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Cleaner Production Opportunities in Leather Tanning in Palestine

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Abstract

Cleaner production (CP) options for leather manufacturing in Hebron are identified and evaluated for the purpose of examining their potential adoption. The approach was descriptive combined with field sampling and laboratory testing from seven factories. All processes in the investigated factories have been monitored, focusing on chromium contamination in wastewater (WW). In addition, pollution sources from every process have been identified, in a parallel paper, and used in this analysis. The determined process efficiency of tanning is found to be low to medium, compared to that reported in previous work. The evaluation of the identified CP options indicates that the most practical options is the improvement of operating conditions of the tanning process, such as pH, for increasing chromium uptake efficiency. This requires further experimental study to investigate the technical feasibility, industrial acceptance and the impacts of process modifications on the quality of the produced leather.

Key words: Leather, tanneries, wastewater, chromium, cleaner production.

1. Introduction

In leather manufacturing, raw hides are transformed stage-wise through various physicochemical processes for cleaning and removing non-collagen materials, then stabilizing the collagen fibers into leather matrix. A detailed review of local leather processing and associated pollutions have been presented in a recent previous publication [1]. The production starts with a soaking the hides in water and detergents, then the cleaned hides are subjected to a liming step for swelling and hair removal, using lime and sodium sulfide (unhairing). Then, the pH is deceased to allow hides to receive chromium, through deliming using ammonium sulfate followed by pickling using acids and salts. In tanning process, a solution of chromium sulfate (7 g/L) is used to allow crosslinking between collagen fibers, which makes the hide resistant to putrefaction and thermal effect. Finally, the hides are re-tanned using dyes and auxiliaries for softening the leather product [2]. Each of these processes releases wastewater (WW) contaminated with various pollution content, resulting from the residuals of the used chemicals (e.g. sodium chloride, sulfide, lime, chromium sulfate…etc) and from the released dirt's, bloods, hair.

Leather industry releases large amounts of WW, with high chemical oxygen demand (COD), biochemical oxygen demand (BOD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), and ions of chromium, chloride, ammonia and others. The pollution loads differ from one tannery to another depending on the applied technology, source and type of hides, amounts of process water and types and doses of chemicals [1]. Chromium is the major environmental concern in leather industry. Only, the non-hazardous Cr (III) is used in tanning, since the hazardous Cr (VI) does not have tanning function [3]. However, minor concentrations

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of Cr (VI) may exist in WW as a result of oxidation of Cr (III) under certain circumstances and from contaminations of raw materials of $Cr_2(SO_4)_3$ tanning agent [1]. The inventory of the generated hazardous waste has been estimated in a previous publication [4].

Previous studies indicated that about 30-40% of chromium input to traditional tanning process is released from the system, whereas the rest reacts with the hides [5]. Previous studies reported that the concentration of chromium in WW released from a tanning process is in the range of 1.5–3 g/L [6]. A previous case study, on one local factory of cow hide processing, indicated that such a WW was highly concentrated with chromium, with a concentration of about 3.5 g/L, equivalent to chromium uptake efficiency of about 47%. Such an efficiency is below the previously reported range of 60–70% [5].

These levels and types of pollutions urge the need for investigating CP options. CP focuses on waste minimization, pollution prevention, eco industrial production, and aims at conserving raw materials and minimizing hazardous raw materials [7]. It is usually based on five prevention principles including: good housekeeping, substitution of raw materials, product modification, equipment modification and better process control. There is a considerable knowledge gap related to CP strategies in Palestine. There is also a lack of awareness on CP in reducing production cost and in environmental protection. Palestinian environmental laws and systems [8] do not focus on advancing CP. There were no previous initiatives of CP practices in tanneries. Previous environmental attempts focused mainly on treating WW contaminated with chromium from the tanning step [9-11]. Currently, a Palestine Dutch Cooperation Program (PADUCO) is gearing new efforts to promote CP in Palestine. This paper is one of the outputs of one of its funded projects, aiming at evaluating CP for leather tanning, as a case study from Palestine, to suggest options for improvement, including a large number of local factories.

