrolidine ring, and aliphatic chain are prone to concentrating to form a hydrophobic pocket[26] (Figure 8).Likewise, since both groups contain hydrophobic regions, the aromatic nuclei of the vegetable tannins and the aliphatic side chains of the collagen amino acids, it would seem equally possible that these would participate in the interaction phenomena. Thus, the mechanism of association between chromium-vegetable tannins and collagen was in favor of hydrophobic bonding. Considering that collagen has very complex structures with a variety of chemical groups of different affinity characteristics, it would, on the other hand, be unreasonable to ascribe the interaction phenomena exclusively to this particular mode. It was in the hydrophobic micro domains collagen molecules that hydrogen bonding would occur, [23] and the hydrogen bonding reinforced the hydrophobic bonding. (as shown in Figure 8)

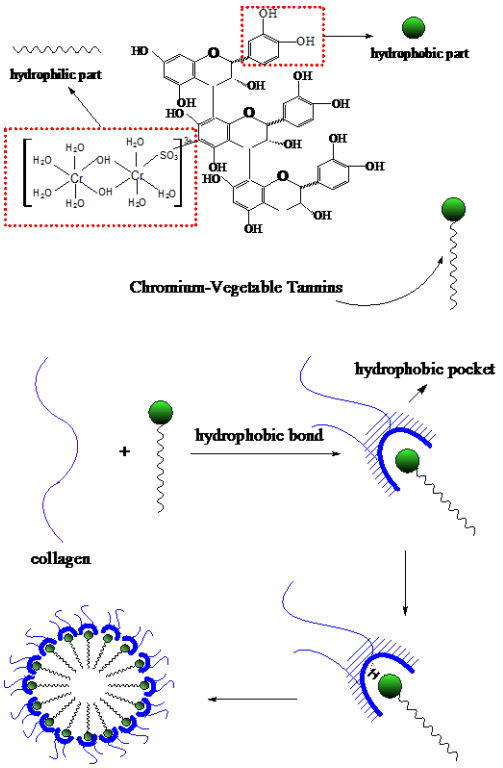

Figure 8 The self-assembly mechanism of collagen with chromium-vegetable tannins

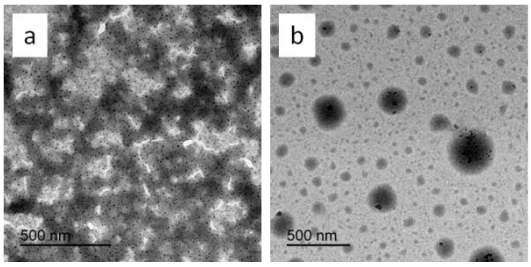

Figure 9 The projection electron microscope of (a) collagen solution, (b) collagen and chromium-vegetable tannins solution

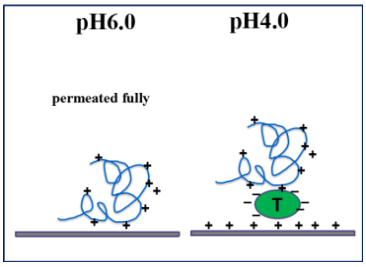

Figure 11 The surface electric charge of collagen and nylon fiber under different pH

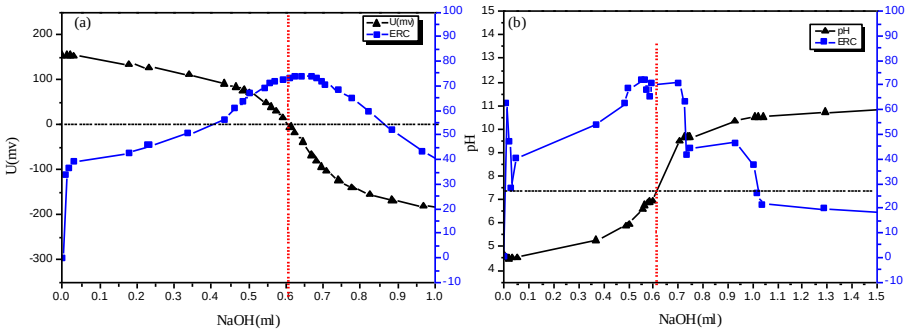

Figure 10 The potentiometric titration of U-NaOH and pH-NaOH

Modification Mechanism analysis. Figure 12 showed that there was the method of grafted C-CrT on the nylon fiber. In the step 2 of the modification, collagen was dissolved in the distilled water firstly while the pH was about 6.0 (collagen solution) and the microsphere did not form (Figure 9). At the same time, it was well-known that nylon had a small amount of residual COOH and NH_2 end group. The pH-rate profiles indicated that ionizations of the residual amino and carboxyl end groups in nylon played important role in the observed pH-sensitive permeation. The nylon formed high barrier to the permeation of the cationic substance in the acidic medium (below pH5.0) but not in the basic medium (above pH9.0), relative to the neutral-pH region (pH 6.0-9.0).[27] The isoelectric point (pI) of the collagen applied in this study was about 7.4 (Fingure 10). Therefore, the collagen was cationic and nylon was neutral in the initial solution with pH 6.0. The collagen was permeated in the USFSLB fully for a given time (Fingure11). Then chromium-vegetable tannins were added and the pH of the collagen solution was adjusted to 4.0 for preventing the chromium precipitate. In the pH 4.0, the collagen, and nylon had cationic charge. But the vegetable tannins had anionic charge. So vegatable tannins was attracted by nylon fiber (Fingure11). At the same time the chromium of vegetable tannins formed the complex with -COOH of nylon fibers by coordination bond (Figure 12). Then the collagen crosslinked with chromium-vegetable tannins by hydrogen bonding and hydrophobic bonding (Figure 12). Following, the chromium of vegetable tannins formed the complex with -COOH of collagen (Figure 12). These ways of cross-linking were alternated repeatedly until the microspheres were formed on the nylon fibers (Figure 12). So the outer surface of microspheres presented in two forms surrounded by chromium tannins layer and by collagen layer.

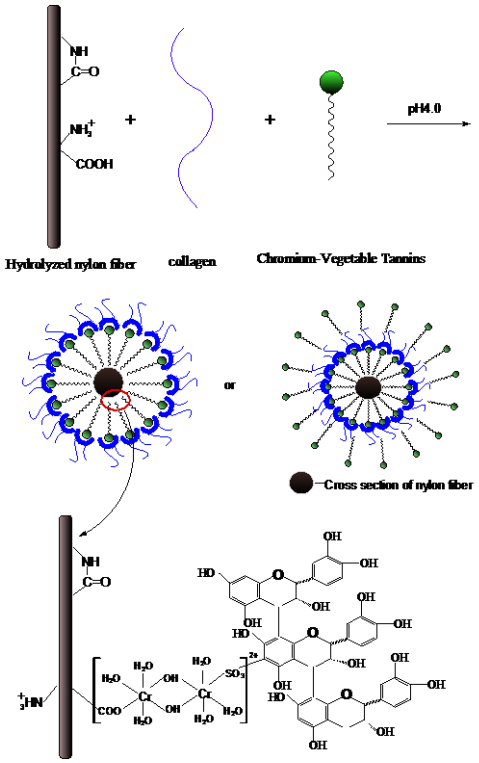

Figure 12 the methods of grafted C-CrT onto nylon fiber

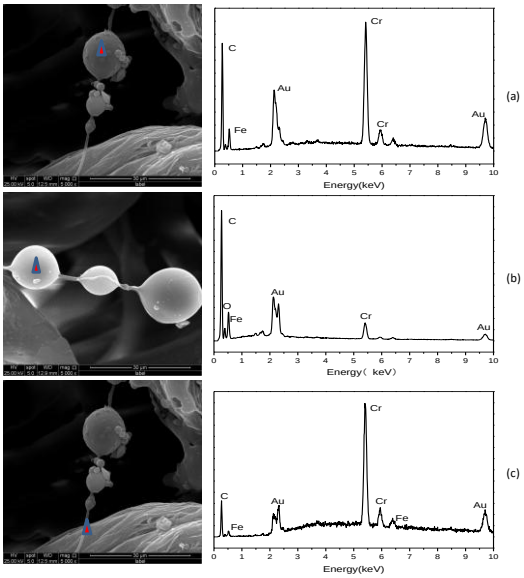

Figure 13 The SEM/EDS of C-CrT-grafted USFSLB on the different spots

SEM/EDS of C-CrT-grafted USFSLB on the different spots were shown (Figure 13). After elemental analysis of different microspheres (Table 3), it was confirmed that there were two forms of the outer surface of microsphere. One was surrounded by chromium tannins layer, as shown Figure 13-(a), and the relative content of element C, O and Cr was 76.32%,7.04% and 9.67% respectively (Table 3). The other was surrounded by collagen layer, as shown in Figure 13-(b), and the relative content of element C, O and N was 56.11%, 19.67% and 22.07% respectively (Table 3).

Table 3 EDS elemental analysis of different spots

Spot	Chemical composition(%)							
	C	O	N	Cr	Si	S	Fe	Au
(a) microsphere	76.32	7.04	*	9.67	*	0.84	0.83	5.31
(b) microsphere	56.11	19.67	22.07	1.04	0.13	*	*	0.99
(c)nylon fiber	63.57	*	*	23.80	0.12	1.36	2.10	0.99

* Not measured

4. Conclusion

The waste biomass materials, collagen and vegetable tannins, was grafted on the nylon fibers of USFSLB successfully. Some physical properties of C-CrT-grafted USFSLB had be improved, such as homogeneity, antistatic property. Importantly, the C-CrT-grafted USFSLB showed excellent moisture absorption and permeability. The modification mechanism what collagen and chromium-vegetable tannins grafted on the nylon fibers of USFSLB was demonstrated to be forming hydrogen bonding, hydrophobic bonding and coordination bond. More meaningfully, this method paved a way for recycling the waste biomass materials, collagen and vegetable tannins.

5. Acknowledgements

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SFS P-28

REDUCE POLLUTION LOAD AND VOLUME BY EFFLUENT REUSE / RECYCLE

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Nowadays the bottleneck for production capacity of a tannery is the restricted quantity of effluent water being let out for treatment to Common Effluent Treatment Plant (CETP). This paper analyzes possibility to reuse or recycle various waste water streams generated from various operations in beam house.

Quantity of waste water generated per Kg of Raw skin or hide by conventional wet blue beam house process is 8.5L to 10L. This reuse and recycle suggests reduction of this fresh water quantity to 1.5 L/Kg, where the balance quantities are from this reused and or recycled waste streams. This implies final discharge as effluent to CETP will be less than 1.5 L/Kg.

Waste water streams in a beam house are generated from Pre-Soak, Main Soak, Lime, Fleshing, Delime prewash, Delime, Delime 1st and 2nd, Pickle, Tanning, Piling. Beam house waste water streams vary in pH, TDS and few other parameters. After required primary treatment, especially removal of Suspended solids these waste streams shall be used in various processes in beam house. Let's recall our traditional long liming process, where we do not use any sodium sulphide, there sharpening action was done by the old lime liquor, this triggers idea of reusing lime liquor after removing suspended solids. We discuss similar such reuse ideas for different waste streams at different stages.

Analysis on paper is done regarding quantity of treated waste water from different streams, and that shall be used for different operations depending on their contents viz TDS, proteins, fats, other chemicals and pH. This suggests number of iterations of reuse and recycle. Chemical requirement shall be reduced as these treated waste streams have some unused chemicals, especially chemicals such as Sodium Sulphide, Sulphuric acid, Chrome which are hazardous to environment and health.

Keywords: effluent water reuse recycle bottleneck reduction Suspended solids pollution load unused chemicals pH

INTRODUCTION

If a tanner is given an opportunity that they can

- increase their wet end (beam house) production capacity by 5.5 folds with given capacity of effluent per day or

- earn by saving an amount of Rs 3.5 to 5.6 per Kg of Raw

imagine how much sustainable the business would be, amidst the situation that tanner's capacity is curtailed by effluent water quantity and cost involved in effluent treatment to meet pollution control boards norms.

This is very much possible with reuse or recycling of effluent water, based on the fact that processing of hides and skins goes with addition of salt to increase upon process water's TDS (Baume). This salt and TDS are problem for environment but are boon for leather processing, say for example, to solubilize globular proteins in soaking, to control swelling in liming, deliming and degreasing, to split fiber bundles and to control swelling in pickling, for dye and fatliqours fixation in dyeing.

This paper is written on the basis of coagulation, discoloration, and physical separation of TSS, TDS etc using mechanical filters with sieves. The possibility of reducing TDS by enzymatic treatment and activated sludge can add value into this project

It is observed here, that how many iterations the water shall be reused or recycled, without affecting process (reuse) water quality

Waste water streams and their properties

Waste water streams that are generated during beam house processes are Soak liquor, Lime liquor, Fleshing water, Delime prewash water, Delime water, Delime I wash water, Delime II wash water, Pickle bath, Tan bath, piling water

Soak liqour

Soak liquor contains dissolved Sodium chloride, major contributor for its TDS, Fat, Soluble proteins, traces of hair, Dirt, Dung, Blood, processing chemicals such as wetting agent, Soak enzyme, Alkaline salts(pH controllers) etc. The pH of soak liquor effluent is between 8.5 to 10.5, TDS may vary between 30,000 to 1,00,000 ppm depending on source and percentage of water used. Its 100% for drum soaking and 200% for paddle soaking based on wet salted raw weight

Lime Liqour

Lime liquor has Proteins (Flesh, Hair), Fat, processing chemicals such as Lime, Sodium Sulphide, Anti-wrinkle agent, Lime enzyme, degrease agent. pH is fully alkaline, high TSS content, TDS shall be 10,000 to 20,000 ppm. Dosage is 100% for drum liming and 200% for paddle liming based on wet salted raw weight or soaked weight.

Fleshing water

Fleshing water is used to prevent rubber feed roller from wear and tear and easy operating condition. Its running water, it has flesh, fat, hair, soluble lime and sodium sulphide. Approximately 100% based on wet salted raw weight or soaked weight., with pH >11

Delime prewash water

It has flesh, fat, hair, hydrogen sulphide, soluble lime, traces of processing chemicals such as Sodium bi sulphite, wetting agent. Approximate quantity is 100% on pelt weight, with pH >10

Delime WatEr

It has soluble lime, traces of sodium sulphide, fat, soluble proteins, processing chemicals such as delime agent, ammonium salts, alkaline bate, degrease agent, hair roots. Approximate quantity of delime waste stream is 30%, based on pelt weight, with pH 8.0

delime wash I

It has fat, soluble proteins, processing chemicals such as degrease agent, wetting agent, salt. Approximate quantity of this waste stream is 100%, based on pelt weight, with neutral pH

delime wash ii

It has fat, soluble proteins, measuring 100% on pelt weight, with neutral pH

pickle bath

It has fat, acid soluble proteins, processing chemicals such as Salt (TDS contributor), acids. Approximate quantity of this waste stream is 30% based on pelt weight, with pH <3.0

Tan bath

It has proteins, traces of fat, processing chemicals such as salt, acids, chrome, fungicide, alkaline salts. Its waste stream measures around 150% based on pelt weight, with pH 4.0

PILING water

Piling water is due to liberation of acid during olation and oxolation after the leathers are piled up. This is similar to tan bath with pH < 3.0

WASTE water treatment and treated waters properties

The waste water is to be treated mainly to separate out TSS, decolorize and preserve from fungal and bacterial activity. The values shown here under are based on waste water treatment in following steps, coagulation, discoloration, physical separation of TSS, TDS etc with mechanical separator having sieves and preservation from fungal and bacterial growth.

The properties of waste streams, what to remove from that waste stream, what method shall be employed in removal of impurity reusable water's pH, TDS and what can be reducing in further processing are given below.

Per 100 Kg of Raw				Reusable Water's	
Operation	Water Cons in L	What to remove	Method of removal	pH	TDS
Soak	200	SS, all dirts	Coagulation, physical separation, discoloration	8.5	30,000
Lime paste	20				
Lime	200	SS, Sludge, Hair	Coagulation, physical separation, discoloration	14.0	3,000
Flesh	100	Fat, SS	Coagulation, Physical separation	12.0	2,000
Pre wash	80	Fat, SS	Coagulation, Physical separation	10.0	2,000
Delime		Fat, SS	Coagulation, Physical separation	9.0	2,000
I Wash	100	Fat, SS	Coagulation, Physical separation	8.0	2,000
II Wash	100	Fat, SS	Coagulation, Physical separation	7.0	2,000
Pickle	50	Soluble protien	Physical separation	2.8	8,000
Tan	50	TSS	Physical separation, acidification	4.0	9,000
Pile			Physical separation	3.0	9,000

where to reuse treated waste water, why

The waste water should be reused in such a way that its properties are as per requirement at the given stage of usage, where by usage of additional chemicals shall also be reduced. Also, consideration is given in such a way that TDS built up on no. of iterations be in control. Based on this concept the waste streams reuse stages are defined as per below table. Read reuse stages column wise and reusable waste stream's source is in rows.

Per 100 Kg of Raw					Re use stages									
Operation	Water Cons in L	Let out	Reusable	Effluent	Soak	Lime paste	Lime	Flesh	Pre wash	De lime	I Wash	II Wash	Pickle	Tan
Soak	200	160	150	10		20	45				85			
Lime paste	20													
Lime	200	170	150	20			150							
Flesh	100	100	90	10	90									
Pre wash	80	80	75	5	75									
Delime		20	10	10					10					
I Wash	100	95	90	5	20				70					
II Wash	100	95	90	5				90						
Pickle	50	10	5	5									5	
Tan	50	80	80	0	5								29	46
Pile		5	5										1	4
Fresh Water					10		5	10			15	100		
	900	815	745	70	200	20	200	100	80	0	100	100	35	50

Soaking bath is made as composite of Fleshing water, Pre-wash water and Delime I wash water and traces of tan bath. Other than tan bath the rest of the waste streams are at pH around 10, which is desired in soaking to prevent bacterial growth, also traces of chrome at very low ppm can also inhibit growth of bacterial colonies.

Lime bath is composite of some soak liquor, major lime liquor and balancing with fresh water, this has soluble proteins and NaHS that helps removal of hair, and some portion of salt to result in controlled lime swelling.

Flesh water is contributed by traces of fresh water and major Delime II wash waste stream, which has deliming property, thereby reducing possibilities for lime blast on drying after fleshing.

Delime pre-wash is contributed by waste stream of delime I wash and traces of delime, this helps in removal of lime without addition of any deliming chemical as in usual practice.

Delime I wash is done with waste stream of soak liquor and traces of fresh water, the salt content in soak liquor is set to start stage for pickling.

Delime II wash be done with fresh water for cleaner pelt and balance of TDS on next iteration.

Pickle reuse water is from waste stream of tan bath (supernatant in chrome recovery), traces of pickle bath and piling water, this totally eliminates use of additional salt as the bath itself is self-sustained.

Tan bath is composite of Recovered chrome, some supernatant water from chrome recovery and pile water. This reduces usage of Chrome for tanning.

WHAT CAN BE REDUCED

The waste streams composition in reuse stages are designed such that chemical dosages shall be reduced, a glimpse of the same is given below

Per 100 Kg of Raw					
Operation	Water Cons in L	Let out	Reusable	Effluent	Reduction in dosage of
Soak	200	160	150	10	Alkali
Lime paste	20				
Lime	200	170	150	20	Sulphide
Flesh	100	100	90	10	
Pre wash	80	80	75	5	Delime chemical
Delime		20	10	10	
I Wash	100	95	90	5	Delime Chemical
II Wash	100	95	90	5	
Pickle	50	10	5	5	Salt, Acid
Tan	50	80	80	0	Chrome

How many iterations can be done

It is studied on how much TDS will be contributed at every reuse stage for every reuse iteration. It is found that Pickle and tanning stabilizes at 9000 ppm from 4th iteration, Soak bath at 52,608ppm from 36th iteration, lime bath at 47,547 ppm from 46th iteration and Pre-wash, delime, delime wash at 45,017 ppm from 40th iteration, after these any number of iterations can be done, the end iteration has to be decided based on practical experience. Find the numbers from below table

Per 100 Kg of Raw					Iteration 1	Iteration 4	Iteration 36	Iteration 40	Iteration 46
Operation	Water Cons in L	Let out	Reusable	Effluent	TDS 1	TDS 4	TDS 36	TDS 40	TDS 46
Soak	200	160	150	10	32,175	44,334	52,608	52,608	52,608
Lime paste	20								
Lime	200	170	150	20	9,050	23,410	47,539	47,544	47,547
Flesh	100	100	90	10	2,000	2,000	2,000	2,000	2,000
Pre wash	80	80	75	5	2,000	29,344	45,016	45,017	45,017
Delime		20	10	10	2,000	29,344	45,016	45,017	45,017
I Wash	100	95	90	5	25,800	36,467	45,016	45,017	45,017
II Wash	100	95	90	5	2,000	2,000	2,000	2,000	2,000
Pickle	50	10	5	5	8,857	9,000	9,000	9,000	9,000
Tan	50	80	80	0	9,000	9,000	9,000	9,000	9,000
Pile		5	5		9,000	9,000	9,000	9,000	9,000
Fresh Water					2,000	2,000	2,000	2,000	2,000

Conclusion

The paper finds clearly that the waste streams be reused effectively, without much of newer technologies, just relying on basic requirements of feed bath in various stages, that effluent can be reduced by 80 - 90%, or indirectly the production capacity based on effluent shall be increased by 5.5 folds.

A savings of effluent treatment cost by Rs. 3.5 to 5.6 per kilogram of raw hides is possible.

Technologies such as use of enzyme to reduce TDS and in activated sludge system, as some proprietary suppliers claim, should be explored as one method of removal and or treatment.

References

1. My teachers in academics and industry
2. My practical experience

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CREATIVE DESIGN CONCEPTS AND NEW PRODUCT DEVELOPMENT STRATEGIES FOR RECYCLING OF FINISHED LEATHER WASTES

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Zero waste or minimization of waste is now a strongly emerging issue for the industrial development especially in leather and leather product industries where an integrated waste management system is the need of the hour to sustain in the leather business. Leather industry generates a significant quantity of solid wastes that are affecting the environment as well as the industry economically. It is estimated that the industry produces about 1.4 Million tons of processed waste per year worldwide, with the majority as sludge, being disposed as landfill. This waste disposal mechanism is in conflict with increasing legislation and environmental drivers to encourage avoidance of waste and waste disposal. The implementation of stringent environmental regulations has led to increasing disposal costs also to the industry. The tanning processes generate even greater quantities of leather wastes, few alternatives are at present commercially available like fuelling. Leather scraps represent a large part of these wastes. In most cases, internal reduction solutions cannot reduce the quantities of waste very much and most of these industries end up selling these scraps to the local collecting agents. It's a loss for these industries when they have to sell these scraps for Rs.10-20 per/kg or sometimes even less, to small vendors.

Also, from the literature review done, it has been found that attempts have been made by the previous researchers to utilize the wastes from the leather industries by turning them into leather boards or composite boards, etc. Not much research work or design interventions have been done in the previous years for converting the leather wastes into commercial leather products for the market.

In this context, the main objective of this research work is to understand the problem of solid leather wastes particularly finished leather scraps that has been generated by the leather industry and to reduce the leather wastes by converting the scrap leathers into useful products thereby reducing the impact on the environment and also minimizing the loss for the industry due to huge disposal of unused leathers and scraps as wastes. The research work presents the strategies for the collection and assortment of different types of finished leather scraps generated by the leather manufacturers, footwear, leather goods and leather garments industries. Then, suitable design concepts and product development techniques are applied for converting the scraps into innovative leather products which are commercially feasible and can be marketed domestically as leather lifestyle products at affordable price to the mass consumers.

Keywords: Design Concepts, Leather Wastes, Leathers Scraps, Life Style Products, Leather Recycling, New Product Development, Sustainable business, Waste Management.

1. Introduction

New technologies are generating a big amount of leather wastes year after years. It would be helpful for the environment if something new from the waste or unwanted scraps of better quality are created. The primary aim was to assess the type, quality and size of leather scrap collected and to incorporate different approaches and techniques to develop value added fashion and home accessories. Leather is a unique and highly versatile material. It is a renewable resource based on a by-product of the meat, wool and dairy industries and used in a wide range of products as diverse as garments, footwear, luggage, bags and portfolios, ladies handbags, belts and several industrial accessories. The cutting and sewing is done according to the pattern/design/size of the product manufactured. This generates small cuttings, side layers from the leather sheets which are abandoned are considered as waste. This generated leather waste disposed into the landfills, which takes long time to decompose and creates environmental pollution. To reduce the elimination of waste and using all the resources appropriately is very necessary. However, leather industry is also accused of being one of the most polluting industries. Not only production but consumption of leather also produces waste. To counter the problem, the industry has taken many measures for reducing its negative contribution towards environment, but there are only few measures that have been implemented towards the design intervention part of this problem.

2. LiteratureReview

Swaminathan(1998) states that sludge from tannery effluent treatment plants in India has been categorised as hazardous waste due particularly to the presence of chromium in it. Whilst the mobility and toxicity of chromium is under review in certain developed countries (e.g. USA, Australia) in many developing countries the presence of chromium limits disposal and / or conversion possibilities of tannery sludge. Three common effluent treatment plants operating in Ranipet area, Tamil Nadu, India, generate about 23 tons of sludge per day (dry matter). With UNIDO's technical assistance, CETP-Ranitec established a temporary safe landfill in October 1997. CETP-SIDCO followed suit with a smaller landfill. A more basic landfill, representing conventional large landfills, has been planned for CETP- Vishtec, Melvisharam, Ranipet. In conventional physio-chemical cum biological treatment system 70-80 per cent of the sludge is produced in the primary treatment and the remaining 20-30 per cent is produced in the secondary biological treatment. The solids content in the tannery effluent will depend upon the raw material, type of process adopted, chemicals used in the process and other in- plant control measures. The main sources of suspended solids generation are first soaking, liming and vegetable tanning that too if carried out in pits using crushed barks and nuts.

Maroquinerie(2000) shows the quantification of the wastes produced is a difficult task; the production data (number of pairs of shoes, number of gloves etcher not available on a worldwide basis except for

leather and for leather footwear. The calculations for the other products have been made from exportation data which do not represent production. However, with the figures obtained, it seems that Asia is the 1st region regarding the production of wastes in the leather sector. It is producing more than 60% of the wastes in the world. Leather scraps represent a large part of these wastes; at the same time, scraps from wet blue (tanning process) are very important too. In most cases, internal reduction solutions cannot reduce the quantities of waste very much and internal recycling solutions can only be applied in large scale to thermoplastics. This is why recycling solutions must be found outside the factories. As the recycling technologies need large quantities of wastes (>2000 t/year), the leather sector must organise the collection, the transport and the recycling operations in order to find a solution. For the other wastes, it will be difficult to find a recycling solution which could be operational rapidly. This is why the valorisation solution seems to be the incineration with energy recovery and under controlled conditions (exhaust gazes treatment). In that way, scraps containing PVC will probably become a problem due to the production of chlorohydrin acid during the combustion. As a consequence, and unlike the other wastes, waste containing PVC will probably continue to need landfills in the next future. These considerations also apply to worn finished products as it contain the same materials. In any case, and in order to start/improve the recycling treatment of wastes, the leather sector will need to develop a new internal organisation and new internal responsibilities in the factories as well as a structured organization between the factories which could deal with these new environmental issues.

Zlin (2000) shows that the leather manufacturing process generates a variety of solid wastes which are well known, we only selected the wastes having a chemical composition comparable to finished leather 1. Wet blue splits, trimmings and shavings, 2.leather trimmings, 3. Leather dust. Footwear is the sector which consumes the major part of leather (60 %). Logically, this industry is producing the largest quantity of leather wastes. However, in spite of the specific application of their products, these industries a have some common points which are described hereafter the process (and even the machines) involves similar production steps and technologies (except for footwear for which the assembling techniques can be sophisticated). With European partners (research institutes, industries of the leather sector, machinery makers), the CTC has just completed a 24 month craft project aiming to develop a cutting system able to “geometrise” the raw hides. The objective of this approach is to generate the solid wastes at the earliest possible stage. This means that the best place is in the tanneries, before the beamhouse stage. Practically the geometrisation consists in automatic (CD camera + water jet cutting) trimming device. Thanks to a specific software, the width to be cut at the side of the hide/skin is optimised; the size of the trimmings are automatically calculated according to the area of the hide/skin itself (belly etc.). In this way, the trimmings contain less chemicals (raw hide) and can be easily recycled. In the whole leather processing chain, the minimum quantity of chrome containing wastes can then be generated.

Karel and Viswanathan (2001) found in their study that a part of wetblue leather shavings is used in leather board manufacture along with vegetable tanned leather (EI) shavings. The wetblue shavings are mixed with EI shavings in the ratio of 1:2 for production of leather board. Unused wetblue shavings are dumped in open areas around tanneries, riverbeds, and etc. in India and elsewhere in the region causing a serious environmental hazard. The presence of chromium in such shavings poses a potential danger.

This technology uses organic amines such as iso-propyl amine, di-isopropyl amine, cyclo-hexyl amine and other chemicals. Use of these volatile amines has the following advantages: Ash content in hydrolyzed products is low. It increases the chromium oxide content in filter cake, thus facilitating regeneration of tanning salt. When concentrating diluted solutions of protein hydrolyzate, a certain regeneration of organic base i.e. amines takes place. The efficiency of protein yield increases from 60% to 80% and more. Plants for treatment of liquid waste have been established in many of these countries. Though many options exist for management of solid wastes from tanneries, solid waste utilization and disposal continue to pose a serious challenge to the tanners.

Steve ABBOTT (2002) is organising a project whose objective is to develop at least one commercially viable recycling route for finished leather, thereby lessening the environmental impact of the footwear industry and improving its competitive edge by reducing waste disposal costs. The use of products containing waste leather would be demonstrated in applications in footwear and other industries. The objective of finding a viable recycling route for finished leather was to be achieved by: - compression molding an intimate mix of binder and leather fibers - incorporating leather fibers into a nonwoven fabric - using leather fibers as a filler for polymeric systems. A comprehensive study would be undertaken to quantify what leather wastage there is in footwear and other industries such as clothing and furniture. SATRA had existing data on footwear production and leather usage, but this lacked detail. For the purpose of this study, information would have to be collected on the composition of the leather market such as type of leather (e.g. cow, pig or goat), type of tannage used and nature of finish. It was possible that these factors would affect the recyclability of the leather. Leather fiber properties would be fully characterised using techniques such as optical and scanning electron microscopy, FTIR, GCMS and wet chemical methods. Activities were also to be undertaken to disseminate information, both during and on completion of the project. This was to include in-house publications, trade journals and two seminars, at which use of the leather fiber containing materials would be demonstrated. Nevertheless, the project has generated a considerable body of knowledge which will be invaluable if and when conditions are favorable. If, or more likely when, the routes for recycling waste finished leather identified in the project become attractive for commercial exploitation then the anticipated environmental benefits (reduced disposal of materials to landfill and incineration, with consequent reduction in emissions of substances to land, water and air) will be achieved. Bowden (2003) states that the leather industry is estimated to produce some 1.4 Million tons of process waste per year, with the majority as sludge, being disposed to landfill. This waste disposal route is in conflict with increasing legislation and environmental drivers to encourage avoidance of waste and waste disposal. This has led to increasing disposal costs and difficult logistics. However, few alternatives are at present commercially available. The research is to provide a degree of industry acceptance of the technology, provide experience in emissions and measurement, process operation, robustness, regulatory issues, licensing, design and an indication of operational issues to be expected when rolled out on industrial sites for risk analyses. The economic and strategic pressures facing the leather industry, the relative success of the technology at demonstration scale suggests that the application of gasification could point therefore to a clean green and efficient waste disposal and energy recovery solution for the leather sector. This is in support of EU policy implementation, and government policy support and yet provides payback periods to each site estimated at 3 years or less. Improvement to

process robustness is currently being addressed, in order to provide even greater (industrial and public) confidence. Gasification of wastes such as sewage sludge, agricultural residues, packaging, municipal solid waste, refuse derived fuel and other residues from paper, tire and leather industries have distinct advantages over simple combustion devices (e.g. incinerators, boilers etc.).In so far as, with well-designed gasifier systems, the product gas is controllable and clean enough to operate combined heat and power (CHP) systems or be applied directly into burner systems of boilers Downdraft gasification would seem to be preferable to updraft gasification for a small site application (e.g. industrial site), on the basis of cost, gas quality and aesthetics. Compliant emissions to atmosphere should be achievable. This stage the technology will need more on site trials before sufficient data can be collected to prove compliance. Also, compliance can only be ascribed according to the choice of application to which the syngas is put. Supplementary RTO (regenerative thermal oxidisers) may be required (secondary combustion) in addition to conventional post combustion abatement plant.

Kanagaraj , Velappan, Chandra & Sadulla (2006) has described in their study that solid wastes by the leather industry cause pollution problems in terms of sludge, BOD and TDS. Raw trimmings and wet blue trimmings can be useful to generate glue and gelatin. Keratin hydrolysate can be used as an exhaustive aid for chrome tanning Fleshing hydrolysate can be used as a tanning agent by proper chemical modification. Fleshing wastes can also develop poultry feed. Chrome ad buffing dust are useful in developing retaining agents, fertilisers and landfill sites. Leather industries in developing countries is facing a lot of solid wastes problem and many tanneries closed for not able to meet bio chemical oxygen demand and total dissolved solids. That's is why it is important to manage the leather waste in to useful products generated by the leather industry.

Persson and Malin (2006) talks about generic development process that was followed throughout the project and the goal was to end up with a number of concept ideas to further develop. In the beginning the range of product possibilities was wide but the usage of different development methods made it possible to eliminate the less suitable. The result was eight final product concepts; bookmark, pocket mirror, serviette ring, lantern, vase, bowl, mug and glass made out of leather. For the concepts a pattern was developed. To evaluate the result of the project, most of the products were shown as test products made in leather at the Nolia fair in Piteå and the visitors of the fair were able to give their reflections. This ultimately led to a few changes of the final products which hopefully will be manufactured and sold in the future. The main goal with the project was to give Bölebyn's Tannery the possibility to use the result in future development of their product range. The result would consist of three to five product concepts. These concepts would be well-made, if possible presented as leather models, and were to be ready for manufacturing. The products would foremost be attractive to a younger market.

