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Ionic liquids: new age materials for eco-friendly leather processing

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The manufacture of leather is a challenging and complicated process, which converts natural biomaterial to various high end applications. There are several stringent regulations in processing this natural biomaterial skin due to the discharge of effluent and impact on environment. In this study, an attempt has been made to use ionic liquids to remove inter-fibrillary materials from the skin. Cleaner leather processing is a new avenue to explore the existing pollution complications during leather manufacture. Herein, an ionic liquid, 1-butyl-3-methylimidazolium chloride, is used as a fiber opening agent. Conventional reliming process was avoided by the treatment of molten salt. Enzymatic unhairing methods have been adopted for the removal of hairs from the skin. After the complete removal of hair, the pelts are treated with various concentrations of molten salts by the drum method. The pelts treated with low concentrations of molten salts showed better appearance and there was no damage to the pelts. After the fiber opening process, the pelts were subjected to conventional chrome tanning and post tanning processes. The shrinkage temperature of the experimental leathers is around 108–116 °C. The physical strength characteristics like tensile strength, tear strength and grain crack index of crust leathers meet the standard norms. Morphological studies ascertain that there was no grain damage and coalescence of fibers. These results show a promising venture for the use of ionic liquid for leather manufacture. This study signifies the role of ionic liquid in the tanning industry and gives a new dimensional approach to existing cleaner processing systems.

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1. Introduction

Pretanning processes/operations from soaking to bating adopted for leather processing mainly intend to purify collagen, which is the leather making protein.[1] Liming is one of the important pretanning processes for the removal of hair, flesh and splitting/separation of the fiber bundles physico-chemically.[2] Hair can be either digested or mechanically removed after loosening by chemical means (conventional process). The conventional lime-sulfide process produces a large amount of sulfide, which is toxic to health and difficult to dispose.[3] Moreover, the pretanning process leads to the destruction of hair, causing increased COD (Chemical Oxygen Demand), BOD (Biochemical Oxygen Demand) and TDS (Total Dissolved Solids) loads in the effluent.[4] Enzymatic unhairing causes loosening of hair by the selective breakdown of cementing substances and presents a hair saving approach.[5] However, the application of enzymes requires special training for workers. Apart from liming, the other important process in pretanning is bating, which aims at the removal of some of the inter-fibrillary materials mainly proteins and proteoglycans. It is facilitated by the use of proteolytic enzymes.[6] The conventional method employed for fiber opening is the use of lime. Lime is applied through various methods using pit, paddle, drum and painting on the flesh side. Lime increases the pH to 12–13, resulting in osmotic swelling of the skin. There is loosening of the fiber bundles and separation of unwanted inter-fibrous materials due to the hydrostatic pressure created. The advantage of the conventional liming method is that it does not require any special labor skills and is cost-effective. However, this method poses significant environmental risks by generating lime sludge, thereby decreasing the efficacy of industrial effluent treatment plants. Hence, there is a need for the intervention of modern science in the traditional sector along the same lines as the use of waste-derived photocatalysts for water depuration and use of light to produce protective coatings on large areas.[7,8]

The most widely used enzymes for lime-free fiber opening processes are α-amylase and protease, as an alternative to conventional lime process. Proteolytic and amylotic enzymes act by cleaving the protein–carbohydrate conjugates, resulting in the removal of interfibrous materials.[9] The application of enzymes requires skilled labors, as usage of enzymes in uncontrolled environment might result in the degradation and destabilization of protein present in the skin matrix.[10]

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This has given rise to exploring alternatives for the removal of inter-fibrillary materials in skin/hide, which are eco-benign, biocompatible, and sustainable with a user-friendly approach.

Ionic liquids are a class of molten salts with low boiling points (<100 °C), negligible vapor pressure, low flammability, and miscibility with water and organic solvents. They are thus termed 'green solvents'. Apart from being environmentally-friendly solvents, the physico-chemical properties of ionic liquids, including multiple solvation interactions with both organic as well as inorganic compounds, high chemical and thermal stability, high ion conductivity and wide electrochemical window, pave the way for a wide range of applications in various industries. Additional characteristic of ionic liquids is the ability to change its cations and anions depending on its application.[11] Therefore, ionic liquids are also known as 'designer' or 'task-specific' solvents.

