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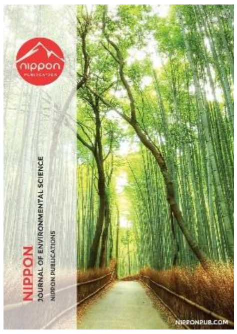

Full Length Research Paper

Development of conventional ammonia free deliming agents in leather manufacturing in regarding the environmental pollution control

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Abstract. Environmental pollution is a major concern for leather industry. During leather processing, a large amount of waste is generated and their disposal into water bodies without proper treatment has a detrimental effects on environment. Tannery effluent is composed of several kinds of liquid waste: soak, lime, delime & bate, pickle & chrome. Deliming is one of the important steps in leather processing which is mainly based on ammonium salts. In conventional deliming process, a significant amount of ammonia is released which leads to further demand for critical wastewater treatment. Ammonia gas is highly soluble in water and responsible to create adverse environment for aquatic life. In this research work some weak organic acids like tartaric acid, propanoic acid, lactic acid, salicylic acid and para-hydroxy benzoic acid were used as deliming agent to decrease the pH of the reaction mixture as well as to reduce pollution load in tannery waste water. Deliming efficiency of used weak acids, physico-chemical properties of tannery effluent and physical properties of leather such as tensile strength, tear strength, lastometer test, water vapor permeability, flexing endurance and color fastness were comparable with the conventional delimed leather. The experimental results showed that the significant amount of pollution load as well as the costing of finished leather processed by developed deliming agent was significantly reduced although the quality of leather remain similar or better than conventional method.

Keywords: Deliming, Tannery effluents, Environment, Pollution load, Tensile strength

1. INTRODUCTION

Leather industry has been attracted a considerable attention due to the environmental pollution. It generates huge amount of solid, liquid and gaseous pollutant that can have adverse impact on the environment. In tanning several major steps such as soaking, liming, deliming, bating, pickling etc. are involved. In leather production, liming operation is performed to remove the epidermal structure, open up fibrillar structure and make it ready for further operation (Chowdhury et al., 2018). The pH in liming operation remains 12-13. At the end of the liming process the pH have to be reduced by adding acid for next operation. Deliming is the process of neutralizing alkali used during liming and unhairing of hides and skins in leather manufacturing (Colak and Kilic, 2007). The main aim of deliming is to remove effectively the alkaline materials in the limed hide and help processing material to penetrate into hide. As a result the pelt becomes partially reversing the swelling which is suitable for the next tanning operation (Datta and Sivakumar, 2015). The removal of alkali from pelt before tanning is important and essential before going to the next step of the process. If the pelts are directly introduced into vegetable tanned liquor without going through the deliming process, the lime present in the grain and flesh sides will quickly darken the color of vegetable tanning and maximum chromium will be fixed to the grain and flesh sides which will prevent further penetration of chromium into the pelt in chrome tanning. This type of uneven distribution of chromium causes stiffness, paperiness of the finished leather and roughness of the grain surface (John, 1997). Conventionally ammonium salts are used as deliming agent because it penetrates quickly into the hide and has a good buffering action (Ghimenti, 1994; Chowdhury et al., 2018). But ammonium salts based deliming agents generate a significant amount of ammonia which is highly soluble in water (Sui et al., 2012). About 70% of the ammonium ions discharged in tannery effluent is the result of the use of ammonium sulphate in the deliming and bating operation (Kolomaznik et al., 1996). When ammonium salts like ammonium chloride and ammonium sulphate are used as deliming agent, they react with lime to form calcium salt, ammonia and water. Reactions involved are given below:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NH_3 + 2H_2O$$

