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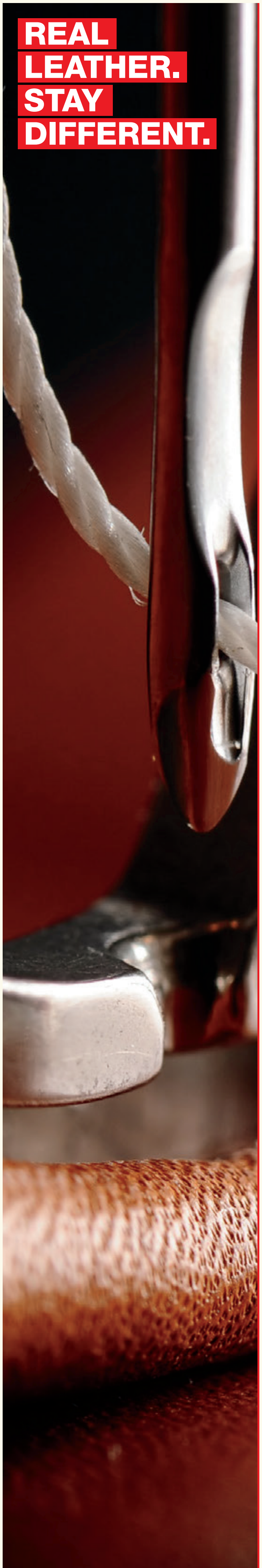

REAL
LEATHER.
STAY
DIFFERENT.

LEATHER BY NUMBERS:

FACTS AND FIGURES FROM THE US LEATHER INDUSTRY AND BEYOND

Note: All figures as of January 2021 or latest available.

ZERO cattle are killed to make US leather. US hides have been valued at **JUST 1-2%** of a cow's total value for the last two years, which is why they are considered a by-product and often end up as waste. The average price per head of US cattle is $2,000-2.200, while hides vary in price from **$5 TO $35 PER PIECE**, if sold at all. (1)

330M hides come from the meat and dairy industries around the world. Approximately **34M** were processed the US. (2) **AS MANY AS 2.4M US HIDES** ended up as landfill in 2019, this is **7%** of the national total.

Worldwide the waste figure is approximately **40%** or **132M** hides. With the average hide weighing 25Kg this means that **3M TONNES** are thrown away ever year.

Leather production turns more than **4.5M TONNES OF** potential waste, every year, into usable, durable goods. This saves **2.7M TONS OF GREENHOUSE GAS EMISSIONS** from landfill sites. (3)

Production, processing and distribution of hides and leather products directly employs an estimated **5,486** individuals, who collectively earn more than **$384M**. US exports of hides and leather was over **$1.5BILLION** in 2021. (4)

The US exports approximately **95%** of all cattle hide and wet blue leather products it produces, worth **$2.85BILLION**. (5)

Around **45%** of global leather production is used to make footwear, **22%** for clothing, bags and accessories, **18%** for car upholstery, and about **15%** for furniture. (6)

Water consumption for the production of leather from cattle hides has fallen by more than **35%** in the past 25 years, down from **60 CUBIC-METERS** per ton of hides to **38 CUBIC-METERS** per ton. US tanneries are required, by law, to connect to effluent treatment plants to prevent pollution. (7)

Leather will biodegrade in **LESS THAN 50 YEARS**. In contrast, it can take **500 YEARS** or more for synthetics, made from petrochemicals, to degrade. (8)

ReFed's conversion rate for food waste is for **EACH METRIC TON OF WASTE DISPOSAL** there is **9.8 7MT** of **CO2 EQUIVALENT** emitted. In this case, mostly as methane. (9)

This factsheet is produced by the Leather and Hide Council of America (L&HCA), established to promote the US leather industry which is responsible for a significant proportion of the international trade in hides. The L&HCA works to establish best practice in US leather production and to share this worldwide. Figures quoted refer to the USA unless otherwise stated.

SOURCE:

(1) https://downloads.usda.library.cornell.edu/usda-esmis/files/rx913p88g/w0893q25p/5d86qb66f/lstk0223.pdf
(2) https://downloads.usda.library.cornell.edu/usda-esmis/files/r207tp32d/pg15cj85z/hd76t466z/lsan0422.pdf
(3) 2020 LHCA Infographic
(4) John Dunham & Associates, Economic Impact of the Meat Industry (2016)
(5) https://thesustainabilityalliance.us/wp-content/uploads/2020/04/US-Hide-Skin-and-Leather-Factsheet-0420.pdf
(6) TBC
(7) 2020 LHCA factsheet
(8) https://en.wikipedia.org/wiki/Leather#:~:text=Leather%20biodegrades%20slowly%E2%80%94taking%2025,or%20more%20years%20to%20decompose
(9) https://insights-engine.refed.org/impact-calculator?inputs=%7B%22sector%22%3A%22manufacturing%22%2C%22type%22%3A%22fresh-meat-seafood%22%2C%22unit%22%3A%22tons%22%2C%22alternative%22%3Afalse%2C%22destinations%22%3A%5B%7B%22key%22%3A%22refuse-discards%22%2C%22current%22%3A1%7D%5D%7D

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self cleaning

Exploring Structural Features of Bovine, Ovine, Fish, Poultry, Reptile, Amphibian, and Porcine Skins through Scanning Electron Microscopy: Insights for Material Science and Sustainable Design

by

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Abstract

In leather research, the Scanning Electron Microscope (SEM) proves to be an invaluable tool, offering detailed and high-resolution images of both the surface and fiber structure. This information plays a critical role in optimizing manufacturing processes within the leather industry, enhancing the quality of leather products, and contributing to the development of new materials. In the current study, our focus is on unraveling the microscopic details of skins sourced from various biological origins. We aim to provide insights into the distinctive morphological features, fiber arrangements, and surface topographies of bovine, ovine, fish, poultry, reptile, amphibian, and porcine skins, which were converted into crust leathers. We captured microphotographs of the surfaces and cross-sections of the leathers through scanning electron microscopy analysis. This paper presents a comprehensive comparison and discussion of the findings, seeking to identify key differences and similarities. Such a comparative analysis contributes to our understanding of material science, fashion, and sustainable design, offering potential implications for these diverse fields.

Introduction

The Scanning electron microscope, often referred to as SEM analysis, has emerged as a pivotal technology with widespread applications across various disciplines, ranging from materials science to biology. The German scientist Max Knoll is credited with building the first scanning microscope, laying the early groundwork in 1935.[1] Manfred von Ardenne further contributed to the development of both the SEM and the Transmission Electron Microscope (TEM) in 1938.[2] The first true SEM was a contribution from U.S. scientists Zworykin, Hillier, and Snyder in 1942.[3] However, the commercial development and widespread use of SEMs occurred in the past four decades.

The SEM has proven to be an indispensable tool, providing researchers with the ability to explore and analyze the surface characteristics and fiber structures of leather materials. In leather science, SEM is extensively employed to understand the impact of tanning and post-tanning systems on the collagen fiber structure.[4-7] This utilization of SEM is crucial in optimizing emerging processes within the leather industry. By providing detailed insights into the structure of leather fibers, SEM enables researchers to assess the effectiveness of different tanning methods and post-tanning treatments, ultimately contributing to the enhancement of product quality and the development of innovative manufacturing techniques.[8,9] Furthermore, SEM plays a pivotal role in examining the fiber structure of new types of raw materials in the leather industry.[10-13] The capability to study the structural details of these materials allows for a comprehensive understanding of their characteristics and properties.

SEM is also used in identifying and characterizing defects or irregularities in leather, such as cracks, pores, or surface imperfections. Understanding the nature of these defects contributes to improving the manufacturing process.[14,15] Thus SEM plays a crucial role in the quality control and improvement of leather manufacturing processes by providing detailed insights into the surface morphology and structure of leather. Identifying and characterizing defects at a microscopic level enables manufacturers to take targeted measures to enhance the quality and consistency of their leather products. Understanding the surface morphology and structure of leather at a microscale helps in optimizing the manufacturing process to enhance the durability and longevity of the material. This aligns with sustainable design principles, prioritizing the creation of products with a longer lifespan.

SEM could also be used to examine the particle size and morphology of leather auxiliaries, aiding in the understanding of the physical characteristics of the materials used in tanneries. SEM, coupled with Energy Dispersive X-ray Spectroscopy (EDX), also provides information on the elemental composition and spatial distribution of metal ions within the leather sample.[4,12] By leveraging SEM in the present study, we aim to provide a better understanding of the structural intricacies of leathers from various biological origins. The comparative analysis seeks to identify key differences and similarities, shedding light on the potential implications for material science, fashion, and sustainable design. The findings have broader implications for the development of innovative materials and sustainable practices.

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Experimental

Materials

This study involves the use of skins from different biological origins, specifically sourced from legal and reputable channels in Africa and India. The various sources of skins used in this study are as follows:

Bovine and Ovine: Cow, Buffalo, Goat and Sheep
Fish: Tilapia, Salmon, Stingray
Poultry: Ostrich, Chicken
Reptiles: Crocodile, Lizard (Teju), Python, Cobra
Procine: Pig
Ambibians: Frog

Material Preparation for Structural Investigation

All skins from diverse biological sources utilized in this study underwent tanning using 8% basic chromium sulfate, followed by fatliquoring, retanning, and drying. The resulting crust leathers were employed for SEM analysis.

SEM Study of Crust Leathers

A systematic and detailed examination of the structural characteristics of leather samples from various biological sources was conducted and compared using a scanning electron microscope. The key steps and procedures involved in the analysis are given below:

Sample Preparation:

Samples were obtained from crust leathers.
Dimensions of the samples: 5mm × 2mm.
Fresh stainless steel blades were used for cutting.

Mounting Procedure:

Samples were mounted on aluminum stubs.
Both vertical and horizontal orientations were used.
An adhesive tape was employed for mounting.

Coating:

Gold coating was applied to the mounted samples.
Hitachi E-1010 sputter coater was used for the coating process.

Scanning Electron Microscope Setup:

A Hitachi S-3400N scanning electron microscope was used.
The stubs were introduced into the specimen chamber.
The stubs mounted on the stage were adjustable for tilting, rotating, and moving to the desired position and orientation.

Imaging Process:

Micrographs for the surface and cross-section were obtained.
The microscope was operated at 10 – 20 kV for imaging.

Results and Discussion

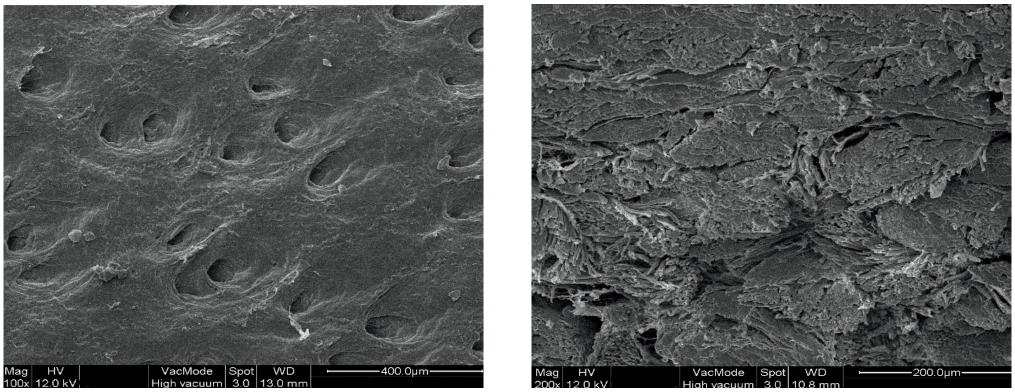
Structural Characterization of Bovine and Ovine Leathers

The scanning electron microphotographs presented in Figure 1 offer insightful visualizations of the surface and fiber structures of cow, buffalo, goat, and sheep leathers. The microphotographs confirms that cow leather surface does not contain any papillation, which accounts for roughness of grain (Figure 1A). The number of hair follicules present in this figure is high compared to the buffalo leather microphotograph. The hair follicle is deep rooted in the case of buffalo which is clear in the microphtograph (Figure 1C) since bufflalo leathers have two types of hair, the coarse hairs are rooted deeper a little below the junction of the grain and corium.[16] The fine hairs present in the buffalo hides are not deep rooted which is also clear in this microphotograph. The Figure 1C reveals the presence of papillation on the buffalo leather surface. This papillation may contribute to the distinct characteristics of buffalo leather and could be a factor influencing its grain texture. The microphotographs in Figrue 1B and 1D reveals that collagen fiber bundles are quite big and are compactly woven in both cow and buffalo leathers which is different from goat and sheep leathers.

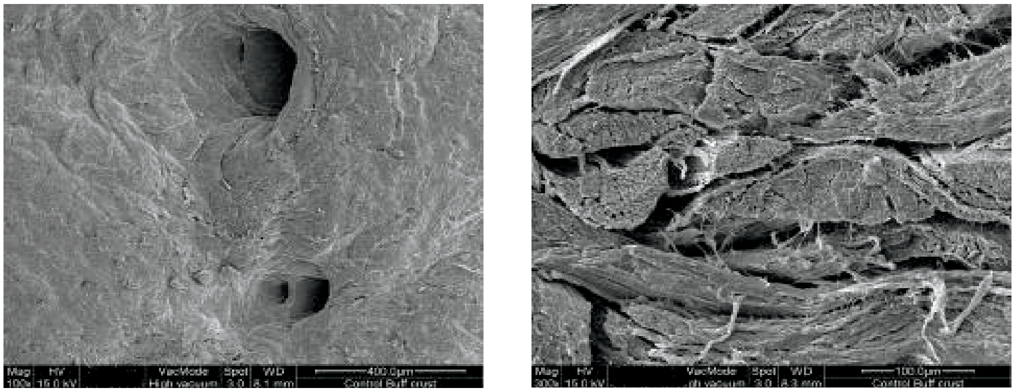
The scanning electron microphotograph of goat leather presented in Figure 1E indicate the presence of a specific trios pattern on its surface makes the leather different from sheep. The cross-section microphotograph presented in Figure 1F reveals that the collagen fibers are firmer and fuller than the corresponding ones in the sheep skins (Figure 1H). The collagen fiber bundles in the sheep leather microphotograph are extremely thin and are not closely interwoven which accounts for the looseness of the structure.

