An Environment-friendly Lime-Free Liming Process based on sodium silicate

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Abstract: As a substitute of lime, a novel liming agent totally based on sodium silicate and enzyme was applied for lime-free liming process. This innovative process achieved equivalent effect on fiber opening, shrinkage temperature (Ts) and mechanical properties of crust leather compared with conventional liming process. Whilst the environmental factors, including total solids (TS), chemical oxygen demand (COD), sludge concentration and biodegradability of wastewater were all superior to the conventional liming process, showing environmental-friendly characteristics. Another interesting phenomenon was that the traditional deliming process based on ammonium salt could be omitted because of no utilization of lime in this innovative process. As a result, the NH_3-N concentration in wastewater was greatly reduced and plenty of water needed to remove lime was also saved.

Key words: Lime-Free agent; Liming Process; Environment-friendly

1 Introduction

Beamhouse processes for leather making are known for environmental unfriendliness since many conventional leather chemicals, organic or inorganic, result in severe pollution. For example, the total $Ca(OH)_2$ content in the sludge in the effluents discharged from tanneries are contributed completely by the so-called dehairing-liming processes, in which a large amount of lime, sodium sulphide and ammonium salts are conventionally employed. In addition, this disreputable process also accounts for more than 60% of the biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total solid (TS) in the wastewater.[1] With environmental pollution coming under intense scrutiny during the past decades, governments have implemented numerous stringent regulations to challenge this long established industry, which simultaneously, sparks researchers' interests in "green leather chemicals" that only impose little influence on the surroundings.

To remedy the unfavorable contamination in dehairing-liming processes mentioned above while maintain various performance of the resultant leathers, considerable effects have been devoted around the world to substituting the commonly used chemicals (sodium sulfide and lime) with environmental sound materials. For example, Qiang He *et al* reported that both sedimentation property and biodegradability of wastewater collected from novel enzymatic unhairing could be better achieved, in comparison with that of conventional Na_2S-lime processes.[2] Moreover, P. Thanikaivelan *et al* claimed that application of sodium hydroxide（NaOH）, which worked as substitute for lime in liming, not only facilitated the open up of fiber bundles, but also omitted deliming process coupled with a 45 percent reduction in total solid load on environment. Nevertheless, the former research did not discard the utilization of lime thoroughly, since a certain amount of calcium hydroxide was still required in the

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following reliming process for further opening up fibers. As for the latter example, although strong alkali exhibited powerful action on swelling, it was probable that uneven effect and worse mechanical properties of final leather could also occur due to the extremely high collagen dissolubility possessed by sodium hydroxide.[3,4] Without doubt, the above facts indicate that tanners and chemists worldwide have more work ahead to fully realize sustainable liming process characterized by zero lime utilization.

In this study, a novel liming agent totally based on sodium silicate and enzyme was used for the liming process. Comparing with strong alkali, basic sodium silicates had a moderate action on hide swelling and fiber opening up without large loss of proteins；The alkaline enzyme was designed to help further fiber opening. With the cooperating effect of sodium silicate and enzyme, a desirable fiber-opening effect and clean lime-free liming process together with non-deliming process were achieved.

2 Experimental

2.1 Materials

Sixteen wet salted goatskins were chosen as raw materials, and they were previously fleshed and washed to remove excessive fats and surface salts. The novel lime-free liming agent used in the present experiment was prepared in our laboratory and referred to as NL (non-lime). The details about NL are shown as follows.

Main Chemical Composition: $Na_2SiO_3.9H_2O$（90 wt%), Urea (3 wt%)，surfactant（2 wt%）and enzyme (5 wt%), 5wt% solution with pH value 12.0-13.0;

Where, the enzyme is an alkaline bacterial protease (named 2709) with activity of 5000 units/g and active at pH 7.5-11.0 and 25-45 ℃.

All other chemicals employed for leather processing are commercial grade, while the chemicals used for analytical techniques are of laboratory grade.