Since ammonia is highly soluble in water, excessive discharge of ammonia nitrogen from waste water results in eutrophication of lakes, river and coastal waters and depletion of dissolve oxygen in receiving water (Yunhang et al., 2011). Besides, the toxic ammonia gas leads to unsafe working conditions and results in diseases like methemoglobinemia and hepatic encephalopathy (Lemberg and Fernandez, 2009). So, the reduction of ammonia in leather industry is important in regarding to the environmental pollution control. To remove ammonia from tannery effluent is often very difficult and expensive in effluent treatment plant (Colak and Kilic, 2008). So, to avoid the formation of ammonia, non-ammonia deliming technology is needed to be introduced. Many non-ammonia deliming method such as citric acid (Colak and Kilic, 2007), epsom salt (Koopman, 1982) carbon dioxide (Ochs, 1953; Deng et al., 2015; Hu and Deng, 2016) magnesium salt (Kolomaznik et al., 1996), extract of leaf of Hibiscus (Putshaka et al., 2013), weak acids (Colak and Kilic, 2008; Wang et al., 2016), mixture of acetic acid and sodium acetate (Kong et al., 2016), sodium gluconate (Zeng et al., 2018), gallic acid (Sivakumar et al., 2015), glycine (Chao et al. 2020), peracetic acid (Sirvaityte et al., 2009) have been introduced in leather production. But, due to their certain limitations, availability and environmental respect etc. most of them could not able to use successful as ammonia free deliming agent in leather production. In CO_2 deliming, it avoid the formation of ammonia but it needs special equipment and only suitable for limed split. Formic acid, lactic acid, and citric acid could prevent pollution during deliming process, but they have little buffering capacity in the pH range of 8.0 to 9.5. They penetrate limed pelt relatively slowly and tend to cause acid swelling of pelt (Chao et al., 2020). Therefore, it is important to find out an alternative deliming agent which would be suitable for industry in environmental respect. Current research is an endeavor to develop an industrially viable deliming agent based on organic acid which evolves no ammonia and low production cost. As part of our ongoing research on the environmental pollution control of tannery effluents, the efficiency of the developed deliming agent, its effect on the quality of leather and discharged effluent have been studied and presented in this paper. Conventional ammonium salt also used as control group to compare its result with the developed deliming agent.

2. MATERIALS AND METHODS

2.1. Materials and Methods

Ten pieces of wet salted Goat skins were taken for the experimental trial. In experiment 1, conventional ammonium sulfate was used as control group and from experiment from 2 to 10 was considered as experimental group. Wet weight of the experimented goat skins were 1-1.5 kg. Soaking, painting and liming processes were done by conventional process to make the skins ready for deliming process. The limed pelts were washed and taken in several drums for deliming with selected deliming agent. Chemicals used for leather processing from raw to full chrome upper leather were commercial grade whereas chemicals used for the determination of pollution load in the effluents and to check the penetration efficiency were analytical grade. All % of chemicals were taken based on wet salted weight.

2.2. Deliming efficiency

Deliming efficiency of used organic acids was determined by using phenolphthalein indicator. The experimental group and control group delimed pelt were cut with a sharp knife during the deliming process done. Then phenolphthalein indicator was used at the cross section area of delimed pelt and no pink color was observed which indicates completion of deliming process.

2.3. Determination of pollution load in deliming effluents

Physico-chemical properties such as BOD_5, COD of the effluents generated from both control group and experimental group were determined by American standard method (APHA, 2012) and TDS was measured by TDS meter.

2.4. Analysis of leather

To ascertain the quality of leather processed by newly developed methods, some physical test such as tensile strength, tear strength, grain crack and distension were carried out according to International Standards regarding IUP methods used IUP 06, IUP-08 and IUP 09 respectively (IUP, 1958), stitch tear strength was carried out according to DIN-53331, flexing endurance, water vapor permeability test, color rub fastness test was carried out according to International Standards regarding SATRA PM 55, SATRA PM-172 and SATRA PM-08 (SATRA, 2011). According to ISO standards, samples for physical and mechanical testing are taken not only parallel to the backbone; they are taken in both directions (parallel and perpendicular) to the backbone. The strength properties and other test results were compared with standard value as well as conventional shoe upper leather.

3. RESULTS AND DISCUSSION

The main objective of deliming is to decrease the pH of limed pelt from 12-13 to 7-9 for the suitable condition of subsequent batting operation. Conventionally ammonium salts are used in this step of leather processing because of their good penetration capacity and formation of better buffering environment of pH 8-9 with alkali in the pelt to make it softer (Leafe, 1999). Due to the generation of toxic ammonia gas in conventional method, weak organic acids were used to replace it in the current research. The results of completion of deliming time of both experimental and control trial, pH of the cross section of pelt after completion of liming and costing of various deliming agents are shown in Table 1. The completion time of present deliming process was less than conventional deliming process.

Table 1. Required time, pH and comparison of cost of several deliming agent

Expt. No.	Chemicals used as a deliming agent[a]	Deliming Time(min)[b]	pH	Cost (USD)
1.*	2.0% Ammonium Sulphate 0.5% Bi-sulphite	45	8.4	0.24
2.	0.4% Tartaric acid	40	7.4	0.19
3.	0.6% Tartaric acid	30	7.6	0.28
4.	0.4% Propanoic acid	40	7.2	0.11
5.	0.6% Propanoic acid	30	7.4	0.15
6.	0.5% Lactic acid	40	7.5	0.19
7.	0.7% Lactic acid	35	7.4	0.23
8.	0.5% Salicylic acid	35	8.2	0.12
9.	0.6% Salicylic acid	30	8.4	0.14
10.	0.4% Para hydroxy benzoic acid	50	7.8	0.14

*Sample 1: conventional deliming process, control group
[a]The percentage was based on the weight of limed pelt.
[b]Time of complete penetration checked by phenolphthalein indicator.

