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Reducing The Use of Lime in Leather Tanning Process

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ABSTRACT:
Leather tanning is associated with high pollution levels due to the use of hazardous chemicals, particularly during the unhairing step. To address this issue, researchers have been exploring ways to reduce or eliminate the use of these chemicals. One approach is to decrease or remove the use of lime in the unhairing process. The current study aimed to evaluate alternative chemicals to replace lime during unhairing and assess their impact on wastewater characteristics and leather properties. Three unhairing methods were tested, including the conventional method using lime, one using sodium hydroxide to reduce lime usage, and one using sodium aluminate instead of lime. Standard procedures were used to measure the wastewater characteristics, including chemical oxygen demand, biochemical oxygen demand, total solids, and dissolved solids. The physical, chemical, and organoleptic properties of the tanned leather were also assessed. The results showed that the alternative methods reduced the environmental parameter values by up to 50% compared to the conventional method, indicating the potential for significant environmental benefits. The tanned leather properties were largely similar among the three groups, and scanning electron micrographs did not show any significant effect on the overall leather structure from the alternative methods. However, the reduction in using lime decreased scratches and deposits on the leather surface, could still benefit the final product quality. Of the three alternative methods tested, replacing lime with sodium aluminate had the least environmental impact without negatively affecting the quality of the produced leather. These findings suggest that using sodium aluminate or sodium hydroxide as alternatives to lime in the unhairing step of the leather tanning process could be an effective approach for reducing pollution levels and improving the environmental sustainability of the industry especially as it is easy to apply.
Keywords: *Hides, Environment, Leather properties, Unhairing.*

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I. INTRODUCTION

The leather tanning industry has been an integral part of human civilization for thousands of years, with leather serving various purposes such as clothing, footwear, accessories, furniture, and more [1]. The leather tanning process is complex, consisting of three primary stages: pre-tanning, tanning, and post-tanning, each with a series of sequential steps that may vary depending on the type of skin and intended end-use of the leather. One crucial step in the process is unhairing, which removes unwanted hair, flesh, and fat from the hides and skins to prepare them for tanning. Unhairing plays a vital role in ensuring that the final product meets quality specifications and is smooth and uniform in color [2,3].

Traditional methods of removing hair from animal hides involve the use of chemicals like sodium sulfide and lime. Lime is a low soluble alkaline in water that increases the pH and causes slight swelling. Additionally, the calcium hydroxide produced from lime reacts with sodium sulfide to form calcium sulfide and sodium hydroxide. The calcium sulfide then reacts with keratin protein in the hair to break the disulfide bonds and dissolve the hair from the hides/skins [3,4]. However, conventional unhairing methods have negative environmental impacts as they can seep into soil and water and cause contamination. Furthermore, the waste generated from this process, such as hair, flesh, and fat, can also contribute to environmental pollution. Although lime can cause gradual swelling due to its low solubility, it is not an eco-friendly option due to the large amounts of lime sludge and total solids it produces [5-7].

Previous investigations have developed various techniques to address these environmental concerns, focusing on three primary approaches: lime reduction as possible by using less dangerous chemicals [7,8], use of unhairing enzymes [9-11], or applying a save hair technique by mechanical hair removal [12]. While the latter two methods are environmentally friendly, requiring less usage of chemicals and generating less waste, their adoption was limited in tanneries due to the need for precise control when using enzymes and the significant energy and water resources required for mechanical hair removal. Consequently, one alternative approach to traditional lime unhairing is the use of other chemicals such as sodium hydroxide or sodium aluminate to reduce the use of lime and sodium sulfide. The amount of lime used in the unhairing step was reduced by adding different ratios of sodium hydroxide instead [8]. Sodium hydroxide is a strong alkaline that is known to dissolve keratin protein [10]. On the other hand, Širvaitytė et al. [7] did not use lime at all in the unhairing step and instead added sodium aluminate. Sodium aluminate reacts with water to produce sodium hydroxide and aluminum hydroxide. The sodium hydroxide produced in the first step then reacts with keratin to form water-soluble keratin, which breaks down the keratin protein in the hair and allows it to be dissolved and removed from the hides [7].

