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Ultrasound processing for high quality leather fat liquor production based on recovered fish oil

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Abstract

Treatment of tanned leather with oil/water emulsion (fatliquor) is well known as leather fatliquoring. The process has to capable of transfer fatty substance into leather backbone brings about leather fibers lubrication and enhancing the tensile properties. Promoting oil affinity to the water involves oil chemical treatment; uneco-friendly exothermic sulfonation is the commonly used method. Finding economical oleo-chemical resources and an eco-friendly oil emulsification process are noble goals. In this work, a trail to offer an economical high- quality leather fatliquor avoiding non-environmental friendly traditional methods based on ultrasound clean technology has been achieved. The ultrasound fish oil recovery from fish tissues byproduct was found to be more efficient 25% over the chemical traditional methods; the oil meets the requirements to be used as a leather fatliquor with chemical properties superiority over that extracted by conventional methods. The ultrasound oil/water emulsification and emulsion stability have been studies, emulsions of 70- 80% oil/water ratio (v/v) show great stability against pH variation; they were able to incorporate the required fatty matter into leather fibers consequently the desired improvement in the mechanical properties of liquored leather have been recognized.

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Introduction

The leather is the oldest fibrous material used by Neanderthal. For thousands of years leather tanning has been proceed through primitive methods depending on plant organs like leafs and barks. Nowadays, the process became more complicated. A lot of chemicals use to tan the leather through long and complex technical operations.

Before tanning, the animal hides have to subject to beam house operations, at which the protein layer, which represents the real skin components is segregated through removing the flesh and the fatty tissues (Habib and Al shammari, 2014).

Removal of flesh and fats layers accelerates interaction between tanning agent and function groups of the protein of the skin (Viktor L *et al.*, 2006). Tanning agents join the function groups of the protein chains [-OH, -COOH, -HN2, -NH-] via multi-link with function groups of the collagen (Fig.1). Due to protein chains fixation, the tanned leather becomes harsh, inflexible and unusable (Anthony D C, 2009). The fat should be over again introduced into tanned leather fibers to restore the durability and softness. The fat is introduced into leather as an emulsion of oil in water. The emulsion should be able to carry the oil into the leather fiber.

The oil accumulation exterior the liquored leather should be forbidden. The emulsification of the fat is achieved through chemical adaptation to insert hydrophilic groups. In a primitive tanning, crude oils of high iodine value (vegetable or animal) were used as fatliquoring agents.

They were used without modification or additives. Therefore, the large numbers of the unsaturated centers enable the oils to attach with the collagen of the hide. However, the primitive methods do not support getting on the leather of the desired specifications (Habib and Alshammari, 2017).

Later on, soap had been used to emulsify the oils. The emulsion exhibit lubricant effect if it is stable up to the time required for completing the process and bring the fatty matter inside the fibers via micro size oil droplets (Ola *et al.*, 2010) (Fig. 2).

Therefore, it should be steady in opposite to dying materials, metallic ions rather than the pH of the medium (Nyamunda *et al.*, 2013; Habib and Alshammari, 2017). Moreover, it must be taken into account the quality standards and tanners requests.

It has to show light color and softness with silky-smooth feel to meet tanneries consumer's demands. Although natural oils are considered as renewable sources, they are not offered in a large quantity and pricey costly. Tanneries Researchers try to develop mineral lubricants. But they face a negative environmental challenge, as well as the shortage and non-renewability. Attempts have been done to modify low- cost bio-based byproducts.

Fish dressing and canning generate large quantities of fish byproducts tissues (fins, scales, eyes, and operculum, skins, tails …act). They considered a wealth because they contain oils of long - chain fatty acids. Unfortunately, in most cases, they don't find the right way for recycling and achieving benefit; discarded into surrounding environment causing environmental pollution.

However, some studies dedicated to taking advantage of them via conversion into value - added products such as biodiesel and energy generation (Fukuda *et al.*, 2001). Cuq *et al.* Try to produce leather fatliquor from seal hides oil (Cuq *et al.*, 1998).

