Leather Manufacturing Wastewater Characterization and Cleaner Production Options

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II

Dedication

"Say: 'Allah will see your works and so will His Messenger and the believers; then you shall be returned to the Knower of the unseen and the visible، and He will inform you of what you were doing. "[9.105]

Praise be to Allah in the beginning and in the end

To our true source of hope, to the people who keep us going through struggles and hardships, our parents.

To our dearest friends, your encouragement and continuous support is only matched by your big hearts and pure souls.

Thank you from the depths of our hearts.

Acknowledgment

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Thank you all and god bless you.

Table of Contents

List of figures

List of Tables

Abstract

This study analyzes physicochemical characteristics of wastewater from all of leather manufacturing processes, and compare pollutants load released from goat and cow hides manufacturing processes.

Results of experimental work for characterization of wastewater released from two local tanneries are presented. By analysis of pH, chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), chloride, ammonia (NH3) and chromium.

Characterization of these process effluents was done in order to identify the waste generation rate and quantities discharged. Highest pH value measured was about 13.5 in liming process while the lowest was about 3 in retanning effluent. COD of liming-hair removal effluent exceeded 160000 mg/l, which contributed to more than 50% of total COD. Analysis of chromium tanning effluent showed that hexavalent chromium concentration was 3.2*10-4 mg/L, which is below the permissible limit.

Future research work for management of chromium containing wastewater in this industry is important. Financial burden from ever-tightening “Israeli” occupation’s legislations on leather manufacturing industry and the associated environmental impacts shall motivate research work for better exhaustion and uptake of chromium.

KEYWORDS

Leather industry, Wastewater, Characterization, Chromium, Cleaner production.

Chapter 1

Concept of the Project

1.1 Introduction

The leather industry occupies a place of prominence for economic growth, employment and exports in Hebron city, Palestine. The products of this industry are the inputs for footwear and leatherwear industries, which are considered leading industries in Hebron city. There are currently fifteen tanneries were established in the West Bank and presently employ about 70 workers, with a total investment of 7 million USD, where eleven of the tanneries are located in Hebron and the rest in Nablus [1,2]. Leather industry has emerged in Hebron city in the early twenties of the past century, and since then, it has faced countless challenges and difficulties in striving for survival, starting from Israeli occupation restrictions to market competition.

Leather production goes through three main steps to attain finished salable leathers, which are preparation of hides, tanning and finishing. Animal skin consists of three layers – the epidermis, dermis and hypodermis. The epidermis is the surface layer and largely consists of hard and dead cells, and the hypodermis is made up of muscle and fat, both of these layers are removed in leather manufacturing processes, leaving some of fibrous dermis. The dermis consists of fat cells, water, proteins, carbohydrates, and minerals; the major protein in the derma is collagen, which is made up of long sequences of amino acids. Collagen structure consists of twined triple units of peptide chains, these chains within the triple helices are held together by hydrogen bonding, and the amino acid residues are joined together by peptide links [3, 4].

Leather industry consumes large amounts of chemicals (approximately 130 different types of chemicals) ranging from common salt (sodium chloride) to toxic chromium sulfate [5]. For each ton of raw salted hides processed between 680 to 850 kg of solid waste is produced, and the amount of wastewater released is estimated to be 20 m^3 with chromium concentrations between 1500-3000 mg/L [6]. The allowable concentration of discharged chromium-containing tannery wastewater according to Germany is 1 mg/L total chromium and 0.05 mg/L hexavalent chromium [7]. In addition to large consumption of water during the manufacturing processes, the water consumption of Palestinian tanneries is estimated at 70000 m^3 /year [8].

Leather industry poses several threats to the local environment and to employees. It releases a large amount of wastewater and solid waste that generate during leather production. Tannery wastewater is highly concentrated with hazardous materials such as sulfide and chromium. About 30-40% of chromium used is released from the system as a solid or liquid waste, which eventually ends up in soil and ground water, whereas the rest react with the hides [9, 10]. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended and dissolved solids, sulfide and high concentrations of organics and salts are discharged to the sewer along with the chromium wastewater [5]. Currently chromium wastewater is discharged without proper treatment risking occupational exposure to chromium that increases the risk of eye irritation and causes many of respiratory effects [11].

The severity of such Palestinian environmental problems is further intensified by the fact that all tanneries are located close to residential areas. In Hebron, tanneries are located in an industrial zone, but some of these tanneries are now just a few meters away from residential homes or main transportation routes. The environmental problems of leather industry are confined mainly to the tanning process, which releases wastewater containing large quantity of chromium. Tannery wastewater is drained into the public sewage network without an appropriate treatment.

