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

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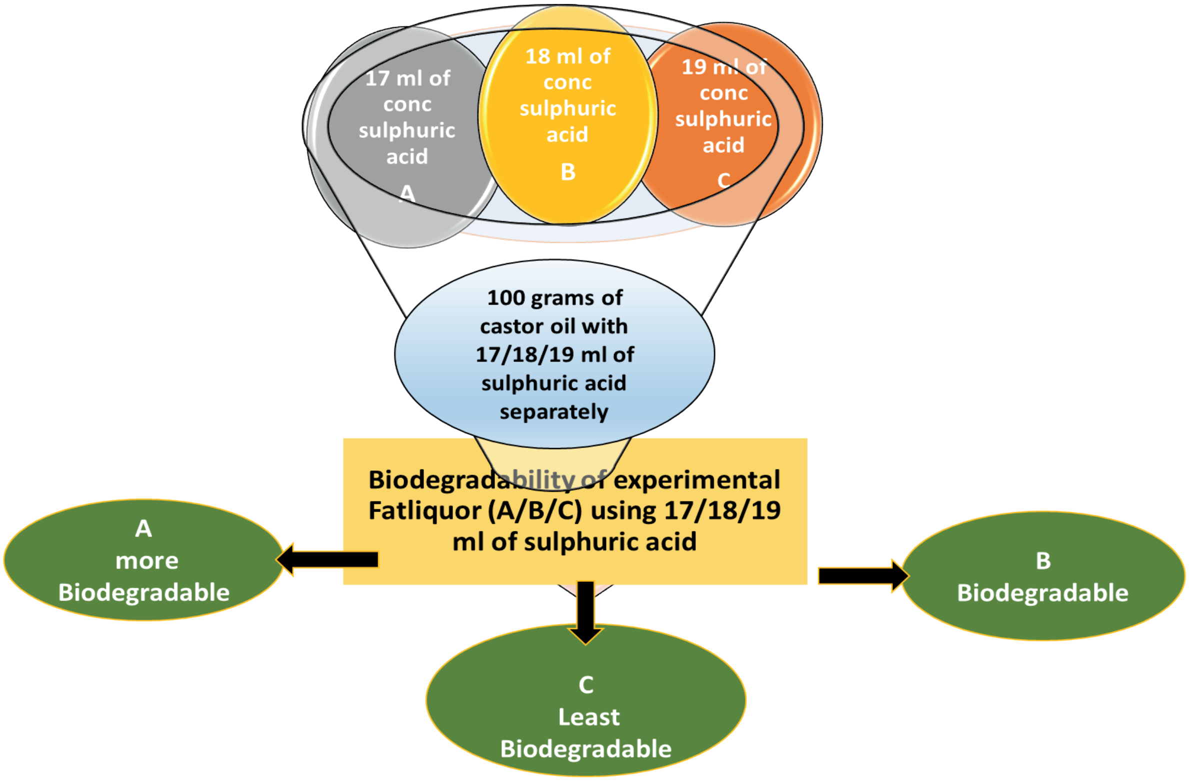
Graphical Abstract



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]

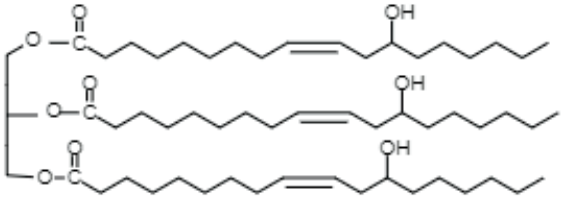


Figure 1. Structure of castor oil[12]