Structural Characterization of Fish Leathers

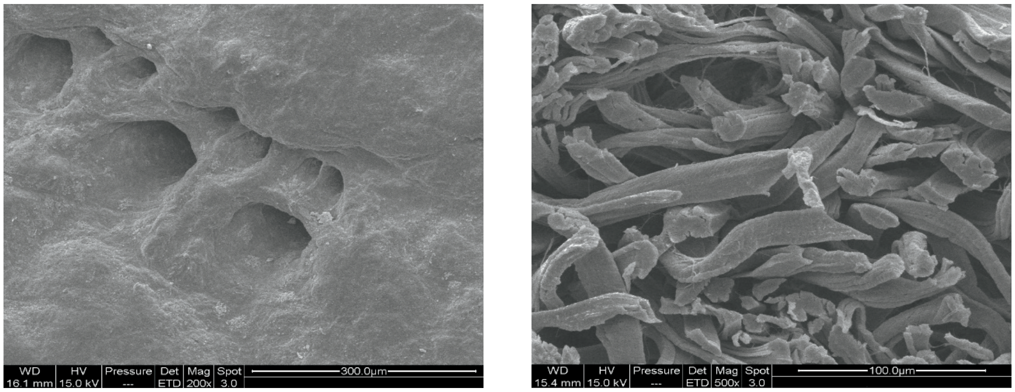
In this study, we have analyzed three different types of fish, namely tilapia, salmon, and stingray. Each fish species exhibits distinct surface morphologies, as illustrated in Figure 2. Both tilapia and salmon exhibit a porous grain structure formed after removing the scales during processing. Despite this similarity, each fish species possesses its own unique surface morphology (Figure 2A and 2C). Due to the porous nature of tilapia and salmon, finishing is typically not applied to these leathers. Unlike tilapia and salmon, stingrays have denticles (Figure 2E) that contribute to their unique skin texture. The stingray leather, characterized by an attractive grain surface, is primarily used in the production of ornamental goods and has also found applications in reflexology.[17] SEM cross-sections



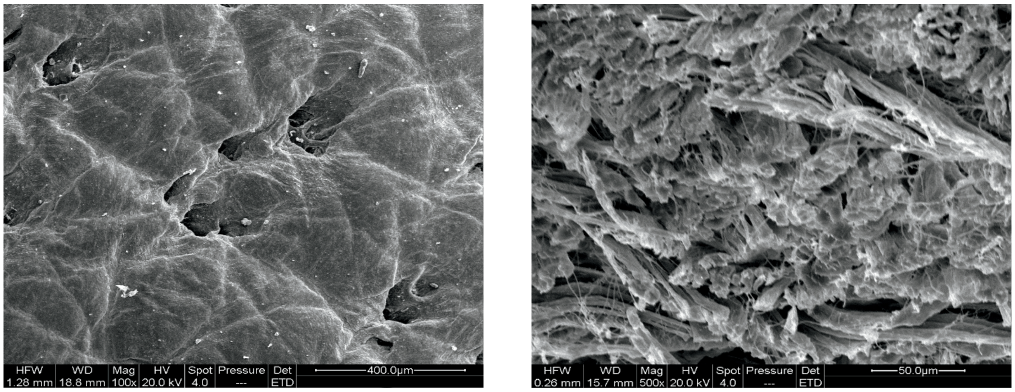
A. Cow surface B. Cow cross-section



C. Buffalo surface D. Buffalo cross-section

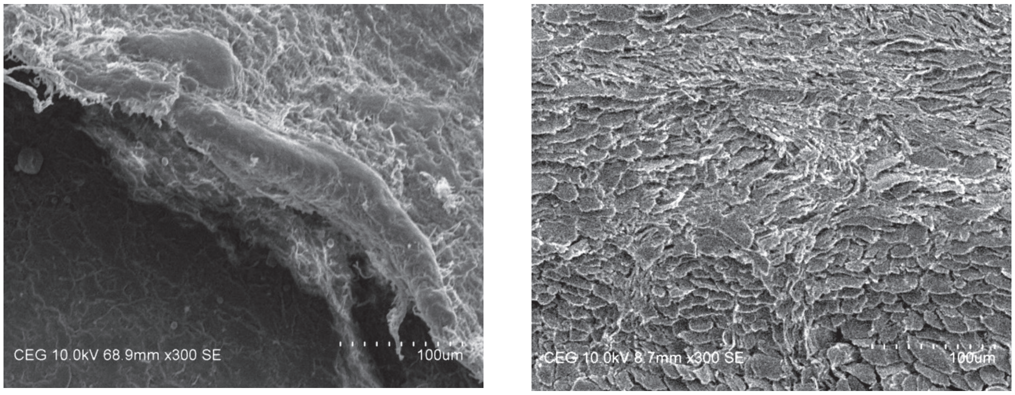


E. Goat surface F. Goat cross-section

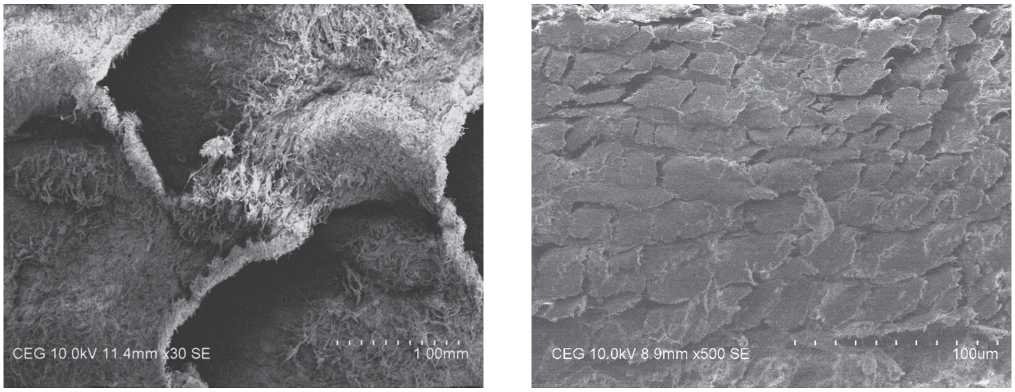


G. Sheep surface H. Sheep cross-section

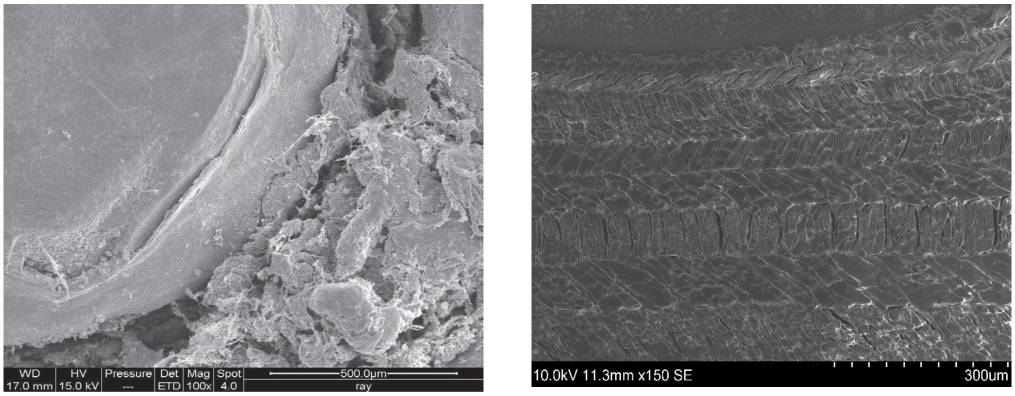
Figure 1. Scanning electron microphotographs of bovine and ovine leathers **A.** Cow surface **B.** Cow cross-section **C.** Buffalo surface **D.** Buffalo cross-section **E.** Goat surface **F.** Goat cross-section **G.** Sheep surface **H.** Sheep cross-section



A. Tilapia surface B. Tilapia cross-section



C. Salmon surface D. Salmon cross-section



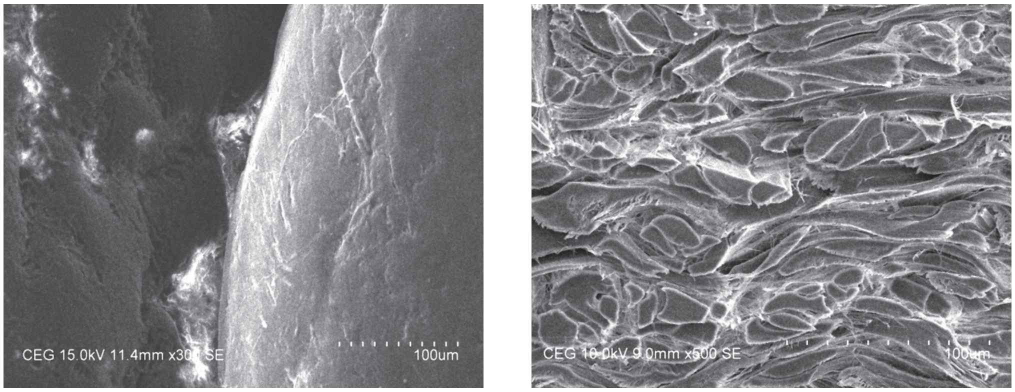
E. Stingray surface F. Stingray cross-section

Figure 2. Scanning electron microphotographs of fish leathers **A.** Tilapia surface **B.** Tilapia cross-section **C.** Salmon surface **D.** Salmon cross-section **E.** Stingray surface **F.** Stingray cross-section

of tilapia, salmon, and stingray are given in Figures 2B, 2D, and 2F, respectively. The microphotographs confirm that tilapia and salmon have loosely packed thin collagen fiber bundles, whereas stingrays have very compactly woven parallel collagen fiber bundles running perpendicular to the grain surface, leading to high-strength properties.

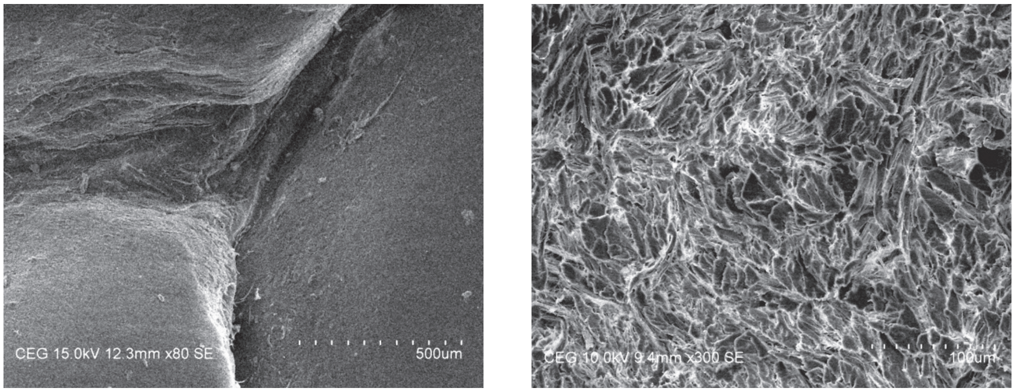
Structural Characterization of Poultry Leathers

Among poultry skins, ostrich skins are very expensive due to their unique natural grain patterns.[18] Ostrich leather is renowned for its distinctive quill or 'diamond' patterns, as illustrated in the microphotograph shown in Figure 3A. These patterns, interwoven by collagen fiber bundles, require careful processing. Each quill mark creates a unique pattern (Figure 3A) that adds to the aesthetic appeal of the leather. Both ostrich leg and chicken leg skins share a similar and unique surface morphology, characterized by reptile-like grain structures without follicles, as illustrated in Figures 3C and 3E. SEM cross-section of ostrich skin is presented in Figure 3B, whereas ostrich leg and chicken leg skin are presented in Figures 3D and 3F, respectively. The microphotographs reveal that ostrich skin has thicker and compactly woven collagen fiber bundles compared to the leg skins of chicken and ostrich.



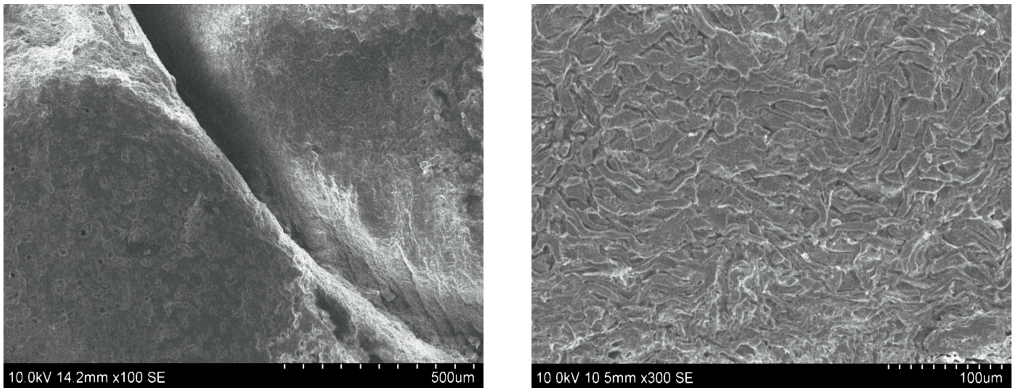
A. Ostrich skin surface

B. Ostrich skin cross-section



C. Ostrich leg surface

D. Ostrich leg cross-section



E. Chicken leg surface

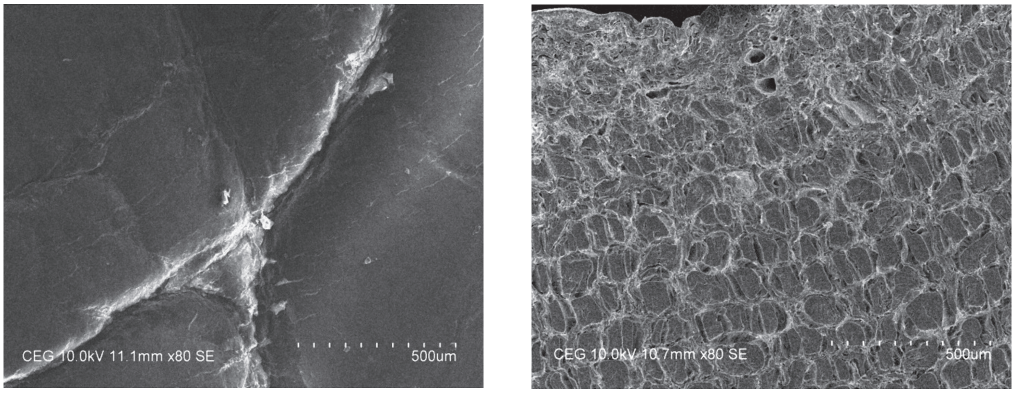
F. Chicken leg cross-section

Figure 3. Scanning electron microphotographs of poultry leathers **A.** Ostrich skin surface **B.** Ostrich cross-section **C.** Ostrich leg surface **D.** Ostrich leg cross-section **E.** Chicken leg surface **F.** Chicken leg cross-section

Structural Characterization of Reptile Leathers

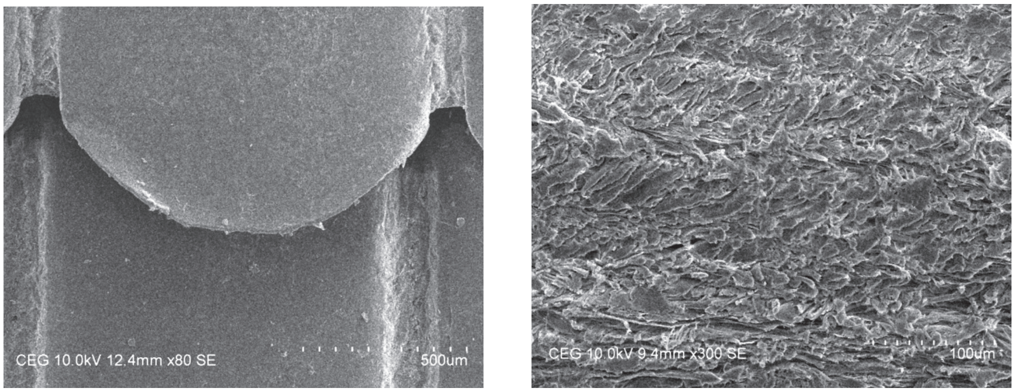
In this study, we have analyzed four species in the reptile class, namely crocodile, lizard, cobra and python. Figure 4A and 4B represents the crocodile leathers' SEM microphotograph for surface and cross-sectional examination. Figure 4A reveals the rectangular morphology of the crocodile skin surface resulting from the removal of the scaly epidermis during the processing of the skin into leather. The intricate geometric pattern left by the scales imparts a distinctive and aesthetically pleasing quality to the finished products, capturing the attention of those who appreciate both the functional and decorative aspects of crocodile leather.[20] In Figure 4B, the cross-sectional microphotograph demonstrates the densely packed and highly organized collagen fiber bundles within crocodile leathers. This distinctive basket-weave meshwork of collagen fiber bundles, as observed in both crocodile and stingray leathers (Figure 2F), plays a pivotal role in enhancing the mechanical strength.