The interaction of ionic liquids with biological macromolecules is not well explained; however, it is speculated that the ions follow Hofmeister series formulated by Franz Hofmeister.[12] Salts such as NaCl and KCl show predictable behavior of stability and solubility owing to the kosmotropicity and chaotropicity of the ions.[13] A combination of kosmotropic cation and chaotropic anion results in the destabilization of protein, whereas the combination of chaotropic cation and kosmotropic anion results in the stabilization of protein.[14] The strong H-bonded kosmotropes cause less breakage to the water surrounding the protein, while the weak H-bonded ions break more H-bonds and interact with protein. It is also likely that Hofmeister series also depends on the ion size for exhibiting stabilization or destabilization behavior on proteins.

Though enzymes are being employed in the industry for the unhairing process, pelts are used for the reliming process after unhairing for fiber opening.[15] This causes serious concern in terms of pollution load.[16] Ionic liquids have been previously explored for various industrial applications in the fields of chemical engineering, energy conversion, electrochemistry and biotechnology. Very few attempts have been made to replace the lime and sodium sulfide technique in the conventional leather processing step.[17] The application of enzymes is currently being practiced in few parts of the world, a further need to explore an alternative, *i.e.* a green and eco-benign, biocompatible, user-friendly, clean technology, stable against heat and pH and recyclable, is necessary. Hence, in this study, 1-butyl-3-methylimidazolium chloride[18] is used as an alternative to amylase and conventional reliming process. Ionic liquid treated pelts are subsequently chrome tanned and post tanned to evaluate the physical strength.

2. Materials and methods

2.1. Materials

Wet salted goat was chosen as the raw material for the study. All chemicals used for leather processing were of commercial grade, whereas the chemicals used for analysis were of analytical grade. Bovine Serum Albumin (BSA), mucin, Folin–Ciocalteu reagent, periodic acid and 1-butyl-3-methylimidazolium chloride were procured from Sigma-Aldrich Chemicals, India and other analytical chemicals were procured from SD Fine Chemicals, India.

2.2. Estimation of protein and proteoglycan

Five wet salted goat skins (one day preserved) were taken and processed for enzymatic unhairing and IL assisted fiber opening process, as given in Table 1.

The pH of the float was adjusted to 8.5–9.0 before the addition of enzyme for effective unhairing treatment. All the samples were filtered through Whatman filter paper. The filtered samples were used for the estimation of protein and proteoglycan spectrophotometrically using standard procedures.

2.3. Proteoglycan estimation

Schiff's assay was carried out to estimate periodate oxidizable glycoconjugates in the effluent liquor. Standard graph was prepared using mucin as a standard and the amount of proteoglycan present in the sample sourced from the IL processes were calculated using the mucin standard graph.[19]

Table 1 Process recipe for ionic liquid application

Process	Chemicals	%	Time (h)	Remarks
Soaking I	Water	300		
Soaking II	Water	300	2	The pH of soak liquor was adjusted to 9–9.5 and left overnight
	Sodium carbonate	0.4		
	Biocide	0.1		
Enzyme (protease) treatment	Water	30	6	The pH of the bath was adjusted to 9–9.5. No. of cycles – 6 (10′ run and 50′ stop and left overnight)
	Protease	2.5		
Washing	Wetting agent	0.2	0.1	Dry drumming
Washing	Water	100	0.1	
	Wetting agent	0.2		
Ionic liquid	Ionic liquid	0.25–1.0	4	
Washing	Water	30	0.1	

Table 2 Process recipe for chrome tanning process

Chemicals	% Offer	Time	Remarks
Pickle liquor	50		Check pH 2.8–3.0
Basic chromium Sulfate	6	1 h	Check penetration
Water	50	30 min	
Sodium formate	1	15 min	
Sodium bicarbonate	1–1.5		
Water	50	4 × 10 min + 1 h	Check pH 3.8–4.0 drain: aged for 24 h

