Minimization of the Environmental Impact in the Chrome Tanning Process by a Closed-Loop Recycling Technology

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Abstract. It is acknowledged that conventional chrome tanning in leather processing discharges significant amounts of chromium, dissolved solids and chlorides. The recycling technology is one of the effective solutions to reduce the environmental impact of chrome tanning waste water at source. In this work, a novel closed recycling technology of chrome tanning wastewater was applied in the tanning process of the goat skins at a pilot scale level. The properties of chrome tanning liquors obtained by the recycling technology and the resultant crust were analysed. The results show that this close recycling process works well. The contents of Cr_2O_3, total organic carbon, and ammonia nitrogen in the waste water tend to accumulate with the increase of recycling times, and finally reach a balance after 5 times of recycling. The obtained leather sample is full, soft and having a shrinkage temperature comparable to that of conventional chrome tanned leather. SEM images indicate that the resulting leather samples by this recycling technology show fine and clean grain and well-dispersed fibrils. Compared with conventional chrome tanning technology, water, salt and chrome tanning agent are saved in this process. The cleaner production technology exhibits promising application prospect for its economic and environmental benefits.

1 Introduction

Tanning operation in leather making is the most important process which convents the perishable hides and skins into useful and durable leathers [1-3]. In this step, many kinds of tanning agents, such as metal salts, aldehyde derivatives, syntans and vegetable tannins, are used single or combinedly to produce leather with different properties and styles. Nontheless, not only the handing qualities but also the hydro-thermal stabilities of leathers tanned by other tanning agents cannot parallel to these of chrome tanned leather [4-5]. Up to now, 90% of the leathers were produced by chrome tanning method [6], which makes them more versatile. Hence, chrome tanning method will still keep its dominant position for a long time and not be replaced entirely in the future.

However, the conventional chrome tanning method is facing the pollution pressure of discharged chrome salt, which potentially negative effects on the environment and human health. Generally, less than 70% chrome tanning agent was fixed on the leather, resulting in the concentration of chrome in spent water is high to 2500-3000mg/L [7-8]. On the other hand, at least 6% of sodium chloride is used in the pickling process to protect the collagen matrix from acid swelling [4], and all of the chloride would be discharged in effluent at the end of tanning. It was reported that approximate 27.5 billion liters of chrome tanning wastewater containing 24 kilotons of chrome salt, 340 kilotons of chloride and 270 kilotons of sulphate are drained from tanneries in worldwide every year [6]. In order to protect our environment, strict statutory limits have been set for chrome, chloride as well as other contaminants in China. According to the Chinese "Discharge Standard of Water Pollutants for Leather and Fur Making Industry", the limits of total chrome discharged into sewage and chloride discharged into water bodies are 1.5mg/L and 3000mg/L, respectively. Therefore, developing much cleaner chrome tanning processing has drawn great attention of global leather technologists.

In order to resolve the chloride pollution, the salt-free or low-salt pickling technologies were developed, in which non-swelling acids were used to replaced formic and sulphuric acid. The non-swelling acids are mainly aromatic sulfonic acids, and some aromatic sulfonic acids such as phenol sulfonic [9], phenol sulfone sulfonic [4], naphthalene sulfonic [10] and naphthol sulfonic acid [4] were applied in the pickling processes to reduce the dosage of chloride. Although a large proportion (at least 80%) of sodium chloride was reduced in these researches, the widely commercial applications of these technologies are limited by the dissatisfactory qualities of result leather.

In the case of the resolution of chrome pollution, the high-exhaustion chrome tanning methods and chrome recovery technologies from wastewater for reuse were reported. The application of varied high-exhaustion auxiliaries such as small molecules glyoxylic acid and aliphatic dicarboxylates [11], low molecular weight acrylic copolymers [12], and hydroxyl-terminated dendrimer [13] is a convenient method to increase the chrome uptakes. Besides of these, new nanocomposites with multiple carboxyl groups were prepared for enhancing the uptake of chrome salt [2, 7]. However, the concentrations of chrome in the spent float were much higher than the limit of 1.5mg/L [2]. In view of this, recovery of chrome from tanning effluents and its reutilization technologies were drawn much more attentions. Some researches on recovering and concentrating chromium salts from exhausted baths through membrane filtration (ultrafiltration and nanofiltration) on laboratory scale were carried out [14-15]. The properties of leathers tanned by recycled chrome were similar to these of leather tanned by traditional methods. Whereas, the high cost of membranes makes this technology difficult to be a popular option.

