Avoiding the Production of Polluting and Toxic Chemicals in the Tanning Process

by

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Abstract

Polluting and potentially toxic chemicals are used in tanning. Sodium sulfide/hydrosulfide are used when the hides are unhaired. These chemicals can be transformed into hydrogen sulfide with a simple change of pH. This gas is highly toxic and is the recurring cause of many deaths and accidents due to suffocation of workers in tanneries around the world. The basic salts of chromium III are the most used chemical to tan. The chromium III used can be transformed by oxidation, even once the leather transformed into a consumer good (shoes, for example), in chromium VI, which is carcinogenic. Both chemicals are present in process floats, in residual floats and in solid waste generated. Chromium III is also present in manufactured leathers. This article aims to describe the problems associated with the use of the aforementioned hazardous materials and deepen the possibility of using less toxic alternative processes to tan. The designed process allows to significantly reduce the pollutant load of the discharged wastewater, facilitates the reuse of the solid waste generated and clearly improve the safety of people at work.

Introduction

The tanning industry is considered very pollutant[1] due to the chemicals used. It is believed that the greatest risk of injuries connected with certain tasks is caused by the greater proximity or contact with agents potentially dangerous.[2] The tanning process follows different steps. Two of the most polluting steps are unhairing and tanning.[3]

The unhairing is part of the beamhouse processes, those that prepare the hide to be tanned. The traditional unhairing process is carried out to separate the hair from the hide with sodium sulfide and/or sodium hydrosulfide and lime.[4] The combination of hydrosulfide (HS^-) and hydroxyl (OH^-) breaks the disulfide bonds of the keratin, main protein constituent of the hair, transforming the cysteine residues, not easily hydrolysable, in cystine residues, that dissolve easily in alkaline solutions. Equation (1) shows one of the possible mechanisms of this reaction:

$$-S\text{-}S- + 2RS^- \rightarrow -S\text{-}S\text{-}R + R\text{-}S\text{-}S- \qquad (1) \quad R = \text{H or organic group}$$

It is a low-cost operation that poses little risks for the hide quality in the whole process. Nevertheless, although the efforts carried out by many researchers, it is still a very polluting process and with high health risk for the operators due to the use of sodium sulfide and sodium hydrosulfide as unhairing agent.

The pollution produced is high.[5] Due to the organic matter detached when dissolving the hair and part of the hide, and to the used chemicals, the residual float has very high chemical organic demand (COD), suspended solids (SS), nitrogen (TKN), and toxicity (TOX). The worldwide total amount of water in beamhouse operations has been calculated[6] in approximately 105 Mm^3, which is about 60% the total amount of water used in all the tanning process.[7] About 75% of COD, 80% of SS, 85% of TKN, and 100% of sulfide (S^{2-}) are generated during beamhouse. Therefore, approximately 0.9 Mt of COD, 0.04 Mt SS, 0.08 Mt TKN and 0.6 Mt of S^{2-} are produced.

On the other hand, sulfide and hydrosulfide ions contained in both unhaired skins and residual floats from the unhairing operation are a major latent hazard. When, for any reason, the pH value of the float is less than 9, hydrogen sulfide is formed. This extremely toxic gas can cause great harm to the human body.[8] Its inhalation has been the cause of numerous fatal accidents in the tanning industry.[9] Inhalation of air with a concentration of 700 ppm of hydrogen sulfide causes instantaneous death. If the exposure is longer, the lethal concentration decreases. If the exposure lasts 30 minutes, a concentration of 500 ppm is already sufficient to produce unconsciousness and subsequent death.[10] The danger of direct inhalation when opening the drum is not the only one. As the density of hydrogen sulfide is higher than that of air, it usually accumulates in low places, for example, the sewage pipes of the unhairing floats, where it can cause casualties when maintenance is performed. It is the typical case of a confined space fatality.[11] Often several consecutive accidents occur: a first person falls unconscious (then becomes a victim) and then all others who, without the necessary protective equipment, come to their rescue[12] are also affected.

