Eco-friendly Chrome Tanning of Leather using Ultrasound Technique

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Abstract

This article describes the development of an environment friendly chrome tanning of leather using ultrasound. Most of the leathers are tanned by the conventional method using basic chromium sulphate. It is one of the most polluting and time-consuming steps in leather processing. In this study, investigations were carried out on ultrasound assisted eco-friendly tanning process so that the chrome tanning agent could provide better quality leather without creating any environmental problem. Effects of using ultrasound in chrome tanning process were studied at different pH, tanning time, tanning agent dosage, and then compared with that of conventional method. Tanned leathers were characterized by scanning electron microscopy (SEM), photomicrographic analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), energy dispersive X-ray (EDX), etc. SEM analyses of the surface and cross-section of the tanned leather showed that fibre structures were not affected by ultrasound. It was also found that the shrinkage temperature of leather tanned with ultrasound was increased by about 5–29°C. Chrome uptake and content were found to increase by 30–50% and 1–7%, respectively. Tanning time was shortened from 6 hours to 2 hours and the quantity of leachable chromium in the leather was also decreased significantly. The noteworthy enhancing effects have been attributed largely because of the increased penetration of tanning agents into pickled leather. Photomicrographic analysis of the cross-section of the tanned leather also showed a higher penetration of tanning agents in presence of ultrasound.

1 Introduction

Leather industry is one of the most ancient and potential industries in Bangladesh that supplies the necessary materials such as leather goods, shoes, and garments using by-products of the meat industry. But leather processing generates huge number of by-products and wastes [1, 2]. It is well known that only 20% of wet salted hides and skins are transformed into commercial leather, whereas 25% is chromium-containing leather waste (CCLW), and the rest is non-tanned waste or lost in wastewater as fat, soluble protein, and solid suspended pollutants [3]. The real problem, however, is that the leather industry presently faces ample challenges due to environmental regulations [4]. In Bangladesh, there are about 165 leather industries, and 93% of them are located in the western part of the capital city Dhaka [5] and others are located at different locations of the country [6]. In Bangladesh, 240 MT hides or skins are processed per day which generates 8.47 million liters of wastewater and 98 MT solid wastes [7]. Leather and Leather Goods (LLG) is the second-largest export product of Bangladesh just after the ready-made garments. Bangladesh aims a target to achieve a total of $60 billion export earnings by 2021 of which $5 billion is expected to be achieved from LLG [8].

Tanning is the process of converting hides or skins into non-putrescible leather having certain physical, chemical and biological properties [9]. The common feature of the hides/skins is that they are composed primarily of collagen and can be made from the skin of any vertebrate. In tanning, raw hides/skins are treated with inorganic and organic tanning agents such as chromium, aluminum, titanium, iron, and zirconium basic salts as well as high molecular weight vegetable substances, aldehydes, oils, and other substances [10, 11]. More than 85–90% of the leather is processed by chrome tanning and it has been used for over 100 years [12].

Due to diffusion limitations of the chrome tanning agents in conventional tanning, only 60–70% of the total chromium applied in the tanning process is consumed in the skin matrix while the other 30–40% remains in the spent liquor [13, 14]. This excess amount of chrome increases the SS, DS, BOD_5, COD of the wastewater which pollutes the environment, and when this polluted water falls into the sea or river it also increases the pollution load of existing water which is very harmful to aquatic life [15]. Therefore, it is crying need to develop a process to speed up tanning without impairing the quality of finished products.

Ultrasound is one of the novel techniques for assisting the tanning process. Ultrasound is a sound wave with a frequency of 20 kHz-10 MHz that is generally used to enhance physical and chemical processes [16, 17]. The use of ultrasound over the last few decades has led to tremendous advances in the provision of versatile equipments for testing, detection, imaging, chemical processing, and research [18].

Sonochemistry deals with the effects of sonic waves and wave properties on chemical systems. Sonochemical activity arises from acoustic cavitation in liquid media [19, 20]. Acoustic cavitation involves nucleation, growth and explosive collapse of microbubbles on a microsecond timescale [21]. In the liquid phase high micromixing will increase the heat and mass transfer and diffusion of species inside the pores of the solid [22]. This study aims at developing eco-friendly leather tanning process using ultrasound.

2 Material And Methods

2.1 Materials

Raw materials used in chrome tanning were divided into two categories: primary raw materials and auxiliary raw materials. The primary raw materials are pickled pelt and basic chromium sulfate (basicity 33%). To operate the tanning process, different types of chemicals (laboratory reagent grade) were used besides the primary raw materials. The percentage of used chemicals is based on the weight of the pickled pelt. The auxiliary chemicals were 150% pickling liquor, 1.5% sodium formate (HCOONa), 0.25% oxidized chitosan (OCS), 1.5% sodium bicarbonate ($NaHCO_3$), 0.25% busan 30L. The percentage of all chemicals mentioned here are on the basis of weight of pickled pelt.

2.2 Experimental set-up

Ultrasonic bath SONOREX DIGIPLUS DL 514 BH of BANDELIN electronic GmbH & Co. KG, GERMANY with a power generation of 860W and 35 kHz frequency was used in this study. Leather samples were taken in a glass beaker clamped inside the ultrasonic bath containing water. Conventional tanning was carried out using a drum in absence of ultrasound with provisions of controlling temperature and rotation per minute (rpm).

2.3 Tanning procedure of pickled pelt

Sample preparation

The samples were cut into 2□ × 2□ taking from the equivalent lateral position of the pelt corresponding to the line of the backbone of the animal and weighed with an electronic balance (Shimadzu ATY224).

