Improvement of Unhairing Operations in Tanning Process in Sudanese Tanneries

Mutasim Ahmed Ali¹, Alim A Haj Ali^{2*} and Mohammed HM Abuuznien¹

¹Department of Chemical Engineering, Engineering College, Karrary University, Omdurman, Khartoum, Sudan

²Department of National Leather Technology Center, Industrial Research and Consultant Center, Khartoum, Sudan

*Corresponding author: Alim Abd Elgadir Haj Ali, Department of National Leather Technology Center, Industrial Research and Consultant Center, Khartoum, Sudan, P.O Box: 5008; Tel: +249 18 531 37; E-mail: alim-ali74@hotmail.com

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Abstract

The negative environmental impact of the leather processing has been regarded as an inevitable consequence of that activity. In addition to high water consumption, soaking and liming with conventional unhairing method is one the most polluting part of the entire process of leather manufacture. The hair-save process proposed in this research utilizes conventional chemicals normally used in the unhairing process, but the hair fibre is firstly partially immunized by an alkali (lime) to be subsequently removed by the action of sulphide and ultimately recovered by filtration. The proposed process conducted in two trials in which 1.5% and 2.0% sodium sulphide of the hide's total weight were used, the process conducted had a significant reduction of the pollution load in comparison with the conventional unhairing in terms of BOD, COD and sulphide load. Results showed decrease in BOD, COD and sulphide levels by 12%, 70.9%, 71.7% in the first trial and 4.4%, 22.5%, 27.3% in the second trail respectively. The reuse of the recovered hair fibre in hair-save process is possible under certain conditions.

Keywords: Leather; Environmental impact; Unhairing; Polluting; Lime; Sodium sulphide; BOD; COD

Introduction

The tanning process aims to transform skins in stable and imputrescible products namely leather. There are four major groups of sub-processes required to make finished leather: beam house operation, tanyard processes, retanning and finishing [1]. Traditionally most of tannery industries process all kind of leathers, thus starting from unhairing to retanning processes. However, in some cases only pre-pickled leather is processed with a retanning process. Acids, alkalis, chromium salts, tannins, solvents, sulfides, dyes, auxiliaries, and many others compounds which are used in the transformation of raw or semi-pickled skins into commercial goods, are not completely fixed by skins and remain in the effluent [2]. The first treatment is unhairing where liming dealing affect the structure of the skin which results in a better reactivity of the skin containing collagen when it is exposed to liming agents. The liming step introduces chemicals such as lime and sodium sulfide which open up the fibre structure of the skin and hence provide more working surface for treatment with tanning agents [3]. The natural fats are partially saponified, most of the interfibrillary proteins such as albumins and globulins, mucoids are degraded and the derma is swelled [4]. The mechanism of unhairing process was described to be through the destruction of cementing substances, such as, keratin and glycoprotein, in the root of the hair. The addition of liming agent helps to break the disulfide bond on amino acid cystine, which is part of the keratin structure [5]. Leather industry has been categorized as one of the high polluting industries and there are concerns that leather making activity can have adverse impact on the environment. The global production of about 1.8 billion m² of leather; presents a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather processing [6]. Most of the steps of a tannery's operations are performed in water. Consequently, waste water is one of the major concerns in tanneries. The characteristics of (untreated) waste water are a high chemical and biochemical oxygen demand, and a high salt and process chemical content. The data have to be interpreted in the context of the processed hide weight and concentrations have to be discussed with regard to the loads. Large variations in concentrations may occur due to different water consumption and process types [7]. In addition to high water consumption, soaking and liming with hair-burning are the most polluting part of the entire process of leather manufacture in terms of nearly all key parameters (BOD, COD, Suspended Solids, TDS/ salinity and nitrogen [8]. The main pollutant in beam house operations is sulphides. The sulphide content in tannery effluents is due to the use of sodium sulphide, (and the breakdown of hair) in the unhairing process thus the objectives of this study to improve unhairing operations using new methods and evaluate the physico-chemical properties of polluted water discharged from these trails, viz., sulfide BOD, COD, TSS, TDS of traditional methods [5].