2.4. Staining techniques

Haematoxylin and Eosin (H&E) and safranin 'O staining[20] are used routinely in histopathology laboratories as they provide the pathologist/researcher a very detailed view of the tissue. Though several new technologies have come up for staining, H&E staining is considered to be a critical assay to study the tissue samplings. This staining is carried out for relimed pelt and ionic liquid treated skin to understand the fiber modifications. From each specimen, color images were acquired with a light microscope and a digital camera running under imaging analysis program.[21]

2.5. Chrome tanning

The ionic liquid treated skins were washed thoroughly and taken for the conventional pickling process. Deliming and bating processes were eliminated in the enzyme and IL assisted fiber opening process as the pH is around 8–9 and also no lime is used. The pickled pelt was subsequently processed for conventional chrome tanning using 6% BCS, as given in Table 2.

2.6. Determination of shrinkage temperature

The shrinkage temperature, which is a measure of the hydrothermal stability of leather, is determined using a Theis Shrinkage Tester. A 2 cm^2 sample cut out from the tanned leather sample was clamped between the jaws of the clamp, which in turn was immersed in a solution of water : glycerol mixture (3 : 1). The temperature of the solution was gradually increased and the temperature at which the sample shrunk was noted.

2.7. Post tanning process

Tanned leathers were shaved to a uniform thickness of 1.1–1.2 mm and post tanned to obtain upper crust leathers, as given in Table 3. After post tanning operations, the leathers were piled overnight. The next day, the leathers were set, hooked to dry, staked and buffed.

2.8. Physical testing of leather samples

The samples for physical testing were obtained as per IULTCS methods. The samples were conditioned at 80 °F and 65% Rh for 48 h.[22] Physical properties, such as tensile strength, % elongation, tear strength and grain crack strength, were investigated as per standard procedures.[23–25] Each value reported is an average of four (2 along and 2 across the backbone) measurements.

Table 3 Post-tanning recipe for the manufacture of upper leather from wet blue

Process/chemicals	%	Duration (min)	Remarks
Washing water	100	10	Drained
Neutralization water	150		
Sodium formate	1.0	10	
Sodium bicarbonate	1.0	3 × 15 + 45	pH-5.0–5.2, drained.
Washing water	200	15	Drained
Retanning, dyeing and fat liquoring			
Water	100		
Grain tightening acrylic syntan	4.0	30	
Semi-synthetic fatliquor	3.0	45	
Acid dye	2.0	30	
Synthetic fatliquor	3.0		
Phenol–naphthalene based syntan	6.0		Mixed in hot water
Melamine syntan	5.0	60	
Semi-synthetic fatliquor	4.0	30	
Wattle	4.0	30	
Formic acid	1.5	4 × 10 + 20	The dye exhaustion was checked. Drained.
Washing	100	15	Drained and dried

2.9. Scanning electron microscopy analysis of the processed leathers

Samples from the control and experimental tanned leathers were cut from the official sampling position from the crust leather. Samples were first washed in water. Subsequently, samples were then dehydrated gradually using acetone and methanol as per standard procedures. A Quanta 200 series scanning electron microscope was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 5 kV with different magnification levels.

2.10. Analysis of waste liquor

Waste liquors from experimental processes were collected after the fiber opening process and analyzed for COD and TDS (dried at 103–105 °C for 1 h) as per the standard procedures.[26] Emission loads are calculated by multiplying concentration (mg L^{-1}) with volume of effluent (L) per metric ton of raw skins processed.

3. Results and discussion

3.1. Application of ionic liquid for fiber opening

Based on the protease activity, 3.0% was offered based on raw weight of the skin. Four different concentrations of 1-butyl-3-methylimidazolium chloride from 0.25 to 1.0% were used based on the raw weight of goat skin. Unhairing and fiber opening process procedures are given in Table 1. The process employs two soaks at 300% water with overnight second soak followed by enzyme treatment in drum method with 30% water and 3.0% enzyme concentration based on raw weight of goat skin. The process includes six hour process duration with 10 min drumming and 50 min rest followed by resting overnight in the drum (12 h). After protease treatment, skins were washed thoroughly and treated with ionic liquid for fiber opening. Control experiment was carried out based on conventional liming and reliming processes.

