# Pollution Loads from Leather Tanning Processing in Palestine

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## Abstract

The present study aims determining the pollution loads from the wastewater (WW) released from the leather tanning industry in Palestine. WW samples were collected from all leather manufacturing processes from seven tanneries located in Hebron, Palestine. The physicochemical characteristics of the WW including, chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), pH and chromium, were analyzed and compared.

The results showed that approximately 10 $m^3$ of WW is generated per processing of one ton of hide. The physicochemical characteristics of the released WW vary according to the manufacturing process and differ from tannery to tannery. For instance, the COD of the WW released form hair removal and liming process was the highest amongst other leather manufacturing processes, with an average value of about 8000 mg/L. The pH of the WW was greatly dependent on the manufacturing process. The WW from pickling and tanning processes was rather acidic with pH values (2-4), whereas, liming and de-liming processes generated alkaline WW with pH values ranged between 8-12. WW resulting from washing process have the highest value of TS, TSS and TDS. The chromium was mainly present in the WW generated from tanning operation with an average chromium of approximately 3500 mg/L. It was mostly existed in the form of trivalent chromium (Cr+3) and only traces of the hazardous hexavalent (Cr+6) could be detected. The pollution loads discharged from leather making processes was rather high. The whole leather tanning sector releases about 29 ton of organic pollutants, 365 ton of total solids and 6 ton of chromium every year.

**Key Words:** *Leather industry, Tannery, Wastewater Characterization, Pollution Load*

## 1. Introduction

Leather manufacturing industry involves conversation of cow or goat raw hides into leather. The raw hides are subjected to a series of chemical and physical processes including soaking, liming, deliming, pickling, tanning and retanning to produce stable and high-quality leather. The salted hides are firstly soaked in water and detergents to remove salts and dirt. Then, the hair is removed through

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liming the hides with lime and sodium sulfide. After that, a deliming step is applied to remove the lime through the addition of ammonium sulfide. The hides are then pickled in an acidic liquor to lower the pH of the hides to be prepared for the tanning step. During tanning process, tanning agent (i.e. chromium sulfate) is added to create crosslinking between collagen fibers of the hides, which increases the durability, flexibility and resistance of the hides to putrefaction. Finally, the tanned hides are subjected to retanning during which dyes and auxiliaries for softening the produced leather [1, 2].

Various types of chemicals (about 130 chemicals) are used during the aforementioned leather manufacturing processes [3]. Most of these chemicals end up in the WW effluents from this industry. The discharged WW is characterized with high chemical oxygen demand (COD), biochemical oxygen demand (BOD), total solids (TS), chromium, chloride, ammonia and others [4-6]. It is worth mentioning that the type of technology, chemicals and amount of process water used during leather production vary from country to country and tannery to tannery, which consequently affect the pollution loads released from this industry. The amount of WW generated from processing one ton of hides ranging from 12-35 m3 [7]. In terms of pollutants, the chromium concentration also varies (1500-3000 mg/L) [8]. The COD ranges from 3000-10000 mg/L. The leather tanning industry produces large amount of solid wastes consists mainly of flesh and hide splits, trimmings and hair. Approximately 850 kg of solid waste is produced per processing one ton of raw hides [9, 10].

Leather manufacturing industry is an important industrial sector in Palestine with a total investment of about 7 million USD (Palestine Federation of Industries, 2011). In total, thirteen tanneries are currently working in Palestine, of which, twelve are located in Hebron and the other one in Nablus. Water availability is one of the major challenges and limitation that the local industry is currently encountered. leather manufacturing sector consumes about 70,000 m3 of water /year [11]. During processing, most of this water is ended up as WW contaminated with various biodegradable and organic maters, chromium, salts and suspended solids. The generated WW is eventually discharged into the sewer system and open environment without proper treatment [3]. In a study that was recently published, the WW from all leather manufacturing processes obtained from tow tanneries in Hebron (cow hides tannery and goat skins tannery) was characterized for the purpose of identifying cleaner production options [12]. The study showed that the WW produced in these local tanneries is much more concentrated with pollutants than tanneries worldwide.

The current study aims at evaluating the pollution loads from leather manufacturing industry through extending the previous characterization work and cover most of the tanneries in Hebron district. WW samples were collected from al

manufacturing processes from six different tanneries of various production capacity. The physicochemical characteristics of WW including, chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), pH and chromium, were analyzed and compared and the pollution loads were eventually determined.

## 2. Materials and Method

### 2.1 Materials

Real samples of industrial WW from all of the leather manufacturing processes were collected from seven local cow-hides tanneries in Hebron, Palestine. The samples were collected in polyethylene bottles and stored at 20oC until testing. Chemicals used during the tests include silver sulfate (Sigma-Aldrich, USA), mercury (II) sulfate (Acros organics, USA) sulfuric acid (Dasitgroup, Italy).

