Ammonia – Reduced Deliming using Glycolic Acid and EDTA and its Effect on Tannery Effluent and Quality of Leather

by

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Abstract

In leather processing, deliming is traditionally carried out using ammonium salt which generates a large amount of ammonia in tannery waste water. This may result in water pollution as well as toxic effect on aquatic organisms. This research work is an attempt to develop an alternative deliming agent to minimize the pollution load o tannery waste water. The current research was performed using mixture of 90 wt. % of glycolic acid and 10 wt. % of ethylenediaminetetraaceticacid (EDTA), which evolves no ammonia and relatively inexpensive. Deliming value, buffer capacity, calcium solubility and penetration in limed pelts of the developed deliming agent were determined to assess its effectiveness. Sulphide content, Ammonia Nitrogen (NH3-N) Content, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values of the resulting discharge water were analyzed and examined in contrast with traditionally delimed discharge water. The developed deliming agent was applied on leather and its properties, such as tensile strength, elongation at break, tear strength, softness, chromium uptake, and morphological characteristics were compared to conventionally delimed leather as well as the standards.

Introduction

Liming, the most important pre-tanning process, is carried out to remove epidermis and open up the fibrillar structure by swelling during production of leather.[1] It is essential to remove lime present in the hides or skins matrix prior to tanning. The lime removal operation is termed as deliming.[2] It is done for removing lime and unhairing chemicals from the pelt, lowering the pH, deswelling and preparing the pelt for following bating operation.[3] Conventional deliming is done employing ammonium salt because it penetrates quickly into the hide and has a good buffering action in the suitable pH range required for deliming. The conventional deliming process discharges ammonia in the form of ammonia nitrogen into the effluent and also emits ammonia gas into the air. The toxic ammonia gas leads to unsafe working conditions and results in diseases like methemoglobinemia and hepatic encephalopathy.[4] High ammonia content in the tannery effluent increases biological oxygen demand (BOD) due to nitrification reaction causing death of fish and aquatic organisms.[5]

Removal of ammonium ions in tannery effluent is also very expensive and time-consuming. In order to reduce the ammonia nitrogen from tannery waste water many ammonia free deliming agents have been developed. But due to some difficulties, none of those could be introduced in the leather processing chain. Mineral acid based deliming agents liberate no ammonia, but it is difficult to control the pH.

Deliming with carbon dioxide requires special types of equipment and it is suitable only for limed split. Formic acid, lactic acid, acetic acid based deliming cause acid swelling of pelts if added in excess.[6]

Glycolic acid is a α-hydroxy organic acid which has high chelating efficiency and thus capable of forming stable complex compound with alkaline earth metals viz. calcium and magnesium ions.[7] Therefore, it is reasonable to presume glycolic acid's capability of removing high extent of calcium during deliming. On the other hand, EDTA is a widely used buffer which can dissolve lime scale because of its ability to sequester metal ions such as Ca^{2+} and Fe^{3+}.[8, 9]

In our preliminary analysis we found that the buffering effect of glycolic acid in deliming bath was at pH 6.6, which might cause acid swelling of pelt. On the contrary, EDTA showed buffering effect at pH 8.8 in deliming bath. Hence, we expected a small amount of EDTA with glycolic acid giving desired buffering action as well as avoiding acid swelling of pelt in deliming. Thus, we decided to develop an environment friendly deliming agent

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in combination with glycolic acid and EDTA in a rational molar ratio. Finally, the efficiency of the developed deliming agent, properties of the discharged effluent and its effect on the quality of leather have been studied and presented in this paper.

Material and Methods

Raw Materials

Goat skins were supplied by commercial hide/skin brokers. Limed skin was produced by following conventional leather processing steps and was made ready for deliming operation. Chemicals used for leather processing were commercial grade. Chemicals for evaluation of deliming agent and effluent treatment were analytical grade.

Deliming Process

After washing of limed pelt deliming was performed. In experimental deliming trials 1.0% of developed deliming agent and 100% water were added and drummed for 60 minutes. The developed deliming agent was prepared by mixing of glycolic acid (90 wt. %) and EDTA (10wt. %). After that further conventional procedure (bating, pickling and chrome tanning) were performed. In control deliming trial 2% ammonium sulphate was added and same procedure was followed as experimental deliming trials.