Figure 4C illustrates the surface morphology of lizard leather, where the distinctive small-scale pattern of the lizard is clearly visible in this microphotograph. The unique features of lizard leather, characterized by uniform scales and a distinctive texture,



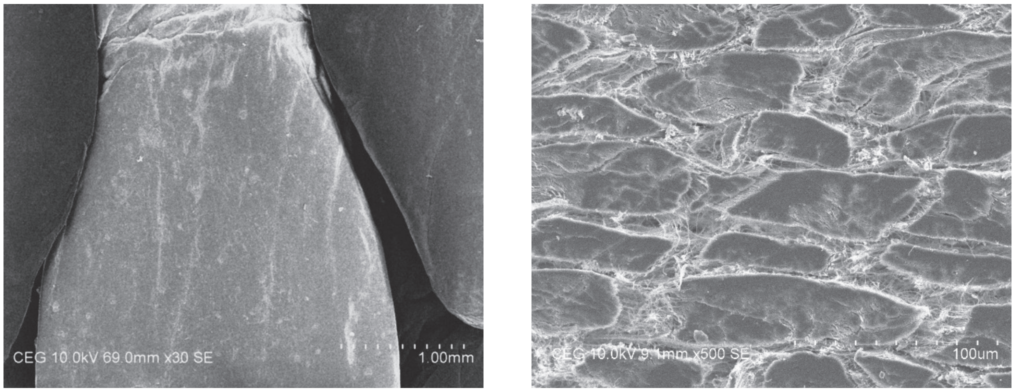
A. Crocodile surface

B. Crocodile cross-section



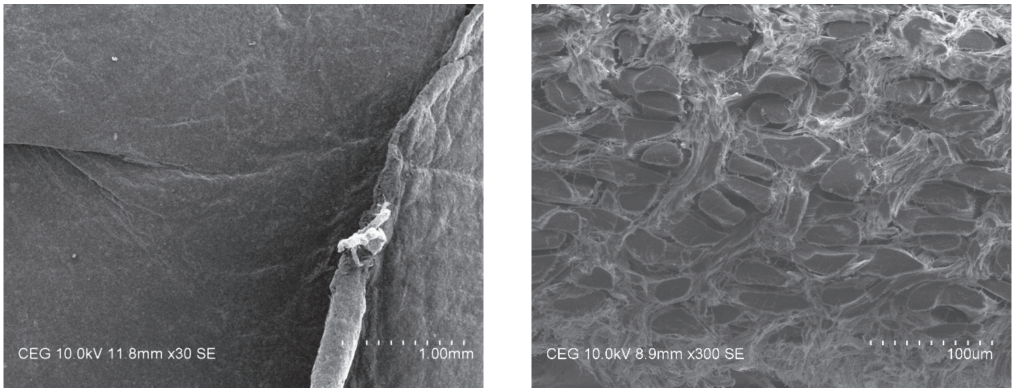
C. Lizard surface

D. Lizard cross-section



E. Cobra surface

F. Cobra cross-section



G. Python surface

H. Python cross-section

Figure 4. Scanning electron microphotographs of reptile leathers **A.** Crocodile surface **B.** Crocodile cross-section **C.** Lizard surface **D.** Lizard cross-section **E.** Cobra surface **F.** Cobra cross-section **G.** Python surface **H.** Python cross-section

contribute to its exclusivity and premium status in the fashion industry. The cross-sectional microphotograph of lizard leather reveals that the skin has very thin, organized collagen fiber bundles that split apart during the leather conversion process.

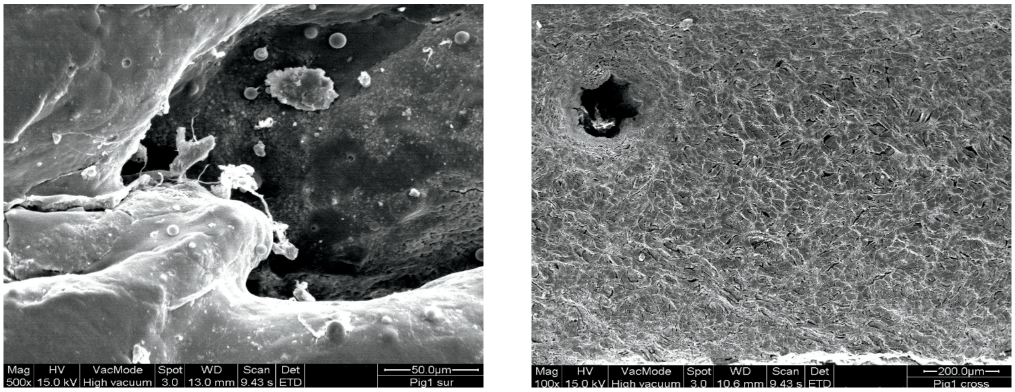
The SEM images of surface and the cross-section of the cobra and python leathers are presented in Figure 4E, 4F, 4G and 4H respectively. The surface morphology reveals that cobra leather is characterized by a prominent and visually striking scale pattern, offering designers a versatile material for creating a variety of visually appealing products. The surface morphology depicted in Figure 4G illustrates that python leather is distinguished by its prominent and sizable hexagonal scale pattern, setting it apart from cobra leather. The symmetrical arrangement of python scales imparts a distinctive texture, forming an intricate and visually appealing pattern in the final leather. This quality makes python leather a preferred choice for high-end fashion items.

SEM cross-sections of python and cobra skins indicate that both species exhibit a stiffer and more organized collagen fiber structure. This structure requires additional fiber splitting during the fiber opening process to achieve fuller and softer skin.

Structural Characterization of Pig and Frog Leathers

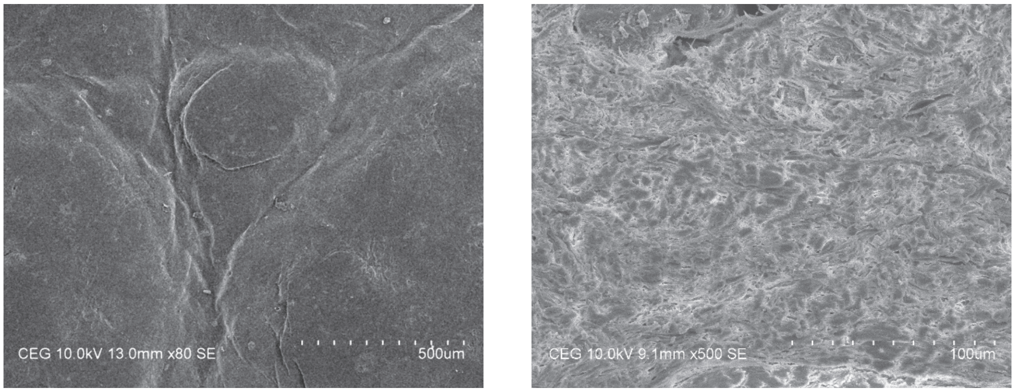
Scanning electron microphotographs of pig leather showing the grain surface and cross section are presented in Figures 5A and 5B, respectively. The pig bristles are generally in groups of three and penetrate through the entire skin, which is evident in these microphotographs. The surface analysis reveals that the hair follicles are deeper compared to other species, and the cross-section analysis indicates the presence of hair follicles below the grain layer, differing significantly from other bovine and ovine leathers used in leather manufacture. Furthermore, the cross-section microphotograph of pig leather reveals that collagen fiber bundles are loosely packed. Due to this structure, pig skins are predominantly used for lining and suede leather manufacture.

Figures 5C and 5D represent the surface morphology and cross-section view of frog skin, respectively. Surface analysis reveals that frog skin has very unique irregular tiny bumps and projections, making it suitable for smaller leather goods. The cross-section analysis shows that frog skin has very thin and loosely packed collagen fiber bundles, leading to poor mechanical properties.



A. Pig surface

B. Pig cross-section



C. Frog surface

D. Frog cross-section

Figure 5. Scanning electron microphotographs of porcine and amphibian leathers
A. Pig surface **B.** Pig cross-section **C.** Frog surface **D.** Frog cross-section

Conclusion

Throughout this study, our focus was directed towards unravelling the microscopic intricacies of skins derived from diverse biological origins, including bovine, ovine, fish, poultry, reptile, amphibian, and porcine sources. The high-resolution images obtained through SEM have provided invaluable insights into the surface and cross-sectional fiber structure of various types of leathers from different biological origins. This information serves as a crucial asset in optimizing manufacturing processes within the leather industry, ultimately leading to enhanced product quality and the potential for the development of innovative materials. The insights gained from this comparative analysis not only deepen our understanding of material science but also bear implications for the realms of fashion and sustainable design. By shedding light on the distinctive morphological features, fiber arrangements, and surface topographies of different leather types, this study opens avenues for informed decision-making in leather-related industries and encourages sustainable practices.

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Potential for using Cattle Hair from Hair-Saving Tanneries as Adsorbent for Crude Oil

by
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Abstract

The oil cleanup potential of discarded cattle hair from tannery operations was investigated by batch adsorption experiments using two crude oils with different viscosities. The results illustrate that cattle hair exhibits higher adsorption capacity for crude oil with higher viscosity. The sorbent can adsorb 5 to 6 times its weight in the two crude oils. Maximum adsorption capacity of 8.72 g/g at 18°C is achieved with pulverized hair powder, and it is comparable to human hair. The sorption can fit better to Freundlich adsorption isotherm and shows the adsorption occurred on heterogeneous sites with a non-uniform distribution of energy. Desorption and reusability experiments confirmed reusability without significant reduction in sorption capacity. This investigation indicates that discarded cattle hair has potential as a low-cost and effective bio-sorbent for scavenging crude oil spillage.

Introduction

Raw cattle hides are basic materials for the leather-making industry. They are processed in tanneries and the hairs in the hides are completely removed. The traditional leather-making process using hair-destruction technology leads to the hair being destroyed and useless. While the presently developed hair-saving unhairing technologies render the removed hair intact,[1] ensuring the utilization of the discarded hairs is feasible. What is more, the output of cattle hairs in tanneries is sizable due to the fact that 40 million pieces of cattle hides are processed in China every year, leading to more than 4×10^5 tons discarded hair. Cattle hairs are often treated as solid waste or used for composting.[2] Thus the development of these discarded cattle hairs into appropriate products should be investigated to avoid problems such as waste of resources and environmental pollution.

Presently, with the development of offshore oil exploration and transportation, marine oil spill accidents have become increasingly serious, as shown by the January 2022 spillage of a tanker ship that released a huge amount of crude oil into the coast of Peru. Spillage demands urgent cleanup and regulatory sanctions to reduce environmental damage because spills spread rapidly and can cause significant ecological damage,[3] placing animal and human health at risk and destroying various natural resources. Multiple cleanup strategies are applied including burning, usage of mechanical skimmers, chemical dispersants, and absorbents when oil spill occurs in marine environments. Among these methods, the use of sorbents is an attractive way due to their simplicity and relatively low cost.[4] Natural sorbents for the cleanup of oil spills have been considered due to their effectiveness, low cost, reusability and eco-friendliness. Several natural bio-sorbents for oil spillage removal have been reported.[5] These include plant fibers and protein fibers, such as cotton fiber, silk fiber, collagen fiber and keratin fiber. Keratin fibers such as wool,[6] yak hair and human hair,[7-9] have attracted great interest for oil spill remediation due to their effectiveness. Human hairs were often publicly called for as an emergency supply for cleanup during the recent oil spill incidents in Cayao (Peru) and Maracaibo Lake (Columbia). However, it is quite inconvenient to collect human hairs and the amounts are nowhere near enough as oil sorbents.

Cattle hairs are similar to human hairs in chemical components. They consist of medulla, cortex and cuticle made up of amino acids. The cuticle content makes hair water repellent and therefore, highly hydrophobic.[10] In addition, they have abundant peptide bonds and CO- as well NH- groups which form hydrogen bonds among the neighboring molecules on the hair surface and have a highly porous cortex.[11] The collection of cattle hair from tanneries is convenient and the cost is quite low. These make it possible for the cattle hair to be utilized as a new oil adsorbent.

The purpose of this paper is to investigate the adsorption capacity of discarded cattle hairs from tannery operations for oil spill cleanup under different conditions, and to provide a theoretical basis for the development and utilization of these cattle hairs in oil-adsorbing material.

Experimental

Reagents and materials

All chemicals used in the experiments were of analytical grade and purchased from Sinopharm Co. Ltd, Shanghai, China. Two light crude oils (No. 201# and 206#) were obtained from a petrochemical plant located in Ningbo City. The characteristics of the oils are outlined in Table I. Discarded cattle hair of 40-60 μm used for the

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Table I

Physical characteristics of used crude oils at temperature 18 °C

No. of Crude Oil	Density (g/cm^3)	Rotary Viscosity (mPa-s)
201#	0.849	12.5
206#	0.853	26.0

adsorption experiments was collected from a tannery in Zhejiang province, and hair-saving technology was used in the unhairing process. Human hair of 30-70 μm used for comparison was obtained from a local hairdressing salon in Jiaxing City. The human hair was sourced mainly from males and was original and free of dyes and dust.

Modification of the cattle hairs

Generally, the discarded cattle hairs from tanneries had been treated in lime solutions. These hairs are quite brittle if dried directly and inconvenient for use. Thus, the hairs were modified prior to use according to the following description. The hairs were first rinsed with 20 volumes of water containing HCl 0.01 mol/L for 30 min. After filtration, the hairs were immersed into 20 volumes of emulsifier solution containing 1% alkyl sulfonyl chloride (called M80) and treated in an ultrasonic bath with 40 Hz for 30 min. The hairs were then rinsed twice in warm water and dried at room temperature and were then ready for use.

Fiber surface morphology observation

The surface morphology of the hairs was examined after spraying gold to make the fibers conductive with a scanning electron microscope model of Phenom Pure from Phenom Scientific Co. Ltd Shanghai.

Adsorption experiments

Adsorption experiments were conducted in artificial seawater as described by Kester et al.[12] Crude oils (10-50 g, in Table I) were poured into separate 500 mL conical flask with 200 mL of seawater. Amounts of the sorbents (strands, 1-6 g) were added with a contact time (2-60 min) under a slight shaking action. All the experiments were conducted at the temperature 18±2°C approaching the average surface temperature of actual seawater.

Oil contents in the sorbent were measured based on EPA Method 1664 by hexane extraction.[13] The oil adsorption capacity (g/g) was calculated based on the weight of oil adsorbed in the hair and the weight of the hair before adsorption. The experiments were performed in triplicate with the average value and standard deviation (SD) calculated.

Effects of time on adsorption

The effects of contact time on the adsorption capacity were tested using the two types of oils (in Table I) separately. A dosage of 2 g adsorbent was used for the experiments. 20 g of crude oil were subjected into 200 mL of seawater in a flask. Tests were carried out with samples withdrawn at intervals ranging from 2 to 60 min.

Effects of particle size on adsorption

The modified cattle hair and human hair were first cut into short fibers (< 3 mm) with electric scissors, and then pulverized with a precise grinder (Retsch ZM200, German). The particle sizes were checked with a Fiber Fineness Meter (Guoliang GL003, China), and the average sizes were almost at the range of 40-80 μm. A dosage of 2 g powder was added into the flask containing 20 g crude oil and 200 mL artificial seawater. The adsorption time was 60 min.

Effects of adsorbent dose on adsorption

This operation was the same as effects of time on adsorption described above, except that dosage of cattle hair strands ranged from 1 to 6 g, and the adsorption time was 60 min.

