Study on the Recycling Technology of Unhairing-liming and Tanning Wastewater

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Abstract .....

The recycling technology is one of the most important ways to realize the clean production in leather industry. In this study, a novel closed recycling technology of unhairing-liming and chrome tanning wastewater has been applied in mass production scale in a local tannery. In the recycling process, the content of various ions and TOC of the wastewater were measured. The collagen fiber dispersion and the distribution of ions in pelts were characterized. The shrinkage temperature and mechanical properties of leather obtained by the recycling technology were also tested.

All the trials showed that the novel closed recycling technology worked well without impairing the quality of the resultant leather and the zero emission of unhairing-liming and chrome tanning wastewater was realized. In the unhairing-liming step of the novel technology, the dosage of water, sulfide and lime were reduced by 80.8%, 33.3% and 23.4%, respectively. The collagen fiber bundles of limed pelts were split well. The distribution of calcium ion and sulfion in limed pelts was more uniform. 70% of salt and 20% of chrome tanning agent could be saved by recycling of chrome tanning wastewater. The shrinkage temperature of wet blue from different recycling times (from the first time to the 30 times) was all above 100°C. With the increase of the recycling times, the grain surface color of the wet blue tended to be similar. Furthermore, the mechanical properties and yield of the leather in the recycling technology were improved.

Keywords: unhairing-liming wastewater; tanning wastewater; recycling technology; zero discharge; mass production

INTRODUCTION

The unhairing-liming and chrome tanning are two of the most important steps in the production process of leather making. The quality of unhairing-liming and tanning process will affect the following process as well as the properties of the finished leather. The traditional unhairing-liming wastewater contains large amount of sulfide, lime, protein and its degradation product. The tanning wastewater contains chrome complex and neutral salt. Therefore, the unhairing-liming and chrome tanning wastewater is the main source of pollution in leather manufacture. The terminal control method is usually used in the liming and chrome tanning wastewater treatment. But the treatment fee is high and the treatment system is not very effective.

The recovery and reuse of wastewater is one of the effective ways to realize the clean production of liming and chrome tanning (Thanikaivelan et al. 2005; Hu et al. 2011; Saravanabhavan et al. 2004; Rao et al. 2003), which has been paid more and more attention by researchers.

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In recent years, several patents have been granted to BIOSK chemical company about closed cycle technology of liming and chrome tanning effluent (Zhang et al. 2009; Zhang 2011; Zhang 2014).

According to the principle of this technology announced by BIOSK, the closed cycle technology of unhairing-liming and chrome tanning wastewater in production of cattle shoe leather was investigated. The aim of this research is to explore the technical points of the recycling technology of liming and tanning wastewater, and evaluate the effect of the process and the quality of the obtained products.

MATERIALS AND METHODS

Materials

The experiment chemicals were as following: Na_2S, NaHS (70% flakes), lime and chrome powder were industrial grade. Degrease agent AN-C was supplied by LANXESS Inc. The liming auxiliary DO-pro and ELIPO, fungicide DK and basifying agent BE were supplied by BIOSK CO., Ltd. Lime dispersing auxiliary CR-2 was purchased from American

BK Company. Especially for special illustration, the dosage of chemicals was calculated according to the weight of salting hide.

Liming wastewater recycling process

The traditional hair persevering process was shown in Tab. 1. The wastewater of experimental process was collected and then reused in the next production batch. Because of the restriction of experimental condition, only 80% of the liming wastewater was collected. The recycling route of the liming wastewater was shown in Fig. 1. A certain amount of sodium sulphide as well as the lime was supplemented in each recycling.