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

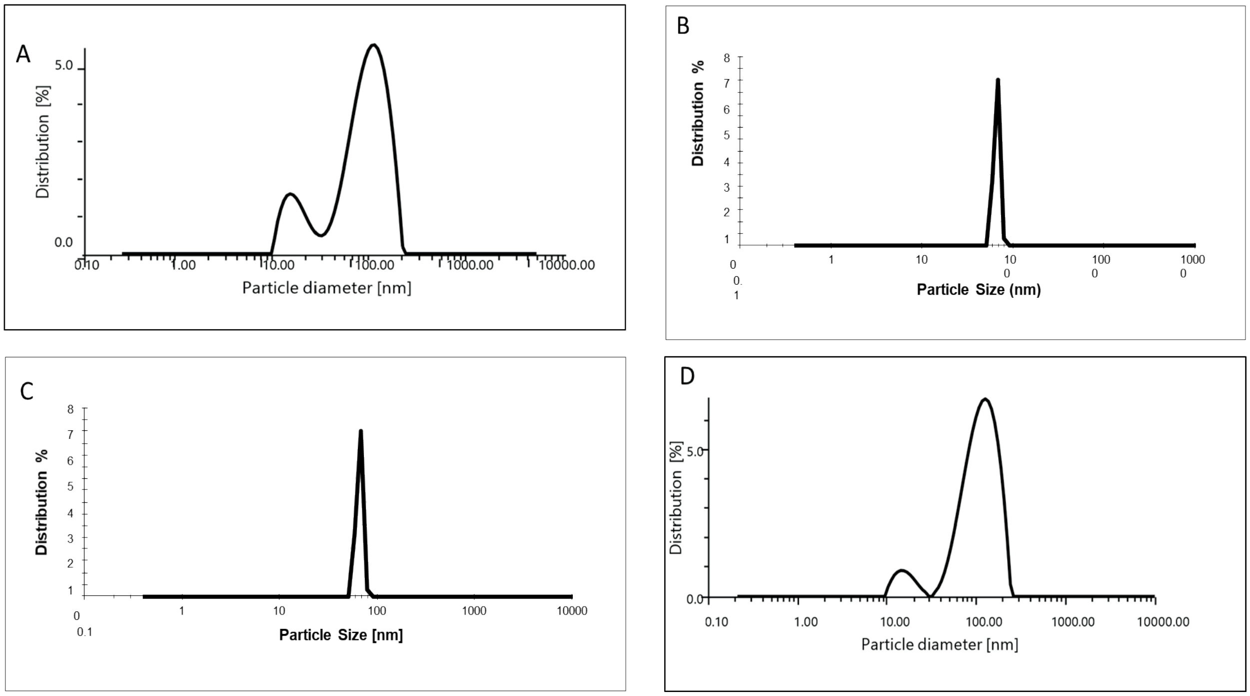


Figure 2 (A-D). Particle Size of experimental fatliquor SF-17, SF-18, SF-19 and control respectively