2.2 Conventional and experimental process of Liming and Deliming

Preliminary trials were carried out to optimize the concentration of NL for fiber opening. Sixteen soaked goatskins were dehaired and weighted before addition of NL. Three skins were used for each experiment including control. Concentration of NL tried in this study varied as 1.0, 1.5, 2.0wt% and 1.5wt% without enzyme (based on the dehaired hide) and the corresponding experiments were termed as E1, E2, E3 and E4 respectively. At the same time, another three skins were treated with 8wt% lime and termed as C (control). Dehairing, Liming and deliming processes were presented in Table 1.

Table 1 Conventional and experimental Dehairing and liming processes

Process		Chemical	wt%	Temp(℃)	Duration
Dehairing		Water	50		
		Na_2S	3	25	3h
Liming	conventional	Water	300		overnight after
		Lime	8	25	drum 3h
	experimental	Water	300		overnight after
		NL	1.0/1.5/2.0	25	drum 3h
Deliming	conventional	$(NH_4)_2SO_4$	2.0	38	1h

	experimental	citric acid + boric acid	0.8	38	1h
Bating, pickling and chroming	As the same as the traditional process				

The optimal concentration of NL was approximately determined according to the percentage increases in weight and thickness after liming process, and confirmed by the following scanning electron microscopic (SEM) analysis as well as other performance evaluation.

2.3 Scanning Electron Microscopic(SEM) analysis

Samples from experimental and control sides were firstly cut from the official sampling position after opening up treatment,[5] then they were washed in water and fixed by soaking with buffered formalin for 18 hours. After dehydrated gradually using acetone and methanol according to standard procedures, excessive solvent in the samples was removed by filtering papers. Finally, the samples were cut into specimens with uniform thickness, which was then cryogenically fractured in liquid nitrogen and then coated using aurum spattering. A JEOL JSM-5900LV scanning electron microscope (SEM) was used for the analysis, and the cross section micrographs of specimens were obtained by operating the SEM with an accelerating voltage of 20KV at a magnification of 500.

2.4 Shrinkage temperature analysis

The shrinkage temperature (Ts) of samples, which is a measure of hydrothermal stability of leather, was determined using a Theis shrinkage meter.[6] Each value reported is an average of three experiments.

2.5 Analysis of hide substance content of leather samples

Total nitrogen contents of leather samples were measured according to GB4689 using BUCHI-339 device. Hide substance contents of leather samples were calculated by multiplying the measured total nitrogen contents of leather samples by 5.62.[7]

2.6 Mechanical properties of crust leather samples

Mechanical properties such as tensile strength, elongation, tear strength and grain crack strength were measured according to standard procedures.[8] Each value reported was an average of four (2 along the backbone, 2 across the backbone) measurements.

2.7 Analysis of wastewater

Wastewaters collected from dehairing process to deliming process were for the testing of total solids (TS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Total solids (dried at 103-105℃ for 1 hour) in wastewaters were determined by using standard methods,[8] and measurements of COD and BOD_5 were carried out by using HANNA HI 99721 and HI 99724A-6(Hanna Instruments, Italy), respectively. The results reported were average values of three experiments for each sample.

2.8 Analysis of total nitrogen in wastewater

Total nitrogen contents of wastewater collected from dehairing process to deliming process were measured respectively according GB4689 using BUCHI-339 device.[7]

3 Results and discussion

3.1 Degree of fiber opening

The fiber opening-up treatment was carried out using various concentrations of NL viz 1.0, 1.5, 2.0wt% and 1.5wt% without enzyme. The percentage increases in weight and thickness of goatskins after liming process for various concentrations of NL were shown in Table 2.

