

Development of Chrome-free Tanning in Supercritical CO₂ Fluid using Zr-Al-Ti Complex

by

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Abstract

In the current study, a green technology for the leather tanning process was developed, based on Zr-Al-Ti complex as a tanning agent in supercritical CO₂ fluid (SCF-CO₂). The operating parameters in the tanning process, including dosage of the tanning agent, reaction time, tanning temperature and tanning pressure, were optimized using the orthogonal testing method. The physicochemical properties, morphological features, organoleptic properties, hydrothermal stability and microscopic fibrous construction of the Zr-Al-Ti tanned leather were also evaluated. The results showed that the optimum process conditions were: a tanning agent dosage of 40% of the bated pelt weight, a tanning time of 1.5h, a final temperature of 40°C and a reaction pressure of 8.5 MPa. The shrinkage temperature, tear strength, tensile strength and elongation at break of Zr-Al-Ti tanned leather in water media and in SCF-CO₂ exhibited no statistically significant differences. However, SEM and histological observations revealed that the fiber bundles of leather tanned using the Zr-Al-Ti complex tanning agent in SCF-CO₂ seemed to disperse more unevenly compared to those in water media, as well as conventional chrome tanned leather. Moreover, the degree of "opening up" of the fiber bundles and the visible interspace among them in the Zr-Al-Ti tanned leather in SCF-CO₂ seemed to be much larger. Based on these results, we infer that the chrome-free tanning process in SCF-CO₂ may endow similar leather characteristics compared to Zr-Al-Ti tanned leather in a water medium, which could effectively reduce the discharge of waste water compared to a conventional chrome tanning process, thus contributing to the development of a greener, or cleaner, technology for the leather tanning process.

Introduction

In recent years, concerns over environmental issues have led to many greener, or cleaner, approaches to leather tanning processes in the leather industry.¹⁻⁴ At present, chrome(III) is still recognized as endowing leather with unmatched hydrothermal stability and excellent organoleptic properties; hence, its use as a tanning agent is widespread in the industry.⁵ Nevertheless, chrome tanning has some negative attributes, including: the possibility that uncombined residues of trivalent chromium in leather may be transformed into hexavalent chromium in some extreme conditions due to the insufficient penetration and combination of the chrome tanning agent;⁶ such agents could give rise to concerns about water treatment issues related to BOD and COD; in some countries, chromium resources may be limited and even restricted to certain purposes only.^{7,8} Therefore, the development of an eco-friendly chrome-free tanning agent is of key importance for leather tanning.^{9,10} The Zr-Al-Ti complex tanning agent, abbreviated DMT-II, is a novel chrome-free tanning agent, which has been prepared by our group based on the interactions of metal molecules through coordination bonds.^{11,12} According to our previous study,¹¹ the combination of the three metal ions in solution results in the regeneration of a more complex multi-heteronuclear composite, which may be conducive to the tanning process. Moreover, it has been confirmed that DMT-II can endow leather with appropriate hydrothermal stability and superior organoleptic properties, comparable to chrome tanning agents.¹²

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Reduction or elimination of sewage discharge at the source might solve certain contaminant concerns in the leather manufacturing industry.¹³ Supercritical CO₂ fluid (SCF-CO₂) has been utilized extensively in many areas, such as printing, dyeing, and cleaning.¹⁴⁻¹⁶ In recent years, the technology of leather manufacturing based on SCF-CO₂ has also been explored, with its core principle being the use of SCF-CO₂ instead of water as a medium in the different parts of the leather manufacturing process.^{17,18} It has been reported that the penetration, distribution uniformity and combination of the chemical reagents used in each working procedure seem to be promoted significantly under SCF-CO₂,^{19,20} as the fluid can effectively control reactivity and reaction selectivity owing to its high compatibility, high dispersion, and low viscosity.²¹ Therefore, the chemical reagents used in the process exhibit relatively high levels of utilization. Moreover, as CO₂ can provide an inert chemical micro-environment, these reagents may be much more easily recycled in SCF-CO₂.

In the present study, SCF-CO₂ was used instead of water as a medium in the chrome-free Zr-Al-Ti tanning process. The process conditions, including dosage of the tanning agent, reaction time, tanning temperature and pressure of the reaction caldron were optimized using the orthogonal testing method. In addition, the physicochemical properties, morphological features, organoleptic properties, hydrothermal stability, chemical components, and microscopic fibrous construction of the Zr-Al-Ti tanned leather were further studied. Our aim is to explore the feasibility of an anhydrous or micro water tanning method using supercritical CO₂ fluid as the medium and Zr-Al-Ti complexes as a chrome-free tanning agent, with a view to the sustainable development of cleaner leather manufacturing process and effluent.