2. Materials and Method

The method for obtaining experimental results was through laboratory testing of collected WW samples from all processes, from seven local leather factories. All processes in local factories had been monitored and pollution loads were determined. The pH of the WW samples was measured using pH Bench Meter (Milwaukee MI150, US). The WW samples were analyzed for chromium content as detailed in a previous publication [1]: The total chromium was measured by ICP-MS. The required information about the inputs and outputs of various processes were obtained through a walk through inspection of the tanneries and by interviews with production managers. Mass balance calculations, and the descriptive approach were used for process auditing and identifying CP options. Various reported CP options in previous literature were reviewed and evaluated for further consideration by the local industry.

3. Results

Results of experimental data from field samples are presented in section 3.1, as concentrations of Cr in ppm for all processes, except for WW from tanning process, which are given in g/L. Section 3.2 summarizes the analysis of the CP options.

3.1. Experimental results of laboratory testing of field samples

Figure 1 shows results of the chromium content in WW from every process of one of the factories involved in this field study. It shows experimental data from three replicates, while the average value is indicated as a number. The values of standard error ranged from 3 to 30%. The data for WW from tanning process exceeds the limits of the vertical axis; the average value is given on the figure (3014) and the standard error is 197. Figure 2 shows results of the measured pH of WW from each process of all investigated factories, as averages of three replicates.

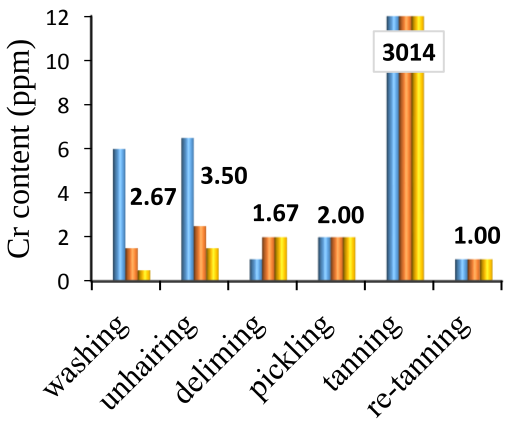

Figure 1. Cr content in each type of WW from each process of a sample factory (F3), (three replicates)

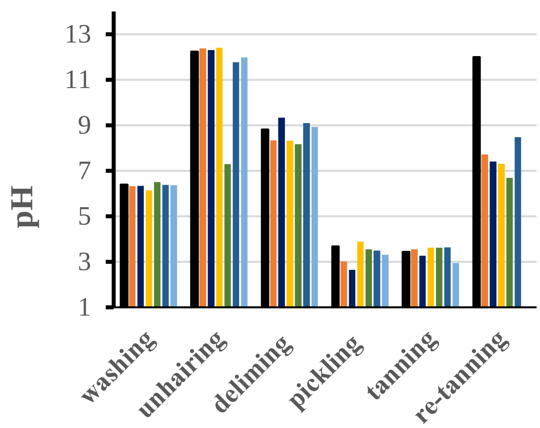

Figure 2. pH of WW from processes of all factories (averages of three replicates)

Figures 3 and 4 show results of the chromium content in WW from washing and unhairing processes, respectively, for each of the seven factories involved in this field study. They show experimental data from three replicates. The standard error ranged from 5 to 37%. In some samples, Cr was not detected and reported as zero. Most of these values are relatively small, except for WW from washing from factory no. 6.

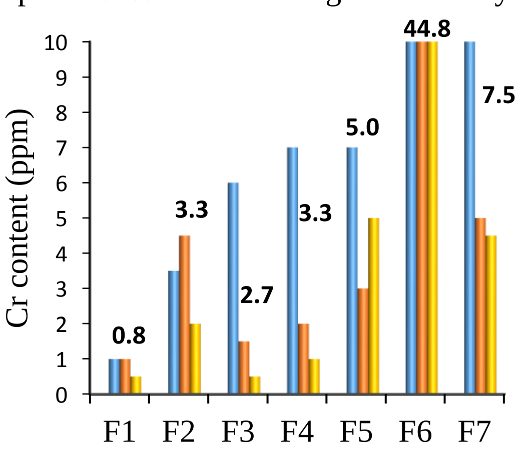

Figure 3. Cr content in WW from washing process from all investigated factories (three replicates).