### 2.2. Wastewater characterization

The COD of the samples was measured using titrimetric method (5220 C. closed reflux titrimetric method). In this method, potassium dichromate was used as a strong oxidizing agent to oxidize the organic content of the sample under acidic conditions. The pH Bench Meter (Milwaukee MI150, US) was used to measure the pH of the samples. To measure the TS, the samples were dried in the oven at 105°C for 48 hours and the material left after evaporation and drying was determined. The TDS were measured using TDS meter (JENWAY 4510 bench conductivity meter, UK). The TSS values were than calculated from the difference between TS and TDS. The total chromium was measured by ICP-MS (Agilent Technologies 7500 Series, Agilent, Santa Clara, CA, USA). The samples for all aforementioned WW characteristics, except for COD, were measured in triplicates and average values were depicted.

## 3. Results

Tannery effluent is generally a dark brown-greenish liquid, characterized with high COD, TDS and chromium content and with great variation in the pH. The average pH values of the WW released from all processes from the seven factories are shown in Table 1. The pH values varied with the manufacturing process. For instance, the beamhouse operations (i.e. liming and deliming) generated highly alkaline effluents with pH ranges 8-12. Whereas, the WW released from tanning processes (i.e. pickling, tanning and retanning) was highly acidic with pH values of around 3. Comparing the pH results between the seven tanneries, one could conclude that the behavior was rather similar and the variation in pH values was minor as can be seen from the standard deviation values in Table 1.

Table 1: The average pH values of the WW generated from various leather processes. Data were obtained from the seven different tanning factories and averaged.

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| Process | pHave | Standard deviation |
|---|---|---|
| Washing | 6.35 | ± 0.11 |
| Liming | 11.48 | ± 1.86 |
| Deliming | 8.71 | ± 0.44 |
| Tanning | 3.26 | ± 0.39 |
| Re-tanning | 3.54 | ± 0.22 |

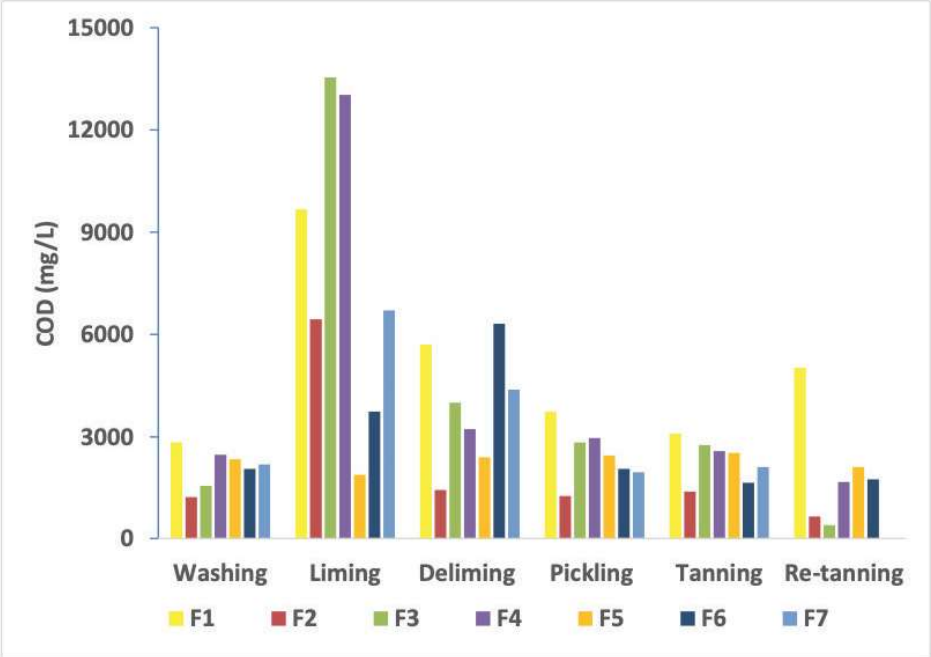


Figure 1

Figure 1 shows the COD of the WW generated from all processes in the seven tanneries, with "F" denotes for the factory number (1-7). Significant differences in the organic load generated from the various tanning processes could be noticed. The average COD of the WW released from beamhouse operations, mainly liming and deliming, was the highest at around 8000 mg/L and 4000 mg/L, respectively. The subsequent tanning processes gave relatively lower COD values of approximately 2000 mg/L. Clear variation in the COD from various tanneries was observed (see figure 1).