TABLE 2 Fiber Opening Using Lime and Various Concentrations of NL

No.	NL (wt%)	Increase in weight (wt%)	increase in thickness(%)	remark
E1	1.0	14.5	52.9	No Grain damage
E2	1.5	21.6	68.8	No Grain damage
E3	2.0	27.4	80.0	No Grain damage
E4	1.5(without Enzyme)	19.0	63.5	No Grain damage
C	control	21.5	69.4	No Grain damage

It can be seen that there was no appreciable swelling compared with control when low concentration of NL (1.0wt%) was applied. However, with the offer of NL increasing, the pelts exhibited obvious fiber opening effect without any grain damage. The degree of swelling employed NL1.5wt% without enzyme was lower than that employed NL1.5wt% with enzyme; this indicates that protease 2709 enzyme has an ability to further open up the fibers. Comparing with the conventional liming process, it was found that comparable swelling or opening up effect on the pelts could be achieved when 1.5wt% NL was employed.

SEM analysis provides another convenient way to observe the extent of fiber opening up. The cross section micrographs of pelts were given in Figure1 (a-e) at a magnification of 500. According to these pictures, when low concentration of NL (1.0wt%) was applied, the fiber bundles seemed to be devoid of interspacing (Figure a), which indicated that inadequate extent of fiber opening was obtained in comparison with conventionally limed samples (Figure d). Nevertheless, pronounced opening up of fiber bundles was observed (Figure b and c) with an increasing offer of NL, and the sample treated with 1.5wt% NL exhibited comparable opening up to that of control in particular. These observations totally keep good consistent with the conclusion mentioned above.