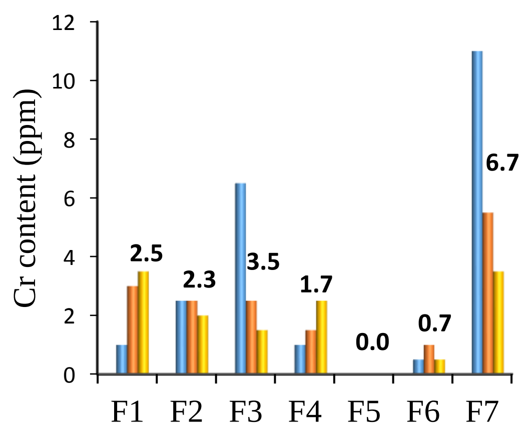

Figure 4. Cr content in WW from unhairing process from all investigated factories (three replicates).

Figures 5 and 6 show results of the chromium content in WW from deliming and pickling processes, respectively, for each of the seven factories involved in this field study. They show experimental data from three replicates. The standard error ranged from 3 to 58%. Most of these values are relatively small and creates no major environmental concerns.

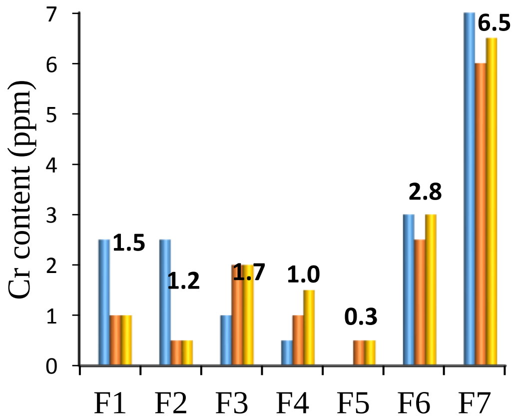

Figure 5. Cr content in WW from deliming process from all investigated factories (three replicates).

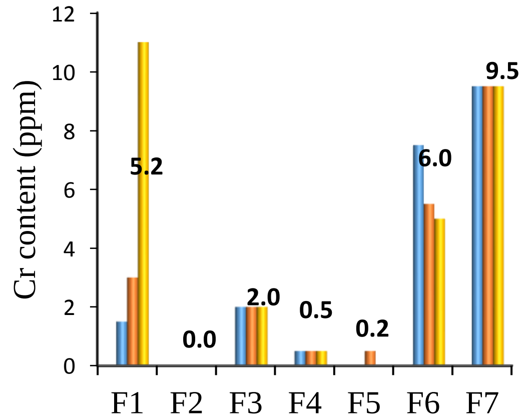

Figure 6. Cr content in WW from pickling process from all investigated factories (three replicates).

Figures 7 and 8 show results of the chromium content in WW from tanning (in g/L) and re-tanning (in ppm), respectively, for each of the seven factories involved in this field study. They show experimental data from three replicates. The standard error ranged from 1 to 25%. The levels of Cr content in WW from tanning are of environmental concern. However, Cr in WW are relatively small and creates no major environmental concerns.

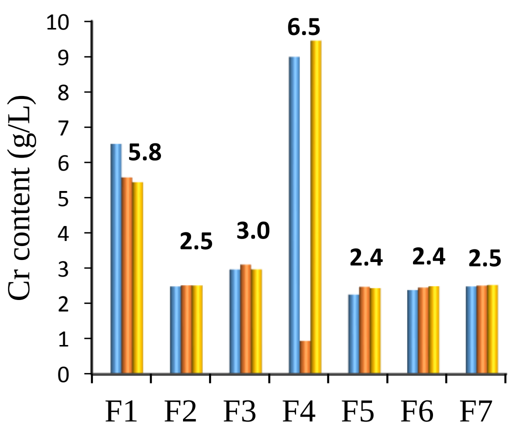

Figure 7. Cr content in WW (in g/L) from tanning from all investigated factories (three replicates).

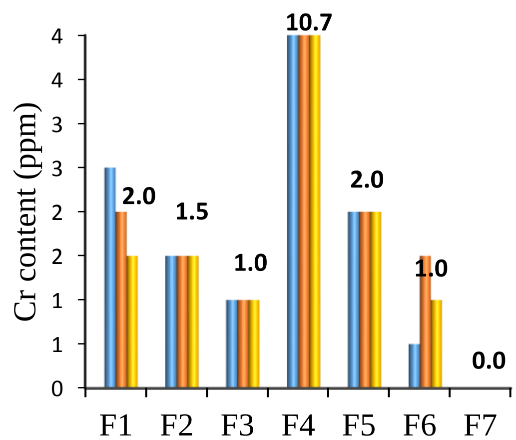

Figure 8. Cr content in WW from re-tanning process from all investigated factories (three replicates).