Chrome tanning

Chrome tanning was performed using ultrasound and conventional techniques. Details of tanning process are described in Table 1. All samples were divided into two parts for carrying out experiments with ultrasound and conventional methods. In the first group, the pickled pelt samples were taken in a beaker that was placed in a water bath to maintain the temperature exposed to ultrasound. Then, the pelts were chrome tanned with 6%, 8%, 10%, and 12% of basic chromium sulfate (BCS) for 2, 3, and 6 hours. At the beginning of tanning half of the basic chromium sulphate $Cr(OH)SO_4$ was added to the pickling liquor (150%) and the other half was added after 30 min and was sonicated. Then sodium formate (1.5% of sample) was added as a masking agent. The tanning bath was then basified using sodium bicarbonate which was divided into three equal portions and was added within an hour. pH of the liquor was monitored during adding sodium bicarbonate.

The second part of the sample was tanned by conventional method where a stationary glass vessel and rotary drum were used instead of ultrasound. A hotplate stirrer was used to control the temperature. In chrome tanning an initial pH of 2.5 to 4.0 and the temperature of 30–50°C was maintained.

Upon completion of tanning operation, the tanned leathers were covered by polythene and were piled up for several days to complete the fixation of tanning chemicals and dried in air. Tanned leathers obtained in both ultrasound and conventional methods were then used for analysis and characterization.

Table 1
Detail of chromium tanning operation

Sample	Tanning condition (For penetration)	Tanning condition (For basification)
1	6% basic chrome sulfate, 1.5% HCOONa and OCS for 1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 1 hour
2	8% basic chrome sulfate, 1.5% HCOONa and OCS for 1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 1 hour
3	10% basic chrome sulfate, 1.5% HCOONa and OCS for1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 1 hour
4	12% basic chrome sulfate, 1.5% HCOONa and OCS for1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 1 hour
5	6% basic chrome sulfate, 1.5% HCOONa and OCS for 1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 2 hours
6	8% basic chrome sulfate, 1.5% HCOONa and OCS for 1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 2 hours
7	10% basic chrome sulfate, 1.5% HCOONa and OCS for 1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 2 hours
8	12% basic chrome sulfate, 1.5% HCOONa and OCS for 1 hour	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 2 hours
9	6% basic chrome sulfate, 1.5% HCOONa and OCS for 2 hours	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 4 hours
10	8% basic chrome sulfate, 1.5% HCOONa and OCS for 2 hours	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 4 hours
11	10% basic chrome sulfate, 1.5% HCOONa and OCS for 2 hours	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 4 hours
12	12% basic chrome sulfate, 1.5% HCOONa and OCS for 2 hours	50% water, 0.25% busan and 1.5% $NaHCO_3$ for 4 hours

2.4 Characterization of tanned leather

Tanned leathers were characterized with field emission scanning electron microscopy (JSM-7600F, JEOL, Japan), photomicrographic analysis (Nikon, K16976, Japan), thermogravimetric analysis (TGA-50, SHIMADZU, Japan), differential scanning calorimetry (NETZSCH STA 499 F3 Jupiter, Germany), energy dispersive x-ray spectrophotometry (JED-2300 Analysis Station Plus, JEOL, Japan), boiling test, toxicity characteristic leaching procedure (TCLP) test etc.

Boling test is used to determine the percentage of shrinkage of the tanned leather. The piece of tanned leather (1□ × 1□) was boiled at 100°C for 10 minutes. Then the distinction from the initial to the final surface area of the tanned leather after was measured and the percentage of shrinkage was calculated by the following equation:

$$\%\text{Shrinkage} = \frac{(A_i - A_f)}{A_i} \times 100$$

where, A_i and A_f are the initial and final area of the tanned leather after boiling.

TCLP is commonly used to measure the quantity of leachable chromium in wet-blue leather. The TCLP extraction solution was arranged through titrating 40 g $C_6H_8O_7$ in 400 mL of distilled water by 1 M NaOH. The utmost pH was maintained to 5.0 ± 0.1. Air-dried chrome tanned leather powder (1 g) was added to 50 mL TCLP extraction solution. The mixture was turned at ambient temperature for 48 hours to a speed of 30 rpm. After 48 hours extraction, the reaction composition was filtered.

In this experiment, UV-Vis Spectrophotometry was used to determine the amount of leachable chromium from the tanned leather.

3 Results And Discussion

3.1 FTIR spectroscopic analysis of tanning agent

The tanning agent used is characterized by FTIR spectroscopic analysis. FTIR spectra indicate specific functional groups present in the chrome tanning agent. Hence, it is possible to determine the chemical structure of functional groups present in the chrome tanning agent. In this study, basic chromium sulfate was used as a tanning agent. FTIR spectrophotometer (IR Prestige-21, SHIMADZU) was used to study the functional groups present in the basic chromium sulfate. Fig. 1 shows the FTIR spectrum of pure basic chromium sulfate ($CrOHSO_4$).

FTIR spectra reveal functional groups present in a compound. Figure 1 shows the FTIR spectra of basic chromium sulfate, $Cr(OH)SO_4$. In the IR spectrum of basic chromium sulfate, the absorption peaks at 609 cm^{-1} and 480 cm^{-1} are attributed to the absorption due to vibration between Cr-O and SO_4^{2-} [23]. The peak at 1132 cm^{-1} are assigned for α-Cr_2O_3 [24]. The absorption peak at 609 cm^{-1} also reveals the vibration of Cr-O. A broad peak centered at 3456 cm^{-1} was observed due to the presence of -OH group [25].

