Application of Ultrasound in Eco-friendly Fatliquoring of Leather

by

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Abstract

This article describes the effect of ultrasound on fatliquoring of leather. Preparations of fatliquor-emulsions as well as fatliquoring of leathers were carried out in presence of ultrasound. Ultrasound aids in reducing the size of fatliquor emulsion and increasing fat content of leather. It was found that the particle size of fatliquor emulsion was reduced by more than 22% and fat contents of leather were increased up to 40% due to using ultrasound. Moreover, smooth penetration and uniform distribution of fat in the processed leathers were observed. Physical properties of both ultrasound-assisted fatliquored leather and conventionally fatliquored leather were also studied in detail. Tensile strength, stitch tearing strength, tongue tearing strength, grain crack load, ball bursting load, Bauman tear strength, color fastness and perspiration of ultrasound assisted fatliquored leather were better compared to that of without ultrasound.

Introduction

Fatliquoring is a very important step of leather processing in which fatliquoring agents penetrate into the empty spaces of leather. It imparts the softness, elasticity, and smoothness to the grain surface.[1] Fatliquors are mainly emulsifying mixtures prepared by the introduction of phosphate, sulphonate and sulphite groups into oils or fats or by the addition of surface-active agents to the mixture of fatliquoring agents.[2]

Ultrasound is a sound wave of 18 kHz–10 MHz and is generally applied for enhancing various processes and to reduce process time and pollution load. The use of ultrasound in the preparation of fatliquor emulsions to leather making is promising because it takes advantage of the typical effect of cavitation.[3] Ultrasound could be used to emulsify fatliquor efficiently and quickly.[4] In leather processing, a widespread change of chemical processes and reactions are also enhanced because of ultrasound.[5,6] This is due to the sonochemical effect called cavitation that is generated by the formation and collapse of microscopic bubbles.[7] Cavitation produces noteworthy mechanical and chemical effects for example intense agitation, dispersion, degassing, emulsification, micro-jetting in addition to making free radicals.[8] The application of ultrasound to leather processing has become more effective due to an increase in commercial availability, the advancement of ultrasound technology, the external applicability of ultrasound to leather making and the strict environmental laws that demand new efficient processing technology.[9,10]

Ultrasound is one of the best alternatives to make high quality dispersions of fatliquor.[11] Furthermore, it has also been shown to decrease the particle size of the fatliquor emulsion. Most commercial fatliquoring agents are provided as a mixture of raw oil and a certain type of surfactant. Fatliquoring agents may be anionic, cationic or non-ionic in nature. The most widely used fatliquoring agent in leather industry are anionic fatliquors that are made of the neutral oil, a sulfated or sulfited oil, and some free fatty acids.[12] The sulfated (-OSO_3Na) and sulfited oil (-SO_3Na) consist of water-soluble groups and act as surfactants to emulsify the neutral oil in order to replace the water molecules in leather resulting in better penetration. The higher the degree of sulfation or sulfitation the better the penetration of the emulsion. But, the lubricating effect of leather is decreased because of the reduction in neutral oil content.[13] Thus, the choice of the fatliquor type is dependent upon the end use of the products. In this study, the effect of ultrasound on fatliquoring process was investigated and compared with that of conventional fatliquoring.

Experimental

Materials

Remsynol ESI, an anionic fatliquor, was collected from Clariant, India and Figure 1 demonstrates the molecular structure of the sulphited fatliquor component.[14] Generally, 85% of the fatliquor emulsions work as active material and the percentage of the sulphited fatliquor component is 50-55%. Wet blue leather with a thickness of 1.2-1.5 mm was collected from Smith Leather International, Dhaka,