However, traditional methods have been used for oil recovery are not considered as clean operations in addition to time and effort. In general, the traditional methods for fish oil extraction include cooking, pressing, and separation through solvent separation or centrifugal. They consume a large amount of solvent and need more energy for solvent separation. Acid digestion and chloroform/methanol/ water extraction methods are a clear example of this (Jayasinghe and Hawboldt, 2012).

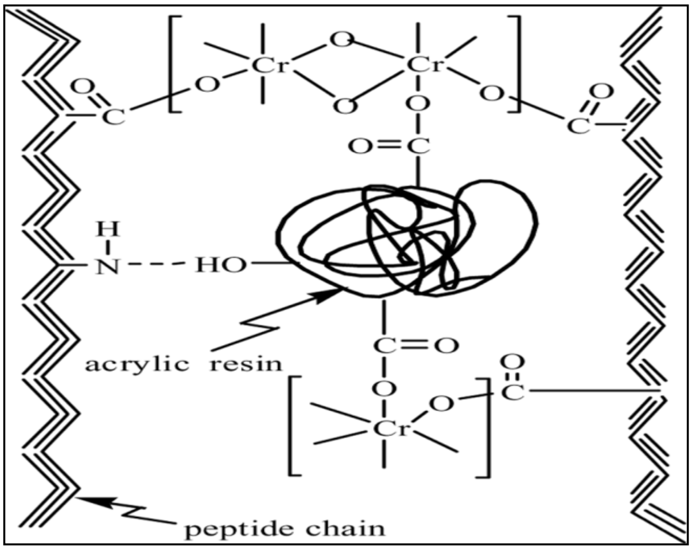


Fig. 1. Multi-link of tanning agents with function groups of the collagen (ChenW Y and Li GY., 2005).

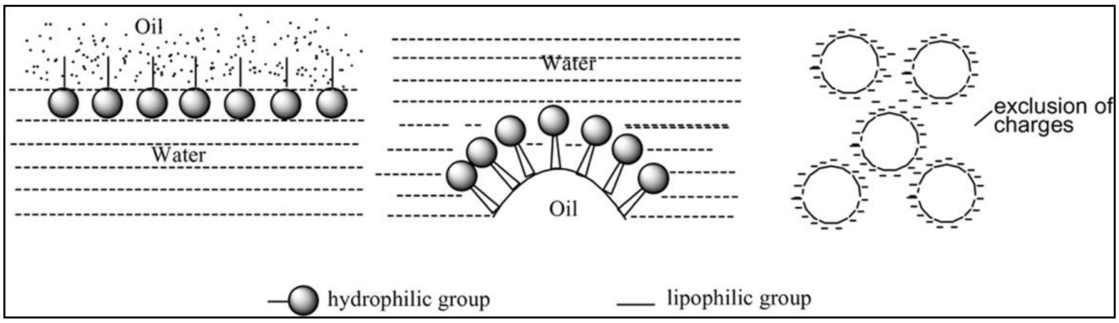


Fig. 2. Emulsification of fat into an aqueous phase (Liao and Shan., 2005).

Enzymatic extraction involves using concentrated mineral acids, in addition to the formation of brown dark oil (Ramakrishnan *et al.*, 2013) . Oil emulsification based sulfonation basically based on using concentrated sulfuric acid through exothermic reaction so the sulfonated product vulnerable to discharge and color change. The basic idea of using ultrasound in the manufacture of leather fatliquoring without chemical treatment using anionic emulsifiers as a wetting agent based on the fact that the power ultrasonic waves (20 – 100 kHz) have a significant effect on increasing the wet properties (Venkatasubramanian *et al.*, 2012). In particular, they raise efficiency oil droplet dispersion into the bulk of the emulsion enhancing the homogeneity and emulsion stability, aiding the efficiency of the liquor to corporate the fatty matters into the leather fiber (Sivakumar *et al.*, 2005; Zwieten *et al.*, 2017). Therefore, they are a clean substitute for exothermic sulfonation.