Therefore, this study aims to compare the effectiveness of sodium hydroxide or sodium aluminate as alternatives to the traditional method of using lime and sodium sulfide in unhairing, assessing their impact on environmental pollution and changes in the quality of the leathers resulting from these methods.

II. MATERIALS AND METHODS

Materials

For this study, a total of fifteen salted camel hides pieces measuring 20 x 20 cm were utilized. The chemicals utilized in the leather processing were of commercial grade and commonly used in leather tanning. Sodium hydroxide and sodium aluminate were obtained from the El-Gomhouria Company, Egypt.

Methods

The leather tanning experiments were conducted in Elshafei Sons's tannery in El-Max, Alexandria, Egypt, while the taken samples were analyzed at the laboratories of Mariout Research Stations, Desert Research Center, Ministry of Agriculture, Egypt.

Leather tanning

The camel hides pieces were treated with tanning chemicals in a small drum that rolled at a rate of 15±1 cycles per minute. The salted camel hides pieces were soaked in water for 24 hours and washed the next day. Before the unhairing step, the hide pieces were randomly divided into three groups. Lime and sodium sulfide were used for the first group (control), while the second and third groups underwent unhairing using sodium hydroxide or sodium aluminate, respectively. Table (1) shows the variations among the three experimental groups during the unhairing step. After the deliming step, the pelt pieces were marked and kept together throughout the subsequent steps of chrome leather tanning, up until the final finishing step.

Table 1. The unhairing step for each experimental group.

Group	Unhairing step*	Reference
Control	The hide pieces were soaked in a solution consisting of 150% H_2O, and 1.5% $Ca(OH)_2$. The drum was then run continuously for 45 min. Next, 1.5% Na_2S flakes were added and the drum was run continuously for 120 min. After this, 50% H_2O and 2% $Ca(OH)_2$ were added and the drum was run continuously for 120 minutes. Finally, the drum was adjusted to run for 5 minutes after stopping for 180 minutes, with a total duration of 24 hours.	[12]
Sodium hydroxide	The hide pieces were soaked in a solution consisting of 100% H_2O, 0.5% $Ca(OH)_2$, 0.25% NaOH and 1.5% Na_2S. The drum was then run intermittently (run 20 minutes and stop 20 minutes). Later, the drum was adjusted to run for 5 minutes after stopping for 180 minutes, with a total duration of 24 hours.	[8]
Sodium aluminate	The hide pieces were soaked in a solution consisting of 100% H_2O, 2.5% $NaAlO_2$, and 1.5% Na_2S. The drum was then run continuously for 8 h. Later, the drum was adjusted to run for 5 minutes after stopping for 180 minutes, with a total duration of 24 hours.	[7]

* All percentages were based on hide pieces weights.

Characteristics of unhairing and deliming wastewater:

After unhairing and deliming steps, the wastewater samples were taken from each group to determine Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Solids (TS), and Total Dissolved Salts (TDS) contents according to APHA [13].

Tanned leather properties:

Different finished leathers underwent physical and chemical testing using ASTM methods [14]. The specimens were conditioned for 48 hours at 20 °C ± 2 °C and 65% ± 4% R.H. Physical properties, such as thickness, tensile strength, elongation percentage at break, and split tearing strength were measured. The reported values were the average of three specimens. Chemical properties, including pH, moisture %, and ash % content, were also studied. The organoleptic properties of the tanned leathers were evaluated by five experienced tanners using the standard tangible evaluation technique [15]. These properties included softness, grain smoothness, grain tightness, fullness, and general appearance, rated on a scale of 1 to 10 points for each property, with higher points indicating better quality.

Scanning electron microscopy:

The tanned leather samples underwent a process of coating with gold ions using sputter coating and were then examined using an electron microscope, specifically the JEOL JSM-5300, to gather micrographs of both the surface and cross section.

