Recycling of Wastewater from Raw Hide to Wet Blues in Leather Manufacture

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Abstract: Waste water generated from soaking to chrome tanning of leather manufacturing processes contains complicated components, which would cause serious impact on environment. Waste water recycling can effectively reduce the environmental problems produced by the tannery. In general condition, defects inevitablely existe when waste water is directly reused in the recycle. For example, soaking and deliming waste water can cause 'rough' grain. When waste limed water was directly applied, pelt' s swelling inhibition phenomenon would result in decrease of rendment of wet blue, and waste chrome water would make crust rougher and its color darker. The waste water direct application would reduce rendment of wet blue, of which waste limed water is the most serious. This paper has focused on the negative impact resulted by waste water directly applied ,and a series of solutions are provided as to achieve that rendment of wet blue increased 0.5-0.8%, shrinkage temperature raised 1.0-1.5℃ (compared to conventional process) ,with convenient handling and low investment. Meanwhile chemical cost can be saved by 7-12%, and effluent discharge can be reduced by 60-70%. Then the waste water recycling in soaking, liming, deliming-bating and pickling-chrome tanning can be achieved comprehensively.
Key words: collection treatment; separate discharge; recycling

1 Introduction:

The leather industry is of high water consumption and waste discharge. In order to meet the environment requirement, the pollution problems must be solved urgently. Pressure from environment protection has prompted tanneries to seek ways to reduce consumption of water and chemicals .It is necessary to reuse the waste water as much as possible, which can be considered as one of the best way at present.

The processes from raw hides and skins to wet-blues produce more than 75% pollutant effluents and contain large amount of toxic and harmful components, such as lime, protein, salts, grease, ammonia nitrogen compound, sulfide, chrome salt, hairs, raw hide pieces, soil and ect. While COD, BOD, sulfide, ammonia nitrogen compound, suspended matter are of a high content. For its various pollutants, complicated composition and odor, the tannery waste water is comparatively hard to deal with.

In today's market, environment protection devices and technology have made great progress. (See the table as followed). But they usually have complicated handling and high-level cost devices, which can not meet the requirement of pollution control in practicality.

Tab. 1 Some technologies for treating tannery wastewater

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Technology	Advantages	Defects
Traditional activate sludge	The removal rate for BOD_5 is more than 90%，COD 60%～80%，chrominance 50%～90%，S 85%～98%.	Stringent for the quality of the wastewater; not fit to the loading impact; cost high on power and capital construction; occupying large area of land that common tannery can not bear; unsatisfying effect on ammoniate and nitrogen compound.
Biological contact oxidation	The removal rate for organic substances and BOD_5 is up to 95%, COD 92%，S 98%.	Easy to plug; difficult to amend and the whole system must be stopped when problems happen.
Oxidation ditch	The removal rate for BOD_5 of more than 95%，S 99％～100%，SS 75%.	Unstable treatment effect; less effective for the northern area with lower temperature than the southern especially in winter.
Biofilter with double layer	Removal rate for SS is 95%，BOD_5 98%，COD 90%，more than 96% of Cr(Ⅲ), S 96%.	Suitable regurgitant ratio and filtered carrier must be needed with high operating cost.
SBR	Removal rate for COD, S^{2-}, SS, Cr respectively 93.3%、99.0%、90.3%、99.4%	Comparatively high cost for operating; small scale with low efficiency; difficult to amend.

In order to deal with pollution problems of tannery wastes in a perfect way, we have concentrated on the process innovation of clean production. Through two years' experiments, a reasonable clean process system was designed to achieve the effluent recycling from raw hides and skins to wet-blues. While the process is convenient, devices are easy to make, such as waste water collecting-reacting pool, filter, channels (pipes) connected with drums. Based on the feature of each waste water and negative impact of direct recycling, a series of antibody control products---ELIPO was designed to treat various waste water to meet the process requirement ,which are of simple and convenient usage that only have to react with waste water for half to one hour. ELIPO of 0.2% is applied in soaking, deliming and bating waste water, while 0.5% applied in waste limed water. Application in the experiment is as followed. Parts of factors are selected to discuss. In the experimental process, all are free of washing, except before and after pre-soaking, deliming and bating are in one bath with a small float, which reduces effluent by 40% more or less.

2 Experimental

2.1 Material and equipment

Cattle hides, high-precision fleshing machine, stainless automatic control drum, digital precision shrinkage temperature apparatus, thickness-measuring calipers, digital infrared thermometer, precision electronic balance, cattle hides mesurement frame, knifives, scissors, puncher, steel tape, high-accuracy splitting machine. The raw hide with high quality and the ELIPO series (pollution control agent) was from Shangqiu Dongyang Leather Chemical Co. Ltd., Shangqiu, P. R. China. While other reagents were industry grade.