Another undesirable effect of the use of sodium sulfide is that the presence of sulfide and hydrosulfide ions in wastewater floats complicates and makes treatment in treatment plants more expensive.[13]

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Another drawback of the type of unhairing method mentioned is that solid wastes, called fleshings, which contain sulfide and are difficult and expensive to recycle and/or reuse are also generated. Although attempts have been made to reuse them in different ways, often such wastes are brought to a landfill.[14]

Several alternative processes have been developed to minimize the pollution generated and to eliminate or reduce the use of sodium sulfide in the traditional unhairing process. An example of this is the unhairing process that allows hair recovery without dissolving it and subsequently allows its separation from the residual float via filtration.[15-19] Another alternative are oxidative unhairing processes, based on the use of unhairing products such as hydrogen peroxide and the like.[20-24] Hydrogen peroxide, at pH values close to 13, is capable of hydrolyzing the hair through an oxidative reaction. The oxidative attack of the S-S bond is due to the formation of peroxy anion from hydrogen peroxide (Equation (2)):

$$H_2O_2 + OH^- \leftrightarrow HOO^- + H_2O \qquad (2)$$

All hydrogen peroxide is consumed. Because the sodium sulfide/hydrosulfide is not used, the toxicity and the problem of the environmental management of waste floats and solid waste decreases greatly. The generation of hydrogen sulfide is avoided, which increases the safety of workers.

Recently, unhairing systems based on the use of enzymes have also been tested.[25-28] Both oxidative and enzymatic unhairing systems can be combined with hair recovery to reduce the pollution generated. Unfortunately, at present, there is no commercial enzyme-based chemical that can completely replace sodium sulfide as a depilatory agent.

Tanning with chromium III salts is also a problematic operation from an environmental point of view.[29] Chromium III binds to the carboxylic groups of the side chains of collagen,[30] thus stabilizing this protein. The hide, which once the animal is dead is easily degradable,[31] is transformed into leather, which is a material suitable for manufacturing large quantities of consumer goods (bags, shoes, etc.).

The chromium III contained in the residual float of the tanning operation must be treated correctly to avoid serious pollution problems.[32]

Subsequently, in many cases, the resulting sludge is deposited in a landfill. In addition, significant amounts of chrome shavings, which are also deposited in a landfill, are generated.[33] The main health problem of chromium III is that, under certain conditions, it can be oxidized to chromium VI, which is carcinogenic.[34] The chromium incorporated in the leather can suffer this oxidation due to the effect of solar radiation at relatively high temperatures.

There are other tanning agents, such as those based on vegetable extracts, which are eco-friendlier.[35] The tannins of these tanning agents react with the hide, mainly through hydrogen bridge bonds.

The replacement of chromium III salts is not always possible, because they confer different properties to the leather than those of other known tanning agents.[36] As in the case of the unhairing with sodium sulfide and lime, tanning with chromium salts is favored by its low cost and the ease of handling. However, every day there is more demand for products made of chrome-free leather.[37]

The aim of this paper is to increase the knowledge that allows to develop more ecological tanning processes, minimizing the pollutant load discharged and using less toxic and dangerous chemicals for health. To achieve this goal, the influence of three innovative types of unhairing in leathers tanned with three different vegetable extracts has been studied. An experimental design of the Latin square type has been followed to carry out the experimentation and the results have been assessed by performing the corresponding statistical analysis.

Achieving such aim will bring new knowledge such as the changes in the physical properties of the final leather produced and the pollution dumped during the oxidant unhairing process comparing if the unhairing process dissolved the hair or not. This comparison is then compared with results from a classical reductive unhairing process.

In most of published research papers about an oxidant unhairing process, hides are tanned with chromium salts. Therefore, another novelty of this paper is the study of the compatibility and the behavior of vegetable tanning agents with different chemical base (two condensed and one hydrolysable) with the proposed oxidizing unhairing agents. This knowledge will contribute to better understand the mechanism of the chemical reaction between the oxidant unhairing agent and the hide.