3.2 Effect of ultrasound on % chromium uptake of leather

Chromium uptake was studied during tanning process for different tanning conditions. In this study tanning was carried out using 6%, 8%, 10% and 12% basic chromium sulfate for 120 minutes. Cr uptake of leather tanned with ultrasound and conventional methods are shown in Fig. 2. From the Fig. 2, it is evident that chromium uptake in case of tanning with ultrasound was more than those tanned without ultrasound. Ultrasound improves the penetration of chromium through the pores of collagen fibres and hence, enhances the percentage of chromium uptake by the leather sample. Thus 87%, 98%, 91% and 90% chromium uptakes were obtained in case of tanning with ultrasound for 120 minutes using 6%, 8%, 10% and 12% basic chromium sulfate, respectively while only 17%, 29%, 33% and 39% chromium uptakes were observed in case of conventional method under same tanning conditions.

The results showed that chromium uptakes of the leather samples tanned with ultrasound increased up to the concentration of basic chromium sulfate at 8% and then decreased. Because pickled pelts can't absorb all the chromium present in tanning liquor if excessive amount of tanning agent is used [26]. Thus, the use of 8% basic chromium sulfate for 2 hours is the best condition for ultrasound assisted chrome tanning to get maximum percentage of chromium uptake.

3.3 Effect of time on chromium uptake

Cr uptake reached 98% when tanning was carried with ultrasound for 180 minutes while only 33% Cr uptake was observed in case of conventional method under same conditions (Fig. 3a). Further increase of tanning time proved to be detrimental for ultrasound process as was evidenced that 79% chromium uptake was observed with ultrasound for 360 minutes. However, it was increased to 63% with conventional process (Fig. 3b). This reduction of Cr uptake might be desorption of some non-chemically bounded chromium ions due to effect of excessive sound wave which generated in sonicator.

3.4 Determination of chromium content in the tanned leather

The chromium content in the tanned leather sample was determined by energy dispersive spectrophotometric (EDS) method. From the EDS spectrum of tanned leather sample, the elemental composition of the leather sample was derived. The tanned leather sample contained several elements e.g., C, H, N, O, Cr, S, P, Na, Ca, Cl etc but amount of H, Na, Ca, P etc. were ignored in EDS analysis. The EDS spectra of samples tanned in presence of ultrasound (a) and in absence of ultrasound (b) are shown in Fig. 4. The spectrum of other samples also showed similar trends.

Elemental analysis of chrome tanned leather with ultrasound and conventional method have been done and the data are tabulated in Table 2. Chromium uptake of ultrasound assisted tanned leather was higher than that of conventionally tanned leather. Uptake of other elements also showed similar trends.

Table 2
Elemental analysis of tanned leather

Sl. No	Tanning Conditions	Ultrasound		Conventional	
		Element	Mass (%)	Element	Mass (%)
1	8% BCS, 2h	Cr	6.16	Cr	0.82
		S	1.47	S	1.43
		Cl	8.67	Cl	8.2
		O	16.49	O	21.18
		N	20.20	N	19.51
		C	47.01	C	48.86
2	8% BCS, 3h	Cr	5.26	Cr	0.89
		S	1.52	S	0.85
		Cl	8.66	Cl	4.46
		O	21.33	O	25.03
		N	17.08	N	21.39
		C	46.14	C	47.38
3	8% BCS, 6h	Cr	4.7	Cr	3.66
		S	1.82	S	2.29
		Cl	7.55	Cl	15.55
		O	21.41	O	14.85
		N	19.65	N	13.14
		C	44.86	C	49.43

3.5 Thermogravimetric analysis of the tanned leather

Thermal stability of leather tanned with and without ultrasound were compared to investigate the effect of ultrasound on leather tanning. Thermal degradation studies of the tanned leather samples were performed using thermogravimetric analyzer under N_2 atmosphere.

The temperature needed for a fixed percentage of weight loss was increased for leathers tanned using ultrasound technique. The improvement of the thermal stability of ultrasound assisted tanned leather samples were due to higher penetration of basic chrome sulfate through the pores of leather leading to the formation of chromium-collagen complexes which acted as a barrier to the decomposition of leather sample [27].

3.6 Effect of ultrasound on hydrothermal stability of tanned leather

There are several thermal analysis methods but differential scanning calorimetry (DSC) comes into prominence in recent years for evaluation of thermal behaviors (e.g., denaturation and shrinkage temperatures) of the raw skin, pickled, tanned, and finished leathers.

Several important temperatures such as peak temperature, onset temperature, extrapolated onset temperature, and end set temperature can be determined from a typical DSC thermogram. In this study, the onset temperature was considered as the shrinkage temperature. The onset temperature is the temperature at which the slope of the thermogram first deviates from the baseline.

The DSC thermograms of the leather samples tanned with ultrasound and conventional method using 8% basic chromium sulfate for 2 hr is shown in Fig. 6 (a, b). The thermograms of the leather sample showed that the shrinkage temperature of sample tanned in presence of ultrasound was 111°C while that of conventionally tanned leather was 82°C. The shrinkage temperature of sample treated under ultrasound was 29°C higher than that of conventionally tanned leather. The main reason for the improvement of shrinkage temperature is that a very small amount of chromium fixation was happened within two hours in the conventional tanning method whereas most of the chromium present in tanning liquor was fixed with collagen fibre in ultrasound-assisted tanning process. Therefore, the fixation of chromium increased with ultrasound.

3.7 Boiling test of tanned leather for evaluating thermal stability

The influence of ultrasound on the hydrothermal stability of the tanned leather was also measured by evaluating the results of the boiling tests. In the present study, the percentage of area loss or area shrinkage was determined by the boiling test.