2.2 Preparation of the leather samples

For washing waste water before and after pre-soaking contains large amount of dung, blood and microorganism and enzyme, ect. which easily results in the damage of the grain. To ensure the quality of

final leather, the experiments are carried out in the processes of liming, deliming-bating and pickling-tanning. At first, this experiment concentrates on one stage to carry out directly recycling (other stages are conducted with conventional process).Then the experiment was carried out with waste water directly reused in every stage. In the end, waste water treated with antibody control agents was respectively applied in the corresponding stages.

Experiments above mentioned show the effect of each method on yield rate, shinkage temperature and grain quality of wet blue. This paper chooses five times recycling of waste water to explain. To insure the accuracy and avoid interruption of mechanical or some other reasons, the comparable experiments are carried out in two drums of the same type simultaneously.

Quality cattle hide was selected and washed for half an hour. Then it was hung on a special shelf for leather measurement and cut symmetrically along the spine line. The symmetric points of the two sides which were not easy to deform for limed pelt were punched and then marked to measure. After kept still for half an hour, the sampled leather was surveyed for their length, width and weight which contributed to the rendment of wet blue. The next is to cut the hide into two parts equally along the backbone line and record the hide weight of the two parts as cardinal number for charging material and calculating the weight increase rate of soaking and liming stages, while in deliming, bating, pickling and tanning stages, the pelt weight should be recorded as the cardinal number. One is conducted with conventional process, the other applied with waste water which was treated for 0.5-1hour by the ELIPO products and used for recycling.

2.2.1 Recycling of soaking waste water

The wastewater of the main soaking was treated by the ELIPO and then applied to the soaking process. The pre-soaking and the main soaking processes for the conventional process and the wastewater recycling process were given in Tab. 2. The water washing from the soaking was added to the processes using wastewater when there was no enough water.

Experimental process

Tab. 2 The processes of main soaking

Process	Material	Temperature/℃	Time/min
Pre-soaking	300% water		10min
	300% water	20℃	
	0.2%bactericide		15min
	0.3% degreasing agent		
	0.3% soda		
	0.2% soaking agent		Run 20min and stop for 40min with 4 times
	300% water		10min
Main soaking	300% water [a)]	20℃	
	300% treated wastewater [b)]	20℃	
	0.2% bactericide		15min
	0.3% degreasing agent		
	0.4% soda		
	0.4% soaking agent		Run 20min and stop for 40min
	0.2% Na_2S		Run 20min and stop for 40min with 2 times, then run 3min and stop for 57min till next day

Note: "[a)]" means the adding material and amount for conventional process;

"[b)]" means the adding material and amount for wastewater recycling process.

Experimental results：

Left side is applied with main soaking waste water. Right side is conducted with conventional process.

▲ Indicates waste water is used.

Tab. 3

Recycle (times)		Rendment of wet-blue（%）	Shrinkage temperature（℃）	Grain appearance
1	left▲	85.23	100.28	No visible difference, both grains have well appearance
	right	85.60	100.45	
	difference	0.37	0.17	
2	left	84.58	101.20	No visible difference, both grains have well appearance
	right▲	84.00	101.20	
	difference	0.58	0.00	
3	left▲	86.35	99.9	Conventional process brings better appearance, and a little damage on the other
	right	86.60	100.45	
	difference	0.25	0.55	
4	left	85.25	102.10	Conventional process brings better appearance, and rough grain on the other
	right▲	84.85	101.80	
	left	0.40	0.30	
5	right▲	83.06	98.95	Conventional process brings better appearance, and rough grain on the other
	right	83.50	99.20	
	difference	0.44	0.25	
Average	lower	0.41	0.25	

2.2.2 Recycling of waste limed water

At the beginning of saving hair method, an additional filter was used to filter the entire hair without effecting on the liming process. The processes of saving hair method for the conventional process and wastewater recycling process were as shown in Tab. 4.