All of the researches above mainly focused on the eliminating of chemicals discharge, while the reduction of water usage in tanning industry has also to be considered. Hence, the recycling strategy of wastewater is considered as an alternative approach to both increase the utilization coefficients of leather chemicals and save a large quantity of water. In present recycling systems, chrome salts are mainly used indirectly, namely the chrome was precipitated firstly and then acidified for using in pickling, tanning, or re-tanning process [16-18]. However, the water bath quality would deteriorate after several recycles and pigmentation would appear on the grain layer, which has negative effect on the appearances of finished leather [16, 19].

In recent years, a closed cycle technology of chrome tanning wastewater developed by BIOSK chemical company has been gradually applied in some cattle tanneries in China. In present work, this novel closed recycling technology was applied in the tanning process of the goat skins at a pilot scale level, and the properties of chrome tanning liquors obtained by the recycling technology as well as the qualities of crust leather were analysed.

2 Experiments

2.1 Materials

The goat skins were supplied by a local tannery in China (Shandong Juncheng Ltd.), and about 105 pieces (150Kg, calculated according to the weight of limed pelts) of skins were used in single recycle. The fungicide DK and basifying agent BE were supplied by BIOSK CO., and other chemicals used in the experiments were industrial grade.

2.2 The recycling formulation of chrome tanning wastewater

The tanning process (the 6th recycle) using chrome tanning wastewater was shown in Table 1. The chrome-contained wastewater was collected at the end of tanning process, and about 90% of chrome tanning effluent was collected due to the limitation of practical conditions. One third of the collected chrome baths was used in the next pickling process and the rest was added into drum at basifying step.

Table 1. The pickling and tanning process of the 6th recycle by using spent liquors.

Process	Chemical	Dosage %	Temp. (°C)	Time (min)	Remark
Pickling	Residual water	20	18		
	salt	4.0			
	5063	0.2		10	Baume degree 5.8
	Formic acid (85%)	0.5		10	1:10 diluting
	Sulfuric acid (96%)	1.0		20	1:10 diluting, ×2
	Chrome tanning effluent (20°C) / Pickling auxiliary D	60/0.15		60	×3, pH 2.6, full penetration
Tanning	Sodium formate	0.5		30	
	Chrome powder	3.0		30	
	Chrome powder	3.0		60	full penetration
	Chrome powder	0.2		30	
	Basifying agent BE	0.25		60	pH ≥ 3.1
	Basifying agent BE	0.25		90	pH 3.4
	Sodium bicarbonate	0.2		20	pH ≥ 3.5
	Sodium bicarbonate	0.1		10	pH ≥ 3.6
	Chrome tanning effluent (70°C)	120		10	39 °C
	Mildew preventive DK	0.15			
	Pickling auxiliary D	0.2		20	overnight, pH ≥ 3.6, Baume degree 8.4

2.3 The chemical analysis of spent tanning wastewater

About 500 mL wastewater of each recycle was filtered twice by double layers of gauze for analysing. The pH values, Baume degrees, chrome contents, and ammonia concentrations of tanning wastewater of 9 cycles were investigated. Additionally, the waste liquors were diluted 500 times and filtered through filter membrane (0.45 μm) for the total organic carbon (TOC) (TOC-L CPH CN20, SHIMADZU) values analysis.

2.4 The characterization of the wet-blue samples

The contents of Cr_2O_3 and shrinking temperatures of wet blues were determined accordance to Chinese standard QB/T 2720-2005 and QB/T 2713-2005, respectively. The morphologies of the grain layers and cross sections of the wet blues were investigated by an Environment Scanning Electron Microscope (ZEISS EVO18, Germany). The L*, a*, b*, C*, and DE* coordinates of the wet-blue samples were measured using a X-rite 8200 spectrophotometer, and the viewing conditions used were illuminant D65, 10° standard observer.

2.5 The physical and mechanical properties crust leathers

The tensile strength, bursting strength, tear strength, and other related properties of the crust leathers were tested due to Chinese industrial standard QB/T 2710-2005, 2712-2005, 2711-2005, et al.