Although the ultrasound utilization in fatliquoring is still in the initial stages, in early time, ultrasound gains an importance in the field of improving leather making method as well as manufacture of leather auxiliaries such as fatliquors and dying manufacture. Castor oil emulsification for leather fatliquoring and natural dye taking out from plant sources are commonly used processes (Venkatasubramanian *et al.*, 2012). Moreover, ultrasound waves are employe in several physical applications (crystallization, cleaning ……act) as well as speeding up the rate of chemical reaction (contamine *et al.*, 1994; Shanmugam and Ashokkumar, 2014). They are very interested becomes of the great superiority over traditional processes include no need to stirring or external heating, in addition to rapid processing and it doesn't increase the pollution load (O'Sullivan *et al* 2015). The superiority of the process also attributes to mechanization with the advantage of heat selectivity and reduction energy dispersion to the surrounding.

In the recent work, we try to adapt an effective ultrasonic clean process to recover fish oil from fish tissues byproduct as well as produce leather fat liquoring agent via emulsifying the oil in an aqueous medium avoiding oil chemical treatment. The research is an attempt to reduce the dependence on traditional sulfonation that achieved by unsafe fuming sulfuric acid or oleum.

Materials and methods

Byproduct discarded fish tissues were collected from medium fish canning factory, Cairo, Egypt. Wet blue leather (chrome tanned bovine leather) with a thickness 2- 4 mm feed from a local tannery, Cairo, Egypt. Commercial sodium lauryl sulfate (an anionic) has been used as a wet agent. All chemicals used are fine grade and were purchased from international markets.

By product tissues dressing

The discarded fish tissues (without inner organs) have been placed in semi sealed glass containers as a single layer. The containers exposed to direct sunlight for 24 hours period of time or complete drying, as the temperature is approaching 40 ◦c in July days of time. The dried tissues were well grinded using an electrical mixer. The grinded tissues have been preserved into plastic sealed containers for further processing.

Fish oil extraction

For the research and efficiencies comparison, two oil extraction methods were carried out. The first was the traditional solvent extraction method (Bligh and Dyer, 1959), at which mixture of methanol, chloroform, and distilled water at ratio of (2:2:1) has been used;100g of dry tissues were mixed with a proper mixture of solvents for 40min under 250rpm stirring speed. The mixture was then filtered by using a Whatman filter paper. The residual tissues were re-extracted to obtain high recovery oil ratio. The filtrate was transferred to a separating funnel and allowing for separation. The upper aqueous phase containing non-lipid compounds was siphoned out and the lower phase was filtered and the solvent has been removed under vacuum distillation. The yield was calculated.

The extraction technique relying on the use of ultrasound has been performed. It has been achieved using ultrasonic device XUB5 50-6-Hz, Grant instruments, Ltd. UK

The dressing tissues have been blended with ethanol in one - liter glass beaker; the beaker has been put into the isolated ultrasonic area at 200 w input powers for one hour (Abdullah *et al.*, 2010). The ratio of the grounded tissues to the solvent has been varied from 0.02 to 0.08m/v keeping the total volume is 500 ml. The maximum yields of the recovered oils of both methods have been recorded.

Preparation of the leather fat liquor emulsion

-The goal is to emulsify the recovered fish oil to former stable emulsion leather fatliquorvia clean ultrasonic process avoiding chemical treatment of oil.
-The ultrasonic power has been controlled around (80-100W) so that the temperature within the ultrasound zone maintained around 55^{o}C.

In order to optimize the ideal oil/water ratio, the ratio of oil to water has been varied (40:60, 50:50, 60:40,70:30,80:20) for total volume 100ml. The wetting agent (sodium lauryl sulfate) has been used as 4% based on the mass of oil. The total time for best emulsification has been recorded. Formation of homogenous one phase solution with the milky aspect is an evidence of complete emulsification.

Evaluation of the emulsion stabilities

The stability of prepared fatliquors against pH variation of the different fatliquor samples has been tested. 10% aqueous emulsion concentrations of the different formulate fatliquor samples were built as milky solutions. To evaluate the stability to acids; 2ml formic acid has been blended with 20ml of 10% aqueous emulsion.