Statistical analysis

To evaluate the differences among the various treatments, the data was analyzed using the statistical package for social science (SPSS) version 25 [16]. The fixed model employed in the analysis of the effect of unhairing method is described by the following equation:

$$Y_{ij} = \mu + T_i + e_{ij}$$

Where, Y_{ij} represents the observation taken (k), μ is the overall mean, T_i represents the fixed effect of the unhairing method (either conventional, sodium hydroxide, or sodium aluminate), and e_{ij} represents a random error that is assumed to be normally distributed with a mean of 0 and a variance of σ^2e.

III. RESULTS AND DISCUSSION

Characteristics of unhairing and deliming wastewater:

As shown in Figures (1, 2, 3 and 4), the wastewater characteristics during the unhairing and deliming steps of the three groups under investigation are presented. It is noteworthy that the levels of COD, BOD, TS, and TDS contaminants were higher in the unhairing step compared to the deliming step. This is due to the high concentrations of the chemicals used and the organic matter that comes out from hides in unhairing step, such as hair, fats, and flesh, which is consistent with previous investigations [5, 7-9]. The conventional method resulted in significantly higher levels of pollutants (P< 0.01) than the other two groups studied, with an increase of approximately 50% in the amount of pollutants. Moreover, the sodium aluminate group had significantly lower levels (P<0.05) of pollutants produced than the sodium hydroxide group in the unhairing step, while the differences between the two groups were insignificant in the deliming step. That may be as a result of using small amounts of lime in the sodium hydroxide group, whereas lime was not used with the sodium aluminate group.

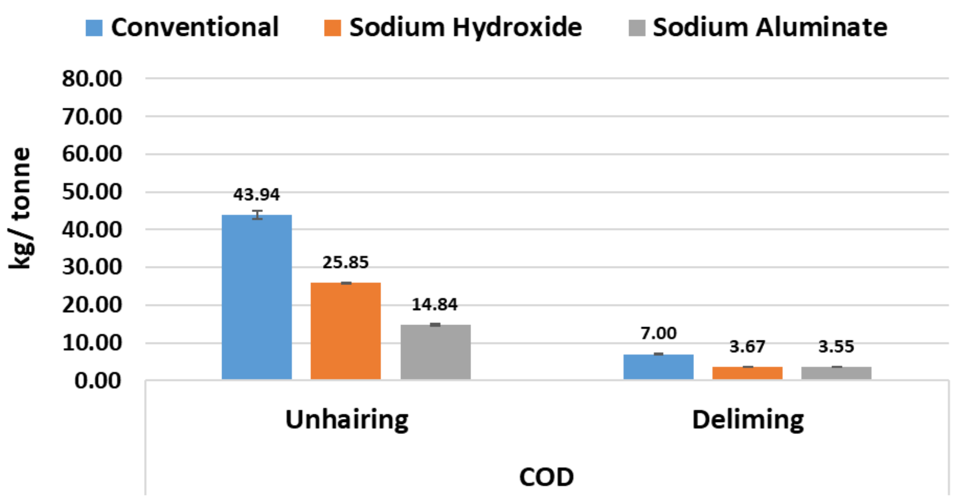

Fig. 1: Chemical oxygen demand of unhairing and deliming steps of studied groups.