General appearance, scud removal, grain smoothness, softness, odor and fluffiness of the pelts are shown in Fig. 1. From the figure, it is clearly evident that ionic liquid treated pelts have similar appearance compared with the relime-assisted process. Scuds were completely removed in the IL assisted processes; this is probably due to their lyotropic effect.[27] The higher concentration of IL removed scud completely. Grain smoothness was matched with relime-assisted process and a concentration of 0.5% of IL exhibited better smoothness than other concentrations. Softness also increased with increase in the concentration of IL. Further studies were carried out to explore the efficacy of IL in terms of proteoglycan release, percentage exhaustion of chromium, physical strength characteristics of crust leather, morphology distribution of fibers due to the IL effect.

3.2. Proteoglycan release after IL treatment

The release of proteoglycans is an indicator of fiber opening during conventional reliming operation.

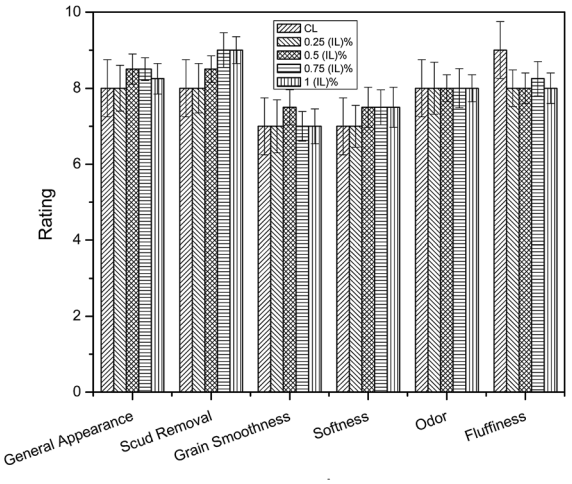

Fig. 1 Subjective evaluation of ionic liquid treated pelts.

In order to examine fiber opening efficiency in the skin due to IL treatment, the release of proteoglycans and protein is estimated in the effluent liquor. The concentrations of protein and proteoglycan were estimated and calculated using their respective standard graphs and the data is given in Table 4. In IL treated liquor there was a significant amount of protein and proteoglycans being released. Higher amounts of protein were released in the IL treated liquor due to the release of albumin and globulins. Proteoglycans were released into the process liquor on washing the IL treated pelt before the pickling processes. Due to lyotropic effect, the glycosidic linkages of proteoglycans, which are predominantly conjugated with skin matrix, are broken down and subsequently proteoglycans are released.

3.3. Histological characteristics of IL treated skins

To study the histological characteristic of the skin during IL treatment, H&E and safranin O staining were carried out for the IL treated skins. Histological study reveals the compactness of the fiber orientation in the skin matrix. The stain differentially shows the fiber orientation in the skin before and after IL treatment. Fig. 2 and 3 show the H&E and safranin O stained samples of IL treated sample of skins. The figures indicate the staining of the entire skin matrix, which consists of proteins such as collagen, reticulin, elastin and other non collageneous proteins. The compactness of corium fiber remains constant before and after IL treatment. From the stained images, it can

Table 4 Release of proteoglycan in the spent liquor

	Proteoglycans (mg g^{-1} of raw weight) for IL offer (%)				
Process	0	0.25%	0.5%	0.75%	1.0%
Spent liquor (IL)	4.9	5.0	5.2	5.4	5.5
Wash liquor I	1.7	2.1	2.4	2.2	1.9
Wash liquor II	0.9	1.0	0.8	0.7	0.4

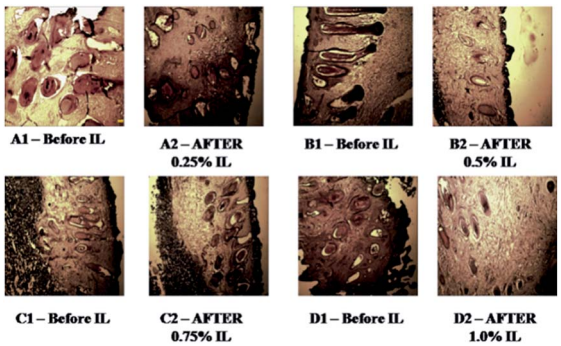

Fig. 2 Hematoxylin Eosin stained images of ionic liquid treated pelts.

