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Minimization of the Environmental Impact in the Unhairing of Bovine Hides

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Abstract

This study tests an alternative method to the traditional unhairing method used during the process of tanning the hides. The new method is based on the substitution of sodium sulfide by hydrogen peroxide as an unhairing agent in both hair recovery and recirculation of the floats employed in the process. The properties of the hides obtained using the two methods have been compared and the results indicate that those hides have similar physical, chemical, and organoleptic properties. However, the differences existing from an environmental point of view are significant. These include reductions of water consumption (approx 70%), Chemical Oxygen Demand (approx 35%), Toxicity (98%) and Total Kjendhal Nitrogen (50%). Also, the risk associated with the production of hydrogen sulfide is eliminated, which implies a great improvement in terms of safety for the workers. Given the large amounts of water and chemical pollution discharged in the process, the reductions in absolute values represent a significant improvement. A financial assessment was carried out to demonstrate that the proposed new system is 16% more economic than the traditional one.

Keywords: Hide unhairing; Unhairing wastewater; Tanning industry; Residual float; Pollution minimization

1. Introduction

The paper deals with the environmental concerns generated by the tanning industry and focuses on beamhouse operations, the most polluting part of the tanning process. The beamhouse procedures are cleaning operations to prepare the hides for the leather making process. The purpose of these operations is to remove raw hide constituents such as dirt, epidermis, subcutaneous tissue and hair. When beamhouse processing is accomplished, the collagen, which is the main protein contained in the skin, is ready to be tanned. In other words, the hide is prepared to be transformed by means of chemical reactions into the useful leather which will be used in the manufacture of shoes, bags, clothing and other goods (Heidemann, 1993; Morera, 2000).

This entails using large quantities of clean water. After usage, the clean water will become highly contaminant wastewater (Rivela et al., 2004; Saravanabhan et al., 2006). In order to provide an estimate of the amount of water involved in the process, recent studies by official organizations (FAO, 2007) estimate that approximately 6 Mt of bovine salted raw hides are tanned yearly worldwide. In accordance with the pollution values from tannery processes under conditions of good practice (IULTCS, 2004), there is an average yearly estimate of beamhouse resulting in approximately 70 Mm^3 of contaminated water, containing approximately 0.85 Mt of Chemical Oxygen Demand and approximately 0.07 Mt of Total Kjendhal Nitrogen (TKN).

Furthermore, sodium sulfide is used as an unhairing reactive agent. This brings about a risk associated with the production of hydrogen sulfide, which in terms of safety poses a permanent threat to the workers. A further adverse effect is the production of solid wastes (i.e. fleshings) which contain sulfide.

Many studies have been carried out lately exploring ways to address the environmental problems mentioned above (Hummel and Germann, 2001; Thangam et al., 2001; European Comission, 2003; Thanikaivelan et al., 2003; Saravanabhan et al., 2005). One of the most successful systems has been a hair-save unhairing system (Vila, 1996; Baba et al., 1999; Manzo et al., 1999). Instead of dissolving the hair by means of a chemical attack as is done in the traditional system, in this system the hair is immunized with lime and separated from the hide, making it possible to recover the hair intact by means of filtering the float. This system thus involves significant reductions in discharged pollution, especially regarding COD and TKN. Another of the experimented systems consists of replacing sodium sulfide with hydrogen peroxide as an unhairing chemical agent, which aims to decrease the toxicity involved in the process (Marsal et al., 2000; Shi et al., 2003; Marmer and Dudley, 2004; Bronco et al., 2005; Morera et al., 2006). The actual reduction of the environmental impact of an oxidative unhairing process by hydrogen peroxide versus the traditional one was recently evaluated performing a Life Cycle Assessment (LCA) (Castiello et al., 2008).

This study compares, both from an environmental and an economical point of view, a process which combines the two ideas exposed (oxidative unhairing and hair recovery) with the traditional process. Also, the fundamental concept of float recirculation is applied in order to significantly reduce water consumption.

This unhairing process incorporates two relevant differences in relation to the traditional process with sodium sulfide and lime. Firstly, the unhairing products employed. Whereas sulfide attacks the hair acting as a reductive in the traditional unhairing process, hydrogen peroxide attacks the hair acting as an oxidative in the new unhairing process. However, the effect on the hair is the same: breaking of the disulfuric bonds of cysteine and the resulting hydrolysis of keratin, the main protein found in hair.

Secondly, there are always remnants of sulfide and sulfydrate on the hide and in the waste float resulting from the traditional liming process. On the contrary, there is no resulting toxicity in the unhairing process experimented here because the reaction of hydrogen peroxide with the hide causes its decomposition into water. This allows for the easy recirculation of part of waste floats since they do not contain toxic products and are quite “clean”.

2. Materials and methods

2.1. Material

The tests were carried out using 1 m-high (i.e. diameter) and 0.4 m-wide stainless steel drums. Drums are cylindrical vessels that rotate around an axle (Fig. 1, Supplementary data). Bovine salted hides were used in order to perform the tests. 40 kg of salted hides were processed in each test. The chemicals and the machinery used in the operations were those normally used in the leather industry. The chemicals used for analytical analysis were of laboratory grade.

2.2. Methodology

First, five 40 kg packs of bovine hides were processed in the beamhouse operations using hydrogen peroxide. Table 1 gives an account of the main operations. Figure 2 shows a diagram of the beamhouse process, where water input, water output and recirculations for each of the operations are detailed. The strategy of reutilization of floats consists of making use of the less polluting waste floats as floats in operations within a same process or to be reused in later cycles.