Determination of Effectiveness of Deliming Agents

The effectiveness of deliming agent depends on the combination of deliming value, buffer capacity and calcium solubility.[10] The penetration of deliming agent in limed pelts and concentration of Hydroxyproline (Hyp) in deliming effluent also evaluates its effectiveness. The deliming value is the amount of deliming agent in gm necessary for neutralizing 1 gm of lime. The deliming value of deliming agents (both experimental and control trials) were calculated by titrating deliming agents against 3% calcium hydroxide.[11] Buffering effect of both experimental and control trial were analyzed by recording the initial pH of the deliming liquor at 10, 20, 30, 45 and 60 minutes respectively by using a pH meter. The extent of calcium removal from pelt (calcium solubility) of both experimental and controlled trial were measured using Atomic absorption spectrophotometer (Agilent 240 AA) according to the method mentioned in literature.[6]

Analysis of Penetration of Deliming Agents

The delimed pelts (both experimental and control) were cut during deliming process with a knife to determine the penetration depth of the deliming agent and checked by using phenolphthalein indicator.[12]

Determination of Concentration of Hydroxyproline (Hyp) in Deliming Effluent

Deliming liquors both from experimental and control trials were collected and filtered through 100 mesh filter cloth and their Hyp concentrations were analyzed according to the described method in literature.[12]

Analysis of Effluents

The collected effluents from both the experimental and control trials were filtered through Whatman no.1 filter paper. The sulphide content, NH_3-N content, Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were analyzed according to the test methods 4500-S2- D, ASTM D1426–15, USEPA Method 405.1 and ASTM D-1252-06 respectively.

Analysis of Leather

To determine the quality of leather the parameters tensile strength, elongation at break and tear strength were tested according to the Society of Leather Technologist and Chemists (SLTC) methods (SLP6; IUP/6), (SLP6; IUP/6) and (SLP7; IUP/8) respectively.[13]

The softness of crust leather was analyzed by an experienced leather expert.

Chromium content of tanned leather (both trials) were measured by using Atomic absorption spectrophotometer (Agilent 240 AA) and the method described in literature.[6]

To evaluate the morphological characteristics of chrome tanned leather (both trials), JEOL Scanning Electron Microscope (JSM-6490 LA, Japan) were employed.

Result and Discussion

Effectiveness of Deliming Agents

From the Table I, the deliming value of the developed deliming agent is 1.68, which is less than ammonium sulphate (1.81) after titration against 3% $Ca(OH)_2$. This explains that less amount of developed deliming agent would be necessary for completing the deliming action in comparison with ammonium sulphate.

Table I
Deliming value of developed and conventional deliming agent.

Sl. No.	Deliming agent	Deliming Value
1	Developed	1.68
2	$(NH_4)_2SO_4$	1.81

One of the main objectives of deliming is to decrease the pH of delimed pelt from 12 to 7-9 for the subsequent bating operation. If pH falls below this level, acid swelling of pelt and liberation of toxic hydrogen sulphide may occur.[14] Therefore, it is necessary for deliming agents to have a buffering action to control the deliming pH in the desired range. From Figure 1, in experimental deliming process the desired pH 7.0 was achieved in about 35 min and an equilibrium pH of almost 7.5 was reached in about 45 min. This indicates that, the developed deliming agent has a trend to form a buffering system in alkaline limed pelt. Although the equilibrium pH of experimental trial (about 7.5) was lower than that of control trial (about 8.9), but was retained at a higher pH than 7.0, so there was no possibility of acid swelling of pelt.

The penetration rate of deliming agent to the pelt is closely related to the deliming time. Ammonium sulphate is conventionally applied in the deliming bath for its quick penetration ability in the pelt. During deliming, we allowed gradual penetrability check of the pelt by using phenolphthalein indicator for the developed deliming agent and conventional deliming agent (Ammonium sulphate). It was found that the whole vertical section of the developed delimed pelt became colorless to phenolphthalein indicator within 25 min, whereas ammonium sulphate delimed pelt required 30 min (Figure 2).

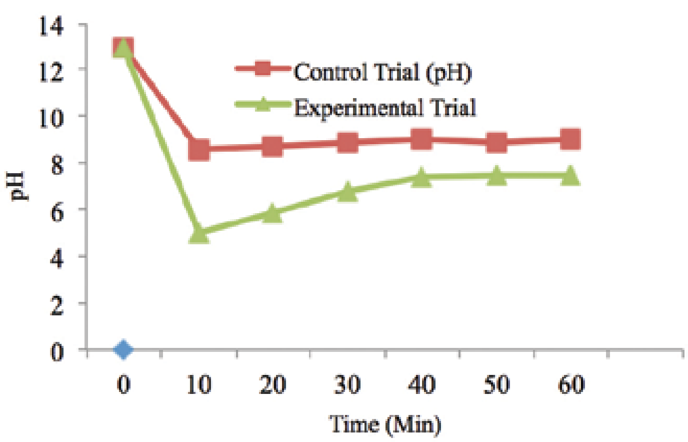

Figure 1. Change of pH of deliming liquor during deliming operation.