Tab.1 Conventional hair saving unhairing process

Process	Chemical	%	Temp.°C	Time
	Water	80	25	
Immunization stage	AN-C	0.1		
	DO-pro	0.8		
	NaHS	0.2		Run: 30 min
	Lime	1.2		Run: 20 min, standing: 20 min
Unhairing stage	NaHS	0.8		
	Na_2S	0.2		Run: 30 min
	Water	20	25	
Hair separation				Filtration with 30 min
Liming stage	DO-pro	0.4		
	Lime	1		
	Na_2S	1		Run: 30 min
				Run: 10min every half hour (4×)
	Lime	0.5		
	Water	50		
	CR-2	0.2		
	Lime	0.8		Run: 30 min
				Run: 5min every hour until next day

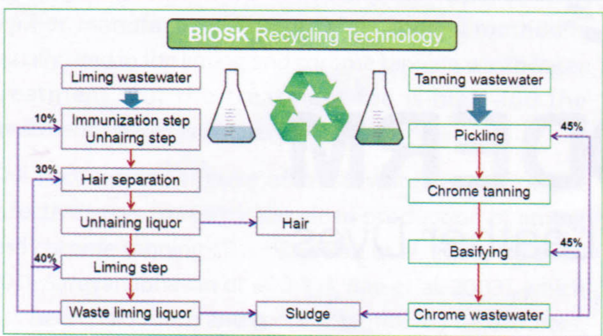

Fig.1 The recycling method of liming and chrome tanning wastewater

The recycling formulation of chrome tanning wastewater

The operating process of the chrome tanning wastewater was shown in Tab.2. The chrome-contained wastewater of experimental process was collected and then reused in the next production batch for pickling and tanning. Due to limitations of the experimental conditions, only 90% of chrome tanning effluent was collected. The recycling route of the chrome-containing wastewater was shown in the right side of Fig. 1.

Tab.2 The pickling and tanning process

Process	Chemical	Dosage %	Temp. (°C)	Time (min)	Remark
Pickling	Salt	2-4	25		
	Chrome tanning effluent	100			
	Formic acid (85%)	0.5			1:10 diluting
	Sulfuric acid (96%)	1.7			1:10 diluting
	Pickling auxiliary D	0.2			1:10 diluting
	Mildew preventive DK	0.2		120	pH: 2.0-2.5
Chrome tanning	Conducted in the pickling solution				
	Chrome tanning agent	5		180	
	Pickling auxiliary agent D	0.2	25		
	Basifying agent BE	0.2		120	pH: 3.2-3.4
	Chrome effluent (60°C)	100		240	Stay for overnight Run for 30min in the next day, pH:3.2-3.4

The chemical analysis of liming wastewater

The sample of liming wastewater was precipitated firstly. After natural sedimentation, 500 mL of the wastewater of different recycling technology was filtered by double layer gauze for two times. The filter liquor was taken to analysis.

The determination of Na_2S content

The content of sulfide in the wastewater was determined by filtration and iodimetry (Balasubramanian et al. 2000)

The determination of Ca content

The content of Ca in liming wastewater

The content of Ca was determined by EDTA complexometry method (Barrows et al. 1962).

The determination of Ca content in the pelt

The leather sample was ashed at 550°C firstly. Then the 1:1 hydrochloric acid was used to resolve the ash. Lastly, the sample was diluted. The titration process was similar to the determination of Ca in the wastewater.

The detection of Total Organic Carbon (TOC)

The TOC was detected by a TOC analyzer (TOC-L CPH CN20, SHIMADZU). The liming liquid waste was diluted 500 times and filtered through filter membrane (0.45 μm) before analysis.

The detection of buffer capacity

The buffer capacity of the liming liquid waste was detected by an automatic potentiometric titrator (ZDJ-4A, Rex Electric Chemical)..

Ts and analysis of chrome tanning wastewater

The TOC of chrome tanning wastewater was detected as mentioned above. The Ts of wet blue and the content of Cr_2O_3 in wastewater were also determined in accordance with Chinese standard QB/T 2713-2005 and GB 30486-2013.