The waste floats from the two soaking operations are discharged with no recirculation as they are highly contaminated. The waste float from the washing which is carried out after the main soaking is recirculated partly for the subsequent unhairing and partly for the first soaking of the next pack of hides. At this point, there is still an excess of part of the waste float discharged. The waste float from the immunization is reutilized in the same operation with the next pack of hides. Wastewater from the unhairing is reutilized for the first soaking of the next pack of hides. Finally, the waste float from the washing subsequent to the unhairing is reutilized in the unhairing of the next pack of hides. The accumulation of polluting agents in the subsequent floats is avoided since there an input of fresh water is supplied each time that a pack of hides is processed.

All waste floats resulting from the five processing cycles were analyzed. The following are the parameters that were analyzed for all the waste floats which were completely or partially discharged: COD, Suspended Solids (SS), Soluble Solids (SOL), Toxicity, Nitrogen (TKN) and Phosphorus.

Neither toxicity nor phosphorous was analyzed in those waste floats which were completely recirculated since it was agreed that the other parameters sufficed to evaluate whether the quality of the floats was being kept constant. As for the immunization float, Phosphorous was not analyzed. Analyses were carried out according to the Standard Methods (APHA, 1998). However, the EN ISO 11348-3 norm for “Toxicity” was followed alternatively.

As Table 1 indicates, the hides were subject to the remaining vegetable tanning processes that are part of the traditional method, once the beamhouse operations had been accomplished. After the last cycle, the resulting hides were subject to a series of normalized physical tests in order to grade them. The following official IUP methods were used to this end:

IUP 6. Measurement of tensile strength and percentage elongation (IUP 6, 2000): To carry out this test a leather sample is fixed on the clamps of a dynamometer. Then the clamps are subsequently separated at a constant speed while the force exerted on the sample is measured with the load cell of the device. The elongation is calculated as the difference between the final and initial separation of the sample. This difference is expressed as a percentage of the initial separation.

IUP 8. Measurement of tear load (IUP 8, 2000): This method is used to determine the capacity of the leather to withhold multidirectional tensions. In order to perform this test the dynamometer is also used by fixing a leather sample with a slot and subsequently separating the clamps at constant speed, causing the leather to tear completely.

IUP 9. Measurement of distension and strength of grain by the ball burst test (IUP 9, 1960): This test assesses the performance of the leather in the upper side of the shoe by using a lastometer, a machine developed by SATRA. The leather is progressively deformed until the first crack appears, acquiring thus a conic shape. Action is not stopped until total break takes place.

IUP 16. Measurement of shrinkage temperature up to 100 ºC (IUP 16, 2000): Shrinkage temperature is a parameter of great importance to measure the degree of stabilization of collagen in leather. It is determined by immersing a strip of leather in a mixture of water and glycerin subjected to a slow temperature increase. Shrinkage temperature is therefore the temperature at which shrinkage of the leather takes place.

A panel of five experts examined the organoleptic properties of the leathers and passed judgment on the suitability of the leathers for commercialization.

In order to carry out a study on the financial feasibility, the cost of unhairing with hydrogen peroxide was compared to the cost of a traditional unhairing under conditions of good practice (IULTCS, 2004). The calculation was based on the cost of the chemical products, the water used, the wastewater and the fleshings produced with sulfur. The costs for the treatment of the wastewater and the fleshings are in accordance with the prices in tanneries in Catalonia (Spain).

Results and discussion

3.1. Effect of the new process on water consumption and generated pollution

Water input and output for the three unhairings carried out with recirculated water and whose floats were recirculated (cycles 2, 3, and 4) were averaged. The amounts of water to be used per tonne of salted hide were calculated. Figure 3 shows the results obtained. Water input and output appears in brackets. Input water exceeds output for two reasons, namely some water is wasted during recirculation and some is absorbed by the hides. The differences between input water and output are the ones expected in the working conditions in which the experimentation was carried out.

The results of the analysis of the different floats used during the five unhairing cycles are shown (Fig. 4; Fig. 7-12, Supplementary data).

The results have to be interpreted bearing in mind that the treated hides are not uniform raw materials. The subcutaneous tissue is eliminated in the fleshing operation, which affects the weight of the hides and the amount of float to be used in the next operations. Therefore, this factor determines the proportion of water that has to be recirculated. In addition, the dirt (organic matter) attached to the hides is not uniform, either. These two factors determine the interpretation of the results and so these have to be regarded qualitatively.

This explains why it would be pointless to include errors in the results. Apart from the lack of accuracy, the analysis of the results obtained indicates that, except in the case of Soaking 1 and Immunization, the values of the pollution parameters are kept relatively constant throughout the five cycles. This means that there is no accumulation of polluting substances in the system despite recirculation. This accumulation might downgrade the quality of the leathers produced.

As far as Soaking 1 is concerned, the values of the pollution parameters in the first cycle are slightly lower than those in the remaining four cycles. This is clearly explained by the fact that the water used in the first cycle is fresh and clean, while approximately 75% of water in the float used in the other four cycles is recirculated and comes from the waste float of the unhairing carried out in the previous cycle. Thus, the increase in values of the pollution parameters was due to the pollution that resulted from the unhairing. The values of the pollution parameters from cycles two to five remained within the same range. The very nature of the operation, a quick wash of the hides, seems to indicate that if the water employed is partially "dirty" it does not necessarily imply a change in the quality of the treated hides. What is really important is that the recirculated water can still dissolve the dirt and soak out most of the salt in the hide.