Experimental process

Tab. 4 The liming process with saving hair method

Conventional process	Wastewater recycling process
100% water at room temperature, 0.2% degreasing agent and 0.4% NaHS, run 30min then stop for 30min; 1.2% lime, run 50min; 0.6%Na_2S, 0.4% NaHS and 1.0% liming agent, run 30min and stop for 30min with 2 times; 0.6% Na_2S and 0.2% liming enzyme, run 30min stop for 30min with 2 times; 0.2% Na_2S, 0.5% liming agent, 1.8% lime run 30min and stop for 30min; 110% water at room temperature, run 30min and stop for 30min; then run 5min and stop for 25min with 2 times, next run 5min and stop for 90min till next day	70% water at room temperature, 0.2% degreasing agent and 0.4% NaHS, run 30min then stop for 30min; adding 1.0% lime, run 50min; 20% liming wastewater treated by ELIPO at room temperature, 0.6%Na_2S, 0.4% NaHS, 1.0% liming agent, run 30min and stop for 30min with 2 times 40% liming wastewater treated by ELIPO at room temperature, 60min for filtering hair; 20% liming wastewater treated by ELIPO at room temperature, 0.4%Na_2S, 0.15% liming enzyme run 30min and stop for 30min with 2 times ; 60% liming wastewater treated by ELIPO at room temperature, 1.5% lime, run 30min and stop for 30min, then run 5min and stop for 25min with 2 times, next run 5min and stop for 90min till next day

Experimental results

Left side is applied with waste limed water. Right side is conducted with conventional process.

▲ Indicates waste water is used.

. Tab. 5

Recycle (times)		Pelt weight gain rate(%)	Rendment of Wet-blue（%）	Wet-blue shrinkage temperature（℃）
1	left▲	19.36	85.28	102.85
	right	20.74	86.02	102.6
	difference	1.38	0.74	0.25
2	left	21.13	86.63	103.20
	right▲	19.74	85.60	102.80
	difference	1.39	1.03	0.40
3	left▲	19.03	84.10	99.20
	right	20.62	85.48	98.70
	difference	1.59	1.38	0.50
4	left	24.35	85.68	100.00
	right▲	23.51	84.43	100.00
	difference	0.84	1.25	0.00
5	left▲	21.57	82.44	103.15
	right	23.10	83.35	102.80
	difference	1.53	0.91	0.35
Average		lower1.35	lower1.06	increase0.14

2.2.3 Recycling of wastewater from deliming and bating

The deliming and bating for the conventional process and the wastewater recycling process were shown in Tab. 6.

Experiment progress

Tab. 6 The process of deliming and bating

Process	Material	Temperature/℃	Time/min
Deliming	100% water [a)]	room temperature	
	100% wastewater treated by ELIPO [b)]	room temperature	
	1.5% $(NH_4)_2SO_4$		
	0.2% degreasing agent		
	0.8%deliming agent		40min
Bating	0.4% enzyme for bating		30min

Note: "[a)]" means the adding material and amount for conventional process;

"[b)]" means the adding material and amount for wastewater recycling technology.

Experimental results

Left side is applied with waste water ,right side is conducted with conventional process.

▲ Indicates waste water is used.

Tab. 7

Recycle (times)		Yield rate of wet-blue（%）	Shrinkage temperature（℃）	Grain appearance
1	left▲	84.00	101.00	No visible difference, well appearance on both grain
	right	84.79	102.05	
	difference	0.79	1.05	
2	left	85.20	102.40	No visible difference, well appearance on both grain
	right▲	86.00	100.90	
	difference	0.80	1.50	
3	left▲	83.43	102.65	No visible difference, well appearance on both grain
	right	84.12	103.65	
	difference	0.69	1.00	
4	left	85.20	102.85	Conventional process brings better appearance, rough grain on the other
	right▲	84.00	101.60	
	difference	1.20	1.25	
5	left▲	83.50	99.30	Conventional process brings better appearance, rough grain on the other
	right	84.66	100.65	
	difference	1.16	1.35	
Average	lower	0.93	1.23	

2.2.4 Recycling of chrome tanning

Waste chrome water are applied in the pickling and post-tanning, waste water should be treated with corresponding ELIPO. After being filtered, the treated wastewater was used for the next pickling and the later stage of tanning.

For pickling:70% of waste chrome tanning water was adjusted to PH value of 1.5 more or less with sulfate. Then apply it in the pickling stage to be recycled .

For post tanning: 50% of waste chrome tanning water was adjusted to PH value of 3.0 more or less with sulfate. Then apply it in the post-tanning stage to be recycled.

The chrome tanning wastewater used for the conventional process and the wastewater recycling process was shown in Tab. 8.