Sorption isotherm study

Batch adsorption isotherm studies were performed with dosage of 2 g hair strands used for the experiment. The operation was the same as effects of time on adsorption above, except that the adsorption time was 60 minutes. The experimental data obtained was analyzed using the Langmuir and Freundlich adsorption isotherm models separately.[14-15]

Reusability test

The hexane extraction method was used to recover the cattle hair for reuse, and the reusability of the sorbent for oil sorption was evaluated. The used cattle hairs were immersed into hexane and extracted for 60 min with ultrasonic assistance for desorption. The recovered hairs were then reused for the batch adsorption experiments in the following continuous cycles. Oils in the hexane were measured and the adsorption capacities were calculated.[13]

Results and Discussion

Morphology of the hair

The surface morphology of the modified cattle hair was observed by scanning electronic microscopy (SEM). Human hair was also examined for comparison. As shown in Figure 1, the SEM images of cattle and human hair are quite similar. They have rough cuticles formed by many layers which look scaly. The cuticles are structural elements of individual hair strands, and they are more hydrophobic as water tends to bead on the hair strands. These contribute to the

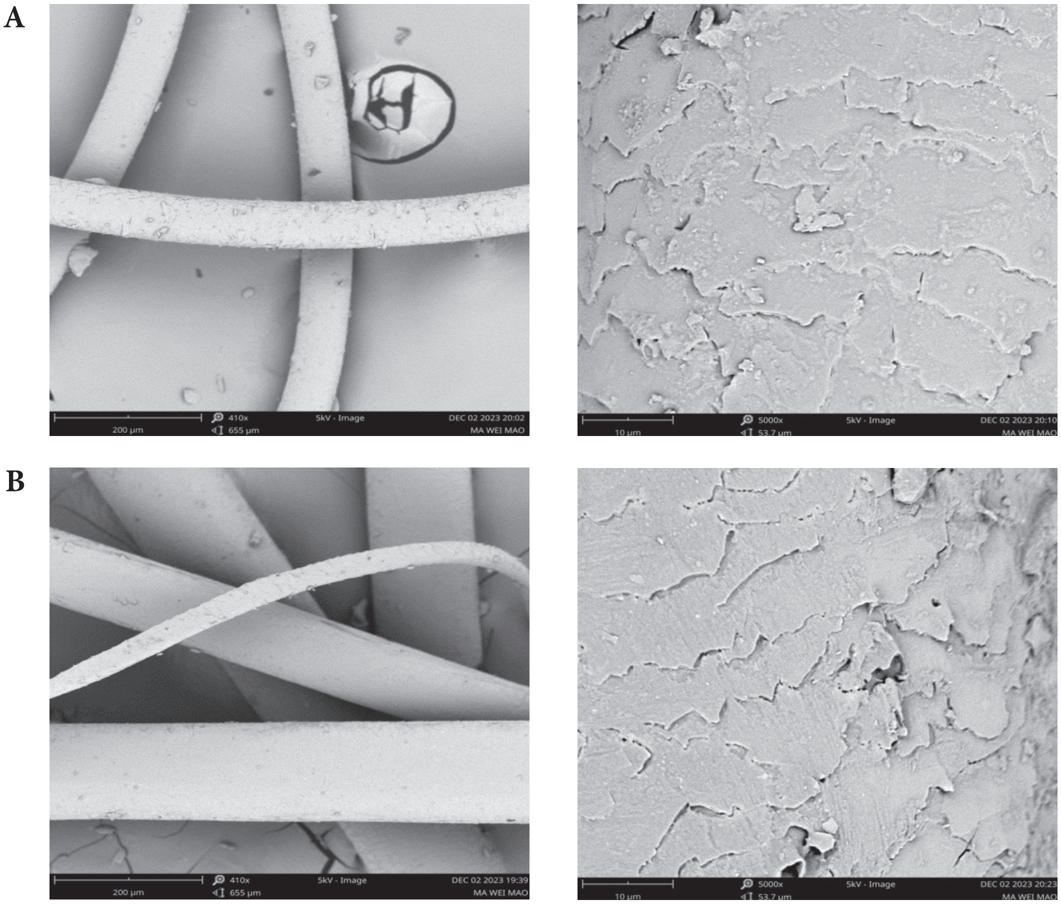

Figure 1. The surface morphology of cattle hair and human hair with magnification ×410 (left) and ×5000 (right). **A** - Cattle hair; **B** - Human hair.

action of the oil at the hair/oil interface and play a significant role in the sorption of oil by hair.

Both cattle hair and human hair are natural protein fibers, and their adsorption of oil is physical adsorption. It is mainly in the form of surface adhesion and adsorption, and the adsorption process is carried out on the surface of the fiber. For the two hairs with similar morphology and structure, their oil adsorption capacities should be comparable.

Effects of time on adsorption

The effects of contact time on the adsorption of cattle hair were tested by batch adsorption experiments at varying times of 2, 5, 10, 20, 30, 40, 60 min with other experimental variables kept constant. The results were illustrated in Figure 2. It was shown that there was a rapid increase in the sorption of the two crude oils in the first 5 minutes. From 5 to 20 min, the oil adsorption rate slowed and the oil adsorption capacities was close to saturation. After 20 min, the oil adsorption rate tends to zero and the oil adsorption capacities are

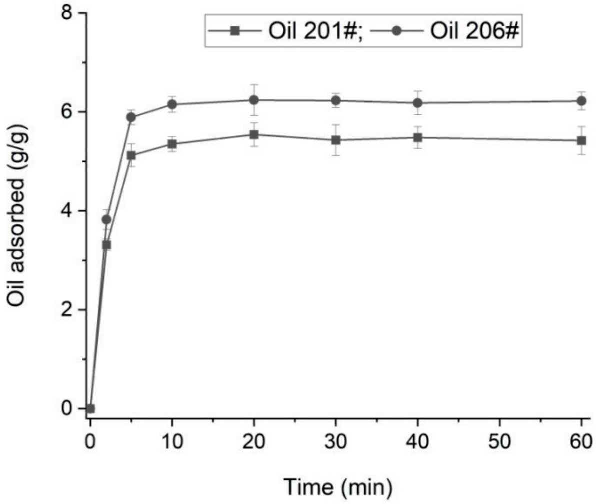

Figure 2. Adsorption rate of oil 201# and 206# on cattle hair strands at temperature 18°C. The hair dosage is 2 g and crude oil is 20 g. The bars represent standard deviation of the mean.

basically similar, which indicates that the sorption has reached the saturated oil adsorption capacities.

The initial high sorption rate might be attributed to the existence of bare sites available for adsorption on the surfaces of the hair. As most portions of these sites became occupied by the oil molecules with prolonged contact time, the adsorption rate decreased until the 20th minute, when there was no more obvious sorption of crude oils. The reasons should rely on the saturation of the surfaces of the hair with oil molecules, as well as the equilibrium between the adsorption and desorption processes that occur after saturation. Similar results were also obtained by other researchers regarding the use of yak hair[8] and human hair[9-10] for oil cleanup. Almost 90% of the total adsorbed oils took place in the first 5 min. These indicate that a certain contact time is necessary in possible field application of cattle hair for oil spill removal.

Effects of particle size on adsorption capacity

Adsorption capacities of cattle hair in strands and powder forms were determined individually with the two crude oils 201# and 206# (as listed in Table I) by batch experiments, as shown in Figure 3. For cattle hair strands, the sorbents showed higher sorption capacity for oil 206# (6.28 g/g), and lower capacity for oil 201# (5.31 g/g), indicating that the hair has more affinity for oil 206# compared to oil 201#. The better adsorption capacity for oil 206# might be due to its higher viscosity (Table I), which enhances the adherence of oils to the surface of the sorbents. The same phenomenon has been illustrated in other references.[8,16] For cattle hair powder with particle size of 40-80 μm, the adsorption capacity improved to 7.63 and 8.49 g/g for oil 201# and 206#, respectively. The reason mainly relies on the enlarged surface area of the sorbents.

The adsorption capacities of human hair in strands and powder forms were also tested under the same adsorption conditions, as illustrated in Figure 3. It was found the cattle hair could compare favorably with the adsorption capacity of human hair, because the adsorption capacities of human hair strands were 5.41 g/g for oil 201# and 6.21 g/g for 206#, and the adsorption capacities of human hair powder were 7.95 g/g for oil 201# and 8.72 g/g for 206#. Considering that human hair has been recognized as a potential sorbent for oil cleanup by many researchers,[8-9] cattle hair can be another low-cost natural adsorbent used for oil spill cleanup.

Effects of adsorbent dose on adsorption capacity

The effect of adsorbent dose (hair strands) on the adsorption efficiency was investigated, as shown in Figure 4. The adsorption efficiencies for the two oils increase with increasing mass of the

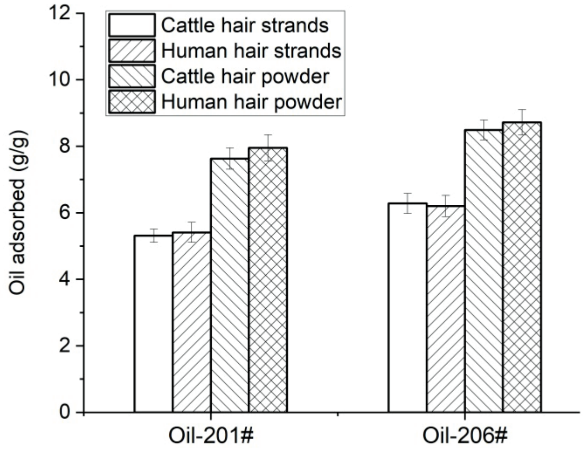

Figure 3. Adsorption capacities of cattle hair and human hair with strands and powder forms in crude oil 201# and 206# at temperature 18°C. The sorbent dosage is 2 g and crude oil is 20 g.

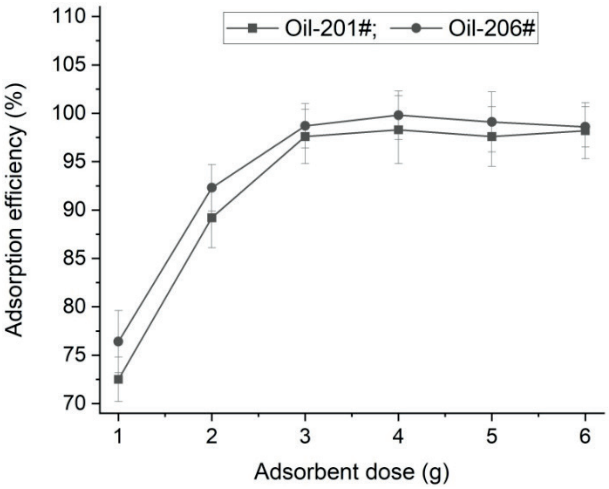

Figure 4. Dosage effect of cattle hair strands on the adsorption capacity in crude oil 201# and 206# at temperature 18°C.

adsorbent. The percentage uptake for oil 206# was found to be slightly higher than 201#. This might be related to the higher viscosity of 206#, as illustrated in Table I.

Adsorption isotherms

An adsorption isotherm helps to understand the interaction between the solute and the adsorbent, and also helps in modeling design parameters. Isotherms were depicted with equilibrium concentrations of the two oils (201# and 206#), as shown in Figure 5. The equilibrium data was further analyzed using the Langmuir and Freundlich adsorption isotherm models. The Langmuir model is often used for monolayer adsorption on a homogeneous surface with identical adsorption sites,[14-15] and is expressed as:

$$\frac{1}{Q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{b}$$

where Q_e - the adsorption capacity at equilibrium (g/g), C_e - the concentration of oil remaining at equilibrium in mg/L, a, b - the constants, a is the coefficient, and b is the maximum amount of adsorbate. A plot of $1/Q_e$ against $1/C_e$ gives a straight line.

The empirical Freundlich model is appropriate for the adsorption on a heterogeneous surface,[15] which can be expressed as:

$$\log Q_e = \frac{1}{n} \log C_e + \log k_f$$

where Q_e - the adsorption capacity at equilibrium (g/g), C_e - the concentration of oil remaining at equilibrium in mg/L, n and k_f - constants derived from the adsorption isotherm by plotting Q_e against C_e on log-log paper which produces a straight line with a slope $1/n$ while the y-intercept is k_f.

The Langmuir and Freundlich coefficients for single solute (crude oil) adsorption isotherms and their corresponding correlation coefficients are presented in Table II. The results illustrated a good fit of the Freundlich model ($R^2 \approx 0.99$) to the experimental data. This fact is not rare as similar findings being previously reported.[17-18] This fact indicates that sites with non-uniform distribution of energy level rather than on a homogeneous site with uniform distribution of energy in cattle hair. In addition, the values of 1/n were less than 1, indicating a favorable sorption of crude oil onto the cattle hair.[19]

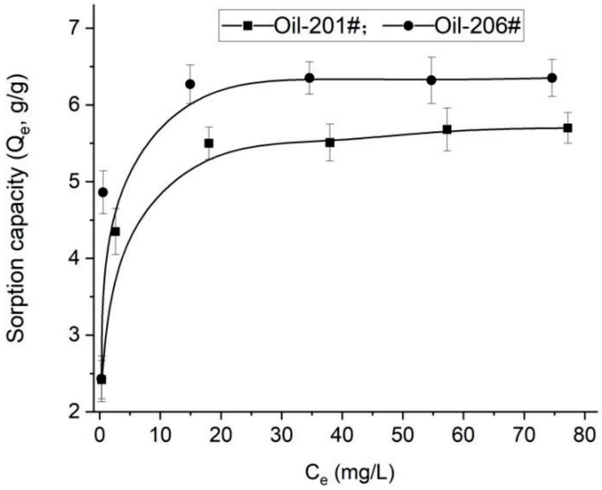

Figure 5. Adsorption isotherms of cattle hair strands to crude oils (201# and 206#) at temperature 18°C.
The hair dosage is 2 g and crude oil is 20 g.

Table II

The Langmuir and Freundlich model parameters for the adsorption of crude oils on cattle hair at temperature 18°C

Solutes	Langmuir			Freundlich		
	a	*b*	R^2	*1/n*	k_f	R^2
Oil-201#	1.146	5.682	0.9689	0.1005	3.770	0.9879
Oil-206#	0.971	6.544	0.9669	0.1149	4.164	0.9892

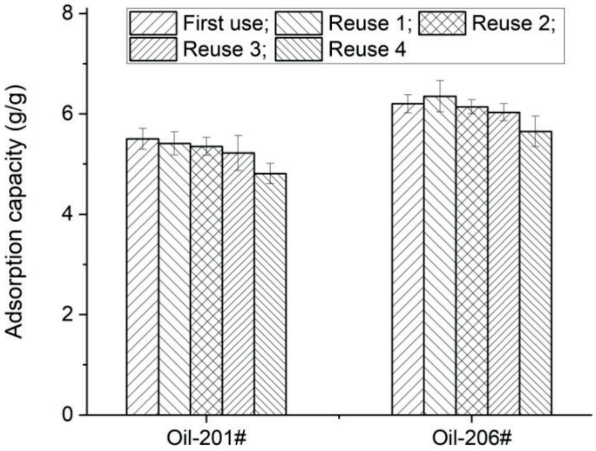

Figure 6. The reusability of the cattle hair strands at temperature 18°C

Reusability of cattle hair sorbent

The recovered cattle hair by hexane extraction method was employed to evaluate the potential of reusing the sorbent without a significant decrease in performance over time. Figure 6 illustrated the results of the reusability test in the two crude oils (201# and 206#). It could be seen that there was no significant decrease in the adsorption capacity after five cycles of reuse. This is similar to other work of Ifelebuegu et al[8] using human hair giving no obvious loss in its adsorption capacity after reusing four consecutive times, indicating the durability of this sorbent.

Conclusion

The characteristics of discarded cattle hair obtained from a tannery adopting hair-saving unhairing technology were investigated to determine its potential for scavenging a crude oil spill. Two crude oils with different viscosities were used as adsorption targets. The results indicated that the cattle hairs exhibit higher adsorption ability for crude oil with higher viscosity, and the adsorption capacity reached 6.28 g/g at 18°C. It could be improved to a maximum of 8.72 g/g when the hair fiber was pulverized to fine powder, and its capacity was comparable to human hair. The sorption showed a better fit to the Freundlich adsorption isotherm, indicating the oil retention occurring on heterogeneous sites with a non-uniform distribution of energy. The sorbent could be reused in several cycles without significant deterioration in sorption characteristics, demonstrating its potential for use as a low-cost adsorbent for oil spill cleanup. Further studies for pilot experiments are underway in the lab.