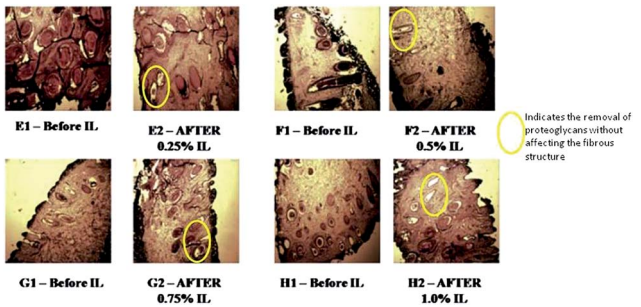

Fig. 3 Safranin 'O stained images of ionic liquid treated pelts.

Table 5 Visual assessment data of the wet blue leather

Parameter	Control	0.25% IL	0.5% IL	0.75% IL	1.0% IL
Color of the wet blue	9	9	9	9	9
Chrome patches	Nil	Nil	Nil	Nil	NIL
Grain smoothness	7	7	8	8	9
General appearances	8	8	8	8	8

be observed that proteoglycans are removed after IL treatment. Moreover, the nature of the fibers is retained. There might be a weak lyotropic effect due to ionic liquid, which can cause damage to fibres. In this case, there is no major distortion observed. Hence, IL can be used to treat the skin without damaging the corium content.

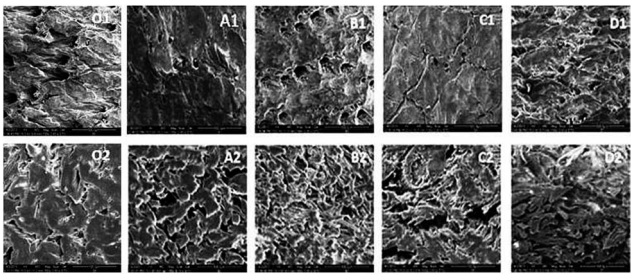

Fig. 4 Scanning electron microscopy images (grain surface (1) and cross section (2)) of IL treated pelts. (O) Control, (A) 0.25% IL, (B) 0.5% IL, (C) 0.75% IL and (D) 1.0% IL (grain-100 μm and cross section-500 μm).

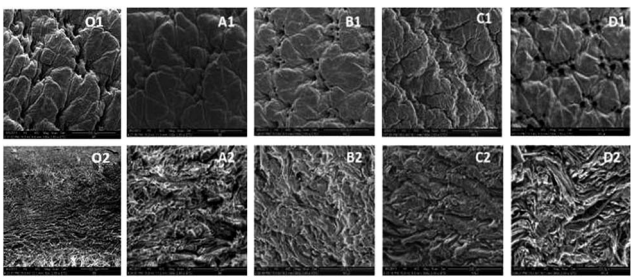

Fig. 5 Scanning electron microscopy images (grain surface (1) and cross section (2)) of IL treated wet blue leathers. (O) Control, (A) 0.25% IL, (B) 0.5% IL, (C) 0.75% IL and (D) 1.0% (grain-100 μm and cross section- 500 μm).

3.4. Characteristics of wet blue leathers

The chrome content in the control wet blue leather was 3.1%. The shrinkage temperature of the wet blue leather was about 112 °C. The chrome contents of IL treated wet blue leathers were 3.15, 3.25, 3.30 and 3.50% of IL for 0.25, 0.5, 0.75 and 1.0%, respectively. The shrinkage temperature of IL treated leathers is between 108 and 116 °C. This indicates that IL effectively scissors the inter-fibrillary materials and aids in tanning chemicals.