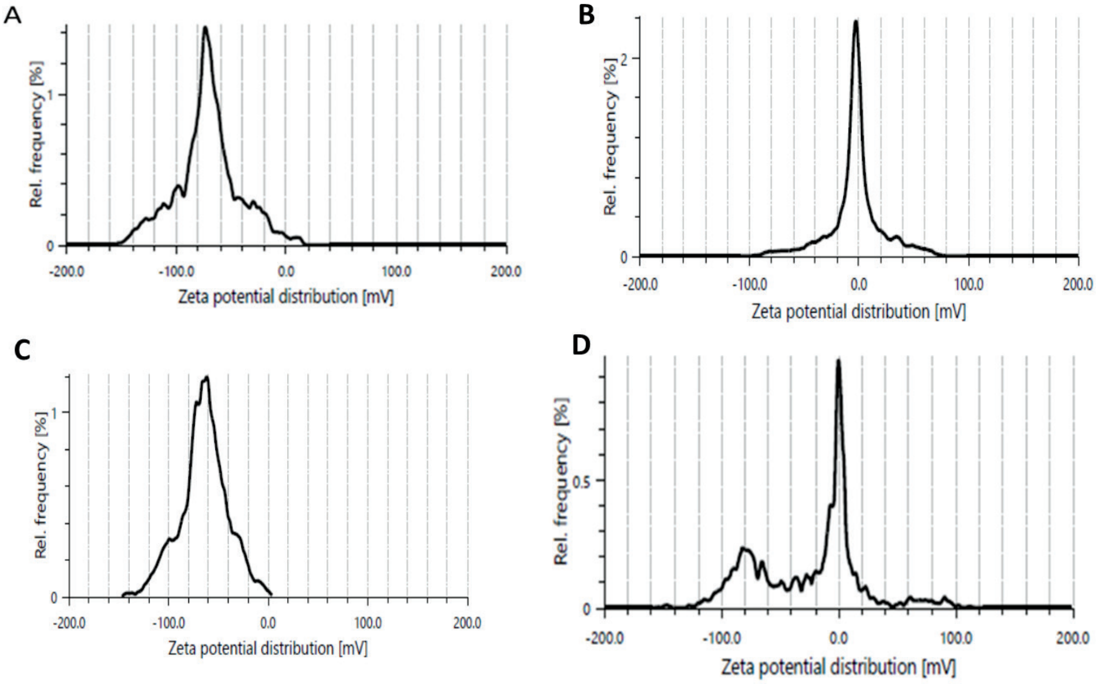


Figure 3 (A-D). Zeta Potential of experimental fatliquor SF-17, SF-18, SF-19 and control respectively