The TS, TDS and TSS from all processes are shown in figures 2, 3 and 4, respectively. Large amounts of solids in all forms were present in the WW generated from first steps of the beamhouse operations (i.e. washing and liming)

Whereas, the WW released from the final tanning operations (i.e. Re-tanning) seem to have lowest amounts of solids.

The results showed also that the chromium was mainly present in the WW generated from tanning operation, as chromium is only added during this production stage. The average chromium concentration in the WW obtained from tanning process was approximately 3500 mg/L. The chromium was mostly existed in the form of trivalent chromium (Cr+3) and only traces of the hazardous hexavalent chromium (Cr+6) could be found.

The total average pollution loads generated from processing of one ton of hides from all manufacturing processes in the seven tanneries were measured and results are shown in Table 2. Based on the results obtained in Table 2, the annual pollution loads released from the leather tanning sector in Palestine was estimated (see Table 3), assuming a total manufacturing capacity of 1000 ton raw-hides/year. The results show that the pollution resulting from this industrial sector is remarkably high, especially the amount of chromium, organics and solid pollutants released to the environment.

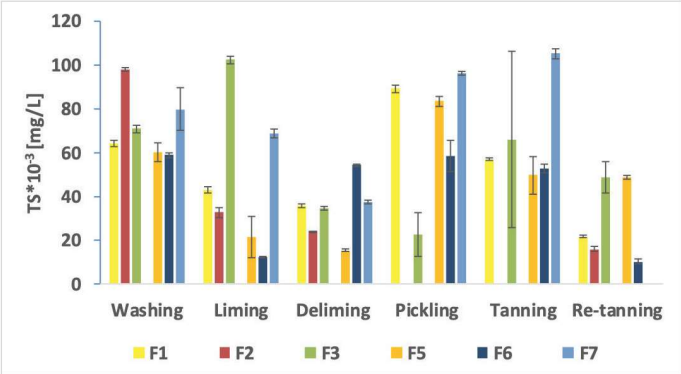


Figure 2

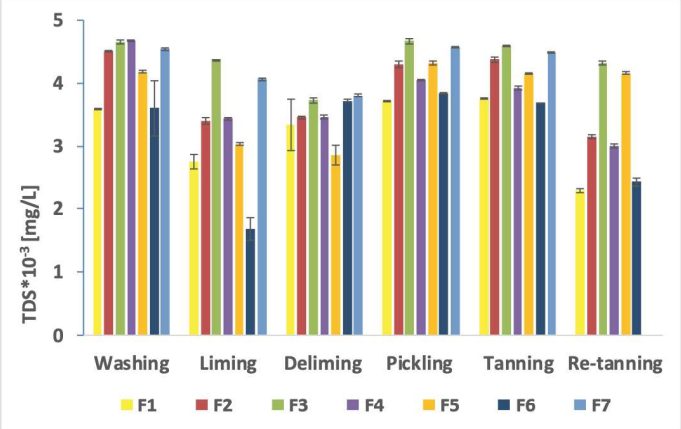


Figure 3

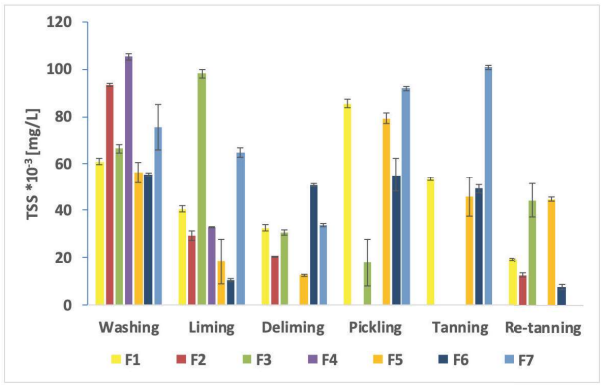


Figure 4

Table 2: The average pollution loads generated from processing of one ton of hides from each leather making process. Data were obtained from seven different tanneries and averaged.

| Process | Volume WW [$m^3$] | kg COD/ton hide | kg TS/ton hide | Kg TDS/ton hide | kg TSS/ton hide | kg Cr/ton hide |
|---|---|---|---|---|---|---|
| Washing | 1.40 | 2.94 | 101.03 | 5.95 | 102.65 | |
| Liming | 1.7 | 13.09 | 77.90 | 5.41 | 69.95 | |
| Deliming | 1.7 | 6.53 | 55.96 | 5.81 | 50.02 | |
| Tanning | 1.7 | 3.83 | 91.96 | 6.90 | 83.00 | 5.84 |
| Re-tanning | 1.25 | 2.42 | 36.34 | 4.04 | 32.26 | |

Table 3: The total annual pollution loads released from the leather tanning sector in Palestine, assuming a total manufacturing capacity of 1000 ton raw-hides/year

| Pollution parameter | Pollution load [kg/year] |
|---|---|
| COD | 28809 |
| TS | 363201 |
| TDS | 28111 |
| TSS | 337886 |
| Chromium | 5840 |

## 4. Discussions

The variation in the characteristics of the WW generated from various processes is ascribed to the difference in the function of each process and the chemicals added during operations. For instance, the low pH values obtained from the pickling and tanning process is due to the use of acids during these operations to

enhance the chromium uptake during tanning and retanning processes. On the other hand, the addition of lime and other alkaline chemicals during liming step, results in high pH of the released WW (see Table 1).