3 Results and discussion

3.1 The chemical analysis of spent tanning wastewater

The pH values and Baume degrees of the spent water from zero recycle (control) to the 9th recycle were shown in Fig. 1. It was observed that the pH values decreased slightly as increase of recycle times, and it was stable at around pH 3.2. On the other hand, the Baume degrees of the wastewater increased gradually with the recycle times as the accumulation of the salts. The pH and Baume degree properties of wastewater make it be suitable for reusing in pickling and tanning processes. Thus we further investigated the chrome concentration, TOC and ammonia nitrogen values in the wastewater of the each recycle.

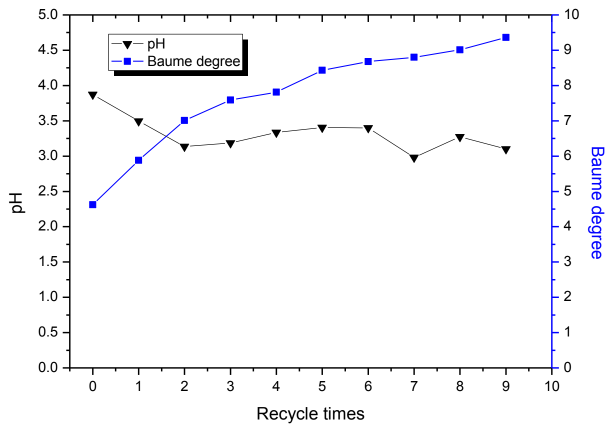

Fig. 1. The pH and Baume degree of wastewater from zero to the 9th recycle.

The Cr_2O_3 contents, TOC and ammonia nitrogen values of the wastewater from zero to 9th recycle were shown in Fig. 2. The Cr_2O_3 concentration increased greatly at the initial several recycles, it accumulated from about 2000mg/L to 4000mg/L. After 9 recycle times, the Cr_2O_3 concentration was stable at around 5000mg/L. It was because the chrome tanning agent could not be adsorbed absolutely by the skins and consequently the residual chromium accumulated in the wastewater. According to the chrome salt contents in the last used water, the dosage of chrome tanning agent was constantly adjusted in the next recycle. Therefore, the quality of the leathers would be guaranteed, while the chromium concentration in the effluents would be at balance. The changes of TOC and ammonia nitrogen values in the wastewaters were similar to that of chrome salts. The TOC values of the wastewater were stable at about 3000mg/L, and the ammonia nitrogen values were balance at around 230mg/L. In the pickling and tanning processes, the TOC and ammonia nitrogen might result from the slight dissolution of some protein of the goat skin, which hardly effected on the penetration and combination of chromium.

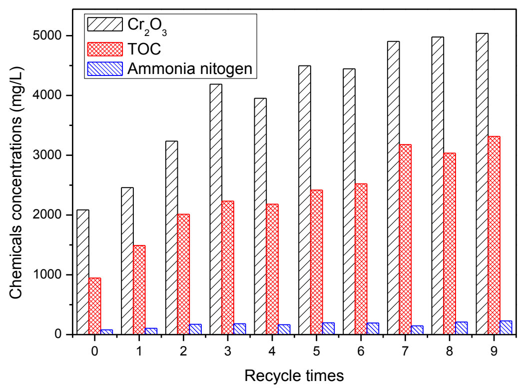

Fig. 2 The contents of Cr_2O_3, TOC and ammonia nitrogen in each recycle spent liquor

3.2 The characterization of the wet-blue samples

Some properties of the wet-blue sample were analysed to research the effect of the usage of wastewater on the qualities of the leather. Firstly, the Cr_2O_3 contents in wet-blue samples as well as their shrinking temperatures (Ts) were measured, and the results were shown in Fig. 3. Totally, the Cr_2O_3 contents in the leather samples produced by recycle processes varied from 3.1% to 3.7%, which were close to that of the control (3.8%). All of the shrinking temperatures of leathers manufactured by this closed recycle process were higher than 104°C. These results proved that the closed recycle process of tanning wastewater was stable for leather making.