The lack of proper treatment for chromium wastewater and the mishandling have caused the closure of many tanneries in Palestine by Israeli occupation in prevention of more environmental damage. Although the leather tanning industry contributes to the national economy, the prospect for this sector is not promising. However, it could be greatly enhanced by the implementation of appropriate cleaner production technologies to deal with the aforementioned problems.

Cleaner production (CP) usually refers to the improvement of industrial production processes. It involves the conservation of raw materials, water and energy, the elimination of toxic raw materials, and the reduction in the quantities and toxicity of wastes at source during the production process. Cleaner production principles lead to cost effective and environmentally sound industrial processes [12].In short, it identifies where and why resources are lost in form of waste and pollution and how to eliminate or minimize these losses.

In tanning process, there are many cleaner production technologies can be implemented to avoid chromium present in effluent or at least to reduce it. Alternative tanning agents can be used to replace chromium completely and high exhaustion technique ensures that more chromium actually affixes to the hides/skin. Chromium can be recovered by alkaline-precipitation.

The current study aims at characterizing the industrial wastewater resulting from all leather manufacturing processes in Hebron-Palestine and comparing results between cow and goat manufacturing processes. CP principles and opportunities for chromium containing wastewater will be applied in the future.

1.2 literature review

Implementation of CP principles in tannery wastewater has been taking place worldwide. Several researchers reported several CP technologies as preventive strategies to eliminate or minimize this industry's wastes. Some of the related researchers results are as follows:

Cleaner Production is a protective strategy that protects the environment and the worker. At the same time, it improves industrial efficiency. CP technologies can be implemented at all steps of leather manufacturing processes to minimize the environmental impacts. Several clean technologies associated with chrome tanning were studied, including replacement of chromium with alternative tanning agents to avoid the presence of chromium in the effluent, in addition to better up-take or recovery and reuse of chromium to reduce it from the effluent [13].

Advanced tanning process aims at minimizing chromium concentration on the effluent by enhancing chromium uptake up to 90% by modifying process parameter and/or tanning process. The results from high exhaustion studies showed that, high exhaustion technique increases chromium utilization, and decreases the amount of chromium used and discharged in effluent. Several masking agents are commercially available, and can increase chromium utilization up to 98% compared to conventional chromium tanning [14, 24].High exhaustion of chromium with near zero chromium discharge is called closed loop tanning system, that leads to protect environment and there is no need to further treatment [25].

Chromium can directly be recycled from chromium tanning back into processed tank. Instead of being discharged into sewer system after one use. Recycling efficiency is only 68 % and it can reduce chromium use up to 20% [24].

The use of alternative tanning agent has been studied intensively. There are many effective alternatives to chromium salts (i.e. aluminum, zirconium and titanium compounds) [16].

Titanium is available in nature and nontoxic. Research on titanium tanning has documented in the past century with not much satisfying results. However, the use of betitanyl sulfate masked with citrate resulted in leather quality close to that tanned with chromium [15, 16]. Titanium tanning agents obtained from the waste of metal industry can be used to produce eco-friendly leather with acceptable physical and chemical characteristics [18].

Combination tanning of titanium with chromium for upper leather has been given higher chromium uptake; this combination leads to less chromium discharge in the effluent and overcomes possible poor exhaustion levels associated with the chromium compounds [17].

Iron can be used instead of chromium in tanning process. From experimental works, iron is suitable in the production of wet brown leather with low resistance to heat, so it must retanned with chromium or vegetable tanning agent [19].

Combination of aluminum and titanium (IV) was tested, and it produced full and soft leather; tanning is processed at pH 3-5.Many scientists used masking agents include carboxylic acid such as lactate to overcome the problem of hydrolysis [20].

Combination tanning of chromium and zirconium was studied, experimental work of 2% as ZrO_2 and 0.5% as Cr_2O_3 has been carried out. The result showed that, the higher exhaustion level of chromium and zirconium and the higher shrinkage temperature were obtained [21].

Precipitation is a very common way in heavy metal recovery. In this experiment, three different precipitating agents calcium hydroxide, sodium hydroxide and magnesium oxide were tested. Tests were carried out in batch experiments to determine the effects of pH, stirring time, stirring rate and sludge volume. As it turned out, magnesium oxide showed the best precipitating abilities for chromium at pH 8-9 with high settling rate and reasonable sludge volume [22].

D-Lysine aldehyde was tested as a substitute for chromium in attempt to develop a greener, eco-friendly tanning process. The shrinkage temperature, mechanical strength and other characteristics of the tanned leather were evaluated and was found to be nearly the same as that conventionally tanned with chromium [23].