Table 3
Percentage of area loss of chrome tanned leather by boiling test

Sample No.	Experimental Technique	Initial area (cm^2)	Final area (cm^2)	Area loss (cm^2)	Area loss or shrinkage (%)
1	With Ultrasound	4	2.90	1.10	27.50
	Conventional	4	2.64	1.36	34.00
2	With Ultrasound	4	2.75	1.25	31.25
	Conventional	4	2.20	1.80	45.00
3	With Ultrasound	4	2.54	1.46	36.50
	Conventional	4	2.15	1.85	46.25
4	With Ultrasound	4	2.58	1.42	35.50
	Conventional	4	2.14	1.86	46.50
5	With Ultrasound	4	2.88	1.12	28.00
	Conventional	4	2.63	1.37	34.25
6	With Ultrasound	4	2.72	1.28	32.00
	Conventional	4	2.21	1.79	44.75
7	With Ultrasound	4	2.64	1.36	34.00
	Conventional	4	2.10	1.90	47.50

Table 3 shows that the reduction in the area of the samples tanned with ultrasound were less than that of the samples tanned by the conventional method. Shrinkage areas of leather samples tanned with ultrasound and conventional method are 31.25% and 45%, respectively. The conventionally tanned leather sample has a lower amount of fixed chromium and consequently, higher shrinkage occurred.

3.8 Field emission scanning electron microscopic (FESEM) analysis

The surface morphology of the wet-blue leathers produced by tanning under ultrasound and conventional techniques were observed by FESEM as shown in Fig. 7.

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The micrographs show the chromium penetration across the cross-sectional view of the wet-blue leathers tanned with 8% basic chromium sulfate for 2 hours using both ultrasound and conventional techniques. In the micrographs, the darker region represents the concentration of chromium. It was observed that ultrasound assisted tanned leather showed higher uniform distribution of chromium throughout the samples than that of conventionally tanned leather. Therefore, FESEM further confirmed that the tanning agent completely penetrates the full cross-section of leather in the process of ultrasound-assisted chrome tanning.

The fibril bundles of the tanned leather were also analyzed from FESEM micrographs which showed that the fibrils and fibril bundles of collagen in the flesh, corium, and grain layers of the chrome tanned leather and observed that the collagen fibrils are intact for the leather tanned with both ultrasound and conventional techniques. These results revealed that collagen fibre structures were not damaged because of the usage of ultrasound in the tanning for 2 hours. But it was observed that in the case of the tanning process for 6 hours, the distance between fibrils is more with ultrasound than that of the conventional process. It means exposure to ultrasound for longer period is harmful for the structure of leather. Thus, in ultrasound-assisted chrome tanning process, 2–3 hours tanning time is optimum to complete the tanning operation.

3.9 Diffusion of tanning agent into leather: Stereo microscopic observations

Ultrasound enhances the penetration of the tanning agent and the degree of penetration was examined with a stereomicroscope. The cross-sectional images of the tanned leather obtained from the stereo microscope are shown in Fig. 8. The depth of penetration of the tanning agent depends on the type of sample and the tanning agent used.

It was observed that the tanning agent distribution in the leather samples treated with ultrasound was about 30–70% higher than that of the conventional method. The principal reason behind this is the effect of acoustic cavitation which enhances the diffusion rate of tanning agents through the pores of collagen fibres [21]. Almost 98% penetration of tanning agent was observed for tanned leather after 2 hours of tanning with ultrasound whereas only 29% penetration was observed for that sample after 2 hours of tanning without ultrasound. Besides this, uniform distribution of tanning agents throughout the whole cross-section of the pelt, even the inner portion of the pelt is possible in the case of ultrasound-assisted chrome tanning, which is quite impossible in the conventional tanning process. Hence, ultrasound can improve the penetration or diffusion of the tanning agent and impart the better-quality leather.

3.10 Determination of leachable chromium content

All the absorbed chromium present in tanned leather is not chemically bonded to the collagen chains. The chemical bonding within the carboxyl groups of collagen fibres and chromium ion is supposed to happen. In this study, chromium physically attached to the fibres was extracted by the TCLP. It helps in determining the quantity of free chromium that can be leached out from the tanned leather to the environment when it is disposed off. The leached chromium present in TCLP liquor was measured by UV-Vis spectrophotometric analysis (Table 4).

Table 4
Leachable chromium of tanned leather

Sample No.	Sample specification	Amount of leachable chromium (mg/gm)		Improvement (%)
		With ultrasound	Without ultrasound	
1	8% BCS, 2h	0.027	0.047	42.55
2	10% BCS, 2h	0.128	0.165	22.42
3	8% BCS, 3h	0.113	0.140	19.29
4	8% BCS, 6h	0.241	0.247	2.43

These results indicated that the amounts of leachable chromium with ultrasound-assisted tanned leathers are lower than that of conventionally tanned leather. It is assumed that chemically bonded chromium in the tanned leather is not easily leached out [28]. Thus, higher hydrothermal stability for the tanned leather might be obtained for ultrasound assisted tanning.

3.11 Estimation of environmental benefits

Ultrasound may be applied to reduce the effluent load to the environment. Ultrasound can improve the diffusion, penetration and fixation of chromium even at a lower concentration of tanning chemicals. As a consequence, Cr content in the spent liquor is reduced (Table 5) resulting the lower pollution load to the environment.

Table 5
Amount of chromium present in the spent tanning liquor

Sample No.	Sample specification	Amount of chromium in the spent liquor (%)		Difference (%)
		Ultrasound	Conventional	
1	8% BCS, 2h	2	71	69
2	8% BCS, 3h	2	67	65
3	8% BCS, 6h	21	37	16

There is a significant reduction in the amount of unused chromium in the spent tanning liquor due to the use of ultrasound was observed. The reductions were 69%, 65%, and 16% for samples 1, 2, and 3 that were tanned with 8% BCS for 120 minutes, 180 minutes, and 360 minutes, respectively.