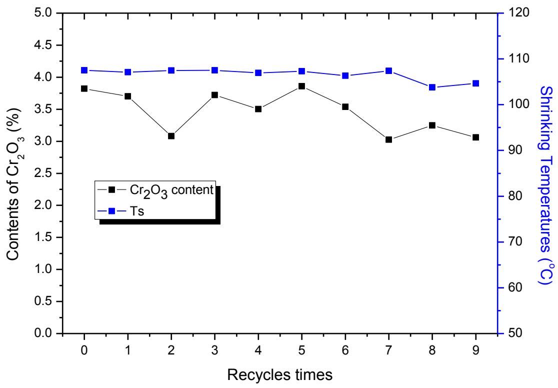

Fig. 3 The Cr_2O_3 contents in wet-blue samples produced by recycle process and the shrinking temperatures of leather samples

Besides of these, the appearances of the wet blue grain layers and the dispersion conditions of collagen fibers on cross sections of samples were observed by SEM, and the images of the wet blues produced in the 0, 5th and 9th recycles were shown in Fig. 4. Compared with the grain layer of the control (Fig. 4a-1), the hair pores on the wet-blue samples produced in the 5th and 9th recycle were also clearly, shown in Fig. 4b-1 and c-1 respectively. Meanwhile, their collagen fibers were opening well and dispersed evenly (shown as Fig.4 b-2 and c-2), which were very similar to that of the control which was shown in Fig. 4a-2. Basing on the SEM images, it can conclude that the close recycle process of tanning wastewater is feasible.

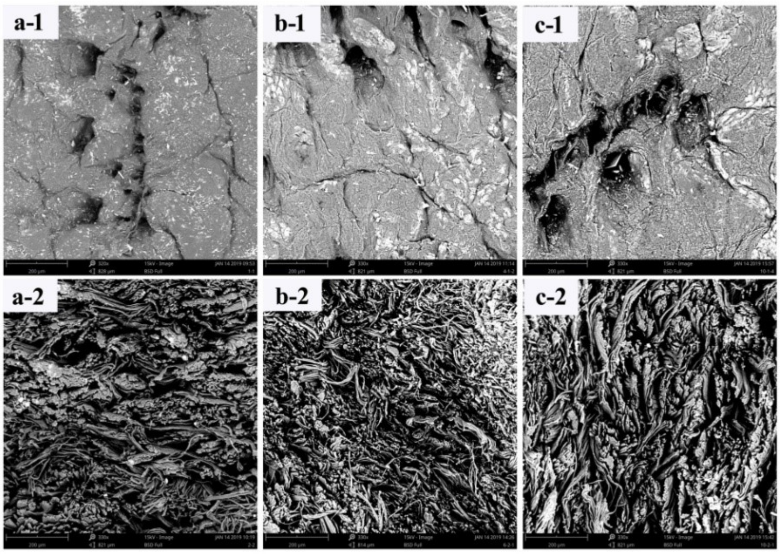

Fig. 4 The grain layer and cross-section SEM images of wet-blue produced in: (a) control, (b) the 5th recycle and (c) the 9th recycle

Table 2. The color coordinates of leather samples.

Samples	*L**	*a**	*b**	*DE**	$\overline{DE}^a$
0	59.00	-6.50	-6.50	42.02	41.89
	58.50	-6.10	-6.30	42.42	
	59.90	-6.70	-6.90	41.24	
1	58.50	-6.40	-7.10	42.59	41.99
	59.50	-6.20	-7.00	41.57	
	59.20	-6.10	-6.80	41.81	
2	58.30	-7.00	-8.00	43.03	42.86
	58.00	-6.90	-7.70	43.25	
	58.90	-6.70	-7.40	42.29	
3	59.80	-6.10	-6.10	41.12	41.56
	59.00	-5.40	-6.30	41.83	
	59.20	-5.80	-6.60	41.74	
4	60.40	-6.10	-7.20	40.71	41.02
	59.70	-6.20	-6.70	41.32	
	60.00	-6.20	-6.70	41.03	
5	60.20	-6.30	-7.50	40.99	41.10
	60.10	-6.40	-7.10	41.03	
	59.80	-6.10	-7.20	41.29	
6	59.90	-6.30	-7.10	41.21	41.10
	60.20	-6.20	-7.20	40.92	
	59.90	-6.10	-7.00	41.16	
7	61.90	-6.90	-7.70	39.48	40.34
	59.90	-6.30	-7.00	41.19	
	60.70	-6.20	-6.70	40.35	
8	61.40	-6.60	-7.80	39.93	40.33
	61.30	-6.50	-7.90	40.03	
	60.30	-6.40	-8.10	41.02	
9	63.00	-6.50	-8.20	38.45	38.84
	61.90	-6.40	-7.90	39.43	
	62.80	-6.50	-8.20	38.64	