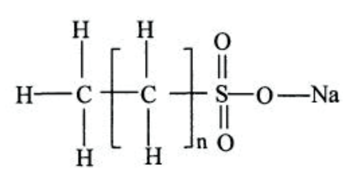

Figure 1. Structure of sulfited fatliquor component

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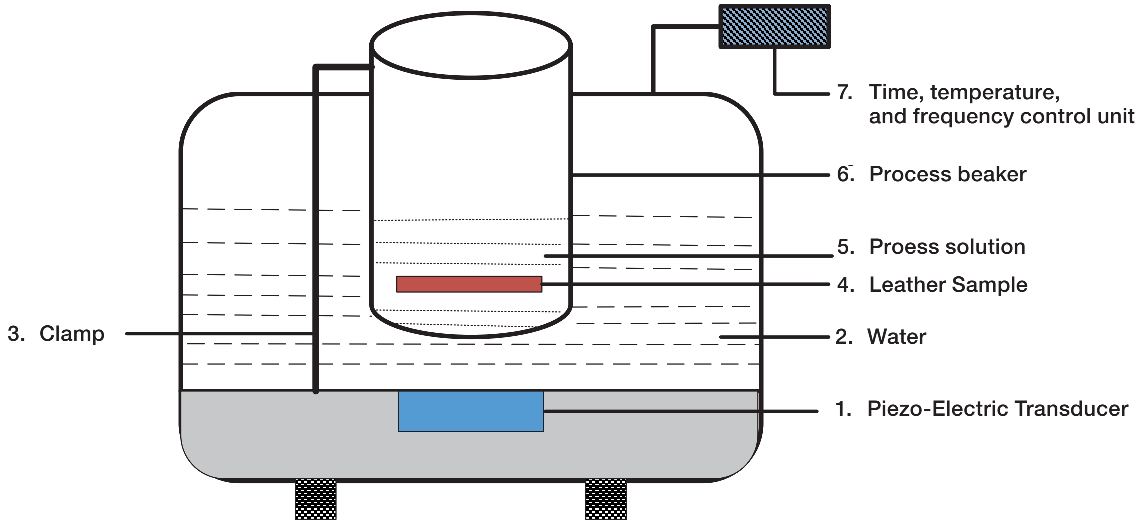

Figure 2. Schematic diagram of experimental setup

Bangladesh. Leather samples were cut (2 inch × 2 inch) adjacently from the same piece of leather to ensure almost similar properties of the samples. Weight of the samples was approximately 4.0 gm. All chemicals used in this study were of analytical grade and purchased from Merck India.

Experimental set-up

In this study, ultrasonic cleaner (HWASHIN TECHNOLOGY CO., KOREA), generating ultrasound at 350W and 40 kHz frequency was used for the experiments as shown in Figure 2. This type of equipment is generally used in the laboratory for ultrasonic experiments.[15] During fatliquoring, ultrasound was applied either continuously or for a short period at different stages, with or without the use of mechanical stirring. In the case of using mechanical stirring in conventional fatliquoring, leather samples were hung from the end of a bladed stirring propeller rotating at 50 rpm.

Fatliquoring of leather samples

All leather samples were first neutralized using alkaline solutions prior to fatliquoring. The gradient of pH across the leather cross section is important for the penetration and deposition of fatliquor. In practice, a pH value of 4.0 – 6.0 is desired. In this study, the neutralization pH was 4.5. Fatliquoring was carried out with 5% Remsynol ESI (5%) and distilled water (30%) either in the presence or absence of ultrasound at different temperatures. All the percentages of chemicals used are based on the weight of wet leather. The fatliquor emulsions were prepared using either ultrasonic irradiation or mechanical stirring for 30 minutes at the predetermined temperature of fatliquoring.

Measurement of particle size

The mean particle size of 1% (w/v) fatliquor emulsions were measured using a particle size analyzer (iSpect DIA-10, SHIMADZU, Japan) prepared by either sonicating or mechanical stirring at different times and temperatures.

Measurement of viscosity

Viscosity of 5% (w/v) and 10% (w/v) fatliquor emulsions were measured over a range of shear rates at 20°C, 30°C and 40°C using a cone-on-plate rheometer (RST-CPS Cone/Plate, AMETEK Brookfield, USA), where, emulsions were prepared at 25°C by either sonicating or mechanical stirring for 30 minutes.

Determination of fat content

Fat content of the fatliquored leather was determined by Society of Leather Technologists and Chemists (SLTC) standard method.[16] Then the samples were air-dried to a certain weight and crushed in a milling machine. Around 10g of ground leather was extracted using a Soxhlet extraction apparatus with dichloromethane (DCM) for at least 5 hours. The weight of DCM extractables was then obtained and expressed as the weight percentage of dried leather sample.