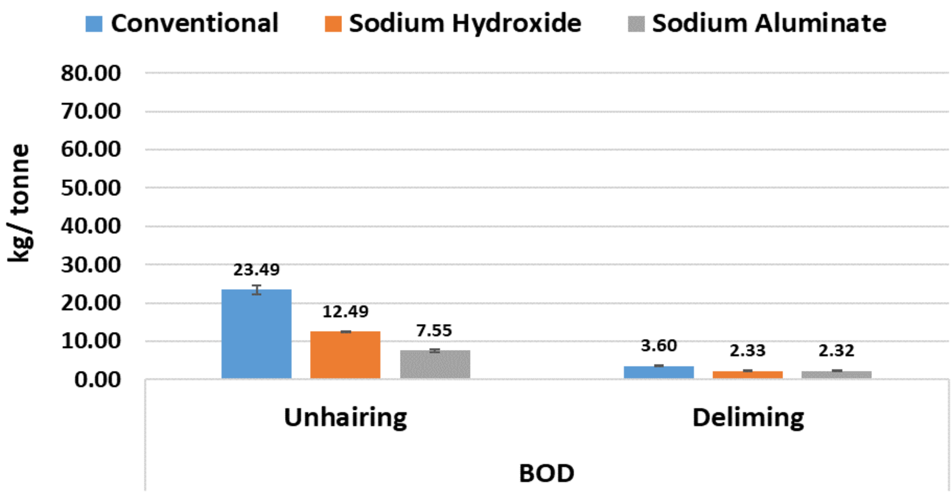

Fig. 2: Biological oxygen demand of unhairing and deliming steps of studied groups.

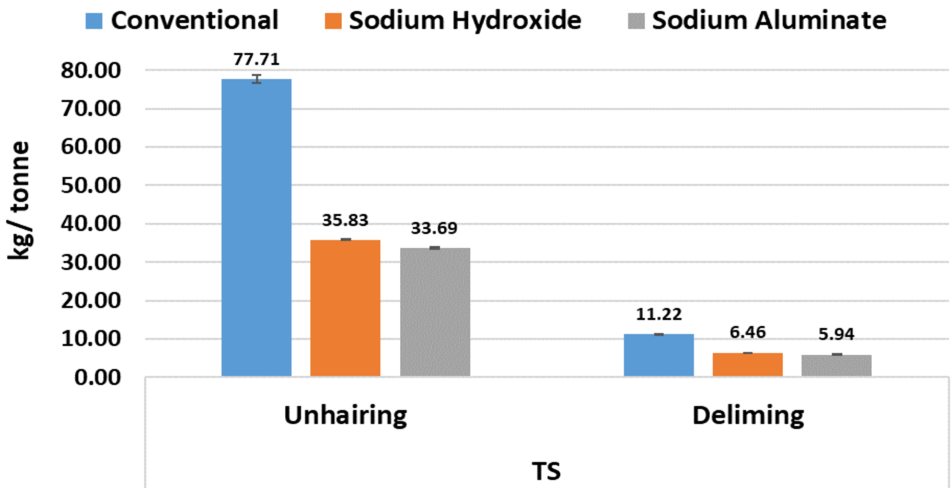

Fig. 3: Total solids of unhairing and deliming steps of studied groups.

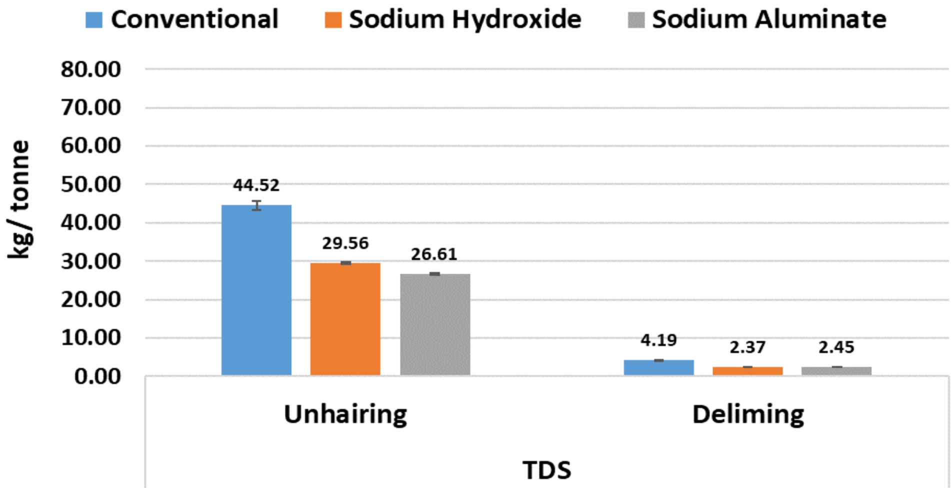

Fig. 4: Total dissolved salts of unhairing and deliming steps of studied groups.