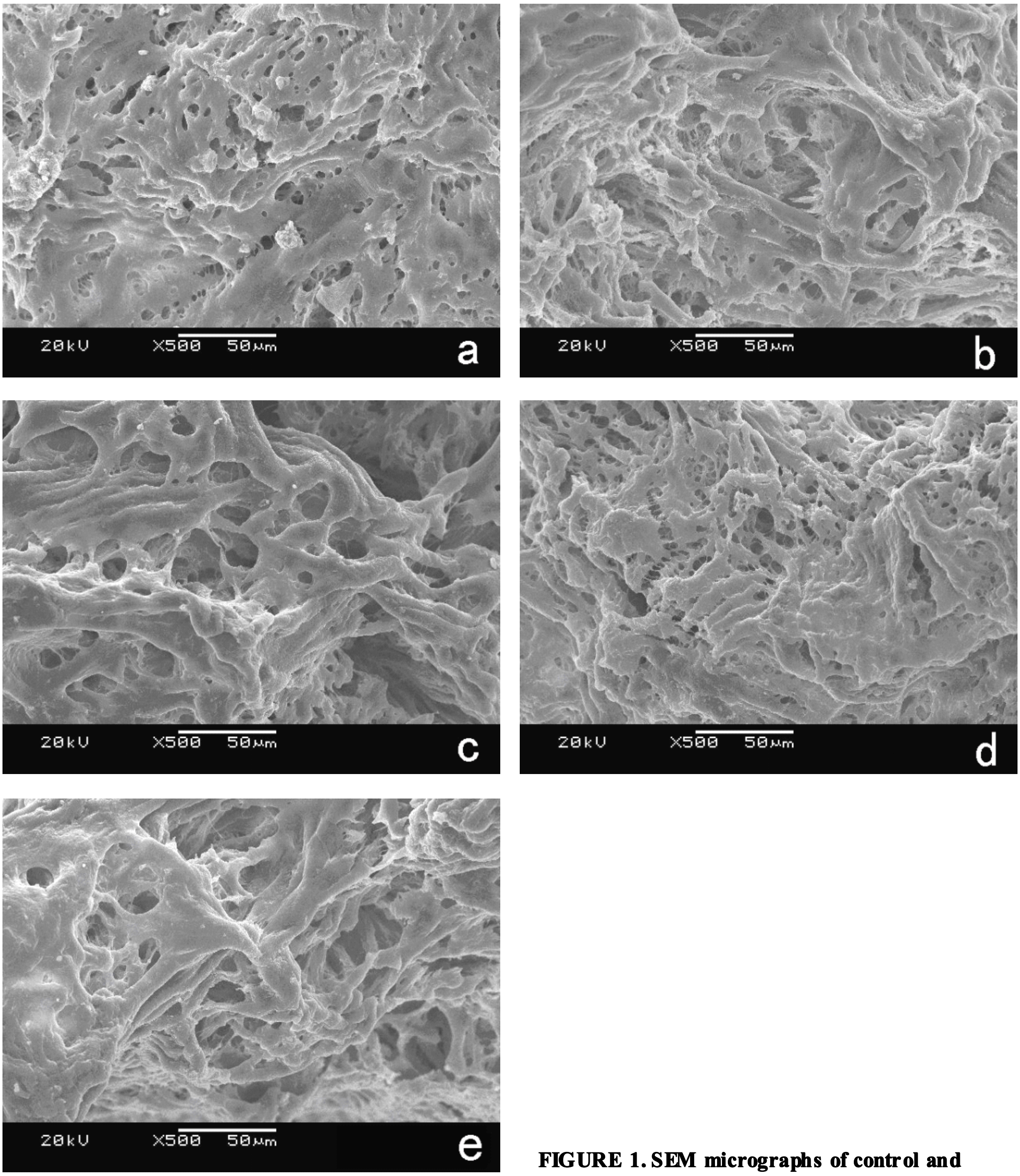

FIGURE 1. SEM micrographs of control and experimental pelts after opening up treatment showing the cross section (×500 magnification) (a) 1.0 wt% NL (E1), (b) 1.5 wt% NL (E2), (c) 2.0 wt% NL (E3), (d) 1.5 wt% NL without enzyme (E4), (e) control sample (C)

3.2 Properties of crust leather

3.2.1 Shrinkage Temperature Analysis

After liming process which removes cementing substances and other unwanted proteins, the opened-up pelts exhibit lower shrinkage temperature (Ts) than ever before. As already known, moderate fiber opening facilitates the penetration and combination of chrome in the following tanning process, which will result in high hydrothermal stability of leathers;[9] whilst opposite results are obtained when excessive liming process is adopted. Table 3 lists the shrinkage temperatures of soaked, limed hides and wet blue from experimental and control treatments changes with the offer of NL. According to the data presented in this table, it could be clearly seen that the shrinkage temperatures of limed hides treated with NL were all lower than those of raw hides and with an increasing offer of NL, the shrinkage temperature of pelts decreased gradually. This phenomenon indicated that the alternative agent prepared in this study was capable of opening the fiber bundles as traditional lime. Moreover, when the offer of NL was 1.0wt%, chrome-tanned leather with low hydrothermal stability was produced, which could be ascribed to inadequate fiber separation as evidenced in the previous parts. With the offer of NL increased to 2.0wt%, excessive opening was responsible for the unsatisfactory shrinkage temperature of wet blue recorded, which was 101.2℃ and relatively lower than that of E2(110.8℃)and C(111.3℃). Meanwhile the shrinkage temperature of wet blue with the offer of NL 1.5wt% without enzyme was lower than that employed NL 1.5wt% together with enzyme. This is because that in absence of enzyme the fibers are not opened up enough, in this case the chrome salt can not fully penetrate and combine with collagen, which results in the decrease of shrinkage temperature. To achieve comparable hydrothermal stability of leather to that of control, 1.5wt% NL seemed to be the optimized offer.