The morphology and energy spectrum analysis of limed pelt

The limed pelt (1.5 cm X 1.5 cm) was dehydrated for four times by 100 mL ethanol overnight and drying 24 h at 40°C. The grain and vertical section of the dried samples were analyzed by super depth of field microscope (ZEISS Smart zoom 5, Germany) and Environment Scanning Electron Microscope (ZEISS EVO18, Germany).

The physical and mechanical properties of the finished leather

The tensile strength, bursting strength, tear strength, contents of Cr_2O_3 and other related properties of the finished leather were tested according to Chinese industrial standard QB/T 2710-2005, 2712-2005, 2711-2005, 3812.15-1999, et al.

RESULTS AND DISCUSSION

Analysis of liming wastewater recycling technology

In our recycling experiment, the weight of leather was about 10 ton every time. The dosage of rawhide, sulfide, water, lime and waste lime solution in the recycling process were shown in Tab. 3. The dosage of water, sulphide and lime were reduced by 80.8%, 33.3% and 23.4%, respectively, as shown in Tab.4. In the whole process, the wastewater discharge was zero. Compared with the normal craft, the pelt obtained by this recycling technology was evenly swelled. The pelts also showed a clean surface and an obvious weight gain.

Tab.3 Information about the dosage of hides, chemicals and water in process

No.	The number of hides	Weight (kg)	Water (t.)	Recycled lime liquid (t.)	Sulphide (kg)	Lime (kg)
0	300	11126	15	0	245.8	389.4
1	243	9458	4	7.5	160.6	283.5
2	324	9370	1	11	149.8	280.7
3	317	11080	2	10	177	331.8
4	311	10586	2.5	12	168.5	307.8

Note: 0 represent the normal liming unhairing craft. “1” represents the first time recycling craft. “2” represents the second time recycling. “3” represents the third time recycling. “4” represents the fourth time recycling.

Tab.4 The saving materials in recycling process

No.	Water-saving rate (%)	Decrease in sulphide (%)	Decrease in lime (%)
1	65.2	34.7	27.2
2	91.7	39.1	27.9
3	83.3	28.0	17.4
4	82.8	31.4	21.0
Average	80.8	33.3	23.4

The Na_2S content analysis of liming wastewater

The Na_2S content of liming wastewater in different recycling time was shown in Fig. 2. The sulfide content of liming wastewater in normal process was higher than 5 g/L. The Na_2S content of wastewater in different time of recycling process was in the range of 4~6 g/L.

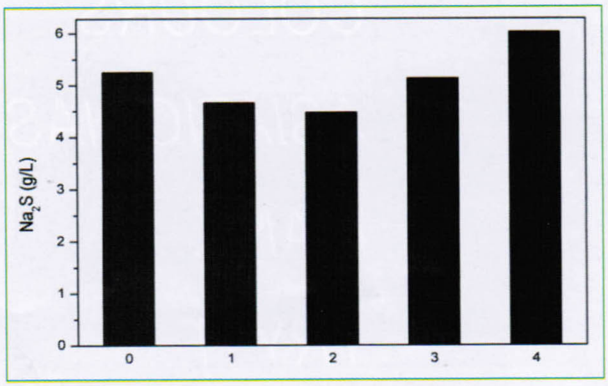

Fig.2 The Na_2S content of liming wastewater in different recycling time

The Ca content analysis of liming recycling wastewater

The variation of Ca content in different liming recycling wastewater was shown in Fig. 3(a). According to the results, the Ca content of wastewater in normal process was the highest. The content was about 2.25 g/L. In the following recycling technology, the Ca content in wastewater was in the range of 1.87~2.03 g/L. The rangeability is small. The variation of Ca content in different recycling process indicated that the recycling technology not only decreased the dosage of lime, but also decreased the residue content in the wastewater. The Ca content in the pelt was shown in Fig. 3(b). Compared with the conventional liming process, the Ca content of pelts in different recycling time decreased a little.