Yimaz, Kantarli, Yuskel and Jale (2007) have found out in their study that Leather industry is the one of the wide spread industries of Turkey and thus it is polluting the country in a large scale. The leather making process generates substantial quantities of solid and liquid wastes (hides and skins, fats, shaving and trimmings, buffing dust, process effluents, sludge). Mostly this wastes are disposed in land. It is reported that the tanned wastes of 0.22 kg/kg of wet salted hides/skins is generated per year in Turkey. Since the chromium metal is the most important tanning agent, the solid wastes from chromium-tanned

leather requires special attention because of the large amount produced and because of the legislative restrictions. In literature, there are many studies on the treatment of tannery wastes. Most of these studies concerns the extraction of chromium from wastes to re-use in the tanning process. On the other hand, pyrolysis may be one of the alternative route for treatment of solid wastes from tannery wastes. Pyrolysis have being widely applied to organic wastes, such as agricultural wastes, scrap tires, sewage sludge and plastic wastes. The pyrolysis process involves heating the carboneous material in an inert atmosphere. The products of pyrolysis are gas, oil and carbonaceous residue. The gas can be used as fuel and the oil can either be used as fuel or as raw material for chemicals. The carbonaceous residue can be burnt as fuel or safely disposed of—since the heavy metals are fixed in the carbonaceous matrix. In addition, this residue is also suitable for production of activated carbon. The physical activation method involves pyrolysis of the raw material and the subsequent activation at high temperature in a carbon dioxide or steam atmosphere. The chemical activation method involves the pyrolysis of the raw material previously impregnated with a chemical agent such as zinc chloride, phosphoric acid, potassium hydroxide, etc. A large number of agricultural by products such as coconut shells, palm-kernel shells wood chips, sawdust, corn cobs, seeds, etc., have been successfully converted into activated carbons. The qualities and characteristics of activated carbons depend on the properties of the starting materials as well as the activation methods and processes. There are few studies related to pyrolysis of tannery wastes. Research was carried out a kinetic analysis of the global thermal decomposition of leather. The pyrolysis of chromium-tanned leather was modelled assuming that it was formed by two different fractions which decompose by two independent reactions. They also studied on the pyrolytic products evolved from the thermal degradation of chromium tannery wastes by two stages pyrolysis. They concluded that the formation of pyrolytic products was influenced by the operation conditions (temperature, heating rate). They also detected significant levels of ammonia, hydrogen cyanide and Sulphur dioxide. The activation at 825 ◦C in carbon dioxide of chromium-tanned leather. The porous texture of carbons has been characterised by adsorption of N2, CO2 and iso-butane. Taking the above considerations into account, the aim of this work was to investigate the production of useful materials from different kinds of leather wastes by pyrolysis. A primary focus of the paper is on the production of activated carbon and investigation of its aqueous adsorption characteristics.

Sekaran, swarnalatha, Srinivasulu (2007) has found in their research that Leather industry generates a significant quantity of solid wastes. They are classified into tanned and non-tanned collagenous waste. The dissolved chromium and other spent chemicals namely proteins, poly phenolic compounds, surfactants, dyes, etc. present in the waste-water are removed through chemical precipitation technique using lime and ferrous sulphate, before the wastewater is allowed to enter the biological treatment process. The precipitated chromium along with the other organic compounds is discharged as primary chemical sludge. The basic component of solid waste is protein. Hence, they undergo microbial degradation, may be at retarded rate. Options such as land fill, vermin composting, anaerobic digestion and thermal incineration were considered for disposal of solid wastes. Leachability study through TCLP on solidified block was carried out to determine the degree of leachate and metals. The percentage of metal fixation was 99.1 99.9 % and dissolved organic concentration in the TCLP leachate was 55-66 mg/l. Index terms - Chrome shaving, bottom ash, sludge, starved air incineration, solid waste, leather industry.

Karabay (2008) has wrote in his study that there are many some salting methods (drying, keeping in a temperature of -3 Celsius degree or putting in the ice bars). Treating leather with salt method is applied since it is economically the best way, it causes an additional treatment cost to the facility. This salt can be detracted from the facility by whipping-by-hand method to a minimum degree. Also, the slaughter houses are near the leather tanning facilities but this does not necessitate that the leathers should be immediately tanned or additional chemicals or technologies should be used. Since this factor is not considered during the foundation of the facilities, this alternative cannot be used in the process of decreasing the salt added into water. In the first facility, waste products from snipping and trimming processes were used as raw material in other industries, but in time, these waste products caused additional pollution since the shipments expenses became costly because of the distance between the facilities. In the other facility, these waste products are sold. Waste products from fleshing process are used as raw material in neither facility. Today the most easily applied method for hair-removing process is using chemicals such as lime, sodium sulphide (arsenic) and kaolin in liming closets, which does not require additional work force. But this method is one of the reasons for the increase of the pollution in the water. Another method is whitening method. In this method, a solution composed of arsenic, lime, sulphide hydrate and kaolin is applied on the sub-section of the leather, and the leather is left for 3 hours, then the hair is removed manually. This whitening method should not be ignored since in this method the process water is used and the chemicals and the pollution in the water are kept at a minimum level, in addition, it can be sold and most importantly this method helps energy saving. Considering the physical characteristics of the leather achieved by the chrome tanning method, this method is used in both facilities for producing desirable quality leather. Vegetative tanning or alternative tanning methods can be used instead of this method. Even though we cannot completely extinguish the pollution that is caused by chrome tanning method, we can recycle chrome by making use of clean technologies to minimise it keeping the pollution of the environment and costs of the chemicals used at a minimum level. The process of minimising the pollution by recycling chrome is applicable in both facilities without any area problem. This technology is perfect for the big or medium-sized facilities. But it is a fact that, considering the additional processes in the future and unplanned construction costs; the modification of the clean technologies should be subtracted. Since the first facility is located in a free leather trade area, it is not required to construct a pre-treatment facility because there is a single treatment facility in this free trade area to minimise the wastes from all of the facilities in this area. But wastes from liming and tanning are elevated to the facility in separate canals together with the process water and discharged in accordance with the rules stated in the Regulations. In both facilities, for the control of the pollution, the most appropriate technologies can be preferred in both refining and operating processes by employing mass balance calculations, which is an additional indicator to the Regulations. The second facility has concentrated on this kind of an activity and is trying to get data for calculations.

Katarzyna Fela (2010) shows in their study that the tendency towards cleaner, waste-free production in the recent years, particularly in the European Union, opens new possibilities for tanneries in terms of waste management. However, new technologies are required that would be able to provide comprehensive solution for tannery waste management. This paper outlines the concept of such technology, utilizing chemical incineration process. Tannery waste management is a serious problem for

all tanneries. Untanned hide waste can, in certain cases, be used as raw material for the production of glues, gelatine, protein casings, as well as forage and fertilizers. There are also technologies of transforming waste into biogas. Furthermore, tanned hide waste can be used for the production of the so-called composition leather. Nevertheless, due to economic reasons and legal regulations prohibiting the use of animal waste in the forage production, the management of this type of waste is minor. The majority of such waste is stored in lands. This creates further environmental hazards due to the emission of odours, washing away of toxic substances, etc. In general, there are no solutions enabling comprehensive disposal of all waste within the economic capabilities of the tannery. Thermal waste neutralization is, in many cases, the alternative to storage, which is considered the most environmentally hazardous method of waste disposal. Also, it is often required by the relevant provisions of the law that order certain types of waste to be incinerated. Rather than a cumbersome burden, waste can become a valuable energy source. To achieve this, appropriate facilities are needed to ensure correct and environmentally friendly waste incineration.

Stanislaw and Krystyna (2011) wrote in their study that the modern leather industry is based on hides which are a by-product of meat industry. In this aspect tanneries reuse waste from other industries. But on the other hand, the tanning processes generate even greater quantities of by-products and waste leather. 1 Mg of wet salted hides yields only about 200 kg of leather. The rest – about 800 kg – becomes waste, including tanned solid waste (about 250 kg), non-tanned waste (about 350 kg) and waste lost in wastewater (about 200 kg). Water required for the processing of 1 Mg of hides amounts to 45–50 m3. The chemical reagents consumption is also high – for 1 Mg of hides about 400 kg of chemicals is needed, including sodium chloride, lime, sodium sulphide, sulphuric acid, basic chromium sulphate and others. Thus, the impact of tanning industry on the environment is significant and the proper waste and wastewater management by tanneries is of great importance. Due to FAO statistics, the worldwide annual production of bovine hides and skins amounts to about 6 million Mg (wet salted weight). Sheepskins, lambskins, goatskins and kidskins are processed for 600 thousand Mg (dry weight). Rough calculations reveal that the world leather production generates about 3–3.5 million Mg of solid waste, which requires appropriate treatment in respect of the environmental protection standards. The production of leather has increased in recent years, mostly in developing countries. The UE-countries process about 11% of world bovine hides production and about 12% of sheep- and goatskins production (mostly Italy, Spain and Germany). The amounts of bovine hides processed in Poland have decreased in recent years, yet the values are still significant – 22.7 thousand Mg in 2009. Other sources give information about the leather production in Poland – about 9.5 thousand Mg of leather from bovine hides was produced in 2008.The proper utilization of this waste not only eliminates the negative environmental impact of its landfilling, but also brings benefit such as energy and material recovery. The combustion process permits to utilize all types of solid tannery waste.

Paul, Antunes, Convington, Evans and Phillips (2013) has found out in their study that zero waste is now a strongly emerging issue for sustainable industrial development where minimisation and utilisation of waste are a priority in the leather industry. In a tannery hides and skins converted in to leather through various processes. Approximately 20% (w/w) of the chrome containing tannery solid waste (TSW) is generated from one ton of raw hides and skins. However, tannery solid waste may also be a resource if

it is managed expertly as we move towards zero waste. Moving towards zero waste requires that industry adopts a circular economy. In Bangladesh, substantial environmental degradation occurs in the crude disposal of tannery solid waste. An increase in the utilisation of potential and traditional feed ingredients by processing industries will lead to the development of new feedstuffs. Tannery solid waste is however a potentially very vital source of protein once dechromed. Dechroming rate can be controlled to produce a final product with a low level of chromium and satisfies the requirement for poultry feed. The chemicals used in this vital process do not impinge of the final quality of the product. Some (Ca, Na) are advantageous in the final product. This paper show how a waste can be changed to a valuable product by adopting a sustainable approach. Further research would needs to be undertaken into these by-products with the aim of establishing their value for a wide range of animal feed. Kim Joo (2014) claims that with the help of 5R (Reduce, Reuse, Recycle, Regeneration, and Refill), the concept of upcycling has been placed as a strong cultural, political, economic, and cultural factors of influence in helping understanding the environmental issues and working on it. In the following research, 29 designs of high value-added up-cycled luxury handbags for the Dubai fashion market were developed from the consumer wastes produced from the manufacturing and sewing process of fashion products like handbags & apparel. The designs resulting from the following study are planned to be sold as a limited exclusive line in Dubai's Harvey Nichols and Bloomingdale's from the 2014 S/S season. The market analysis and proposed design model in the present study are generally applicable in the future development of the trading markets. Through the following study, it is hoped that Korea will no longer be the passive consumer of the global luxury markets but instead develop as a leader of the fashion industry and lead international exchange through strengthened national competitiveness. Up-cycled handbags have manufacturing disadvantages where the materials and supplies are limited and are only available through order-made service. However, these disadvantages are rather advantageous for Dubai's upper-class consumers where order-made service and the right to choose their own color, material, and shape of the design is considered as the opportunity in creating high values in Dubai's luxury fashion accessories market. Second, Dubai's upper-class women prefer couture accessories where the designs might be similar but are unique in material, color, and detail. Thus, application of three-dimensional appliqué techniques as design elements can be seen as the key strategy for stimulating consumers' interests. Third, the key element in the consumption patterns of Dubai's upper-class women is the preference of purchasing whole items instead of a single item.

Md Ola, Youssef and Bloch’s (2015) study focuses on two problems: (i) the valorization of industrial waste, in leather industry, (ii) the prevention of fire, or at least the flame burning tendency of paper materials. One of the most significant problems of the leather industry is waste generation: About 60% of leather substance processed in tanneries are eliminated, mainly after shaving process, in the form of protein wastes containing about 10–15% chromium. Leather waste shavings were disintegrated in a multistage way to obtain a powder, and then sieved through a sieve (0.3 meshes). The resultant leather powder was divided into three parts: (i) untreated leather powder, (ii) leather powder treated with triethyl phosphate and (iii) leather powder treated with Bromine (treated II). The treated samples were filtered and dried at 60°C for 2 hours in an air oven and sieved again through a sieve (0.3 meshes); then they can be included in the preparation of hand sheets. These wastes are mainly deposited and burned causing hazards to the environment. In the last few years, chrome shavings as filler in polymer, rubber

and paper were studied. Improvement of flame tendency may impact both society and industry preventing fire losses in previous study flame retardant of leather were reduced. Worldwide, paper, plastic, and polymers make up a large amount of materials used in everyday life and in many cases they contribute significantly to fire when ignition sources due to their ability to firing. In this study, leather wastes were grinned to Nano size, treated with flame retardants, and then added as filler during the paper sheets formation. Using of these wastes help in reduce their hazards and give an economical benefit to paper making and an effective solution for paper firing. Paper contributes to fire because they have low flame due to their cellulosic nature while plastic materials are inherently flammable owing to their chemical based upon petrochemical feedstocks. Among the pyrolysis components, the most significant is cellulose, which is the principal component in forest species, comprising 41–53% (w/w) of the total weight. The thermal degradation of cellulose takes usually place between 250 and 400 ◦C, through two competing pathways: one is the dehydration which leads to char and gases (mainly, CO, CO2, and H2O) and the other is the depolymerisation which leads to tar and volatiles through the formation of laevoglucose. Fire retardant is that any substance that by chemical or physical action reduces or inhibits combustion, decreasing thereby both the rate of spread and the fire line intensity of a forest fire. Many studies of retardant effectiveness were carried out based on water solutions containing different chemicals. The long-term retardants consist of flame inhibiting chemicals dissolved in water. They remain effective even after water has been removed by evaporation. Jiang, Junsheng and Wei Han (2016) claims that the genuine leather cannot be obtained via an artificial method and must be converted from raw skin/hides. The fabrication of leather from raw skin/ hides to finished leather must undergo various complex steps. The procedures usually include such operation steps as: pre-tanning, tanning and post-tanning. In these steps, large amounts of leather solid wastes (LSWs) and wastewater are produced. It was reported that about 1000 kg of wet salted hides would yield only 200kg of finished leather (ca. 20% of raw hides); while it would generate more than 600 kg of solid wastes and byproducts (beyond 60% of the raw hides). The conversion of raw skin/ hides into the finished leather needs the use of about 100 chemicals to remove unwanted components, which will also generate various LSWs or wastewater. Thus, pollution to the environment inevitably will occur. As a result, the contamination caused by leather-making severely threatens the environment and the health of human beings. How to treat these pollutants attracts much attention. Consequently, developing new strategies to treat leather wastes is urgent. Presently, there are two dominating material streams and systems for leather waste treatments: Wastewater and solid waste. The former is directed to obtain purified water. Whereas the latter places more emphasis on the removal of toxic pollutants, such as chromium, and the recovery of some useful products, such as collagen. Whether it is wastewater or solid waste treatment, efficiency, operation cost and adaptability of techniques are the major concern of cleaning technologies. For the direct dechroming of CTSWs, more research needs to be done for optimising the operation parameters, reducing the operation costs and improving the device's performances. The process integration of high-temperature pyrolysis and biochar dechroming techniques might be more efficient.

3. Research Method

Modelling

The aim of this research method is to make design concepts and fabricate from leather scraps and wastes collected from the Kalyanam & Co. tannery, Chennai for the commercial use and market or simulate by referencing it to existing and usually commonly accepted knowledge.

4. Research Implementation

4.1. Introduction

The leather scraps and wastes has been collected that is generated by Kalyanam & Co. during the tannery process. Some scraps have been also collected from their footwear company. These scraps contains different sizes and thickness of leather which are scraped during the tanning process for the better treatment of the leather. These scraps are segregated according to their size, thickness and finish to accordingly create design concepts for the products.

4.2. Materials-Waste/Scrap Leathers

The leather scraps that has been used for the research work has been collected from a tannery. These scraps includes both finish and semi-finished leather that has been scraped during the tanning process.

4.3. Collection and Selection of Scraps

The leather scraps are segregated according to their sizes, thicknesses and finishes. Though there are full leather skins that has cut outs of the patterns that has been used to make footwear. To sort that out, the leather sheet has been cut into smaller pieces in order to segregate the leather.

-Sizes: 1, 1.5, 3 sq. ft. are available

-Finishes: Patent leather Cow, full grain Cow, Oil pull up Cow, Matte black Cow

-Thickness: 6mm, 7mm, 8mm & 10mm

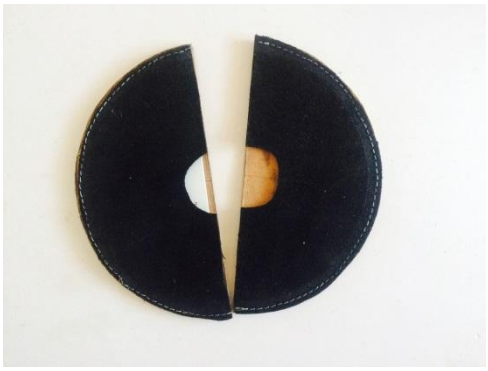
4.4. New Product Development Strategies

The research have been conducted to check on the existing products that are being made by only leather scraps that comes out from the industry. These products line category are divided into 5 major sections:

1. Flat goods
2. Desktop small accessories
3. Jewellery
4. Small Leather goods
5. Patched goods

4.5. Development of Design Concepts

The Concepts have been created keeping the market in mind. the products should be commercially marketed and user friendly. The final products are a Key holder, table coaster cum card holder, Pen holder and a earphone holder.

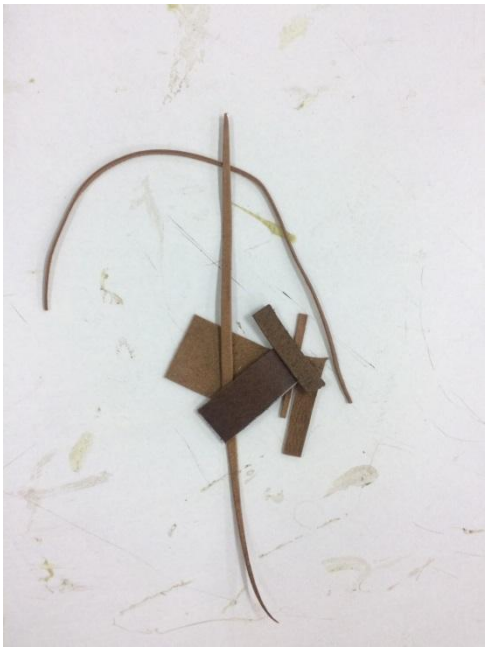


4.6. Development of Prototypes

4.7. Conclusion

The leather scraps that is being generated by the leather industries can be used in many possible creative ways in everyday life. These products are just an example of how small lifestyle products can be fabricated with leather scraps that can be marketed and commercially used. The products that has been

created from the scraps has generated almost no waste and most of the selected leather scraps has been utilised for creating these products.



5. Results and Discussion

Design plays a major role in any field. In leather, its been observed that in a past few decades the industry have been trying to experiment with leather from design point of view. Similarly, these research papers target the design are on how to use the scraps that comes in huge amounts from the leather industry. It will make a huge difference to the leather industry economically if the products that are made from these scraps are commercially used and will also make a difference if there is zero waste generation to the environment.

6. Future Scope

This research would be of a great use in leather industry as there are tons of leather scraps that gets wasted every year around the world. If the products are made keeping in mind the trends and data analysis of current market and are distributed in a manner that it reaches a huge part of the market, it can make a major difference to leather industry economically and also to the environment.

Conclusion

The leather industry is one of the major leading industry in current scenario around the world. With that comes the problem of environment pollution by waste disposal. Research centres has already came out with ideas to turn leather wastes and sludges into boards which is commonly done by the industry and are equally useful but after a point those boards are useless and becomes only a space to waste. There has to be other ways to use these scrap for a better use in the market.

Acknowledgement

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We thank Kalyanam Tannery & Co. for assistance with the collection of scraps and information.We would also like to show our gratitude to the (Name Surname, title, institution) for sharing their pearls of wisdom with us during the course of this research, and we thank reviewers for their so-called insights. We are also immensely grateful to all the authors for the reference papers (The names are listed in the Reference section) for their comments on an earlier version of the manuscript, although any errors are our own and should not tarnish the reputations of these esteemed persons.

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FLS P-12

A COMBINATION OF ANALYTICAL METHODS TO COMPARE THE THERMAL STABILITY AND EVOLVED PRODUCTS OF LEATHER TANNED BY DIFFERENT TANNING AGENTS

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Tanning is the most important process of treating skins and hides of animals to produce leather, which is more durable and less susceptible to decomposition. Tanning hide into leather involves a process which permanently alters the protein structure of skin. In this paper, much progress has been made in elucidating relationship between tanning solution concentrations and thermal stability of leathers. We studied the thermal stability by TG-DSC and compared the thermal stability of hide powder tanned by 2.5g/L, 5g/L, 7.5g/L, 10g/L and 12.5g/L chromium solutions. Thermogravimetric analysis simultaneously coupled with mass spectrometry was employed to study the thermal modification and degradation of leather through in depth analysis of the evolved gases. The information on the evolution of gaseous compounds during pyrolysis under the conditions revolved in this work was provided by TG-MS method and their evolution were different. The evolved products were similar while the distribution is not the same, and the thermal stability is different for the different concentrations of tanning agents. It was demonstrated that the concentration less affects the thermal stability. In DSC curves, we found the peaks in hide powder tanned by 12.5g/L chrome solution are lowest, indicating that high concentration is not a good one.

Keywords: thermal stability, leather, decomposition, tanning

Introduction

Tanning is the most important process of treating skins and hides of animals to produce leather, which is more durable and less susceptible to decomposition. Traditionally, tanning used chromium, formaldehyde, and glutaric dialdehyde(Gil 2012). Tanning hide powder into leather involves a process which permanently alters the protein structure of skin. Tanning can be performed with either vegetable or mineral methods. Chromium has long been regarded as the most efficient and effective tanning agent(Technology 1997). In this paper, we studied the thermal stability and thermal decomposition. So far, to our knowledge, no systematic thermal analysis on leather tanned by different tanning agents has

been reported. In recent years, the environmental pollution problems involved the emission of tannery sludge with chromium are increasing, which brings a big challenge for society(Sethuraman 2014). The quality of leather is excellently prepared by chrome tanning. The tanning process provides leathers with excellent hydrothermal stability, good dyeing characteristics, and softness. With the development of the economy and the improved of life level, the demand for leather products is also increasing significantly. However, only 70-80% of chrome is absorbed by leather during the process of chrome tanning, and the rest is discharged in effluent. There are still excessive amounts of chrome in the biological sludge after the tannery waste treatment, which results in the accumulation of the metals in soil. We compared the thermal stability of hide powder tanned by chromium and glutaric dialdehyde with different concentrations. The influence of solution concentration to thermal stability of hide powder was studied. It was demonstrated that there little difference in thermal stability and evolved products.

Experiments

Samples tanned by chromium and glutaric dialdehyde with different concentration were subjected to thermal analysis. Hide powder was tanned by 2.5g/L, 5g/L, 7.5g/L, 10g/L, 12.5g/L potassium chromium solutions. The process is the same as reference(Keyong 2004). Open platinum crucible, a heating rate of 10K/min, sample size of 10-20mg, and flowing argon atmosphere (20ml/min) was used for purging the thermoanalytical furnaces during the evolved gas analysis measurements.

The TG-EGA-MS-FTIR apparatus consists of a SETSYS Evolution 16/18 Thermogravimetric Analyzer (SETRAM Instrumentation Inc.), OmniStar (Pfeiffer) and a Tenso27 (Bruker) FTIR spectrophotometer equipped with a TGA/IR Accessory gas cell and an outer DTG detector. The furnace and the gas cell were coupled through a heated (T=280^{o}C) 0.8m stainless steel tube with the diameter of 3mm. The OPUSTM software accumulated 40 interferograms in every second, and they were transformed to one IR-spectrum (600-4000cm^{-1}). Temperature calibration was carried out using indium. Baseline curves were obtained under the same experimental conditions. The FTIR spectrometer obtains spectra every 7s to quantitatively determine the evolution rate and composition of several compounds. Species identification and analysis are discussed in details below. The components of released gaseous mixtures were monitored and identified on the basis of their FTIR and MS reference gas spectrum available on NIST mass spectrometry library and EPA.

A mass range between *m/z*=1-100 was monitored in multiple ion detection mode (MID) with a measuring time of 0.5s/channel.

Results and discussion

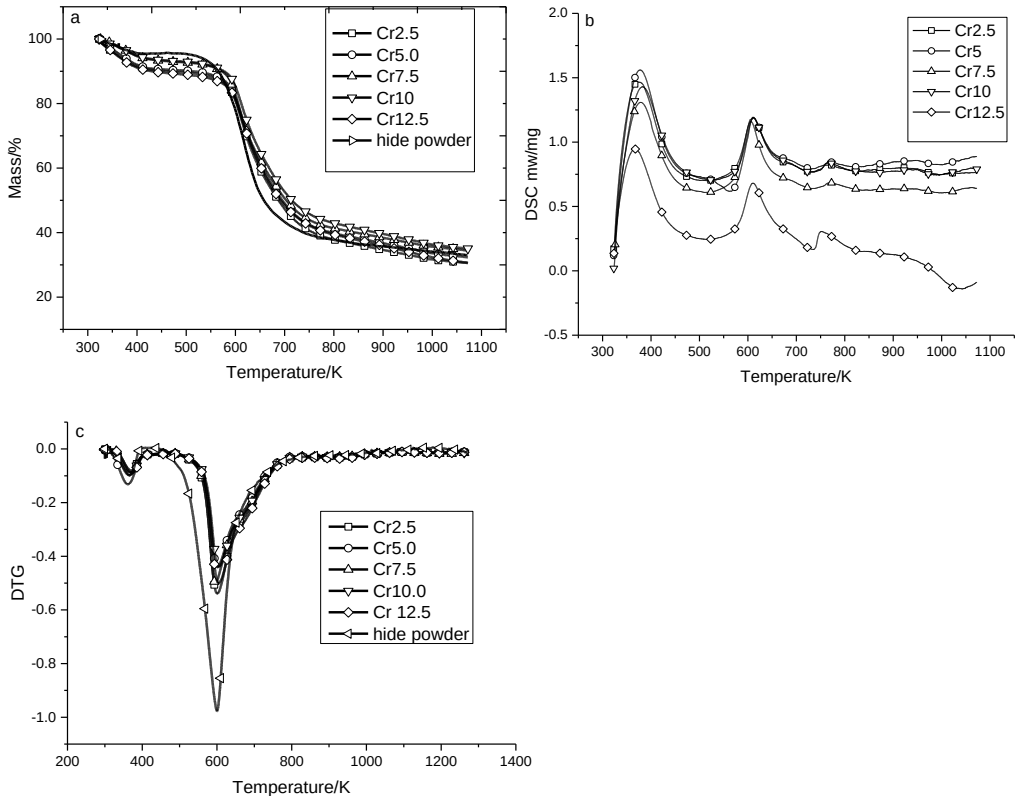

Fig 1a TG curves of leather tanned by different concentrations of tanning solutions, b DSC curves of leather tanned by different concentrations of tanning solutions, c DTG curves of leather tanned by different concentration chrome tanning solutions.

Fig 1 showed the TG/DTG and DSC curves of leather tanned by different concentration tanning solutions. There are two stages in TG curves. Two main mass loss regions were detected in all samples. The first peak of DTG curve at about 373K, corresponding to dehydration of leather bound water. It is most likely that hide powder decomposed at lower temperature in second stage. Moreover, the decomposition rate of hide powder is higher than tanned leather. The hide powder was decomposed at about 450K, and max decomposition rate is at about 600K. When the temperature is above 850K, no obvious mass loss is observed in argon atmosphere. The largest DTG peak can be attributed to thermal decomposition of leather. This is main evolution temperature range of many decomposition products. The decomposition temperature of chrome tanned leather are the highest, which demonstrated that chrome tanned leather is more stable than untreated leather. In Fig.1c, the decomposition temperature of hide powder is lower than other samples, and decomposition rate is higher than other samples. It showed that chrome tanned leather has better thermal stability than untreated leather. The concentration of tanning solutions has little effect on thermal stability of leathers.

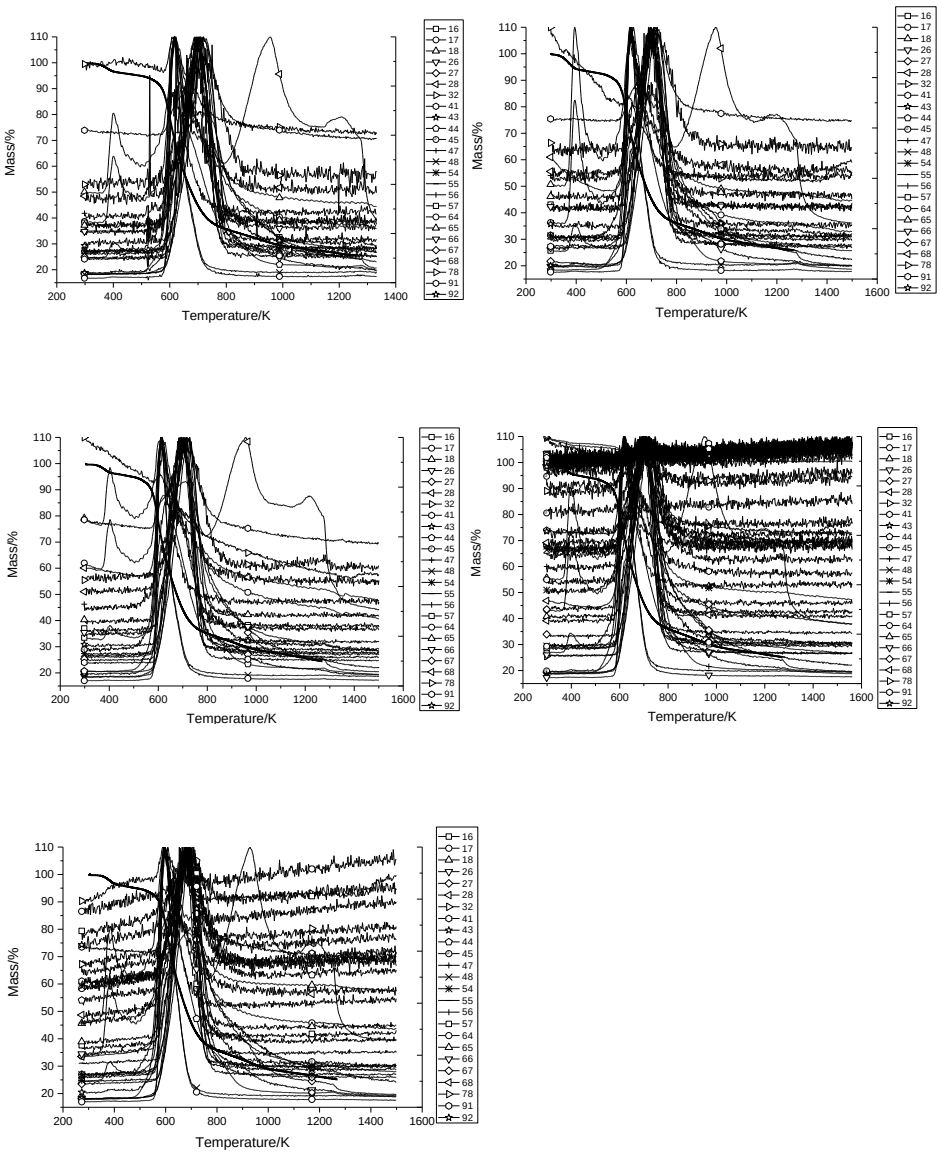

Fig.2 TG-curve and mass spectroscopy of chrome tanned leather with different tanning solution concentrations: a)2.5g/L b)5.0g/L c)7.5g/L d)10g/L e)12.5g/L

As a part of the EGA-MS studies on chrome tanned leather with different tanning solution concentrations, a comparative *in situ* evolved gas analysis was reported. Fig.2 shows TG-curve and mass spectroscopy of chrome tanned leather with different tanning solution concentrations. As reported in literature, the organic fraction occurring in leather measureable by TGA is composed mainly of collagen. It cannot be excluded the contribution of a minor fraction deriving from non-collagenous proteins. We found that species of evolved products decreases with the increase of tanning solution concentrations. No more differences among chrome tanned leather with different tanning solution concentration was found.

Table 1 evolved products analysis

Fragment mass/amu	Molecular formula	Possible molecule	Reference
16	CH_4	Methane, ammonia	(Lopez-Anton 2015)
18	H_2O	Water	(Lopez-Anton 2015)
28	N_2, CO	Nitrogen, carbon oxide	(Caballero 1998)
30	NO, CH_2O, C_2H_6	Nitrogen monoxide, Formaldehyde, Ethane	(Caballero 1998)
32	O_2	Oxygen	
44	CO_2	Carbon dioxide	
54	C_4H_6, HCCCHO C_3H_5N	Butadiene, Cyclobutene, Butyne Propynal, Propanenitrile Propane nitrile	(Sethuraman 2014)
64	SO_2	Sulphur dioxide	
67	C_6H_{10}	Crotonitrile, Pyrrole. allyl cyanide, methacrylonitrile, 2-Pyrimidinamine, toluene	
70	C_5H_{10}, C_4H_6O	Pentene, cyclopentane	
72	C_5H_{12}, C_3H_4O,	Pentane, acrylic acid	
78	C_6H_6	Benzene, 2,2'-Bifuran	
81	C_5H_7N, C_7H_{12}	Methyl pyrrole, methl cyclohexane, resorcinol, 1,2-Benzenediol	
91	$C_2H_5NO_3$, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, C_6H_5-C_2H_6	2-nitroethanol, ethyl nitrate Toluene 1,4-, 1,3- and 1,2-dimethyl benzene ehylbenzene	

In Fig.2, the evolved products in main decomposition stage evolved in different temperatures, which demonstrated that leather decomposed in a complex method. Some products evolved at about 600K, and some at 700K. So leather decomposed more than three stages when being heated. Compared to high concentration of tanning solution, leather tanned with 2.5g/L tanning solution were decomposed earlier than other samples. In Fig.2a, the second peak of carbon monoxide evolved earlier than other samples, probably because that lower concentration of tanning solution provides less crosslinking for leathers. In Fig.2d and Fig.2e, the species of evolved products are less than others, which might be because of the high saturation of protein with the metal in high concentration of tanning solutions. Chrome has also been shown to stabilize polypeptide chains in either random-coil or spiral conformation and to prevent thermal transition from one to another. This conclusion was based on the fact that chrome tanning caused an increase in *ΔH*, which was not found with any other tannage. The high yield of carbon dioxide and ammonia measured by TG/MS indicates that some amino acids probably lose

their amino, imino and carboxylic side groups during pyrolysis. Carbon dioxide and oxygen was evolved in argon atmosphere, because oxygen was deleted by carbon-monoxide or nitrogen monoxide.