Experimental Procedures

Materials

The bated cattle pelts used in the tanning process were self-prepared according to the method describe in our previous report.¹² The chemicals used for the synthesis of DMT-II and for tanning the leather were of analytical grade and purchased from Chengdu Kelong Reagent Chemical Factory, P. R. China. In addition, the supercritical CO₂ fluid equipment, with operating temperatures between -20 and 300°C, was designed in-house. Figure 1 shows a schematic of the SCF-CO₂ reaction unit. The maximum operating pressure and effective working volume of the equipment were 20 MPa and 1000 mL, respectively.

Preparation of Zr-Al-Ti Complex Tanning Agent

The Zr-Al-Ti complex tanning agent (DMT-II) was self-prepared according to the method detailed in a previous study, with slight

modifications.¹¹ A brief description of the preparation process is as follows: first, zirconium sulphate, aluminum sulphate, titanium sulphate and citric acid, in a ratio of 5:4:1:2 (w/w), were dissolved in 1 L of water under continuous magnetic stirring. Then, the mixture was heated and maintained at a constant temperature of 90°C for 30 minutes. Finally, the solution was dried using spray drying (GPL5, Sichuan Wang Chang Drying Equipment Co. Ltd.) to obtain the DMT-II.

Leather Tanning Process

The tanning process was carried out using bated cow pelts with a pH of 7.0–7.5. The bated cow pelts were soaked in the Zr-Al-Ti complex tanning solutions with different concentrations (based on the pelt weight) for 12 h and then drained for 30 min. Subsequently, the flesh side of the pelts was further soaked in a sodium bicarbonate solution with a stock concentration of 30 mg/ml. Finally, the pretreated pelts were placed in the supercritical CO₂ fluid reaction unit to undergo the tanning reaction. The detailed operating conditions for the tanning process are shown in Table I according to the design principles

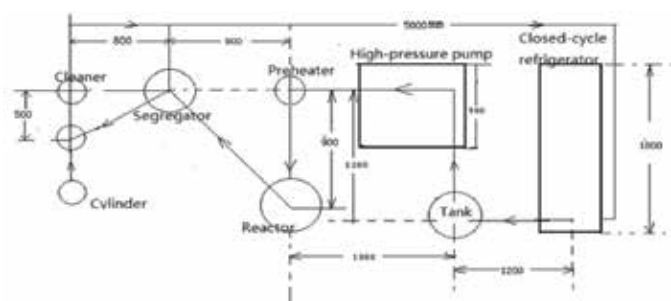


Figure 1. Schematic of the SCF-CO₂ reaction unit.

Table I
The factors and levels of orthogonal tests for the Zr-Al-Ti complex tanning process.

Level	Factors			
	Tanning time /h	Tanning temperature /°C	Tanning pressure / MPa	DMT-II offer /% ^a
1	2	45	9.5	24
2	1.5	40	8.5	32
3	1	35	7.5	40

^aThe DMT-II tanning solution was used in the tanning process and its dosage was based on the limed pelt after weight gain to 1.2 times.

of the orthogonal test method. Simultaneously, samples of chrome-free tanned leather and chrome tanned leather, both using water as the medium, were also prepared as a control, based on the methods from our previous report.¹²

Shrinkage Temperature Analysis

The shrinkage temperature of the leather specimens from each tanning group was measured using a MSW-YD4 shrinkage meter from the Yangguang Research Institute of the Shanxi University of Science Technology, according to the Chinese Industrial Standard QB/T 2713-2005.

ICP Analysis

The leather specimens from each tanning group were split into three layers (grain layer, middle layer, and flesh layer) with the same thickness, using a precise splitting machine. Each layer of the leather specimens was placed in a drying oven for over 4 hours, following which a certain number of the dried samples were digested and further analyzed using an inductively coupled plasma (ICP) spectrometer (Optima 2100DV, Germany). The homogeneous degree of DMT-II in the leather specimens was calculated using the following formula (1).

$$\text{homogeneous degree} = \frac{2 \times A_2}{A_1 + A_3} \times 100\% \quad (1)$$

where A_2 represents the metal ion content of the middle layer, and A_1 and A_3 are the metal ion contents of the grain layer and flesh layer, respectively.