3.2. Results of the analysis of the CP options

The manufacturing processes are summarized in Table 1: The local tanneries receive preserved salted dry hides. The production process starts with a mechanical shaking for salt removal. The hides are then soaked with water and detergents in order to remove salts and dirt. Then, lime and sodium sulfide are used to remove the hair and non-collagen materials, through swelling and hair disintegration. Then, deliming is performed using ammonium sulfate, where the pH is decreased. The pH is decreased further in the pickling step by using formic acid, since sulfuric acid is not available due to local restrictions. Then, tanning is performed by adding chromium sulfate, which creates crosslinking between collagen fibers. Finally, the hides are re-tanned using dyes and auxiliaries to obtain better softness.

Table 1 also summarizes the amounts of solid waste and the volumes of released wastewater from these processes. In a previous publication [1], pollution loads from all processes in selected two local factories have been determined, only one of them processed cow hides. The amount of WW generated locally is much lower than that generated by tanneries worldwide. This makes the WW pollution parameters of TS, TDS, SS, COD, chloride, ammonia and chromium generally higher than those reported worldwide in previous literature. The discharged WW does not comply with the legal permissible limits for the investigated characteristics. Liming process releases the highest COD at the highest pH value. The released WW contains no ammonia content before deliming. Ammonia concentration increases when proceeding from tanning to retaining. Another paper, presented in this conference, involves the determination of pollution loads of the seven factories involved in this study. Based on all these information, the identified CP options for each process are listed table 1.

Table 1. Leather manufacturing processes in Palestinian Tanneries and the identified CP options.

Processes and Conditions	Pollution Loads	Identified CP options
Mechanical Shaking	Salts	• Collecting salts and sending for reuse in salting fresh hides.
Fleshing	100 kg of solid waste per ton of processed cow hide (fats and non-collagen proteins)	• Performing it after liming. • Investigating protein recycling (e.g. in soap or poultry feed manufacturing).
Soaking (24-48 hrs) Detergents (0.3%) Fat remover (0.3%) Enzyme (0.5-1%) Water (150%)	≈ 1.5 m^3 WW/ton (Salt, dirt, fats, soap)	• Counter current soaking. • Using detergents and disinfectants in a shorter period: 8-20 hours.
Washing (2 hrs) Water (120%)	≈ 1.2 m3 WW /ton (Salt, dirt, fats, soap)	• Increasing pH by adding Na_2CO_3 and NaOH, for better effects.
Unhairing and Liming (18 hrs) Lime (4%) Sodium Sulfide (2-3%) Water (120%)	≈ 1.2 m^3 WW/ton Sulfide, lime and hair	• Performing in two stages. • Using sharpening agents (HNaS and Na_2CO_3). • Intacting hair removal or hair-save dehairing techniques. • Using enzyme assisted unhairing to reduce the level of COD and reduce sulfide content in effluent. • Recycling of spent liquor.
Additional **fleshing** step	50 kg of solid waste per ton of processed cow hide (flesh, fatty tissues,	• Investigating recycling of solid wastes in soap or poultry feed manufacturing.

	hair and excess lime and Na2S). Little WW	
Deliming (3.17 hrs- stagewise: 40, 90 then 60 min). Stages 1 & 2 at 35^{o}C Soap (0.3%)-Ammonium sulphate (1%) - Fat remover (0.3%) - Water (100%) Stage 3: Dekeltal (2.5%) and Orpone (containing NH4Cl) (0.5%)	1 m^3 WW/ton from each stage	• Performing a single stage. • Organic acid based deliming. • Carbon dioxide based deliming. • Reusing deliming liquor.
Pickling (2.7 hrs shaking) Then, hides are left in the drum overnight, targeted pH 2.5-2.8. Salt (10%) - Formic acid (1%) Alternative acid (2.5) -Water (60%)	No waste	• Decreasing pH value (e.g. to 2.4) for better tanning conditions. • Using salt free organic acid pickling.
Tanning: (8 hrs mixing) Then. hides are left in the drum for 24 hrs - $Cr_2(SO_4)_3$ (7%) - Water (20%) for 6 hrs (Added to the same water used in pickling). Then, Soda ash (0.2%) for 2 hrs.	0.8 m^3 WW/ton (Chromium)	• Adjusting p: –first lowering pH to 2.4, then increasing to 4.1, by the addition of soda ash or sodium bicarbonate, to improve the chromium uptake.
Pressing	70% of entrapped tanning liquor from the fiber network.	
Splitting and Trimming	Solid waste: 40-80% of the hides as solid waste	• Performing splitting at liming stage, to reduce the required chromium for tanning and to increase chromium uptake. • Performing a feasibility study for using splits and trimmings for manufacturing glue, gelatine, protein flavor and reconstituted collagen.
Retanning stage 1 (1hr) Soap (0.5%), then, after 20 mins: Formic acid (0.5%) Hot water (100%) At 40oC	1 m^3 WW /ton	
Retanning stage 2 (1.5 hrs) Sodium formate (1.5%) Sodium bicarbonate (0.1%) Water (100%)At 40 oC	0.8 m^3 WW/ton (Oils and dyestuff) Air emission VOC	
Retanning stage 3		• Using non-spraying dying methods