Results and Discussion

Effect of sonication time on the particle size

Particle size is a very significant factor that characterizes the nature and performance of emulsion. It also influences the stability and penetration of fatliquor. Generally, the smaller the particle size of a fatliquor emulsion, the easier penetration into leather.[17]

Figure 3 shows the changes in particle size as a function of sonication time at 40°C. As seen from the graph, after sonication for 10 minutes the particle size becomes 72 nm that is almost similar to the size prepared by conventional method. After sonication for 30 minutes the particle size obtained was 59 nm and further

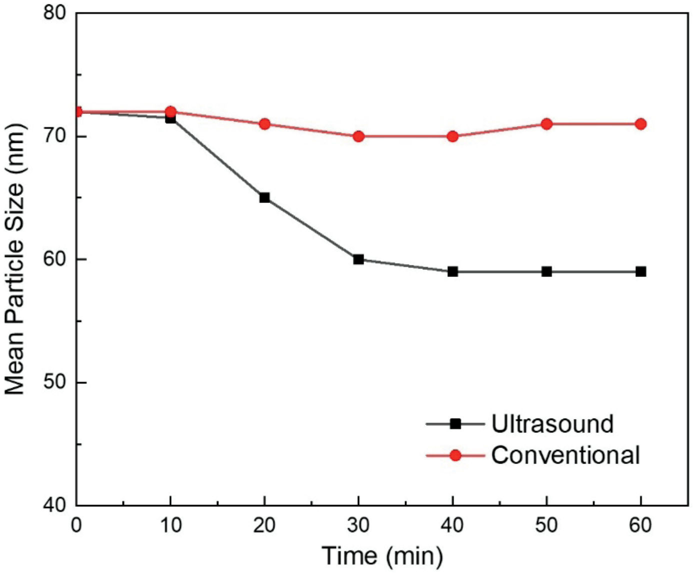

Figure 3. Mean particle size of fatliquor emulsion

sonication did not show any effect on the particle size of fatliquor. That means 30 minutes ultrasonic irradiation was optimum to maximize the reduction of particle size. It is assumed that this reduction in fatliquor particle size happened due to cavitation energy generated by ultrasound. The cavitation energy produced shock waves that raised local pressure and reduced the particle size.[18, 19]

Effect of ultrasound on the viscosity of fatliquor emulsions

The viscosity of fatliquor is another important parameter that influences the penetration of oil into leather. The lower the viscosity of a fatliquor, the better is its penetration. In this study, 5% and 10% Remsynol ESI fatliquor emulsion were made by both ultrasonic technique and conventional method. Figures 4 and 5 show the viscosity of fatliquor emulsion as a function of shear rate at different temperatures under ultrasound and conventional method. It was observed that viscosity of fatliquor produced by ultrasound was