As for the Immunization, most of the pollution parameters of the waste floats progressively increase with the fulfillment of the new cycles. Therefore, this operation needs to be adjusted. The logical adjustment would entail not recirculating the whole float and discharging part of it. This means that some fresh water has to be added to the float with every new immunization. At the same time, lime additions should have to be adjusted to lower levels, and such adjustments are easily made. After the adjustments made for the immunization, we concluded that the process was valid since the unhairing of the hides could be accomplished with important savings in water use.

In order to determine the cost of wastewater discharge, the pollution load discharged during the cycles with recirculation was averaged. The average values of the discharged water and its pollution load of both the process using hydrogen peroxide and the traditional process of unhairing are presented in Fig. 5.

Considering the fact that 6 Mt of bovine salted raw hides are currently processed worldwide, the use of an unhairing with hydrogen peroxide and recirculation may result in water savings of approximately 70 Mm^3, which represents 70% of the amount of water used nowadays. This would imply a yearly reduction of approximately 0.3 Mt (35% reduction) of COD, 0.035 Mt (50% reduction) of Nitrogen, and 12 million kiloequivalents (98% reduction) of Toxicity. There is a 41% increase in soluble solids, as shown in Fig. 5. This result is misleading since what is actually measured is the conductivity.

The 70% of water savings brings about a proportional decrease in the amount of soluble salts discharged. Finally, there is an 80% increase in SS. Two factors may account for the increase: a poor filtration of the hair on the one hand, and an attack of the hydrogen peroxide on the hair on the other. First, the filtration was done manually as there was no automatized filtration system at pilot plant level. Nowadays, drums are equipped with very efficient automatized systems of filtration and recirculation at industrial level. Second, the hair recovered after filtration appeared to be a little dissolved. This might result in part of the hair filtering through to the float and increasing the value of SS.

The process with hydrogen peroxide has other advantages. The first is that the production of sulfides is completely eliminated. Such thing prevents the formation of sulfydric acid, which is a highly toxic gas. The formation of this gas presents a permanent risk that is far from being solved. Many workers in tanneries have been intoxicated with the gas, an intoxication which can easily kill the worker. The fact that most leather production is progressively moving to countries with poor safety measures makes this problem more acute. An estimated 5.5 kg of sulfide per tonne of bovine salted raw hides is generated under conditions of good practice (IULTCS, 2004).

A second advantage is an important decrease in the presence of sulfates in waste floats. This is accounted by the fact that ammonium sulfate is often employed in the traditional system as a means to remove and eliminate lime from leather when the unhairing process has been carried out. The system of unhairing using hydrogen peroxide avoids sulfates production because the quantity of lime added in the process is so small that it is simply absorbed by the epidermis and then eliminated by the unhairing process. An estimate 0.075 Mt of sulfate are discharged yearly. These sulfates become a problem when wastewaters are treated at water treatment plants.

A third advantage is the elimination of fleshings, the primary contaminant among the solid by-products. In the traditional process a tonne of salted hides generates an approximate production of 300 kg of fleshings. As fleshings contain sulfide, recycling is extremely costly and therefore they usually end up in landfills. Alternatively, by unhairing with hydrogen peroxide the fleshings generated are sulfide-free, which enables a complete and easy reuse of the fleshings by basically transforming them into fats.

3.2. Effect of new process on leather properties

The results from the physical tests on the finished hides in the last cycle are shown in Table 2. After evaluating the organoleptic properties of the leathers obtained in the last cycle and bearing in mind the results from the physical tests (Table 2), the panel of experts confirmed that the leathers were suitable for commercialization as leather goods.

3.3. Economical considerations

The economic calculation was done in accordance with the regulations which are applied in Catalonia (Spain). Figure 6 shows the comparison between the traditional system and the new system in economic terms. The economical analysis indicates that, with the parameters indicated, unhairing with hydrogen peroxide is 16% more cost-effective than using the traditional unharing method. However, it is important to ponder this issue. In Spain, the discharged water is usually paid in accordance with the total pollution load, although the approach taken instead is one to punish any savings of water rather than reward it. Indeed, the regulation sets a limit on the concentration of pollution in discharged water but not on the total amount of pollution discharged. This is a contradiction because it promotes the use of water to dissolve the pollution load so as to avoid surpassing those limits set by law. However, there is much more social concern with the increasingly shortage of water. As a result, there is already a charging system used to pay for fresh water where the price increases with consumption. It also seems clear that in the next few years cost of disposing of sulfide-laden fleshings in landfills will grow much faster than costs of the unhairing process. Therefore, it seems likely that unhairing with hydrogen peroxide will increasingly result in considerable financial savings.

It is also worth mentioning that hydrogen peroxide at high pH values reacts with wood. Some years ago, the drums were almost exclusively made of wood. In later years, though, the drums have been manufactured using other materials such as polypropylene as they are immune to hydrogen peroxide attack. Having said this, the constant development of the tanning industry brings about new factories which are already equipped with this new drumming technology. Accordingly, the problem as regards infrastructure owing to the use of hydrogen peroxide is being progressively reduced.

4. Conclusions

The aim of this study was to check the advantages of introducing an alternative method to the traditional unhairing system. This new method is based on the replacement of sodium sulfide by hydrogen peroxide as an unhairing product and on the resuse of part of the residual floats in subsequent processes. The conclusions are outlined below.

The first conclusion is that the tests conducted indicate that the changes introduced result in leathers with physical and organoleptic properties that comply with the necessary requirements to be put on the market. The second is that the new unhairing system results in considerable savings in water supply (70%), COD (35%), nitrogen (50%) and toxicity (98%). In addition, production of fleshings with incorporated sulfides is completely eliminated. Also, the new system dramatically reduces the chances of serious injury to tannery workers by preserving the formation of sulphuric acid. We can also conclude that the change in system cuts the unhairing expenses by 16%. Finally we can assert that the proposed modification will have a positive impact both on the environmental and economic aspects of the tanning process, thus enhancing its sustainability.