Experiment progress

Tab. 8 The process of chrome tanning

Process	Material	Temperature/℃	Time/min
Pickling	70% water [a)]	room temperature	
	30% water [b)]	room temperature	
	0.15% fungicide		
	8% salt [a)]; 5.5% salt [b)]		10min
	1.0% HCOOH		20min
	adding 1.2% H_2SO_4 in all		Run 10min for 3 times, then run 90min [a)]
	with three times		Run 10min for 3 times [b)]
	40% treated wastewater [b)]		90min [b)]
	0.5% cation oil		30min
Tanning	3% chrome powder		30min
	4% chrome powder [a)]		60min
	3% chrome powder [b)]		60min
	0.5% sodium formate		30min
	0.4% magnesia		240min
	50% water [a)]	40℃	180min
	50% treated wastewater [b)]	40℃	180min

Note: "[a)]" means the adding material and amount for conventional process;

"[b)]" means the adding material and amount for wastewater recycling technology.

Experimental results:

Left side is applied with waste tanning water. The right side is conducted with conventional process.

▲ Indicates waste water is used.

Tab. 9

Recycle (times)		Rendment of wet blue（%）	Shrinkage temperature（℃）	Grain appearance
1	left▲	84.73	100.55	Waste water brings darker color, well appearance on both grain
	right	85.24	101.70	
	difference	0.51	1.15	
2	left	85.17	102.00	Waste water brings darker color, well appearance on both grain
	right▲	84.42	100.70	
	difference	0.75	1.30	
3	left▲	85.24	99.00	Waste water brings darker color, well appearance on both grain
	right	86.03	100.80	
	difference	0.79	1.80	
4	left	84.85	102.80	Waste water brings darker color and rougher grain
	right▲	83.76	101.10	
	difference	1.09	1.70	
5	left▲	81.53	101.95	Waste water brings darker color and rougher grain
	right	82.39	103.20	
	difference	0.86	1.25	
Average	lower	0.80	1.44	

2.2.5 Comprehensive recycling of each process

Concentrate all waste water on one side of cattle hide according to the process above mentioned (collect waste water of each stage to recycle). The other side is conducted with conventional process.

▲ Indicates untreated waste water is used.

Tab. 10

Recycle (times)		Pelt gain rate (%)	Rendment of wet blue（%）	Shrinkage temperature（℃）
1	left▲	18.51	86.31	97.40
	right	19.35	87.37	99.30
	difference	0.84	1.06	1.90
2	left	22.37	84.95	98.20
	right▲	20.88	83.41	96.50
	difference	1.49	1.54	1.70
3	left▲	22.32	85.98	99.70
	right	24.72	87.80	101.10
	difference	2.40	1.82	1.40
4	left	24.23	88.54	102.95
	right▲	21.73	85.99	100.10
	difference	2.50	2.55	2.85
5	left▲	20.00	85.72	101.00
	right	20.95	87.69	103.00
	difference	0.95	1.97	2.00
Average	lower	1.64	1.79	1.97

2.2.6 Comprehensively recycling of waste water having been treated respectively

Concentrate all waste water having been treated with corresponding agents on one side of cattle hide according to the process above mentioned (collect waste water of each stage to recycle). The other side is conducted with conventional process.

Experimental results:

Left side is applied with waste water that treated by antibody control agent, the right side is conducted with conventional process.

▲ Indicates treated waste water is used.

Tab. 11

Recycle (times)		Pelt weight gain rate (%)	Rendment of wet blue（%）	Shrinkage temperature（℃）
1	left▲	26.95	86.36	99.15
	right	26.00	85.57	98.10
	difference	0.95	0.79	1.05
2	left	19.51	83.77	98.90
	right▲	20.35	84.43	100.10
	difference	0.84	0.66	1.20
3	left▲	19.98	85.64	100.00
	right	19.46	84.84	98.90
	difference	0.52	0.80	1.10
4	left	20.95	84.00	98.70
	right▲	21.30	84.52	100.00
	difference	0.35	0.52	1.30
5	left▲	20.37	83.82	98.60
	right	19.88	83.05	97.60
	difference	0.49	0.77	1.00
Average	increase	0.63	0.71	1.13

3 Results and discussion

Experiment results indicate that direct recycling from soaking to tanning has many defects, which would make pelt weight gain rate and rendment of wet-blue both reduce 1-2.5%, and shrinkage temperature decrease in 1.5-2.5℃. Meanwhile the grain of wet-blue would be damaged and become rougher and darker. Soaking process requires great amount of water, and the waste water contains a lot of chloride, surfactants, water-soluble protein and other pollutants. Recycling of soaking waste water can not only save water, but also reduce pollution visibly. When the soaking waste water are directly used in main soaking, experiment results indicate that the rendment of wet blue reduced by 0.3-0.6%,and‘rough’ grain is also appear on the wet blue, especially in summer. The rough grain will be removed when the waste control agent applied.