Experimental results show that deliming time in the experimental group was lower than the control group. Among the weak acids used in this research as deliming agent, 0.6% tartaric acid, propanoic acid and salicylic acid delimed pelt became colorless to phenolphthalein indicator by 30 minutes whereas ammonium sulphate delimed pelt required 45 minutes. This faster penetration capability of developed deliming agent will prevent excessive mechanical action on the pelt that may cause a creak of fibers and a looseness of the leather. The pH of liming float was determined as 13. The pH of the developed deliming float of the experimental group was similar to the control group, ammonium sulfate deliming. Most important concern in conventional method was formation of toxic ammonia whereas in current system there is no chance to produce ammonia gas.

The physio-chemical test results such as BOD_5, COD and TDS of discharged waste water are given in Table 2. BOD_5 is the biological oxygen demand of the effluents generated from both control and experimental group measured over 5 days at constant temperature which estimated the amount of oxygen required for biochemical degradation of organic matter by metabolic activity of aerobic microorganism (Zeng et al., 2018). The BOD_5 value of the experimental group was in the range of 240 – 530 mg/L which was very much lower than that of conventional deliming agent (1090 mg/L). The BOD_5 of the experimental group was reduced by 51% to 88% which indicates the reduction of significant amount of pollution load in these methods. 0.6% salicylic acid gave the best result (88% reduction).

Table 2. BOD_5, COD and TDS value of the effluents

Expt. No.	Type of Leather Effluent	BOD_5 (mg/L)	COD (mg/L)	TDS (ppm)
1.	2.0% Ammonium Sulphate, 0.5% Bi-sulphite	1090	3744	332
2.	0.4% Tartaric acid	430	1920	158
3.	0.6% Tartaric acid	480	960	202
4.	0.4% Propanoic acid	420	1440	157
5.	0.6% Propanoic acid	470	960	154
6.	0.5% Lactic acid	370	1440	134
7.	0.7% Lactic acid	400	480	124
8.	0.5% Salicylic acid	240	2400	171
9.	0.6% Salicylic acid	260	1440	164
10.	0.4% Para hydroxy benzoic acid	530	2496	184

The COD and TDS values of conventional deliming process were 3744 mg/L and 332 ppm respectively which were higher than those generated in currently developed deliming process. The COD value and TDS could be reduced to 87% and 62% respectively by using 0.7% lactic acid as deliming agent. Since BOD_5, COD and TDS value of experimental group were very much lower than the conventional ammonium salts delimed which indicates that these delimed effluents contain less pollutants as a result cost of waste water treatment also will be reduced significantly.

3.1. Physical testing

Table 3. Physical testing result of various leather:

Expt. No.	Deliming agents	Name of Test						
		Tensile Strength (N/mm^2)	Stitch Tear Strength (N/mm)	Baumann Tear Strength (N/mm)	Water Vapor Permeability ($mg/cm^2/hr$)	Flexing Endurance (After 50000 cycle)	Color Rub Fastness	
							Color Change	Felt Rating
1.	2% AS and 0.5% BS	21.9	95	38	4.81	3/4	5	5
2.	0.4 % TA	20.8	88	38	3.12	3/4	5	5
3.	0.6 % TA	20.6	92	45	2.99	3/4	5	5
4.	0.4 % PA	25.0	95	50	3.36	3/4	5	4/5
5.	0.6 % PA	23.0	85	42	3.01	3/4	5	5
6.	0.5 % LA	24.6	101	56	5.53	3	5	5
7.	0.7 % LA	20.6	102	44	2.99	3/4	4/5	4
8.	0.5 % SA	20.5	106	50	5.80	3/4	5	5
9.	0.6 % SA	27.7	107	54	2.65	3/4	5	5
10.	0.4 % PHBA	26.0	102	43	4.40	3/4	5	5
Standard Value [UNIDO]		Min 20.0	Min 80	Min 30	Min 1.0	Max 3/4	Min 3	Min 3

Expt. 1- Conventional method, AS- Ammonium Sulphate, BS- Bi sulphate, TA- Tartaric Acid, PA- Propanoic Acid, LA- Lactic Acid, SA- Salicyclic Acid, PHBA- Para Hydroxy Benzoic Acid