Conclusion

Comparing the changes in the composition of the pyrolysis products of hide powder tanned by different concentrations of tanning solutions, it can be found that the chromium tanned hide powder are more stable than untreated hide powder. The enhanced water evolution between 473K and 523K originate from the free hydroxyl groups or structural water. The second peak of *m/z* 18 is lower, indicating the altered structure of the hydrogen-containing functional groups as a result of tanning. TG-MS is suitable to sensitively monitor the degradation of the polypeptide components in the hide powder samples. There are much ammonia and nitrogen yielded due to the rich content of glycine, proline, alanine and hydroxyproline. The existence of histidine, tyrosine and tryptophan results in some aroma compounds evolved during the late stage of decomposition.

Acknowledgment

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DIP P-07

REJUVENATION OF TRADITIONAL LEATHER CRAFTS WITH INNOVATIVE SURFACE DESIGN INTERVENTIONS - A CASE STUDY APPROACH

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Indian handicrafts have a deep dug history behind its existence of over 5000 years from now. The tradition of crafts in India has grown around religious values, needs of the common people and also the needs of ruling elites. In addition to these factors, growth of foreign and domestic trade has also played an important role in the evolution of crafts in India.

In this paper, the researchers explored on leather Batik craft which is the form of art and craft in which the technique of dye resisting is applied. The resistor used on leather is Babol Gum. In this process babol gum is applied on leather where ever one want to maintain the surface hue and the rest of the surface is dyed with a dye of a particular colour which results into an aesthetically appealing surface which can be used to create various artefacts.

Thus the objective this research work is to give create new designs on the leather, to hide various defects on leather using innovative batik technique, to increase the market value of leather by promoting batik leather products. Major intervention is done in textures and motifs. As crack effects remain the signature texture for the background so few new textures are developed using leaves, petals, stems and other natural products which can be easily found everywhere. Few new motifs are also being developed taking various animals silhouettes like snake, butterfly, and frog as inspiration for creating interesting designs.

Batik can turn out to be a very useful technique for industries as it doesn't require any special machinery for carrying out the process it requires primitive tools like bowl, brush, pencil etc to create wonders on the surface. Secondly it can be a very useful technique for hiding various defects on leather as this process can increase its market value. This technique and process can end up with innovative products ensuring eco friendliness and cost effectiveness for leather fashion industry leading to more profits and better scope for creating new products.

Keywords: Batik, leather craft, surface design, innovative techniques, fashion inductry

Introduction

‘When the real history of India will be unearthed, it will be proved that, as in matters of religion, so in art and craft, India is the primal Guru of the whole world.”

The above quote is by the famous Indian saint Swami Vivekananda who wanted to describe Indian historical depth and implies on the fact that India is a solitary country which is known for its rich cultural heritage and religions.

India being the paradigm of unity in diversity because of it diverse culture and tradition which constitutes of festival, cuisine and handicrafts. Amongst all, Indian handicrafts have a deep dug history behind its existence of over 5000 years from now. The tradition of crafts in India has grown around religious values, needs of the common people and also the needs of ruling elites. In addition to these factors growth of foreign and domestic trade have also played an important role in the evolution of crafts in India.

Traces of crafts found in Indus valley civilization had high degree of technical excellence in the field of pottery, sculpture, jewellery and weaving. In the Vedas there are numerous references of artisans involved in pottery, weaving, woodcraft etc. rig veda refers to the variety of pottery made from clay, wood and metal. In the mauryan age there was great development in the field of sculptures and in this period more than 84000 stupas are said to be built in India including the famous sachi stupa. Moving from the historical past to modern India the country is fortunate enough to have skilled artisans who are carrying forward the legacy of their forefathers.

“Handicrafts” commonly refer to handmade crafts or artisanry are practiced in all Indian states. Amongst them west Bengal situated on the eastern bottle neck of Indian peninsula known for its sanctity of hoogly, the beauty of eastern Himalayas , diversity of sundarbans, freshness of tea gardens, serenity of its culture, its luscious cuisine and magnificent art and craft of the state. The unique rustic and mystic charm of Bengal crafts is admired by the art lovers all over the world. From embroidery to sculpture and sketching to metal craft, the state has unique specialization in numerous forms of craft. The age old traditional crafts of Bengal have been so well mouldedaccording to the present day demands that seem that these artisans, apart from their traditional skills, have an expertise in the art of survival as well. Amongst all the craft practiced in the state, craft of batik on leather practiced in the district of Bolpur at the famous college of art and craft, Sriniketan.

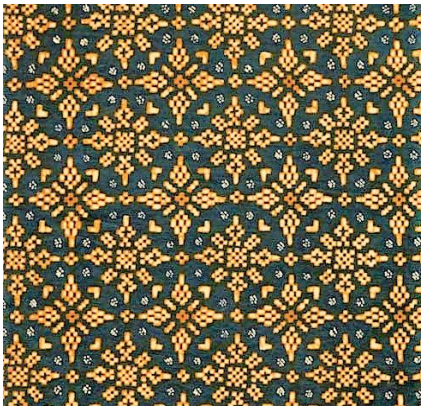
Batik

The word batik originates from Javanese “tik” which means to dot. Thereby, to define the word batik we can refer it to be a form of art and craft. This is basically a form of decorating a cloth or a leather piece in a way, using wax for fabric and babul gum for leather to block the area of the surface where we want to retain a original hue and dry the rest. And this process results into aesthetically designed surface which can be used for production of various artefacts.

Types Of Batik Design

Nitik patterns :-

Nitik patterns can be recognised by the rows of dots and short stripes that run parallel and at right angles in a pattern that intimates woven decoration. This style probably derives from the early rudimentary batik technique of dripping wax on cotton, which creates a pattern of small dots.

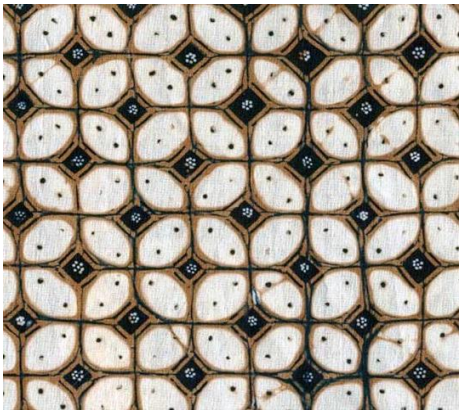


Banji :-

Banji is the oldest type of ornamental motif used in batik. Its basis is swastika a simple cross with arms of equal length each arm bent at right angles pointing in the same direction. The use of banji is the ornamental art of south Asia certainly dates back to the hindu-buddist period. The word “swastika” is a word coming from Sanskrit, meaning “well being” but the word “banji” is of Chinese origin. The chinese symbolic meaning of the ornament is similar to the Sanskrit version : happiness, longevity and wealth.

Kawung

Kawung is very old design consisting of intersecting circles, known in Java since at least the thirteenth century. This design has appeared carved into the walls of many temples throughout Java such as Prambanan near Jogjakarta and Kediri in East Java. For many years, this pattern was reserved for the royal court of the Sultan of Jogjakarta. The circles are sometimes embellished inside with two or more small crosses or other ornaments such as intersecting lines or dots. It has been suggested that the ovals might represent flora such as the fruit of the kapok (silk cotton) tree or the Aren (sugar palm).



Ceplok

Ceplok is a general name for a whole series of geometric designs based on squares, rhombus, circles, stars, etc. Although fundamentally geometric, ceplok can also represent abstractions and stylization of flowers, buds, seeds and even animals. Variations in colour intensity can create illusions of depth. The Indonesian population is largely Muslim, a religion that forbids the portrayal of animal and human forms in a realistic manner. To get around this prohibition, the batik worker does not attempt to express this matter in a realistic form. A single element of the form is chosen and then that element is repeated again and again in the pattern.

Parang

Parang was once used exclusively by the royal courts of Central Java. It has several suggested meanings such as 'rugged rock', 'knife pattern' or 'broken blade'. The Parang design consists of slanting rows of thick knife-like segments running in parallel diagonal bands. Parang usually alternated with narrower bands in a darker contrasting colour. These darker bands contain another design element, a line of lozenge-shaped motifs called “Mlinjon”. There are many variations of this basic striped pattern with its elegant sweeping lines, with over forty parang designs recorded. The most famous is the 'Parang Rusak' which in its most classical form consisting of rows of softly folded parang. This motif also appears in media other than batik, including woodcarving and as ornamentation on gamelan musical instruments.

History Of Batik Around The World

Evidences of early batik have been found in far east, middle east, central Asia and India over 2,000 years ago. The craft spread from Asia to the Islands of Malay and West to the Middle East through the Caravan route. Batik was practised in China as early as Sui Dynasty (AD 581-618). These works silk batiks and the similar were also discovered in Nara, Japan (AD 710-74) in the form of screens. These batiks consisted of decorative trees, animals, flute player, haunting scenes and stylised mountains.

No evidences of very old cotton batik have been found in India but frescoes in the Ajanta and Ellora caves depict head wraps and garments which endow the feeling of batik. In Java and Bali Temples ruins contain figure whose attires are patterned in a manner suggestive of batik by 1677, there is evidence considerable export trade, mostly on silk from China to Java (Indonesia), Sumatra, Presia and Hindustan.

Indonesia most particularly the Island of Java, is the area where batik has reached as the greatest peak of accomplishment. The Dutch brought Indonesian craftmans to nurture the plant of craftsmanship in them in 1835. So, the batik became an vital part of Javanese cultural life. Batik was originally reserved as an art form for Javanese royalty as splendid nature of the kingdom was clear as the certain patterns were reserved to be worn by the princely people.

The birth of leather batik was on Indonesian land as Javanese dalang (puppeteer) who was not only responsible for wayang puppets but also an important source of batik. The wayang puppets were usually made out of goat skin which was perforated and dyed to create the batik patterns on them, so as to give a illusion of cloths on the puppets.

History of Batik In India

The history of Indian batik can be traced as far back as 2000 years in 1st century AD. Indians knew resist method of printing designs on cotton fabrics long before any other country had even tried it. Indian cotton and dyes were very popular. The indigo blue was one of the earliest dyes to be used. The religious tapestries of ancient India hold the proof of batik printing. The elaborate process of dyeing and waxing was one of the hitches that caused the art to decline. The Khatri community of Gujarat were the only set of artisans for this art.

But in 20th century batik art received an impetus when it was introduced as a subject at the famous university of Sriniketan in Calcutta. Chola Mandal in Madras is also popular for its Batik product.

Modern batik

The horizon of batik is continuing to widen. While the design process has remained basically the same over the last century, the process shows great progress in recent decades.. Now, not only is batik used as a material to clothe the human body, its uses also includes furnishing fabrics, heavy canvas wall hangings, tablecloths and household accessories. Batik techniques are used by famous artists to create batik paintings which grace many homes and offices.

Fine quality handmade batik is very expensive and the production of such works is very limited. However, in a world that is dominated by machines there is an increasing interest in materials that have been handmade. Batik is one of these materials.

Modern batik, although having strong ties to traditional batik, utilizes linear treatment of leaves, flowers and birds. These batiks tend to be more dependent on the dictates of the designer rather than the stiff guidelines that have guided traditional craftsmen. This is also apparent in the use of color that modern designers use. Artisans are no longer dependent on traditional (natural) dyes, as chemical dyes can produce any color that they wish to achieve. Modern batik still utilizes canting and cap to create intricate designs.

Fashion designers such as Iwan Tirta have aggressively introduced batik into the world fashion scene. They have done much to promote the Indonesian art of batik dress, in its traditional and modern forms.

Tjanting work is time consuming when compared with that of tjap. It might take months, week, days to complete the richly patterned batik whereas the same intricate patterns can be executed in half the time with the help of “Tjap”. But the tjap is also replaced by the modern machinery.

Dyes have been affected by the progress; aniline and other commercial dyes are taking over the vegetable dyes. These newly invented dyes are posses more colour fastness and impart better wear and tear strength to the surface. So it has become very difficult to mark the difference between the hand made batik and machine made batik only experts in the field can know the difference.

Advantages Of Traditional Batik

Batik permits an enormous amount of spontaneity and freedom of expression. Startlingly beautiful colour combination may suddenly appear when one colour is dyed over another. The dyeing may produce two or more colours depending upon the colour of the fabric and the colour of dyes.

Aside from being a versatile medium, batik promises that each effort will have a hand crafted personal look as no two people apply wax in precisely the same way, nor do they handle colour with the same intensity or create line with same movement. Even if we want to duplicate the hand made batik it won't be possible

Limitation Of Traditional Batik

When We Are Working With The Wax We Cant Correct Our Mistakes And The Traditional Also Takes Time As The Time Needed To Dry After The Dye Bath Is The Greatest Consideration.

Batik Cluster At Amar Kutir Society Of Rural Development, Bolpur,West Bengal

History

Batik has a very deep rooted history in India but the craft never got acclaimed so during 1920s Rabindranath Tagore went on a tour to Indonesia and he saw the batik craft being the very important part of the a Java life. The intricacy, vibrancy and beauty of batik left a mark on the minds of Mr. Tagore so on returning back to India he planned to send his son Rathindranath Tagore and Pratima Devi, his daughter in law to learn the craft. And after returning from Indonesia Pratima Devi started teaching the craft to the near by village people of Bengal so that they can earn their livelihood. She even opened the night school for the people who wanted to learn the craft.

The son of Mr. Tagore started experimenting this craft on leather and he succeeded in this craft by using gum as the dye resistor instead of wax. Later on in 1926 he made the first copper stamp which could cast impression on the leather and the work was reduced to quite an extent as the stamped leather can be used for batik instead opf drawing the motif one by one. Soon the craft got acclaimed and was practiced by the people of the nearby villages. Soon it became the major source of earning for the people.

The Raw Materials

The basic raw materials used for carrying out the process of batik:-

Babul gum:- The babul tree is a close relative of kikar(Acacia nilotica subspecies indica) and quite prolific in the Punjab region of Pakistan. It is a native of the Indian subcontinent and Egypt going through the African continent to South Africa where it is called lekkerruikpeul or the scented thorn, into the Arabian Peninsula through to Myanmar. It has a fairly slender trunk about 20 – 30 centimetres in diameter and is a slow-growing but reasonable long-lived tree. It is a pioneer species which can regenerate waste land as the seeds with their hard outer husks can germinate within two weeks.

It is a source of gum, used as an emulsifier and in the cloth manufacturing industry and in the manufacturing of paper. It is also used in the production of matches, ink and candles. The red gum from the babul is of good quality. The gum will exude spontaneously from the trunk for about five weeks, but the process of harvesting it is helped by making incisions into it. The gum hardens into 'tears' the size of a pigeon's egg.

The babul gum is in form of solids balls so to convert it in the thick solution, the gum is soaked over night in water. The water is added just half the quantity of babul gum and the next day morning the water has penetrated the solids gum to form the thick solution. But to remove the dirt, few solids particles and excess water from the solution, the thick mixture is passed through a cotton fabric piece and the solution to apply for batik is ready. For the crack effect on leather same thick paste can be used but for the making the motifs small amount of water is added to make it thinner.

Leather:- Vegetable tanned goat crust leather is the leather used for batik by the artisans in the cluster. Vegetable-tanned leather is tanned using tannins and other ingredients found in different vegetable matter, such as tree bark prepared in bark mills, wood, leaves, fruits, and roots. It is supple and brown in colour, with the exact shade depending on the mix of chemicals and the colour of the skin.

Leather which has been tanned but not yet underwent the finishing process. Such leathers referred to as being "in the crust leather. Leather from which the grain has been removed after tanning, by splitting, abrading or other process the key features of crust leather.

Vegetable tanned leather is used because the base colour is very light as compared to chrome tanned leather and vegetable tanned leather posses a good stiffness which is required for making bags and clutches. Goat leather is preferred by the cluster as these people manufacture bags so goat skins have enough surface area and correct thickness which is required for the bags. Crust leather is taken for the processing because the crust is the just one stage before dying so thereby the surface of crust is ready to be dyed and batik is all about dying the leather. The leather for the batik is imported from Kolkata tanneries.

Dyes:- The synthetic dyes are used in the process for dying the crust leather. Since the dyes are supplied from Bolpur so they don't have any information regarding their chemical combination. The dyes they get in 100 grams or 250 grams packs in powdered form. To prepare the dyes for applying on the leather, the equal amount of spirit is added and it's liquefied. The basic colours of dyes used in the cluster are red, yellow, green, blue, brown and black.

Jute:- The jute is used to scrape the gum from the batik surface of leather when the batik is completely done. The leather with batik on it is kept under the running water the jute is used to scrape the gun on the leather which was applied as the dye resistant on the surface.

Cotton Fabric:- Cotton small pieces of fabric are used for applying dyes on the leather. The left over pieces of fabric are folded in such a manner that they form a pointed edge at one end through which you can apply colour very easily.

The Tools

Brush:-The brush is tool used for applying the gum on the motifs drawn on leather.

Small bowl:- A small bowl is required to keep the gum to be applied as a dye resistor on the leather and bowls are also required for keeping dyes which are to be applied on leather.

Container:- A container quite big in size is required to keep the babul gum for soaking the babul gum solid balls to form the liquid solution in an over night process.

Pencil:- Pencil are used for drawing or tracing the motifs on leather for further process.

Modular:- This is used by the expert artisans to directly draw motifs on the surface of leather.

The Process

Step-I

The babul gum are in form of solid balls which needs to be converted into the thick paste by soaking them in the water and keeping it for overnight in a big container covered with the plate to avoid the loss

of moisture from the content. Then the next morning the solution is filtered using the cotton fabric to remove the dirt and excess water to form the thick paste which can be used for making textures but a small amount of water is added to the solution for drawing the motifs on leather

Step-II

The babul gum paste is transferred into small bowls and bigger container with the paste is kept air tight to avoid drying of solution.

Step-III

The leather on which batilk has to done is taken and the desired motifs are transferred on it using pencil or tracing paper or modular.

Step-IV

Then the babul gum is applied on the area where the surface colour is supposed to be maintained as babul gum act as a dye resistor.

Step-V

Then the leather is kept under the sun to dry in sunlight. Sun is must for batik because babul gum looses it full moisture content under the sun not even over night drying can get the batik results as if the babul gum is not dried properly the dyes will penetrate inside and batik process will not properly take place. So dry the leather with babul gum in the sun until the babul gum starts getting cracks on it. There is no fixed time limit to be kept in the sun light it depends on the drying of leather.

Step- VI

Meanwhile the leather is drying take the dye powder of dye and add the similar amount of spirit as the measure of dye powder to from the solution to be applied on leather drying in sun. We can make the tint and tones of same colour by changing the measure of dye powder and spirit in the solution as if we add more spirit then we will get lighter shades and more dye powder darker tones. The bowl containing the colour should be covered with a plate so the spirit content is not lost from the dye solution.

Step-VII

After the leather is dried then the first coat is applied on the leather using a cotton cloth bud. As many coats of colours we will apply to the leather darker tones will be darker on leather.

Step-VIII

Since these synthetic dyes dry out very soon with in 2 to 3 mins so we can apply the coat of gum where we want to retain the dye colour we applied right now and let it again dry in the sun.

Step-IX

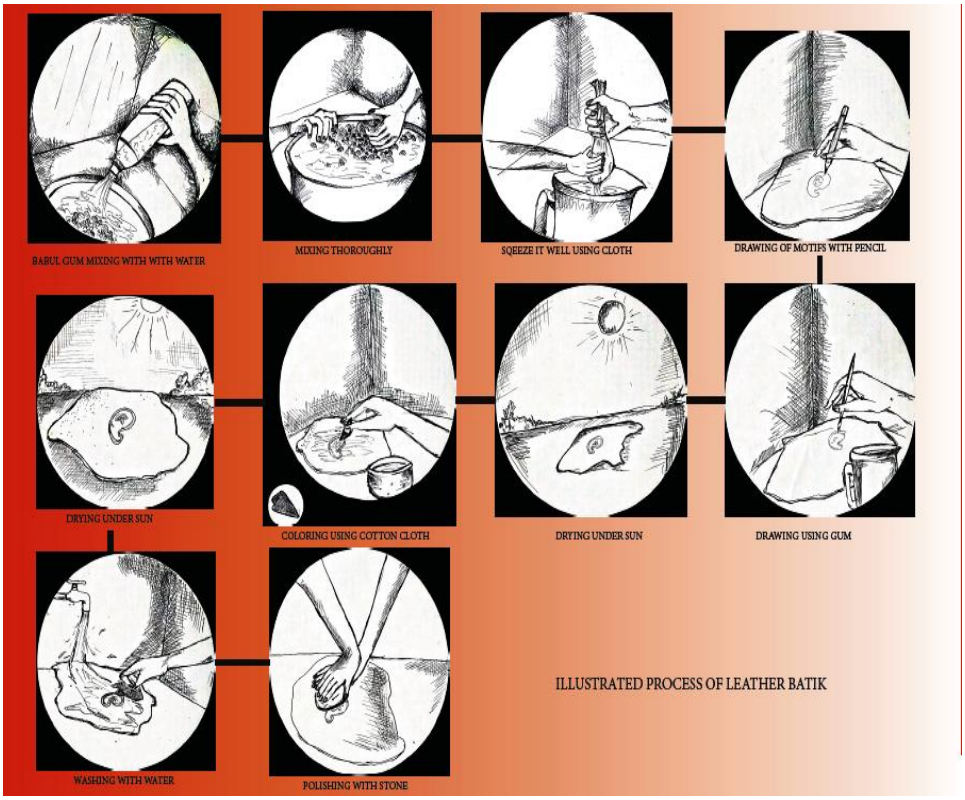
The process of gaining dye with the darker tone is repeated and the process of applying the dye and gum continues according to the number of colours we want on our leather batik. But it is basically preferred to have maximum two to three colours on single batik.

Step-X

When the batik is completely done then the leather is washed under the running water with jute for scraping the gum out of the surface.

Step-XI

The washed batik is kept in sun for drying and then the dried batik is polished with stone and coconut oil to give shine and enhancement to the surface



For Textures

Step-I and II remain the same but in step-III the desired material for making the texture is dipped in the gum and the impression is taken on leather and other similar process line is followed. But for the crack effect on batik the thick paste of gum is applied and dried it sun and crushed to get cracks on the surface and then dyed and polished similarly.

Conclusion

Batik can turn out to be a very useful technique for industries as it doesn't require any special machinery for carrying out the process it requires primitive tools like bowl, brush, pencil etc to create wonders on the surface. Secondly, it can be a very useful technique for hiding various defects on leather as this process can increase its market value. Since this technique is carried out in the crust stage of leather so there is no need to spend a lot on hiding the defects by applying expensive finishes. It can even serve as a trend to the fashion world as alike garments now customised leather products can be developed according to consumers need.

Since batik is simple process which doesn't require any sort of huge machines or technical advancements. There is no need of very skilled labour force for carrying the process as this technique can be learned in few days so thereby this process will serve as a priceless advancement for leather fashion industry which can be used to earn a lot of profit and create new products.

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TREAMENT OF CETP WARANGAL TANNERY WASTEWATER

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In Warangal the common Effluent Treatment plant (CETP) has a tannery cluster of 10 tanneries. The tanneries are engaged in Raw to finish operations with production capacity of 750 skins/day and wastewater discharge of 20 m^3/day. The tannery cluster is equipped with Common Effluent Treatment Plant consisting of Primary Chemical treatment, Secondary biological treatment and tertiary treatment. The CETP faces issues such as huge sludge generation and difficult to meet the discharging standard. The main cause for the above two issues may be due to recalcitrance of the organic compounds. The recalcitrance of the organic compounds can be eliminated by fragmenting the organic compounds. The fragmentation of organic compounds can be derived by incorporating advanced oxidation process using hydroxyl radicals. The hydroxyl radicals are generated from Nano Porous Activated Carbon and molecular oxygen from air at ambient conditions. The fragmented organic compounds in wastewater can be mineralised in Fluidised Immobilised Cell Carbon Oxidation reactor (FICCO). The FICCO system incorporates both biological and catalytic oxidation processes i.e. biological oxidation is facilitated by immobilized bacteria in nano porous activated carbon and the biologically fermented organics are subjected to catalytic oxidation The nano porous activated carbon (NPAC) serves for two purposes, one is to act as a carrier matrix for the immobilisation of bacteria and the second one is to generate hydroxyl radicals using the free electrons of the activated carbon matrix. The scheme of treatment of tannery wastewater consists of Fenton oxidation of acidic post tanning wastewater and is neutralised with alkaline beam house wastewater. The neutralised wastewater is further treated in FICCO reactor to meet the discharging standard. The refractory organics [wetting agents] in treated wastewater was further treated in enzyme immobilized reactor.

Key words: FICCO, FAACO, HFO, NPAC, Post tanning and Beam house.

Introduction:

Conversion of raw skins and hides into useful leather products were involved through many tanneries by process it discharges highly polluted water which affect the environment in many ways (Rathinam Aravindhan et al.,2004). An industrial district in Telangana has a cluster of tanneries, most tanneries resource the raw materials from their native state and some are drawing from the neighboring states. The common Effluent Treatment plant (CETP) should meet the discharging standards prescribed by local pollution control regulatory agencies. The CETP was functioning to the expected results for some time and thereafter it was not properly utilized. Only very few industries those have individual Effluent Treatment Plants are actively involved in production of leather. The focal theme of the treatment option is to reduce sludge production without addition of

coagulants and substantial reduction in reject stream (http://www.wefnet.org, http://www.patoczka.net). Elimination of coagulants such as lime and alum will reduce silt index, one of the important parameters which affect the membrane separation process (Jun Wanga 2008). The proposed scheme for the treatment of CETP wastewaters are immobilized Cell Reactor systems as post treatment to biological treated wastewater. The immobilized wastewater systems consist of Fluidized Immobilized Cell Carbon Oxidation system (FICCO) and Fenton Activated Carbon Catalytic Oxidation system (FACCO) (John Kennedy.L 2004,Parken GE 1983.). The wastewater will be pretreated with substantial reduction in COD without generation of sludge and discharged into existing biological treatment unit.

Materials and methods:

FACCO system consists of Nano porous activated carbon, having pore size in the range 35-39 nm (Karthikeyan.S et al 2013), is packed in a cylindrical reactor containing multi grade strainers of height 0.7m to support carbon matrix and to allow permeation of water to collection unit provided at the bottom of the reactor. The water collection unit consists of header and laterals are provided with perforations. The header pipe is connected to an outlet pipe which is elevated at a height of 0.4m from the bottom level of the reactor. The oxygen required for the oxidation of organics in wastewater is supplied in the form of air through an air blower. The pressurized air is distributed across the NPAC bed through air distributor. The water to be treated is distributed across the cross sectional area of the reactor. The water level in the reactor is maintained at constant level above the NPAC bed using automatic flow controller. The top portion of FACCO reactor may be closed, with a provision to vent out the unused air and gaseous end products discharged during FACCO reaction (Ramani.K et al**)**. FICCO system consists of immobilization of bacteria in nano porous activated carbon and oxidation of organics in biological treated wastewater is facilitated by the immobilized organisms. The nano porous activated carbon (NPAC) serves two purposes, one is to act as a carrier matrix for the immobilised organisms and the second one is to generate hydroxyl radicals using the free electrons of the activated carbon matrix (Karthikeyan.S, 2014., Murugandham,2004., Sun J.H,2007., Zhang.H2006.). The objective of supplied air is to fluidize the NPAC and to generate hydroxyl radicals for the oxidation of organic compounds from wastewater (Raphael Altai Bach, 2011.,zeolites, 2008.,Karthikeyan, 2011).The FICCO reactor can oxidize the labile organic s and complicated or refractory organics can be oxidized in FACCO reactor.

The post tanning stream (Re-tanning, Acid wash and Dye&Fatting) will be treated separated through Heterogeneous Fenton Reaction [HFO]. After mixing of the post tanning wastewater (Mixture I) its pH was dropped to pH 3.5 by adding 1.58ml/L of 6N Sulphuric because at this point only the fenton reaction favors for the oxidation of organic molecules present in the wastewater. Then it was heterogeneously oxidized in fluidized bed reactor for 12h then the water was carried to Fenton Activated carbon catalytic Oxidation [FACCO]. After this stage wastewater will be neutralized with beam house wastewater. The remaining beam house wastewater will be neutralized with sulphuric acid. When pH goes beyond the neutral it was adjusted to neutral using sulphuric acid likewise it consumes 16.5ml/L of then it is carried to microbial oxidation of FICCO process for 12 h The neutralized wastewater streams are mixed together to get a homogeneous composition. The composite wastewater will be treated in Fluidised immobilised carbon catalytic oxidation [FICCO] reactor to eliminate dissolved organics. The FICCO

treated wastewater will be treated further in conventional biological treatment unit. The refractory organics [wetting agents] in treated wastewater will be further treated in enzyme immobilized reactor.

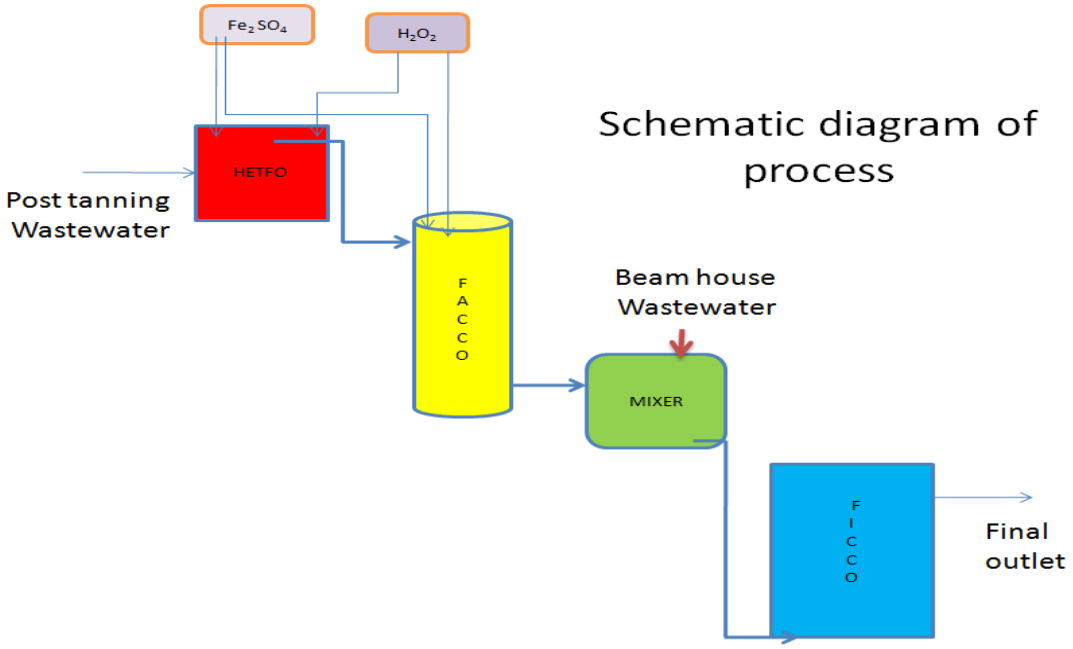

Fig.: 1 Schematic diagram of treatment process

Results and Discussion

Initial parameters

	ACID WASH		DYE&FATTING		LIMING		DELIMING		RETANNING	
	Average	Deviation	Average	Deviation	Average	Deviation	Average	Deviation	Average	Deviation
pH	1.64	±0.21	4.065	±1.415	12.755	±0.045	8.325	±0.755	6.01	±0.268701
ORP	-226.2	±135.9	-244.05	±147.25	-590.2	±19.9	-313.15	±132.55	-183.4	±8.768124
COD ,mg/L	3680	±280	4720	±2040	10520	±7800	1700	±140	5100	±311.127
BOD ,mg/L	1131	±44	607.5	±367.5	577.5	±202.5	256.25	±143.75	1188.575	±108.0813
BOD:COD	0.30825	±0.0115	0.11685	±0.0273	0.153555	±0.133315	0.15875	±0.09765	0.232841	±0.006988
COD:TOC	6.700	±1.5818	5.008	±0.9473	11.71676	±4.517181	5.154681	±0.195113	2.719355	±0.063137
NH_3 mg/L,	214.2	±21	201.6	±84	92.4	±75.6	562.15	±74.95	302.8	±24.32447
TN ,mg/L	387.35	±26.15	440.5	±104.5	1415.4	±1188.6	857.15	±294.35	555.2	±60.52834
TOC ,mg/L	592.05	±181.55	897.45	±237.55	753.15	±375.35	331.3	±39.7	1877	±158.3919
TS ,mg/L	52315	±1735	14002.5	±1517.5	36435	±15730	11195	±965	17557	±702.8641
TDS ,mg/L	49095	±15	12480	±1070	29966.5	±16746.5	9507.5	±467.5	16669.5	±444.7702
TSS ,mg/L	3220	±1720	1022.5	±52.5	6468.5	±1016.5	1687.5	±497.5	887.5	±258.094

Table: 1 Average Initial parameters of Acid was, Dye&fatting, Liming and Retanning waste water with standard deviation.

Optimization:

Optimization of factors such as pH, Time, Dosage of peroxide, ferrous sulphate and HRT was taken from related work which was done by the same author for tannery wastewater treatment process. Based on optimization the HRT for Hetero fenton is 12h, FACCO 1h and FICCO 24h. The dosage of peroxide and ferrous sulphate is 0.4ml/L of 30% w/v peroxide and 0.1g/L of ferrous sulphate was taken for the oxidation process. (Karthikeyan.S et al.,2013,**Ramani .K et al., Prabhakaran.N et al.,)**

Overall process:

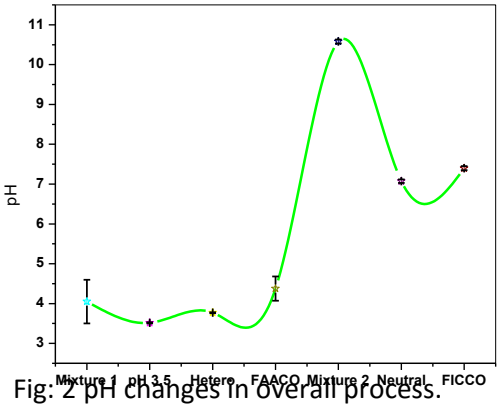

Fig: 2 pH changes in overall process.

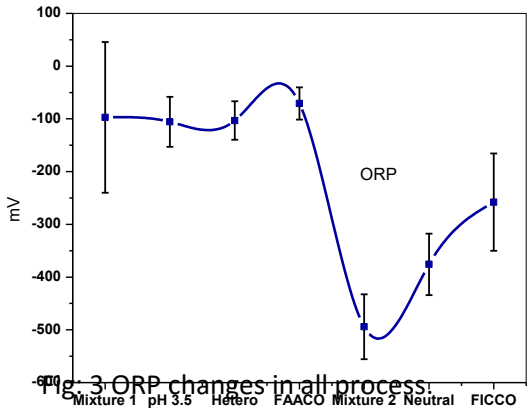

Fig: 3 ORP changes in all process.