Liming stage produces 70% pollutants in the leather manufacturing. Recycling waste liming water will largely reduce the pollutants discharge and water consumption and minimize the cost. Compared to other processes, waste limed water is the most difficult to recycle. Direct recycling of waste limed water would bring visible swelling inhibition, which results in 1-2% reduction of pelt gain rate and 1-1.7%

reduction in rendment of wet blue. There is no remarkable change in shrinkage temperature, while pelt is thin and wet blue has low-level of fullness. The most serious problem is area shrinkage in high degree. We believe that swelling inhibition factors (antibody) are existed in the waste water to protect the raw hide and skins from attack of lime and alkali. ELIPO can remove the swelling inhibition effectively and ensure pelt swell moderately.

Hair saving liming process can recover hair by using a filter. When waste limed water are reused, a filter should be installed outside the drum. Then whole hairs can be removed without any effect on liming process in the primary stage, which can reduce the organic wastes from hair solution and provides more suitable condition for chemicals' penetrating, so chemical consumption can be lowered.

To save water and reduce pollution, deliming and debating are carried out in one bath. Large amount of ammonium and calcium salt, protein and enzyme are existed in deliming and debating waste water. Directly discharge not only has serious impact on environment, but also results in the lost of available chemicals. The experiment suggest that there would be 0.6-1.2% reduction of rendment of wet blue, 1-1.5℃ reduction of shrinkage temperature, and rough grain when waste water are directly reused. Meanwhile enzyme's amount and variety are difficult to control and waste water would easily have odor, especially serious in summer. Problems above mentioned can be solved when the antibody control agents are applied.

As one of the most serious pollution sources, trivalent chromium in the waste tanning water brings serious impact on environment and human beings. Accomplishment of such recycling not only solves the pollution problems, but also reduces the consumption of heavy metal chrome. When waste water are directly reused, the rendment of wet blue reduced 0.5-1% and shrinkage temperature reduced 1.0-1.8 ℃.As the recycle times increased, the macromolecular complex in waste water would increase as well. Binding among molecule happens easily, which results in crust grain rougher and color darker. Specialized antibody control agent to waste chrome water can transfer and disperse complex, which would provide better penetration to make chrome combine with collagen protein uniformly and moderately. The leather would have perfect grain and 10-15% chrome powder can be saved.

Untreated waste water applied with direct recycling would easily result in damaged grain, area shrinkage, rougher grain, darker color of wet blues. Especially when the recycle was up to four or five times, the crust quality would be damaged. This experiment is conducted with the process innovation, decrease in chemical consumption and antibody control agent application, which brings that 0.5-0.8% increase of rendment of wet-blue, 1.0-1.5℃ increase of shrinkage temperature (compare to conventional process), and quality wet blue. Meanwhile performance indicators of the final leather would meet standards, the rate of loose grain is lowered efficiently, chemical cost is saved for 7-12% and pollutant discharge is reduced by 60-70%. Soaking, deliming and chrome tanning waste water can be recycled for unlimited times. As times of recycle increased, deposition of lime, waste pieces of raw hides and filth would make waste water too sticky to recycle. To solve the problems, membrane filter press instrument can be used to separate solid matter from liquid. The liquid can be used in further recycling, and solid matter would have other application, so water recycling is unlimited. In fact this solution would not be perfect enough to bring about harmony of economic returns and contribution to society and environmental protection, so that related study has progressed continuously. As the recycle process and pollution treatment advanced, waste water recycling of leather industry would have huge breakthrough in future.

4 Conclusions

Treated by corresponding waste control agent, waste water from main soaking, liming, deliming-bating and pickling-tanning would effectively solve the problems above mentioned that damaged grain, shrinkage area, rougher grain and darker color. There would be 0.3-1% increase of limed pelt weight gain rate, 0.5-0.8% increase of rendment of wet blue, and 1-1.5℃increase of shrinkage temperature (compare to conventional process). Meanwhile, final leather compaction is strengthened and the rate of loose grain is reduced, then quality final leather is gained.

Waste water recycling not only can reduce the pollutant discharge by 60-70%, but also save chemical cost by 7-12%, which brings about harmony of economic returns and contribution to society and environmental protection. Pollution control can be achieved in practicality.

This method just need simple operation with low investment, such as waste water collecting-reacting tank, filter, and channels (pipes) connected with drums. The antibody control agent is required to applied with waste water, and then mix together and react for 30 min to 60 min.

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