Tensile strength is the force per unit area of cross section required to cause a rupture of the test specimen. It depends upon the number of collagen fibers acting in the direction of applied load. According to IUP-06 method the test was carried out and UNIDO prescribed the standard value for tensile strength of shoe upper leather is minimum 20.0 N/mm^2. The tensile strength values of the leather samples were above the acceptable. The highest tensile strength value (27.7 N/mm^2) was observed with 0.6% salicylic acid delimed leather. Stitch tear strength is defined as the load required breaking the leather sample when the two holes diameter is 2 cm and they are 6 cm apart (IUP, 1958). Stitch tear strength test was carried out according to DIN-53331. The UNIDO standard value of stitch is minimum 80 N/mm and tear strength value of all analyzed leather were higher than the UNIDO standard, where some leather shown outstanding results.

Baumann Tearing strength values of all the leather obtained above the UNIDO standard 30N/mm which indicate all of them meet the international standard. The highest Baumann tearing strength (56 N/mm) was observed with 0.5% lactic acid delimed leather. Water vapor permeability is done to assess the breath ability of leather. The method is mainly applicable to leather and textile because it gives a measure of the ability to remove perspiration from the surface of the wearers skin. The water vapor permeability values of the analyzed leather were in a range 2.65-5.8 mg/cm^2/hr. According to UNIDO, leather must have water vapor permeability of minimum 1.0 mg/cm^2/hr. And all the samples showed a great performance with two to five times higher than the minimum requirement.

Flexing endurance test is simple folding of the leather in several times with the grain side out. This property is very important in case of shoe upper leather because during walking the vamp portion undergoes repeated flexing and by this test result the quality of leather can be easily determined. The leather and its finish shall have high flexibility to prevent the appearance of cracks (IUP, 1958). The samples were used for vamp flex applying the IUP 20 testing method by using flexometer. The test result of this method has been presented in Table 3. According to UNIDO the performance requirement for leather after 50000 cycles in break pipiness scale rating is maximum 3/4. The laboratory test results show that all the finished leather meet the UNIDO standard except 0.5% lactic acid delimed leather. According to SATRA PM-08 the leather samples were rubbed by wet or dry circulated cotton felt under a constant contact force. After 1024 cycle the color change on felt and leather should be 5-3 in gray scale rating and all type of leather meet standard value. Poor quality leather causes bleeding of color and creates uneven color.

Lastometer test results of shoe upper leather processed by developed deliming agent as we as conventional ammonium sulphate delimed leather are shown in Figure 1.

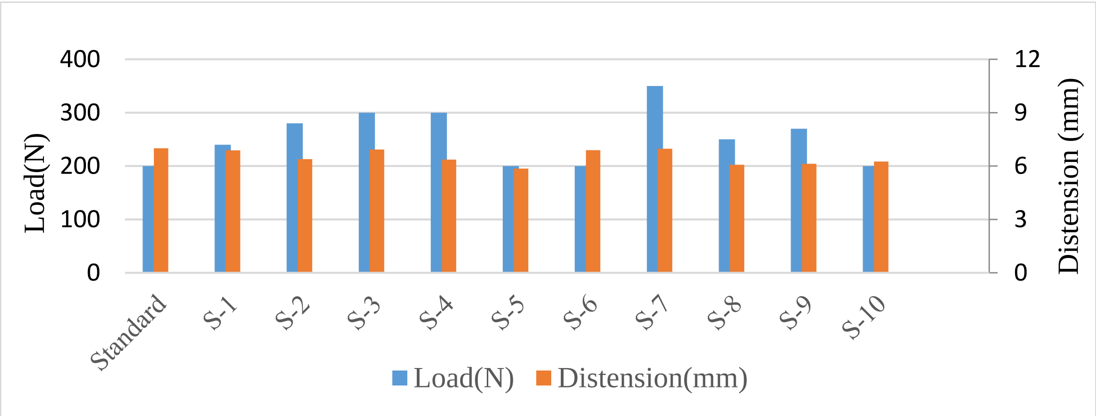

Figure 1. Lastometer test value of leathers

Lastometer is one of the most important tests for shoe upper leather. It is the load required to crack the leather sample. The high value of grain crack strength indicates that the upper leather will not crack at the sharp edge of the last during lasting operation of shoe making. The load required just to crack the grain and the vertical lift of the load is distension. Lastometer test result shows that the experimental value of all analyzed leather were higher than the minimum acceptable limit, 20 Kg (UNIDO, 1996) in load whereas distension values were less than 7 mm which indicates the good quality of leather.