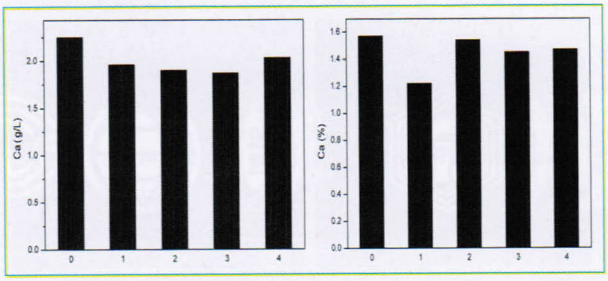

Fig.3 The content of Ca in liming waste liquor (a) and pelt (b)

The TOC analysis of liming wastewater

In order to analysis the content of organic material in the wastewater, the TOC was determined to characterize the pollution of organic material in the wastewater. The results were shown in Fig. 4. The TOC of wastewater from conventional method was 14750 mg/L. This was due to the dissolution of interfibrillar substance in liming process. In the liming process, the interfibrillar substance as well as part of collagen fiber would dissolve in the liming wastewater. Therefore, the content of organic material in waste water would increase. At the same time, the collagen fiber was dispersed sufficiently.

With the increase of recycling time, the TOC of wastewater increased due to the dissolution of organic material. After 4 times recycling, the TOC of waste water tended to be constant. Furthermore, the viscosity of liming wastewater did not tend to thicken. These might attribute to the hair persevering technology. In the hair filter process, part of the organic material would be absorbed into to the shedding hair and then filtered out the recycling system. So the recycling process could be carried out.

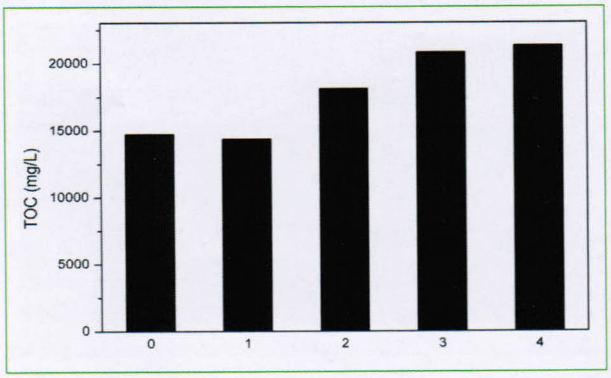

Fig.4 The TOC content of liming wastewater

The buffer ability of liming wastewater

The solubility of lime is limited, so the pH of saturated lime solution is in the range of 12~13. The mild liming condition makes the alkaline swelling slowly and uniformly. The operable and safety of lime swelling are attributed to the chemical property of lime. The potentiometric titration results of liming wastewater of different recycling time were shown in Fig. 5.

According to Fig. 5, the titration curves of $Ca(OH)_2$ solution had an obvious pH abrupt points. On contrary, no obvious abrupt point appeared in the titration curves of liming wastewater. So the liming wastewater displayed the outstanding buffering ability. This might be attributed to the existence of degradation products of interfibrillar substance in wastewater. Polysaccharose substance and protein showed a good buffering property, so the pH of the liming wastewater changed slowly when the acid was added. In the liming recycling system, the buffering properties of the liming wastewater would slow down the swelling rate of the raw hide. Furthermore, the occurrence of liming wrinkle in the liming pelt decreased. Then the obtained pelt became smoother and the yield of crust increased.