In the same manner, the high COD from the liming and deliming operations is attributed to the fact that the alkaline medium helps in the removal of most of the organic materials from the hides including hair, epidermis, protein, and fats, hence, resulting in organic levels in the released WW.

The discharged WW from soaking and washing step contains high levels of TS, TSS and TDS because most of extraneous organic and inorganic matters are removed during these operations, including, salts, dirt (blood and other foreign materials), and soluble non-fibrous proteins and residuals. Besides, the use of detergents and fat remover chemicals during soaking and washing contributes to the high solid levels in the discharged WW. As most of the solids and dirt were already removed during the initial beamhouse operations, the TS in the final operations, i.e retanning, were quite low.

The difference in the WW characteristics between various tanneries might be related to the variation in the operational procedures, types of added chemicals and quality of the salted raw hides. For example, some of the tanneries may conduct some of the processes at several stages (i.e. two or three stages), while, others perform same processes in a single stage. Furthermore, the amount of process water varies from factory to factory and from process to process, which considerably affects the pollutants concentration in the resulting WW. In general, the amount of process water used in tanning industry in Palestine is much lower than other tanneries worldwide, which explains the high values of pH, COD, TS, TDS and TSS as compared with literature. It is worth mentioning, that the measured WW characteristics from various processes in the local tanneries, exceed most of the standard allowable limits including Palestinian, Jordanian, and WHO standards limits. This is agreement with the results obtained in the previous publication [12].

The WW generated from tanning industry is among the highly polluted WW compared to other industrial sectors. This is clear from the high pollution loads from each process (Table 2) and from the whole leather tanning sector (Table 3). This is due to the variety of toxic chemicals used during leather manufacturing such as chromium, detergents, ammonium, sulfides, acids, chlorophenols, biocides and dyes. In addition, the raw-hides release large amount of organic and biological maters during hide processing, which may provide a chance to a variety of pathogenic bacteria to grow and contaminate the released WW.

The discharge of the WW from leather industry without proper treatment may result in significant levels of water and soil pollution. For instance, the high salt content in the WW can increase the salinity of the water and soil which deteriorates the fertility of the soil. Besides, high sulfide loads in the WW can lead to deficiency of some micronutrients in soil such as Zn, Cu and Fe [13]. Furthermore, the release of chromium contaminated WW into the surrounding open environment and valleys, may give the opportunity for the oxidation of (Cr+3) into the more toxic and hazardous chromium (Cr+6). This critical environmental problem requires urgent mitigation measures to reduce the environmental impacts from this industry. In Palestine and most of the developing countries, the leather making processes are rather traditional and poorly controlled. Advanced and effective WW treatment techniques should be applied to reduce the pollution load in the discharged WW. Besides, optimization of chemical and water consumption as well as implementation of cleaner production strategies are needed to make this sector more sustainable and environmentally sound.

## 5. Conclusions

Physicochemical characteristics of WW characteristics from all manufacturing operations from seven leather tanning factories were measured. The pollution load resulted from each production process and from the whole tanning sector was determined. The beamhouse operation generated high alkaline WW with high COD, TS, TDS and TSS loads, whereas, subsequent processes i.e. tanning operation, gave acidic WW with high chromium content. The pollution loads discharged from leather making processes and from whole tanning sector is quite high. Approximately, 29 ton of organic pollutants, 365 ton of total solids and 6 ton of chromium are released from this industry every year. This requires immediate actions to reduce the resulting environmental pollution.

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## Figure captions:

**Figure 1**: The COD in mg/L of the WW generated from various leather man

ufacturing processes. Data were obtained from seven different tanning factories.

**Figure 2**: The average TS values in mg/L of the WW generated from various leather manufacturing processes. Data were obtained from seven different tanning factories.

**Figure 3**: The average TDS values in mg/L of the WW generated from various leather manufacturing processes. Data were obtained from seven different tanning factories.

**Figure 4**: The average TSS values in mg/L of the WW generated from various leather manufacturing processes. Data were obtained from seven different tanning factories

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