4 Conclusion

Ultrasound showed significant effects on both penetration and basification of chromium ion through hide or skin by enhancing the tanning operation. Ultrasound decreased chrome tanning time from 6 hours to 2 hours. In presence of ultrasound, the percentage of Cr uptake was 70% for leather tanned with 8% basic chromium sulfate in 2 hours while it was only 35% for conventionally tanned leather. These results revealed that the use of 8% basic chromium sulfate and duration of 2 hours are the optimum conditions for ultrasound-assisted chrome tanning to get the maximum percentage of chromium uptake. The amount of unused chromium in spent liquor was also determined. A reduction of about 69% of unused chromium in the tanning effluent liquor was obtained by using ultrasound. EDX studies of tanned leather showed that chromium contents of ultrasound assisted tanned leather were about 7% higher than that of conventionally tanned leather. Thermal characterization of ultrasound assisted chrome tanned leather was carried out by DSC and TGA. The shrinkage temperature of ultrasound assisted leather was 5–29 ºC higher than that of conventionally tanned leather. TGA analysis revealed that the thermal stability of ultrasound assisted tanned leather was better than that of conventionally tanned leather. Thus, it can be concluded that application of ultrasound in leather processing might be a potential alternative to develop an eco-friendly leather manufacturing technique.

Declarations

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Authors' contributions

Professor Dr. Md. Zahangir Alam, Professor Dr. Md. Nurnabi and Dr. Md. Abu Sayid Mia planned and designed the research. Dr. Md. Abu Sayid Mia and Shamima Yeasmin conducted the experiments and wrote the manuscript. Professor Dr. Md. Zahangir Alam and Professor Dr. Md. Nurnabi supervised the whole research and revised the manuscript.

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Availability of data and materials

All data from this study are presented in the paper.

Competing interests

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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Figures

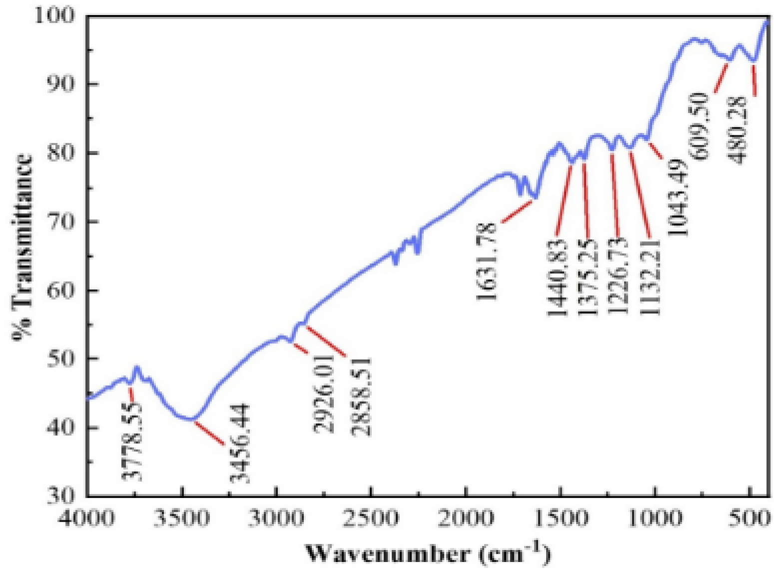

Fig. 1. FTIR spectrum of basic chromium sulfate ($CrOHSO_4$)

Figure 1

FTIR spectrum of basic chromium sulfate (CrOHSO4)