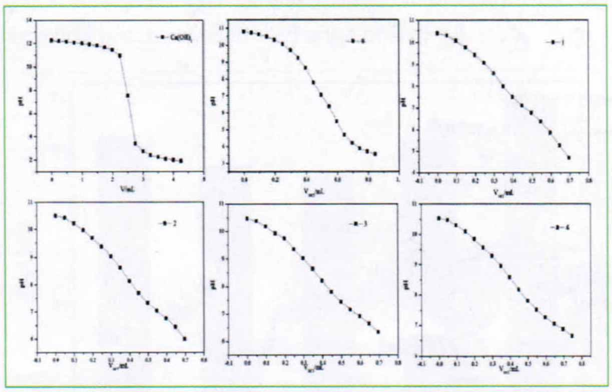

Fig.5 The potentiometric titration curve of liming wastewater at varied cycles

The fiber morphology of limed pelt

The morphology of grain of limed pelt was investigated by super depth of field microscope. The morphology of grain of limed pelt obtained by normal hair persevering process was shown in Fig. 6(a). The morphology of grain of limed pelt obtained by fourth times recycling process was shown in Fig. 6(b). The results indicated that the hair of two pelts was removed thoroughly. The hair pores were both clearly visible. This mean the hair root was also removed thoroughly. So the recycling technology of liming wastewater was safe and reliable. The SEM pictures of limed pelt from the original

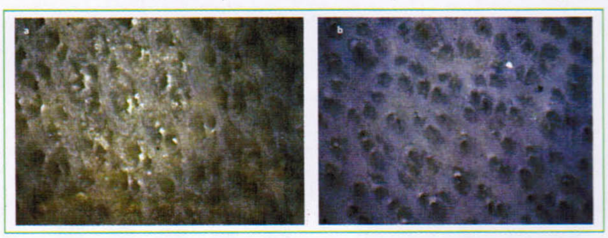

Fig.6 The grain of pelt from conventional process (a) and recycling process for 4 times (b)

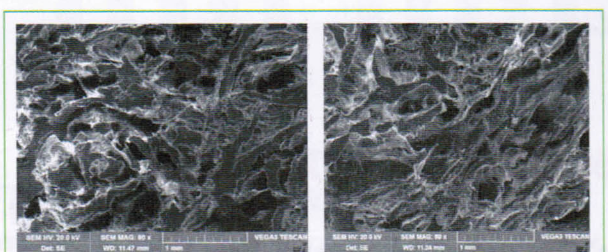

Fig.7 The SEM of cross section of pelt from conventional process (a) and recycling process for 4 times (b)

technology and the fourth times recycling process were shown in Fig. 7. According to Fig. 7, the dispersion of collagen fiber obtained by the fourth times recycling craft was similar with the normal craft.

The distribution test of Ca and S and SEM analysis

The EDS spectrum of the leather sample obtained by the conventional technology was shown in Fig. 8(a). The EDS spectrum of the sample obtained by the fourth time recycling process was shown in Fig. 8(b). It indicated that the Ca content (red) of grain layer and flesh side was higher than that of the middle layer. After 4 times recycling, the distribution of Ca was uniformly distributed in the whole vertical section of limed pelt. This might attribute to the existence of large amount of organic material in the recycling liming wastewater. The swelling process was assuasive. The liming process was more uniform. As a result, the penetration of Ca was better. The S (blue) distribution in the samples from the conventional technology and the fourth time recycling process were similar. This might attributed to the solubility of sulfide. The penetration property of sulfide was higher than lime.

The distribution of Ca in the pelt obtained by the normal craft and the fourth time recycling craft were shown in Fig. 9. The Ca distribution in the pelt of the grain layer, middle layer and flesh side were 37.29%, 6.14% and 27.97%, respectively. Compared with the normal craft, the Ca distribution of pelt obtained by recycling craft in the grain layer, middle layer and flesh side were 29.33%, 12.95% and 23.91%, respectively. The results were in accordance with Fig. 8. The distribution of Ca in different layer was more uniformly.