TABLE 3 Shrinkage temperatures of soaked, limed hides and wet blue of Experimental and Control

No.	Ts of Soaked hide (℃)	Ts of Limed hide (℃)	Ts of wet blue (℃)
E1	63.5	52.0	97.5
E2	63.5	50.8	110.8
E3	63.6	49.8	101.2
E4	63.5	51.2	101.5
C	63.5	50.5	111.3

(E1: 1.0 wt%NL; E2: 1.5wt%NL; E3: 2.0 wt%NL; E4: 1.5 wt% NL without enzyme; C: control)

3.2.2 Analysis of hide substance content of crust leathers

Hide substance, which is defined as the remaining protein ratio after various treatments in the leather manufacture is a key parameter to determine whether the hides have been through correct treatments or not. Generally speaking, the hide substance for upper leathers ranges from 50 wt% to 60 wt%. If excessive operations have been imposed, low content of hide substance is supposed to be recorded, which results in empty leathers with declined mechanical properties. On the contrary, inefficient combination of chrome salt accounts for high hide substance, which results in leathers with rough handle and lower shrinkage temperatur.[10] In this study, the hide substances of crust leathers from experimental and control treatments were examined and the results were illustrated in Figure 2. From this diagram, relatively higher hide substances (62.0 wt%) were obtained when 1.0 wt% NL was offered, and 2.0wt% NL brought about crust leather with lower recorded value (48.0wt%). Obviously, the former was due to inadequate opening up of fiber bundles, and the latter could be explained as that exorbitant amount of proteins was removed from the hides. In comparison with control, moderate content of hide substances was left in sample from E2 treatment, which indicated that 1.5wt% NL was quite reasonable in the opening up/liming process.

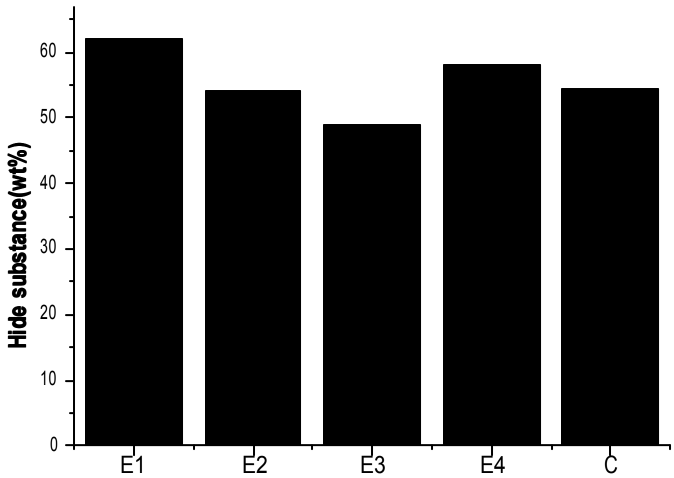

FIGURE 2. Hide substance (wt%) content of leather samples

(E1: 1.0wt% NL; E2: 1.5wt% NL; E3: 2.0wt% NL; E4: 1.5 wt% NL without enzyme; C: control)

3.2.3 Mechanical properties of crust leather samples

Tests of mechanical properties were carried out for all the crust leather samples both along and across backbone line. The results corresponding to the two directions were averaged for each crust for each strength character. The mean values of three crusts, which were processed in each experiment, were calculated and given in Table 4. It could be clearly seen that E1 and E4 process characterized by low NL concentration or by NL without enzyme resulted in crust with lower tensile and tear strength than those of control, which was ascribed to inadequate opening up of fiber bundles. Crust made from E3 process, due to the excessive opening up of fiber bundles, showed higher broken elongation but lower mechanical properties. In addition, sample from E2 process presented comparable tensile strength, broken elongation, tear strength and burst strength respectively when compared with crust made from traditional liming. These facts validated not only that sufficient opening up was crucial to the mechanical performance of the resultant leather, but also that 1.5wt% NL was quite enough to achieve leather with comparable qualities to control.