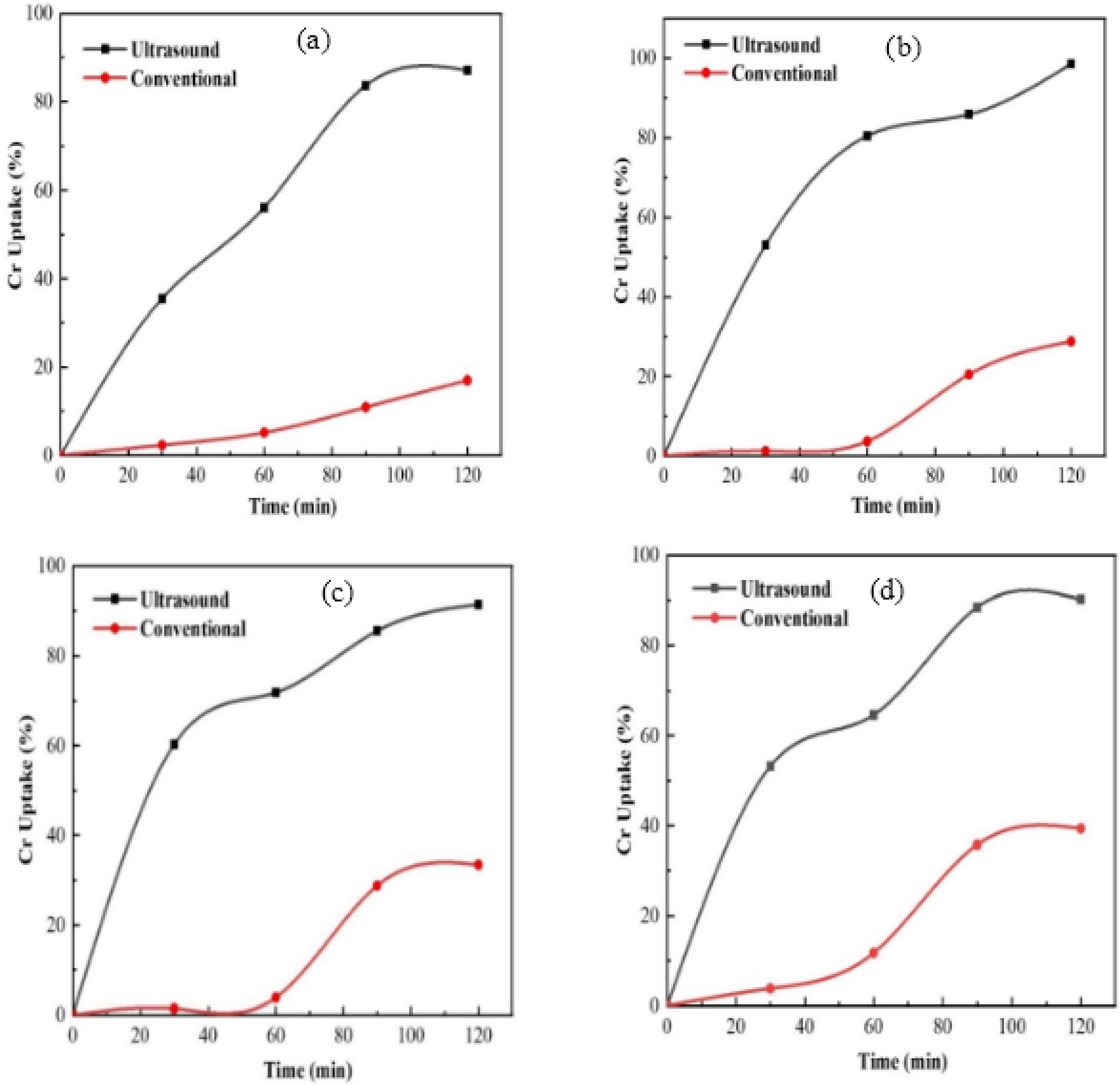

Fig. 2. Cr uptake of leather (%) as a function of time (a) Sample 1, (b) Sample 2, (c) Sample 3, and (d) Sample 4

Figure 2

Cr uptake of leather (%) as a function of time (a) Sample 1, (b) Sample 2, (c) Sample 3, and (d) Sample 4

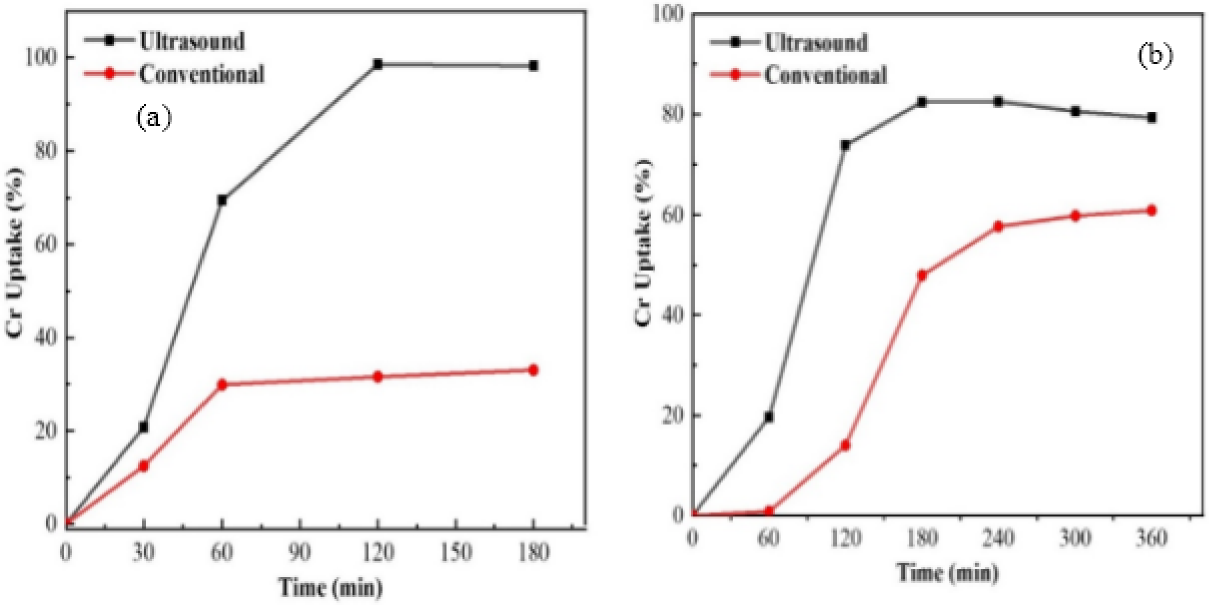

Fig. 3. Cr uptake of leather (%) as a function of time (a) Sample 6 (b) Sample 10