3.2. Thermogravimetric analysis (TGA) of leather

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption, adsorption and desorption; as well as chemical phenomena including chemisorption's, thermal decomposition, and solid-gas reactions (Coats, A. W., 1963). The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. In order to test leather sample temperature from 100°C to 700°C was used. Two experimental group and one control group finished leather were analyzed by TGA. Their results are shown in Figure 2.

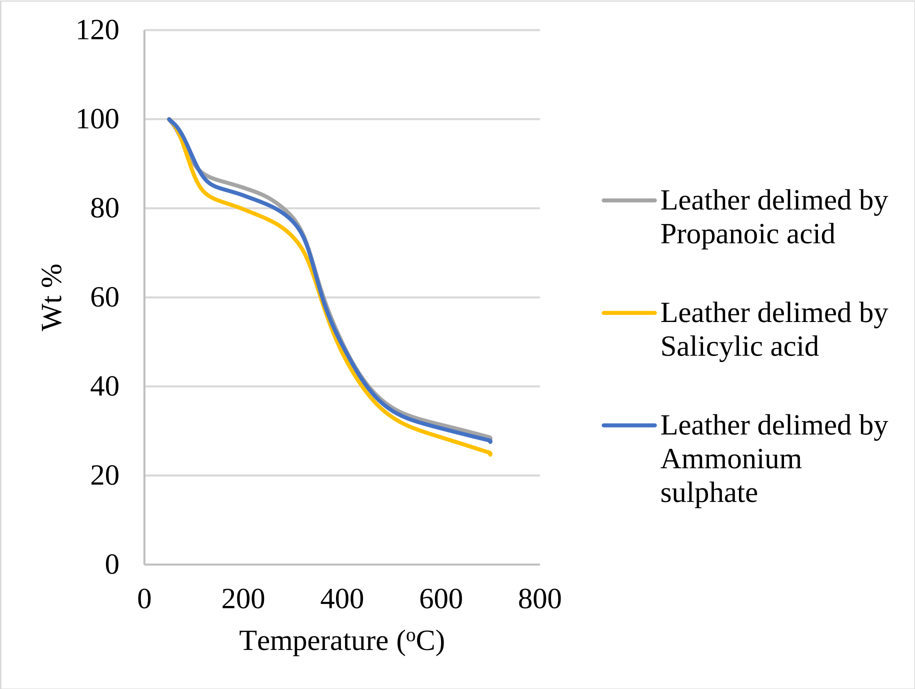

Figure 2. TGA curve of leather sample

Three very similar curves were obtained from TGA analysis which indicate that use of alternative chemicals in deliming process do not have much impact on leather. So, these alternative chemicals can be easily used as deliming agent. Curves showed initial weight loss of each sample at around 100^{o}C due to the evaporation of volatiles with the elevated temperature and 2nd time sharp weight loss of leather at around 300^{o}C due to the breaking of bonds and finally decomposition of leather fibers.

3.3. Cost estimation

In order to make the calculation easy, all the cost was calculated based on 1 kg weight of goat skin even in experiment different weight were used. The cost of conventional deliming agent and several developed deliming agent are given in Table 1. The cost for conventional deliming agent was 0.24 USD per 1 Kg wet weight goat skin. The cost of all developed deliming agent were lower than that of conventional ammonium sulphate and bisulphate except 0.6% of tartaric acid. Other way, since the delimed liquor from the newly developed deliming agents contains less amount of pollutants than conventional method which would be significantly reduced waste water treatment cost. Considering the chemical cost and other physical test results propionic acid would be the best deliming agent among other weak acids used in this research.

4. CONCLUSION

In leather processing it is a burning issue for liberation of ammonia because ammonium salt are used in deliming step which has an adverse effect on worker's health as well as on environment. To address the environmental pollution control, tartaric acid, propanoic acid, lactic acid, salicylic acid and para-hydroxy benzoic acid were used as deliming agent to replace the ammonium salts. The BOD_5, COD and TDS content of the waste water generated from experimental group trial were less than the conventional deliming agent trial. These results revealed that the developed system could be reduced a significant amount of pollutants in leather processing. In addition to that, no ammonia could be generated in this process which is also significant for the environmental pollution control. Cost of developed deliming agents also less than conventional ammonium sulphate and bisulphate. Due to high penetration rate of experimental deliming agents the pelt became delimed within short time and prevented excess mechanical damage to the pelt. Physical test results show all categories of experimented leather meet the international standard values. Considering above all, newly developed deliming agent could be an excellent alternative system as ammonia free deliming process which would more environmental friendly and cost effective for leather production.

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