In fig: 2 the pH of mixture of post tanning wastewater (mixture I) is acidic so it reduces the high addition of acid to adjust pH 3.5 the pH varies upto FACCO from 3.5-4.65 for neutralization when we mix with beam house wastewater in certain ratio it pH is raised to 10.5 then it was neutralized with acid then carried to FICCO. In Fig.3 shows the changes in oxidation and reduction potential the mixture I is -100 when oxidation takes place to moves towards positive side, addition of mixture II increases the presence of reduced species it also oxidized to further in neutralization and FICCO process.

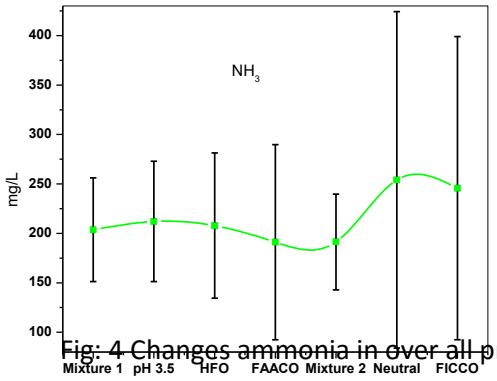

Fig: 4 Changes ammonia in over all process.

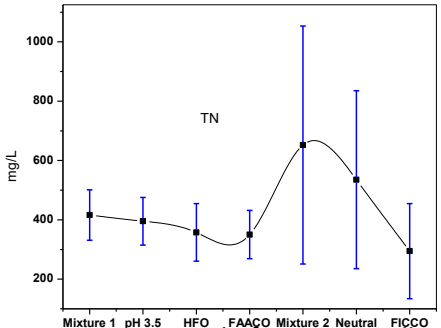

Fig:5 Removal of TN in overall process

Fig.4 Shows formation of free ammonia in treatment processes because of cleavage of protein molecules present in the wastewater this shows changes occur in macro molecules on other words in Fig

5 shows decreases in total nitrogen in all process this may be due to conversion of nitrogen dioxide it may be escaped to the atmosphere . The reduction in TN observed in all treatment process.

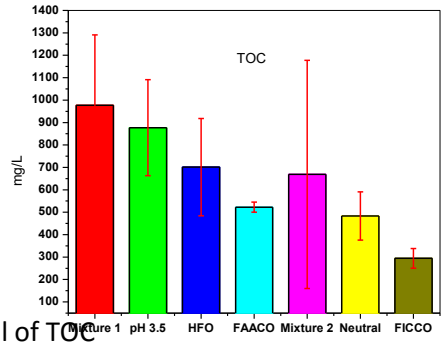

Fig:6 Removal of TOC

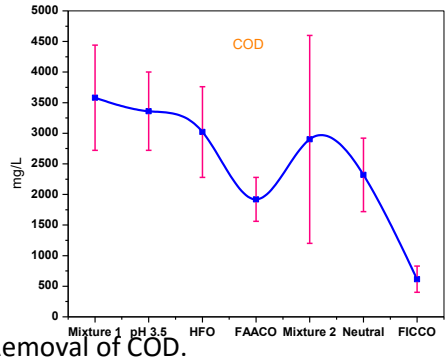

Fig:7 Removal of COD.

The reduction in Total organic carbon(Fig:6) from mixture I to FICCO process observed in all process except mixture II because there only we adding the beam house wastewater it is the source of increase in total organic carbon. The reduction in COD was observed in all stages of the treatment process. The initial COD was 3580mg/L after FACCO 46.36% of COD was removed when we mix with mixture II it raised to 2900 mg/L after FICCO 78.79% of COD was reduced (Fig:7).

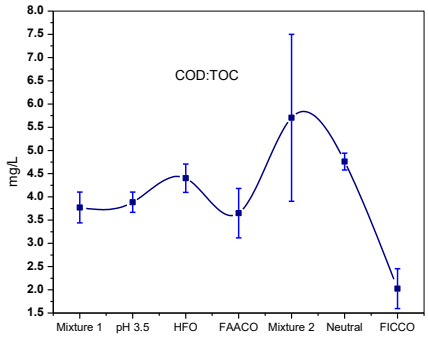

Fig: 8 Changes in ratio of COD: TOC.

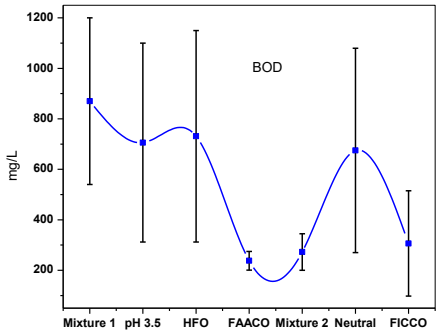

Fig: 9 Removal of BOD.

The COD:TOC ratio(fig:8) shows changes in ratio it confirms the degradation of macro molecule takes place because of this changes takes place in treatment process. Fig; 9 The BOD of the wastewater was reduced in all process well reduction in BOD was observed in FICCO process.

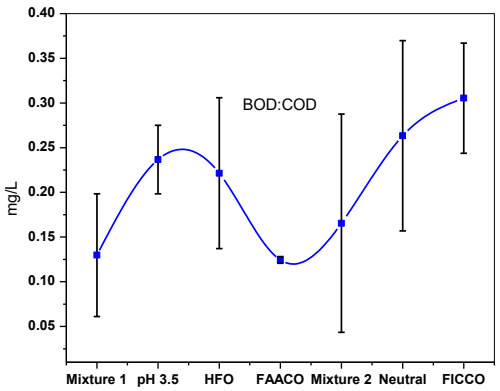

Fig: 10 changes in BOD: COD.

The mixture I BOD: COD shows in fig.10 very poor biodegradability of the wastewater on chemical treatment well increase in the biodegradability observed because of this only FICCO technology placed at end of the process after increasing the biodegradability the efficiency of FICCO increases more.

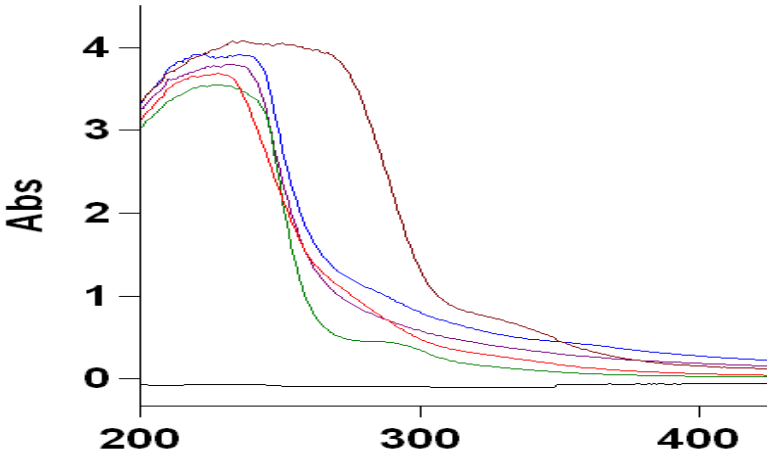

Fig.:11 UV/Visible spectroscopy images of treatment process.

The UV/Visible spectroscopy images of all treatment process shows decrease in intensity and hypso-chromic shift was observed this shows the removal of population in means of organic compounds in wastewater.

FT-IR spectroscopy study of treatment process:

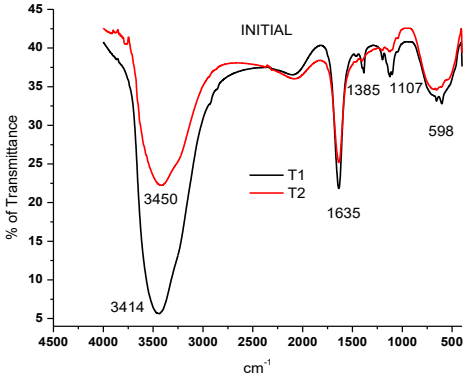

Fig:12 FT-IR Spectroscopy study of Mixture I of two tannery samples.

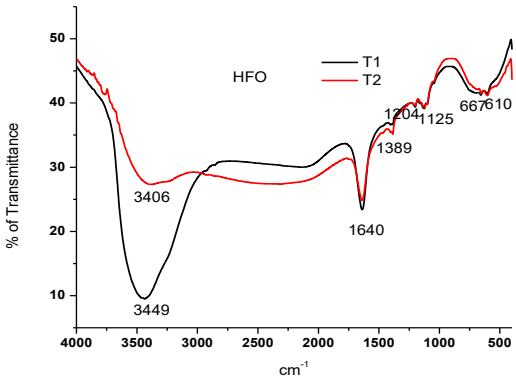

Fig:13 FT-IR Spectroscopy study of HFO of two tannery samples.

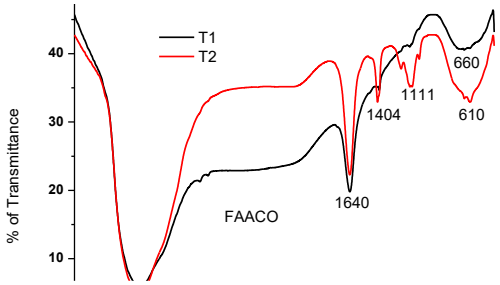

Fig:13 FT-IR Spectroscopy study of

Fig:14. FT-IR Spectroscopy study of FACCO of two tannery samples.Fig:

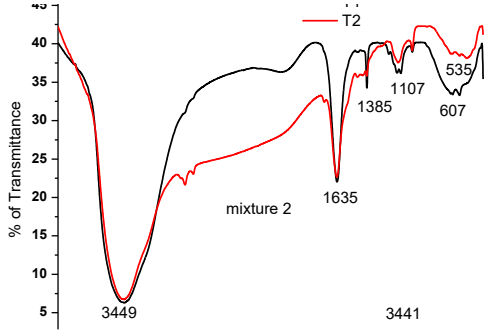

Fig:15. FT-IR Spectroscopy study of mixture of two tannery samples.Fig:

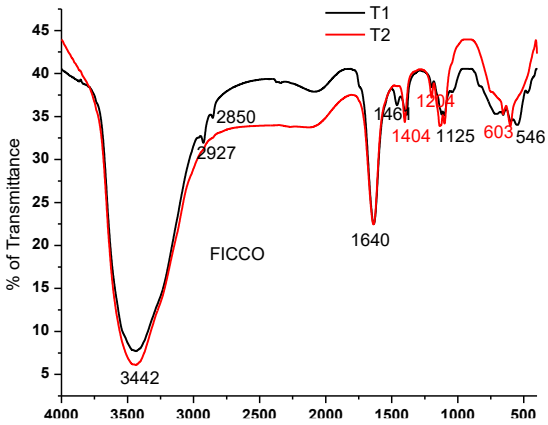

Fig: 16 FT-IR Spectroscopy study of FICCO of two tannery samples.

The FT-IR Spectroscopy studies of all treatment process shown in Fig.11-15. The Fig11 is initial sample of mixture I two set of sample were shown in single graph a broad band at 3414 cm^{-1}, 3450 cm^{-1} is due to the stretching frequency of –OH group in organic molecule. A peak at 1635cm^{-1} is due to the stretching frequency of C=O of amide group present in the protein molecule. A small sharp peak at 1385

cm^{-1} may be due to the C-N stretching of amines this confirms presence of macro protein molecule in wastewater. A moderate sharp peak at 1107 cm^{-1} C-O stretching of secondary or primary alcohol this is also supported with the –OH stretching frequency , during the entire treatment process changes in stretching frequency of –OH, C=O, C-O and C-N only observed. The wave numbers below 700 cm^{-1} region present may be due to the in plane, out plane pending and deformation of C-H groups present in chain of organic molecules. So by the treatment, because of change in structure of the compound only the changes in frequency of corresponding functional groups observed.

Fluorescence spectroscopy:

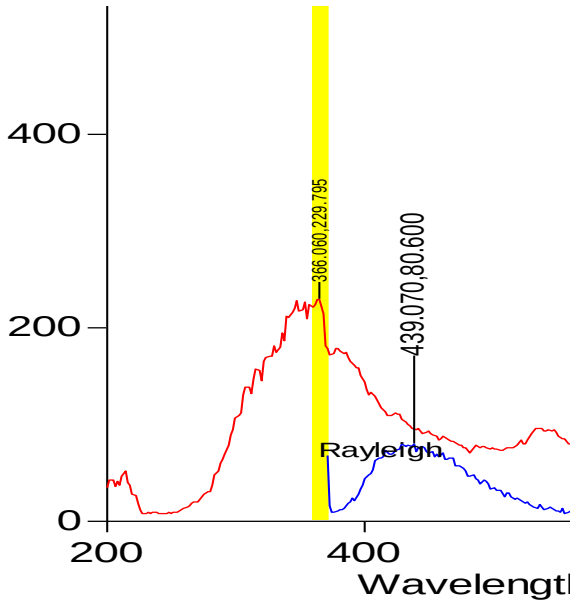

Fig: 17 Fluorescence Spectroscopy images of FACCO

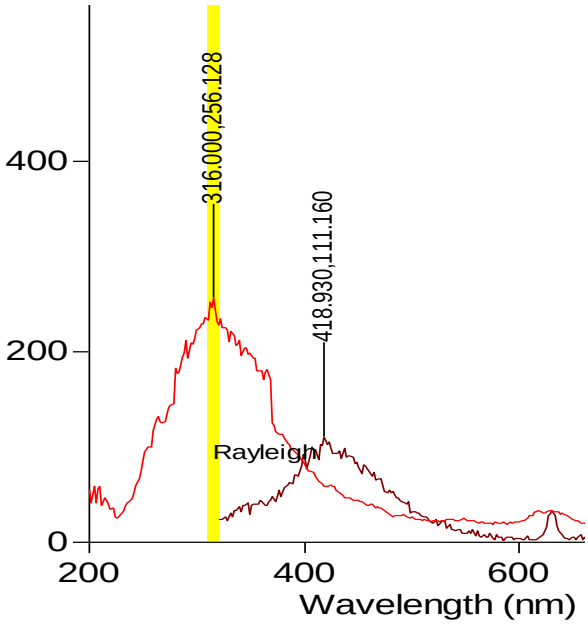

Fig: 18 Fluorescence Spectroscopy images of FICCO

The fluorescence spectroscopy of all the samples except FACCO and FICCO were inactive after the HFO the fluorescence active compound formed in FACCO process. In FICCO the changes in λ max were observed this shows the active compound may be modified of changes in its structure taking place.

Conclusion:

The poor biodegradable tannery wastewater thus catalytically oxidized and immobalised reactor system (FACCO and FICCO) used for the oxidation refractory organisms present in wastewater. The biodegradability of the wastewater was gradually increased in all the treatment process this favors the effective oxidation by immobilized cell system to the oxidation.The mixture of post tannin wastewater COD was 3580 mg/L and mixture of beam house wastewater was 2900 mg/L. The treatment process has the efficiency of COD82.82%, 69.90% of TOC and 64.82% removal of BOD.

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ECT P-36

TREATMENT OF HIGH COD AND REFRACTORY ORGANICS CONTAINING INDUSTRIAL WASTEWATER BY INTEGRATED FLUIDIZED BED BIO-REACTOR AND HETEROGENEOUS FENTON OXIDATION PROCESS

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The work was focused on the treatment of high COD containing wastewater having low biodegradability nature due to the presence of high refractory organics and the variety of solvents used in the various industrial processes. The biodegradability of the wastewater was increased by Immobilized Cell Carbon system named Fenton Activated Carbon Catalytic Oxidation system (FACCO) followed by the heterogeneous Fenton oxidation, which is one of the advanced oxidation processes (AOP) and a fluidized bed bio-reactor namely "Fluidized Immobilized Catalytic Carbon Oxidation (FICCO)" reactor was used for the treatment process. FICCO comprises of Nano porous activated carbon as the carrier matrix in which the microbial culture for the degradation of organics was immobilized and added. The immobilization of microorganisms on the surface of activated carbon increases the catalytic activity of the microbial oxidation by providing the active sites for the organic adsorption onto support matrix. The hydraulic retention time (HRT), pH, temperature, organic load and the concentration of microbial culture for the maximum degradation of organics were optimized. The combination of AOP- FICCO process results in the removal percentage of NH_3, COD, BOD and TDS upto50-80% 65-93%, 70-82% and 25-38% respectively. The instrumental analyses such as UV-Visible spectrophotometer and FT-IR spectroscopic analyses were carried out to confirm the degradation process.

Key words: High COD wastewater, Low bio degradability; Advance Oxidation Process; Fluidized bed bio-reactor

Introduction:

All pharmaceutical industries consume lot of solvents for production of its own products.The toxic solvents and unreacted toxic organic compounds discharged with wastewater (Chanti Babu Patneedi et al, 2015.,Halling-Sorensen.B,2002). Here we have taken the synthetic and utility wastewater which was generated from pharmaceutical industry collected as condensate water from evaporator which consists of high COD and refractory organic compound due to presence of solvents, un reacted compound. The solvent from waste water can cause mutagenic and teratogenic effects to the living organism, when it mix with river or sea will spoil the life cycle of aquatics (Sanderson H,2004). When spread in land it will penetrate and mix with ground water affect the total ecosystem (Glassmeyeret al., 2005, Wu .M,2009). The water characteristics will change industry to industry initial characteristics two type of wastewater and mixture were presented in Table:1. By mixing the synthetic wastewater with utility water COD

comes around 4400mg/L. Then it was catalytically oxidized via FACCO, HFO and followed by FICCO I and FICCO II in all these processes activated NPAC was used as heterogeneous catalyst for the oxidation refractory organic present in the wastewater.

Materials and methods;

Sample collection:

The waste water from a pharmaceutical industry was passed through primary treatment consists of equalization, neutralization, Flash mixer, floccualtor followed by sand filter and Carbon filter which are present in the industry. The secondary treatment involves of Multiple effect evaporator system (MEES) the condensate from evaporator (synthetic) and Utility wastewater are boiler blowdown water, regeneration water and cooling tower water. Both Synthetic condensate water and utility water are mixed for further treatment process.

Analytical method:

The analysis of COD, BOD, TKN, NH_3 and TDS was followed APHA 1995 method. For TOC and TN Shimadzu TOC/TN analyzer was used. For UV/visible and FT-IR Cary win UV/visible spectrophotometer, Perkin Elmer FT-IR spectrophotometer was used respectively. All the chemicals were bought from SDFCL chemicals and used.

Reactor:

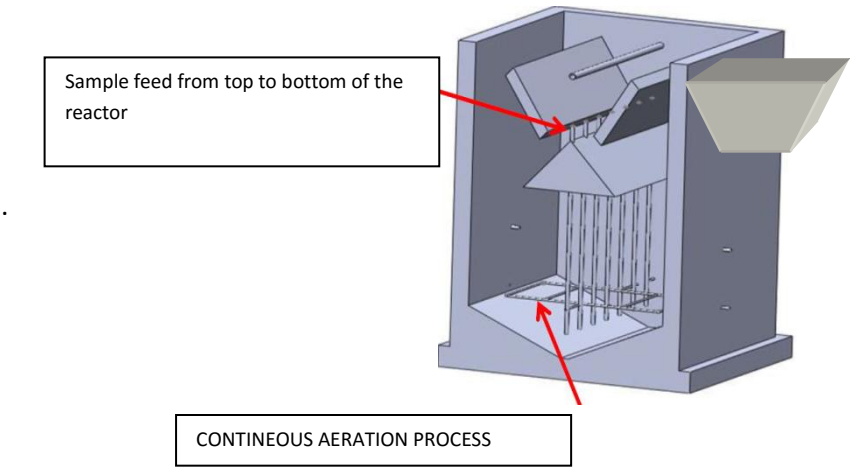

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Fig:1 Schematic diagram of fluidized bed reactor.

The Reactor mainly consist of three zone first one Aeration zone here air was diffused upward direction in inverted triangle shape at the bottom of the reactor. Because inverted triangle shape the well fluidization of NPAC and wastewater takes place and the second one is the triangle zone which was placed to distribute and recycle the unspent air inside the reactor. It increase the efficient of fluidization

and oxidation using atmosphere compressed air. The third zone is settling tank purpose of this tank is to settle the biomass bottom of the settling tank and its outlet will be carried to further treatment or discharge purposes (Karthikeyan.S et al,2011).

Scheme of treatment process:

For the condensate from wastewater is treated through Fenton Activated Cell Carbon Oxidation (FACCO), Heterogeneous Fenton oxidation process followed by and Fluidized Immobilized cell carbon oxidation (FICCO) process used for reduction of COD, Suspended solids, Ammoniacal Nitrogen, Total Kjeldahl Nitrogen(TKN), Total organic carbon(TOC), Total Nitrogen(TN) (Zielińskaet al 2004). In Heterogeneous Fenton oxidation (HFO) and in FACCO 0.3 ml of hydrogen peroxide is added per liters. Continuous aeration is required for Fluidized which reduces of COD and other parameter (K.Ramani et al.,). In FICCO (Fluidized Immobilized Carbon Catalytic Oxidation) Reactor, Advance Oxidation process takes place through immobilized microbial and carbon used as catalyst (John Kennedy.L 2004,Parken GE 1983). No chemicals involve in FICCO process only the supply of aeration to the conventional aerobic biological system along with carbon catalyst. Carbon Catalyst (NPAC) used in FICCO reactors is 30 gm/liters. NPAC catalyst produced from rice husk. Life time of Catalyst is 15 Years (Karthikeyan.s et al, 2014). It improves the water quality after treatment of FICCO reactor consists of different dimensions of upper hopper and aeration for Fluidization. In addition to these the raw water and FICCO treated water were analyzed for characteristics which include pH, COD, total solids, dissolved solids and suspended solids ,Ammoniacal Nitrogen, TKN, TOC, TN. FICCO reactor with generates of minimum sludge by the treatment process.

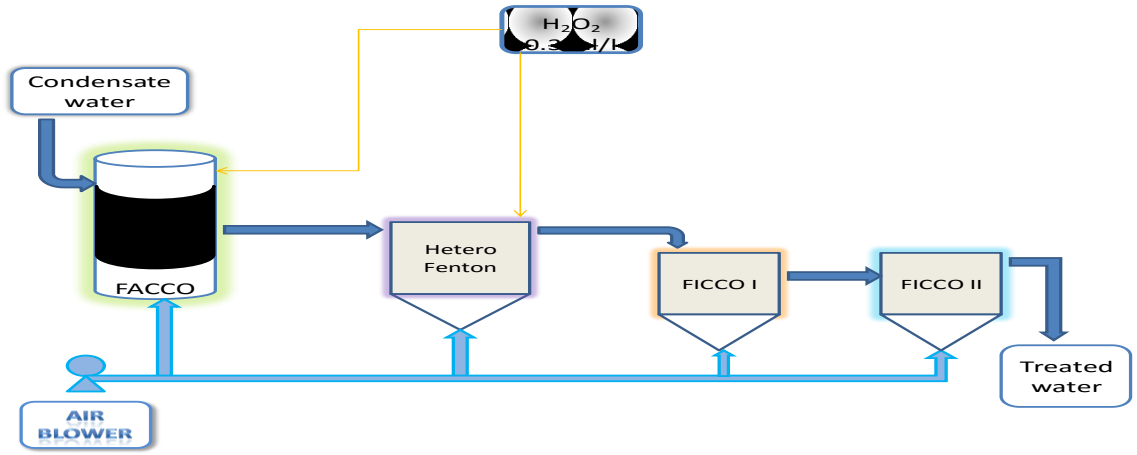


Fig:2 Schematic Flow Diagram for the treatment of waste water

Results and Discussion

The physicochemical analysis of synthetic, utility and mixture was carried out and tabulated below.

Synthetic wastewater

Parameters	Synthetic	Utility	Mixture
pH	8.1	8.97	8.6
ORP	-253	54	-123
COD ,mg/L	7720	800	4460
BOD ,mg/L	2050	250	1230
BOD:COD	0.2655	0.3125	0.2758
COD:TOC	3.8938	6.6225	4.1411
NH_3 ,mg/L	159.6	21	92.4
TN ,mg/L	305.4	22.5	299.8
TOC ,mg/L	1998	120.8	1077
TDS ,mg/L	3184	1579	2312
TKN ,mg/L	302.4	79.8	192.3

Table:1 Initial parameters of the synthetic, utility and mixture of wastewater

Optimization:

Optimization of Time and H_2O_2:

The composite of wastewater, it was passed to FACCO for 1 hr. The HRT of FACCO process was taken from Ramani.K et al research paper and NPAC 30g/L was arbitrarily fixed. Then before going to feed Hetero Fenton process it was optimized with different volume of say 0.1, 0.2, 0.3 and 0.4 ml/L 30% peroxide was taken and observed the COD reduction upto 24 hrs. It was shown in Fig:3 after feed up the peroxide a gradual decrease observed upto 6 hrs after that a static line was observed so it may be the optimum condition for the treatment of these types of wastewater among the four hr different volume 0.3ml/L of peroxide dose and 6h HRT was fixed as optimum condition.

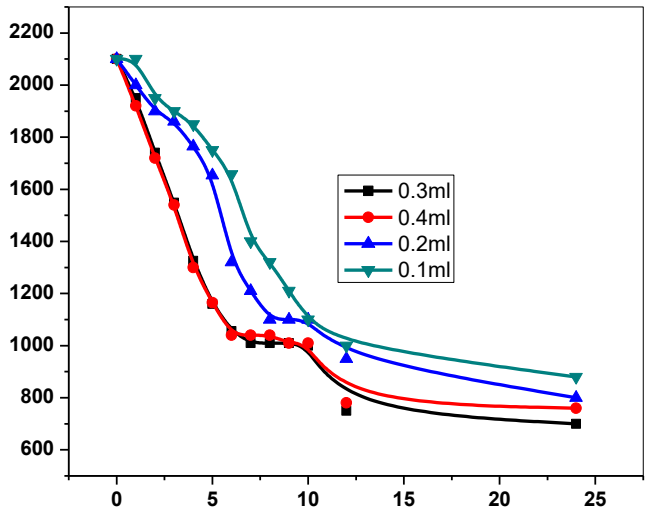


Fig:3 Optimized results of peroxide and time.

Overall treatment process:

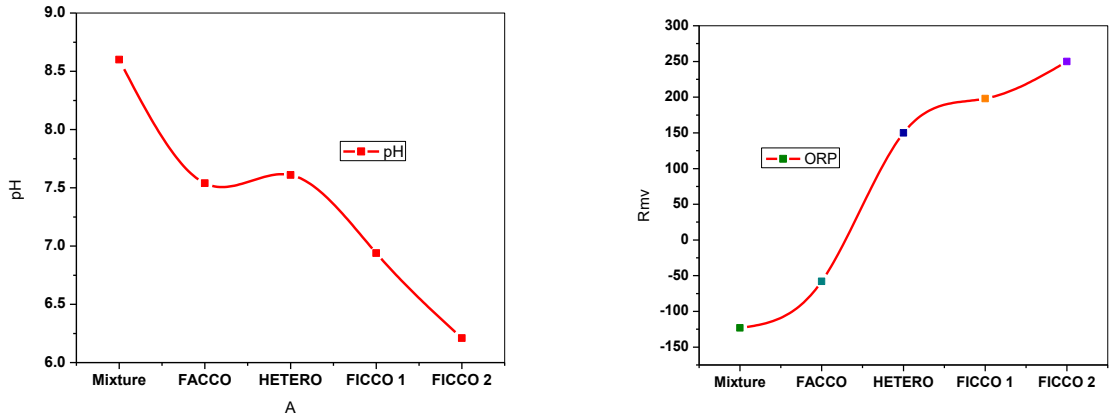
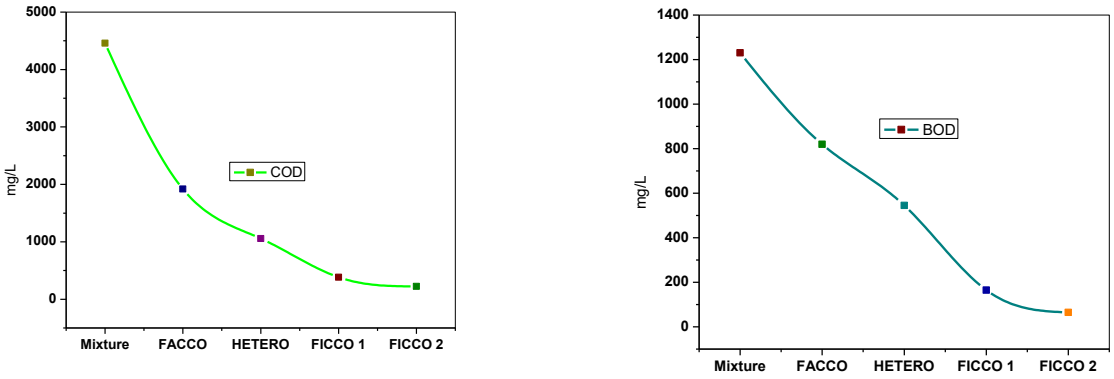


Fig:4 Changes on pH and ORP of the treatment process.

The pH of the mixture was above 8.5 when we pass into the FACCO reactor it was dropped nearly neutral this may due to the formation of acidic compound in wastewater by the heterolytic cleavage of organic compounds by forming acidic compounds. After HFO, FICCO1 and FICCO2 it was observed continuous decrease in the pH was observed. The Oxidation and Reduction Potential (ORP) of the mixture was in negative (-123Rmv) means that it has some of the reduced species it was continuously oxidized by all the method finally it achieved Positive (250). This is the supporting evidence for the oxidation of the organic compounds takes place (Fig:3).

Fig:5 Removal/oxidation of COD and BOD during



the treatment process.

The important parameters COD was analyzed in wastewater it found that mixture has 4460 mg/L during the treatment process found that continuous decrease in COD was observed with the

efficiency of 94.95% and within the dischargeable limit of pollution control board. The BOD of the initial waste water was 1230 mg/L it is also found in continuous reduction of BOD after the treatment it has the efficiency of 94.71%.

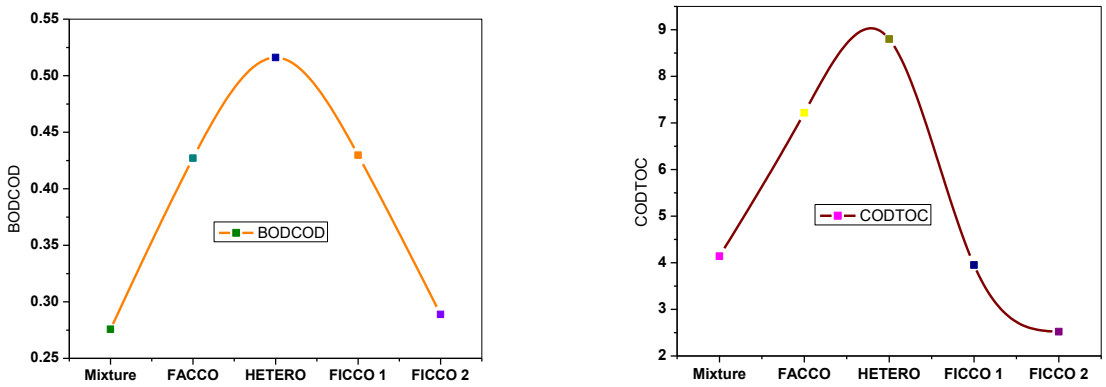


Fig:6 Changes in BOD:COD and COD:TOC.

Biodegradability of the wastewater determined based on the B0D:COD in that way the ratio of the mixture was 0.2758 this shows less amenable to degrade biologically. The heterogenous catalytic oxidation of the wastewater increases the biodegradability of the wastewater upto 0.5160 then when we go to FICCO process microbial decomposition of wastewater takes place after FICCO1 and FICCO2 all the biologically degradable compounds was degraded. The COD:TOC ratio shows increase in chemical oxidation and decrease in biological treatment process.

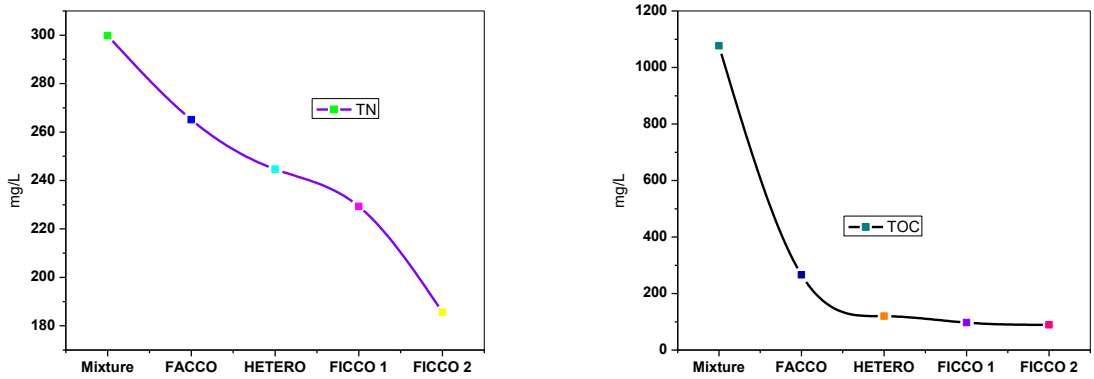


Fig:7 Removal of Total nitrogen and Total organic carbon.

The Total Nitrogen of the mixture was 299.8mg/L after the treatment 38.09% of removal of TN was observed. The TOC of the mixture was 1077mg/L after the treatment 91.73% of removal of organic

compound was found out the carbon content may be converted in to carbon dioxide and it may be escaped into the atmosphere.

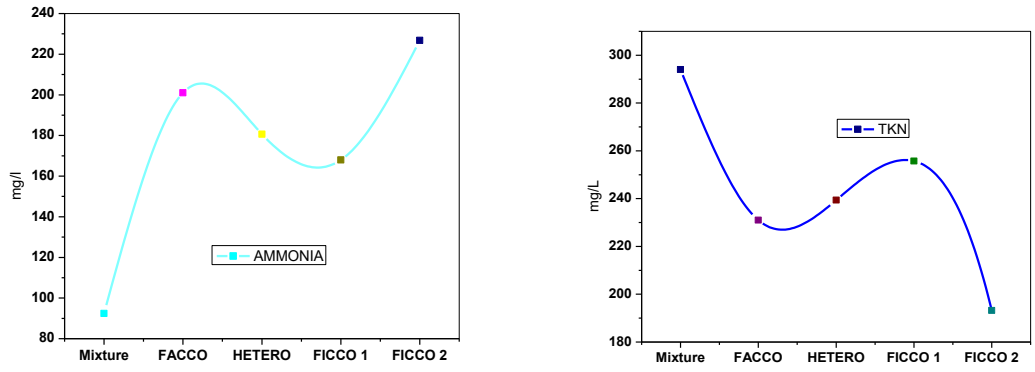


Fig:8 Removal of Ammonia and TKN

The formation of ammonia was observed because of the TN may be converted in to ammonia on the treatment process likewise the decrease in the TKN also observed it support the formation of ammonia in the wastewater.