For measuring the stability in an alkaline medium; 2g sodium bicarbonate was added to 20ml of the 10% emulsion. The emulsions were shaken until complete mixing and their aspects as homogenous, non-homogenous or oil separation has been observed over thirty minute periods of time (Cuq *et al.*, 1998).

Fat liquoring process

In order to testthe performance of the emulsified oil as leather fat liquoring agents, the fat liquoring process using different formulated samples has been individually carried out, wet blue leather sample (chrome tanned bovine leather) has been cut into pieces of 5x5cm², well soaked into plenty of water for 15 min.

The soaking water has been siphoned out and the samples have been neutralized by sodium carbonate and sodium format solution until pH = 6.5 - 7. The weight of the neutralized samples has been recorded. The leather pieces charged into a stainless steel container equipped with stirring bars and heater. Floating water (500% based on the weight of leather) has been added accompanied by adding 4-10% fatliquor, based on weight of neutralized leather (in four times individually). The goods have been stirred for 90 min (50 rpm stirring time) at 50ºC. After that the liquoring fluid are siphoned out and the liquored leather samples have been hang up in open air until complete drying.

Evaluation of the suitability of the fatliquored leather

The amount of oil introduced into liquored leather has been evaluated according to the method reported by the society of leather technologies and chemists STLC, at which the fatty matter is extracted from liquored leather in a soxhlet using dichloromethane as solvent (SLTC, 1996). The percentage of extracted oil = weight of extracted oil (g) / weight of the leather in the soxhlet (g) x 100. To evaluate the mechanical properties enhancement of the fatliquored leather (Tensile strength and elongation % at break) have been measured by Zwick' 1425, The appearance of the fatliquored leather fibers have been evaluated by using scanning electron microscopic (SEM), Jeol scanning microscope (Japan) JSM-T20 (sputter coater-Edwards-Model S-150 A, Eng.).

Results and discussion

The chemical properties of the recovered fish oils have been illustrated in table 1. The data indicate that the ultrasonic extracted oil has significant chemical properties superiority. Iodine and saponification values are of particular importance in the utilization of the biomass as oleo chemical recourse. The iodine and saponification values superiority of the ultrasonic extracted oil over the traditionally extracted oil is attributed to the advantage of ultrasound processing (heat selectivity and reduction energy dispersion to the surrounding). The waves deploy into bulk creating high - pressure cycles which enhance the oil diffusion and time reducing with no need to long time external heating (Bdullah *et al.*, 2010). In addition, the ultrasonic operation has yield superiority over the traditional method. Therefore, The utilization of ultrasound irradiation offers a rapid, easy way to enhance the extraction rate with time processing reducing , they break the walls of the cells by the cavitations cutters power boosting the way out of oil from the cell (Adeniyi and Bawa, 2002).

Table 1. chemical properties of the recovered fish oil.

Property	Recovered oil	
	Ultrasonic extracted	Traditional extracted
Colour	Pale reddish brown	Pale reddish brown
Moisture %	0.92	1.30
Ash %	0.89	1.20
Iodine value mg I_2/g oil	166.80	155.55
Acid value mg KOH/g oil	2.12	4.11
Saponification value mg KOH/g oil	198.63	187.40
Unsaponified matter	0.61	1.17
Yield per 100 gm discarded tissues (g)	8.52	6.01

Oil emulsification and emulsion stability evaluation

Table 2 illustrates the relation between the times of oil emulsification and oil/water ratio. The data in the table clearly reveal to the incremental relationship between the amount of oil and the time taken for emulsification. This result is consistent with the fact that the more oil in the solution, the longer time is taken for emulsification at constant source power (Sivakumar *et al.*, 2007).

Emulsion stability is considered an important factor to judge the performance in the liquoring process, as the process may take up to 90 minutes and assumes that there is no emulsion destruction throughout this period. In addition, the emulsion has to resist the change in pH value. The stability of the emulsion retains to the ability of oil droplet in the bulk as a fine particles and not to be gathered and float into the surface forming a non-homogenous emulsion or oil separation. Consequently, the oil will accumulate on the leather surface and cannot successfully penetrate the leather to reach the inner net of the fibers causing the desired lubricating effect. Therefore, emulsions of high oil concentration exhibit stability resistance with the time or pH variation and long shelf life (Sivakumar *et al.,* 2008).