Figure 3

Cr uptake of leather (%) as a function of time (a) Sample 6 (b) Sample 10

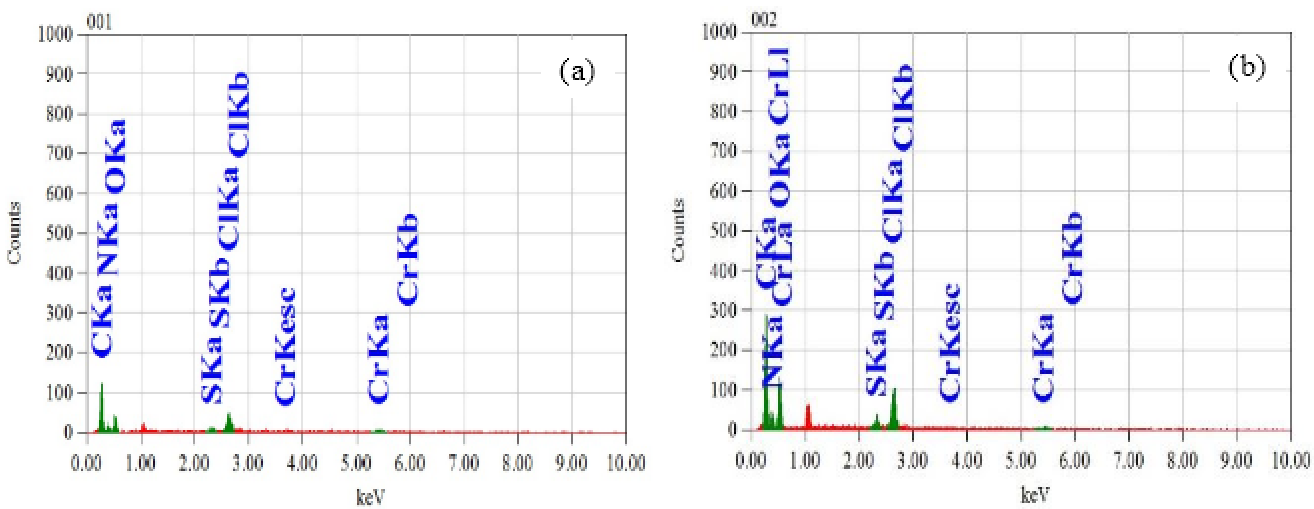

Fig. 4. The EDS spectrum of sample tanned with ultrasound (a) and without ultrasound (b)

Figure 4

The EDS spectrum of sample tanned with ultrasound (a) and without ultrasound (b)

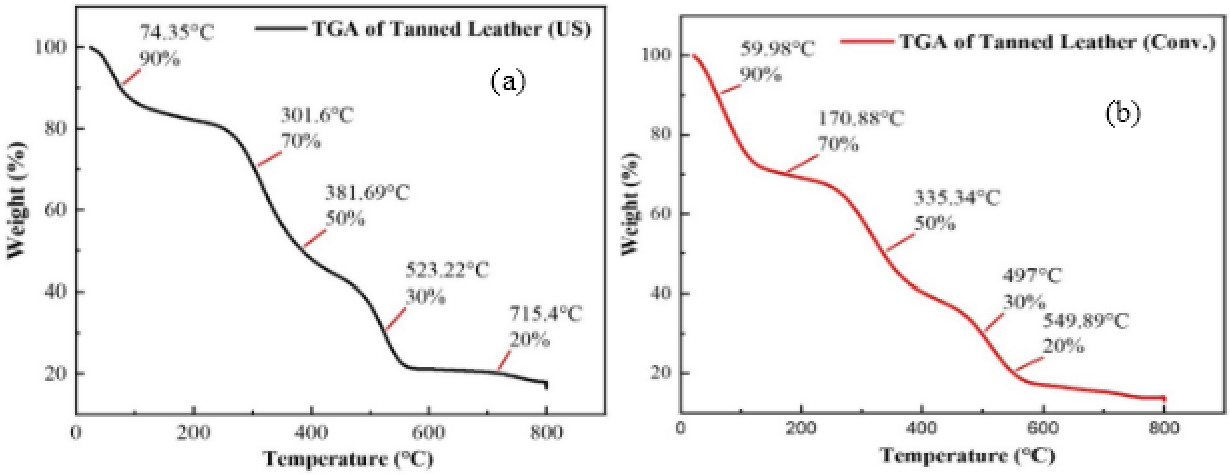

Fig. 5. TGA of leather sample tanned with 8% of basic chromium sulfate for 2 hours (a) with ultrasound (b) conventional method

Figure 5

TGA of leather sample tanned with 8% of basic chromium sulfate for 2 hours (a) with ultrasound (b) conventional method

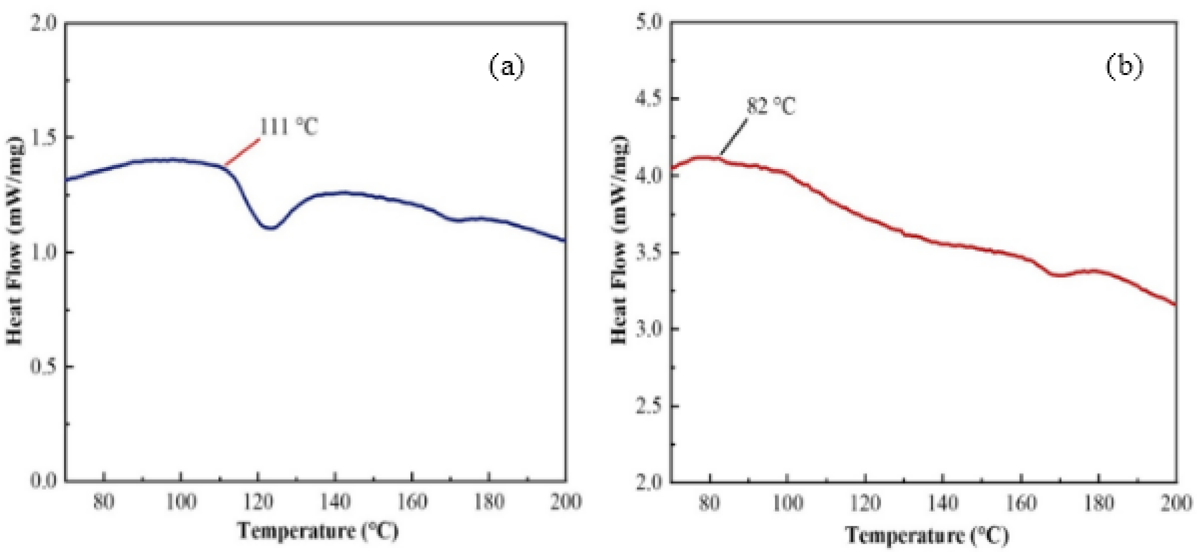

Fig. 6. DSC thermograms of leather sample tanned (a) with ultrasound and (b) without ultrasound