The reported values in earlier studies for COD, BOD, TDS, and DS in the unhairing step of the leather tanning process ranged between 30-100, 15-40, 90-200, and 70-120 kg/tonne, respectively, while in the deliming step, the corresponding values were between 2.5-14, 1-6, 4-20, and 2.5-10 kg/tonne, respectively [5-7,12,17]. The statement indicates that the values obtained in the current study for both the unhairing and deliming steps fall within the ranges of these investigations, suggesting that the findings of the current study are consistent with earlier research. Additionally, the ratio between COD and BOD was found to be close to 2:1, which is in agreement with the findings reported by Page [18].

Therefore, these findings of environmental parameters suggest that the use of sodium aluminate may be a more environmentally friendly alternative to conventional method in the leather industry.

Tanned leathers properties:

The scanning electron micrographs of tanned leathers of the three studied groups in Figure (5) confirmed that the conventional method resulted in some precise scratches on the leather surface, which may be caused by the mechanical effect of non-dissolved lime particles during subsequent operations such as fleshing. Additionally, deposits were found inside the hair follicles, which could be attributed to lime particles that were not completely dissolved or to some parts of the hair that remained within the follicles.

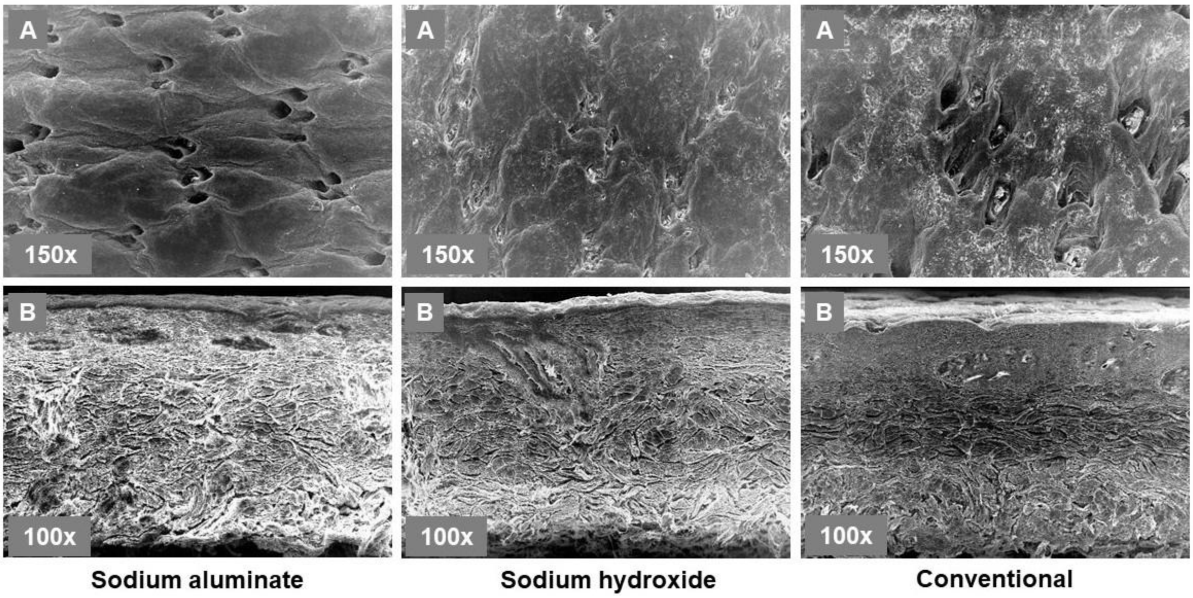

Fig. 5: Scanning electron micrographs of studied tanned leathers:
A: transverse image of surface
B: vertical image of cross section

The alternative methods of using sodium hydroxide resulted in lower scratches on the leather surface compared to the conventional method. The surface of the sodium aluminate group sample had the best results, with no scratches on the surface or deposits inside the follicles. These alternative lime chemicals can dissolve the hair more completely and leave fewer residues behind, which can reduce the likelihood of scratches forming during subsequent mechanical operations. Despite the lack of discernible differences in the vertical cross-sectional images resulting from the unhairing process, the application of sodium aluminate resulted in a more significant expansion of collagen fibers, suggesting a notable impact of sodium aluminate on the hide's structure. As noted by Širvaitytė et al. [7], the use of sodium aluminate is associated with the elimination of non-collagenous proteins, resulting in improved removal of these proteins and increased porosity of the hide. This increased porosity may explain the observed expansion of collagen fibers in the current study.