3.5. Visual assessment of wet blue leathers

In order to establish the final quality of the wet blue leather obtained following the IL treatment, a visual assessment is made and the data is presented in Table 5. All the parameters, namely, grain smoothness, color and chrome patches and general appearance remained suitable. The general assessment

Table 6 Strength characteristics of the crust leather

Sample	Tensile strength (kg cm^{-2})	Extension at break (%)	Tear strength (kg cm^{-1})	Grain strength	Crack
				Load (kg)	Distension (mm)
Control	260	65	43	25	7.92
0.25% IL	255	62	45	24	7.38
0.5% IL	240	68	42	28	6.95
0.75% IL	238	66	39	26	7.24
1.0% IL	230	72	35	28	7.56

Table 7 Waste liquor analysis

Process	COD ppm	TDS Ppm	Emission load (kg/metric ton of raw skin processed) COD	TS
Control	6850	3000	31	175
0.25% IL	2740	6000	14	30
0.5% IL	3048	8000	16	42
0.75% IL	3602	6000	23	41
1.0% IL	3426	8000	25	53

indicated that the IL processed leathers were similar to conventional chrome tanned leathers.

3.6. Physical characteristics of crust leather

The strength characteristics like tensile strength, tear strength and grain crack strength of the crust leathers processed from IL treated wet blue leathers are given in Table 6. The tensile strength of the control goat upper leather was 260 kg cm^{-2} and the tear strength was 43 kg cm^{-1}. The experimental leathers showed tensile strength between 230 and 255 kg cm^{-2}. From the table, it is observed that with increase in the concentration of IL, there was minimal decrease in the strength properties. This might be due to sample to sample variation or due to higher concentration of salt. Higher concentrations of IL show lytropic effect, which might result in the distortion of the fibers. This may be a reason for the marginal reduction of strength properties. However, even at higher concentration, crust leathers met the stipulated norms. The IL processed crust leather passed grain crack strength as per norms. It was elucidated from the table that IL processed leathers exhibited better tensile and tear values to meet the standard norms.

3.7. Scanning electron microscopy evaluation of IL effect on skin matrix

The scanning electron micrographs of IL treated pelt and wet blue goat leathers showing the grain surface and cross-section are shown in Fig. 4 and 5. There is no change in the surface characteristics of IL treated skin, Fig. 4. The wet blue sample of goat exhibits a well-ordered and compact structure especially between the grain layer and corium major junction. The fiber structure of the crust leathers is more compact and uniformly