Microstructure Characteristics

Scanning Electron Microscope Observation

The leather specimens from each tanning group were sampled in official sampling position. The samples were lyophilized in a vacuum chamber (0.05 bar) for 48 hours and their cross sections were observed microscopically using a scanning electron microscope (SEM, Hitachi S3000N, Hitachi, Ltd., Japan).¹² All the specimens were coated with aurum and imaged at an accelerating voltage of 5 kV.

Histological Observation

The leather specimens from each tanning group were sampled adjacently and symmetrically from the same hide, and fixed in a 10% formaldehyde solution for more than 24 hours. The cross- and longitudinal- sections of the specimens were prepared using a CM1950 freezing microtome (Leica, Germany) to a thickness of 12 μm , and adhered to glass slides. Morphologic observation was performed using the Van Gieson staining method with picric acid and fuchsin acid. Finally, an E400 optical microscope (Nikon, Japan) was used to carry out a histological examination of the stained samples.¹²

Physical-mechanical Properties and Organoleptic Assessment

The dried crust leather samples from each tanning group were tested using an AI-7000S Versatile Material Experiment Machine (Gotech High Technology Co. Ltd., Taiwan, China) according to the standard procedures for testing physical and mechanical properties. Physical properties such as tensile strength, elongation at break, and tear strength were examined as per the standard procedures IUP 6 (2000), IUP 8 (2000), and IUP 9 (1996).²² Further, the specimens from each tanning group were assessed by hand for softness, grain tightness, grain smoothness, strength, and fullness, through the visual examination of experienced tanners, who have worked in the leather-manufacturing industry for more than ten years.

Chemical Composition Analysis

The leather specimens from each tanning group were subjected to chemical composition analysis to determine the moisture, sulfate ash, and fat content, according to the methods laid out by the Chinese Industrial Standard QB/T 2706-2722 (2005).

Results and Discussion

Orthogonal Experiment Analysis

Table II shows the results of orthogonal experiments determined by the shrinkage temperature, T_s . The influence of the tanning conditions on the shrinkage temperature of the leather specimens from each tanning group are directly reflected by the R values. As shown in Table II and Figure 2, the tanning conditions for the shrinkage temperature of the leather specimens, ranked in order from the most to the least influential, are: (DMT-II offer) > (tanning time) > (tanning temperature) > (tanning pressure). Figure 2 shows the effects of each tanning operating condition on the shrinkage temperature of the leather specimens. The T_s values increased dramatically for DMT-II dosages of less than 32%. As the DMT-II offer was increased, the T_s tended towards a steady value; however, operating under these conditions would be more costly. Generally, with an increasing concentration of DMT-II, the coordination probability between carboxyl groups in collagen fibrils and DMT-II would increase,¹² thus increasing the combined amount of DMT-II and further improving the shrinkage temperature. Furthermore, our previous study indicated that the reaction between collagen fibrils and DMT-II reaches chemical equilibrium when the DMT-II offer reaches 40%.¹² In addition, when the tanning process starts within 1 h, the penetration of the tanning agent could promptly penetrate into the leather. By prolonging the rotation time to 1.5 h, the combination of the tanning agent with the carboxyl of the collagen chains approaches an equilibrium point. Furthermore, increasing the tanning temperature accelerates the hydrolysis and polycomplexation of the DMT-II molecules,¹² resulting in bigger molecular dimensions; this may promote the permeation of DMT-II into the pelts and

further the combination of the metal complex with the collagen. However, when the tanning temperature is set too high, DMT-II molecules might become too large and react with the collagen too early, leading to the case hardening of leather,²³ which would negatively affect the permeation of DMT-II molecules. In summary, taking into account the cost and tanning results, the optimum operating conditions of the Zr-Al-Ti tanning process in SCF-CO₂ were determined to be: a tanning agent dosage of 40% of the bated pelt weight, a tanning time of 1.5 h, a final temperature of 40°C, and a reaction pressure of 8.5 MPa.