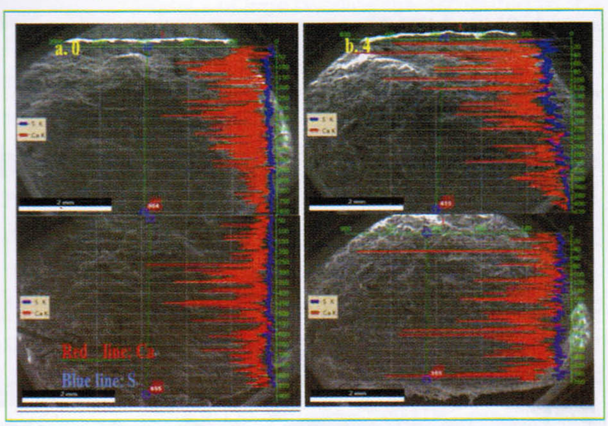

Fig.8 The EDX photo of cross section of pelt from conventional process (a) and recycling process for four times (b)

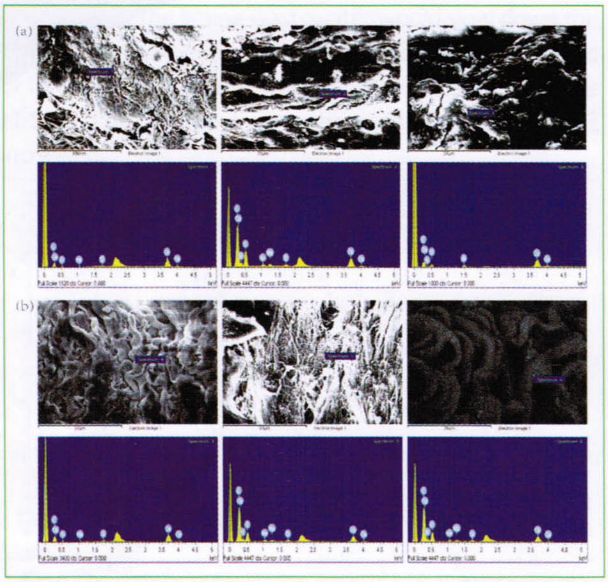

Fig. 9 The distribution of Ca in the pelt obtained by the normal craft (a) and the fourth times recycling craft (b) (three layers form grain to flesh side of limed hide)

Chrome tanning wastewater recycling process

The Ts of wet blue obtained by different recycling time was determined. The experimental results were given in Tab. 5 and Fig. 10. According to Tab. 5, the Ts of wet blue didn't change so much with the increase of recycling time. The Ts of wet blue was in the range of 101~107°C. The color of the grain surface of wet blue was consistent with the increase of recycling time as shown in Fig.10.

The variation rule of TOC and Cr_2O_3 content in the chrome tanning wastewater in different recycling time was shown in Tab. 6. According to Tab.6, the content of TOC and Cr_2O_3 in the recycling wastewater increased with the increase of the recycling time until the tenth time recycling. Then, the total organic compounds and remaining Cr component in the tanning wastewater reached equilibrium.

Tab.5 The variation of Ts of chromed leather with recycling times

Recycling time	0	1	2	5	10	15	25	30
Ts (°C)	103.2	100.8	101.1	103.7	104.8	104.5	106.5	102.5

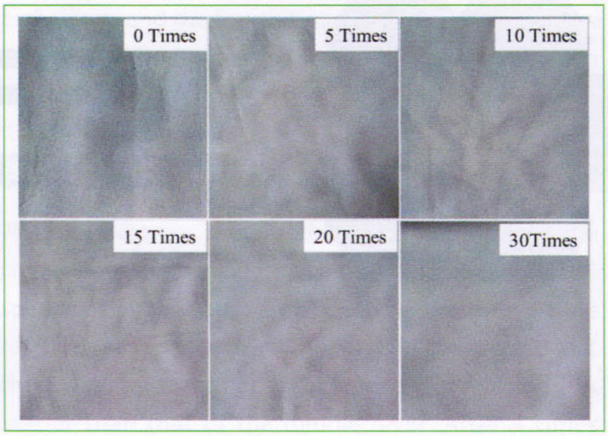

Fig.10 The relationship between the colour of chrome leather and recycling times

Tab. 6 The variation of the content of TOC and Cr_2O_3 with recycling times in chrome waste liquor