TABLE 4 The mechanical properties of crust leathers

NO.	[1]Tensile strength (MPa)	[1]Broken elongation (%)	[2]Tear strength (N/mm)	[2]Burst strength (Kg/cm^2)
E1	20.5	59.0	40.6	12.2
E2	26.9	70.0	43.2	13.4
E3	25.3	75.5	40.1	12.5
E4	24.5	65.2	41.0	13.0
C	26.7	69.6	42.8	12.0

([1] Average of 4 samples (two along the backbone and two across the backbone)
[2] Average of two measurements
E1: 1wt%NL; E2: 1.5wt%NL; E3: 2.0wt%NL; E4: 1.5 wt% NL without enzyme; C: control)

3.3 Environmental impact of novel liming process

3.3.1 TS, COD and BOD_5 analysis of wastewater

To valuate the impact of wastewaters from dehairing process to deliming process on the environment, total solids (TS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were analyzed after experimental and control treatments respectively. According to Table 5 which shown the calculated results, it was obvious that with an increasing concentration of NL, both increasing COD and BOD_5 were recorded. Compared with those of control, COD and BOD_5 for effluent from E1 were lower, which could be attributed to inefficient removal of cementing substances and other unwanted proteins. On the contrary, excessive opening up was responsible for higher COD and BOD_5 values for effluent from E3. For the case of E2 and E4, although the same offer of NL was employed, the BOD_5 is greater for E2 than for E4, which should be attributed to the application of enzyme in E2 process. Another important result was that the TS values in all experimental cases were much lower than that of control(, which was due to the fact that the NL prepared in this study was totally based on sodium silicate and enzyme, namely) because no lime was applied in E1, E2, E3 and E4 processes.

The value of BOD_5/COD is commonly adopted to evaluate biodegradability of wastewater, although this value is not always consistent with the biodegradability in some special situations.[11] It is recognized that the higher the BOD_5/COD value of wastewater, the better its biodegradability is. When the value is larger than 0.45, the wastewater is usually considered to be easily biodegradable.[12] From this point of view, the data in Table 5 indicated that all the wastewaters from experimental cases were easily biodegradable. Comparatively, wastewater from control treatment showed worse biodegradability than that of NL-based treatments。

TABLE 5 Characteristics of Wastewaters

Effluents	BOD_5 (mg/L)	COD (mg/L)	TS (mg/L)	BOD_5/COD
E1	1508	3016	8450	0.50
E2	2910	5291	9375	0.55
E3	3800	6552	10153	0.58
E4	2350	5222	8925	0.45
C	3182	9200	32950	0.35

(E1: 1wt%NL; E2: 1.5wt%NL; E3: 2.0 wt%NL; E4: 1.5 wt% NL without enzyme;C: control)

3.3.2Analysis of total nitrogen in wastewater

Nitrogen is found in wastewaters in the form of ammonia nitrogen, nitrate nitrogen and organic nitrogen. They almost come from dehairing, liming and deliming processes. In traditional process, ammonia salts are the most commonly used as deliming agent because of their quick penetration, buffering action, regulating the pH at optimal values and removing calcium from the hide.[13] But ammonium salts discharged into natural water sources have toxic effects on living organisms. In this liming-free process, the “limed” hide does not contain calcium, only some acids are needed to regulate the pH to satisfy the buffering condition, which can totally decrease the pollution of NH_3-N caused by addition of ammonia salts. Figure 3 is the total nitrogen values of wastewater samples taken from dehairing to deliming processes. As could be seen from this figure, total nitrogen values varied from 750 mg/L to 1800 mg/L. Total nitrogen values of all the wastewaters from experimental cases were lower than 830 mg/L, which were far below the total nitrogen value of wastewater from control (1800mg/L).