Shrinkage Temperature Analysis

The shrinkage temperature determines the thermostability of leather. Table III shows the shrinkage temperatures of the leather specimens from each tanning group. The shrinkage temperature of the Zr-Al-Ti tanned leather in SCF-CO₂ increased by around 24°C compared to the bated cattle skin, which indicates that the hydrothermal stability of leather may be efficiently improved by the tanning agent.²⁴ Note that the shrinkage temperature of the Zr-Al-Ti tanned leather in SCF-CO₂ was somewhat lower than that in the water fluid. This may be because the pelts could not

achieve sufficient mechanical interaction in the SCF-CO₂ reaction unit compared to the conventional drum. On the other hand, though the combination of the DMT-II in the tanned leather under SCF-CO₂ was higher, as confirmed by the ICP analysis, the effective combination with collagen fibrils (i.e. the multipoint attachment) was insufficient.¹⁷ Additionally, as is well known, hydrolysis and polymerization of metal tanning agents usually occur in an aqueous medium; thus, the aforementioned reaction of the Zr-Al-Ti tanning agent would be inhibited to some extent in SCF-CO₂, leading to a lower shrinkage temperature. Therefore, the tanning process taking place in an almost anhydrous environment may be very beneficial for saving tanning water and reducing tanned effluent discharge. At the same time, unlike for the conventional chrome tanning process, there was no need to introduce any additional sodium bicarbonate to increase alkalinity in the tanning process occurring in the SCF-CO₂ reactor. Meanwhile, 1.5 h of tanning time, which was significantly lower than that of the Zr-Al-Ti tanned leather in water fluid, was quite enough in the SCF-CO₂. This would undoubtedly substantially save on energy consumption and labor costs.

Table II
Results of orthogonal experiments.

	Tanning time /h	Tanning temperature /°C	Pressure /MPa	Dosage /%	Ts /°C
1	2	45	9.5	24	82.0
2	2	40	8.5	32	87.5
3	2	35	7.5	40	83.3
4	1.5	40	9.5	40	85.7
5	1.5	35	8.5	24	84.8
6	1.5	45	7.5	32	86.7
7	1	35	9.5	32	83.6
8	1	45	8.5	40	84.3
9	1	40	7.5	24	82.8
Ts	K ₁	84.3	83.7	84.3	83.2
	K ₂	85.7	85.5	85.3	85.9
	K ₃	83.6	84.3	83.9	84.4
	R	2.1	1.8	1.4	2.7
Significance	DMT-II offer > Tanning time > Tanning temperature > Tanning Pressure				

ICP Analysis

Table IV shows the ICP results for the Zr-Al-Ti tanned leathers in the SCF-CO₂ and water fluids. The DMT-II contents of each layer of the tanned leather in SCF-CO₂ were higher compared to those in water, which indicates that the penetration and combination of the DMT-II is promoted under SCF-CO₂. Moreover, the DMT-II in the tanned leather exhibited a significantly higher homogeneous degree in the SCF-CO₂ compared to the water.

Physical-mechanical Properties Analysis

Table V shows the results of the physical-mechanical property analysis for the Zr-Al-Ti tanned leathers in the SCF-CO₂ and water fluids, and the conventional chrome tanned leather. The tear strengths, tensile strengths and elongation at break of the three samples were not very different, and ensures that all three fulfilled the fundamental requirements for the mechanical strength of leathers.¹² However, it is still noteworthy that the Zr-Al-Ti tanned leather in SCF-CO₂ exhibited a slightly lower tensile strength than the other two specimens, while possessing the highest elongation at break.

The organoleptic properties of the three different leathers were also evaluated. All of the professional, skilled tanners consulted in this study believed that there were no visible differences

among these leathers in respect to the strength, fullness and hand feeling; some differences were noted in respect to the softness, grain tightness and grain smoothness. More specifically, the softness and grain smoothness of the Zr-Al-Ti tanned leather in SCF-CO₂ was superior to that in water, while its grain tightness exhibited a slight inferiority.

Chemical Composition Analysis

The chemical compositions of the leather specimens from each tanning group were studied using the methods outlined in the Chinese Industrial Standard QB/T 2706-2722 (2005), as shown in Table VI. According to the proximate composition results, the moisture content of the Zr-Al-Ti tanned leather in SCF-CO₂ was slightly higher compared with that in the water. Generally, the moisture content of leather or fur should be between 12–18%, as the density, thickness, area, and tensile strength of the leather vary greatly with the moisture content. Leathers with lower moisture content appear much harder and crisper, whereas those with higher moisture content tend to be much easier to deform and mildew. A higher content of sulfated ash was found in the Zr-Al-Ti tanned leather in SCF-CO₂ compared to that in the water, which might suggest that the amount of infiltration and combination of DMT-II was significantly higher due to more loosely weaved collagen fibrils. Meanwhile, the Zr-Al-Ti tanned leather in SCF-CO₂ exhibited lower dichloromethane extract