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A Concept on Biodegradability of Fatliquors-
A Sustainable and Cleaner Leather Processing

by
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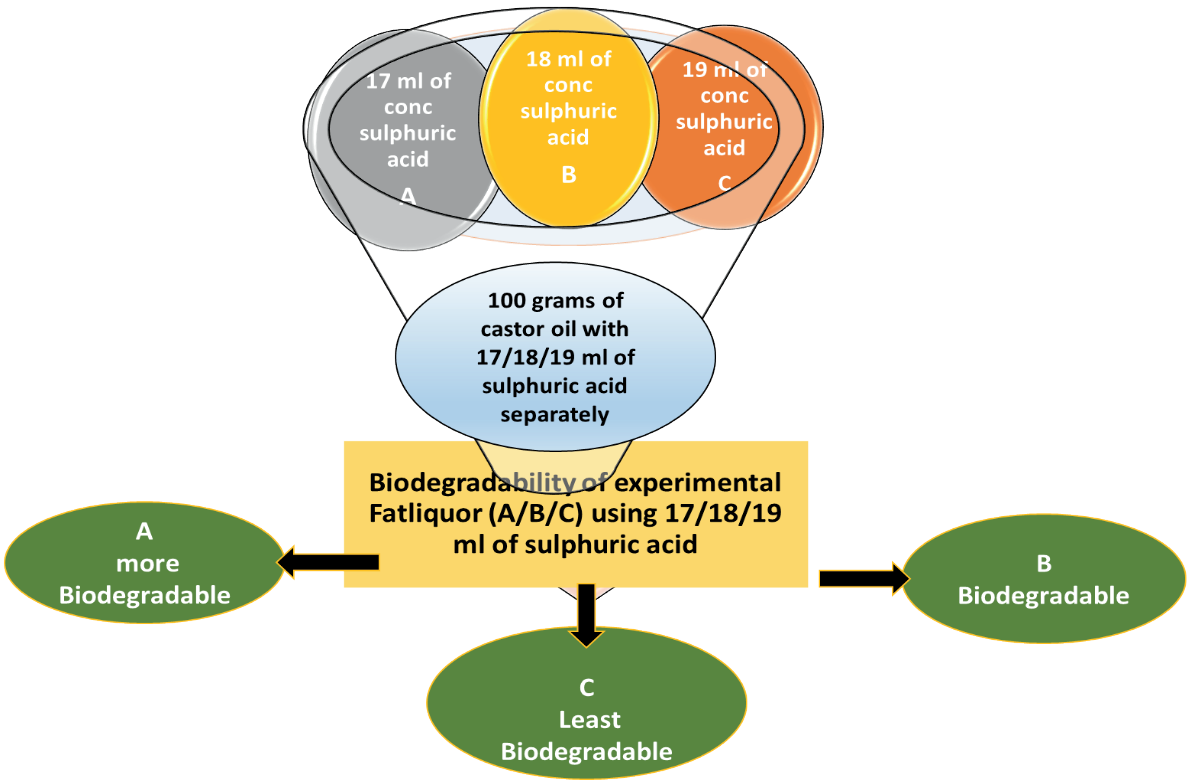
Graphical Abstract



Abstract

The biodegradability of a fatliquor is an important parameter to consider in leather processing as it is critical to obtain an easily treatable waste effluent leading towards a more sustainable and cleaner environment. Fatliquor biodegradability depends upon the functional groups (double bond or hydroxyl) present in the oil after chemical modification, the level and ratio of functional groups impact the degree of biodegradability. In the present investigation, the chemical modification of castor oil was achieved via the sulfation method by varying the level of concentrated sulfuric acid H_2SO_4 (17 to 19 ml per 100 gm of castor oil) is tested for fatliquoring properties against a control (Turkey Red Oil). The sample treated with 17 ml concentrated H_2SO_4 shows better biodegradability than the other samples. The FTIR, particle size and zeta potential analysis of experimental fatliquors and morphological and physical strength (tensile strength, and elongation) characterization of the experimental leathers are comparable to the standard values.

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Introduction

Fatliquor plays an important role in lubrication and is formed by mixing oil with water through different proportions and techniques. Chemical modification of oil is a highly explored way of fatliquor preparation. Different chemical treatment methods of oil such as transesterification, sulfation, sulfitation, epoxidation, and sulfochlorination were explored in this regard.[1-4]

The leather processing consists of multi-step operations which involve post-tanning operations where oil in the form of fatliquor is applied. The fatliquors are essential to lubricate the leather fiber during the fatliquoring process. The enhanced penetration of fatliquors in leather fibers improves the softness of the leather.[5-6]

The post-tanning process requires a high load of different chemicals e.g., fatliquors, syntans, and dyes. During the process around 10–15 % of unutilized fatliquor is discharged as waste effluent increasing the risk of environmental pollution due to the non-biodegradable nature of the fatliquors. Since fatliquors are made up of long-chain hydrocarbons with unsaturated double bonds the presence of unutilized non-biodegradable hydrocarbons hinders the natural aerobic biodegradation process. In addition, oil or fatliquors cause a coat on the top layer of the water surface and hinders the oxygen transfer between ambient air and the natural water bodies.[7,8] This phenomenon causes anaerobicity in the natural waterbodies and destroys the aquatic ecosystem. The pre-treatment technologies in effluent treatment plants such as grease-trap, tilted plate separators, dissolved air flotation systems, hybrid separation processes involving gravity settling, two-step coagulation, nano-filtration, reverse osmosis, and physiochemical separation are used to remove unutilized floating oil from the water.[9] However further managements of this excess non-biodegradable oil is challenging and available treatment technologies are uneconomical or less effective. Improper management of the floating oil separated from the waste streams may cause further possibility of contamination.[10]

Considering the above aspects, the biodegradability of fatliquor or fatliquors is directly linked to the environmental concern and sustainability of leather processing. The biodegradation process involves the participation of microorganisms and the complete breakdown of fatliquor into smaller hydrocarbons such as carbon dioxide and water. Different research indicated that the rate of biodegradability of fatliquor is closely associated with the presence of the functionality (double bonds or hydroxyl groups) that remain after the chemical modification of oil. The order of biodegradability of different fatliquors can be represented as phosphated> sulfonated> oxidized- sulfited> and sulfated, depending upon the utilization of functionality present in the oil.[11] The present study focuses on the modification of functional group present in castor oil.[12]

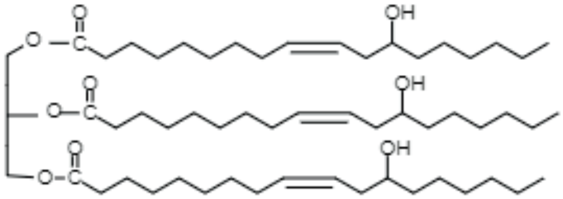


Figure 1. Structure of castor oil[12]

The main aim of the present research is to make fatliquor by using sulfonation of castor oil by adding the varying quantity of concentrated H_2SO_4 from 17 to 19 ml per 100 gm of castor oil and processing it in a specific process to obtain the desired fatliquor product. The target of the investigation is to enhance the biodegradability of a fatliquor for the post-tanning operation of leather processing. Enhancing the biodegradable nature of the fatliquors will increase the biodegradable nature of the post-tanning waste effluents. It is proposed that the conventional biological treatment technologies will be sufficient to manage the fatliquor-bearing effluent leading to a more sustainable leather effluent treatment.

Materials and Methods

Materials

Commercial-grade castor oil was procured from the local supplier from Chennai. Analytical grade sodium chloride (NaCl), sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) were procured from Sigma Aldrich (India) and used for the preparation of fatliquor. Locally grown seeds were purchased from the local market of Chennai.

Preparation of sulphated castor oil fatliquor with varying concentration of sulfuric acid

The fatliquor preparation process was carried out by taking 100 gm of castor oil in 10 separate beakers followed by the addition of concentrated H_2SO_4 dropwise (From 10 ml to 19 ml in different beakers) with constant stirring at 25°–28°C temperature.[5] The addition of concentrated H_2SO_4 in all the beakers was performed very slowly and required 3 hours to complete the reaction. Further, the obtained products were blended with 200 ml of 10% sodium chloride solution and kept for separation in a separating funnel overnight. A 30% sodium hydroxide solution was added dropwise to all of the 10 beakers to the separated products to reach a pH of 6.0. The sample prepared by adding 10ml to 19 ml of concentrated H_2SO_4 in 10 beakers is named as follows along with their visual stability (Table I).

Table I

Nomenclature of the experimental fatliquors

Sample	Concentrated H_2SO_4 in ml	Inference
SF-10	10	10% solution of the product with water is unstable and separated into two layers
SF-11	11	
SF-12	12	
SF-13	13	
SF-14	14	
SF-15	15	
SF-16	16	
SF-17	17	10% solution of the product with water is stable and not separated into two layers therefore can be used as fatliquor
SF-18	18	
SF-19	19	

Characterization of fatliquor

Particle size analysis of fatliquor

Particle size analysis of fatliquors under investigation was carried out by Zeta potential analyzer (Zeta sizer 3000, Malvean instruments HSA:2004) at Inorganic and Physical Chemistry Lab, of Council of Scientific & Industrial Research- Central Leather Research Institute (CSIR-CLRI).

FTIR analysis of fatliquor

To determine the chemical interactions of oil and concentrated sulfuric acid, the Fourier Transform Infrared (FTIR) analysis of experimental fatliquors was carried out at the Centre for Analysis, Testing, Evaluation and Reporting Services (CATERS), Council of Scientific & Industrial Research- Central Leather Research Institute.

Biodegradability test of fatliquors

The biodegradability test of the sulfated fat liquor samples was performed by determining the ratios of 5 days BOD5 and COD of each sample.[13] The BOD5 and COD analysis was performed by following the standard method.[14] Aerobic bacterial seeds from an aerobic reactor treating synthetic tannery wastewater sample in the Environmental Engineering Laboratory Council of Scientific & Industrial Research- Central Leather Research Institute is used for performing BOD5 analysis.

Fatliquor Application in post-tanning operation

The three fatliquors are made up of adding 17, 18, and 19 ml of concentrated H_2SO_4 in 100 grams of castor oil separately, applied in post tanning operation of leather making. The systematic process and different chemicals used in the post-tanning leather processing are expressed in Table II.

Table II

Process recipe for fatliquoring

Process	Materials	Amount (%)	Time	Remarks
Neutralization	Water Neutralizing syntan Sodium bicarbonate + Water	100 0.5 0.2 10	30 min 2 × 10 min + 30 min	pH:5.0-5.2, drained and wash twice
Retanning	Water Melamine syntan + Phenolic syntan + Tara powder	50 5 5 4	60 min	
Fatliquoring	Water	50	2 × 15 min + 60 min	
Control	Terkey red oil	10		
Experimental process	Sulfated fatliquor with 17ml (SF-17), 18ml (SF-18), 19ml (SF-19)	10		
Fixing	Formic acid + water	2 + 10	3 × 10 min + 60 min	Check exhaustion and pile

Four tanned wet-blue leathers were obtained from the Leather Process Technology Department of the Council of Scientific & Industrial Research- Central Leather Research Institute. The four wet blues were treated with experimental fatliquors and compared with the control fatliquor which is Turkey red oil. Turkey red oil is well-established fatliquor commercially used for leather softening and is prepared by sulfonation of castor oil.[15]

Scanning Electron Microscopic (SEM) analysis

The morphology of both control and experimental leather was analyzed by Thermo Fisher Scientific, India from CATERS, Council of Scientific & Industrial Research- Central Leather Research Institute. The SEM analysis of leathers was carried out to evaluate the surface and cross-sectional morphology of the fibers.

Physical strength characteristics and organoleptic properties of leather

The physical characterization such as tensile strength, and % elongation at break of control and experimental leathers was carried out according to the standard methods[16] at CATERS, Council of Scientific & Industrial Research- Central Leather Research Institute. The experiments were also performed to evaluate different organoleptic properties of leathers such as softness, grain smoothness, fullness, and overall appearance by hand and visual examination by an experienced tanner from the leather industry. They have been rated on a scale of 1-10, where a higher point indicates better properties.

Effect of fatliquor on the germination of *Vigna radiata L. Wilcze*

The germination of plant seed was investigated in fat liquor solutions and the growth of the sprout length was evaluated to understand the possible plant growth in fatliquor solution at Inorganic and Physical Chemistry Lab, Council of Scientific & Industrial Research- Central Leather Research Institute. The *Vigna radiata L. Wilcze* seeds were used in this process to perform the experiments. Initially *Vigna radiata L. Wilcze* seeds were placed in three different petri plates containing 10 ml of 6% spent fat liquor (SF-17; SF-18; SF-19) solutions.[5] The petri plates were kept under observation for four days at room temperature ~30°C at atmospheric pressure and the growth of sprout length was evaluated.[17]

Results and Discussions

Fatliquor Particle Size and Zeta Potential Analysis

The emulsion stability depends upon the chemical and physical factors that affect the size of the dispersed phase. Temperature, addition of external solvents, aging of emulsion and charges present on the emulsion are key factors that decide the stability of emulsion over a period of time. Reduced particle-size will allow for more particles to be distributed on the interface, forming a more stable emulsion.[18.19]

The particle size and charges present on the experimental fatliquors using a minimum (17ml) concentration of sulfuric acid with respect to SF-18, SF-19 and control are shown in Figure 2 (A-D) and 3(A-D) respectively.

From the Figures 2 (A-D) it has been concluded that the size of the particles of the experimental fatliquors (SF-17 SF-18 and SF-19) is very close (89.29 nm, 108.3nm, 87.53nm respectively) to the control values (99.16 nm) and therefore suitable for the proper fatliquoring

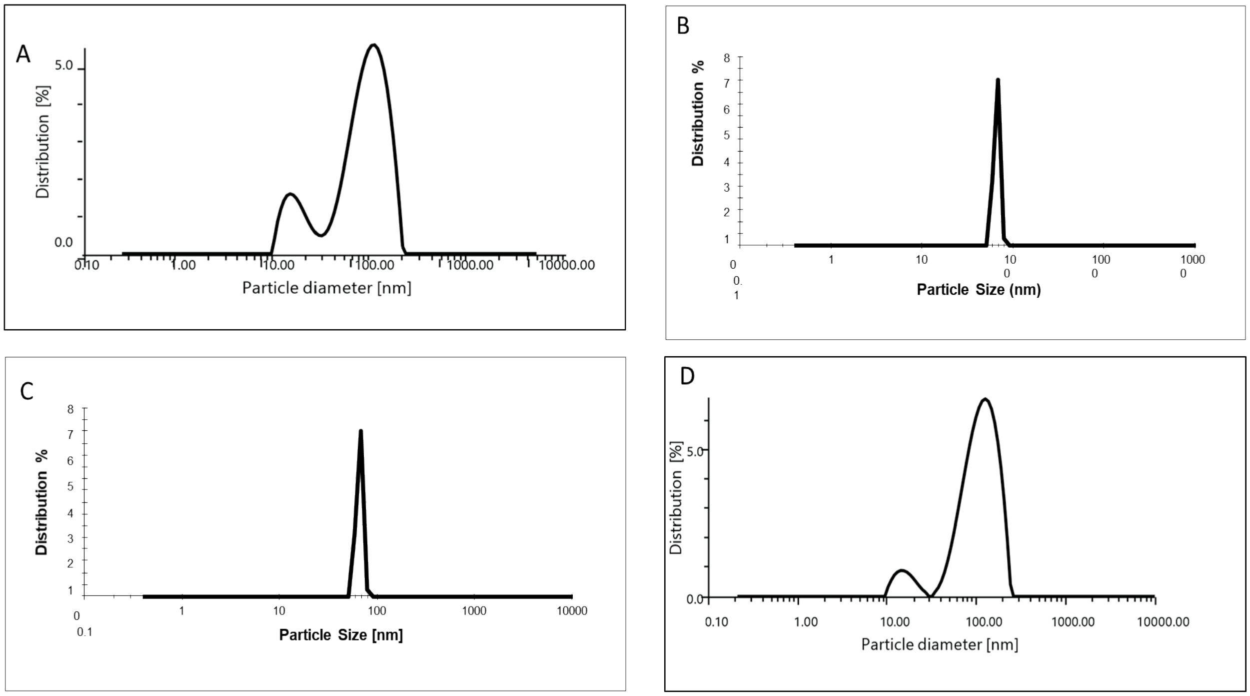


Figure 2 (A-D). Particle Size of experimental fatliquor SF-17, SF-18, SF-19 and control respectively