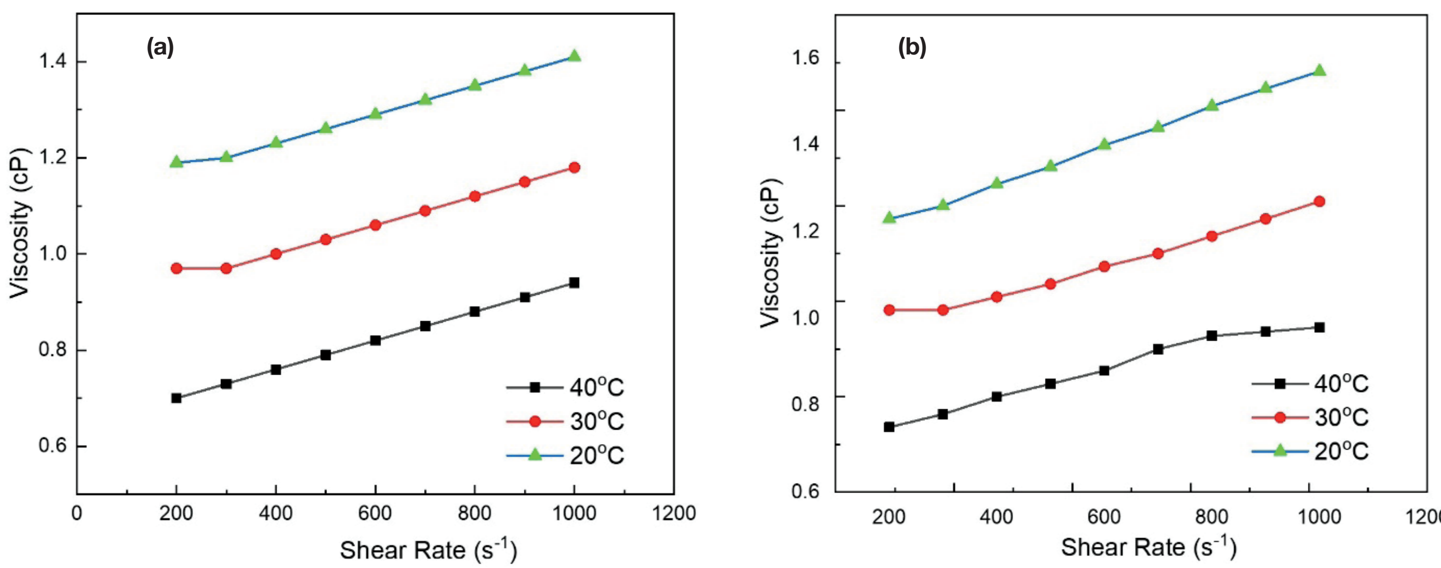

Figure 4. Viscosity as a function of shear rate of fatliquor emulsion at 5% (w/v) concentration using **(a)** ultrasound and **(b)** conventional technique.

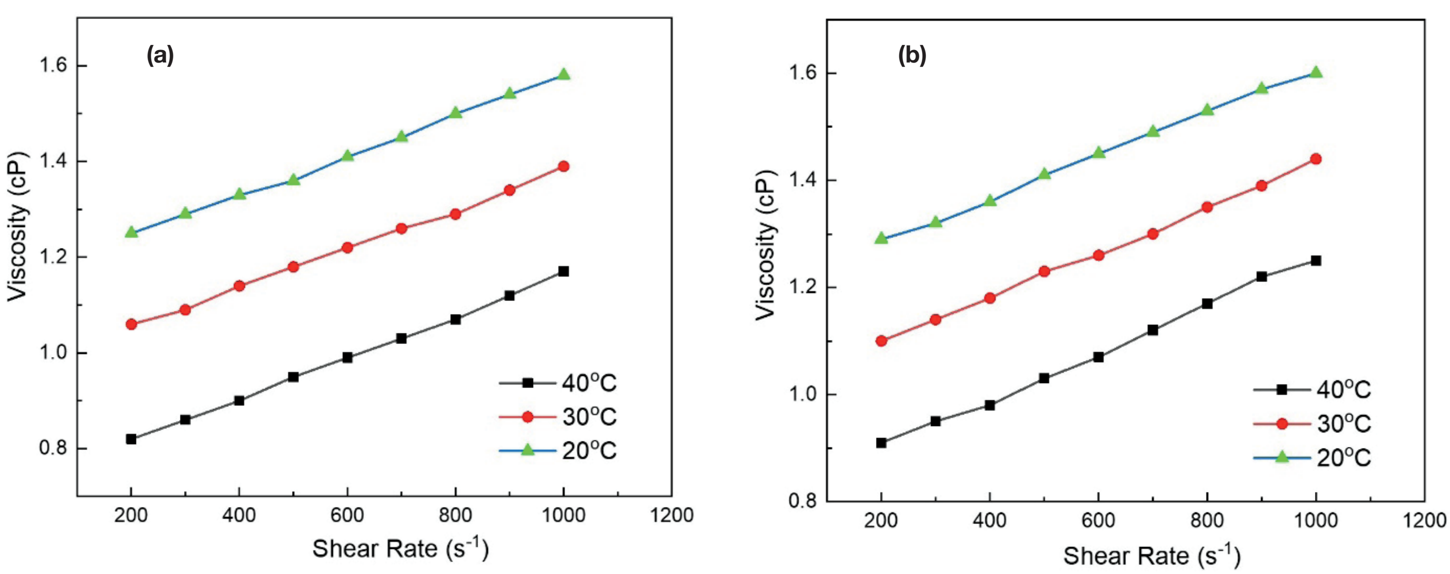

Figure 5. Viscosity as a function of shear rate of fatliquor emulsion at 10% (w/v) concentration using **(a)** ultrasound and **(b)** conventional technique.