Figure 6

DSC thermograms of leather sample tanned (a) with ultrasound and (b) without ultrasound

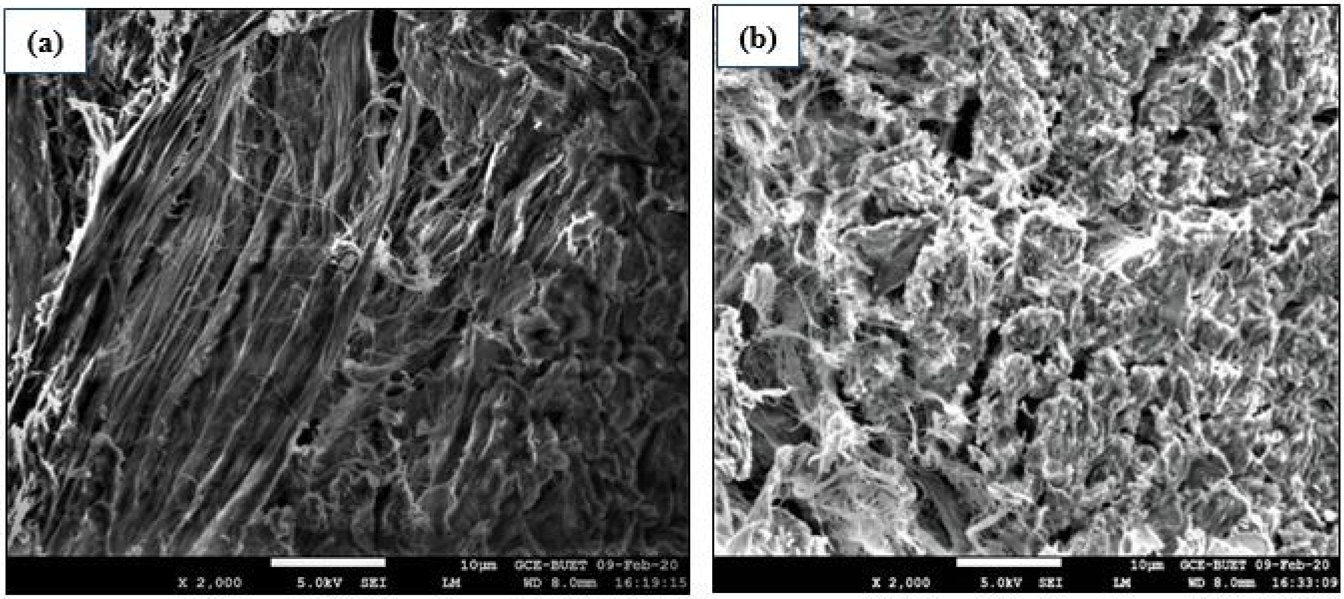

Figure 7

Field emission scanning electron micrographs of the cross-section of tanned with 8% basic chromium sulfate for 2 hours (a) with ultrasound and (b) without ultrasound at magnification ×2000

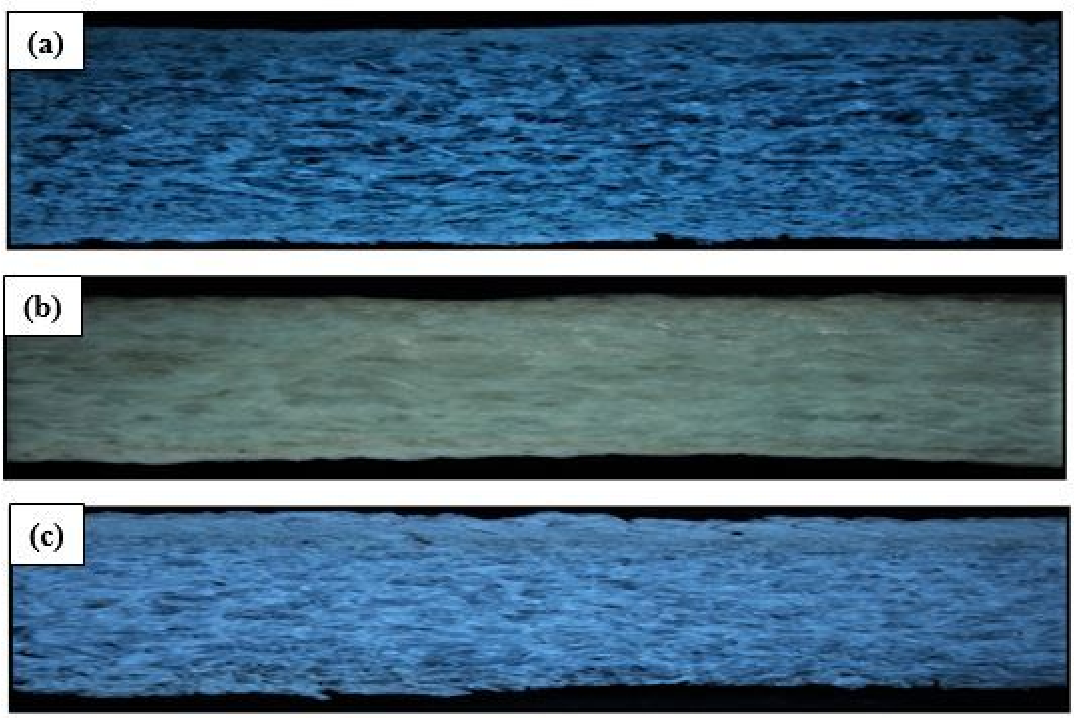

Figure 8

Stereo microscopic images of the (a) cross-section of wet blue leather tanned presence of ultrasound, (b) cross-section of pickled pelt and (c) cross-section of wet blue leather tanned with conventional method