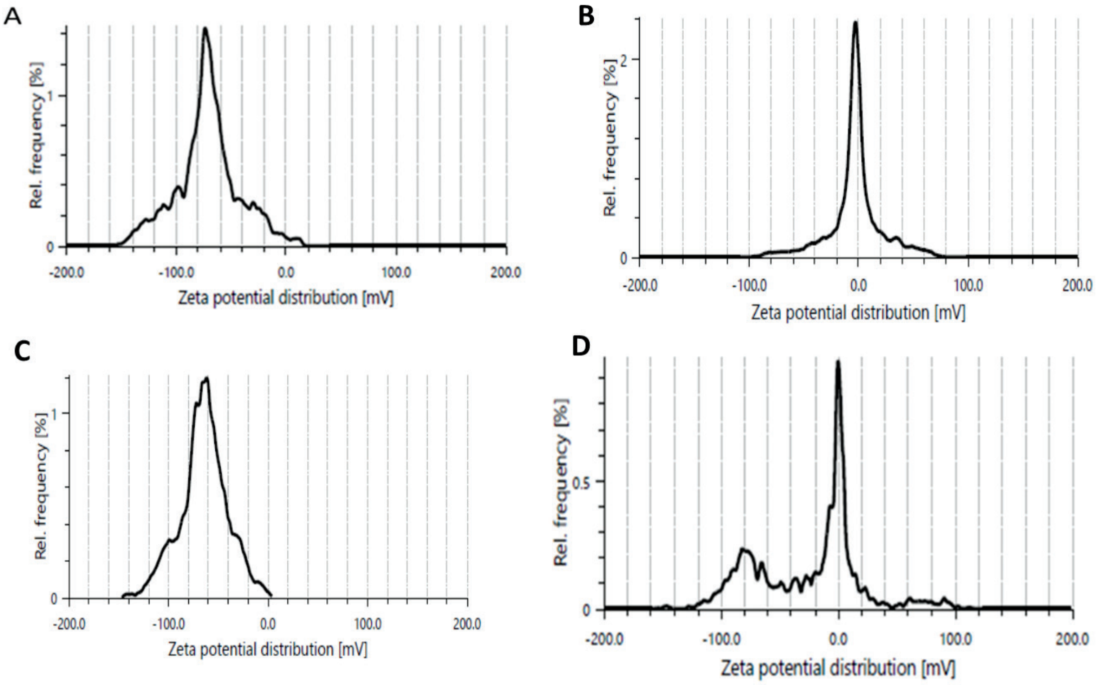


Figure 3 (A-D). Zeta Potential of experimental fatliquor SF-17, SF-18, SF-19 and control respectively

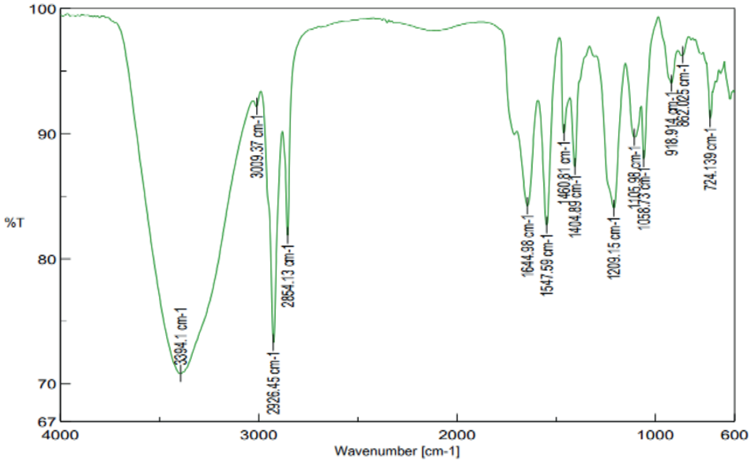


Figure 4A. FTIR of Fatliquor using SF-17

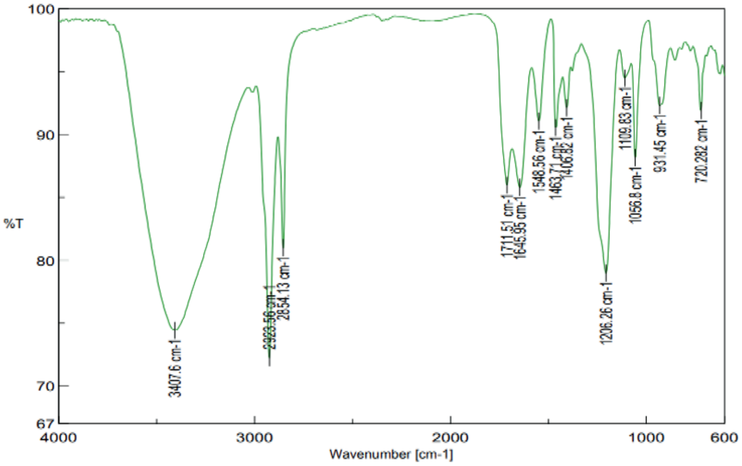


Figure 4B. FTIR of Fatliquor using SF-18

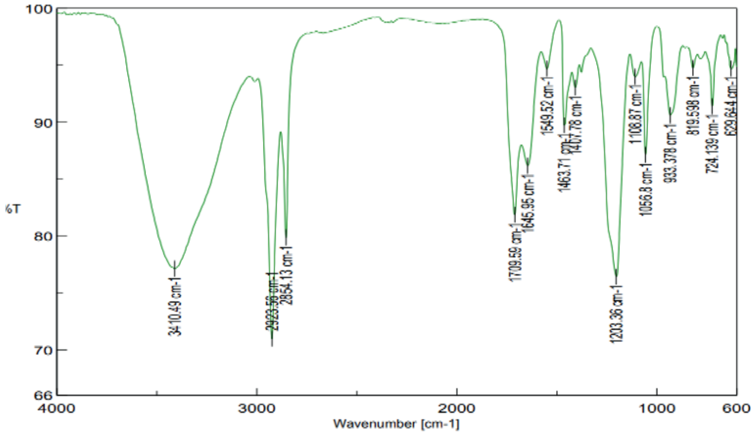


Figure 4C. FTIR of Fatliquor using SF-19

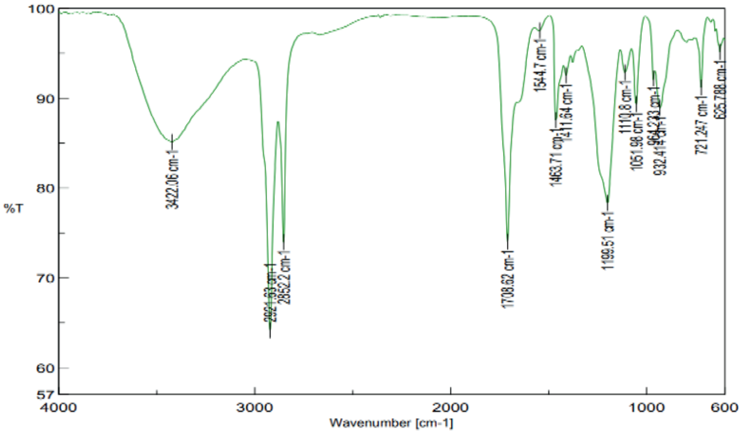


Figure 4D. FTIR of control Fatliquor (Terky Red oil) of the experimental leathers. The particle sizes of the experimental fatliquor are in the range of ±20nm with respect to control which are sufficient to lubricate the leather fibers.

Charges present on the emulsion are key factors for its stability, oppositely charged particles tends to reduce the stability of emulsions. Zeta potential analysis of the emulsion provides information about the charges present on the emulsion particles and can predict the stability of the emulsion.[20] As per the figure 3A-D the negative values indicates that the dispersed particles in the experimental fatliquors have a negative charge.

FTIR Analysis of fatliquors

The Fourier transform infrared spectroscopic analysis of functional groups of control and experimental fatliquors is shown in Figure 4(A-D). The C-H symmetric and asymmetric stretching vibrations of CH_2 groups have been detected at 2926 and 2864 cm^{-1}. The band at 1742 cm^{-1} is due to CO stretching and the absorption bands at 1200±05 cm^{-1} are due to the $-SO_3$ group. The presence of a broad peak at 3400±50 cm^{-1} in all four spectra implies the intramolecular hydrogen-bonded OH group present in fatliquor. The peak at near 1223 and 712±50 cm^{-1} corresponds to =CH group.

Biodegradability test

Fatliquor biodegradability broadly depends upon the availability of functional groups higher functionality (double bond or hydroxyl bond) correlates with higher biodegradability.[20] In the present research, the sulfonation of castor oil was carried out by adding varying amounts (17 to 19 ml) of concentrated sulfuric acid. As the concentration of sulfuric acid increases, the availability of the hydroxyl group decreases due to the interaction with sulfuric acid and the same may be observed in the FTIR spectra where the intensity of the peak of the hydroxyl group getting reduced and the intensity of the $-SO_3$ group is increasing indicating hydroxyl groups are replaced by $-SO_3$ groups as more H_2SO_4 is added. Therefore, the biodegradability of sample SF-17 might be higher than that of SF-18, SF-19, and control samples. The biodegradability test in the subsequent section confirms the present hypothesis.

Table III

BOD/COD of different fat liquor samples

S. No.	Sample	BOD/COD
1.	SF-17	0.337
2.	SF-18	0.235
3.	SF-19	0.226
4.	Control	0.019

A higher ratio of BOD_5/COD indicates higher biodegradability of the fat liquor. The BOD_5/COD values of each sample are presented in Table III. The sequence of the BOD_5/COD ratio of the samples was observed SF-17> SF-18> SF-19> Control, which indicates SF-17 is comparatively more biodegradable than other fat liquors and control is the least biodegradable fat liquor. Considering this sequence this can be inferred that SF-17 fatliquor is a more suitable chemical for leather processing and effluent generated due to the use of SF-17 fatliquor can be biodegraded more efficiently.

Effect of Spent Fat Liquors on the Germination of *Vigna radiata L. Wilcze* and Stem Length of Sprouts

The length of sprouts as shown in Figures 4A to 4F represents the growth of *Vigna radiata L. Wilcze* in the presence of as-synthesized different fatliquor. The Figure 4A-C and Table IV represents the

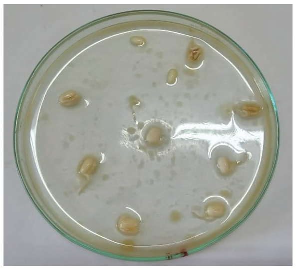
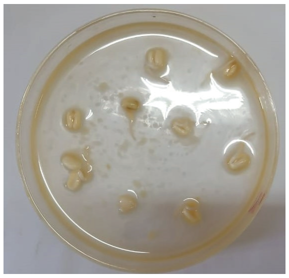
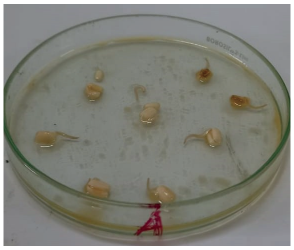
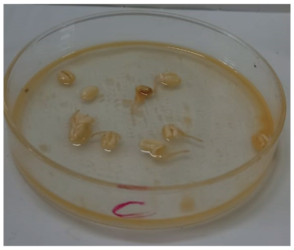
Days	A (SF19)	B (SF18)	C (SF17)
Day-1			
	5A	5B	5C
Day-4			
	5D	5E	5F

Figure 5(A-C). represents day 1 and **5(D-F)** represents day 4 of sprout growth

Table IV

Sprout growth of experimental samples of *Vigna radiata L. Wilcze*

S. No.	Sample	Name	Sprout growth in cm	
			Day 1	Day 4
1.	SF-19	A	0.8±2	1.5±2
2.	SF-18	B	0.6±2	1.2±2
3.	SF-17	C	0.7±2	3.5±2

mean values of sprout growth in day one in Petri plate A (SF-19) B (SF-18) and C (SF-17) which corresponds to 0.8 cm, 0.6 cm and 0.7 cm respectively. The same plates were re-observed after the 4th day and the mean value of sprout growth of experimental seeds was measured at 1.5 cm, 1.2 cm and 3.5 cm for A (SF-19) B (SF-18) and C (SF-17) respectively shown by Figure 4D-F and Table IV. Therefore, the SF-17 spent fat liquor was found to be more suitable for sprout growth and having lesser toxic effect on plant.

Scanning Electron Microscopic (SEM) Analysis

The grain morphology of the leathers processed by the fatliquors under investigation is almost similar to the leather processed by the control fatliquor Turkey Red Oil. This indicates the better diffusion of as-synthesised fatliquors at inter fibril level. Considering this observation can be understood that by using SF-17 fatliquor replacing the control Fatliquor (Turkey Red Oil) the quality of the leather product will not be compromised.

Physical Strength Characteristics and Organoleptic Properties of Leather

The physical properties of the leather produced by using different as-synthesized fatliquors were also evaluated and significant deviations between the physical parameters were not observed (Table V). Comparable physical parameters such as tensile strength, elongation, and softness again ensure that the use of SF-17 as a substitute fatliquor will not cause any significant variation in the physical properties of the leather. In addition, the physical properties are also within the suitable range for commercial usage of leather processed by using these fatliquors.