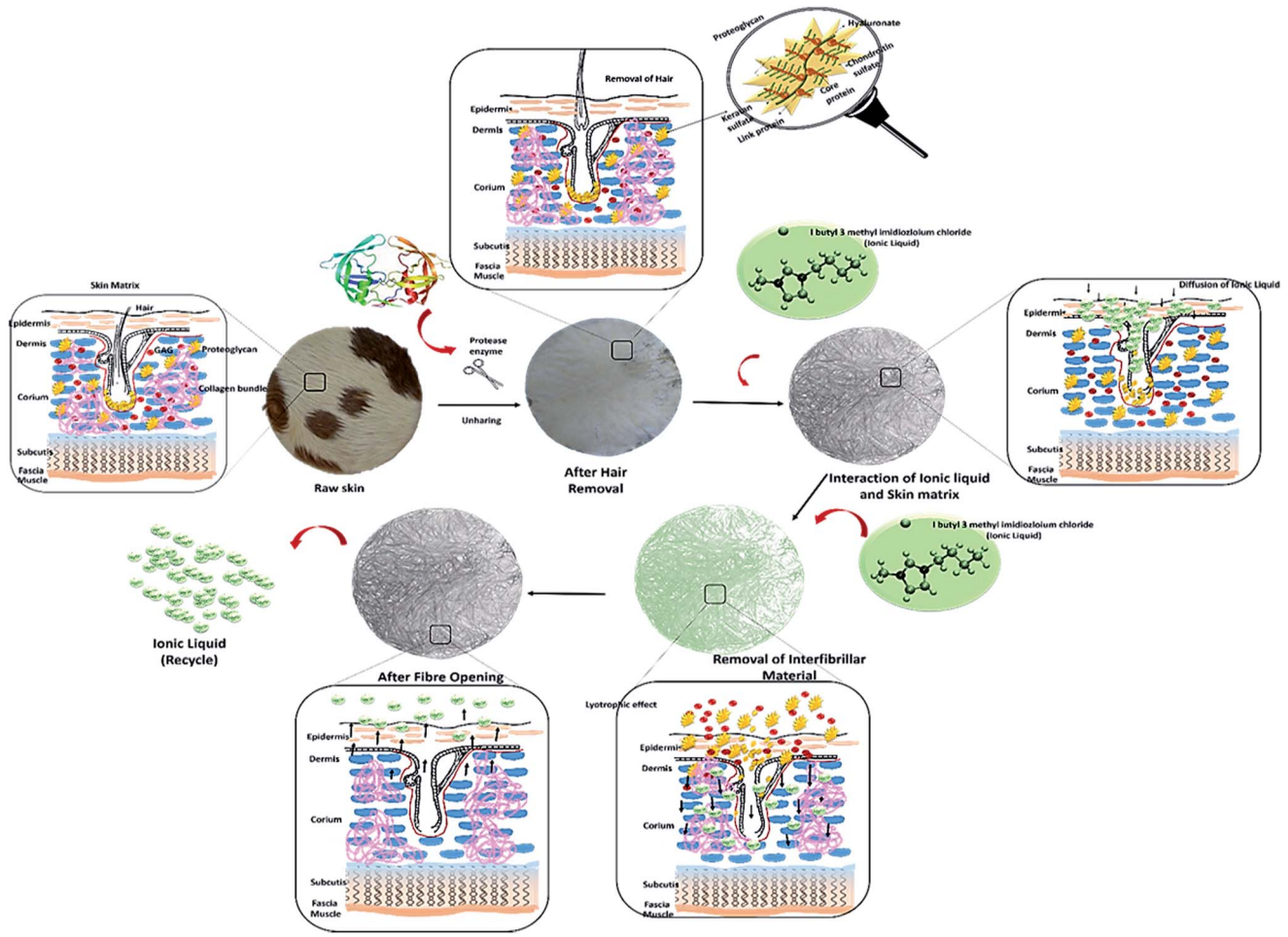

Fig. 6 Mechanism of fiber opening process using ionic liquid.

relaxed throughout the cross-sections. This is due to higher exhaustion of tanning chemicals.

At higher concentration of IL, Fig. 4 D1 and D2 show looseness in the grain surface. This is probably due to higher concentration gradient and lyotropic effect, which apparently damage the skin. However, the cross-section images confirm that there is no looseness and coalescence of fibres. In the case of 0.5% IL treatment, grain structures were prominent with uniformly split fibers, as seen in the cross sectional images, Fig. 4-C2. The orientation of fibers is uniform and regular in the wet blue samples, Fig. 5.

3.8. Environmental assessment

The waste liquor was analysed for TDS and COD after treating the skin with ionic liquid. The estimated pollution values are converted to emission loads for better understanding. The TDS and COD values are given in Table 7.

Ionic liquid treated waste liquors show reduced emission loads. Moreover, the experimental effluent liquor is free of lime and sulphide. However, with increase in concentration of IL, it is observed that there is increase in TDS and COD. However, the emission loads are significantly lower compared with conventional liming and reliming (COD-10 000–20 000 mg L^{-1}; TDS-10 000–30 000 mg L^{-1}) processes. From the results, it can be ascertained that at lower percentage of IL, the emission loads are minimized, paving a way towards a greener approach in leather processing.

4. Conclusion

Natural material processing is always a great challenge due to its inherent complexity. However, the manufacture of leather from skin has been a well-known art for many centuries. Recently, many stringent regulations have been implemented to control pollution discharge from industries. To combat this situation, several cleaner and greener technologies have been researched among the science fraternity. In the present research, a novel dimensional approach was implemented using IL for removing inter-fibrillary materials from skin, Fig. 6. The IL used for the effective fiber opening employed an offer of 0.5% on raw weight of goat skin. There was complete removal of short hairs and better opening of fiber bundles, and this was confirmed by the proteoglycans release study. The efficacy of fiber opening was ascertained through visual appearance, staining techniques and scanning electron microscopic evaluation. The physical characteristics of the crust leathers meet standard norms, which is indicative of an effective process. The morphological features studied through SEM confirm the splitting of fibers during IL treatment. The compactness feature of crust leathers establishes higher exhaustion of post tanning chemicals. The study exposes the leather fraternity to a new era in green technology and meets the existing concerns faced by the leather industry.

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