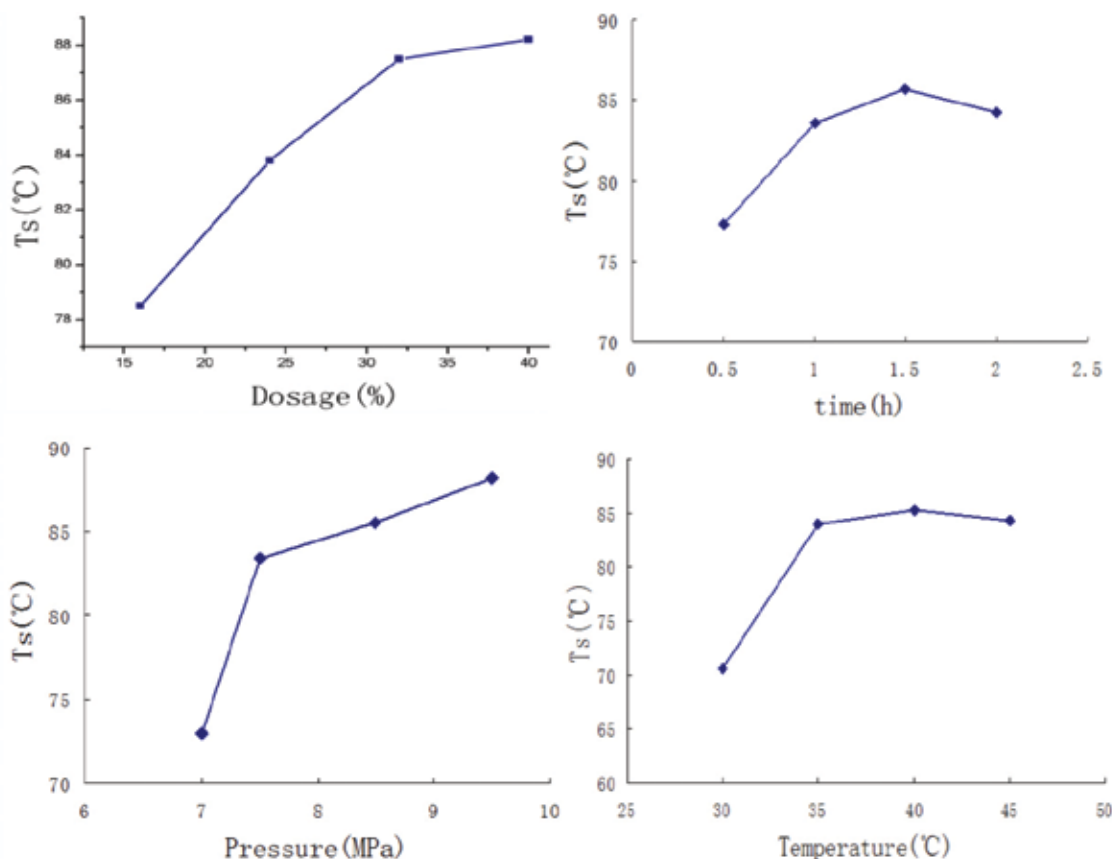


Figure 2. The effect of each tanning operating condition on the shrinkage temperature of the leather specimens.

content, as the SCF-CO₂ was able to extract a small amount of grease from the bated pelts. As is well known, the dichloromethane extract content of leather is closely associated with its water resistance performance, extensibility and breathability. The lower dichloromethane extract content may be beneficial for the breathability of the leather, especially when used as shoe upper leather. In addition, the Zr-Al-Ti tanned leather in SCF-CO₂ was found to have a significantly higher protein content than that in water fluid, which indicates that the tanning process in supercritical CO₂ fluid does not excessively damage the basic framework of collagen fibrils in leather. Overall, the chemical compositions of the two leathers were similar but still showed some differences, which may be closely related to their specific leather properties.

Table III
Shrinkage temperatures of the leather specimens from each tanning group.

Specimens	Ts /°C
Bated cattle pelts	63.7 ± 2.1
Zr-Al-Ti tanned leather in SCF-CO ₂	87.4 ± 2.6
Zr-Al-Ti tanned leather in water fluid	94.6 ± 3.5
conventional chrome leather	105.1 ± 5.3

Table IV
ICP results for the leather specimens from each tanning group.