Experimental

Materials

The tests were carried out using 0.85 m in diameter and 0.4 m wide stainless steel drums with rotating rate and temperature control. The machinery and the chemicals used in the processes were those normally used in the leather industry.

The chemicals used specifically in unhairing and tanning operations were: sodium hydroxide (50% w/w), calcium hydroxide (95% w/w), sodium sulfide (60% w/w), hydrogen peroxide (50% w/w), unhairing auxiliary based on secondary amines (Ribersal PLE Base) and unhairing auxiliary based on enzymes (Riberzym MPX) both provided by Cromogenia Units S.A., formic acid (85% w/w), ammonium sulfate (99% w/w), bating agent based on enzymes (Oropon OR) provided by TFL, phenolic pretanning

Table I

Experimental design

Experimental design: variables and levels

Variable	Level		
	-1	0	1
Part of the hide	Belly	Shoulder	Butt
Unhairing type	Reductive	Ox. Rec.	Oxidative
Vegetable extract type	Mimosa	Quebracho	Chestnut

Experimental design: latin square

	Mimosa	Quebracho	Chestnut
Belly	Ox. Rec.	Oxidative	Reductive
Neck	Oxidative	Reductive	Ox. Rec.
Butt	Reductive	Ox. Rec.	Oxidative

Selected experiments

Experiment	1	2	3	4	5	6	7	8	9
Part of the hide	-1	0	1	-1	1	0	0	-1	1
Unhairing type	0	1	-1	1	0	-1	0	-1	1
Vegetable extract type	-1	-1	-1	0	0	0	1	1	1

agent (Basyntan RS-3) provided by BASF, naphthalene sulfonic pretanning agent (Blancotan SN-20) provided by Silva SRL and vegetable extracts of mimosa (68% w/w tannin content) provided by Tanac S.A., quebracho (72% w/w tannin content) provided by Unitan Saica and chestnut (76% w/w tannin content) provided by Silvateam.

The experiments were carried out three times. Three salted bovine hides were used in order to perform the tests.

Preliminary operations

The three hides were soaked to rehydrate them, and to remove the salt and dirt they contained. Subsequently, the subcutaneous tissue was removed with the fleshing machine.

Experimental design

The hide is anisotropic. Three clearly differentiated parts can be distinguished in terms of their structural properties: the shoulder or neck (upper part), the butt (central part) and the bellies (outer parts). This fact was taken into consideration when choosing the experimental design.

On the one hand, the influence on the physical properties of the leather obtained of three types of unhairing and three types of tanning was studied. On the other hand, the toxicity generated by each of the unhairing tested was compared.

To carry out the experimentation, a Latin square design was followed with three variables and three levels for each variable. The first variable considered was the hide part. Its three levels were the shoulder, the butt and the belly. The second variable was the type of unhairing. Its three variables were a classic reductive unhairing (Reductive), an oxidative unhairing with hair recovery (Ox. Rec.) and an oxidative unhairing with hair destruction (Oxidative). The third variable was the type of vegetable extract used in tanning. The three levels corresponded to each of the three most used vegetable extracts worldwide: mimosa, quebracho and chestnut. Table I shows the coded variables and levels, the selected experimental design and the nine experiments carried out.

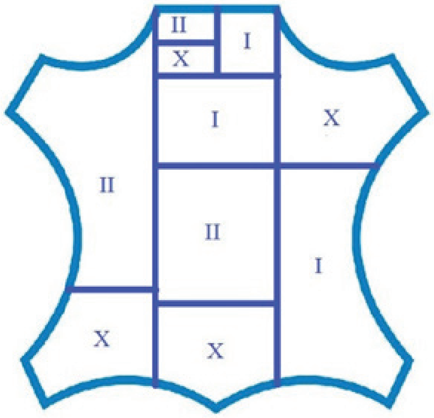

Figure 1. Sampling.