UV/Visible

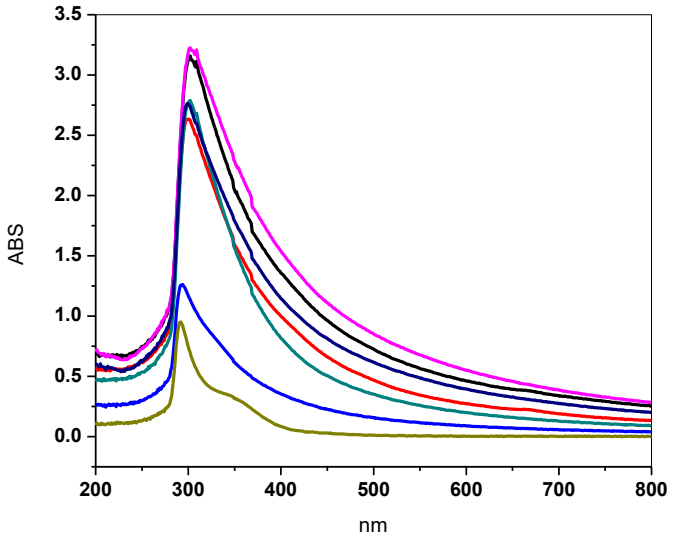


Fig:9 UV/Visible spectroscopy study of treated wastewater on treatment process.

The UV/Visible spectroscopy results shows continuous decrease in intensity may be due to the mineralization of organic compounds takes place as well as hypso chromic shift was observed during all the treatment process which means removal or oxidation of the content of the wastewater in terms of

organic compound was takes place this also one of the supporting evidence of the treatment process. (Raghu.S et al, 2007., Hea.Zet al, 2008).

FT-IR:

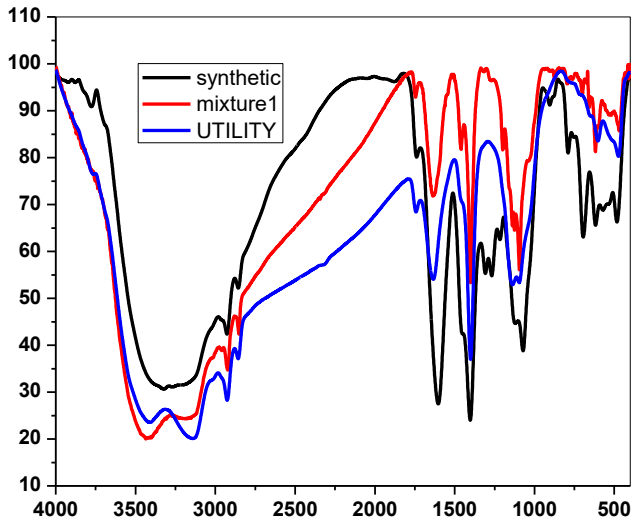


Fig:10 FT-IR spectroscopy study of Synthetic, utility and mixture taken for the treatment process.

In FT-IR spectra of synthetic wastewater shows 3326cm^{-1} peak due to intermolecular association of –OH stretching the same –OH stretching found in utility water when we mix both together mixture1 also shows both peak presences in wastewater. In 2927,2866 cm^{-1} region due to the C-H stretching of methyl or methylene group. A peak at 1742 cm^{-1} present in all the three due to the presence of C=O stretching of free ketone or ester this confirms presence of aliphatic groups present in the wastewater this also supported with at peak at 1634 C=C stretching of conjugated diene or C=O stretching of intermolecular hydrogen bonded ketone or stretching of amide or these three functional groups may be present in the wastewater. A combination band observed in 1400 region this confirms the presence of aromatic groups in wastewater this supports a stretching peak at 1094 region due to C-O stretching in aromatic compound. A peak near 1198 cm^{-1} confirms the presence of phenol group also confirmed with additional peak at 1125 cm^{-1} due to C-O stretching. A characteristic peak of ether observed at 1138 cm^{-1} . So the functional group region shows the presence of functional group of keton, ester, ether, alcohol, amide, conjugated diene present in the wastewater. In finger print region a peak at 874 cm^{-1} confirms the presence Meta-disubstituted compounds in the aromatic compound and two strong bands at 798 and 700 cm^{-1} confirms the presence of mono substituted group present in aliphatic compounds in the wastewater.

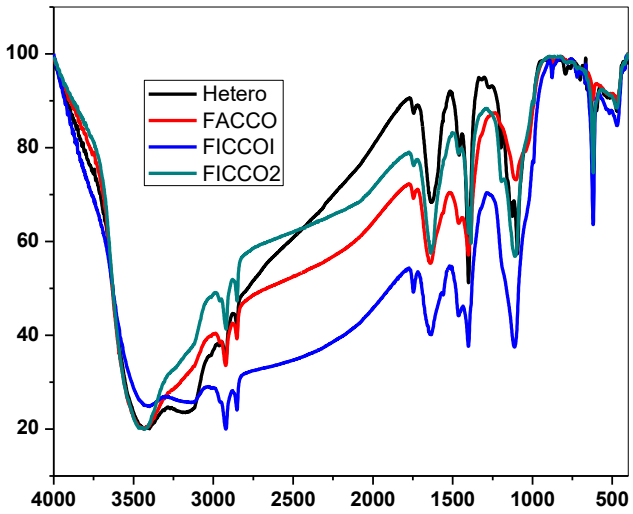


Fig:11 FT-IR spectroscopy study of FACCO, HETERO, FICCO1 and FICCO2 treatment process.

On treatment processes all process shows presence of –OH stretching but the N-H stretching was vanishingly present in FACCO then well peak was observed in HETERO and FICCO1 process then this too disappeared in FICCO2 process. All the C-H stretching peak observed in 2800-2900 region. Stretching of free ketone C=O was disappeared after FACCO process. A peak at 1109-1110 cm^{-1} is due to the C-O stretching of alcohol groups present in the treated wastewater. Amide stretching was present in all the process. Disappearance of C-O stretching of phenol group confirms the degradation of aromatic compounds taking place by hetero catalytic oxidation. A peak at 1400 cm^{-1} due to the C-C stretching of saturated compounds the disappearance of stretching of C=C conjugated diene confirms the formation of saturated compounds by oxidation process.(Raghu.S et al, 2009, Teresa Zayas, 2011).

Conclusion:

The heterogeneous catalyst named NPAC has active sight which involves in both chemical and biological oxidation of the organics. The immobilization takes place in the NPAC thus microbial decomposition takes place. Using this catalyst suggested scheme for the treatment of this type of pharmaceutical wastewater works well in the reduction and oxidation of refractory content present in the wastewater. The spectroscopic results are the notable evidences for the degradation or catalytic oxidation of the wastewater taking place on the treatment process. The high efficiency of the treatment process for COD, BOD, TOC and TN were 94.95%, 94.71%, 91.73% and 38.09% respectively.

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FLS P-15

CHEMICAL CHARACTERIZATION OF VEGETABLE TANNINS FOR LEATHER INDUSTRY

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During the leather making process, tanning is one of the most important operations, which improves the durability and practicability of leather products and prevent putrefaction, in which the tanning agents react with the collagen molecule, stabilizing the triple helical structure of collagen matrix; thereby the leather acquiring resistance towards chemical, thermal and microbiological degradation. Among the various tanning options, vegetable tanning is a traditional and recognizable method. In this work, the percentage of total tannin polyphenols from Acacia, Chestnut, Tara and Quebracho tannins were quantified by the hide-powder method and the UV colorimetric method for identifying the total phenols percentage. Condensed tannins showed the highest total tannin polyphenols, indicating that they may have a greater interaction with collagen protein than hydrolizable tannins. The spectra of the tannin samples were recorded by Fourier-Transform Infrared Spectroscopy (FTIR) and Attenuated Total Reflectance cell (ATR), showing a clear separation between the two tannin groups. Finally, GPC (gel permeation chromatography) technic was useful to compare relative molar mass and polydispersity between tannins. Acacia showed the lowest result of molar mass, indicating that it may penetrate more easily in the hide than the other tannins. These characterization methods are applicable for identifying properties that may explain tannins properties and their performance in leather tanning.

Keywords: tanning, vegetable tannin, FTIR, hide powder, GPC.

1. Introduction

Untreated raw hides have limited value, because they are susceptible to bacterial attack and so they putrefy (Pinto et al., 2013), otherwise if they are dried without tanning they become inflexible and useless for purposes such as clothing.
The collagen structure of the hides must be stabilized by means of the tanning process to avoid its degradation. The reaction of tanning substances with collagen involves the crosslinking of its chains with modifies the chemical properties of the hide. In order for tannin reactions to occur, the tanning particles and molecules are absorbed into the hide by diffusion through the fibers, interfibrillar spaces, fibrils and into the aggregates of collagen molecules. The tanning process occurs in two stages. First, tannin

molecules diffuse into the hide and on a second stage, the molecules are finally fixed during the fixing phase. The factors that influence the diffusion are: particle size, viscosity of the solution, temperature, pH, concentration of tanning, mechanical action, etc. (Faber K., 1990) It is difficult to predict the mode of interaction of plant tanning agents with hide's collagen due to the variability of chemical interactions and the vast number of classes of substances. The pH causes changes in the loading state of the collagen in the side chains of the amino acids, which influences the binding of certain tanning agents (Schroepfer and Meyer, 2015).

Vegetable tannins (e.g., acacia, chestnut tree, tara, mimosa and quebracho extracts) are used for leather tanning and retanning. Tannins are natural phenols or polymers of polyphenolic compounds, synthesized in plants as secondary metabolites for protective purposes (Farah and Donangelo, 2006) with molecular weights ranging from 500 to over 20 000 Da (Online and Grasel, 2016).Types of tanning include basically the vegetable tanning, with the use of vegetable sources; mineral tanning, with the use of metal salts (eg, chromium), and synthetic tanning with the use of synthetic tannins. Vegetable tannins are divided chemically into two groups: hydrolysable and condensed tannins (Grasel et al., 2016). Hydrolysable tannins including chestnut (*Castanea sativa*), myrabolans (*Terminalia* and *Phyllantus* tree species), divi-divi (*Caesalpina coraria*), tara, algarobilla, valonea, oak and several other commercial tannin extracts are reputed to be mixtures of simple phenols such as gallic and ellagic acids and of esters of a sugar, mainly glucose, with gallic and digallic acids, and with more complex structures containing ellagic acid. Notwithstanding their alleged lack of a polymeric nature, they can form complex structures (Belgacem and Gandini, 2008).

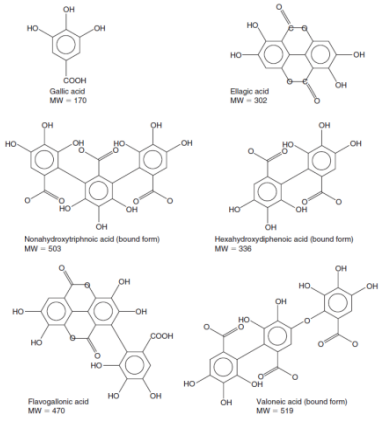

Fig. 1. Structures of hydrolysable tannins (Belgacem and Gandini, 2006).

The other major class of polyphenols is of the condensed tannins (proanthocyanidins). Proanthocyanidins are oligomers or polymers of the basic structure of flavan-3-ol, (Koleckar et al. 2008) as shown in Fig. 2. Condensed tannins can be extracted from the heartwood of the quebracho (*Schinopsis lorentzii*) and black wattle bark (*Acacia mearnsii*) (Grasel et al., 2016). These tannins are extracted in an aqueous medium, and Quebracho usually is sulphited to improve the extraction of polyphenols.

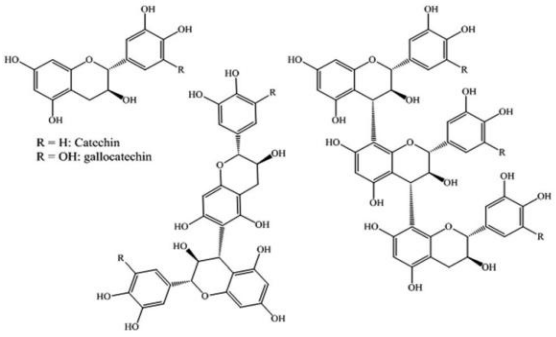

Fig. 2. General structures of condensed tannins (Grasel et al. 2016).

In addition to the application in leather tanning, these extracts are also used to obtain natural coagulant agents (Beltrán-Heredia, Sánchez-Martín, and Martín-García 2012) adhesives for wood panels, (Nakanishi, G. et al., 2008) flame retardant foams, (Tondi et al., 2009) anticorrosion compounds, (Martinez, 2003) and medicines (Mumper, 2010). Furthermore, leathers tanned with vegetable tannins are known to be environmentally friendly products and have aroused great interest in the Market . The tanning activity of tannins is therefore related with multiple hydrogen-bonding and/or ionic interactions with the protein functional groups that stabilizes the hide (Pinto et al., 2013; Schroepfer and Meyer, 2015).

It was investigated the ability of hide collagen substrate to absorb and fix vegetable tannin of Acacia mearnsii at different pH, through the use of UV-visible spectroscopy and zeta potential for elucidation the tanning process (Spier et al., 2015). The results showed that the substrate, the concentration of tannin and even the type of tannin used, influenced the ability of the bovine hide collagen to absorb and fix the vegetable tannin of Acacia mearnsii. Using the technique of near infrared spectroscopy (NIR) was reported that the tanning of hide powder tanning was completed in 120 minutes, meanwhile for the complete diffusion and fixation of the tannins in the bovine hide 24 hours was necessary (Gutterres, 2007).
A method widely used for determining the degree of hydrothermal stabilization of collagen by tannin is differential scanning calorimetry (DSC). This method measures the shrinkage temperature of collagen, that is, the temperature in which the leakage of the hydrogen bonds occurs and the collagen structure denatures. The hydrothermal stabilization of collagen depends on the tannin type applied. Recent studies show (66–69)°C for chestnut, (74–75)°C for mimosa, (77–79)°C for quebracho (Cars and Gatta, 2016) and 85°C for black wattle (Kanth et al., 2009) .

Authors developed a method using Fourier transform infrared spectroscopy (FTIR) associated with multivariate analysis to identify commercial tannins. By means of both principal component analysis (PCA) and hierarchical cluster analysis (HCA), a well-defined separation between condensed and hydrolysable tannins was observed. Among the tannins, chestnut and valonea samples showed the greatest similarity, indicating that these extracts have an equivalent chemical composition.

The literature also shows works aiming at the optimization of tannin extraction parameters. In

experiments to optimize the extraction of Valonea from acorns, optimum extraction parameters were elicited as 100 ml/g for solvent/feed ratio, 6 h of process duration and solvent mixture ratio of 62% methanol–38% water. The filling coefficient of the leathers tanned with extracted valonea (57.81%) and the shrinkage temperature (75.5◦C) was superior to the commercial valonea (52.83%; 73°C).(Onem et al., 2014)

In this context of understanding tannins molecular properties of four commercial tannins: Acacia, Tara, Quebracho and Chestnut. The aim of this study was to improve the knowledge about characterization of tannins, applying four methodologies: FTIR (Fourier Transform Infrared Spectroscopy) for identifying hydrolizable and condensed tannins, the hide powder gravimetric method for determining tannin polyphenols and non-tannin polyphenols percentage, the GPC (gel permeation chromatography) technic to compare relative molar mass and polydispersity between tannins and UV Folin-Ciocalteu method to quantify total polyphenols. These characterization methods are helpful to justify different tanning abilities of these vegetable extracts.

2. Material and Methods

2.1. FTIR (Fourier Transform Infrared Spectroscopy)

In the FTIR transmission experiment, Perkin Elmer FT-IR Spectrometer Frontier model equipped with a MIR TGS detector and an accessory with universal attenuated total reflectance (UATR) in the spectral range of 4500–600 cm−1 was used. The attenuation of the beam after passing the tannin samples was recorded in the frequency domain, providing an absorption pattern for Tara, Acacia, Chestnut and Quebracho. The raw data were recorded in transmission mode (T%), meaning the percentage of initial intensity of the source remaining after the absorption of the sample. The specimens chosen to be analyzed in this work were dried aliquots from the analytical solutions prepared from the commercial tannin products.

2.2. Gravimetric Method with Hide Powder

The gravimetric method of Roux (1951) is used to determine the proportion of the total soluble solids which are soluble non-tannin polyphenols and the proportion which are tannin polyphenols in a solution of vegetable extract. By this method, the soluble non-tannin polyphenols are defined as the portion of the soluble solids which are not absorbed or bound by a prepared hide powder material, while the tannin polyphenols are defined as the portion of the soluble solids which are absorbed or bound by a prepared hide powder material.

2.3. Total Phenols Content

Tannins were prepared for photometrical measurements of total phenols content (TPC) (Sartori, 2012). Firstly, the calibration curve was constructed with an alcoholic solution of tannic acid (100 mg/50 mL), 5 mL was retained and completed to 50 mL of ethanol. Aliquots of 0,3; 0,5; 0,7; 0,9 and 1,1 mL of this solution were taken and each volume was filled to 2 mL. Then, 0,5 mL of each solution was completed to

3 mL with the Folin-Ciocalteau solution 10% (v/v). Finally, 2 mL of a sodium carbonate solution 4% (m/v) was added and the tubes were protected for 30 min from the light for the reaction occur. The absorbance measurements were perfomed with a UV/visible spectrophotometer (T80 UV–VIS spectrophotometer, PG Instruments, Leicester, LEC, UK) at 760 nm. After 0,5 mL of solutions containing the four extracts of Acacia, Quebracho, Tara and Chestnut were reacted with 2,5 mL of the Folin-Ciocalteu solution 10% (v/v), 2 mL of a sodium carbonate solution 4% (m/v) and the tubes were protected from light, letting the reaction occur for 30 min. This procedure was repeated in triplicate, in order to quantify TPC of each sample. The TPC for each sample was then read in the spectrophotometer and the absorbance value in was converted in % of total phenols.

2.4. Aquous Gel Permeation Chromatography (GPC)

A column ViscoteK PC MAX VE 2001 with a viscotek VE 3580 RI detector was used to perform the GPC method. Columns SHODEX SB-806 M HQ, SB-807 HQ,SB-807G in series were used, and the solvent was $NANO_3$.. The samples were diluted previously in water and then injected in the columns.

3. Results and Discussion

3.1. Characterization By FTIR

The ATR-FTIR technique takes advantage of specific crystals exhibiting high refracting indexes. These crystals are able to interact with the thermal source of the FTIR spectrometer, creating an evanescent wave on the crystal surface where adsorption occurs.The characterization of plant extracts according to their phytochemical components is also a widely documented application of ATR spectroscopy (Ortiz et al. 2003; López-Sánchez, Ayora-Cañada 2010;Bharudin et al. 2014;Falcão and Araújo 2013;Ping et al. 2012). Several researchers have exploited this technique for the characterization of tannins interacting with different substrates (Yuranova et al. 2006; Cocciardi et al. , 2005;Çakar, S, Güy, N, Özacar, M. , Findik 2016).

Analysis of the FTIR-ATR spectra ranging from 3500–3000 cm^{-1} shows the sum of the –OH stretching derived from different chemical environments, which is characteristic of polyphenolic extracts (Grasel, Flôres, and Rodolfo 2016). The 1800-1680 cm^{-1} region is significant for qualitative analysis, because it exhibits a distinctive peak for carbonyl stretching of the hydrolysable tannins (Ricci et al., 2015). That is, Tara and Chestnut showed a peak in this range, whereas no signal occurs for the condensed tannins from Acacia and Quebracho.

The 1620 to 1400 cm-1 region is mainly occupied by vibrational motions of C=C groups in the aromatic rings with several strong peaks. The region 1450-900 cm-1, with its complex structure, can be considered the most significant for the description of ring substituents. It is usually characterized by an envelope of strong bands resulting from the combination of C-H aromatic bending, C-O streching and C-OH deformations.

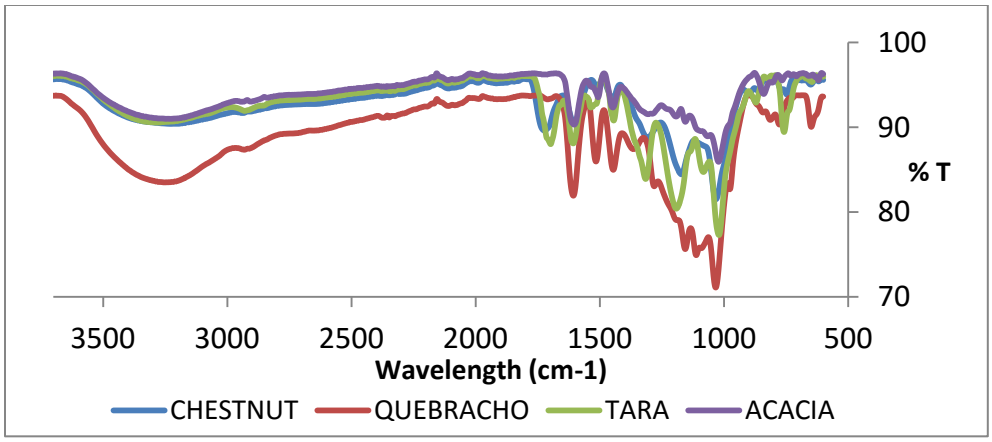

Fig. 3. FTIR Spectrum of vegetable tannins

For the hydrolizable tannins Tara and Chestnut, the region 1326 to 1322 cm-1 represents the symmetric and assymetric streching for C-O in aromatic –OH group. The region between 780-850 cm^{-1} detected peaks only for the condensed tannins. Regions between 1575-1625 cm-1, 1500-1525 cm-1, 1425-1475cm-1, 1000-1050 cm-1 and 1150-1200 cm-1 showed peaks for both condensed and hydrolizable tannins, so these regions are not enough to discriminate both tannin categories.

3.2. Tannin and Non Tannin Determination

This method to evaluate tannins showed to be laborious and time-consuming. Acacia showed the highest total tannin polyphenols percentage (57%), followed by Quebracho (53%), Chestnut (51%) and Tara (44%), as it can be seen in Figure 4. This can be explained by the oligomeric nature of condensed tannins, which contrasts with the non-polymeric nature of hydrolysable tannins (Belgacem and Gandini, 2008). Therefore hydrolysable tannins may be less reactive with collagen.It has been reported that the true affinity of flavanoid compounds for proteins only becomes apparent from the triflavanoid level (Roux, 1951; Yazaki et al., 1993). This indicates that lower molecular weight polyphenols may not react with protein, making Tara and Chestnut less reactive in this case. There was also a tendency of decrease the soluble solids (% SS) from Acacia (87%) to Tara (67%).

The non-tannin polyphenols are chemical components that do not bond so strongly to proteins, being smaller molecules (Synge, 1975) and they may be subdivided into carbohydrates, hydrocolloid gums, sugars and small amino and imino acid fractions (Belgacem and Gandini, 2008). Tara showed the lowest non-tannin polyphenols percentage (23%) and it can be explained by the fact that these tannins come from the pods of tara, different from Acacia tannins that come from tree barks and Quebracho and Chestnut tannins that come from wood. Tara showed the highest insoluble content (20%). The insolubles, on the other hand, are defined as the amount of material present in any vegetable tanning extract that are not soluble in water. It consists of cellulosic matter and owing to the size of the particles it will not penetrate the hide or skin, remaining on the surface as a sludge. What sets the tara tannin apart from other commercial tannins is the fact that it is not an extract, but a finely ground powder from tara pods. Therefore, tara tanning agent has a lower tannin content, a high amount of insoluble

substances and its use involves loading effluents with significant amounts of organic matter (Gaidau et al., 2014).

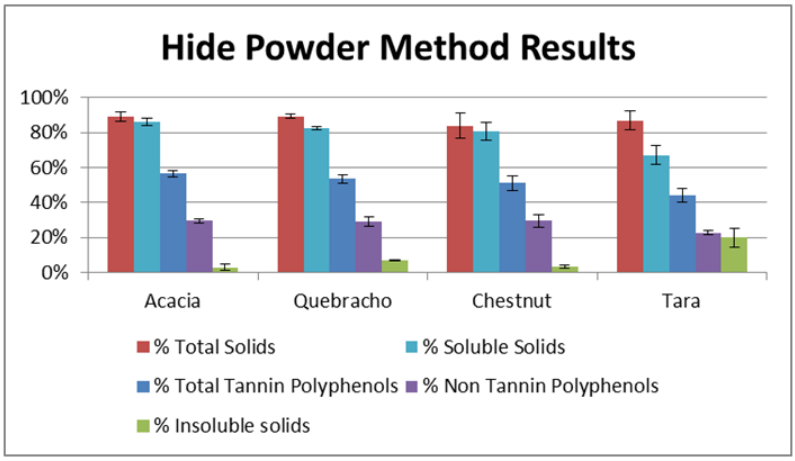

Fig. 4. Gravimetric analysis of vegetable tannins

3.3. Total Phenols Content

The calibration curve showed the effect of the dilution, that is, the more diluted the tannic acid for a certain concentration of Folin-Ciocalteu reagent, the lower is the absorbance and less intense is the blue color. On reaction with a reductant, the molybdenum blue and the tungsten blue of the Folin-Ciocalteau phenol reagent are formed. The hypothesis is that this methodology should quantify higher amounts of polyphenols than the hide powder method does. This is explained because not all polyphenols have the ability to tan (W. Bamforth, 2009). Therefore, in comparison with hide powder method, which measures the interaction of the polyphenols with collagen, Folin-Ciocalteu method should indicate higher values of TPC. This hypothesis is confirmed by the results showed in table 1.

Table 1. Total phenol contents of vegetable tannins.

Total phenol Contents			
Acacia	Quebracho	Chestnut	Tara
57%	69%	61%	69%

These results were calculated based on the absorbance values converted in % of total phenols through a standard curve of tannic acid.

Acacia showed the lowest result of TCP, which corresponded to the same result obtained from the hide

powder method (TT%). This could indicate that Acacia shows a higher extraction yield for the total tannin polyphenol, that is, almost all polyphenols contained in the extract have tanning ability. The other extracts, on the other hand, showed TCP results higher than the TT% results, indicating that for leather tanning purposes, a higher amount of tannin extract should be used to obtain the same performance of Acacia.

3.4. GPC (Gel Permeation Chromatography Results)

A monodisperse or uniform polymer is composed of molecules Monomers?? of the same mass. Natural polymers are typically monodisperse. This is not the case of the tannins analyzed (Table 2), where the polydispersity showed high values. This indicates that their chain lengths vary over a wide range of molecular masses, representing complex structures.

Types of average molecular weight include the number average molecular weight (Mn), the weight average molecular weight (Mw) and z-average molecular weight (Mz). Acacia showed the lowest result for Mn, indicating that its molecules could penetrate more easily into the hide. Also, Tara and Acacia showed more narrow molecular weight distributions, as a result of the lower Mw.

Table 2. Relative molar mass and polydispersity of the the vegetable tannins.

	Peak RV (ml)	Mn (Daltons)	Mw (Daltons)	Polydispersity(Mw/Mn)
Chestnut	33.992	663	44.417	67.033
Tara	34.092	347	458	1.319
Quebracho	33.250	685	4.201	6.134
Acacia	34.142	334	492	1.470

4. Conclusions

Among the four vegetable tannins analyzed by FTIR, Quebracho and Acacia showed the greatest similarity, as well as Tara and Chestnut, indicating that these extracts belong to different groups of tannins: condensed and hydrolizable, respectively, as it can be noted in the 1620 to 1400 cm^{-1} and 780-850 cm^{-1} regions. The results of hide powder method showed that Acacia and Quebracho tannin samples had the greatest total tannin polyphenols percentage. The TPC (total phenol content) showed to be a rapid method to measure phenols and polyphenols. For Acacia, these two methods showed great similarity in terms of results, showing that all or almost all polyphenols have the ability to tan. The GPC analysis showed high polydispersity results for all tannins, confirming that they are complex molecules from different sizes. Hence, this characterization of tannins showed its importance, because it provided evidences to justify tannins interactions with collagen.

5.0 Acknowledgments

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DIP P-08

STANDARDIZATION OF FOOT SIZES OF PATIENTS WITH DIABETIC FOOT ULCER THROUGH ANTHROPOMETRIC SURVEY

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It is well proven clinically that the off-loading of plantar pressure at ulcer site is one of the therapeutic interventions for fast healing of diabetic foot ulcer (DFU). Due to peripheral neuropathy and vascular disease, the foot anatomy of patients with diabetes is significantly different from that of normal persons. Presently the therapeutic footwear or other off-loading devices for patients with DFU are customized which will ultimately delay the treatment intervention. The objective of the present study is to derive standardized foot anthropometric data for patients with DFU to use as a reference for developing pressure off-loading devices. The measurement of foot dimensions for 100 patients with DFU and 50 age matched control subjects were recorded using 3D laser foot scanner. The statistical analysis of data such as regression analysis and cluster analysis was done using SPSS software. By regression analysis the significant difference and correlation between normal and patients with DFU were studied. By cluster analysis 3 groups for male and 3 groups for female were derived. The groups were homogeneous within themselves and as much as possible heterogeneous to other groups. From the statistical analysis of groups, 3 average sizes for male and 3 average sizes for female that can accommodate 70% of patients with DFU had been derived. Development of pressure off-loading devices based on the developed sizes and trial with patients are on-going projects of this study.

Keywords: Diabetes complication, Foot dimension, Cluster analysis, Standard sizes.

1. Introduction

Among the other complications of diabetes, foot complication plays the major role. Foot ulcer is the major cause for patients with diabetes for getting admitted to hospital (Pinzur MS et al 2005). Every 30 seconds one foot is amputated somewhere in the world because of foot ulcer (Bakker K et al 2005). Offloading devices like ankle foot orthosis (Hanft et al 2011), rocker bottom shoes (Hanft et al 2011) removable cast walkers (Vijay Viswanathan et al 2013), felted foam half shoes and air cast shoes (Vijay Viswanathan et al 2013) are used as a treatment aid for diabetic foot ulcer (DFU). Presently the therapeutic footwear or other off-loading devices for patients with DFU are customized (Bus et al 2011) which will ultimately delay the treatment intervention. To make the offloading devices available off-the -shelf, the size of the lower limb (below knee) and foot need to be known. The aim of this study is to collect and understand the foot anthropometric data of patients with DFU. This data would help in

standardizing the size of the diabetic foot having the active ulcer because foot deformities influence the risk of developing a foot ulcer in patients with diabetes (Boyko EJ et al 1999) which in turn changes the anatomy of the foot.

In the past works, the length and breadth of normal and diabetic population's feet were studied (Hanft et al 2011). McInnes AD et al. emphasized the need for a standardized approach to foot length measurement in diabetic peripheral neuropathy population as they use either too short or too long footwear (McInnes AD et al 2012). Bogdan Sarghie et al. studied the foot anthropometric data of 23 normal male subjects in the age group of 30 - 40 years using 3D foot scan (Sarghie et al 2013). In this study, about 20 parameters were measured and analyzed statistically. There is no such database of anthropometric data of patients with DFU available so far. We have collected and analyzed foot anthropometric data of DFU patients like the length of the foot, breadth of the foot, ball girth, joint girth, instep girth, ankle girth, heel girth, calf height and calf circumference. Studying the dimension of the ulcerated foot will help in finding out the standard sizes for fabrication of off-loading devices for patients with DFU.

2. Materials & Methods:

2a. Subjects:

The patients with DFU who visited the Podiatry Department of M.V. Hospital for Diabetes and Research were included in this study. The study involved 100 subjects with 70 male and 30 female. The employees of various departments of CSIR – Central Leather Research Institute were included for control category. The control subjects include 43 male and 9 female. Patients were requested to read, understand and sign the consent form before the measurements were taken. The demographic data of subjects is given in Table 1.

1: Demographic data of subjects

S NO	PARAMETER	DFU (100)	CONTROL (52)
1	Age (years)	59.33 ± 8.95	53.58 ± 8.62
2	Height (cm)	163.87 ± 9.64	162.31 ± 9.10
3	Weight (kg)	70.27 ± 12.74	65.04 ± 9.86

2b. Foot Survey I:

The demographic data of patients were recorded from the hospital record. The measurement of the foot for 100 patients with DFU and 50 normal (Non- diabetes) persons of equal age group were recorded using 3D laser foot scanner (I-Ware Laboratory's INFOOT USB High Type, Model: IFU – H – 01). Criteria of normal (Non-diabetic) persons were the absence of foot pain or any other complaints, foot deformity and gait abnormality. The foot dimension data included foot length (Fig1a), breadth (Fig1a), ball girth

(Fig1b), waist girth (Fig1b), instep girth (Fig1b), heel girth (Fig1b), ankle girth (Fig1b), calf height (Fig1c) and calf circumference (Fig1c).

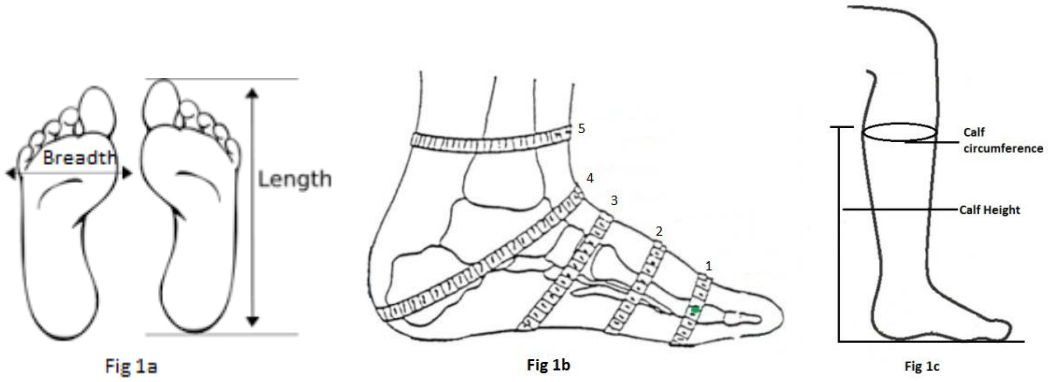

Figure 1: Foot dimensions recorded from Foot Scanner

The data collected were analyzed statistically using the tools such as regression analysis for investigating the relationships between variables and cluster analysis for generating groups which are similar. The SPSS software was used for this analysis. From the analysis, three average sizes for male and female were obtained.

2c. Validation of measured foot dimensions:

A second foot survey was done to check and validate the statistically derived foot sizes. This survey was also done at the Podiatry Department of MV Hospital for Diabetes and research. A total of 19 patients (Male - 9; Female – 10) participated in this survey. In the case of male patients, it was found that 3 out of 9 patients fall under size I group, three patients fall under size II and remaining three patients have their feet measurements distributed over all the three sizes. In the case of female patients, 4 out of 10 patients fall under size I category and three patients fall under size III. Among the remaining three patients, two of them have their measurements in both sizes I and size II whereas one patient has a foot measurement which does not fall in any of the standard sizes.