Overall, this may indicate that the alternative methods did not have a significant effect on the overall structure of the leather. Nonetheless, the reduction in scratches and deposits on the surface of the leather can still have a positive impact on the quality and aesthetic appeal of the final product.

Table (2) shows the physical and chemical properties of tanned leathers with the three studied groups of unhairing. The results indicate that there were no significant differences in most properties among the three groups. However, the tensile strength of the sodium hydroxide group was significantly lower than that of the conventional and sodium aluminate groups ($P<0.05$). This may be attributed to the fact that the sodium hydroxide method can dissolve the collagen fibers of the leather more completely, leading to a weaker mechanical strength [8]. This result highlights the importance of selecting an appropriate unhairing method that balances the desired level of hair removal with maintaining the mechanical properties of the leather.

After comparing the physical and chemical properties of the leather samples with the limitation ranges introduced by BASF [2] and UNIDO [19], it can be concluded that all of the studied tanned leather samples are suitable for use in certain manufacturing applications, such as footwear. The acceptable quality of the leather samples indicates that the alternative unhairing methods tested in this study, including the use of sodium hydroxide and sodium aluminate, do not have a detrimental impact on the final product quality. This suggests that these alternative methods have the potential to be used in commercial leather tanning operations as a more environmentally sustainable alternative to the conventional method that uses lime. As a whole, these results demonstrate the potential to reduce the environmental impact of the leather tanning industry while maintaining the quality of the final product.

Table (3) presents the results of the organoleptic properties of the three studied groups, which include fullness, grain tightness, grain smoothness, softness, and general appearance. The results indicate that there were no significant differences among the three groups in terms of these characteristics. This suggests that the alternative methods of unhairing, such as using sodium hydroxide or sodium aluminate, can produce leathers with similar organoleptic properties as the conventional method.

Table 2: Physical and chemical properties of tanned leathers.

Parameters	Unit	ASTM	Study Group			Overall means	SEM	Sig.
			Conventional	Sodium Hydroxide	Sodium Aluminate			
Physical properties								
Thickness	mm	D1813	1.96	1.85	1.99	1.93	0.055	ns
Elongation	%	D2211	27.43	31.71	20.68	26.61	2.033	ns
Tensile strength	kg/cm^2	D2209	219.20^a	186.77^b	214.68^a	206.88	5.765	*
Tear Strength	kg/cm	D4704	40.62	35.71	37.12	37.81	2.016	ns
Chemical properties								
Moisture	%	D6403	16.28	16.35	16.62	16.42	0.075	ns
Ash	%	D2617	5.13	4.9	5.03	5.02	0.18	ns
pH	mmol/L	D2810	4.49	4.53	4.56	4.53	0.02	ns

Means in the same row with different superscripts letter are significantly different (P<0.05).
SEM means standard error of means.
Sig. means Significant, ns means not significant, * means significant at P<0.05.

Table 3: Organoleptic properties of tanned leathers.

Group	Fullness	Grain tightness	Grain smoothness	Softness	General appearance
Conventional	8.80	8.00	8.00	8.80	8.60
Sodium hydroxide	8.60	8.00	8.00	8.40	8.40
Sodium aluminate	8.60	8.20	8.00	8.60	8.60
Overall means	8.67	8.07	8.00	8.60	8.53
SEM	0.13	0.18	0.22	0.12	0.14
Significant	ns	ns	ns	ns	ns

SEM means standard error of means.
ns means not significant

IV. CONCLUSION

This study suggests that alternative methods of unhairing, such as using sodium hydroxide or sodium aluminate, can produce leathers with similar physical, chemical, and organoleptic properties as the conventional method, while potentially improving the surface quality, as well as reducing the environmental impact of the unhairing process by a percentage that may reach 50% compared to the conventional unhairing method.

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