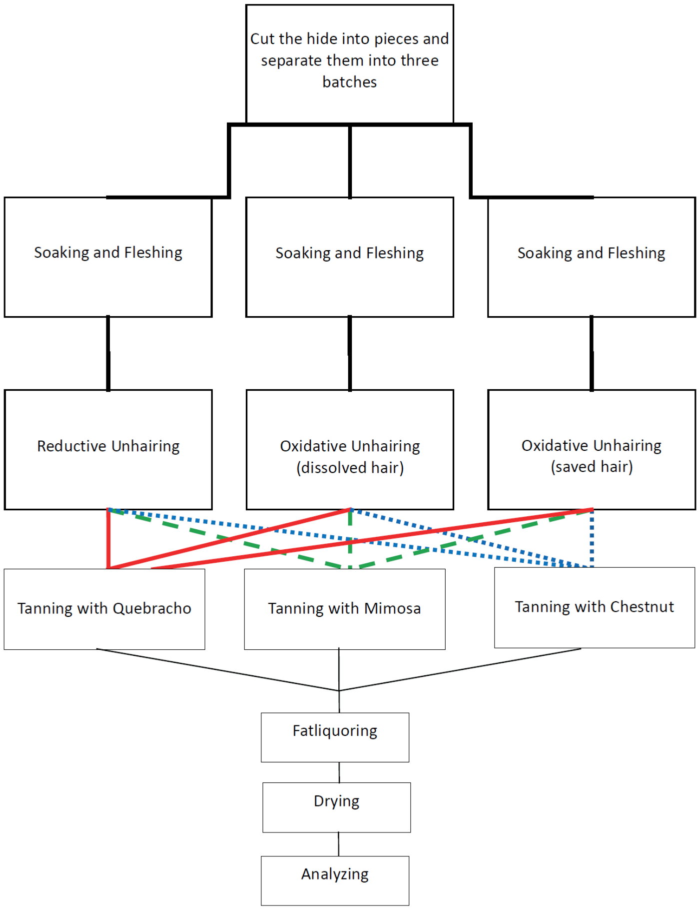

Figure 2. Procedure scheme.

Process

Each hide was cut into different pieces in order to carry out the nine tests (Figure 1).

Figure 2 shows an outline of the procedure followed to perform the nine tests.

The formulations used to perform the different tests are shown in Tables II and III. The formulation used for tanning (Table III) only varies in each case in the vegetable extract used.

Once tanned, the hides were fatliquored, dried and the following physical properties were analysed: tensile strength and elongation,[38] tear load,[39] distension and strength of grain,[40] and shrinkage temperature.[41] With the results obtained, the statistical analysis was performed.

Samples of the residual floats from soaking to pickling were quantified and a representative sample of the mixture of the different floats was analyzed. The sulfide content (S^{2-}) was determined through the Sulfide Test Kit, reference 114779, Merck brand, which is a photometric method. The "Toxicity" analyses were carried out according to the ISO 11348-3 norm. Analyses of Chemical Oxygen Demand (COD), Suspended Solids (SS), Conductivity and Nitrogen (TKN) were carried out according to the Standard Methods[42].

Table II

Unhairing formulations

Reductive unhairing	Oxidative unhairing with dissolved hair	Oxidative unhairing with hair recovery
(% on fleshed weight):		
Unhairing 200% Water at 25°C 3% Sodium sulfide 4.5% Calcium hydroxide Rotate 8 hrs. Night at rest. pH = 12.8 Drain and wash	*Unhairing* 30% Water at 25°C 0.2% Sodium hydroxide Rotate 15 min. pH=10-11 0.3% Amine product Rotate 30 min 6% Sodium hydroxide 4.5% Hydrogen peroxide Rotate until unhairing pH =13 2% Formic acid 200% Water Rotate 3 hrs. Night at rest pH=8. Drain and wash	*Unhairing* 100% Water at 25°C 0.5% Calcium hydroxide Rotate 15 min. Drain 200% Water at 25°C 0.2% Sodium hydroxide 1.5% Amine product Rotate 15 min. pH=10-11 0.1% Enzyme Rotate 1 hr 4.5% Sodium hydroxide 4.8% Hydrogen peroxide Rotate until unhairing 2% Formic acid Rotate 3 hrs. Night at rest. pH=8. Hair filtration, drain and wash
Deliming and Bating 100% Water at 37°C 1.2% Ammonium sulfate Rotate 30 min 0.5% Sodium bisulfite Rotate 15 min. pH=8 1% Bating agent Rotate 45 min Drain	*Bating* 150% Water at 30°C 0.6% Bating agent Rotate 45 min Drain	*Bating* 150% Water at 30°C 0.6% Bating agent Rotate 45 min Drain