Recycling times	0	1	2	5	10	15	20	25	30
TOC(mg/L)	1750	1753	1767	2498	2823	2800	2872	2904	2787
Cr_2O_3 (g/L)	1.72	1.70	1.73	1.91	2.36	2.46	2.64	2.55	2.61

The physical mechanical properties test of finished leather

In order to assess the novel recycling technology, the physical mechanical properties of the finished leather samples obtained by conventional process and the recycling technology were compared. The results were shown in Tab. 7. The results indicated that the physical mechanical properties of finished leather were not influenced by the recycling technology. On the contrary, the tensile strength and tear strength of leather sample from the recycling technology were better than that of the sample obtained by the conventional technology. Furthermore, the yield of leather in the recycling technology was 95%, while the conventional technology is about 93%. This might attribute to the uniform swelling process of the collagen fiber in the recycling of liming wastewater, and the loss of the collagen content was less.

Tab.7 The physical and mechanical tests of the resultant leather

Samples No.	Tensile strength Crosswise (N/mm^2)	Tear strength Crosswise (N/mm)	Bursting strength (N/mm)	Cr_2O_3 (%)	Yield of leather (%)
0	10.58	54.35	22.38	4.82	93
4	10.86	59.60	21.83	4.98	95

CONCLUSION

A novel closed recycling of wastewater technology was applied and the zero discharge of liming and chrome tanning wastewater was realized. Compared with the normal process, the novel recycling technology could save more than 80.8% water, 33.3% of sulfide and 23.4% lime in liming process.

While in the chrome tanning wastewater recycling craft, 20% of the chrome tanning agent as well as 70% of salt were saved.

In the liming wastewater recycling process, the reduction of the dosage of lime and sulfide didn't affect the removing efficiency of hair. The distribution of lime in the limed pelt was more uniform. In the chrome tanning recycling process, the special auxiliary can prevent the deterioration of the chrome tanning wastewater.

The physical and mechanical properties of the leather sample obtained by recycling craft were similar with the sample obtained by the normal craft. Furthermore, the yield and the chrome content in the leather sample obtained by recycling craft are higher than the leather sample obtained by the conventional process.

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REFERENCE

1. Thanikaivelan P, Rao J R, Nair B U, et al. Recent trends in leather making: processes, problems, and pathways[J]. Critical Reviews in Environmental Science and Technology, 2005, 35(1): 37-79.

2. Hu J, Xiao Z, Zhou R, et al. Ecological utilization of leather tannery waste with circular economy model[J]. Journal of Cleaner Production, 2011, 19(2): 221-228.

3. Saravanabhavan S, Thanikaivelan P, Rao J R, et al. Natural leathers from natural materials: progressing toward a new arena in leather processing[J]. Environmental science & technology, 2004, 38(3): 871-879.

4. Rao J R, Chandrababu N K, Muralidharan C, et al. Recouping the wastewater: a way forward for cleaner leather processing[J]. Journal of Cleaner Production, 2003, 11(5): 591-599.

5. Zhang Z D, Yang Y L, Xu F, et al. Recycling of wastewater from raw hide to wet blues in leather manufacture[C]. XXX Congress of the International Union of Leather Technologists & Chemists Societies, Proceedings. 2009: 119-128.

6. Zhang Z D. Leather production process for recycling waste water from soaking to dyeing[P]. CN10253405, 2011-01-05.

7. Zhang Z D. Circular project for realizing near zero discharge of tanning waste water[P]. CN:104843807, 2014-02-15.

8. Balasubramanian S, Pugalenthi V. A comparative study of the determination of sulphide in tannery waste water by ion selective electrode (ISE) and iodimetry[J]. Water Research, 2000, 34(17): 4201-4206.

9. Barrows H L, Simpson E C. An EDTA method for the direct routine determination of calcium and magnesium in soils and plant tissue[J]. Soil Science Society of America Journal, 1962, 26(5): 443-445.