Specimens	Layer classification	DMT-II content / (mg/g)	homogeneous degree of DMT-II
Zr-Al-Ti tanned leather in water fluid	Grain layer	36.32	89.77%
	Middle layer	32.86	
	Flesh layer	36.89	
Zr-Al-Ti tanned leather in SCF-CO ₂	Grain layer	37.65	93.97%
	Middle layer	35.13	
	Flesh layer	37.12	

Microstructure Characteristics

SEM Analysis

The scanning electron micrographs of the leather specimens from each tanning group, presented in Figure 3, show that the degree of “opening up” of the fiber bundles in the Zr-Al-Ti tanned leathers in both media were higher compared to the bated pelts. Moreover, no apparent dense blocky crystals of DMT-II were observed between the collagen fibers, which indicates that all the inner layers were well tanned.²¹ The fiber bundles of these two leathers were weaved very tightly and the fibrous clearance was relatively close. As a result, the tanning effects achieved by DMT-II were clearly apparent compared to the bated pelts, which implies that the DMT-II tanning process was conducted successfully in the SCF-CO₂.

Table V
The mechanical properties of each leather specimen.

Specimens	Zr-Al-Ti tanned leather in SCF-CO ₂	Zr-Al-Ti tanned leather in water fluid	Chrome tanned leather
Tear strength/ (N/mm)	45.7 ± 3.5	44.8 ± 2.8	46.4 ± 1.3
Tensile strength/MPa	10.6 ± 0.6	13.7 ± 1.6	12.3 ± 1.1
Elongation at break /%	95.2 ± 3.7	75.3 ± 6.0	78.9 ± 5.5

Table VI
Chemical compositions of each leather.

Specimens	Zr-Al-Ti tanned leather in SCF-CO ₂	Zr-Al-Ti tanned leather in water fluid	Chrome tanned leather
Moisture /%	15.91 ± 2.52	14.98 ± 2.31	13.13 ± 1.98
Sulfated ash /%	17.95 ± 1.28	16.70 ± 2.13	6.93 ± 1.65
Dichloromethane extracts /%	0.78 ± 0.02	1.05 ± 0.05	2.31 ± 0.59
Protein /%	48.66 ± 3.12	36.50 ± 2.91	38.79 ± 2.61

Histological Analysis

Histological examination mainly showed the intact total framework of the cross and longitudinal sections of the three different specimens, as shown in Figures 4 and 5. The degree of “opening up” of the fiber bundles and the visible interspace among them seemed to be much larger in the SCF-CO₂ specimen compared to the one in water, which may be beneficial for the infiltration and combination of DMT-II, since most of the penetration time is determined by the efficiency of DMT-II assimilating into the collagen fibrils.²⁵ In this case, the CO₂ can directly infiltrate the grain and reticular layers of crust leathers, which should have a positive impact on the penetration of the DMT-II. In addition, the fibrils of the Zr-Al-Ti tanned leather in SCF-CO₂ seemed to be more loosely weaved, which corresponds with the results of the physical-mechanical property and organoleptic assessment analyses. Based on these results, it may be inferred that the gaps between the collagen fiber bundles would be increased in the SCF-CO₂ due to its function of “decentralizing fibers.”

Conclusions

A green technology for a leather tanning process in supercritical CO₂ fluid media (SCF-CO₂) was developed and evaluated based on Zr-Al-Ti complex as tanning agent. The operating conditions of the tanning process were optimized using the orthogonal test method, with the following conditions found to be optimal: a tanning agent dosage of 40% of the bated pelt weight, a tanning time of 1.5 h, a final temperature of 40°C and a reaction pressure of 8.5 MPa. The shrinkage temperature of the Zr-Al-Ti tanned leather in water media and in the SCF-CO₂ exhibited no statistically significant differences. ICP analysis confirmed that the distribution uniformity and combination of the Zr-Al-Ti tanned leather in SCF-CO₂ was better compared to the conventional Zr-Al-Ti tanned leather in water fluid. The slightly lower tensile strength and higher elongation at break of the Zr-Al-Ti tanned leather in SCF-CO₂ were due to its more loosely woven fibrils. Meanwhile, histological observations showed that the degree of “opening up” of fiber bundles, and the visible interspace among them in the Zr-Al-Ti tanned leather in SCF-CO₂ seemed to be much larger compared to that in the water fluid. SEM analysis confirmed that all the inner layers were well tanned. As a whole, the fundamental properties and microscopic fibrous construction of the Zr-Al-Ti tanned leather in SCF-CO₂ exhibited no remarkable differences compared to the conventional Zr-Al-Ti tanned leather in water. However, this chrome-free process could help with waste water treatment by eliminating the chromium discharge at the source, thus contributing to the development of sustainable leather manufacturing processes.