Table III

Tanning with different vegetable extracts

Pickling
80% Water at 25°C
8% Sodium chloride
Rotate 20 min
1% Formic acid 1:5
0.5% Sulfuric acid 1:10
Rotate 2 hrs, night at rest. Drain pH=3.5

Tanning
80% Water at 25°C
6% Phenolic pretanning agent
3% Sodium chloride
Rotate 5 hrs. °Bé=7.5
1% Naphtalene sulfonic pretanning agent
30% Vegetable extract (Mimosa, Quebracho or Chestnut)
Rotate 8 hrs. pH=3.5-4

Results and Discussion

Table IV shows the results of the physical tests performed to the nine tests of the Latin square design.

An analysis of variance was carried out to determine which variables were significant and how they influenced the physical parameters obtained.

Table V indicates the analysis of variance performed for tear load. The P-value indicates whether a variable influences the result of a given parameter. The quantity (1 - P-value) x 100 is the percentage of possibilities that the variable influences the result. In the case of leather, and taking into account the anisotropy of the raw material, it is considered that at P-value equal to or higher than 90%, such influence exists.

Once the relationship of the analyzed variable-parameter was established, this influence can be determined. The results of the P-value indicate that the variables “part of the hide” and “unhairing type” influences the tear load.

Figure 3 shows the “unhairing type” influence. In this case there are significant differences between all results. The unhaired hides with the oxidative unhairing with hair recovery show tear resistance values higher to those of the reductive unhairing and this in turn, presents them superior to those of the hides subjected to the oxidative unhairing with dissolved hair. The results obtained are related to the collagen denaturation capacity by each of the depilating agents tested and with the way they are applied.

The analysis of the variable “Part of the hide” shows that the values obtained in the bellies are slightly inferior to the rest.

Table IV

Physical tests results

Test	Tensile strength (N/mm^2)	Elongation (%)	Tear load (N/mm)	Grain strength (N)	Grain distension (mm)	Shrinkage temperature (°C)
1	28.14	31.6	148.1	88.1	11.78	78
2	24.08	31.6	106.4	124.2	11.43	77
3	33.40	29.6	134.1	169.7	10.37	77
4	18.27	42.2	87.6	66.0	12.58	82.5
5	35.67	35.6	157.4	173.6	11.66	79
6	31.58	50.2	132.8	111.6	13.41	83
7	35.26	47.8	150.5	114.7	10.95	69.5
8	32.54	52.7	120.8	141.2	12.15	70.5
9	15.31	46.5	96.8	94.5	10.90	71

Table V

Analysis of variance for Tear load (N/mm)

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A: Part of the hide	235.049	2	117.524	9.13	0.0987
B: Unhairing type	4593.95	2	2296.97	178.51	0.0056
C: Vegetable extract type	70.1089	2	35.0544	2.72	0.2685
RESIDUAL	25.7356	2	12.8678		
TOTAL (CORRECTED)	4924.84	8			

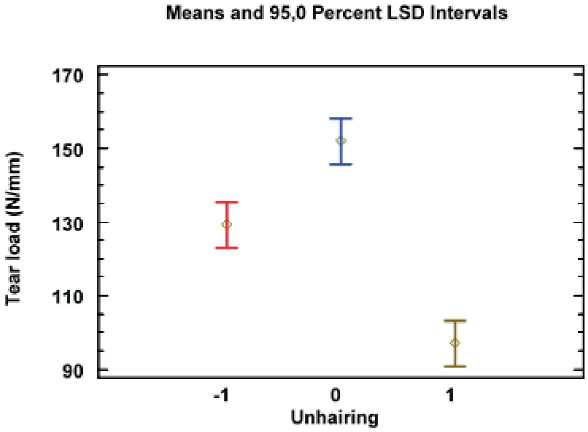

Figure 3. Influence of different unhairing systems on hide tensile strength (-1 = Reductive unhairing; 0 = Oxidative unhairing with saved hair; 1 = Oxidative unhairing with dissolved hair).