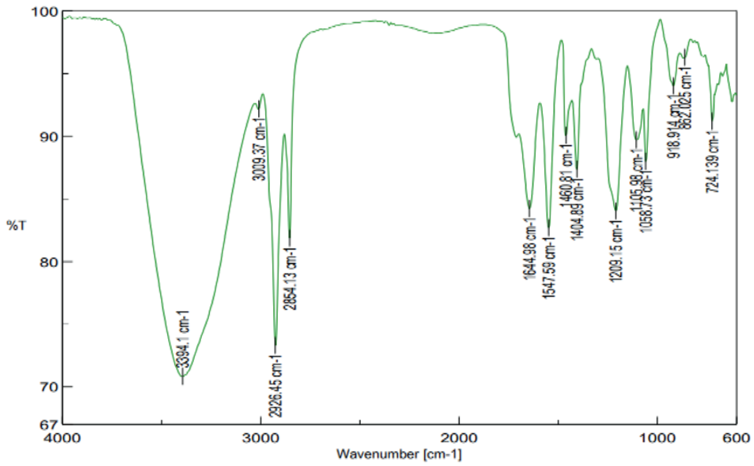


Figure 4A. FTIR of Fatliquor using SF-17

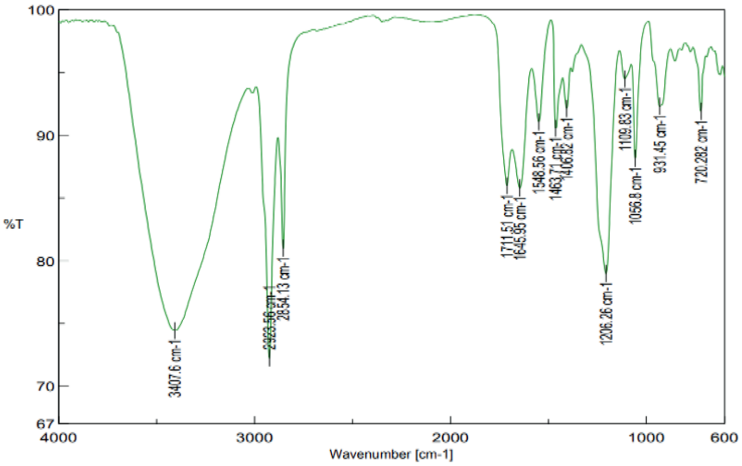


Figure 4B. FTIR of Fatliquor using SF-18

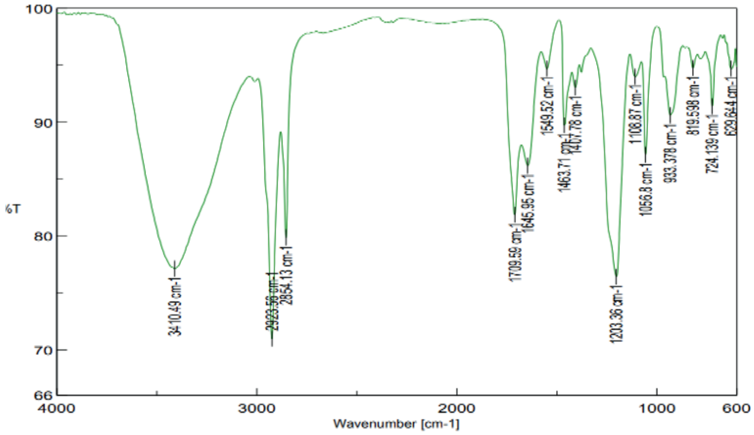


Figure 4C. FTIR of Fatliquor using SF-19

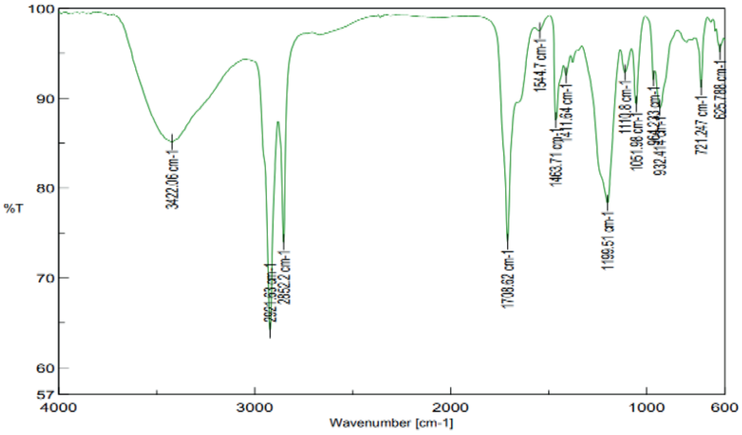


Figure 4D. FTIR of control Fatliquor (Terky Red oil) of the experimental leathers. The particle sizes of the experimental fatliquor are in the range of ±20nm with respect to control which are sufficient to lubricate the leather fibers.

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

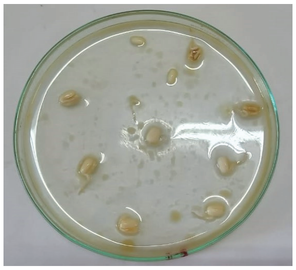
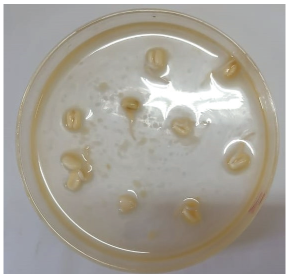
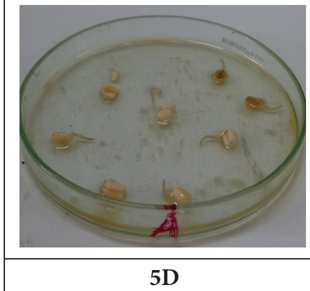
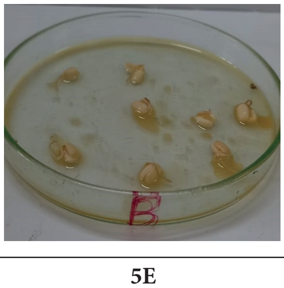
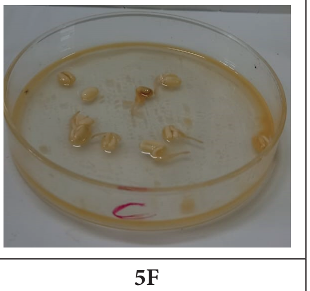
Days	A (SF19)	B (SF18)	C (SF17)
Day-1			
	5A	5B	5C
Day-4			
	5D	5E	5F

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.