Materials and Methods

Source of materials

The samples were collected after preservation using a mixture of salt and boric acid from ELKadaro slaughter, Khartoum North, Khartoum , Sudan, latitude, and 15° 29' 29° N, and longitude 32° 29' E. Chemicals used for the experiment and analysis were of analytical grade.

Experimental design

The experimental design was outlined in randomized complete design with three treatments; t1 indigenous method; 3.5% sodium sulphide; and t2 modified method; 2% sodium sulphide and t3 modified method; 1.5% sodium sulphide and the treatments replicated three times.

Unhairing trail

Four pieces of cow pelts; 40 kg; were weighed and soaked in experimental drum and run for 30 minutes with 40 litres of water. The pelts were re-soaked in a tank using 60 litres of water and then left overnight. In the second day the pelts were transferred to the drum and washed for 10 minutes then 10 litres of water and of 200 g calcium hydroxide were added and the drum was run for 15 minutes fallowed by adding 400 g of calcium hydroxide and 400 g of sodium sulphide and run for 20 minutes then rest for 20 minutes after this step the hair started to remove from the hide then 400 g of calcium hydroxide was added and run for 20 minutes then water in the drum was discharged and filtered and pumped again to the drum and then 400 g and 200 g of calcium hydroxide and sodium sulphide respectively was added then run for 30 minutes, the pelts were take overnight. The method was repeated using four pelts; weigh ~40 kg and 1400 g and 800 g of calcium hydroxide and sodium sulphide as the blank, and the samples of waste water collected and stored at 4°C to physico-chemical tests. The trail was repeated using traditional method in the paddle and utilizes 3.5% of sodium sulphide.

The tanning trials were completed to produced crust leather and produced leathers were stored to mechanical and physicochemical tests.

Physico-chemical proprieties of unhairing waste water

The physico-chemical analysis (pH, TSS, BOD, COD and sulphide) were measured according to ASTM [9-12] and the results in **Table 1.**

Mechanical and physico-chemical proprieties of leather

The samples were prepared according to SLP 1 and 2 then the specimens were subjected to conditioning according to SLP3. Thickness, tensile strength and elongation, tear strength and distension were measured according to (SLP 4, 6, 7 and 9) [13] and strength of grain, stitch tearing strength and tong tears strength were measured according to ASTM [14-16] and the results in **Table 2**.

Statically analysis

The data analysis of variance performed for comparison was conducted by using a computer program equipped with SPSS statistical analysis method at a significant level p=0.05.

Results and Discussion

Physico-chemical properties of unhairing waste water of traditional and modified methods

The **Table 1** showed the parameters of physico-chemical properties of unhairing waste water for traditional as control and the two modified methods, these results showed that there is significant reduction in terms of chemical oxygen demand, sulphide and biological oxygen demand and increase in total suspended solids which can be explained by existence of the remain of dissolve hair and keratin in epidermis layer.

Total suspended solid levels the yielded waste water of were shown in **Table 1.** The results showed that there is significant difference in the levels between both improved methods wastewater in compare to indigenous unhairing method wastewater.

S. No.	Description	T1	T2	Т3	Mean	Std	Sig. 0.05
1	рН	12.64	12.42	12.45	12.5	0.104	0
2	TSS/ppm	1550	400	350	813	554	0.002
3	BOD/ppm	825	426	489	580	186	0.002
4	COD/ppm	14250	4150	6200	8200	4624	0.001
5	Sulphide/ppm	1408	397	560	788	470	0.001

 Table 1: Physico-chemical properties of unhairing waste water

The amount of saved waste-hair was dropping the reading of this load which can be explained by the inexistence of the

remaining undissolved hair particles in the discharge wastewater, which was collected by the filter used in the trials.