Dying (6 hrs) Enzymes (6%) - Limosa (6%), Auxiliaries (6%), Dyestuff (0.25%), Water (80%) Oil (5%), Formic acid (1%)		such as curtain and roller coating, use of liquid and low dust dyes.

Table 2 lists the determined chromium uptake for each of the investigated seven factories (F1 through F7), based on information of feed preparation of 7 g/L of Cr for each factory and based on the analysis of Cr content in WW. The average percentage chromium uptake (of all factories) is 48.6%. However, if the data for factories 1 and 4 are excluded, the average percentage Cr uptake is 63.2%.

Table 2. Percentage Cr uptake or chromium tanning process efficiency.

tanning	Measured	Estimated
	Cr-out (g/L)	**Cr uptake**
F1	5.85	16.5%
F2	2.51	64.2%
F3	3.01	56.9%
F4	6.46	7.7%
F5	2.39	65.8%
F6	2.44	65.1%
F7	2.51	64.2%
average	3.60	48.6%

The most feasible options seems to be the improvement of tanning process towards increasing process efficiency (maximizing chromium uptake by hides), as well as chromium recycling and reuse. Table 3 summarizes the CP options related to chromium tanning process.

Table 3. Summary of CP options related to chromium tanning process.

CP Option	Advantages	Disadvantages	Application feasibility
Replacing tanning agents (e.g. titanium or aluminum compounds)	- Claimed to be effective for producing leather with the same quality of chromium tanning. - Elimination of chromium discharge in the effluent.	- Producing leather with high rigidity. - Requires additional chemicals. Very expensive.	Research level only. Not accepted by the industry.
Reducing Chromium in the effluent by improving chromium	- Cost saving of chromium - Reducing level of chromium in WW. - Good leather quality.	- More energy cost (when heating) with a longer running time and a higher temperature are needed.	- Acceptable by the industry. - Local motivations for this option. - Requires experimental

uptake		- Increasing fixed and operating costs (energy and improved drum).	CP investigations.
Recovery Cr reuse	- Cost saving of chromium Reducing chromium consumption. - Reducing Cr level in WW	- Increasing fixed and operating costs (WW treatment facility, chemicals and man power.	Local constraints on the availability of the required sulfuric acid for regeneration of the precipitated Chromium hydroxide.
Recycling Of Chromium	- Reducing Cr level in WW - Reducing consumption of water. - The simplest form of Cr management.	- Requiring changes to tanning procedures. Increasing the capital cost. - Resulting in changes in leather quality and color.	- It is viewed as a theoretical option only.

4. Discussion

These results indicate that the Cr contents, in WW released from processes other than tanning, are very small: in most cases they are below 10 ppm, and in many cases within 1-3 ppm. Only one sample of WW from washing (from F6) has a high value of to 44.8 ppm. These contents are detected although chromium is added in tanning step. This is attributed to possible residuals attached to the wooden processing drums, from previous batches of tanning and then released slowly in every time fresh water is loaded for a new process.

The alakinity or the acidity of the WW may lead to labelling some of these streams as hazardous waste, such an environmental concern may be reduced by creating a collection tank for highly alkaline WW streams and other one for highly acidic WW streams, then feeding them at a required proportions to an equalization tank to level of pH, and minimize hazardous characteristics of corrosivity [4].