a: the average of *DE**

Generally, the color of the wet-blue is a key quality standard in leather making. Hence, the colors of the wet blue samples produced by traditional tanning process and the closed recycle process of wastewater were characterized by color coordinates, namely L*, a*, b*, and DE* values. According to the definition of color coordinates, the *L** value reflects the brightness of the sample, while the negative b* value indicates that the sample is blue. Principally, the *L** value and the absolute of *b** increased slightly with the increase of recycle time, as listed in table 2. It manifests that the blue appearance qualities of the wet-blues produced by the closed recycle process of wastewater had no obvious batch differences. Except the sample produced in the 9th recycle, the average of DE* value was close to each other, which indicated that the color differences of these samples were hard to find by naked eyes. The SEM and color coordinates analysis above verified that the closed recycle process of tanning wastewater can run stably in pilot scale.

3.3 The characterization of the crust leather samples

Furthermore, the physical and mechanical properties of the crust leathers were measured to evaluate the effect of the closed recycle process of tanning wastewater on the performances of the crust leather, which results were listed in table 3. The tensile strength of the crust leathers were approximate to that of the leather produced by traditional chrome tanning method. However, compared with the control, the variation of the tearing strength and bursting strength of the samples was much larger. It was probably because these mechanical properties were much closer to the fiber structure properties of individual goat skin.

Table 3. The physical and mechanical properties of the crust leathers.

Samples	Tensile strength (N/mm^2)	Bursting strength (N/mm)	Tear strength (N/mm)
0	23.75	399.02	39.40
1	24.11	392.15	38.85
2	23.01	391.40	38.28
3	23.22	366.88	29.35
4	22.46	343.41	28.43
5	20.48	310.94	30.96
6	22.85	308.04	45.55
7	21.84	379.75	29.14
8	19.68	321.27	36.82
9	21.05	319.97	45.32

3.4 Economic analysis

The advantages of the closed recycle process of tanning wastewater were saving water and chemicals dosage, meanwhile the discharge of wastewater was almost zero. The approximate dosages of main chemicals and fresh water in different tanning processes and their discharges of effluents were listed in table 4. In our experiments, about 1500kg goat skins were produced and about 270000Kg fresh water would be used in traditional tanning process. However, totally 51300Kg fresh water was used when the same amount of goat skins were produced by the closed recycle process of tanning wastewater. Above 4 fifths fresh water was saved. Moreover, the discharge of wastewater in the closed recycle process was only 1% of the traditional method, which was attributed to the technological limit. The closed recycle process can be considered as a zero discharge technology, which is very helpful to the sustainable development of the leather making industry and the protection of the environment. Additionally, the main chemicals such as sodium chloride and chrome tanning agent used in the tanning process of leather were saved greatly. Both the produce cost and the charge for wastewater treatment were decreased highly. Therefore, the closed-loop recycling technology of chrome tanning wastewater minimized the environmental impact in the chrome tanning process.

Table 4. The approximate dosages of main chemicals and fresh water in different tanning processes and their discharges of effluents.

Tanning Method	Weight of limed pelt (kg)	Water (Kg)	Sodium chloride (Kg)	Chrome powder (Kg)	Effluents (Kg)
Traditional	1500	270000	90	120	270000
Closed Recycle	1500	51300	30	90	2700

4 Conclusions

A closed-loop recycling technology of tanning wastewater was applied in the tanning process of the goat skins at a pilot scale level. It was found that the properties of the tanning wastewater were suitable for the reused in the pickling and tanning processes. The high contents of chrome salt, chloride sodium could save the dosage of relevant chemicals, while the TOC and ammonia nitrogen values of the wastewater had little influence on the fixation of chrome according to the close shrinking temperatures of wet blue sampled produced in each recycle. The qualities of the wet blue were stable, which was estimated from the SEM and color coordinates results. Importantly, more than 4 fifths fresh water was saved and the discharge of wastewater in the closed-loop recycling process was only 1% of the traditional method in 10 times of tanning producing. It can be predicted that the water saving rate will be increased greatly with the recycling times, while the discharge of effluent will be decreased tremendously. Thus, this technology can minimize the environmental impact in the chrome tanning process and is deserved for researching deeply for further employing in large-scale tanning production.

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