The nonhomogeneous emulsions haven't the fine oil droplets which can penetrate the leather surface and add mass to the fibers. Therefore, low oil content emulsions (samples 1 & 2) were excluded.

Table 2. Relation between the times required for emulsification and oil/water ratio.

Sample	% Oil	% water	Time (min.)
1	40	60	6
2	50	50	7
3	60	40	11
4	70	30	13
5	80	20	16

Table 3. Evaluation of the emulsion stabilities.

Sample No.	Oil : water ratio	pH		
		Acidic	Basic	Neutral
1cf	40:60	OS NH	OS NH	H H
2cf	50:50	OS NH	OS NH	H H
3cf	60:40	NH H	OS H	H H
4cf	70:30	H H	H H	H H
5cf	80:20	H H	H H	H H

*OS oil separation, NH non-homogeneous, H homogeneous - cfcommercial fatliquor.

Evaluation the performance of the prepared fatliquor samples

The ability of the fatliquor to transfer the fatty matter from the bulk of the solution into leather fibers is the real measure of the performance efficiency of the liquor. Therefore, the fatliquor emulsion should be able to add the amount of oil needed to improve the mechanical properties of the leather. Fig. 3 illustrates the performance of samples 3 & 4 at different fatliquor emulsion concentrations (4-10%). Knowing that the amount of fatty matter has to be added to the liquored leather in order to improve the mechanical properties is approximately from 7 to 10% (based on the weight of the liquored leather) (habib and al shammari, 2017**)**, the data in Fig. 3 revealed that the samples 3 & 4 able to add the required fatty matters needed to improve tensile properties of the leather only at higher fatliquor concentrations (8 -10%, based on the weight fatliquored leather concentration).

The data also confirm that the performance of the samples (3 & 4) comes near to the commercial fatliquor at the same concentration.

Evaluation of the fat liquored leather

The data presented in Fig. 4 & Fig. 5 Illustrates the direct relationship between the improvement in mechanical properties of the liquored leather (tensile strength and elongation at break %) and concentration of liquor.

A progressive enhancement in the mechanical properties with the increase in liquor concentration was well observed. However, the recommended values of tensile strength and elongation at breaks have been reached at 7-10% emulsion concentration.

The performance of ultrasound prepared samples was found to be close to commercial liquor, whereas the enhancement of tensile strength and elongation at break caused by the three liquors (sample 3, sample 4 and commercial one) were nearly close to each others.

Fig. 6 (a-b) shows the SEM images (scanning electron microscope) of the leather fibers before and after fatliquoring with 10% emulsion concentration of sample 4 (80% oil content).

The comparison of the two images clearly shows great enhancement in leather fibers after fatliquoring. The bright and shiny appearance of the liquored leather fibers supports the fact that a fatty substance has been added to the liquored leather fibers. Therefore, the oil droplet has been reached to the leather fibers causing the desired lubricating effect.

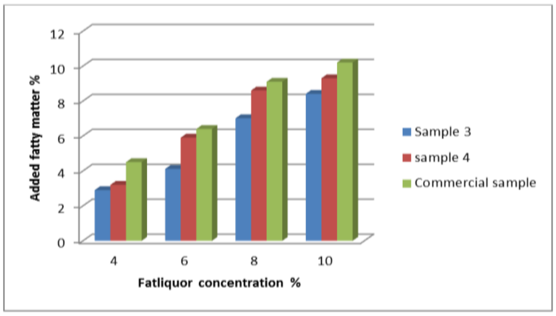


Fig. 3. Total fatty matter add by different fatliquor samples.