In the case of tensile strength, although clearly significant differences are not obtained, there is a trend that the lowest values are obtained with oxidative unhairing. This result would also be related to the collagen denaturation capacity by each of the depilating agents tested and with the way they are applied.

It is important to note in both cases that the values obtained in the leathers subjected to an oxidative unhairing with dissolved hair are clearly inferior to the rest. This result means that the oxidative unhairing with hair destruction hydrolyses more collagen fibers than the other two tested unhairing methods.

The analysis of the elongation results revealed that it depends only on the type of extract used (P-value = 0.0312). The tanned leathers with mimosa give significantly lower results than the others. The interpretation of these results is that the elongation depends on the type and number of bonds that are established between the collagen fibers and the vegetable extract used, which are mostly of the hydrogen bridge type. However, it should be remembered that the vegetable extracts used are not natural, they are chemically modified. This means that not all extracts from the same family behave the same.

Finally, it is found that the shrinkage temperature depends solely on the type of vegetable extract used as tanning agent (P = 0.0258). It is a logical result since the stabilization of collagen (degree of tanning) depends on the number and type of links between the collagen and the tanning agent. When quebracho or mimosa are used as tanning agent, higher shrinkage temperatures are obtained than chestnut is used.

The results of the physical tests make it possible to affirm that the leathers obtained by performing an oxidative unhairing and a tanning with vegetable extract are valid for manufacturing a significant number of leather articles to be used, for example, in leather goods, upholstery or saddles.

It should also be highlighted that with the oxidative unhairing process with hair recovery, similar (or better) values of physical properties to those obtained with reductive unhairing are achieved; on the other hand, with the oxidative unhairing process with hair dissolution those values are lower. Taking into account that with the oxidative unhairing process with hair recovery more H_2O_2 and less NaOH are used than with the same unhairing process with dissolution of the hair, it could be considered that NaOH is responsible, directly or indirectly, for the greater hydrolysis of collagen fibers which results in the loss of resistance of the hide. Confirming this assumption would require specific research and would be interesting since it could open the door to solving one of the problems presented by the oxidative hairing removal studied, which is precisely the loss of physical resistance in the finished leather. This solution could come, for example, from the partial or total substitution of NaOH as a basifying agent.

Finally, it is shown that the type of chemical base of the commercial vegetable extract used only influences the shrinkage temperature. In the other physical properties analyzed, the results are independent of the type of vegetable extract used, which indirectly indicates that the behavior of the vegetable extracts is very similar, regardless of whether an oxidizing or reducing hairing process is used. This is in contrast to chrome salt tanning, where leathers subjected to oxidative unhairing absorb more chrome. This is surely due to the fact that due to oxidation, more carboxylic bonds appear in the hide. Chromium reacts with these bonds and tanning occurs. On the other hand, for tanning, the tannins of the vegetable extracts react preferentially via hydrogen bonding.

Figure 4 shows the results of the chemical analyses carried out to the residual floats.