Whereas the results showed that there are significant differences in biological oxygen demand of both modified unhairing methods wastewater, it presented that it was lower in compare to indigenous unhairing wastewater and suggested that the utilize 1.5 g and 2 g of sodium sulphide and lime in the drum was very effective where was accelerate unhairing processed, increased collagen swelling, saved the waste hair and changed the resultant wastewater behavior whereas drops the biological oxygen demand values as a result of this trail so that the wastewater carried appositely level. Generally biological oxygen demand is a measure of the oxygen consuming capacity of water containing organic matter. Organic matters by itself do not cause direct harm to aquatic environment, but it exerts an indirect effect there by depressing the dissolved oxygen content of the water. The oxygen content is an essential water quality parameter and its reduction causes stress on the ecosystem. As an indigenous unhairing wastewater, a total lack of dissolved oxygen as a result of high biological oxygen demand which can kill allnatural life in an effected area. Chemical oxygen demand of the yielded wastewater of both modified unhairing methods and traditional method were shown in Table 1. Which were showed that there are significant differences between both improved unhairing measured parameters compare to indigenous unhairing methods, the results postulate that reduced the sodium sulphide and using drum vary the nature of unhairing and accelerate the unhairing from collagen fibre whereas lower of improved trail wastewater chemical oxygen demand are indicates that the amount of inorganic wastes and the other chemicals are lower compare to indigenous tanned wastewater. If effluent with the high demand oxygen the

sensitive balance maintained in the water becomes overloaded. Oxygen is stripped from the water causing oxygen lack so dependent plants, bacteria, and fish impel to die. The outcome is an environment populated by non-oxygen dependent (anaerobic) bacteria leading to toxic water conditions these agree with conception which says that the healthy wastewater can tolerate substances with low levels of oxygen demand.

Total sulphide content of the yielded wastewater was shown in **Table 1** where showed that there is significant difference in the levels between both improved methods in compare to indigenous unhairing method wastewater. The amount of sodium sulphide was added was drops the levels of this parameter which Twice as much as those used in the traditional method. The results from the Hair-save limesulphide unhairing (improved unhairing process), both trials show significant reduction of the pollution load in compassion with the conventional unhairing.

Physical and physico-chemical properties of tanned leather unhairing using traditional and modified methods

The **Table 2** showed the parameters of physical properties of traditional unhairing tanned leather as control and the two modified methods, these results showed the convergent result between first trial and second trial, and this disparity can be explained by the difference in tanning operations applied for leather samples and the deference of hide fiber.

S.No.	Test name	T1	T2	Т3	Mean	Std	Sig. 0.05
1.	Thickness mm	1.8	1.82	1.59	1.74	0.1107	0.00
2.	Tensile strength (Kg/cm ²)	230	238	250	239	0.9526	0.00
3.	Elongation (%)	43	46	35	40	5.123	0.00
4.	Tear strength (kg/cm)	100	120	132	117	14.44	0.00
5.	Double tear strength (kg/cm)	120	156	163	146	20.149	0.00
6.	Tongue tear strength (kg/cm)	80	70	71	73.7	5.074	0.00
7.	Elasticity (kg/cm)	12	13	12	12.3	0.522	0.00

Table 2: Physical and physico-chemical properties of tanned leather

Conclusion

- Using Hair-save lime-sulphide unhairing gives excellent full unhairing in both trials. The improved unhairing process reduces the amount of sodium sulphide used by 50% in the first trial and 37.5% in the second trial reducing the overall production cost.
- The sulfides discharged from unhairing operations and pollution load had significant reduction compared to conventional unhairing process in both trails applied using improved unhairing process.
- Using the Hair-save lime-sulphide unhairing (improved unhairing process) for local tanneries will reduce production cost, save chemicals and protect the environmental.

Recommendations

The following points can be recommended:

• Designing of full-scale Hair-save unhairing system that can be applicable in the local tanneries.

 Inventing a new method to benefit from the collected hair produced from the process, so that it can be commercially exploited.

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