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Research Article

AMMONIA-FREE DELIMING USING GLYCOLIC ACID AND EDTA AND ITS EFFECT ON TANNERY EFFLUENT AND QUALITY OF LEATHER

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ABSTRACT

In leather processing, deliming is traditionally carried out using ammonium salt which generates a huge amount of ammonia in tannery waste water resulting in toxic effect on aquatic organisms. This research work is an attempt to develop an alternative deliming agent using mixture of glycolic acid and EDTA, which evolves no ammonia and relatively cheap. Deliming value, buffer capacity and calcium solubility of the deliming agent were determined to assess its effectiveness. Sulphide content, NH3-N content, BOD and COD values of the resulting discharge water were analyzed. The developed deliming agent was applied on leather and its physical properties were compared to conventionally delimed leather as well as standard.

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 (Colak and Kilic, 2007). It is essential to remove lime present in the hides or skins matrix prior to tanning. The lime removal operation is termed as deliming (Murali, et al., 2013). It is done for removing lime and unhairing chemicals from the pelt, lowering the pH, deswelling and preparing the pelt for following bating operation (Sivakumar, et al., 2015). 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 (Abraham and Maria, 2009; Chemours). High ammonia content in the tannery effluent increases biological oxygen demand (BOD) due to nitrification reaction causing death of fish and aquatic organisms (Streicher, 1988).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

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 (Yunhang, et al., 2011).

Glycolic acid can be used for non-ammonia deliming because it penetrates hides rapidly, reduces operation

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time and improves grain quality by eliminating excessive pelt swelling (Chemorous). Since glycolic acid has a lower pH, EDTA was mixed with glycolic acid in our research work because it can act as buffer at pH higher than 7.0 and also has super lime dissolving capacity (Cube Bitech).(College of Science). 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.

MATERIALS AND METHODS

Materials

Goat skin was supplied by commercial hide brokers. Limed hide was produce 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% developed deliming agent and 100% water were added and drummed for 60 minutes. The developed deliming agent was prepared by mixing 70 wt.% of glycolic acid in water and EDTA in the ratio of 10: 1 (v/w). After that further conventional procedure (batting, 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 (Germann and Eberle, 2001). 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 (Putshaka, et al., 2013). 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 calcium solubility (extent of calcium removal) was measured using Atomic absorption spectrophotometer (Agilent 240 AA) according to the method mentioned in literature (Yunhang, et al., 2011).

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 Chemist and Technology (SLTC) methods SLP 6, SLP 6 and SLP 7 respectively (SLP 6 and SLP 7, 1996).

RESULT AND DISCUSSION

Effectiveness of deliming agents

From the Table 1, the deliming value of the developed deliming agent is 1.86, which is almost similar to ammonium sulphate (1.81) after titration against 3% $Ca(OH)_2$.

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 (Michael, 1990). Therefore, it is necessary for deliming agents to have a buffering action to control the deliming pH in the desired range. The developed deliming agent shows the buffering action in the pH range 7.5 to 8.0, whereas ammonium sulphate shows in the range of 8.5 to 9.0. As buffering effect of developed deliming agent occurs in pH higher than 7.0, so there is no possibility of acid swelling.

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 (Ping, 2001). (Fig. 1 and 2) shows that the extents of calcium removal of delimed pelts in experimental and controlled trials were approximately 51 and 54% respectively. It suggests that the developed deliming agent has excellent action in calcium solubility and elimination of uneven dyeing and fatliquoring which results in improvement of leather quality.

Table 1. Deliming value of developed and conventional deliming agent

Deliming agent	Deliming value
Developed	1.89
$(NH_4)_2SO_4$	1.81

The above analysis of deliming value, buffer capacity and calcium solubility 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 ammoniacal 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 2.

From Table 2 the ammonia nitrogen generation in experimental deliming process is about 3.50 mg/L which is 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 (approximately 1150 and 3500 mg/L respectively). The control trial results high amount of sulphide content 5280 mg/L whereas the experimental trials shows the value about 25 mg/L. This result suggests that, sulphide content is remarkably reduced (99.5%) by developed the deliming agent.

Analysis of leather

The physical properties of experimental and control crust leathers are illustrated in Table 3. From the table tensile strength of experimental crust leather

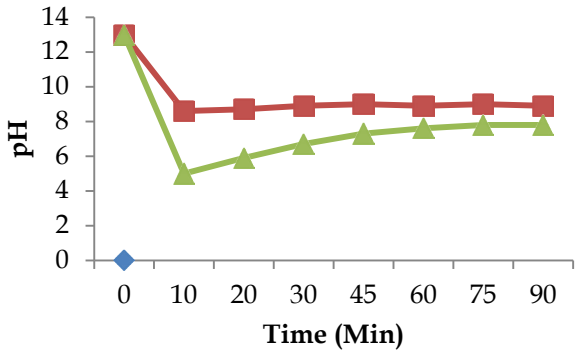

Fig. 1 Change of pH of deliming liquor during deliming operation.

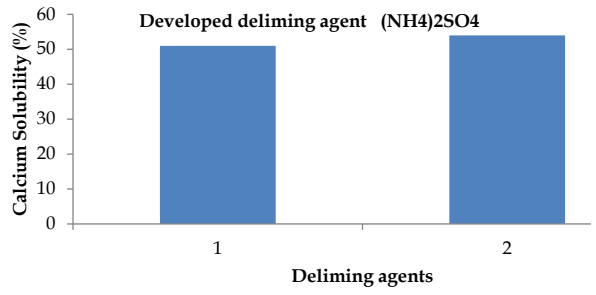

Fig. 2 Calcium solubility of deliming agents.

Table 2. 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 3. Evaluation of physical properties of goat crust leather

Deliming agent	Tensile Strength (daN/cm^2)	Elongation at break (%)	Tear Strength (N/cm)
UNIDO	min. 100	max. 60	min. 15
Ammonium sulphate	135.0	59.2	28.7
Experimental crust leather	132.31	57.17	25.5

is 132.31 daN/cm^2, which is above the minimum acceptable limit (100 daN/cm^2) reported by UNIDO (New York, 1976). The elongation at break value of experimental leather was 57.17%, which is very close to the limit (max. 60%). Tear strength obtained for experimental trials is (25.5 N/cm) also above the sub-limit (min. 15 N/cm).

CONCLUSION

The developed deliming agent has higher deliming value, strong buffering action in the pH range 7.5-8.0 and excellent action in calcium solubility. Combination of these values proves the effectiveness of the glycolic acid and EDTA based deliming agent. The BOD, COD values and sulphide content are quiet 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 from ammonia. The physical 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 later.

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