3. Results:

3a. Regression Analysis

The regression coefficients of both DFU and control group are given below in Table 2 and Table 3. The correlation was not significantly symmetric between left and right for DFU group (Table 2) whereas it was somewhat symmetric for normal population (Table 3) except length vs. breadth correlation in normal female population. This may be because of very small sample size in the normal female group.

It is observed from the measurement, that though an anatomical difference between left and right feet of the patients exists, it is not statistically significant. In female DFU subjects (n=30), the correlation between breadth and ball girth of the left foot is better than the correlation between length and breadth of left foot. The regression graph between the length of the left foot and its corresponding calf

height shows a poor correlation with R^2=0.013 in female subjects. Thus, it is observed that breadth Vs ball girth is correlated in a better way than that of length Vs breadth. Also, the correlation between length Vs calf height is poor. The R^2 values of diabetic population and normal population are shown in Table 2 and 3.

Table 2: Regression coefficients of diabetic foot ulcer population

	Male (R^2)		**Female (R^2)**	
	Left	**Right**	**Left**	**Right**
Length Vs Breadth	0.34	0.199	0.401	0.061
Breadth Vs Ball girth	0.674	0.543	0.650	0.111
Length Vs Calf height	0.218	0.247	0.013	0.074

Table 3: Regression coefficients of normal population

	Male (R^2)		**Female (R^2)**	
	Left	**Right**	**Left**	**Right**
Length Vs Breadth	0.4195	0.3919	0.2892	0.4772
Breadth Vs Ball girth	0.9008	0.9327	0.8467	0.9674

The Pearson's coefficient of length and breadth shows that the correlation is moderately positive for both DFU (r=0.493 for right and r=0.716 for left) and normal group (r=0.607 for right and r=0.670 for left).

The R^2 values of regression graphs for normal population (Table 4) reveals that the length and breadth are better correlated in male population than female. This correlation may be because of small sample size in the normal female category. Also, the correlation between breadth and ball girth in the normal population is better than the DFU population. This result confirms the significant difference in girth measurement of DFU population.

3b. Cluster Analysis

Instead of averaging the measurements, cluster analysis of data was done to segregate the sizes according to the relationship between the measurements. The mean value of cluster 1 in all the parameters corresponds to size 1. The mean value of cluster 2 in all the parameters corresponds to size 2. The mean value of cluster 3 in all the parameters corresponds to size 3. The mean values for left and right foot for all the three sizes for female and male were tabulated in Table 4 and 5 respectively.

Table 4: Standardized foot sizes – Female

Parameters	**Size I**		**Size II**		**Size III**	
	Left	Right	Left	Right	Left	Right

Length (cm)	22.95	23.37	23.72	23.68	24.82	24.59
Breadth (cm)	9.20	9.03	8.90	9.00	9.90	10.04
Ball girth (cm)	21.62	21.83	21.3	21.67	23.70	23.75
Waist girth (cm)	21.50	21.83	21.00	21.58	22.90	23.50
Instep girth (cm)	25.00	25.50	23.33	23.92	26.00	26.55
Heel girth (cm)	30.42	30.42	29.50	30.00	32.45	33.00
Ankle girth (cm)	23.75	24.25	23.00	24.08	25.70	26.55
Calf height (cm)	33.50	33.33	31.33	31.17	33.70	33.50
Calf width (cm)	38.83	39.17	31.83	32.17	36.35	35.75

Table 5: Standardized foot sizes – Male

Parameters	**Size I**		**Size II**		**Size III**	
	Left	Right	Left	Right	Left	Right
Length (cm)	25.34	24.94	25.87	26.05	26.96	27.08
Breadth (cm)	9.44	9.76	10.26	10.54	11.12	11.06
Ball girth (cm)	22.50	22.63	24.11	24.45	26.00	26.41
Waist girth (cm)	22.50	22.67	23.58	23.92	26.25	26.03
Instep girth (cm)	25.50	25.79	26.37	27.24	29.44	29.56
Heel girth (cm)	32.33	32.38	33.63	33.66	36.50	36.50
Ankle girth (cm)	24.08	25.17	26.32	26.66	28.75	28.84
Calf height (cm)	34.17	35.17	35.37	35.21	35.69	35.63
Calf width (cm)	33.33	34.13	35.42	35.74	38.88	39.00

4. Discussion:

In a previous anthropometric study by T. Spahiu et al. (2015), 20 parameters were measured which includes length, breadth, height, circumference, girth and angles involved in the foot using 3D foot

scanner. The mean and standard deviation of right and left foot measurements shows that there was no significant difference between left and right. The mean and standard deviation of 9 parameters which was measured in this work also show that there was no significant difference between left and right, whereas the results of linear regression show that there exists an important difference between left and right of DFU patients (Table 2).

4a. IS 1638-1969 Vs. Derived Standardized sizes for Patients with DFU

IS 1638-1969 is the Indian standard specification for sizes and fitting of footwear. The English, American and Paris point are widely used sizing systems for making conventional footwear. The English size ranges from 1 to 12 for adults and 1 to 13½ for children. The Paris size varies from 33 to 47 for adults and 18 to 33 for children. The American size ranges from 2½ to 13½ for adults and 1 to 13½ for children. The size interval in English and American size is 8.5 mm whereas for Paris point it is 6.6 mm. According to IS 1638, there are six categories under which all the sizes will fall (Indian Standard Specification for sizes and fitting of footwear IS: 1638-1969). They are infants, children, Boys & Girls, Youths & Maids, Women and Men. We have considered the sizes of women and men for comparison purpose because the experiment population's age group will match better with this category. As per the standard, men fall under size 5 to 11 of English size and women fall under size 2 to 7 of English size. The corresponding English and French sizes with respect to the length measurement for the three standardized sizes derived from patients with DFU are given in Table 6.

Table 6: Corresponding English and French Sizes with respect to the length measurement

Standardized Size	**Corresponding English Size**		**Corresponding French Size**	
	Male	**Female**	**Male**	**Female**
Size I	6	3	39	36
Size II	7½	4	41	37
Size III	8	6	42	39

Human feet differ not only in length but also in its volume, i.e., for the same length, thin feet, fat feet and normal feet do exist (Mohan Kumar S 1999). According to Indian standard specification for sizes and fitting of footwear, there are five fittings for each size (Indian Standard Specification for sizes and fitting of footwear IS: 1638-1969).

When comparing the DFU patient's girth measurements with the girth measurements of standard sizes, it was observed that 63.157% (male) of girth measurements belong to XH fitting which implies that most of the DFU patients have broader feet which were already reported in a study by Chantelau E et al (2002). The standard sizing system says that G is the average fitting for Indian population. From the results, it was found that three standardized sizes of the male have 63.16% of XH fitting, and three standardized sizes of the female have 52.38% of XH fitting. Further, male standardized sizes have

15.79% of G fitting, 10.53% of F fitting and 5.26% of H fitting. The female standardized sizes have 4.76% of each E, F and G fitting; 23.81% of H fitting.

4b. Proportional Measurements of last

Last is the base for any footwear as it is the replica of the foot. The last has the critical measurements of foot required for making footwear. The derived standard sizes of DFU population are ultimately going to be used for making offloading devices like ankle foot orthosis which require a lower limb mould. So we need to compare the proportional measurements of conventional last with our derived dimensions for understanding the DFU population's feet dimension. The proportional measurements of last based on the French point system are (Indian Standard Specification for sizes and fitting of footwear IS: 1638-1969),

Length of the last (cm) = (French point x 2)/3

Fitting girth or ball girth (cm) = (French point + indicative fitting)/2

Instep girth (cm) = Fitting girth + 0.5 cm

Heel girth (cm) = Length of the last + indicative fitting

Ankle girth = Fitting girth - 0.5 cm

The six sizes derived from statistical analysis of DFU patient's data do not follow the proportionality mentioned above. The proportionality followed in the conventional sizing system was not observed within the standardized sizes. This disproportion shows that DFU patients cannot go with the conventional shoe sizing system, and they need a separate sizing system to fit in.

5. Conclusion

The three standardized size for male and female DFU patients derived from this study shows that DFU patients have broader feet and larger girths than normal subjects. These standardized sizes will be useful for fabricating off the shelf offloading devices like ankle foot orthosis and therapeutic footwear which in turn helps to save the time taken for making customized foot mould and offloading device. The time interval between prescription of an offloading device and initiating the treatment will be less if the offloading devices are readily available. This work can be further extended by taking more number of patient's data to get few more sizes that can include the entire population.

6. Acknowledgement

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Metric System

1. Length: cm – Centimeters; mm – Millimeters

2. Mass: kg - Kilogram

Symbols

% - Percentage

Abbreviation

DFU – Diabetic Foot Ulcer

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12. Indian Standard Specification for sizes and fitting of footwear IS: 1638-1969

DIP P-09

A NEW APPROACH TO DESIGN FOOTWEAR BASED ON FOOT BIOMECHANICS

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Footwear is an essential product for the entire population of the world. Although fashion plays an important role while designing footwear, comfort and functionality also needs to be considered. Last, the replica of foot is the base for any footwear on which the shoe will be made. The last will have the proportional measurements of foot in order to have a proper fit. The main purpose of footwear is to give protection and comfort to the feet while performing many activities like standing, walking, running, trekking, etc. The footwear should not hinder the respective activity. At present, this objective is achieved by providing the proper fit of the footwear. Proper fitting is achieved using anthropometric dimensions of the feet. Thus, feet dimension plays the vital role in providing fit and comfort to the user. But the biomechanics that are involved while performing particular activity is not considered while thinking about the fit and comfort. It is suggested to consider the Biomechanical actions involved in the feet before designing a shoe. It is challenging to consider all the mechanics involved in the feet for designing a footwear, because multiple movements are involved in each activity. Thus it is suggested to incorporate the kinetics, kinematics, electromyography of few important muscles and plantar pressure distribution data along with anthropometric data before designing footwear.

Keywords: Biomechanics, Gait, Footwear design, electromyography, plantar pressure

Introduction

Footwear is a protective and functional accessory. The three main objective of footwear is function, fit and comfort. Based on these parameters, product performance can be evaluated. The product design of footwear depends upon the trend and fashion rather than function and comfort. The fit of footwear is achieved by designing an appropriate base (i.e., last) on which the footwear is developed. This last will have proportional measurement of the foot in order to fit the footwear precisely. Human foot anatomy is complex and the shape of the foot for every individual will not be the same. Even the left and right foot is not identical in terms of dimensions. Thus, making the footwear perfectly fitting onto the foot is a challenging task for a footwear manufacturer. This fitting issue is mainly due to that the length and width of the foot alone are considered while manufacturing the footwear whereas girth measurements are rarely considered (Goonetilleke 2003). Further the use of footwear is not restricted only to the static conditions. It can undergo several dynamic movements during walking, running and other sports activities. But the dimension of 3D mould (last) out of which the footwear is made was measured in static condition. Thus the movements involved and the changes in dimension of foot while performing various activities are not considered while making the footwear. In order to consider the movement

involved while performing each task, 3D movement analysis need to be performed for understanding the movement pattern. The significant biomechanical parameters based on which the footwear need to be redesigned in order to provide fit, comfort and function to the wearer was identified with the help of present research work.

Materials and Methods

The methodology involves three main steps, first step understanding the biomechanics of human locomotion by conducting biomechanical analysis for a huge normal population whereas second step is categorising the population based on biomechanical data and the final step would be redesigning the footwear for each category. The anthropometric data was collected using 3D laser foot scanner (I-Ware Laboratory's INFOOT USB High Type, Model: IFU – H – 01). The BTS Smart DX motion analysis system integrated with two Kistler force platforms and two AMTI force platforms were used for performing 3D motion analysis. The data acquisition and processing was done using Smart Clinic software. The kinetic, kinematic and electromyography data was acquired and processed using BTS system. The Plantar pressure data was collected using BTS P-walk system during both static and dynamic condition.

The biomechanical data will be categorised and different groups based on biomechanics will be generated for which footwear designing will be done.

Results and Discussion:

The above said biomechanical data acquired from various instruments for 6 subjects are tabulated below. The male and female adult population within the age group of 35 years to 55 years are recruited for this study. The data is limited and for categorising the subjects there is a demand for more number of data. The data collection is still in progress for arriving at a precise conclusion.

Demographic data:

S No	Age (years)	Height (cm)	Weight (Kg)	BMI
1	50	161	71.5	27.58
2	55	168.6	82.5	29.02
3	49	164.1	71.8	26.66
4	54	164.1	78.9	29.30
5	38	160.7	49.6	19.21
6	44	156.9	67	27.22

Table 2: Demography of Subjects

It is understood from the demographic data that parameters which influence gait like age, height and weight are not widely distributed to categorise into groups. As the age increases, the weight of the subject increases. This may be due to reduced physical activity like walking. Due to the limited data, individual biomechanical data can be used to give guidelines for designing an appropriate shoe based on biomechanics.

Spatial Temporal Parameters:

S No	Stride length (m)				Step width (m)		Cadence		Stride time (s)			
	Right		Left						Right		Left	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	1.26	0.03	1.26	0.03	0.15	0.02	118.575	3.599	1.02	0.03	1.01	0.03

2	1.21	0.02	1.21	0.02	0.18	0.04	102.66	5.783	1.15	0.01	1.21	0.19
3	1.27	0.05	1.28	0.04	0.16	0.01	99.525	4.484	1.19	0.05	1.23	0.1
4	1.25	0.04	1.25	0.04	0.16	0.01	124.35	4.427	0.97	0.03	0.97	0.04
5	1.22	0.02	1.22	0.03	0.10	0	96.75	1.552	1.24	0.03	1.24	0.02
6	1.13	0.02	1.13	0.01	0.16	0.02	106	2.993	1.14	0.05	1.12	0.02

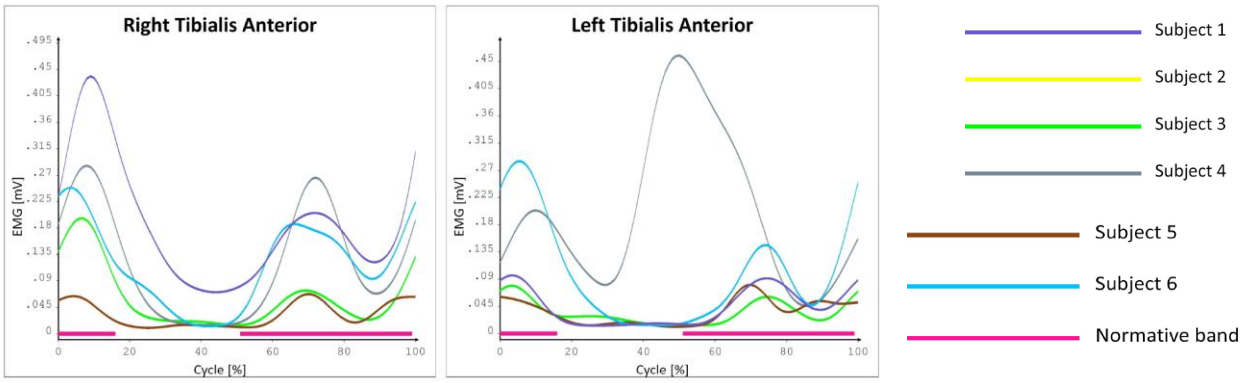
Table 3: Spatial Temporal Parameters of subjects

The spatial temporal data given in Table 2 reveals, there is no significant difference among the six subjects except the reduced stride length for one subject. This can be associated with the reduced height of the particular subject compared to other five subjects which supports the previous study by Landers et.al in 2011 that a positive correlation exists between height and stride length. The cadence i.e., number of steps per minute is widely distributed. The footwear sole design can be modified according to the cadence values i.e., for those who have less cadence, a rounded heel profile (as shown in the figure 1) can be given in their shoes so that the propulsion of foot will be improved which further increases the cadence. But the increase in walking speed is not guaranteed as per Myers KA et.al (2006). The other advantage of providing rounded heel sole is, either 15 degrees or 30 degrees heel flare will prevent maximum pronation and total rear foot movement compared to that of zero degree heel flare shoes (Clarke TE 1983).

Figure 1: Shoe with rounded heel

Electromyography:

Muscles are responsible for the joint movements. In walking biomechanics, ankle and knee movement plays a major role. Among that, footwear influences ankle biomechanics because of the fact that most of the footwear except boots are worn up to the ankle. The ankle dorsiflexion and plantar flexion are the significant movement while considering walking. The major muscles responsible for these two movements are tibialis anterior and gastrocnemius respectively.



Graph 1: Muscle activity of right and left Tibialis anterior

From the *Graph 1*, the activity of right tibialis anterior appears to be unique for each subject. Though the pattern of muscle action is similar the magnitude varies for each subject. This may be due to their physical strength. Also, except two subjects all others have their tibialis anterior muscle activity pattern different for right and left limb. An extended activity of dorsiflexor is noted in most of the cases i.e., even after 15% of gait cycle the muscle is still engaged which is not a normal pattern. Thus muscle activity can be altered by using heel and toe rocker profiles in sole of the footwear (Harris GF, 2000). It was suggested to use toe rocker alone to reduce the tibialis anterior activity during mid-stance (i.e., 10-30% of gait cycle) and increase the gastrocnemius activity during mid – stance. The plantar flexor muscle activity of left limb reveals there is a delay in muscle activity (from 30 - 50% of gait cycle instead of 10 – 50% of gait cycle) for three subjects. This can be initiated early by using toe – only rocker as shown in the *Figure 2*.

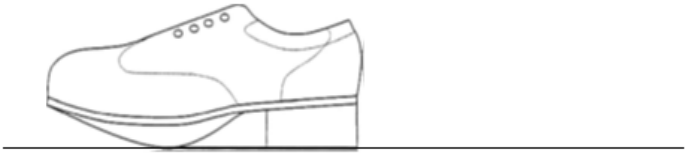


Figure 2: Toe - only rocker profile

Kinetic and Kinematic:

The ankle kinematics of six subjects during walking is given in *Graph 2*. The effect of rocker profiles is significant in ankle kinematics especially in sagittal plane (Hutchins, 2009). Thus we are concentrating on ankle dorsiflexion and plantar flexion data. From the Graph 2, the right ankle range of motion pattern for 4 subjects out of 6 tends to fall within the normal range. One subject had early onset of dorsiflexion during the mid-stance phase and the other subject had early onset, increased dorsiflexion and reduced plantar flexion throughout the gait cycle. In left ankle kinematics, the range of motion falls under normal range during initial contact for 5 out of 6 subjects. After initial contact and till the end of stance phase, almost 3 out of 6 subjects shown early onset and increased dorsiflexion. Only one subject has both dorsiflexion and plantar flexion in excess throughout the gait cycle. Thus, those who have reduced plantar flexion during terminal stance can be given a negative heel rocker in their footwear as shown in the *Figure 3.*

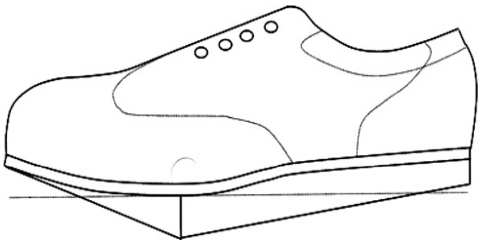
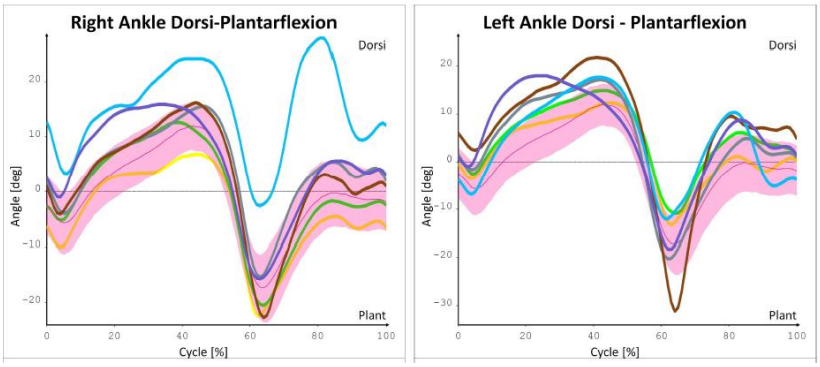
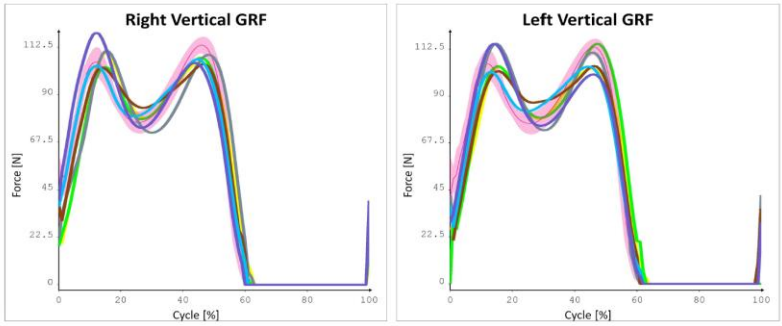


Figure 3: Negative heel rocker profile



Graph 2: Right and Left ankle range of motion during walking

Though the shoe influences internal joint moments and joint power involved in walking, we are considering the external ground reaction force for this discussion because the bottom of the shoe directly influences ground reaction force.



Graph 3: Right and Left Vertical Ground Reaction Force of six subjects

Graph 3 shows that, all the subjects achieved normal double peak pattern in both left and right sides. Thus based on this data it can be suggested to have all of them in one group but this is not possible because they differ in rest of the biomechanical characteristics recorded. According to Kerrigan (2014), impact force is important for maintaining bone density. Thus it is suggested to optimise the material properties of the sole to respond to the impact force and joint torques during walking.

Plantar Pressure:

The plantar pressure was recorded during both static and dynamic (walking) conditions and the average pressure all over the plantar area and surface area data is tabulated in *Table 3* and *Table 4*. From these data, it is understood that there exists a significant difference in average pressure and surface area between two conditions. The change in surface area from static to dynamic is not as much as the pressure value changes. This data found to have more significance in designing an in-sock material for any footwear. Presently customized in-sock or orthotics is made with the help of plantar pressure data as one of the input for patients who have lower limb problems. So by adopting the same method of considering plantar pressure data and foot scan data (for getting the actual bottom profile of the foot), the in – sock for footwear can be made using milling machine. This evidence based design of in – sock will provide better comfort for the wearer as it matches the exact profile of the bottom of foot. Also, from the plantar pressure data, the vulnerable location of the foot can be identified and given more concentration while designing the in –sock.

Static Condition:

Subjects	Average Pressure (Kpa)		Surface area(cm²)		Location of max pressure
	Left	Right	Left	Right	
1	45.6	41.1	102	97	Rt MH
2	41.7	47.4	118	117	Lt MH
3	36.7	41.8	108	109	Rt MH
4	44.3	48.5	105	112	Rt MH
5	41.9	50.6	86	76	Rt M3
6	54.5	46.4	90	100	Rt MH

Table 4: Static plantar pressure (Kpa) and surface area (cm^2)

From the static plantar pressure data, it was found that five out of six subjects load more on their medial heel out of which four subjects load maximum on their right foot and one subject on the left foot. This is a common pattern of loading more pressure on the heel area. Thus in – sock can be designed in two varieties in which one offloads the left medial heel and the other offloads the right medial heel. The surface area of the foot is inversely related to pressure. From table 3, it is understood that only 50% of the subjects have this inverse relation between their plantar pressure and surface area. This cannot be the conclusion as the number of data is minimum. The dual density foam material that can distribute the pressure all over the area can be optimized and used for fabricating the in – sock to achieve better comfort.

Dynamic (Walking) Condition:

Subjects	Average Pressure (Kpa)		Surface area (cm^2)		Location of max pressure
	Left	Right	Left	Right	
1	80.6	69.2	120	121	Lt M2
2	72.9	71.3	138	135	Rt M2
3	77.4	87	136	131	Rt M3
4	68.8	88.2	135	135	Rt MH
5	80.5	74.4	112	100	Lt M1
6	79.3	75	112	111	Lt M1

Table 5: Dynamic plantar pressure (Kpa) and surface area (cm^2)

Though the common pattern of loading the medial heel during static condition was observed in 83.33 % of the subjects, loading pattern during walking is not common for all the subjects. The maximum load was observed in various locations of the feet for each individual which implies, the walking pattern is unique for each individual. It was observed that five out of six subjects load their maximum pressure on the metatarsal area while walking. This is a common phenomenon because of the shift in centre of path of pressure from heel to toe during walking. Though the pattern of loading in metatarsals during walking is common, the difference was noted based on which metatarsal subjected to maximum pressure. The same subjects who have got the inverse relation between pressure and surface area during static don't have the same relation while walking. But the other subjects who doesn't have this inverse relation during static have achieved it during walking. Thus, by designing an in – sock which also provides better

comfort at the metatarsals along with medial heel will be the suitable product to manage both static and dynamic condition.

Anthropometric data:

The anthropometric data obtained from the 3D scanner was used to find the appropriate shoe size of the individual and the bottom profile of the foot can be extracted from the scanned image. The six subjects who are under the study have their shoe sizes in the range of French point 41 and 43 (IS 1638-1969) based on the length of their foot. This is not a significant distribution to categorise as far as shoe size is concerned because normally the adult shoe size ranges from 33 to 47. For categorising shoe size based on anthropometric data large volume of data has to be collected from groups of persons having same BMI.

Conclusion:

Though footwear is a fashion oriented product, it demands a lot of science and engineering for design and development. The influence of science along with engineering technique will provide a comfortable product to the end user. Thus, in that aspect the biomechanical data which can be measured using the latest technologies available are considered to give design guidelines for making the footwear. The importance of spatial temporal data, plantar pressure data and foot anthropometric data in designing a footwear are discussed in this paper.

Limitations:

This work is limited to very small group of people and considered only walking biomechanics. This work can be further extended with large group of people which may give new insights for shoe design and also can be extended to movement patterns of different activities like running, jumping and other sports activities and design the shoes for each activity.

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ECT P-38

RECOVERY OF SALTS FROM REVERSE-OSMOSIS-RETENTATE FROM DOWNSTREAM OF COMMON EFFLUENT TREATMENT PLANT PROCESSING TANNERY WASTES – A SUSTAINABLE SOLUTION TO SOCIETY

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The main focus in this work is to address the issues in evaporator at the downstream of effluent treatment plant from the tanneries operating in a typical cluster through analysis based on mathematical approach. Since Common Effluent Treatment Plant (CETP) undergoes separation of salts through Reverse Osmosis (RO) method, the reject streams are left behind for the further processing/ enrichment in a multiple effect evaporator. A dynamic model for the Seven Effect Backward feed Evaporator with bleed is developed and is validated using observed real-time data. To ensure the operational safety, a Model Predictive Controller (MPC) based on the resulting model is proposed for closed-loop analysis. Parameters such as temperature, mass flow rates, enthalpy of vapour & liquor, density of liquor, boiling point elevation for each effect were calculated. Using the estimated parameters, the mass and energy balance equations are formulated for the seven effect evaporator system. Open loop study was carried out to find sensitivity of parameters on performance of evaporator and on the behavioral dynamics of formation of nuclei for the growth of crystals. An advanced control technique known as Model Predictive Control (MPC) was then formulated and applied on the total system to control the crystal size. The MPC-controller requires the complete state information to be available for feedback and since this is often either very expensive (requires a great number of sensors) or at times even pose difficulty (difficult to measure), a full-state observer was implemented. The MPC was designed for disturbance rejection in the feed concentration. The performance of the MPC scheme was compared with conventional controller.

Keywords: Common Effluent Treatment Plant, Multi-effect Evaporator, Dynamic model, Model Predictive Control

Introduction: As per the recent statistics, 152 tanneries are present in Pallavaram area situated in Chennai, among them 150 tanneries are in the operating condition for processing raw hides/skin for the past several decades. Totally 9 tanneries are working on chrome tanning, 12 on wet blue and 131 tanneries on vegetable tanning method for the leather manufacturing[2] . Raw materials used are Buffalo/cow half hides and goat / sheep skin. In average, per day production of this cluster of tanneries touches 47,000 Kg. For treating the tannery effluents, Common Effluent Treatment Plant (CETP) is erected in 0.8 hectare area coverage. CETP at Pallavaram treats around 30-40 tonnes/day of waste water from the tanneries using Reverse osmosis technique. Reverse osmosis involves in the process of separating dissolved solid particles from industrial wastewater with the help of appropriate semi

permeable membrane to render pure water in edible form. The outlets of RO process includes RO Rejects (Molecules retained by the membrane) and Permeate (molecules passed through the membrane). High salinity of RO reject makes it difficult to dispose in local sewer facility. In such a case we need a treatment method proven to be inexpensive, reliable and efficient. Evaporators act efficiently in the conversion of water portion in RO reject into vapor leaving behind the higher boiling contaminants. Evaporators work on heat transfer mechanism which can be controlled by natural convection or forced convection methods. Evaporators are used to concentrate solutions or to recover dissolved solids. A solution containing a desired product is fed into the evaporator and is heated by a heat source like steam. Because of the applied heat, the water in the solution is converted into vapor and is condensed while the concentrated solution is either removed or fed into a next evaporator for further concentration. If a single evaporator is used for the concentration of any solution, it is called a single effect evaporator system and if more than one evaporator is used for the concentration of any solution, it is called a Multiple Effect Evaporator System. In a Multiple Effect Evaporator system, the vapor from one evaporator is led to pass into the steam chest of the other evaporator. In such a system, the heat from the original steam fed into the system is reused in the successive effects. Evaporation is also used in laboratories as a drying process where preservation of long time activity is required. It is also used for the recovery of expensive solvents and prevents their wastage like hexane [4]. If most of the wastes can be vaporized, the industry can greatly reduce the money spent on waste handling. The multiple effect evaporator system considered in the present work is used for the concentration of RO Rejects from the RO Reject Concentration plant at Pallavaram (PITIE). It consists of seven effects. The feed flow sequence considered here is backward and the system is supplied with live steam in the first effect and a part of vapor from the effect is used to preheat the liquor entering that effect in order to improve the overall steam economy of the system. The main objective of this work is to formulate a dynamic model for the evaporator system which can be validated with the real-time data obtained from RO Reject Concentration plant at Pallavaram (PITIE) and to design a MPC controller system with observer for Evaporator system in order to achieve desired system performance comparing the conventional control strategy. For the better understanding of the works carried out in this paper, contents are well organized in the following order, chapter 2 provides detailed problem description, chapter 3 has mathematical formulations based on mass and energy balance equations to determine transient response of the system, Process model identification is dealt in chapter 4 and design of controller in chapter 5 whereas results and discussion and conclusion part are drawn in subsequent chapters.

2.PROBLEM STATEMENT:

A seven-effect backward feed evaporator[2] is used for concentrating liquor with an input concentration of 3% to an output concentration of 35%. The schematic of multi effect evaporator is shown in Fig1 and the basic operating parameters are listed in Table1 . The feed flow sequence is backward, that is the feed is fed to the 7th effect, from there the liquor moves to the sixth effect, and from sixth to the next consecutive effects. Live steam is fed to the 1st effect only.

Table 1: Operating parameters for a seven-effect backward feed problem

S.No.	Parameter(s)	Value(s)
1	Total no of effects	7
2	Number of effects supplied with live steam	1
3	Sequence of feed	Backward
4	Sequence of steam	Forward
5	Cross sectional Area of each effect, A	2357 m^2

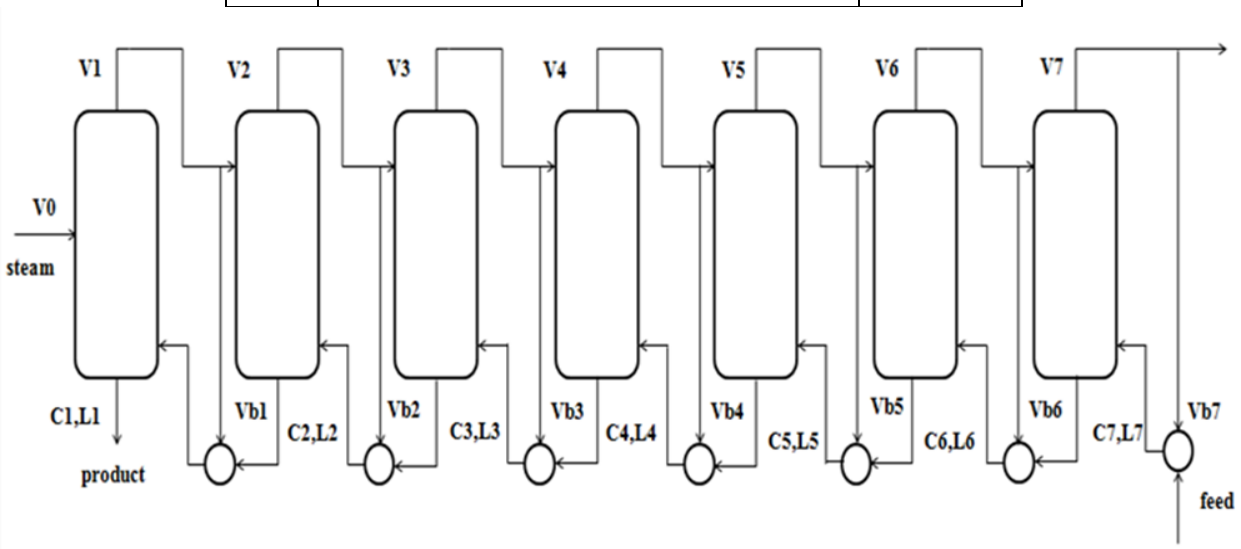


Fig 1: Schematic diagram of Multi effect Evaporator

Since there is no control system implemented for the concentration of RO rejects from CETP, it is necessary to address the issue with modelling, Identification and synthesis of controller .

3. Mathematical modeling of the seven effect back feed evaporator

The dynamic model of seven effect backward feed evaporator with bleed system of a **Common Effluent Treatment Plant** (CETP) is developed by using energy and material balance equations to study the transient behaviour of the system [2,3]. Each effect in the process is represented by a number of variables

which are related by the energy and material balance equation for the feed, product and brine flow. These equations are solved simultaneously to predict the time dependent parameters under various transients. In backward feed evaporator system the steam input is given in the first effect and the feed input is fed in the last effect. The material and energy flow for each effect is given in the Fig 2. The following assumptions are made to develop the model.

- The vapor and liquor in each effect are in equilibrium
- The vapor generated by the process of concentration of brine solution is saturated.
- The energy and mass accumulation in the vapor lump is neglected as it is very small as compared to the enthalpy of the steam.