Chemical analyses carried out to the residual floats revealed when a reductive unharing is used, approximately 5 kg of HS^- per tonne of rawhide was wasted. This value is in accordance with that accepted by the International Union of Leather Technologists and Chemists Societies (IULTCS),[6] which places this value between 2-9 kg of S^{2-} per tonne of rawhide. No sulfide was found in the analyses carried out in the residual floats of the two oxidative unhairing methods used. “Toxicity” results depended on the unhairing method: 1953 eq/t hide for the reductive unhairing, 190 eq/t hide for the oxidative unhairing with dissolved hair and 25 eq/t for the oxidative unhairing with hair recovery. As expected, replacing the unhairing product eliminates any presence of sulfide or hydrosulfide in the residual floats. Consequently, all toxicity problems related to hydrogen sulfide disappear. The use of hydrogen peroxide as an unhairing agent does not cause any toxicity problems, since at the end of the unhairing

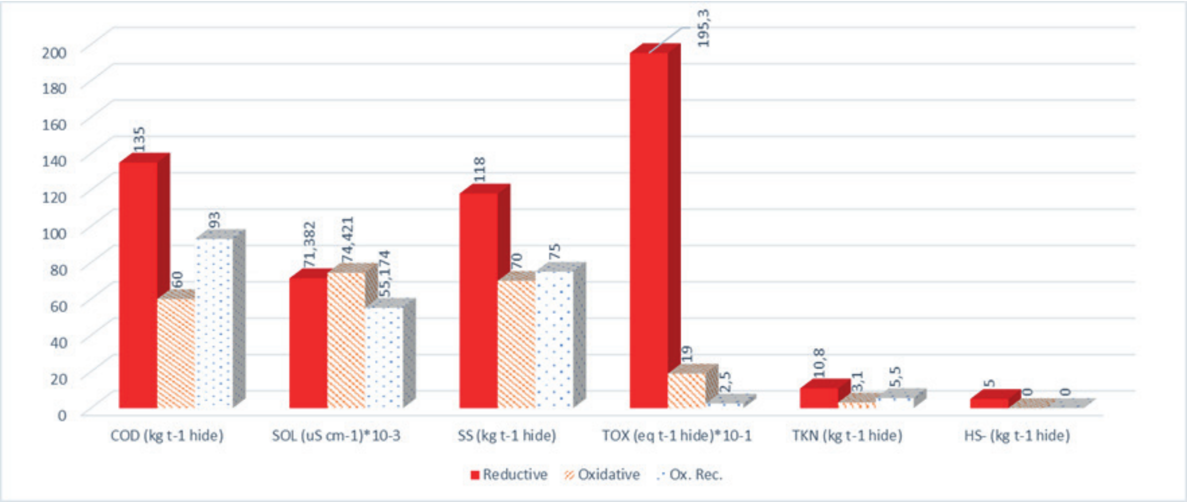

Figure 4. Pollution load of wastewater (Reductive = Reductive unhairing; Oxidative = Oxidative unhairing with dissolved hair; Ox. Rec. = Oxidative unhairing with hair recovery).

process the entire compound has been converted into water. The decrease in the main polluting parameters is also remarkable when replacing the Reductive unhairing with an Oxidative unhairing. In the case of Oxidative unhairing with dissolved hair, the COD decreased by 56%, the SS by 41% and the TKN by 71%. In the case of Oxidative unhairing with hair recovery, a 31% decrease in COD and SS and a 49% decrease in TKN was obtained.

Similarly, the substitution of chromium as tanning agent by the different vegetable extracts allowed to eliminate the presence of Cr III in the residual tanning floats, thus avoiding the risk of serious toxicological problems (mainly generation of Cr VI) that this product can produce.

Regarding the solid waste generated in the process, the absence of sulfides and chromium III greatly facilitates its reuse since it avoids having to carry out laborious and expensive processes to eliminate these toxic chemicals.

Conclusions

The results of the tests carried out show that many leather items suitable for various purposes (leather goods, upholstery, saddles, etc.) can be manufactured avoiding the latent toxicity problems involved in the use of hazardous materials such as sodium sulfide / hydrosulfide and chrome salts. These compounds, in themselves highly polluting, can be transformed into others (hydrogen sulfide and chromium VI) that are very harmful to human health, and can lead to the death of the person affected by inhalation or intake. The replacement of the reductive unhairing by an oxidative one and the replacement of the tanning chromium salts by vegetable extracts makes it possible to manufacture leathers bypassing the mentioned hazards, significantly reducing the pollutant load of wastewater and greatly facilitating the reuse of solid waste.

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