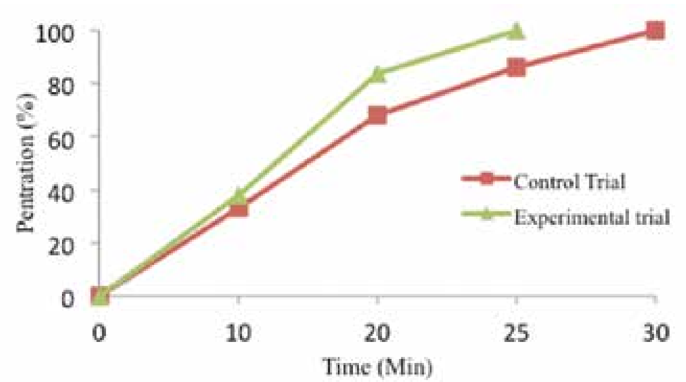

Figure 2. Percentage of penetration of experimental and control trial

Thus, the penetration speed of developed deliming agent was slightly faster than ammonium sulphate which will prevent excessive mechanical action on the pelt.

Excessive calcium salts remaining in the delimed pelt causes uneven reaction with dyes and fatliquors in tanned leather. The precipitated calcium salt in pelt or on its surface cause "cracked grain" and poor strength leather.[15] So, to evaluate the effectiveness of deliming agent the extent of calcium removal from pelt is a crucial criterion. Figure 3, shows that the extents of calcium removal of delimed pelts in experimental and control trials were approximately 51 and 54% respectively. It suggests that the developed deliming agent could also remove calcium salts efficiently. The satisfactory calcium removing capacity of developed deliming agent could be due to the fact that both glycolic acid and EDTA can form soluble complexes with Ca^{2+} for their strong chelating efficiency.[7]

The Hyp concentration of experimental deliming liquor was lower than that of control deliming liquor (Figure 4). This indicates that the developed deliming agent reduces the pelt collagen damage.

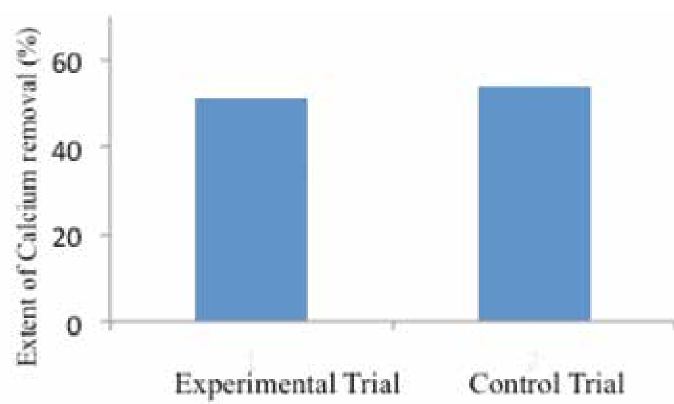

Figure 3. Extent of Calcium Removal of deliming agents.

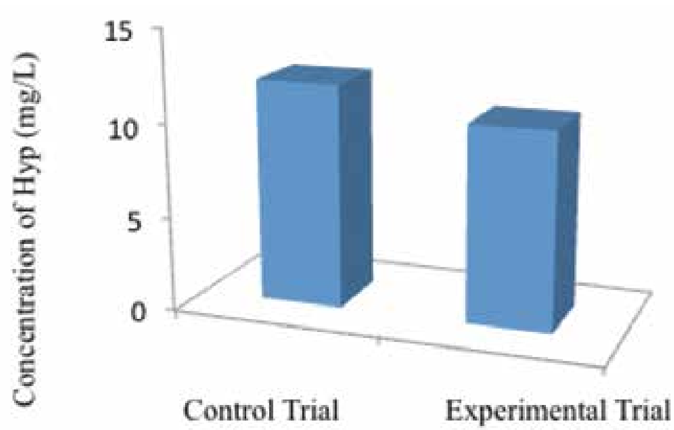

Figure 4. Hyp concentration of Deliming effluent.

The above analysis of deliming value, buffer capacity, penetrability, calcium removing capacity and hyp concentration of the developed deliming agent proves its effectiveness as a deliming agent.

Analysis of Effluents

In this research work conventional ammonium salt based deliming is replaced with mixture of glycolic acid and EDTA to eliminate the ammonia nitrogen and also to reduce COD, BOD and sulphide content in waste water. The pollution load of experimental and control delimed liquor is shown in Table II.

Table II

Pollution load of developed and conventional deliming agent.

Deliming agent	COD (mg/L)	BOD_5 (mg/L)	Sulphide content (mg/L)	Ammonia Nitrogen content (mg/L)
$(NH_4)_2SO_4$	3500	1150	5280	986
Developed deliming agent	1360	850	24.60	3.50

Table III

Evaluation of Physical Properties of goat crust Leather.

Sample	Tensile Strength (daN/cm^2)	Elongation at break (%)	Tear Strength (N/cm)
UNIDO	min. 100	max. 60	min. 15
Ammonium Sulphate	135.00	59.20	28.70
Experimental crust leather	142.05	60.11	30.10

Table IV

Chromium content of chrome tanned leather.