Acknowledgements

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Table 1

Formulation Using Hydrogen Peroxide

Soaking (the hide is wetted and an initial cleansing is carried out)		
Fleshing (the subcutaneous tissue is mechanically removed from the hide) *and weighing*		
Main soaking (the hide is thoroughly washed with water and a tensoactive i.e. emulsifier)		
Washing		
(on fleshed weight):		
Immunisation	100% H_2O 25 ºC	
(the hair is protected)	0.5% $Ca(OH)_2$	Rotate 15' and drain
Unhairing	200% H_2O 30 ºC	
	0.2% NaOH (50%) (1:4)	Rotate 15' ; pH = 10-11
	1.5% Chemical based on secondary amines	Rotate 1 h
	0.1% Protease enzyme for unhairing	pH = 13 Rotate 7 h
	4.5% NaOH (50%) (1:4)	pH 9-9.5
	3.8% H_2O_2 (50%)	Rotate 6 h
	2% HCOOH (1:5) (slowly)	Overnight float Hair filtration and drain
Washing, Fleshing, Splitting, Bating, Pickle, Vegetable Tanning, Resting (48 hours), Shaving, Fatliquoring and Drying		

Table 2

Physical tests results

Analyzed parameters	Results
Tensile strength (Pa)	22.3±0.3
Elongation (%)	39.2±1.3
Tearing Load (N mm^{-1})	89±6
Grain Crack Load (N)	823±49
Grain Crack Distension (mm)	10.10±0.27
Shrinkage temperature (ºC)	79.0±0.1

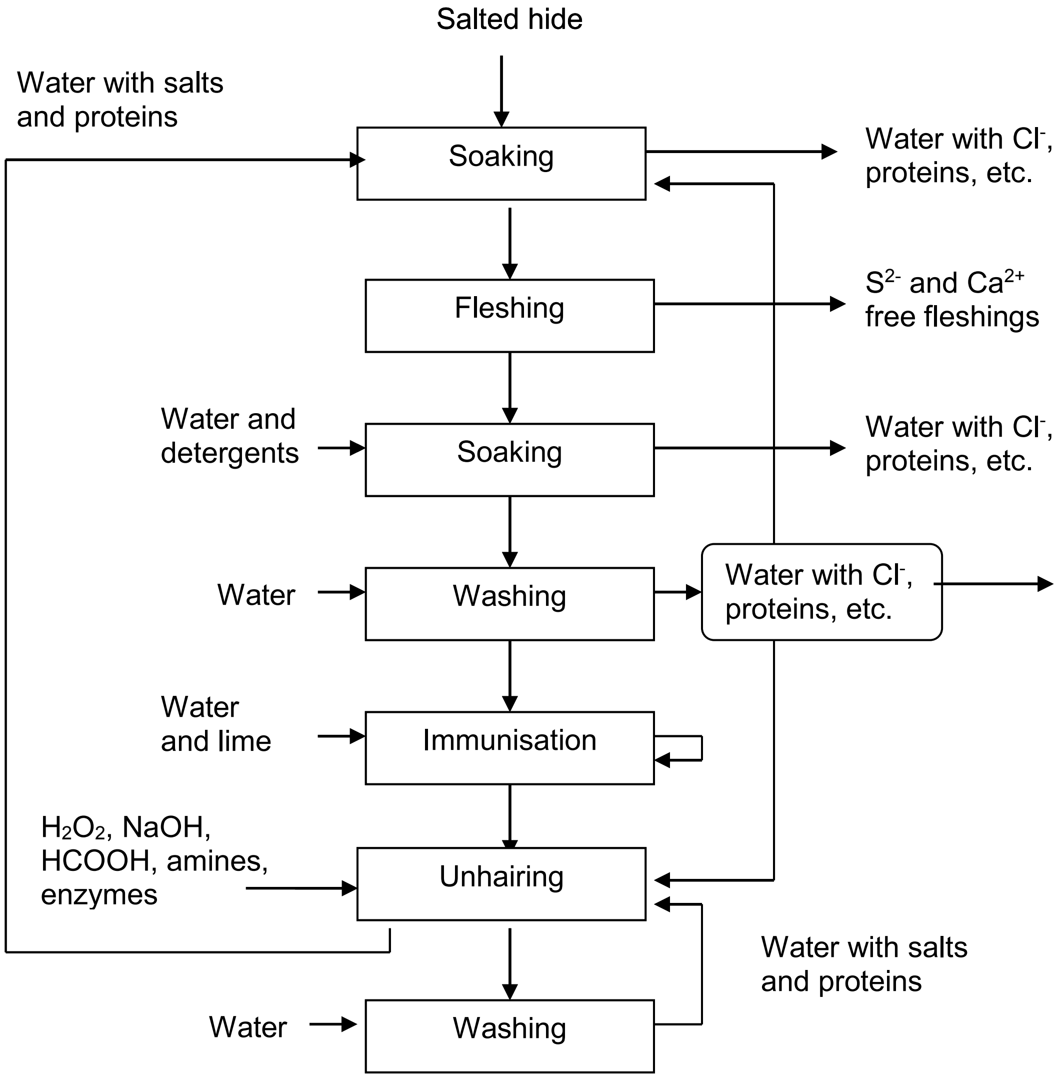

Fig. 1. Diagram of the whole process.