The Mass balance for liquor in the i[th] effect:

$$\frac{d(ml_i(t)}{dt} = wl_{i+1} - wl_i - wv_i \tag{1}$$

The Energy balance for liquor in the i[th] effect:

$$\frac{d(ml_i(t) * hl_i(t)}{dt} = wl_{i-1}hl_{i-1} - wl_i hl_i - \left(wv_i - vb_i\right)hv_i + \left(wv_{i-1} - vb_{i-1}\right)hv_{i-1} \tag{2}$$

Where ml_i can be written as:

$$ml_i = a * pl_i * l_i \tag{3}$$

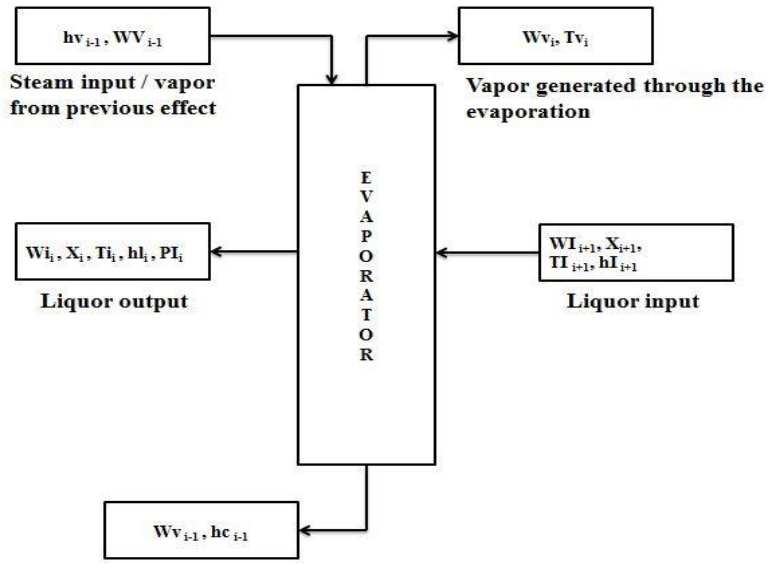


Figure 2 Evaporator schematics for i[th] effect

For the seven effect backward feed evaporator system, ordinary differential equations are formed based on the material and energy balance equations. The system of simultaneous ordinary differential equations given by equations are solved by Runge kutta method to obtain the following equations.

$$\frac{dx_i}{dt}=\frac{(c1\times c11\times c6 - c11\times c2\times c5 - c1\times c10\times c7 + c10\times c3\times c5 - c2\times c7\times c9 + c3\times c6\times c9)}{(c2\times c7 - c3\times c6 - c11\times c2\times c8 + c11\times c4\times c6 + c10\times c3\times c8 - c10\times c4\times c7)} \quad (4)$$

$$\frac{dl_i}{dt}=\frac{(c1\times c7 - c3\times c5 - c1\times c11\times c8 + c11\times c4\times c5 - c3\times c8\times c9 + c4\times c7\times c9)}{(c2\times c7 - c3\times c6 - c11\times c2\times c8 + c11\times c4\times c6 + c10\times c3\times c8 - c10\times c4\times c7)} \quad (5)$$

where a is the shell area, h is the enthalpy, m is the mass, W is the mass flow rate, i is the effect number, pl_i is the density of the liquor, l is the liquor, v is the vapor, x is the concentration of the liquid , l is the level of the liquid, C_i is the constant(i varies from 1to 11).

3.1 PARAMETER CALCULATIONS FOR THE MODEL

The various parameters that are required to develop the seven effect backward feed evaporator are as follows

1. **Mass flow rate of liquor and vapor** $wl_i = \frac{wf * xf}{x_i}$
2. **Vapor flow rate** $wv_i = wl_{i+1} - wl_i$
3. **Boiling point elevation** $bpe_i = 1.78x_i + 6.22x_i^2$
4. **Temperature of vapor & liquor** $tl_i = tv_i + bpe_i$ **where** Temperature of Vapor is obtained from the vacuum pressure of each effect.
5. **Density of liquor** $\rho=\rho_0+As+Bs^{1.5}+Cs^2$
6. **CONCENTRATION** $x_i=\frac{wf*xf}{wf-(wd*(k+1-i))}$

where $wd=\frac{wf-wp}{k}$ and $wp=\frac{wf*xf}{xp}$; xf=concentration of feed; wf=feed flow rate; xp=desired concentration of product; i = effect number; k= number of effects; x_i=concentration at i^{th} effect; T= temperature of liquor, s=concentration of liquor. The calculated parameter values are used for the model development of the seven stage back feed evaporator.

4. IDENTIFICATION OF TRANSFER FUNCTION OF THE EVAPORATOR SYSTEM

To compute the transfer function of the seven effect backward feed evaporator system, the system identification toolbox in the MATLAB is used [5]. The evaporator system itself as a whole is assumed to be a SISO model. The system identification toolbox is used to estimate and validate nonlinear model from

single-input/single-output (SISO) data to find the model structure that best suits the system dynamics. The transfer function model (relating exit concentration and steam feed rate) thus computed with 95.21% of best fitting percentage using the system identification toolbox is as follows

$$\mathbf{G(s)} = \frac{2.525}{12.5575s+1} e^{-6.7824s}$$

The actual evaporator system has inputs: steam pressure, cooling water feed rate and recycling feed rate. The outputs are: liquid level in separator in recycle path, product concentration and pressure in separator / recycle line. But we consider here only a SISO process as discussed above.

5. Design of state observer and MPC control algorithm

The closed-loop analysis of the seven effect backward feed evaporator with bleed requires measurement of the product liquor concentration. Since, the measurement is not directly available, a state observer is designed to compute the product concentration [7,8]. The block diagram representation of Evaporator system with controller is shown in fig 3.

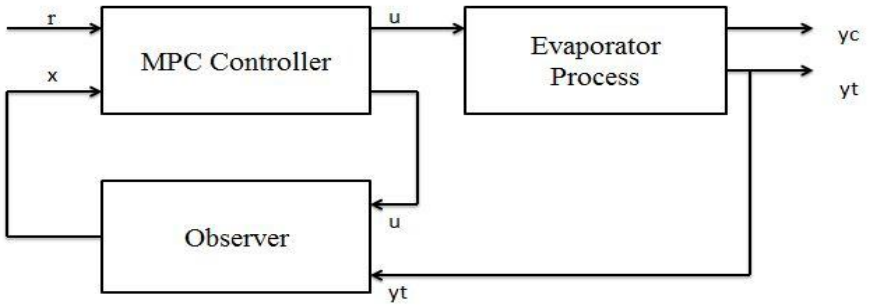


Figure 3: Block diagram of Evaporator Process with Controller.

Where r – Reference Value for Concentration; yt – Known State - Product Temperature; yc – Unknown State - Product Concentration; x – Estimated - Product Concentration; u - Input Steam Pressure

6. Results and Discussion:

The parameters required for the open loop analysis are calculated from the mass and energy balance equations. The calculated parameters are tabulated in Table 2

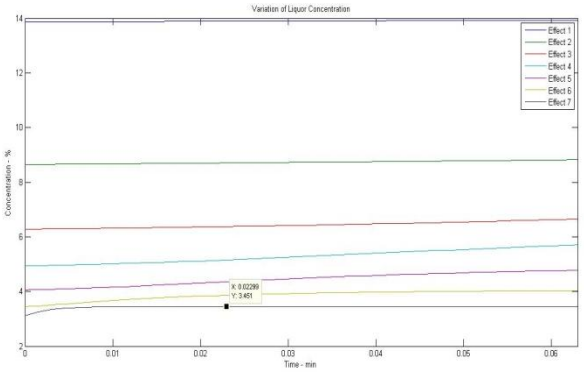
Table 2: Calculated parameters for evaporator

Effect no	C(%)	Bpe $(^{\circ}C)$	T$(^{\circ}C)$		W(Kg/s)		h$(KJ/Kg.^{\circ}C)$		ρ (Kg/m^3)
			L	V	L	V	L	V	
1	35.0000	1.3849	83.6227	82.2378	0.0005	0.8163	539.6557	3365.3	1253.8
2	13.8679	0.3665	80.6970	80.3305	0.0014	0.8163	520.4081	3351.4	1078.6
3	8.6471	0.2004	76.2955	76.0951	0.0022	0.8163	491.8447	3320.7	1040.0

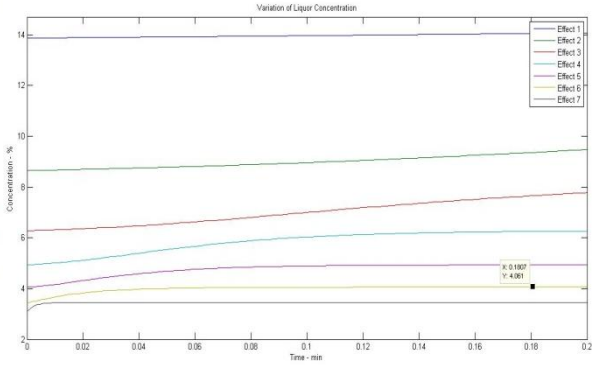
4	6.2821	0.1364	75.4430	75.3066	0.0030	0.8163	486.3656	3315.0	1022.6
5	4.9329	0.1029	66.6757	66.5728	0.0038	0.8163	430.9871	3252.6	1016.3
6	4.0608	0.0825	65.4589	65.3764	0.0046	0.8163	423.4367	3244.1	1010.5
7	3.4507	0.0688	41.6744	41.6055	0.0054	0.8163	281.8809	3080.4	1016.9

6.1 Mathematical modelling of the evaporator system

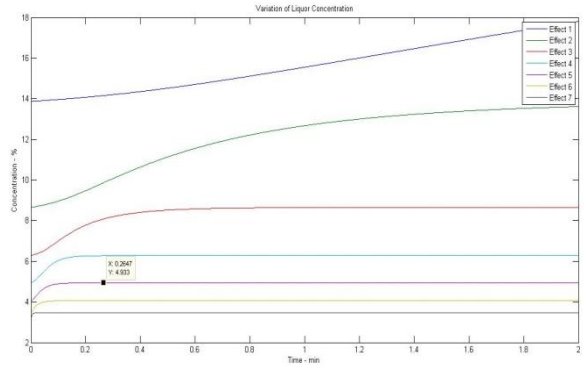
MATLAB codes have been developed to generate simulation results. The 4th order Runge-Kutta method is used to solve the differential equations obtained in the model. The open-loop evaporator performance simulation results for the liquor concentration in each effects and liquid level are presented below.



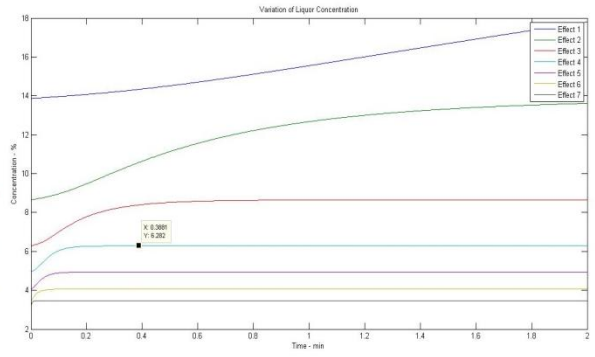
(a)Variation of liquor concentration in Effect 7



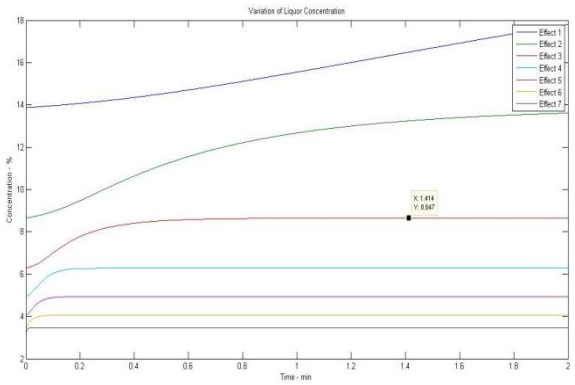
(b)Variation of liquor concentration in Effect 6



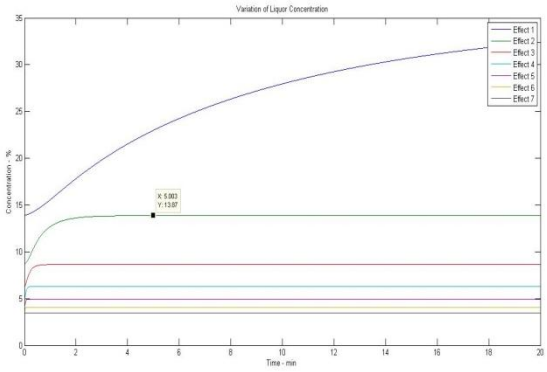
(c)Variation of liquor concentration in Effect 5



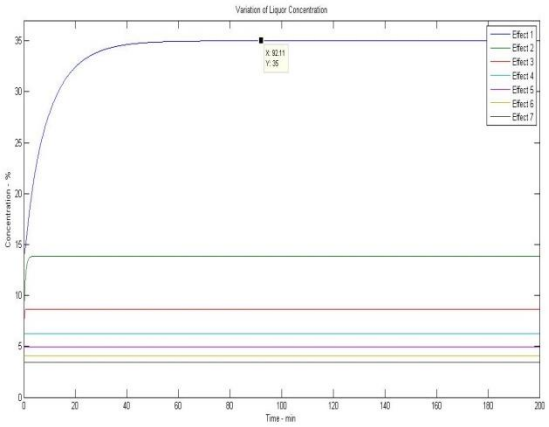
(d)Variation of liquor concentration in Effect 4



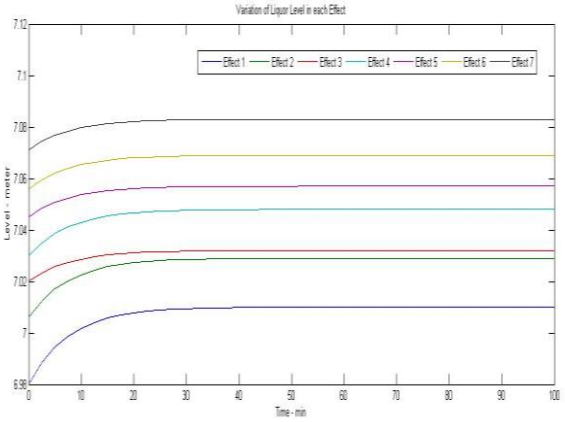
(e)Variation of liquor concentration in Effect 3



(f)Variation of liquor concentration in Effect 2



(g)Variation of liquor concentration in Effect 1



(h)Variation of level in each Effect

Figure 4 Modelling response of the Evaporator system

Steady-state level values of each effect obtained from the simulation results are Effect 1 –7.01m; Effect 2–7.02; Effect 3–7.032; Effect 4–7.048; Effect 5–7.057; Effect 6–7.069; Effect 7–7.083. From the simulation results (Fig 4) we can infer that the steady-state liquor level increases from the first effect to the last effect. This is because as we travel from the last effect to the first effect the liquor concentration increases, decreasing the overall liquid level content in the evaporator system.

6.2 VALIDATION OF THE MODEL WITH REAL TIME DATA

The model validation is used to test whether the developed model addresses the right problem, provides accurate information about the system being modelled and check whether the model can actually be used. Thus we validated our model based on the real time data obtained from the **Common Effluent Treatment Plant** (CETP) at Pallavaram and the result is presented below in the fig5

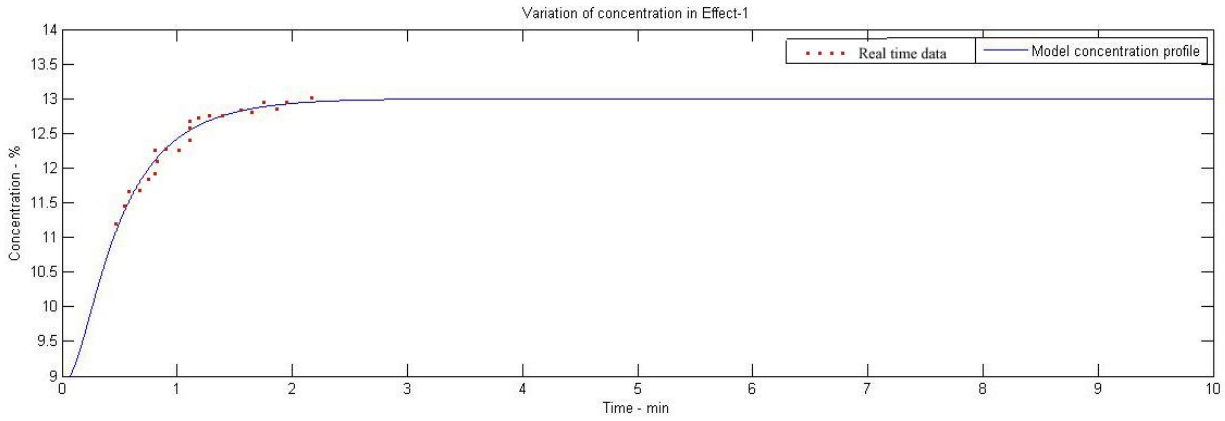


Figure 5 Validation of model with real-time data

From the figure 5 we can infer that the developed model closely follows the real time data.

6.3 Design of Model Predictive controller:

The following figures (Fig 6)show the response of the evaporator process under controlled condition.

6.3.1 MPC RESULTS WITHOUT NOISE

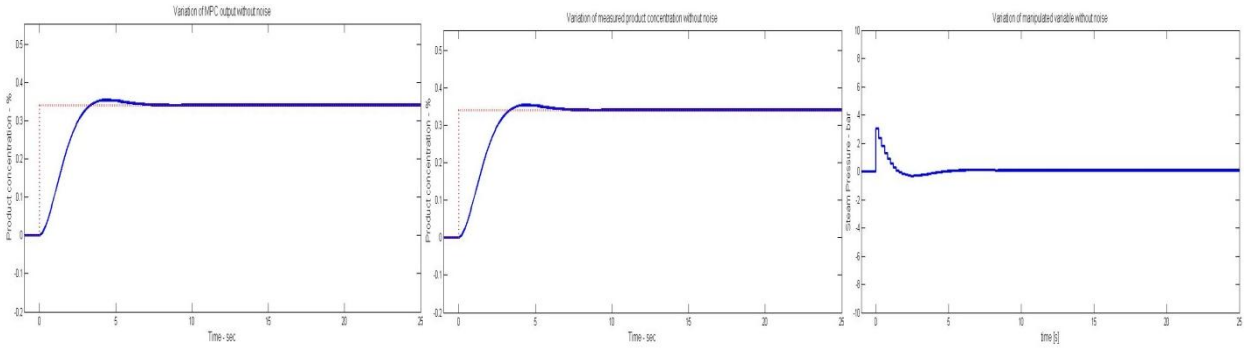


Figure 6: MPC Performance without noise. First: Variation in Product concentration wrt MPC Prediction using model. Second: Variation in Measured Product Concentration. Third: variation in Steam Pressure – Manipulated Variable.

Table 3 shows the performance analysis of controllers designed for the evaporator system.

Table 3 Performance Evaluation with different controllers

Performance Criteria	MPC	Conventional(PI)

IAE	3.0496	16.937

From the IAE values it is inferred that MPC provides better performance than the conventional PI controller. Comparative response is shown in figure 7.

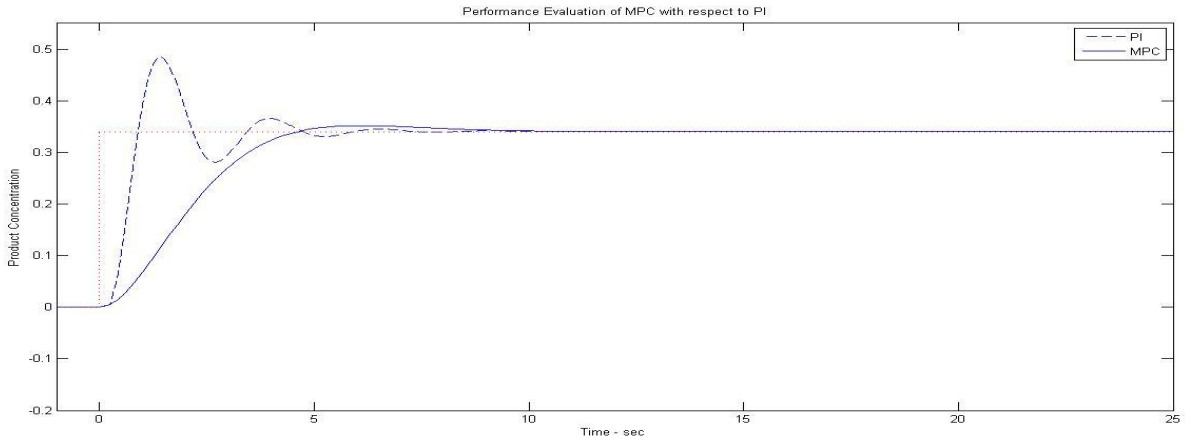


Figure 7: Performance evaluation of MPC

7 CONCLUSION

In the present work, modelling of seven-effect backward feed evaporator with bleed is done along with designing Model Predictive Controller. This control algorithm has been designed and tuned for disturbances rejection. The performance of this control algorithm is very satisfactory and is much better than the conventional control strategy. The model is successfully validated using the data obtained from the plant.

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SFS P-32

COMBINED AND SUSTAINABLE MANAGEMENT OF TANNERY EFFLUENT THROUGH A NOVEL BIOPROCESS METHOD

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Water resources are the significant source for the survival of living organisms. The effluent from leather industries contains many hazardous chemical components and complex biowaste that are toxic to the environment when they mix with water sources it damage the ecosystem. Hence, the present investigation was carried out to treat and manage the tannery effluent with a novel bioprocess using microbes and enzymes combination. Initially, the effluent was treated with enzyme an proprietary formulation that contain highly active enzyme mixture that helps in breaking down the large and complex biomolecules in to simple peptides. Subsequently, the treated effluent undergoes biomass utilization using microorganism is a combination of specialised microorganisms mixture effectively utilize the organic biomass that are already digested by enzyme. Then, in the third process, enzyme mixture was added to remove the odour form treated effluent. Practically, the entire effluent treatment process (ETP) was designed into three section, primarily, the enzyme was added at the concentration of 50 to 100 ppm mixed/stirred well for 30-60 minutes. Secondly, Microbes was added at the concentration of 20 to 50 ppm for 24 hours and enzyme mixture was added at the concentration of 500 to 1000 ppm for 2-4 hours. After completion of the bioprocess treatment, the physicochemical parameters are analysed compare to before treatment. The results indicated that combined bioprocess treatment had effectively reduced the TDS, TSS, BOD, COD, odour and colour of treated effluent.

Keywords: Bioprocess, Effluent treatment, Microbes, enzyme, odour

Introduction

The insufficiency of natural resources and the accumulation of pollution caused by industrial revolution have required the development of biological technology that is less harmful and eco-friendly to the environment. The concept of biological technology has been used in tanneries in order to mitigate their impact and reduce the usage of chemicals, water and raw materials (Dargo and Ayalew 2014). According to Rajamani et al. (2009), the world volume of leather processing is 15 million tons of hides and skins per year. The average wastewater discharge is more than 15,000 million liters/day. Solid waste generation from the tannery process is estimated at 6 million tons/year. The dumping of huge quantities of sludge, approximately 4.5 million tons/year, and effluent from treatment plants is a major issue. The amount and type of waste generated during leather production is variable and depends on numerous factors such as breed, slaughtering procedure, conservation of hides, and the technology used for hair removal

and tanning. Lime/sulfide is widely used in hair removal because it is more efficient and cheaper than other currently available technologies. Chromium salts are the most common tanning agents (Gupta 2003). The sulfur present in the effluent comes from organic matter (especially hair) and from compounds used in the processing of hides including surfactants and unhairing agents, such as sodium sulfide (Na2S). Sulfur is found in effluents in the form of sulfates and sulfides.

The hazard of hydrogen sulfide (H_2S) formation during effluent treatment poses a serious environmental problem. To avoid generating hydrogen sulfide from the effluent, the sulfide should be oxidized, which requires an additional step in wastewater treatment. The unhairing process can be performed using bacteria or chemicals such as hydrogen peroxide and sodium hypochlorite to oxidize substances (Thanikaivelan et al. 2005). Traditionally, tanneries apply enzymes in the bate step to achieve deep cleaning of the hide. However, enzymes were also used in the hair removal process at the beginning of the last century before the development of chemical processes for hair removal (Choudhary et al. 2004). These proteins are gaining more prominence because they are considered to be environmentally friendly technologies and because of advancements made in the purification, development and improvement of enzymes. Enzymes are currently applied at various stages of leather processing, from beamhouse operations until the final stages. (Dettmer et al. 2011, Alexander 1988, Taylor et al. 1987 and Feairheller 1985).

The main enzymes that are of interest to the leather industry are as follows: Proteases because they hydrolyze the protein fraction of dermatan sulfate, making the collagen more accessible to water and reducing the attachment of the basal layer. In addition, they act in the removal of globular proteins; ƒ Lipases, which hydrolyze fats, oils and greases, present in the hypoderm; Keratinases, which hydrolyze the keratin of hair and epidermis and break down the disulfide bonds of this molecule. In the last few decades, research on eco-friendly hair removal has increased substantially with the growing environmental awareness (Bhavan et al.2008). Enzymatic unhairing technologies are interesting because they can preserve the hair and contribute to a reduction in the organic load released into the effluent. These processes eliminate or reduce the dependence on harmful chemicals such as sulfide, lime and amines.

Biosurfactants are mainly produced by aerobic microorganisms in aqueous media and provides a wide range of advantages over chemical surfactants, such as biodegradability due to their simple chemical structure, environmental compatibility, low toxicity, which allows use in different industries such as leather, textile, cosmetic, pharmaceutical and food industry (Kapadia and Yagnik 2013). The Biosurfactant are highly selective for the industrial applications, due to presence of specific functional groups, allowing specificity in the detoxification of specific pollutants (Lawniczak et al. 2013; Banat et al. 2010). In addition, environmental friendly biopolymers could play an important role in leather processing industries. These polymers are produced from natural sources and readily biodegradable in the environmental conditions. Chitosan play a important role as fungal resistant coatings in the leather and fillers along with vegetable syntons. We are in the stage of experimenting chitosan in place of acrylic polymers.

The traditional processing of leather may contain restricted chemicals, but the usage of enzymes for leather processing will be eco-friendly in nature. In ancient days, the costs of enzymes are slightly higher than the chemicals. Currently, the costs of enzymes are cheaper than the chemicals, due to technical development in the field of biotechnology. Different types of natural sources contributing for the production of enzymes such as plants and microbes. The enzymes obtained from plants and microbes are highly stable, specific and easy to harvest. Application of these type of biological substances in leather processing, definitely it will help to reduce the usage of restricted chemicals and also the effluent from industries will be free from toxic substance and the usage of these biological substances will create the eco-friendly atmosphere.

Materials and Methods

Sample collection

The leather industry effluent samples were collected from different locations such as Ranipet, Dindugal, Ambur, Vaniyambadi and Kanpur. The effluent samples were directly collected from the effluent tanks. Samples were collected in sterilized container and transferred to the laboratory and stored in refrigerator at 4°C until further processing.

Isolation of bacteria

Isolation and enumeration of bacteria were performed on basal media such as Nutrient agar. The effluent samples were serially diluted up to 10-7 and one milliliter of the serially diluted samples were inoculated into media. All these media are supplemented with cyclohexamide (100µg/ml) to avoid fungal contamination. Inoculated plates were incubated at room temperature for 7days.

Effluent treatment process

Sample processing

The raw effluent samples were collected from equalization tank, the collected effluent was processed for primary screening to remove the macromolecules and solid particles. After primary screening, the effluent water samples were treated with lime powder to adjust the pH range from 8 to 8.5. After pH treatment the effluent samples were allowed to settle for the period of 1 hour. Then, the supernatant samples were collected for further studies.

Primary Treatment

The different types of enzymes were used for enzyme treatment such as protease, lipase and catalase. After primary treatment, the 500 ml of pH adjusted effluent supernatant was collected and treated with and without the combination of enzymes. The enzymes were added at the dosage of 50 to 100 ppm level, and allowed for the enzymatic reaction for the period of 3 to 4 hours with slow agitation. After treatment enzyme added effluent samples were allowed to settle for the period of 1 hour and the samples were analysed for COD.

Secondary and tertiary treatment

The enzymatic treated effluent samples were further treated with microbial process. The bacterial cultures were isolated from the industrial effluents. Further, the potential microbes were mixed with effluent sample for further digestion at the dosage of 20 to 50 ppm/ litre. Then, the samples were allowed for incubation with aeration for the time of 24-48 hours. After incubation, the effluent supernatant samples were collected for further process. Furthermore, in tertiary treatment the mixture of enzyme substances were added at the concentration of 500 to 1000 ppm in collected effluent sample to remove the smell and color. Then, the samples were analyzed for BOD, COD and other characterization studies.

Estimation of BOD and COD

The Biochemical oxygen demand 5-day (BOD) tests of effluent sample were carried out according to the method described in standard methods for examination of water and wastewaters. The inoculums was prepared by inoculating one loopful of all the individual potential bacterial isolates separately in 25 mL sterilized nutrient broth. The inoculated broths were incubated in an orbital shaker at 35°C for 16–24 hours so as to obtain actively growing mother cultures. After achieving the desired growth (1.2 optical density), the cultures were centrifuged at 7000 rpm for 15 min at 4°C. The cell pellet of individual bacterial isolates thus obtained was resuspended in 2 mL of same buffer and mixed at the time of performing BOD analysis of wastewater.

COD: A sample is refluxed in strongly acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced dichromate is titrated with ferrous ammonium sulfate to determine the amount of potassium dichromate consumed and the oxidizable matter is calculated in terms of oxygen equivalent.

Results and Discussion

Biodegradation as the biologically catalysed reduction in complexity of chemical compound (Alexander 1994). Microorganisms either takes organic pollutant as a sole source of carbon or else degrade organic compound in the presence of growth substrate, that is, use primary carbon as a source of energy. During the decomposition process the DO in the receiving water may be utilized at a greater rate than it can be replenished, causing oxygen depletion, which has severe consequences for the stream biota. Prevention of all these adverse consequences can be done by adopting efficient water pollution management strategies. Quantitative measurement of pollutants is necessary before water pollution can be effectively managed. Microorganisms are used in the monitoring procedures from last to many years. They are the eco-friendly degraders of the organic matter. Industrial wastes are probably the greatest single water pollution problem as they contain large fraction of organic matter which acts as substrate for microorganisms when released in to water course.

Isolation of Bacteria from collected effluent sample:

A total 64 no. of bacterial colonies were isolated from the collected effluent sample. After isolation of 64 bacterial isolates were chosen randomly from all 39 bacterial isolate on the basis of their growth rate. Selected individual bacterial isolate were then used as seeding material for estimating BOD and COD of industrial wastewater. The BOD in all cases was assessed and the results are presented. Among, the bacterial isolates only 15 to 20 isolates showed significant reduction of BOD and COD.

The effect of pollution strength in wastewater can be determined by measuring oxygen demand. The preliminary parameters for observing wastewater quality are COD and BOD. COD gives the total load either in the form of organic or inorganic. The BOD test has been widely measured the organic load of wastewater in terms of carbonaceous matter. Hence, it can give a far more reliable estimation of the possible oxygen demand that a waste will have on a river than a COD test. The defined BOD as a measure of oxygen required for the biochemical oxidation of the organic matter. Although the BOD test is not specific to any pollutant, yet it continues to be one of the important general indicators of the potential of a substance for environmental pollution of surface waters.

S.No	Bacteria Isolated from industrial effluent	BOD mg/L		
		Sample 1	Sample 2	Sample 3
1	Isolate 1	1989	1786	2012
2	Isolate 2	155	784	341
3	Isolate 3	693	982	756
4	Isolate 4	360	492	456
5	Isolate 5	590	742	498
6	Isolate 6	1538	1389	1864
7	Isolate 7	1869	1457	1961
8	Isolate 8	1373	924	1207
9	Isolate 9	989	981	765
10	Isolate 10	588	487	782
11	Isolate 11	1705	1621	1486
12	Isolate 12	2158	2678	3012
13	Isolate 13	335	548	559
14	Isolate 14	560	625	841
15	Isolate 15	1896	1769	1542
16	Isolate 16	789	621	486
17	Isolate 17	1387	1257	1104
18	Isolate 18	1308	1467	1238
19	Isolate 19	789	987	462
20	Isolate 20	1310	824	945

Table-1: Different types of bacterial isolates showed significant reduction of BOD (BOD mg/L)

Biological reduction of BOD and COD along with enzyme and Selected Consortia.

On the basis of the results obtained in the primary experiment, further selections were carried out according to the ability of the selected consortia and enzymes to biodegrade the constituents of effluent waste water. The mixture of enzyme treatment showed a partial reduction of BOD in waste water when compare to initial level. However, after enzymatic treatment there is no reduction of COD levels in waste water. After primary treatment with enzymes, the selected bacterial consortia were treated with effluents and incubated for the period of 24-48 hours. After incubation, the effluent supernatant samples were collected and analysed for BOD. In this study, the selected bacterial consortia showed significant reduction of BOD and COD. The microbial treatment showed prominent reduction of COD, whereas there is no reduction of COD in enzymatic treatment. In tertiary treatment, the treated effluents were further analyzed to remove using the odour and smell with the help of enzyme mixture. In this experiment, enzyme mixtures showed significant removal of color and odour.