Sl. No.	Deliming agent	Chromium content (%)
1	Developed	3.89
2	$(NH_4)_2SO_4$	3.61

From Table II, the ammonia nitrogen generation in experimental deliming process is about 3.50 mg/L which is almost negligible. On the contrary, ammonium sulphate deliming this value is about 986 mg/L. The BOD_5 and COD value for experimental trials are about 850 and 1360 mg/L respectively, which is very much lower than that of ammonium sulphate deliming (approximately1150 and 3500 mg/L respectively). The control trial results high amount of sulphide content 5280 mg/L whereas the experimental trial shows the value about 25 mg/L. This result suggests that, sulphide content is remarkably reduced (99.5%) by developed deliming agent.

In primary chemical cost analysis, we found that the cost of experimental deliming was almost two times higher than that of conventional deliming. On the contrary, the delimed liquor from experimental trial contains a trace amount of pollution load which reduces the waste water treatment cost significantly. Therefore, overall cost for the experimental deliming is an in-extensive issue in term of cleaner technology.

Analysis of Leather

The physical properties of experimental and control crust leathers are illustrated in table-III. From the table tensile strength of experimental crust leather is 142.05 daN/cm^2, which is above the minimum acceptable limit (100 daN /cm^2) reported by UNIDO[16].The elongation at break value of experimental leather was 60.11%, which is very close to the limit (max. 60%). Tear strength obtained for experimental trials is (30.10 N/cm) also above the sub-limit (min. 15 N/cm).

The softness values of both trials were rated on a scale of 1-10 (Figure 5). This shows that, the leather obtained from experimental trial was softer compared with control trial.

From Table IV chromium content of experimental trial and control trial were 3.89 and 3.61% respectively. This suggests that

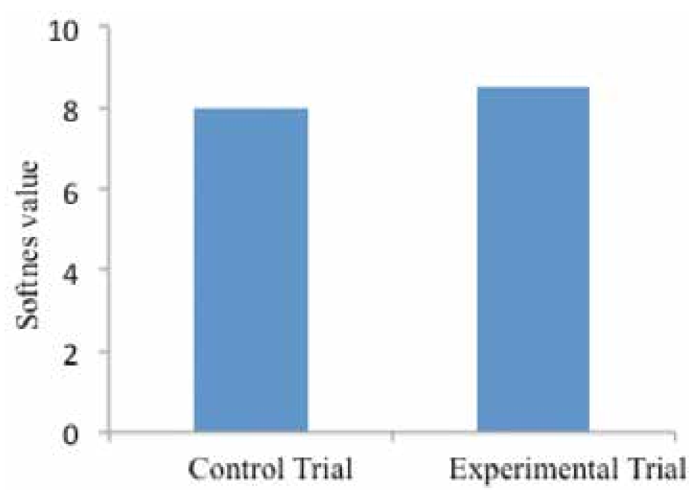

Figure 5. Assessment of Softness value of leather

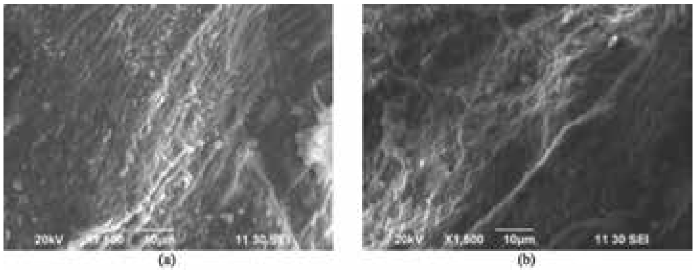

Figure 6. Scanning electron micrographs images of experimental (a) and control (b) tanned leather respectively.

the developed deliming agent shows more chromium uptake capacity compared to conventional one. This was so because glycolic acid has both carboxyl and hydroxyl groups which have high affinity with Cr (III).[17]

The SEM images of chrome tanned leather of both trials at a magnification of 1500x are shown in figure 6. The micrograph of control trial (b) shows separation of fiber. On the other hand, the experimental trial (a) shows slightly dispersed fiber structure which describes improvement in leather fullness. This explains the slightly greater firmness, strength and elongation of experimental trial than the control.

Conclusion

The developed deliming agent has improved deliming value, strong buffering action, excellent action in calcium solubility and rapid penetration capacity. Combination of these values proves the effectiveness of the glycolic acid and EDTA based deliming agent. The BOD, COD values and sulphide content are less than the conventional deliming agent which shows that it also lessens environmental pollution load. In addition to that, the ammonia nitrogen content indicates the developed product is almost free of ammonia. The physical, chemical and morphological test report shows that the final leather quality was highly satisfactory. Since, the developed product was applied only on goat skin, its efficiency in case of other hides and skins can further be studied.

Acknowledgement

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