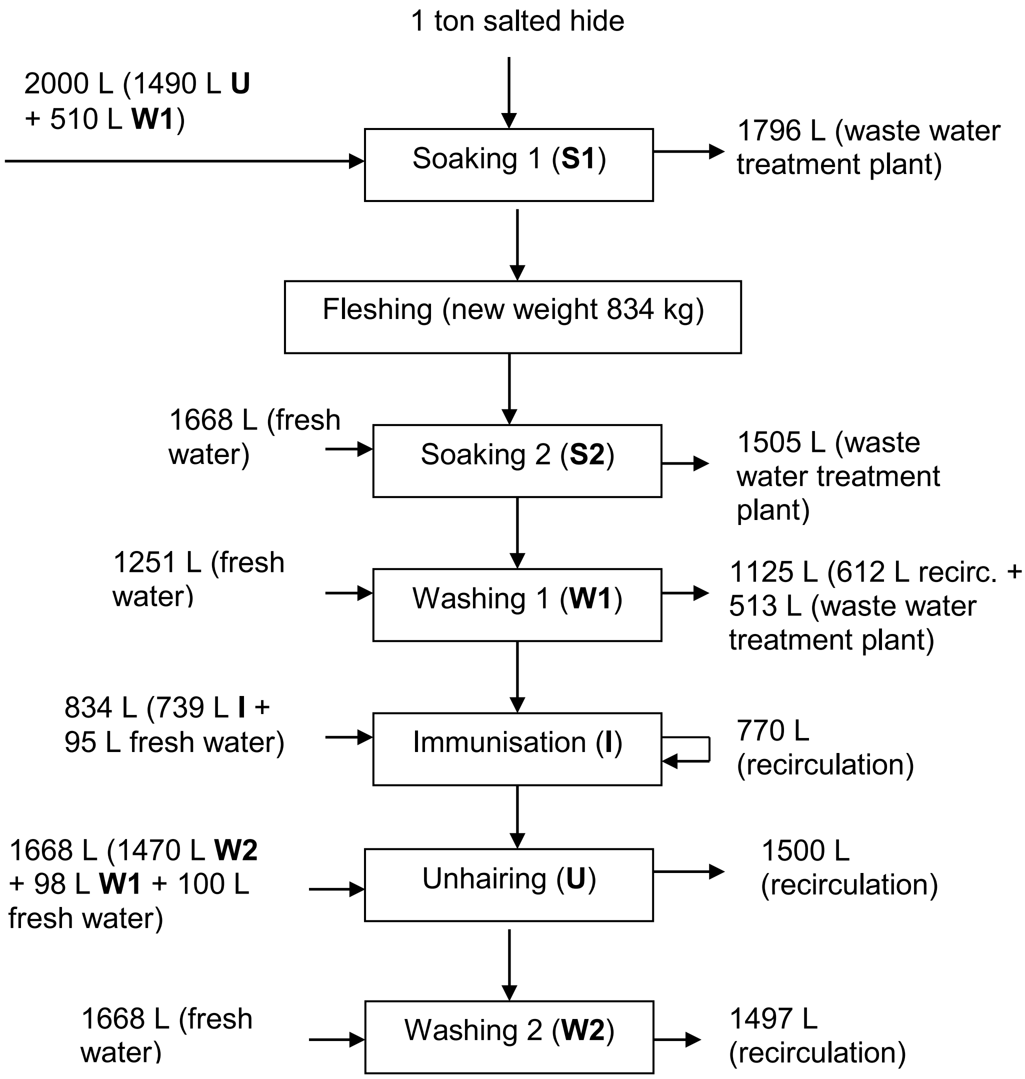

Fig. 2. Diagram of water flow used in the beamhouse with H_2O_2.

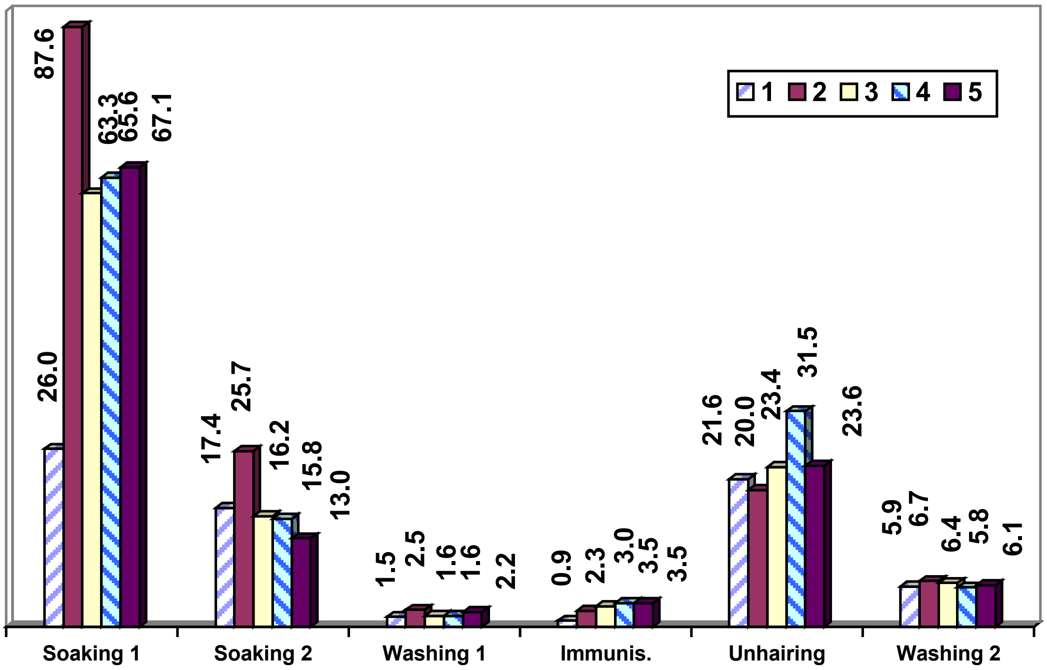

Fig. 3. Pollution Load of Floats. Chemical Oxygen Demand (kg t^{-1} Salted Hide)