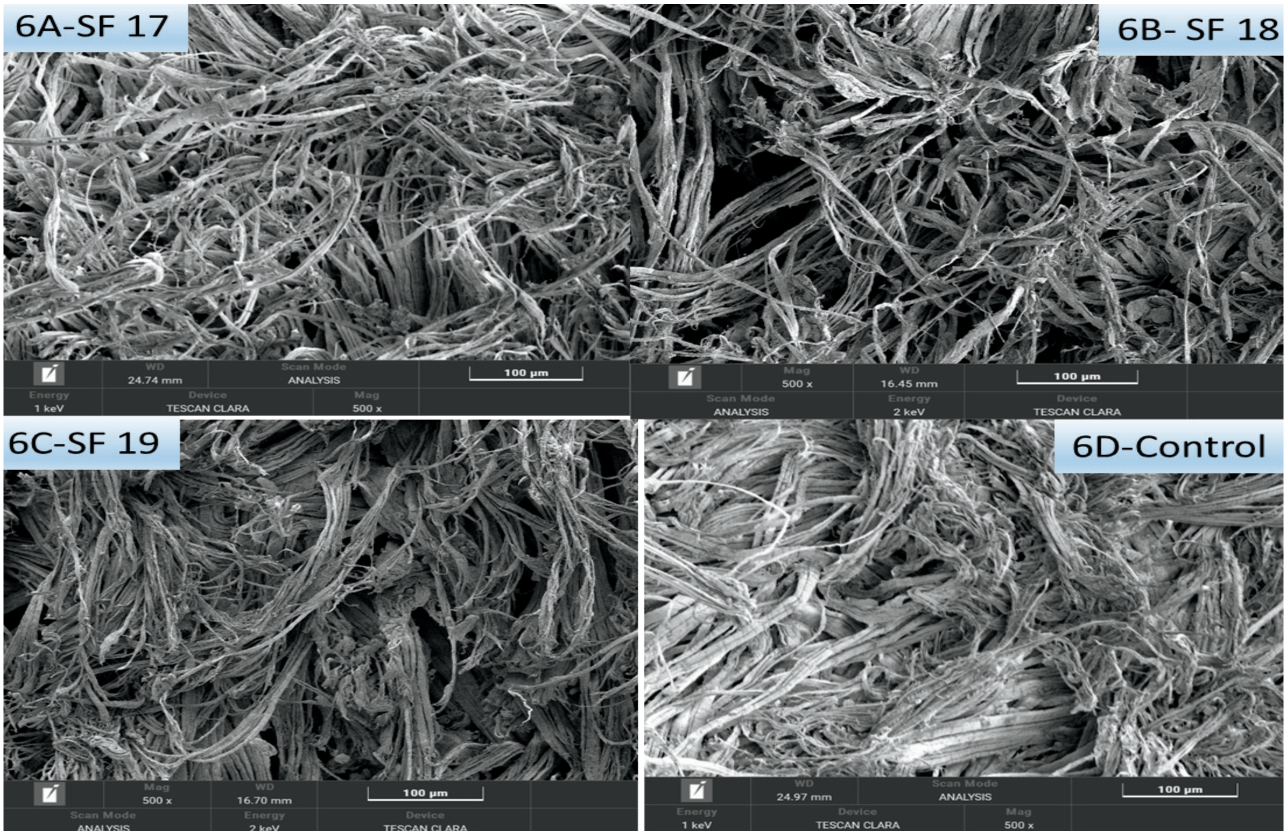


Figure 6 (A-D). SEM images of experimental leathers SF-17, SF-18, SF-19 and control respectively

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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