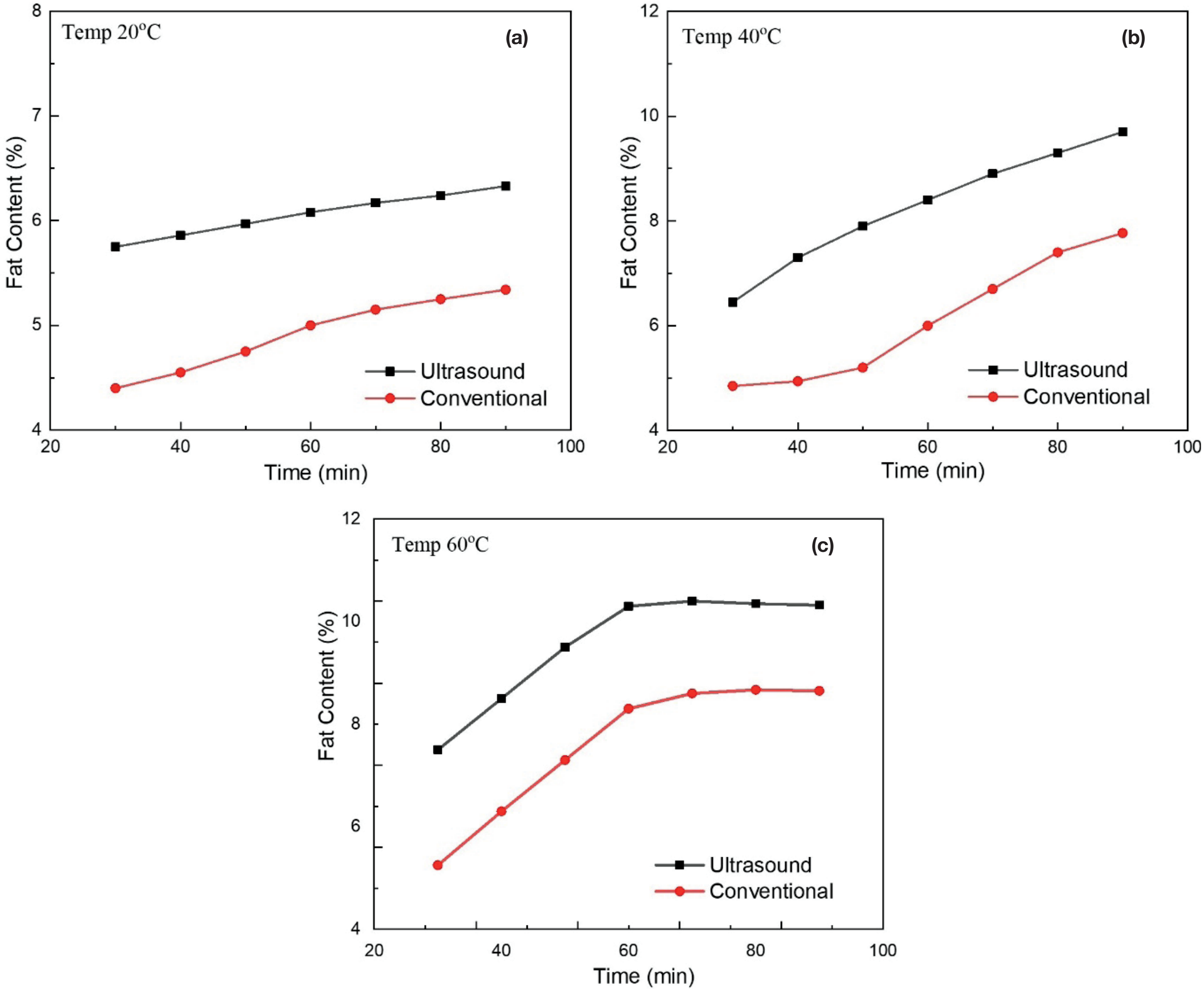

Figure 6. Fat content of leather fatliquored with 5% Remsynol ESI emulsion using ultrasound and conventional technique at **(a)** 20°C, **(b)** 40°C and **(c)** 60°C.