The levels of Cr content in the released WW from the tanning process (Fig. 7) are relatively high, ranging from 2.4 to 6.5 g/L. The high values of 6.5 g/L (F4) and 5.8 g/L (F1) are way beyond the reported range in the literature of (1.5–3 g/L) [6]. This is partially attributed to the ineffective adjustment of pH in the picking process; the pH values for F1 and F4 are higher than that for the other factories (Fig.2). This indicates that pH is an important factor in process efficiency. However, for all other cases (F2, F3, F5, F6 and F7) the measured Cr in WW had very close values with the range of 2.4 to 3 g/L, which are within the reported range (close to its upper limit). They are less than the value reported in our previous case study, on one local factory of cow hide processing (3.5 g/L) [1]. These variations are attributed to day-to-day and factory-to-factory possible variations in operating conditions. Creating production log book may assist in monitoring and controlling such operating conditions.

The determined average percentage uptake of all factories (48.6%) is close to the value reported in our previous case study for one factory (47%) [1]. However, excluding the data for factories 1 and 4, for possible inaccurate handling or processing at the day of sampling, the average percentage of Cr uptake is 63,2%, which is within the reported range of Cr uptake for traditional tanning processes (60-70%) [5]. In addition, high process efficiency can be accomplished with better adjustment of the pH, before tanning (lower pH at pickling step at 2.4 instead of the measured values above 3.0, as shown in Fig.2. These pH values are better for Cr uptake than the value reported in our previous case study (4.65) [1]. As explained above for the variations in Cr contents, the pH variations may be also attributed to day-to-day and factory-to-factory possible variations in operating conditions.

In addition to lowering pH at initial tanning period, a higher pH after, by adding alkaline materials (see Table 3), can improve process efficiency. This pH controlling approach assists in enlarging the chromium complex after its penetration inside the hides (during the initial tanning period), and consequently improve chromium fixation and collagen networking within the hides. This is proposed to be done by adding soda ash or sodium bicarbonate to increase the pH after the initial tanning period. These recommendations are proposed for our future testing on the pilot scale tanning drum. It is also worth to note that the Cr content in the re-tanning process for F4 (Fig. 8) was relatively higher than all other cases. This may indicate that chromium fixing during tanning was not sufficient, since larger amount of Cr is released in the re-tanning step.

The proposed CP options of replacement of chromium with alternative tanning agents (such as aluminium oxide and titanium compounds), or combined tanning approach of these chemicals with chromium sulphates, does not seem practical to local factories; chromium tanned leather leads the best leather quality for shoes making in terms of mechanical characteristics. The level of acceptance of such CP options is planned to be investigated in our future field survey. For the time being, the CP approach of increasing the Cr tanning process efficiency is preferred. This is recommended to be accomplished through process modification (e.g. using of masking agents such as potassium tartrate and dicarboxylic organic salts and acids), and operation optimization (pH, Cr feed concentration, temperature, tanning period and drum rotation speed). An investigation approach will be based on testing the obtained leather product –from each tested process modification- for its mechanical properties of product quality (e.g. tensile test).

The above CP options represent an approach for reinforcing of environmental ethics. This is part of our moral responsibilities to future generations, while there voice in making environmental decision, is not available yet to be addressed. In addition, eco-manufacturing represents an ethical approach for industrial development. Environmental issues are more ethically driven that economic motivations. Some international companies in the field of leather and shoes industry are currently highlighting such ethical issues in their business literature, by explaining how their brands rate when it comes to its treatment of people, planet and animals. Local industry may need to give these aspects more attention, while moving ahead towards better professional business.

Conclusions

The current chromium tanning process efficiency is low to medium. The best operating conditions, it does not exceed 66%. WW from all processes of all factories contain low concentrations of chromium, but might create major environmental concerns. WW from tanning process must receive great attention for CP options, by focusing on the improvement of operating conditions for increasing efficiency.

The following recommendations are stated:

- A better approach for pH control must be developed.

- Ensuring full segregation of the WW line from tanning process from other WW streams.
- Mixing alkaline WW streams with acidic WW streams in an equalization tank to level out pH and minimize hazardous characteristics of corrosivity.
- Performing experimental studies to investigate the technical feasibility and the impacts of process modifications on the quality of the produced leather.
- Additional focus should be given on the high COD content in the discharges from beamhouse operations, and for responding to the sulfide content from unhearing process.
- A feasibility study is recommended for the recycling of the solid waste.

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