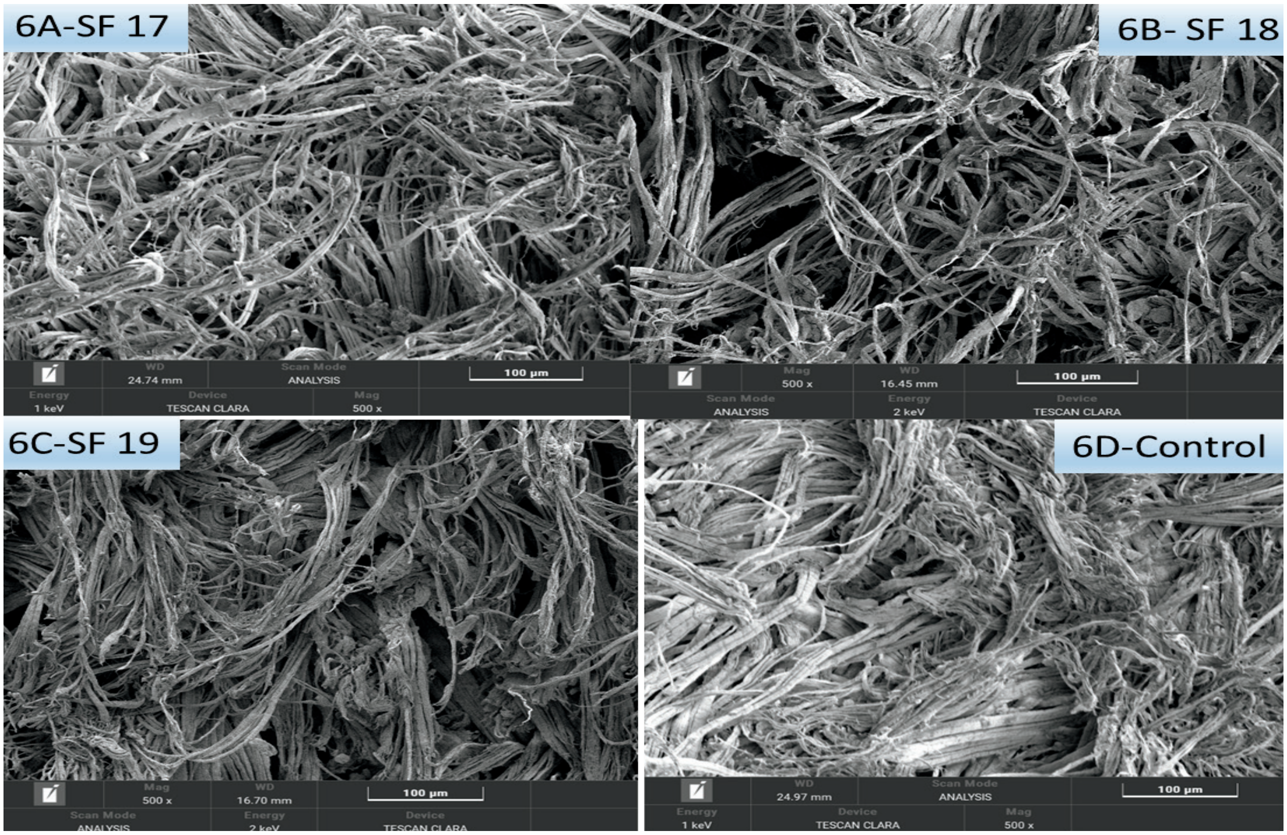


Figure 6 (A-D). SEM images of experimental leathers SF-17, SF-18, SF-19 and control respectively

Table V

Physical properties of the leather processed by as-synthesized fatliquors

S. No.	Characteristics	SF-17	SF-18	SF-19	Control
1.	Tensile strength (N/mm^2)	14±1	15±1	15±1	15±1
2.	Elongation at break (%)	50±2.5	66±2.5	50±2.5	64±2.5
3.	Softness	6.30	6.47	6.38	6.48

Conclusion

The current research proposed the fundamental understanding of the utilization of the functionality of oil for fatliquor preparation and the biodegradability of the same. It could be concluded from the study that the functional groups present in the castor oil in the form of unsaturation and hydroxyl groups correlates with biodegradability. The hydroxyl group present in castor oil is chemically modified by the sulfonation process. A correlation exists in that the higher the level of hydroxyl consumed, the lower the level of biodegradability. Therefore, experimental Trial I where SF-17 is used for complete emulsification of castor oil shows better biodegradability than experimental Trial II (SF-18), experimental Trial III (SF-19), and control where Turkey red oil is used.

Acknowledgments

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Bisphenol Reduction in Syntans and Examples for Extraction and Migration of Bisphenols from Leather Articles

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Abstract

Bisphenol S and F play a major role in the synthesis of syntans. Bisphenol S can be a starting material or undesired side product, while bisphenol F can form as an undesired side product. They can be found in basically all syntans in a range from close to the detection limit up to several thousand parts per million and can be detected in most leather articles by extraction or by migration. In an initiative by the European Chemicals Agency (ECHA) to drastically reduce bisphenols in consumer goods and in the environment, challenging limits were proposed in 2022. These limits would have had a strong impact on syntan portfolios of the leather chemical manufacturers and on many leather articles. After a public a consultation, ECHA has temporarily withdrawn the restriction proposal and wants to re-work it. Examples for reductions of both bisphenols in leather chemicals and the impact on extractions and migration from leather articles down to detection limits will be outlined in this article.

Introduction

Bisphenol A (BPA) is common building block in the chemical industry, especially for plastic materials and is on the ECHA list of substances of very high concern since 2017 due to its toxicity for reproduction.[1] Other studies about the toxicity of bisphenol A have been published abundantly.[2] BPA is seldomly found in leather articles and leather chemicals.

In 2020 efforts were started in the EU to restrict BPA further and to prevent substitution of bisphenol A with similar structures, called bisphenols of similar concern (BosCs) including bisphenol S (BPS) and bisphenol F (BPF). Both play a major role in syntan synthesis. In 2020 and 2021 two calls for evidence were run by national affiliates working on behalf of ECHA for BPA and BosCs restrictions. After the end of the second call for evidence, ECHA published a restriction proposal with a limit of 500 parts per million (ppm) as the sum of all bisphenols for both leather chemicals and leather articles for a period of five years after the resulting regulation would come into force. After that time a limit of 10 ppm was proposed for the sum of all bisphenols in leather chemicals and leather articles. In case these values could not be met, a migration value of 0.04 mg/L as the sum of all bisphenols was proposed for leather. This proposal was published end of 2022 and open for public consultation until the end of June 2023. With the input of this consultation, ECHA wanted to finalize a restriction proposal for the European Commission, that would have entered the legislative process in the EU. However, as a result of the public consultation, ECHA has temporarily withdrawn the restriction proposal and wants to re-work it, as announced end of August 2023.

In leather chemicals BFS and BPF are not used as BPA substitute. Several studies about the reproductive toxicity of BPS have been published, more recent ones also include BPF.[3] While BPS is already classified reprotoxic 1B in the EU, this process is still in preparation for BPF. Reprotoxic 1B means that animal studies have clearly shown reproductive effects and that it is suspected to have a similar effect on humans. This classification in the EU requires BPS to be mentioned in the safety data sheet of a chemical if the concentration exceeds 1,000 ppm and to label the whole product with a hazardous warning notice if the concentration is larger than 3,000 ppm.

Experimental

In the synthesis of syntans two chemistries are applied: phenolic syntans starting from phenol and sulfone syntans starting from BPS. In the latter BPS is condensed with formaldehyde leading to a poly-condensate, as can be seen in Figure 1.

The condensation can be carried out either in presence or absence of naphthalene or phenolic chemistry. In either case, BPS remains as a rest monomer in the product, due to the low reactivity of BPS.[4]The chain length of the poly-condensate, reflected by “n” in Figure 1, dominantly depends on the amount of formaldehyde added and indicates that the structure inside the parenthesis is repeated “n” times. It can be measured in a size exclusion chromatography and

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Some data of this Technical Note was presented at the IULTCS conference in Chengdu, China, October 18-20, 2023, as a PowerPoint presentation, subsequently converted to this manuscript and significantly extended with recent data, including migration results.

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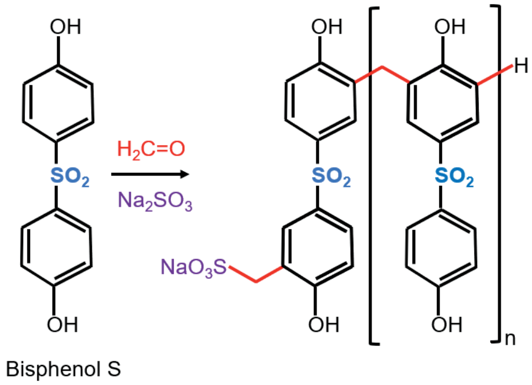

Figure 1. Synthesis of sulfone syntans

related to a standard or reference compound.[5] This value is important to maintain in the optimization of existing products, otherwise performance properties like fullness, softness, and grain tightness could change significantly.[6] BPS levels of the sulfone syntans in the market range from several hundred to several thousand ppm, depending upon reaction conditions. In case this chemistry is carried out in the presence of phenol, BPF can be detected in this chemistry as well. The products are analyzed for BPS and BPF via calibrated high pressure liquid chromatography (HPLC) analog to DIN EN ISO 11936.

In phenolic syntans, phenol is partially sulfonated and condensed with formaldehyde.[7] The synthesis is depicted in Figure 2. Here BPS forms as a side product in the first step, the so called sulfonation, in a range between double digit ppm and several hundred ppm, depending on reaction conditions. Many products from this chemistry in the market have 200 – 500 ppm BPS. BPF is the reaction product of unreacted phenol and formaldehyde and can form between below detection limit and above 10,000 ppm, again depending upon reaction conditions. Synthesis of the syntans described here were carried out in reactors between five tons and twenty tons.

Re-tanning was carried out with wet blue, obtained from the treatment of pickeled pelt with 6-8% chromium sulfate. In a typical example, 100 g of wet blue of southern German origin with a strength of 1.7 mm was treated in a 3.5 L tanning drum with 100 g water, 1.2 g sodium formiate and 0.3 g sodium bicarbonate and the drum was turned for 90 minutes. The resulting float had a pH of 4.5. Approximately 6 g of the retanning agent referring to active material were added and turning of the drum was continued for 90 minutes. The float was discharged and the leather washed with 200 g water. Subsequently, the leathers were treated with three percent of a standard brown dye and with two percent of a standard fat liquor in 200 g water for 90 minutes, before the float was acidified with 0.7 g 85% concentrated formic acid and the drums were turned for 20 minutes. The float was discharged and the leathers were dried via hang drying over night without vacuum at room temperature and subsequently stacked.

For the extraction of BosCs from leathers, the DIN EN ISO 11936 was applied. For this, one gram of leather was cut into small pieces and extracted with 20 mL methanol at 60°C for one hour in an ultrasonic bath, which provided agitation. The extraction solutions

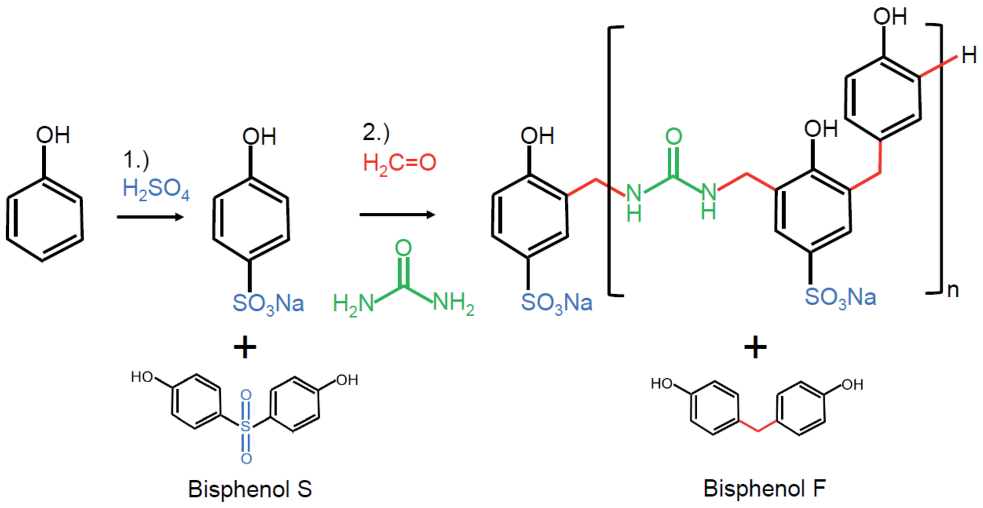

Figure 2. Synthesis of phenolic syntans

were analyzed via calibrated HPLC. This is also applied for the determination of the bisphenols in the products for which they are dissolved in water. The latter modification of DIN EN ISO 11936 can also be used for the analytics of bisphenols in the application floats.

For the migration of BosCs from leathers, the DIN EN ISO 11641 was applied. This procedure derives from color migration tests in which the textile soaked in an artificial sweat solution is pressed on a piece of leather for 3 h at 37°C. For migration the sweat solution was analyzed for BosC's via calibrated HPLC analog to this step in extraction assays via DIN EN ISO 11936.

For leather application evaluation the softness can be quantified according to DIN EN ISO 17235, or via haptics. Grain tightness and fullness were evaluated via haptics. Bleaching and dye penetration were evaluated after application with a brown dye. The lightfastness and heat ageing properties were determined via Xeno test in a Suntester according to DIN EN ISO 105-B06.

Results and Discussion

Examples of bisphenol reductions in syntans

In the sulfone syntans BPS is the starting material and remains as a rest monomer. Through process optimization, changing the parameters like equivalents of starting materials, time, pressure, and pH, the BPS content in sulfone syntan 1 could be reduced from 25,000 ppm in the old version down to 2,700 ppm. The product contained also BPF. Results are depicted in Table I. With a sum of 5,400 ppm bisphenols in syntan 1 the intended level of 500 ppm was still clearly exceeded. For further improvements the chemistry of syntan 1 was changed from sulfone chemistry to phenolic, leading to syntan 1.LB, in which "LB" stands for low bisphenols. In extensive application trials the maintenance of the performance on leather of syntan 1.LB compared to syntan 1 and syntan 1 old were positively tested. Evaluation included fullness, softness, grain tightness, dye penetration, bleaching, as well as fastness properties. The only measurable differences between the "LB" version, the current or the old version of syntan 1 are the bisphenol contents. The content of the sum of bisphenols could be lowered by more than 99% from syntan 1 to syntan 1.LB. These products are spray dried powders with dry matter equal or larger than 95 percent. Due to the high BPS content syntan 1 old is not marketed anymore.

Extraction results of bisphenols from re-tanned leather

For the extraction of BosCs from leathers, we approached two research institutes, FILK in Freiberg, Germany and CTC in Lyon, France to extract our leathers. The leathers were made with 6% of the syntan as a powder. We extracted the leathers ourselves as well and compared the results. Measurements at three different sites, FILK, CTC, and our lab, came out within a reasonable and realistic margin of error. The values for the sum of bisphenols ranged from 970 ppm to 1,230 ppm. As can be seen in Table II, the approximately tenfold reduction of BPS in the product from syntan 1 old to syntan 1 is reflected in the BPS extraction values from leathers re-tanned with these products. With syntan 1 a BPS level of 150 ppm and 100 ppm BPF were extracted at the FILK institute leading to 250 ppm as the sum of bisphenols extracted. This is identical to what was extracted in Stahl and 80 ppm higher than the level extracted at CTC institute. This is showing that with optimized products like syntan 1 leathers with below 500 ppm bisphenols extracted can be achieved. Since the level of all bisphenols in the product in syntan 1 with 5,400 ppm clearly exceeded the initially proposed limit of 500 ppm, work continued to develop syntan 1.LB. Here a level of 35 ppm BPF was achieved while the BPS level was below a detection limit of 10 ppm. At the FILK institute less than the detection limit of twenty ppm of BPS and BPF could be extracted from crust made with syntan 1.LB.

Table I

BPS and BPF in syntan 1

	BPS [ppm]	BPF [ppm]	Σ (BPS + BPF) [ppm]
Syntan 1 old (until 2020)	25,000	2,700	27,700
Syntan 1 (since 2020)	2,700	2,700	5,400
Syntan 1.LB (LB = low bisphenols, since 2024)	< 10	35	< 45

Table II

Extraction from leathers made with 3 types of syntan 1 in re-tanning (6%)

	Measurement in product at Stahl [ppm]	**DIN EN ISO 11936 measurement in [ppm] after extraction from leather at:**		
	BPS / BPF (S = BPS + BPF)	Stahl BPS / BPF (S = BPS + BPF)	FILK BPS / BPF (S = BPS + BPF)	CTC BPS / BPF (S = BPS + BPF)
Syntan 1 old	25,000 / 2,700 (Σ = 27,700)	860 / 140 (Σ = 1,000)	1,100 / 130 (Σ = 1,230)	730 / 140 (Σ = 970)
Syntan 1	2,700 / 2,700 (Σ = 5.400)	130 / 120 (Σ = 250)	150 / 100 (Σ = 250)	80 / 90 (Σ = 170)
Syntan 1.LB	< 10 / 35 (Σ = < 45)		< 20 / < 20	

For the theoretical amount extractable from crust, it was taken into account that six percent of a syntan was used on wet blue for re-tanning. It was again assumed that wet blue has about a fifty percent water content and that it takes therefore two grams of wet blue to obtain one gram of crust, which is the relevant amount for extraction. This leads to the maximal calculated amount of twelve percent syntan inside the crust. In this calculation, depicted in the third column of Table III, it is assumed that all the syntan is taken up and none remains in the float. We wanted to determine the recovery rate of BPS and BPF in extraction and analyzed extracting the same crust three times. As can be seen in Table III, the amount BPS collected after the first extraction with 150 ppm BPS and 150 ppm BPF corresponds to 46 percent of the calculated amount of 324 ppm of each bisphenol. A second extraction still accesses 49 ppm BPS and 37 ppm BPF. The sum of the two extractions collected 199 ppm BPS and 187 ppm BPF. This corresponds to 61% recovery rate for BPS and 58% for BPF after two extractions. A third extraction of the same crust showed BPS and BPF below detection limits of 20 ppm, as given by the FILK institute for these HPLC measurements. The third extraction did not contribute to raise the recovery rate. From a scientific view this is important to realize that single extraction leads only to a partial and lower recovery rate. From a practical view, repeated extraction is less feasible for large throughput. With smaller amounts of extractable bisphenols, the recovery rate increased.