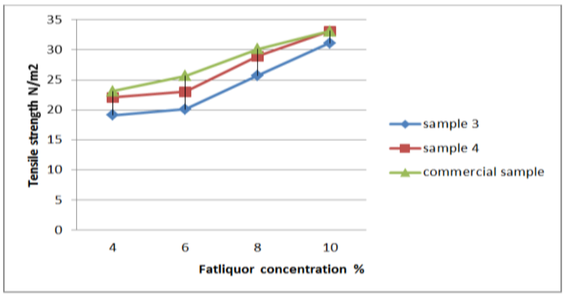


Fig. 4. The relation between tensile strength and fatliquor concentration of different fatliquor samples.

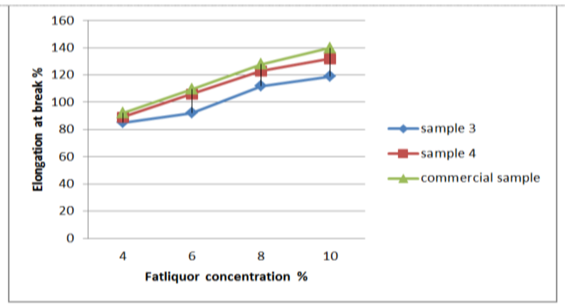
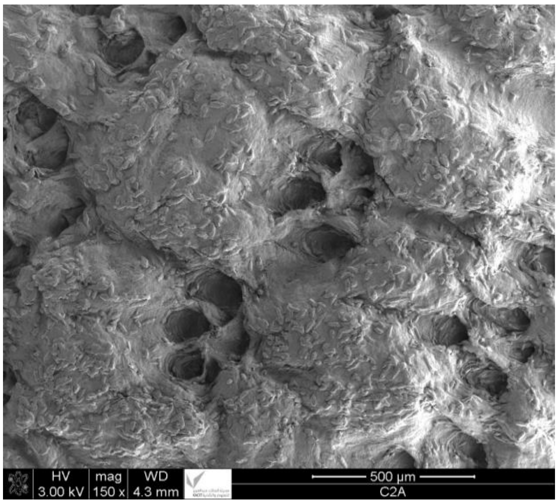
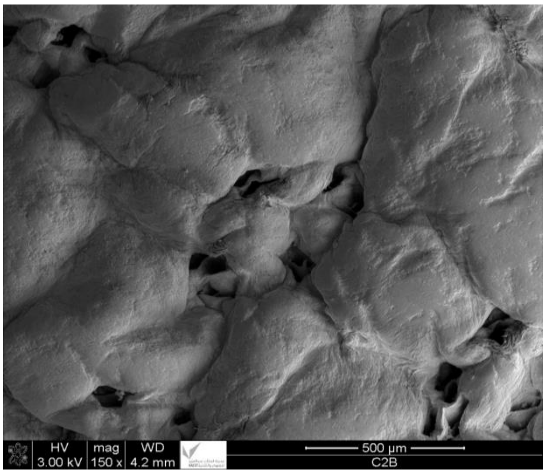


Fig. 5. The relation between elongation at break % and fatliquor concentration of different fatliquor samples.



(a) Un-fatliquored leather.



(b) Fatliquored leather.

Fig. 6. (a-b) SEM (X150) of wet blue bovine leather.

Conclusion

High quality leather fatliquor has been produced from recovered fish oil using clean ultrasound technology to recover and emulsification the oil instead of traditional methods. The prepared fatliquor samples show great emulsion stability and were able to add the required fatty matter into leather fibers causing fibers lubrication. The mechanical properties of the lubricated leather were well enhanced in addition good softening and visual appearance.

References

Abdullah S, Abdul Mudalip SK, Sharrani S, Md Che Pi NA. 2010. Ultrasonic extraction of oil from monopterusalbus: Effect of different ultrasonic power, solvent volume and sonication time. Journal of Applied Science **10 (21),** 2713-2719.

Adeniyi OD, Bawa AA. 2002. Mackerel (scomber scrombrus) oil extraction and evaluation as raw material for industrial utilization. Leonardo Journal of Sciences **8,** 33-42.

Anthony DC. 2009. Tanning Chemistry: The Science of Leather. Royal Society of Chemistry, UK. Thomas Graham House, Science Park, Milton Road, Cambridge CB4 OW F.