S. No	**Summary of ETP Progress**								
1.	**Source of Effluent**	Sample 1		Sample 2		Sample 3		Sample 4	
2.	**Nature of Effluent**	WETBLUE		WETBLUE		WETBLUE		RAW HIDES	
		Initial	End	Initial	End	Initial	End	Initial	End
3.	**TDS (ppm)**	4390	3185	5819	3489	14290	11181	31600	23491
4.	**TSS (gm/L)**	2655	550	9832	673	2371	481	3025	542
5.	**BOD**	2437	208	1320	294	3581	345	3538	1402
6.	**COD (mg/L)**	3808	570	2088	1138.5	5689	1166	5800	3900
7.	**pH**	6.08	7.83	3.90	7.88	4.38	7.91	7.23	8.02

Table-2: Summarize the complete biological treatment of waste water using enzymes and bacterial isolates

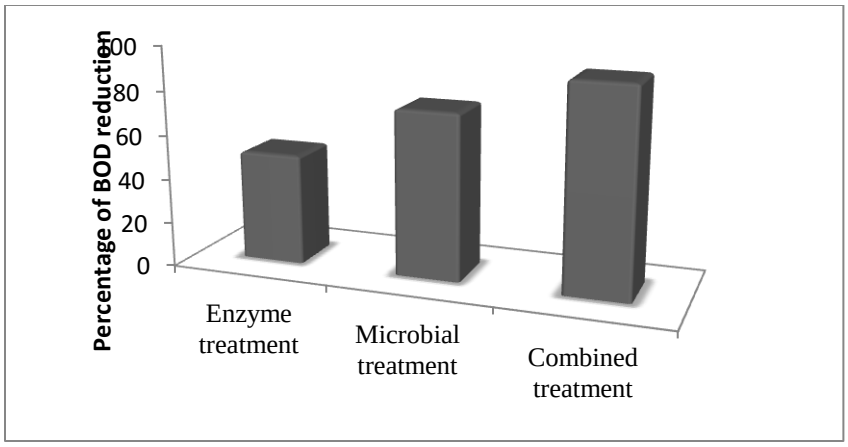

Figure-1: BOD reductions using enzymes, microbial and combine treatment of both enzymes and microbes

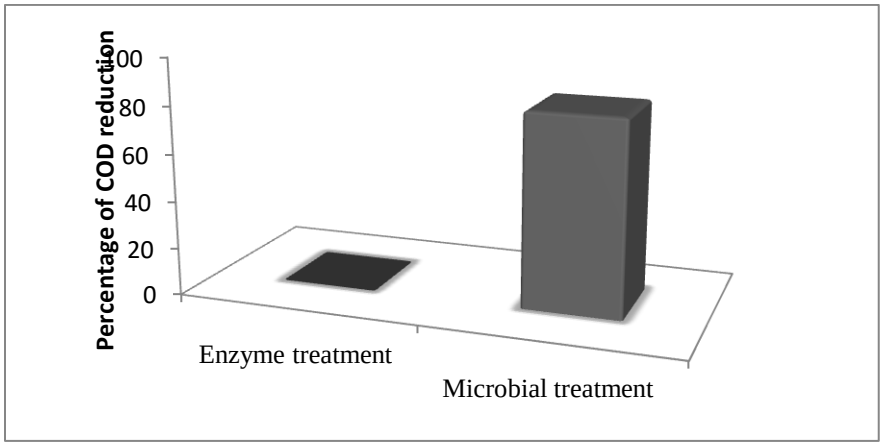

Figure-2: COD reductions using enzymes and microbes

Conclusion

This Bioprocess method was successfully applied on pilot plants to biologically treat the tannery effluent. This technology could be adopted for all large scale treatment plants without any modifications in infrastructure. We, at Caprienzymes bring a new path in effluent treatment process to support tannery industries and to protect the environment.

Acknowledgment

We would like to thank the Aura Biotechnologies Private Limited Chennai, India, for providing a technical assistance for the completion of this work.

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FLS P-16

LIME AND SULFIDE FREE UNHAIRING OF SKINS USING PROTEASE ENZYME AND SODIUM HYDROXIDE

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The conventional lime-sulfide based unhairing process followed in leather industry accounts for major pollution loads both in the form of gaseous and liquid pollutants. Use of proteolytic enzymes for the unhairing process can be observed as an alternative technique. Nevertheless, the two major shortcomings of enzyme-based unhairing are the exorbitant cost of enzyme and the need for stringent process control. Using cheaper agro industrial wastes like wheat bran for enzyme production reduced the cost of enzyme. The criticality of process control was minimized by using fermented bran directly for unhairing, which created a simple two step gradient process involving the transfer of enzyme from bran to process liquor and then from process liquor into the skin matrix. Drum based unhairing application was standardized as 20% enzyme (fermented bran) offer with 40% Hide-Float ratio and drum rotation speed of 5 ± 1 RPM at pH 9.0. The problem of lime sludge formation during the fibre-opening step was addressed by replacing lime with 0.5% sodium hydroxide. Further, the better strength properties of leather produced after enzymatic unhairing in comparison to that of the conventionally produced leather showed that the enzyme based unhairing system can positively replace the polluting conventional lime-sulfide method.

Keywords: Protease; Solid-State Fermentation; Unhairing; Lime-sulfide free; Sodium hydroxide

1. Introduction

Leather industry is one of the growing industries that use several chemicals to achieve its product of utmost quality. Leather manufacturing process includes pre-tanning, tanning, and post tanning and finishing. Leather manufacturing also leads to pollution generation. Of all the processes, 80% of the pollution is caused by the pre-tanning operation. Liming, a unit operation involves the usage of lime and sodium sulfide that adds up to the high COD and the hair that is removed as pulp contributes to the increase in BOD in the final effluent (Nancy et al 2014). The solubility of lime that is used for the plumping and opening up of the fibre structure of animal hides and skins is very low (1.3 g/ L) leading to the formation of lime sludge, which is another solid waste coming out of pre-tanning operation (Saravanabhavan et al. 2003). Resorting to enzymes from microbial origins has been considered as sulfide – free greener alternative for the purpose of unhairing (Dettmer et al. 2012). Protease enzymes are substrate specific enzymes that would help in achieving the objectives of liming operation. Although enzyme assisted unhairing processes have been researched for years, the unit cost of enzymes and stringent process control makes it unapproachable by tanners.

The present work deals with the possibility of using a protease enzyme that effectively dehairs the animal skin with fewer process controls. The production of unhairing enzyme was carried out using solid-state fermentation technique using *Brevibacterium luteolum* (MTCC 5982). Wheat bran, an agro industrial waste was used as the medium for enzyme production so as to reduce the cost of the final product. Sodium hydroxide based plumping up of animal hides and skins had been tried out to replace the lime in leather manufacturing.

2. Materials and Methods

2.1 Maintenance of the microbial culture

Brevibacterium luteolum (MTCC 5982) was previously isolated in the laboratory and its proteolytic activity qualitatively assayed on skim milk agar plates. The microorganism was sub cultured on the nutrient agar medium at 37 ^{0}C and stored at 4 ^{0}C. This culture was used for the production of protease enzyme using submerged fermentation technique.

2.2 Estimation of protease activity

Sigma's Non-specific protease assay was followed for the determination of the protease activity of the enzymes (Cupp-Enyard 2008). To 5 mL of 0.65% casein solution pre incubated at 37 ^{0}C for 5 minutes, 1 mL of enzyme was added and incubated at 37 ^{0}C for 10 minutes. The reaction was terminated by adding 5 mL of 110mM tricholoroacteic acid solution and filtered after incubating the solution for 30 min at 37 ^{0}C. For blanks, 1 mL of enzyme was added after the addition of TCA solution. To 2 mL of the filtrate, 5 mL of 500mM sodium carbonate solution was added along with 1 ml of Folin's reagent and incubated at 37 ^{0}C for 30 minutes. Absorbance of the sample was measured at 660 nm using a spectrophotometer. Tyrosine solution of concentration 10 to 100 µg was used as standard. One unit of protease enzyme activity was defined as the amount of enzyme required to liberate 1 µg of tyrosine under standard assay conditions. This activity was divided by fermented bran concentration (weight of fermented bran taken = 10 g, amount of water added = 100 mL; concentration = 0.1 g/mL) to obtain protease activity in terms of units per gram of fermented substrate.

2.3 Determination of Protein Content

Protein content of the cell-free supernatant was determined using Lowry's protein estimation (Lowry 1951). To 0.2 mL of sample, 2 mL of alkaline copper sulphate reagent (analytical reagent) was added.

The contents of the test tube were mixed well by inversion. This solution was incubated at room temperature for 10 min. Then 0.2 ml of Folin- Ciocalteau solution was added to each tube and incubated for 30 min. The UV-Vis spectrophotometer was zeroed with blank and the optical density (absorbance) of the solution was measured at 660 nm. The absorbance was recorded and the concentration of the unknown sample was found out. Bovine Serum Albumin (BSA) of concentration ranging from 0.05 to 1 mg/mL was used as protein standard.

2.4 Standardization of Unhairing process parameters

The unhairing process was segregated into two different modes of application based on the type of raw material used for the leather production. For skins that were of low thickness, unhairing was done by applying concentrated enzyme as paste. For hides, fermented bran was directly used for unhairing process in drum. The unhairing process parameters like concentrated enzyme offer and water for paste based application and enzyme offer level (fermented bran without any downstream processing), drum rotation speed and the Hide-Float ratio (amount of water offered during unhairing process based on the weight of the cowhide) for drum based application were standardized by visually analyzing the extent of hair removal from cowhides. The fermented bran was shade dried and stored at 4 ^{o}C prior to use. The process pH was optimized by measuring the activity of the enzyme at various pH. All the experiments were conducted in triplicates and the corresponding observations were made.

3. Results and Discussion

3.1 Unhairing enzyme production

The unhairing enzyme was produced using *Brevibacterium luteolum* (MTCC 5982) under solid-state fermentation using wheat bran and rice flour as the source of carbon and nitrogen for the growth of the microorganism. To 1 kg of wheat bran, 50 g (5 %) of rice flour and 1.2 L (120%) of tap water was added and sterilized. This medium was spread on a plastic tray pre-sterilized using ethanol and 15% w/w 24 h microbial pre-inoculum was added and kept in a sterile incubator at 33 ^{o}C for 96 h (Renganath Rao et al 2016). The fermentation medium was mixed thoroughly twice a day using a sterile glass rod to avoid anaerobic condition (Fig. 1). 5 g of fermented bran was taken after the completion of fermentation process and the enzyme was extracted in 25 mL of tris buffer (pH 7.4). The solid bran and the microbial cells were removed by centrifugation at 10,000 rpm for 10 mins. The protease activity of the supernatant was found to be 250 U/ mL. Thus the protease activity of the fermented bran was found to be 1250 U/g. The extracted enzyme was concentrated by lyophilization and the activity was adjusted to 350 U/ mL prior to unhairing application.

Fig. 1. SSF enzyme production on sterlised platic trays; Image from left to right shows the changes in visual appearance of the wheat bran on first and last day of fermentation process

3.2 Pasting based unhairing of sheepskins using concentrated enzyme

The casein solution was prepared in different buffer solutions of pH ranging from 5.0 to 10.0. The enzyme exhibited better activity at pH range of 7.0 to 10.0 with maximum activity of 346 U/ mL at pH 9.0 (Fig. 2). Thus the unhairing process pH was standardized as 9.0.

This pH was set during soaking process by addition of 0.1% w/w (based on raw material weight) sodium bicarbonate. The enzyme offer level was varied from 3% w/w to 9% w/w with an increment of 2% and the enzyme was made up to 10% w/w with water. All the w/w calculations were made based on the soaked weight of the sheepskins. This solution was applied on the flesh layer of the sheepskins and then piled flesh to flesh (Fig 3).

Fig. 2. Standardization of Unhairing process pH by validating the activity of enzyme at various pH

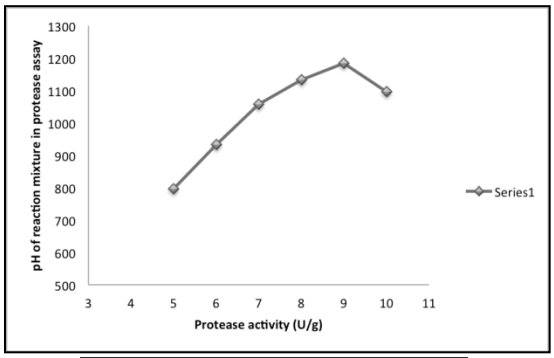
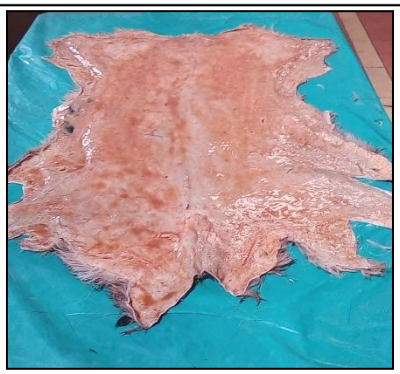


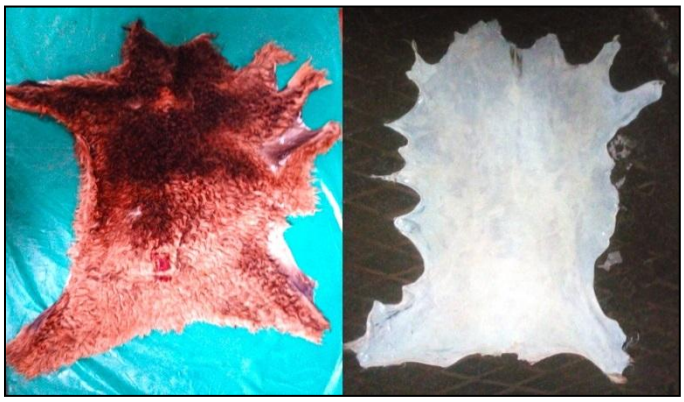
Fig. 3. Manual application of concentrated enzyme on flesh side of sheepskins



The onset of loosening of hair follicle was observed after 3 h of application with the enzyme offer greater than 5%.It was found that 5% of enzyme solution was capable of unhairing the sheepskin

completely after 6 h of application. 0.25% w/w wetting agent was added to ease the penetration of enzymes and 0.25% w/w preservative was added to prevent the microbial growth. The unhairing was done using blunt knife after 6 h of application manually and further processing was carried out. (Fig. 4)

Fig. 4. Pasting method of unhairing the sheepskins



3.3 Drum based unhairing of cowhides

3.3.1 Drum based unhairing of cowhides using concentrated enzyme

A set of 12 experiments was conducted in which the parameters like enzyme offer (3% to 9%), Hide-Float ratio (10% to 30%) and drum rotation speed (3 to 7 RPM) of the process were varied and its effect on unhairing process was studied (Table 1). Trial 1 resulted in incomplete removal of hair throughout the hide surface owing to low amount of enzyme offer level. Trial 2 resulted in improved degree of hair loosening after 4 h of drumming process but ended up with incomplete hair removal on neck and backbone regions of the cowhide even after running for more than 9 h. Trial 3 overcame all these shortcomings with the onset of hair loosening after 4 h of application with complete hair removal within 8 h. But as the enzyme offer increased with trial 4, formation of micro abrasions on the grain side of the cowhide was observed. Thus with the above findings, the optimum enzyme offer level was set at 7 %. Further to reduce the process time, the effect of other process parameters was studied. With trial 5, due to the reduction of hide-float ratio, the impact created by the mechanical action of the drum was clearly observed on the grain surface of cowhides as the micro abrasions started enlarging itself into bigger pores. But this problem was overcome with trial 6 where sufficient water level of 20% was available to absorb the impact caused. Hair loosening was observed after 3 h of application with complete hair removal in just 6 h. Thus the process duration was significantly reduced from 8 h of trial 3 to 6 h in trial 6. Trial 8 to Trial 12 was conducted to find out the optimum drum rotation speed in which the unhairing process can be carried out without affecting the grain surface. Trial 8 showed complete hair removal after 9 h of processing, as there was not much of mechanical agitation while Trial 12 showed complete hair removal in 5 h with high level of grain damage due to the excess mechanical agitation.

Process parameter	**Variation of process parameter**	**Process conditions**				**Experiment legend**
		Enzyme offer	**Hide-Float ratio**	**Drum rotation speed**	**pH**	
		(% w/w)	**(% w/w)**	**(RPM)**		
Enzyme offer	3	-	30	6	9.0	Trial 1
	5	-	30	6	9.0	Trial 2

(% w/w)	7	-	30	6	9.0	Trial 3
	9	-	30	6	9.0	Trial 4
Hide-Float ratio (% w/w)	10	7	-	6	9.0	Trial 5
	20	7	-	6	9.0	Trial 6
	30	7	-	6	9.0	Trial 7 (Trial 3)
Drum rotation speed (RPM)	3	7	20	-	9.0	Trial 8
	4	7	20	-	9.0	Trial 9
	5	7	20	-	9.0	Trial 10
	6	7	20	-	9.0	Trial 11 (Trial 6)
	7	7	20	-	9.0	Trial 12

Table 1. Standardization of drum based unhairing process

Trial 9, Trial 10 and Trial 11 (Trial 6) showed complete hair removal in 6 h without any damage to the grain surface. To further reduce the impact of mechanical agitation of drum on the hides, the drum was run intermittently (20 min for every 1 h). Thus the enzyme based unhairing process parameters were optimized as 7% enzyme offer with 20% Hide-Float ratio and drum rotation speed of 5 ± 1 RPM at pH 9.0 for complete unhairing process in 6 h.

3.3.2 Drum based unhairing of cowhides using fermented bran

The unhairing process parameters were followed as standardized by (Renganath Rao et al 2016) wherein the fermented bran itself was used as the unhairing agent. Unhairing process parameters using SSF enzyme were standardized as 20% enzyme offer (fermented bran as such without any extraction process) with 40% Hide-Float ratio and drum rotation speed of 5 ± 1 RPM at pH 9.0. The major advantage of this method is that the solid bran, which is present as a solid waste after the unhairing process, can be separated by filtering the process liquor in a metallic mesh filter and can be directly used as fuel for boilers present in the tanneries without any pretreatment.

3.3.3 Mechanism of drum based unhairing

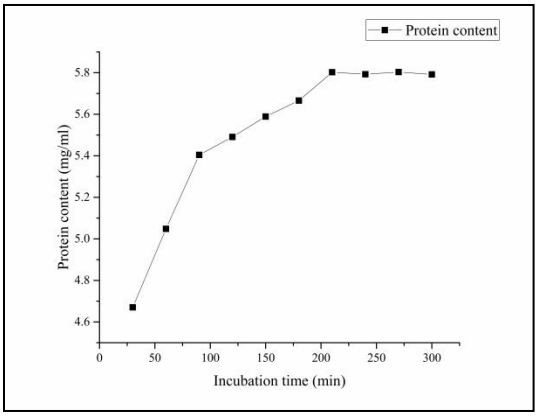
The rate of release of enzyme into solution is another important aspect as the whole fermented medium was used for unhairing. During unhairing, the enzyme needs to be released into solution and then it needs to penetrate into the hide network. The penetrated enzyme then reacts with proteoglycan of the hair bulb and disintegrates the latter (Sivasubramanian et al 2008).

The protein leaching profile revealed key information on how the transfer of enzyme from the fermented bran takes place resulting in the unhairing of hides. It was found that mechanism of unhairing of hides using fermented bran followed a two-step gradient process wherein the first step involved the transfer of enzyme from fermented bran into the process liquor and the second step involved the transfer of enzyme from process liquor into the hide matrix. In first step as the concentration gradient was initially high, the leaching rate of protease from fermented bran was higher during the first 2 h. With progress in time, the enzyme-leaching rate attained a maximum saturation level. In step two, as the protease enzymes penetrates into the hide network through a concentration gradient between the hide matrix and the process liquor leading to decrease in concentration of protease enzyme in process liquor. This again restarts the step one to maintain the enzyme leaching gradient between the

fermented bran and the process liquor. Thus a cycle of enzyme leaching from fermented bran into process liquor and from process liquor into hide matrix takes place in a controlled manner. The enzyme leaching profile followed a polynomial trend of $Y= -2E-05X^2 + 0.0115X + 4.4265$ with R^2 value of 0.9741 where X= Time in min and Y= Protein content in mg/mL.The enzyme release studies showed that the total time of 210 min was required for the complete release (Fig. 5). This regulated release of enzyme ensured the availability of optimal quantity of enzyme for unhairing process and therefore the action of enzyme on substrate was not drastic. This facilitates lowering of criticality of process control.

For the purpose of fibre opening, the unhaired hides and skins were dipped overnight in 300% w/w water with 0.5% w/w sodium hydroxide. Next day the hides and skins were acidified to pH of 3.0 and chrome tanning was done. The chrome-tanned leathers were converted into crust leathers and its physical properties were tested.

Fig. 5. Protease enzyme leaching profile from fermented bran into process liquor



3.4 Physical testing of the crust leather

Property	Result		CLRI recommendation	Test method
	Enzymatic Unhairing	Conventional Unhairing		
Tensile Strength, N/mm^2			Min 15.0	SATRA TM 43:2000
Along	21.4	20.4		
Across	15.6	17.0		
Elongation at break, %			40 - 80	
Along	41.7	46.7		
Across	49.7	53.6		
Tear Strength, N			Min 40 (Thickness 1 mm)	SATRA TM 162: 1992
Along	40.6	42.7		
Across	32.1	34.7		

Lastometer				
Load at grain crack, kg	30.3	26.0	Min 20.0	SATRA TM 24: 1992
Distension at grain crack, mm	11.0	9.99	Min 7.0	

Table 2. Properties of leather made after enzymatic and conventional unhairing method

The crust leather produced by both the conventional method of lime sulfide unhairing system and enzymatic unhairing system was tested for various properties like tear strength, tensile strength, grain crack and elongation at break was determined by standard procedures (Table 2). It was found that the properties of the crust leathers from enzymatically unhaired skins were in par with the conventional leather manufacturing process. This proved that the enzymatic unhairing as in both paste form and in drum method could completely replace the conventional lime-sulfide system.

4. Conclusion

Protease from *Brevibacterium luteolum* (MTCC 5982) exhibited excellent capability towards unhairing the hides and skins in leather processing. Unhairing process parameters for paste-based application were standardized as 5% concentrated enzyme with 5% water and 0.25% wetting agent and 0.25% preservative. Drum based unhairing application was standardized as 20% enzyme offer with 40% Hide-Float ratio and drum rotation speed of 5 ± 1 RPM at pH 9.0 in case of using fermented bran directly. The enzyme offer and hide float ratio for concentrated enzyme based drum application was standardized as 7% and 20% respectively. The better strength properties of leather produced after enzymatic unhairing showed that the enzyme based unhairing system can positively replace the polluting conventional lime-sulfide method.

5. Acknowledgement

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INVESTIGATIONS ON IRREVERSIBLE DEFORMATION PROPERTIES OF LEATHER

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In the premium sector of upholstery and automotive interior genuine leather material is well established for applications. Affected by users body weight as well as exposure to heat and moisture the leather material is intensively loaded during usage. Consequently, relevant deformations can occur. Next to an unaesthetic appearance, resulting waves and wrinkles induce a reduction of comfortability. Potentially, premature failure is caused to the covering material. In consequence, customer complaints are associated with high costs to the industry.

The quantification of an appropriate elongation and relaxation behaviour of leather by means of relevant parameters like elasticity, viscoelasticity and permanent distortion were investigated. Leather specific deformations were examined in pre-defined application adapted test scenarios by adjustment of different loading modes and constructional upholstery setups as well as varied microclimatic conditions. In order to evaluate leather qualities, compared to standard physical leather testing a more close to reality test method is introduced and a newly developed testing instrument is presented.

Keywords: leather, structure-property relationship, deformation, elongation, elasticity, viscoelasticity, permanent distortion.

1. Introduction

Genuine leather material is well established for premium applications in both, upholstery and automotive interiors, respectively. Affected by users body weight as well as environmental heat and moisture impact the leather material is intensively loaded during usage. Consequently, relevant deformations in leather (mainly in the seating area) can arise. Next to an unaesthetic appearance, resulting waves and wrinkles induce a reduction of comfortability. Potentially, premature failure is caused to the trim material. In consequence, customer complaints are associated with high costs to the industry.

Among others, variations in leather properties are caused by local, structure-related distinctions (structure-property relationship).[1] With respect to the heterogeneity in leather's physical properties as well as economic constraints in material testing in general, quantification of, for example, leather's elongation and relaxation properties in quality management established standardised testing methods is still not sufficient. In contrast to large-area leather applications, physical leather testing for quality

control issues is performed using a limited number of small sized specimens, however, exhibiting the properties of the respective area of sampling only. Detailed and statistically reliable data within the whole leather material cannot be generated. Besides, in some arrangements of standardised test protocols the way of specimens loading in whole or in part differs compared to real loading scenarios (e.g. tensile test). In addition, material testing of leather is performed under defined standard climate conditions (e.g. 23 °C / 50 % rel. humidity). Variations in environmental temperature and humidity conditions while loading are (mostly) not in the scope of consideration.

In order to overcome these limitations, a new test method for the determination of elongation and relaxation properties of leather under compression stress was developed. The new testing approach incorporated loading scenarios with practical relevance as found in upholstery and automotive interior trim applications. In accordance to the designated application, appropriate sized leather specimens were tested. By use of an automatically operating testing instrument, continuous force-deformation curves were recorded. The relevant single parameters of elasticity, viscoelasticity as well as permanent distortion could be extracted for leather qualification. In particular, leather's deformation properties affected by varied microclimatic conditions of temperature or/and moisture while compressively loaded were analysed. Based on the methodology developed, a multiplicity of individual leathers in various qualities as well as leathers with varying constructional upholstery setups were examined.

2. Material and Methods

The investigations were performed using a new designed test device featuring automatic operating units for controlling as well as data recording and evaluation (Figure 1). The instrument was developed in collaboration with the company of ZINS Ziegler-Instruments GmbH.[2] In general, multiple variations of compressive load and microclimatic conditions could be applied to the material. The rate of load ($F_{max.}$ 1000 N), the load duration and the type of loading are adjustable. Two types of pistons (50 mm, 200 mm diameter) for compressive stress application are available. By using the 200 mm piston and therein-integrated heating elements an external partial heat treatment was applied to the leather material. By continuously detecting the force-deformation curves, information on the elongation and relaxation behaviour were available each time of the measurement.

Figure 1: Schematic depiction of the test device for determining leather's elongation and relaxation properties.[2]

Leather fixation was implemented by a special designed spring frame allowing the clamping of samples with an effective test area of (400 x 400) mm. The apparatus design ensures a uniform and reproducible adjustment of sample clamping. In addition, the frame allows a wide range of experimental setups of both leather without and leather with padding of, for example, PUR foam and non-woven materials.

For the investigation of the elongation and relaxation properties, various types of leather were used. Next to standard upholstery qualities, leathers which tend to premature stretching as well as stretch resistant articles were procured. Sampling was carried out according to a methodology already established in previous research projects.[3] For observation of thermal or/and microclimatic effects to the leathers, external heat treatment of temperatures of 23, 50 or 70 °C were applied to the sample's surface. The moisture was applied by placing a defined moistened cotton cloth on the leather surface. The degree of moistening could be adjusted accordingly.

3. Results and Discussion

Prior to the definition of the loading scenarios to be considered, on-road tests were performed in order to analyse common stress cases affecting the use of leather in upholstery and automotive interior trim applications. Thus three basic types of mechanical loading could be identified:

- **[A] Statical** (single long-lasted loading, followed by longer release phase):
  200 mm piston, static 500 N load, 1 h stress, 3 hrs release, 5 repetition.
- **[B] Periodical** (repetitive cyclic loading):
  200 mm piston, alternating 500 N load/zero load, 60 s each, 1 h stress, 3 hrs release, 5 repetition.
- **[C] Impulsive** (impact loading, single cycle with maximum force amplitude):
  50 mm piston, static 500 N, 1 h stress, 3 hrs release, 5 repetition.

Based on the stress scenarios determined, specific algorithms needed for test sequence description for test device implementation were generated. Corresponding to the respective type of load application (statically, periodically, impulsive), load cycles were generated individually by sequences of partial phases.

The operating instrument recorded all force-deformation curves continuously. The leather sample specific parameters like viscoelastic deformation of the stress phase (ε_1) as well as elastic deformation (ε_2), viscoelastic deformation (ε_3) and permanent deformation (ε_4) of the release phase could be extracted for the qualification of leather's elongation and relaxation properties (Figure 2). Parameter (ε_4) reflects the irreversible deformation properties of leather and is further used for quantification of the tendency to form waves and wrinkles.

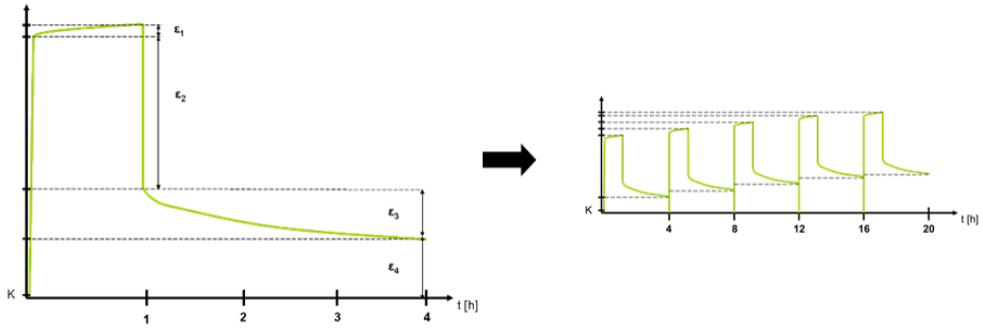


Figure 2: Parameters for the determination of elongation and relaxation properties of leather: single load cycle (left), sequence of five load cycles (right).

Initially, the reproducibility of the applied test method was determined using statical scenario type [A]. For these experiments, instead of leather coated textile material was used as reference material. The measurements revealed minor variance (high reproducibility).

For leather materials tested statically, within the different sampling positions of the same hide no significant differences on irreversible deformation properties could be found. Due to the sample size of (400 x 400) mm, sample-specific (local) structural inhomogeneity showed less influence on the deformation properties. However, significant differences were found evaluating (ε_4) of various leather articles of both same and varied batches, respectively. Nevertheless, a distinct influence of leather thickness on the deformation properties could not be identified, as the samples showed slight thickness variations only. In general, leather materials exhibiting lower thickness are more deformed.

In addition, repetition of individual statical test cycles were performed (Figure 3). The consecutive sequence of test cycles permitted the investigation of temporal changes in the material properties like material fatigue phenomena. Increasing the number of test cycles, the proportion of the permanent deformation increased, characterised by an additive behaviour. Accompanied to the increasing proportion of the irreversible deformation (ε_4), decreasing proportions of (ε_2) and (ε_3) were found. The decline of the total relaxation capacity of the leather and the increasing material fatigue phenomena induced the formation of waves and wrinkles.

In contrast to statical loading [A] or periodical loading [B] scenarios, for impulsive loading [C] a size reduced piston of 50 mm in diameter was used. Accordingly, by applying the same load (F = 500 N) the resulting compressive stress to the material is highly increased. Whereas loading procedures [A] and [B] exhibited similar results in irreversible leather deformations, significant changes in elongation and relaxation properties occured if impulsive loading of type [C] is applied (Figure 3).

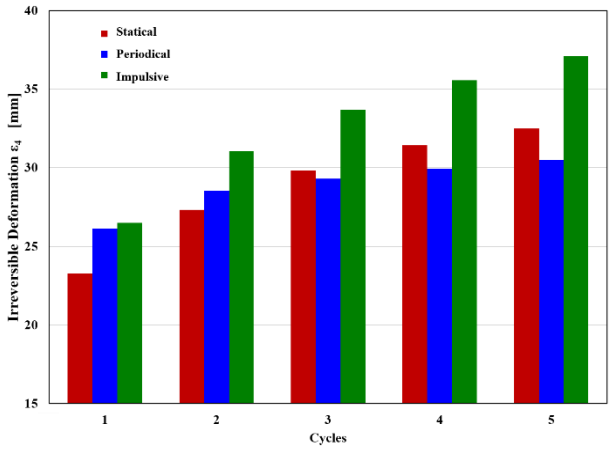


Figure 3: Statical, periodical and impulsive loading results for comparison.

As explained previously, an essential feature of the test apparatus is the possibility of examining the expansion and relaxation properties of complete multiple padded structures. Using the developed spring frame for fixation, an experimental arrangement consisting of the leather sample to be analysed as well as a PUR foam material and a polyester non-woven could be set up. The results indicated a markedly reduced irreversible deformation of the leather under PUR foam cushioned conditions. The elastic material properties of the PUR foam were dominating the complete experimental set up (Figure 4). Furthermore, individual differences between leather samples were less pronounced.

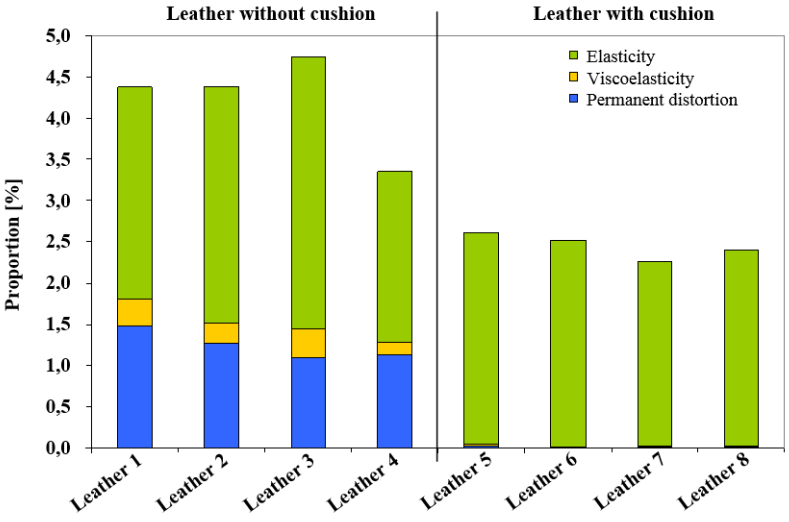
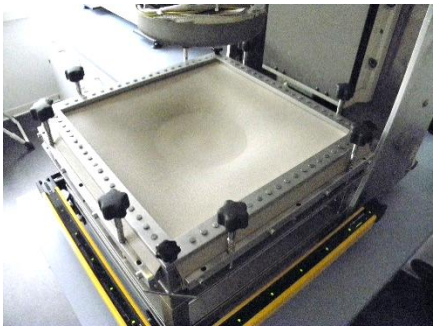


Figure 4: Comparison on proportions of elastic, viscoelastic and irreversible deformation properties of pure leather and leather cushioned with PUR foam, applying statical load type [A].



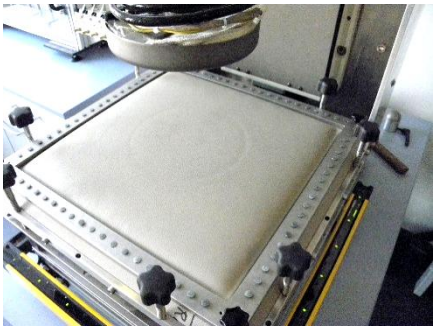


Figure 5: Images of clamp-fixed leather samples after five test cycles without (left) and with PUR foam cushion (right).

The influence of temperature increase on the elongation and relaxation properties was analysed. In the range under consideration (23, 50 and 70 °C), no significant effect on leather sample properties could be observed. By trend, the permanent deformation slightly decreased with increasing temperature. Low drying effects could suppress irreversible sliding of the leather fibres under load and thus favour the effect of the (visco-)elastic material properties of the leather.

The content of moisture influenced the stretching and relaxation properties. The irreversible deformation increased significantly with the increase of the moisture level. Water between the leather fibres acts as a lubricant and thus reduce the frictional resistance. Fibre sliding can occur more easily, which was reflected in a higher leather deformation. Repeated moisture input led to an even higher deformation.

4. Conclusion

The newly developed testing instrument associated with the generated test procedure are well suited for the investigation on elongation and relaxation properties of leather. Analysing a wide variety of types of upholstery leather, specific parameters of elasticity, viscoelasticity as well as permanent distortion were extracted for leather qualification. Compared to standardised mechanical test procedures, considering different types of loading scenarios, varied padding arrangements as well as thermal and microclimatic loadings a new method of more relevant to the application of leather testing could be established.

5. Acknowledgements

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