For the phenolic syntans both BPS and BPF are relevant, but as described earlier, BPS only to a minor extent. As can be seen in Table IV, the optimization of phenolic syntan 2 revealed a reduction of both BPF and even BPS by 99%. The performance on leather could

Table III

Repeated extraction from leathers made with 6% syntan 1 in re-tanning

	Measurement in product [ppm]	**Calculated extractable from crust [ppm] = 12%**	**1st Extraction [ppm]**	**2nd Extraction [ppm]**	**3rd Extraction [ppm]**
	BPS / BPF (Σ = BPS + BPF)	BPS / BPF (Σ = BPS + BPF)	BPS / BPF (Σ = BPS + BPF)	BPS / BPF (Σ = BPS + BPF)	BPS / BPF (Σ = BPS + BPF)
Syntan 1	2,700 / 2,700 (Σ = 5.400)	324 / 324 (Σ = 648)	150 / 150 (Σ = 300)	49 / 37 (Σ = 86)	< 20 / < 20 (Σ = < 40)

Table IV

Extraction results from leathers made with phenolic syntan 2 and 3 in re-tanning; values measured internal, as well as at the FILK (Freiberg) and PFI (Pirmasens) institutes

	Measurement in product			**Measurement after extraction (8% retanning)**		
	BPF [ppm] (source)	**BPS [ppm] (source)**	**Σ (BPS + BPF) [ppm]**	**BPF [ppm] (source)**	**BPS [ppm] (source)**	**Σ (BPS + BPF) [ppm]**
Syntan 2	8,400 (Stahl)	400 (Stahl)	8,800	510 (PFI)	15 (PFI)	525
Syntan 2.LB	85 (PFI)	< 5 (PFI)	< 90	< 5 (PFI)	< 5 (PFI)	< 10
Syntan 3	< 10 (Stahl)	60 (Stahl)	< 70	< 20 (FILK)	< 20 (FILK)	
Syntan 3.LB	< 5 (PFI)	< 5 (PFI)				

be maintained in re-tanning in all aspects. The detection limit of ten ppm for both bisphenols was measured with our HPLC. In an extraction measurement at the PFI institute in Pirmasens leathers re-tanned with 8 percent syntan 2.LB had BPS and BPF levels below the detection limit of five ppm leading to less than ten ppm as the sum of bisphenols. This advanced detection limit could be reached through mass coupling (LC/MS) of the identified peak in HPLC. Syntan 2 and syntan 2.LB are spray dried powders with dry matter equal or larger than 95 percent.

Phenolic syntan 3 showed double digit values of BPS and BPF values below the detection limit of ten ppm in the product. This is the detection limit of our HPCL. Extraction from leathers re-tanned with this product came out below detection limit of twenty ppm for both bisphenols. This detection limit was given by the measurements of the FILK institute that conducted the extraction.

In an effort to lower BPS in syntan 3 further, syntan 3.LB was developed. Here BPS levels could be lowered to below five ppm while maintaining BPF below the detection limit. This measurement was carried out at the PFI institute in Pirmasens, where five ppm is the detection limit. For the sum of both bisphenols, a value smaller than ten ppm could be reached for the first time. Again, it was important to test the performance of syntan 3.LB in all re-tanning aspects as well as on heat and light fastness properties compared to syntan 3 to enable same applications. This was achieved. Note that syntans 3 and syntan 3.LB are liquid syntans with a concentration of forty percent.

Migration results of bisphenols from leather re-tanned with syntans 2 and 2.LB

In the ECHA restriction proposal from 2022 it was envisioned that after a period of five years, in which a limit of 500 ppm BosC's would be applicable, a new limit of 10 pm of BosC's would be enforced for the sum of all bisphenols in leather chemicals and leather articles. In case these values could not be met, a migration value of 0.04 mg/L of BosC's was suggested for leather as the sum of all bisphenols, measured via DIN EN ISO 11641. In this test, a textile soaked in an artificial sweat solution was pressed on a piece of leather for three hours at 37°C. Afterwards, the sweat solution was analyzed for BosC's that have migrated from leather via calibrated HPLC analog to this quantification step in the extraction assay DIN EN ISO 11936. As can be seen in Table V leathers re-tanned with eight percent syntan 2 showed migration values of BPS and BPF below the detection limit of 0.04 mg/L. This was surprising, since this was the unoptimized version of the product. With the optimized syntan 2.LB, the same results were achieved as well.

Table V

Results of BosC's migration from leathers made with phenolic syntan 2 and 2.LB measured at PFI institute

	Measurement in product			**Migration measurement (8% retanning)**		
	BPF [ppm] (source)	**BPS [ppm] (source)**	**Σ (BPS + BPF) [ppm]**	**BPF [mg/L]**	**BPS [mg/L]**	**Σ (BPS + BPF) [mg/L]**
Syntan 2	8,400 (Stahl)	400 (Stahl)	8,800	< 0.04	< 0.04	< 0.08
Syntan 2.LB	85 (PFI)	< 5 (PFI)	< 95	< 0.04	< 0.04	< 0.08

Conclusions

Through process optimization we improved a major sulfone syntan and we lowered the BosC's level by 99 percent by changing from sulfone chemistry to phenolic condensation. This reduction is also reflected by a corresponding reduction of BosCs after extraction from leather. The performance of the product concerning fullness, softness, grain tightness, dye penetration, bleaching, as well as fastness properties remained unaffected even after the change from sulfone to phenolic chemistry.

A single extraction of leather with methanol does not collect the whole quantity of bisphenols from leather but resembles the current state of the art for this analytical method.

For a major phenolic syntan the BosC's level could be reduced from 8,800 ppm to smaller than 90 ppm as the sum of bisphenols. The performance on leather of this syntan remained the same, but the extracted BosC's levels declined from 525 ppm to below detection limit. In migration the limit of smaller than 0.04 mg/l was even achieved with the unoptimized version of syntan 2.

With phenolic syntan 3 we achieved leathers from which less than 20 ppm bisphenols could be extracted. In the optimized syntan 3.LB bisphenol S and F levels were brought to below detection limit in the product, maintaining the performance of syntan 3 with syntan 3.LB on leather.

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I want to thank Roberta Gamarino (Stahl, Palazzolo, Italy) and her team for their lab trials, production scale trials, for analytical support, and their impressive dedication. I am obliged to Marcus Breulmann, Debora Spengler, and Cenk Basoglu for their support with application. I wish to express my gratefulness to my collaboration partner Markus Kalt (BASF, Ludwigshafen, Germany) and his team for the production scale trials in Ludwigshafen. Ute Morgenstern and Ines Stachel from the FILK institute I want to acknowledge for their work to optimize the extraction methods. Special thanks go to Ines Anderie and Oliver Haubrich from PFI institute for analytical support.

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Lifelines

Tamrat Tesfaye (Associate Professor), Scientific Director (Vice President) of Ethiopian Institute of Textile and Fashion Technology of Bahir Dar University studied at UKZN and obtained PhD in Chemical Engineering in 2018. A highly accomplished higher education executive with substantial management experience, Tamrat is a pre-eminent scientist in the field of Chemical Engineering and specifically in Biopolymers and Biomaterials. He has successfully graduated over 36 Masters & 4 PhDs students. Tamrat has published in excess of 113 peer-reviewed papers and has presented in excess of 50 papers at conferences. He is the founder of Biorefinery Research Centre. He serves as Editor-in-Chief of Ethiopian Journal of Textile & Apparel and Ethiopian Electronic Journal of Innovation and Technology Foresight. He is a recipient of various national & international awards & a member of various industry & academic bodies, amongst others the African Scientists forum, African Academy of Sciences & Ethiopian Journal's Editors forum.

R. Karthikeyan currently holds the position of Professor of Leather Technology at the Ethiopian Institute of Textile and Fashion Technology, Bahir Dar University, Ethiopia. He completed his doctoral studies in Leather Technology at Anna University in Chennai, India, earning his PhD in 2010. Karthikeyan's academic journey includes roles as an Assistant Professor of Leather Technology at Addis Ababa University in Ethiopia, an Associate Professor of Leather Technology at the Federal TVET Institute in Ethiopia, and a Visiting Faculty member at both Arba Minch University in Ethiopia and Dedan Kimathi University of Technology in Kenya. With over 30 research publications to his credit, Karthikeyan has also secured five patents from the Indian Patent Office.

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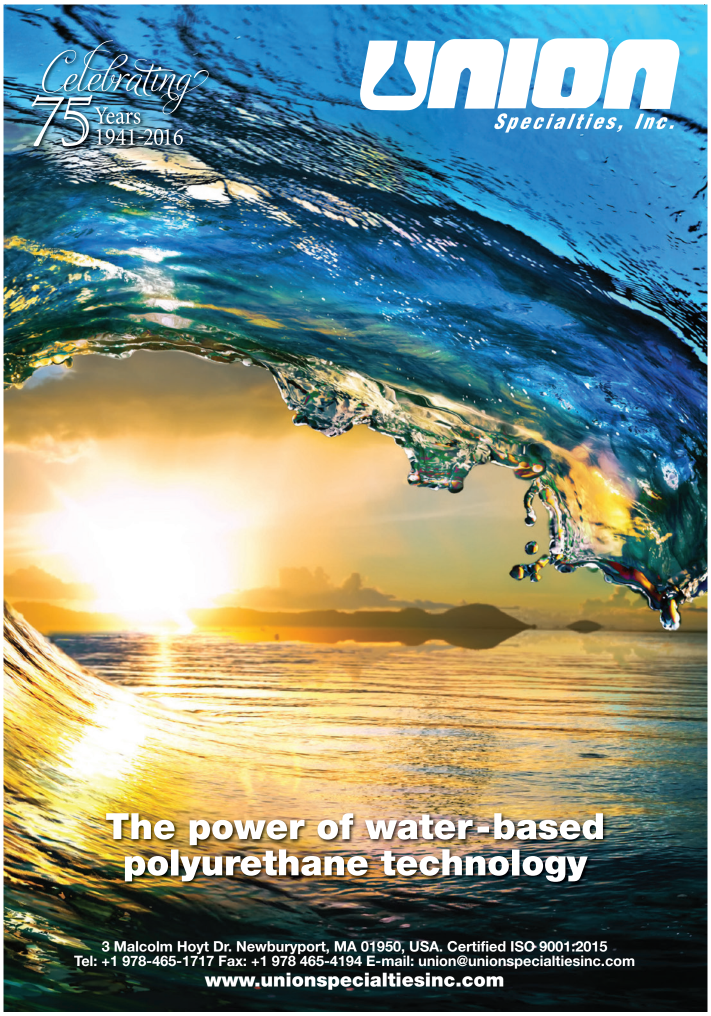
Indrasis Das is a scientist from the Environmental Engineering Department, CSIR- CLRI. He has expertise in environmental engineering, water and wastewater treatment and bio-electrochemistry. He published in 20 peer-reviewed Scientific journals, five book chapters and one Indian Patent. He reviewed more than a hundred manuscripts from high impact journals. He was involved in the analysis of biodegradability and toxicity of different fat liquors in this manuscript.

Akash Bhalla please see *JALCA*, **118**(8), 355, 2023

Ravi Banothu is a technical officer in CSIR CLRI and has expertise in physical and chemical testing of leather.

Jochen Ammenn obtained his Ph.D. in chemistry in 1995 at the university of Goettingen with an emphasis in organic synthesis. After 3 positions in Medicinal Chemistry in Switzerland, Germany and the United States he joined BASF in 2009 for process development and product development of poly-condensates. After the take-over of the BASF leather business by Stahl in 2017, he joined Stahl with the same position.



Obituary

Robert Joseph Masker, 69, of Atkinson, NH passed away on April 13, 2024 in Boston, MA after a courageous battle with cancer. Bob was born on September 6, 1954 in Gloversville, NY, the son of Bernard Masker and Gene Martin Masker.

He was a graduate of Gloversville High School and earned a Bachelor of Arts in Political Science from Union College in Schenectady, NY, where he was a member of the Sigma Chi fraternity. He worked as a leather chemist, specializing in the Asian market. He joined the ALCA in 1989. Throughout his career, he traveled the globe, most recently spending several weeks each year in China and India. At the time of his passing, he was employed by Tannin Corporation in Peabody, MA as an International Sales Manager. As a result of his generous and reliable nature, Bob maintained lifelong close relationships in numerous countries.

Bob excelled as a devoted husband and father. He is survived by his wife of 48 years, Elizabeth (Hladik), four children: Stephanie Masker (Terrence Accoo) of Washington, DC; Bobbie Miles (Donald) of Gloversville, NY; Jessica L'Abbe (Jonathan) of Auburn, NH; and Zachary Masker (Laura Primus) of Boston, MA, and sister, Sally Seeley of Delanson, NY. He had seven grandchildren: Anthony, Bruno, Benicio, Gino, Jonathan, Carmita, and Aretee, and several nieces and nephews. Bob is also survived by his beloved dog, Henry, and three "pea brained" cats, Felix, Oscar, and Jack.

Bob was predeceased by his parents, sister Lois, and brother-in-law, George.

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Abstracts are due by March 1, 2024
Full Presentations are due by May 1, 2024

They are to be submitted by e-mail to the
ALCA Vice-President and Chair of the Technical Program:

John Rodden
Union Specialties, Inc.
3 Malcom Hoyt Dr.
Newburyport, MA 01950
E-mail: johnrodden@unionspecialtiesinc.com

The **Abstract** should begin with the title in capital letters, followed by the authors' names. An asterisk should denote the name of the speaker, and contact information should be provided that includes an e-mail address. The abstract should be no longer than 300 English words, and in the Microsoft Word format.

Full Presentations at the convention will be limited to 25 minutes. In accordance with the Association Bylaws, all presentations are considered for publication by *The Journal of the American Leather Chemists Association.* They are not to be published elsewhere, other than in abstract form, without permission of the *Journal* Editor. For further paper preparation guidelines please refer to the *JALCA* Publication Policy on our website: leatherchemists.org

Full Presentations are to be submitted by e-mail to the *JALCA* editor:

Steven D. Lange, *Journal* Editor
The American Leather Chemists Association
E-mail: jalcaeditor@gmail.com
Mobile Phone (814) 414-5689

118th ALCA ANNUAL CONVENTION May 21 - 24, 2024 Hershey Lodge, Hershey PA

<u>Featuring the 63nd John Arthur Wilson Memorial Lecture</u>

"Material Matters"

A connection of market trends, consumers, creatives, manufacturing and actual materials.

By Panos Mytaros Chief Executive Officer
ECCO

Tentative Schedule

Tuesday, May 21

Golf Tournament, Opening Reception and Dinner

Wednesday, May 22

John Arthur Wilson Memorial Lecture All Day
Technical Sessions, Fun Run, Reception and Dinner

Thursday, May 23

All Day Technical Sessions, Annual Business Meeting
Activities Awards Luncheon
Social Hour, Banquet Dinner

Visit us at www.leatherchemists.org for full details under Annual Convention as they become available