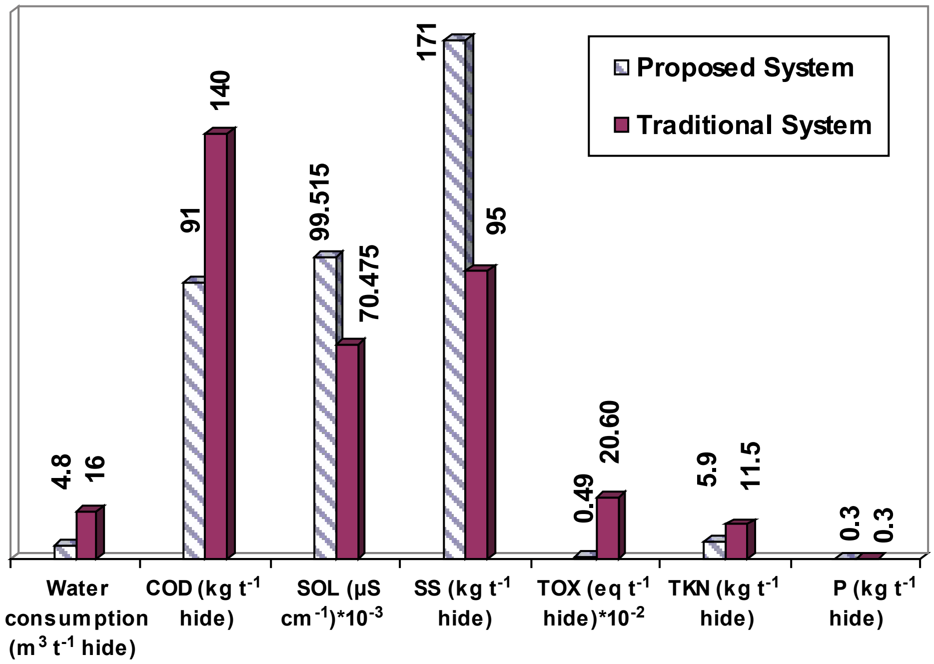

Fig. 4. Discharged water and pollution loads.