similar to that produced by conventional method. Both fatliquor emulsions were non-Newtonian in nature. It was also observed that viscosity of fatliquor decreased with an increase in temperature and viscosity of fatliquor increased with an increase in concentration. Thus, the effects of temperature, shear rate and concentration on viscosity of fatliquor emulsion are in good agreement with the behavior of emulsion.[20]

Effect of ultrasound on fat content of leather

Ultrasound plays a vital role in the fat content of leather. The effects of ultrasound on fat content of leather had been studied at different temperatures. Figure 6 (a, b, c) shows fat contents of leather fatliquored with 5% Remsynol ESI emulsion as a function of processing time using ultrasound and by conventional method at different temperatures. Fat content of leather at 20°C using ultrasound for 90 minutes was 6.3% whereas in conventional method it was only 5.1% (Figure 6a). Using ultrasound, the maximum fat content (10%) was obtained in 90 minutes at 40°C (Figure 6b) and 60 minutes at 60°C (Figure 6c). From the above data it can be concluded that using ultrasound same or even higher fat content can be obtained in shorter processing time or at lower temperature compared to conventional fatliquoring. Moreover, ultrasound aids in much better distribution throughout the whole cross section of the leather.

Physical properties of the fatliquored leathers

Physical characteristics namely tensile strength, stitch tearing strength, tongue tearing strength, Bauman tearing strength, grain crack load, and ball bursting strength of the leather fatliquored using ultrasound and conventional method were determined according to

Table I

Physico-chemical properties of leather fatliquored with 5% (w/v) Remsynol ESI emulsion using ultrasound and conventional method

Strength properties	Ultrasound-assisted fatliquored leather	Conventionally fatliquored leather	Standard Value
Tensile strength (Kg/cm²)	332 ± 2	250 ± 7.64	Min. 200
Percentage elongation at break	64 ± 1.52	37 ± 4.04	Min. 30%
Stitch tearing strength (kg/cm)	98.5 ± 2.02	83.5 ± 3.68	80-100
Tongue tear strength (kg/cm)	60.5 ± 2.56	33.5 ± 3.01	Min. 30
Bauman tear strength (kg/cm)	71 ± 3	35 ± 3.21	Min. 30
Grain crack load (kg)	69.75 ± 2.60	46.5 ± 2.18	Min. 16
Grain crack distension (mm)	15 ± 1.53	9 ± 1	Min. 7
Ball bursting load (kg)	74 ± 2.52	52.5 ± 2.50	Min. 20

Table II

Fastness properties of the fatliquored leather

Experimental conditions	Fastness properties		
	Wet	Dry	Perspiration
Ultrasound-assisted fatliquored leather	4-5	4-5	4
Conventionally fatliquored leather	3	3-4	2

the standard procedures and tabulated in Table I. It was observed that all physical properties of fatliquored leather with ultrasound were found to be significantly higher than those of without ultrasound. It is assumed that this is due to the higher fat-fiber interaction in presence of ultrasound resulting in higher fat penetration into the leather.[21] Consequently, fastness of ultrasound treated fatliquored leather was increased significantly (Table II).

Conclusion

Potential application of ultrasound in fatliquoring of leather was studied in detail. Ultrasound helped to provide finer emulsion particle size distribution resulting in better penetration and uniform distribution of fat in fatliquoring of leather. Therefore, this study revealed the potential use of ultrasound to prepare fatliquor emulsion as a greener leather production option. The use of ultrasound reduced the discharge of unconsumed chemicals in the effluent, enhanced diffusion rate, reduced processing time, and improved the leather quality which will lead the leather industry towards a cleaner image. Thus, application of ultrasound in fatliquoring of leather will be a very environmentally benign technique for leather industries in Bangladesh.

Acknowledgements

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