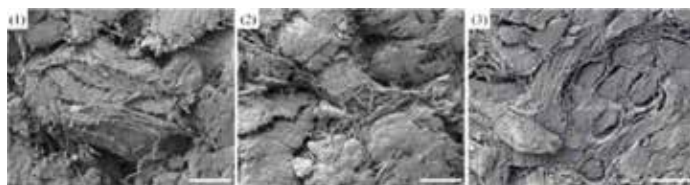


Figure 3. Scanning Electron Microscope cross sections of crust leathers: (1) Bated cattle skin (×200); (2) Zr-Al-Ti tanned leather in SCF-CO₂ (×200); (3) Zr-Al-Ti tanned leather in water fluid (×200).

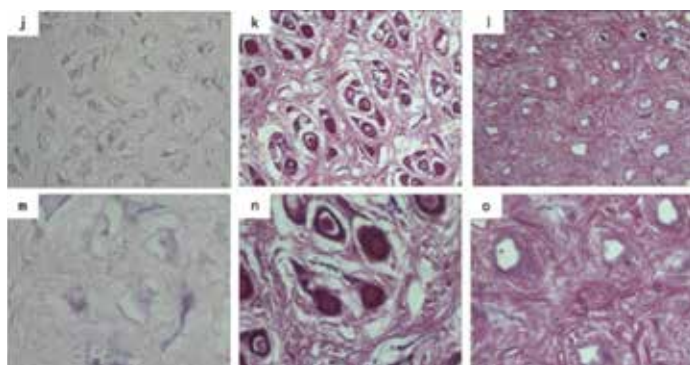


Figure 5. Histological observation of the cross sections of crust leathers j. Bated cattle skin (×40), m. Bated cattle skin (×100); k. Zr-Al-Ti tanned leather in SCF-CO₂ (×40), n. Zr-Al-Ti tanned leather in SCF-CO₂ (×100); i. Zr-Al-Ti tanned leather in water fluid (×40), o. Zr-Al-Ti tanned leather in water fluid (×100).

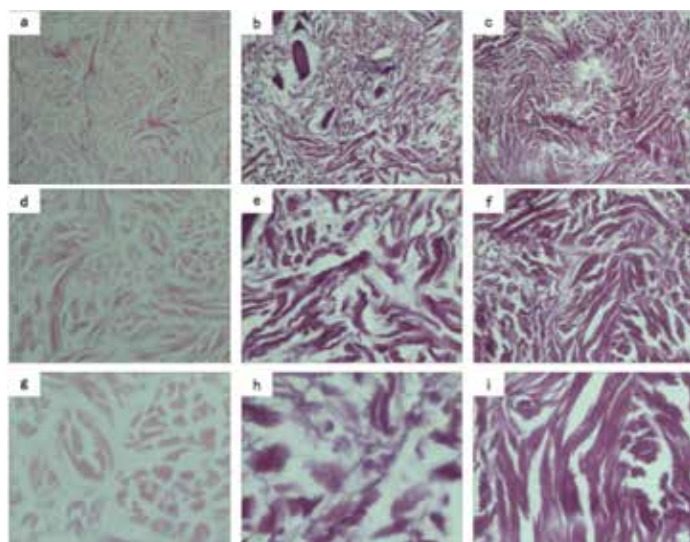


Figure 4. Histological observation of the longitudinal sections of crust leathers. a. Bated cattle skin (×40), d. Bated cattle skin (×100), g. Bated cattle skin (×200); b. Zr-Al-Ti tanned leather in SCF-CO₂ (×40), e. Zr-Al-Ti tanned leather in SCF-CO₂ (×100), h. Zr-Al-Ti tanned leather in SCF-CO₂ (×200); c. Zr-Al-Ti tanned leather in water fluid (×40), f. Zr-Al-Ti tanned leather in water fluid (×100), i. Zr-Al-Ti tanned leather in water fluid (×200).

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