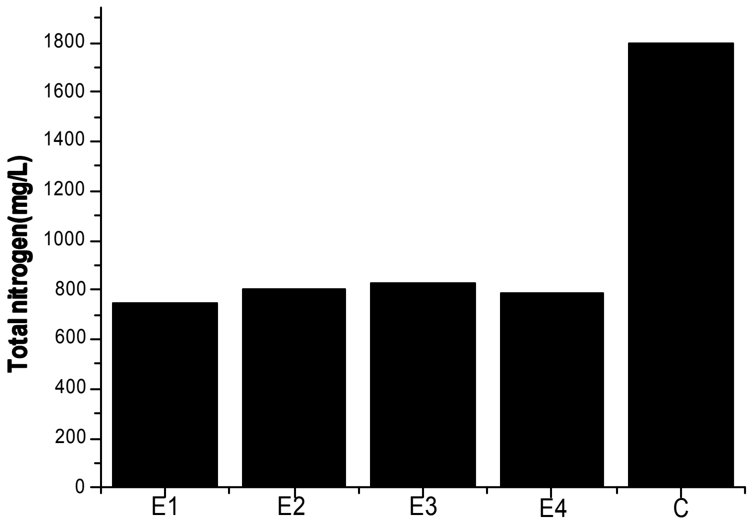

FIGURE 3 Total nitrogen values of wastewaters from dehairing process to deliming process

4 Conclusions

As a substitute of lime, a novel liming agent (NL) totally based on sodium silicate and enzyme was applied for lime-free liming process. Preliminary trials revealed that moderate opening up of fiber bundles could be achieved by employing 1.5wt% NL in opening up treatment; meanwhile, desirable hydrothermal stability and mechanical properties of crust leathers were obtained. In terms of environmental benefits, there was reasonable reduction in chemical oxygen demand (COD) and total solids (TS), whilst the utilization of NL which contained no lime at all was advantageous for reducing sludge and improving the biodegradability of wastewater compared with conventional process. More importantly, the conventional deliming process based on ammonium salt could be omitted because of no utilization of lime in this innovation process. As a result, the NH_3-N concentration of wastewater could be greatly reduced.

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References

[1] Ludvik, J., Study on the scope for decrease of pollution load in leather processing. United Nations Industrial Development Organisation Report, March 1997.

[2] Qiang He, Kai Yao Bi Shi etc. Biodegradability of wastewater from enzymatic soaking and unhairing process in leather manufacture. JALCA 217-222,

[3] P. Thanikaivelan, J. Raghava RAO, Balachandran Unni Nair , et al. Approach toward zero discharge tanning: Exploration of NaOH based opening up method. JALCA, 96, 222-233, 2001

[4] P. Thanikaivelan, B. Chandrasekaran, C. K. Bharath , et al. Single step hair removal and fiber opening process: Simultaneoue and successive addition of proctease and α-amylase

[5] A.D. Covington, R.A. Hancock, I.A. Ionnidis, J. Soc; Leather Technol. Chem, 73, 1, 1989.
[6] McLaughlin, G. D. and Theis, E. R.; The chemistry of leather manufacture. Reinhold Publishing Corp., New York, 133, 1945.
[7] Jiang Weiqi. Chemical and physical analysis in leather processing. Light Industry Press (Chinese), Beijing, 1999.
[8] Chandrasekaran, B., Rao, J.R., Prasad, B.G.S. and Nair, B.U.; Management of chromium wastes in tanneries. J. Indian Assoc.Environ.Manag.16, 168, 1989.
[9] Wang jiangen, Yang zongsui, Ma jianzhong, et al. Liming control and its effects on leather quality. China Leather, 30, 26, 2001.
[10] Dai Hong, Analysis of chemical engineering in light industry, Chemistry Industry Press, Beijing, 2001.
[11] Guo, W. C. and Wu, Q. H.; The biodegradability evaluation of wastewater based on BOD5/CODcr. Environmental Science and Technology (Chinese) 82, 39-41, 1998.
[12] Gao, Z. B. and Shu, C.Y.; Treatment of wastewater from Leather-making Industry. Chemistry Industry Press, Beijing , 2001.
[13] Ghimenti, D. G., Clean technologies in the tanning process life project. Stoneham, 371-391, 1994
[14] Patterson, W. J., Industrial wastewater treatment technology. Butterworth Publishers. 235-255, 1985