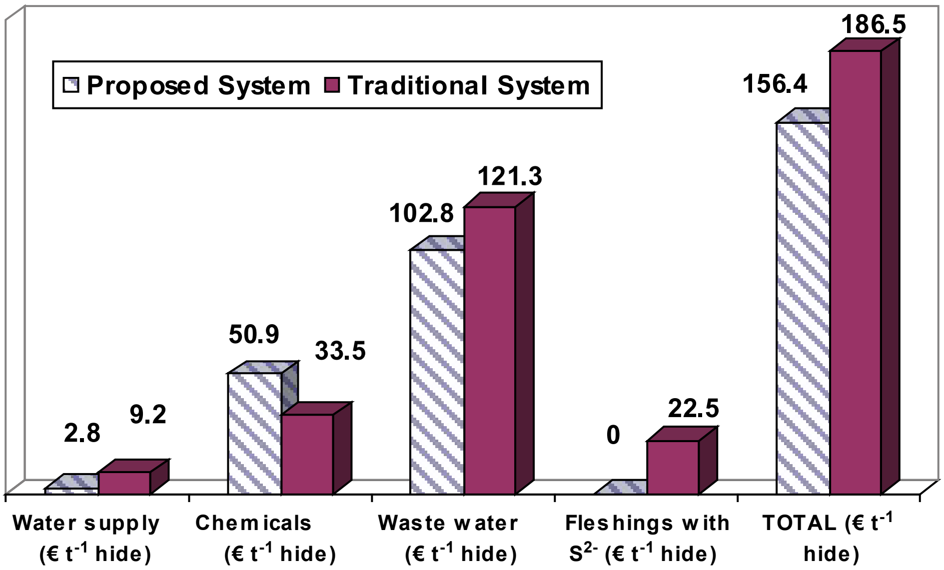

Fig. 5. Analysis of costs

Supplementary data

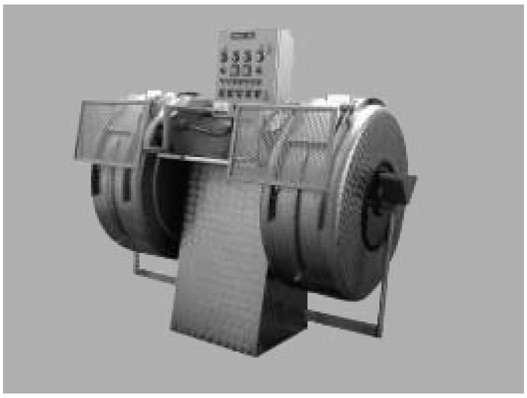

Fig. 1. Drums

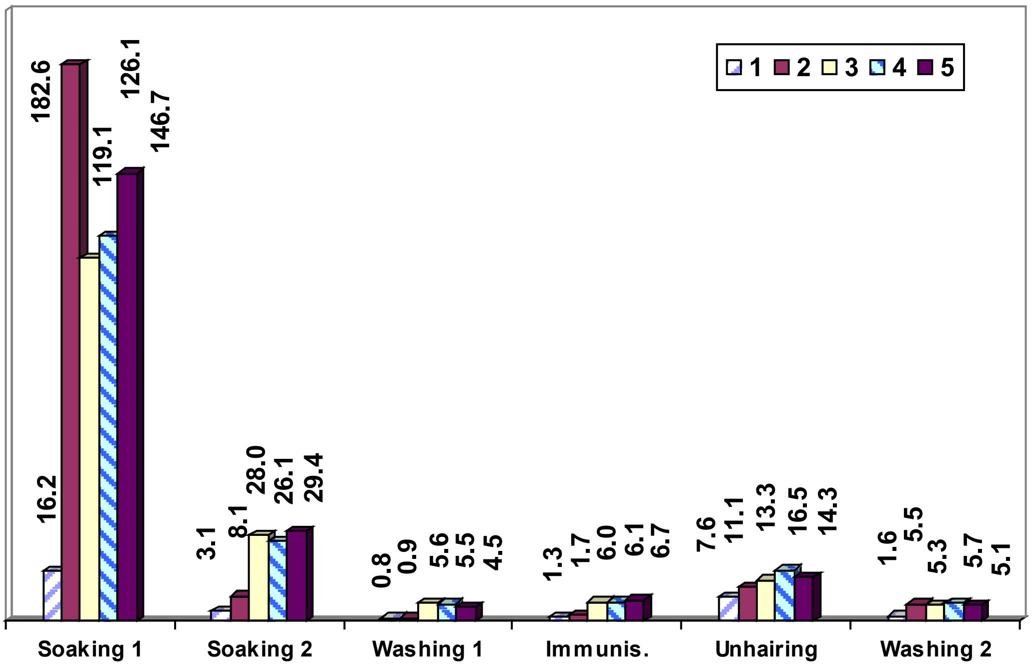

Fig. 7. Pollution Load of Floats. Suspended Solids (kg t^{-1} Salted Hide)

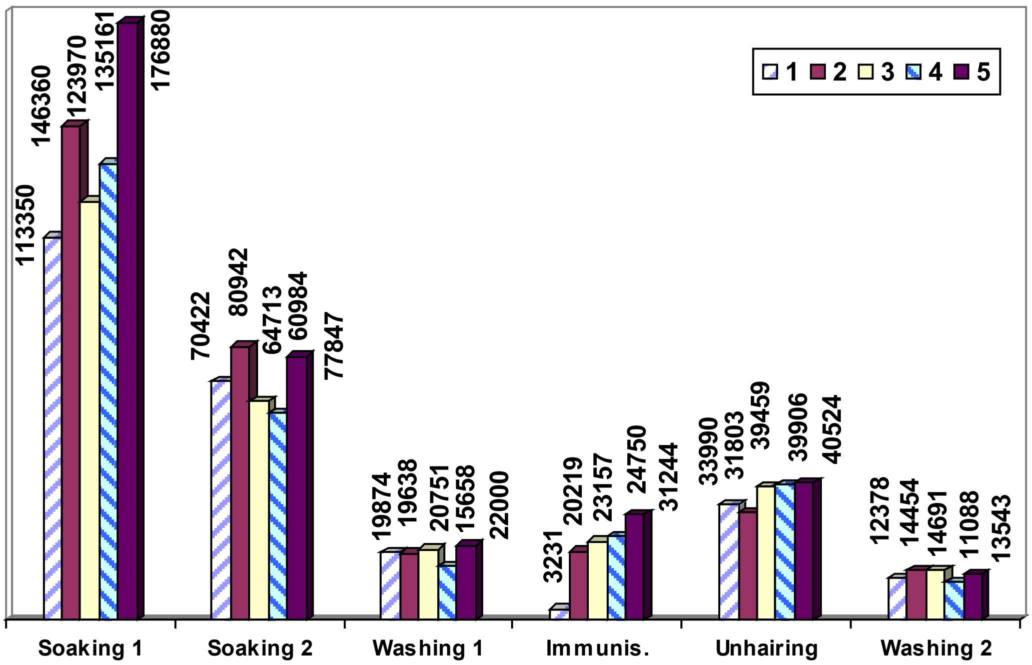

Fig. 8. Pollution Load of Floats. Soluble Solids (μS cm^{-1} Salted Hide)

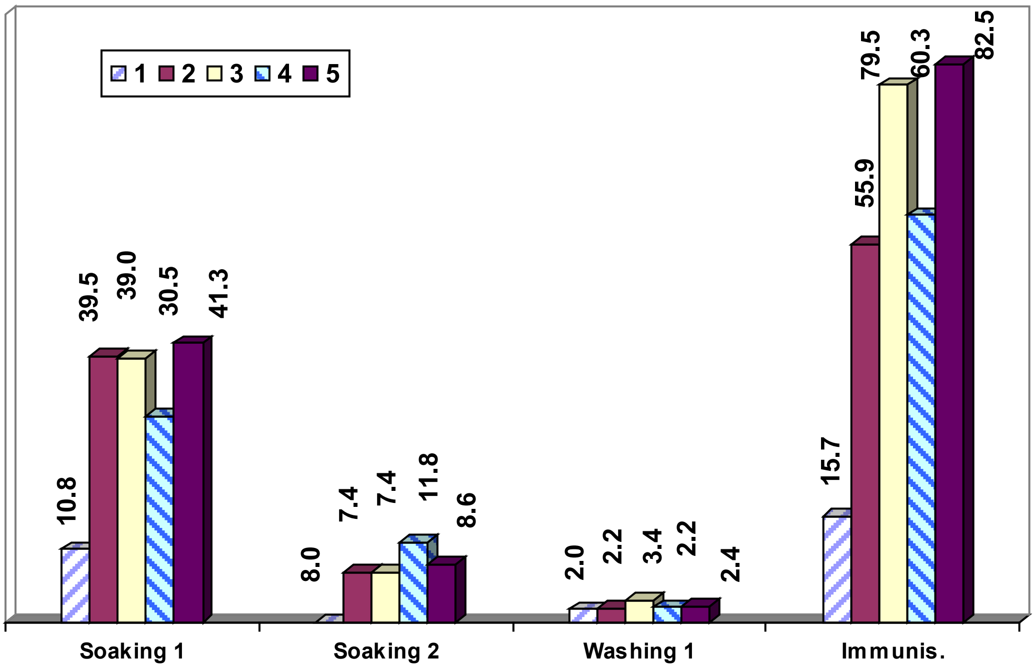

Fig. 9. Pollution Load of Floats. Toxicity (eq t^{-1} Salted Hide)