Bligh EG, Dyer WJ. 1959. A rapid method of total lipid extraction and purification. Canadian Journal of Biochemistry and Physiology **37,** 911-917.

Chakraborty R, Bepari S, Banerjee A. 2011. Application of calcined waste fish (Labeorohita) scale as low-cost heterogeneous catalyst for biodiesel synthesis. Bioresource Technology **102,** 3610-3618.

Chen WY, Li GY. 2005. Leather Chemical, Light Industry Publishing Company Beijing.

Contamine F, Faid F, Wilhelm AM, Berlan J, Delmas H. 1994. Chemical reactions under ultrasound. Chemical Engineering Science **49(24b),** 5865-5873.

Cuq MH, Benjelloun- Mlayah B, Delmas M. 1998. Oil extracted from seal hides: Characterization and use as leather fat liquor. Journal of the American Oil Chemists' Society **75,** 1015-1019.

Fukuda H, Kondo A, Noda H. 2001. Biodiesel fuel production by transesterification of oils. Journal of Bioscience and Bioengineering **92,** 405-416.

Habib MA, Alshammari AG. 2014. Leather fatliquor from hide flestings. Journal of the Society of Leather Technology and Chemist **98(5),** 199-205.

Habib MA, Alshammari AG. 2017. Recycling and utilization waste deep frying oil in leather industry. Indian journal of Chemical Technology **24,** 198-205.

Jayasinghe P, Hawboldt K. 2012. A review of bio-oils from waste biomass: Focus on fish processing waste. Renewable & Sustainable Energy Reviews **16(1),** 798-821.

Norziah MH, Nuraini J, Lee KY. 2009. Studies on the extraction and characterization of fish oil from wastes of seafood processing industry. Asian journal of food and agro - industry **2(04),** 959-973.

Nyamunda BC, Moyo M, Chigondo F. 2013. Synthesis of fatliquor from waste bovine fat for use in a small scale leather industry. Indian Journal of Chemical Technology **20,** 116-120.

O'Sullivan J, Murray B, Flynn C, Norton I. 2015. Comparison of batch and continuous ultrasonic emulsification processes. Journal of Food Engineering **167,** 114-121.

Ola MA, Habib MA, El sayed MH. 2010. Leather fatliquoring agent prepared from phosphorylation of local animal bone. Journal of Indian Leather Technologists' Association. fat Lx **6,** 456-468.

Ramakrishnan VV, Ghaly AE, Brooks MS, Budge SM. 2013. Extraction of oil from mackerel fish processing waste using alcalase enzyme. Enzyme Engineering **2(2),** 115-125.

Santos LM, Gutterres M. 2007. Reusing of a hide waste for leather fatliquoring. Journal of Cleaner Production **15,** 12-16.

Shanmugam A, Ashokkumar M. 2014. Ultrasonic preparation of stable flax seed oil emulsions in dairy systems – physicochemical characterization. Food Hydrocolloids **39,** 151-162.

Sivakumar V, Gayathri k, Pranavi PS, Francis Chandrasekaran C. 2012. Ultrasound assisted cleaner alternate emulsification method for oil and fats: tallow emulsion – fatliquor preparation for leather application. Journal of Cleaner Production **37,** 1-7.

Sivakumar V, Poorna Prakash R, Rao PG, Ramabrahmam BV, Swaminathan G. 2008. Power ultrasound in fatliquor preparation based on vegetable oil for leather application. Journal of Cleaner Production **16(4),** 549-553.

Sivakumar V, Swaminathan G, Rao PG. 2005. The application of power ultrasonic in fatliquoring process. Journal- American Leather Chemists Association **100(5),** 187-195.

Viktor L, Viktoriya P, Anatolij D. 2006. Transformation of the collagen structure during beam-house processes and combined tanning. The Proceedings of the Estonianof Sciences **12(3),** 188-198.

Zwieten R, Verhaagen B, Schroën K, Rivas DF. 2017. Emulsification in novel ultrasonic cavitation intensifying bag reactors. Ultrasonics Sonochemistry **36,** 446-453.