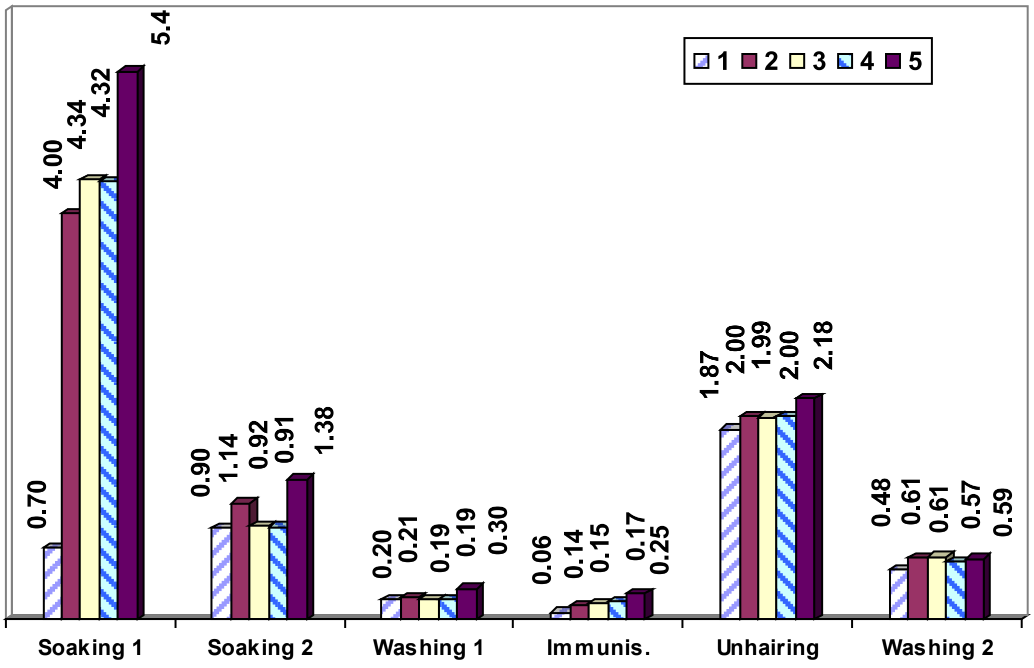

Fig. 10. Pollution Load of Floats. Total Kjeldahl Nitrogen (kg t^{-1} Salted Hide)

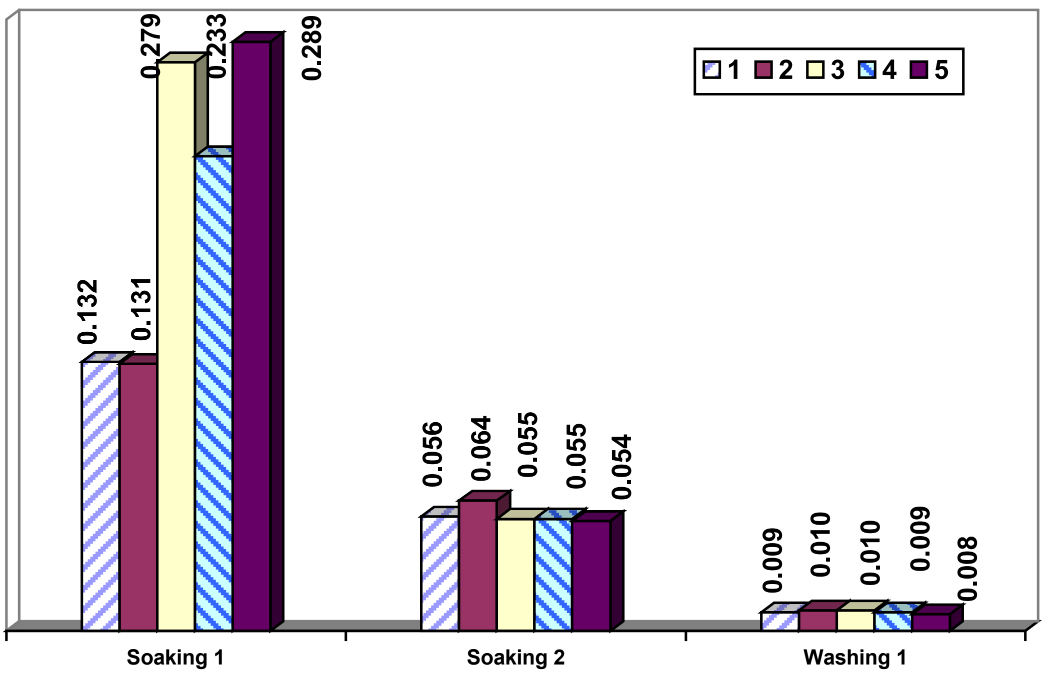

Fig. 11. Pollution Load of Floats. Phosphorus (kg t^{-1} Salted Hide)