1.3 Problem Statement

This research project will respond to the following main and sub main questions:

- **Main Question**

  For leather manufacturing processes, what are the main physicochemical characteristics of whole leather processes streams?

- **Sub questions**

  1- How do trends of COD, pH, ammonia, chloride and total solids change among all processes?

  2- How does pollutants load change between cow skins and goat hides manufacturing processes?

  3- Do tannery wastewater characteristics comply with allowable discharge limits?

  4- Can cleaner production (CP) principles be applied for efficient chromium-containing wastewater management?

  5- What is the sustainable approach for better chromium uptake for the tanning process?

  6- How does tanning parameters change affect the final product in terms of quality and cost?

1.4 Goals and Objectives

The main goal of this study is to characterize all leather manufacturing processes' wastewater and select the most appropriate CP option to be applied in leather industry to induce chromium elimination/minimization as the main source of concern. This study will adopt a CP option chosen based on technical as well as financial evaluations.

The project targets the following specific objectives:

- Reviewing the leather manufacturing processes and study the possibility of CP implementation.
- Characterizing the manufacturing processes to establish a full mass balance study.
- Establishing a focus on the major environmental issues regarding leather industry.
- Carrying out a quantitative analysis for consumed materials and waste generation.
- Preliminary evaluation for the suggested CP opportunities.

1.5 Significance of Study

The importance of this study lies in characterizing tannery wastewater from all manufacturing processes as a key step for management of this industry, in order to determine wastewater generation rate and pollutants quantities. Also to manage chromium-containing wastewater, where the pressure of the ever-tightening "Israeli" occupation's legislations increases due to the lack of proper treatment and mishandling and forces the manufacturers to have financial burden in order to dispose their wastes. Therefore, CP technology implementation would be financially effective and environmentally protective at the same time.

1.6 Methodology

1- **Pre-assessment phase.**
    - Walk-through inspection.
    - Pre-assessment of the leather tanning manufacturing process
    - Preparation of leather manufacturing processes flowchart
    - Establish a focus.

2- **Assessment phase**

- Collection and characterization of tannery wastewater
- Full mass balance study.
- Identifying CP opportunities.

3- **Evaluation and feasibility study**

- Preliminary evaluation.
- Economic evaluation.
- Environmental evaluation.
- Selection of a viable option.

4- **Implementation and continuation**

- Prepare an implementation plan.

1.7 Budget

This project is expected to have a total cost of 2000JD, detailed as table1.1.

Table 1.1: The total estimated cost for implementing the project

No.	Item	Cost (JD)
1	Chemistry lab tools (Beakers, flasks, cylinders, etc.)	330
2	Chemicals for tests (Potassium dichromate, 1.5 Diphenylcarbazide solution, etc.)	350
3	Equipment(Drums and motors)	450
4	Lab testing kits and trials	300
5	Heating plates	250
6	UV-visible spectrophotometer tests	200
7	Transportation	120

1.8 Action plan

Table 1.2: Action plan for the first semester

TASKS	1st Month				2nd Month				3rd Month				4th Month			
	Wk_1	Wk_2	Wk_3	Wk_4	Wk_1	Wk_2	Wk_3	Wk_4	Wk_1	Wk_2	Wk_3	Wk_4	Wk_1	Wk_2	Wk_3	Wk_4
Identification of Project Idea	■	■														
Literature Review			■	■	■	■	■	■								
Pre-Assessment Phase					■	■										
Assessment Phase						■	■	■	■	■	■					
Feasibility Analysis Phase										■	■	■				
Characterization of wastewater											■	■	■			
Documentation					■	■	■	■	■	■	■	■	■	■	■	
Presentation																■

Table 1.3: Action plan for the second semester

TASKS	1st Month				2nd Month				3rd Month				4th Month			
	Wk_1	Wk_2	Wk_3	Wk_4	Wk_1	Wk_2	Wk_3	Wk_4	Wk_1	Wk_2	Wk_3	Wk_4	Wk_1	Wk_2	Wk_3	W
Preparation of leather manufacturing processes flowchart																
Collection of effluent samples																
Characterization of effluents																
Preparation of CP implementation plan																
Documentation																
Final Presentation																

Chapter 2

Literature Review

2.1 Background

2.1.1 Skin structure

Skin forms about 16% of the body weight, it consists of water, proteins, fats, mineral salts and others (pigments i.e.) as shown in figure 1, and it consists of three structural layers; epidermis, dermis and hypodermis [4].

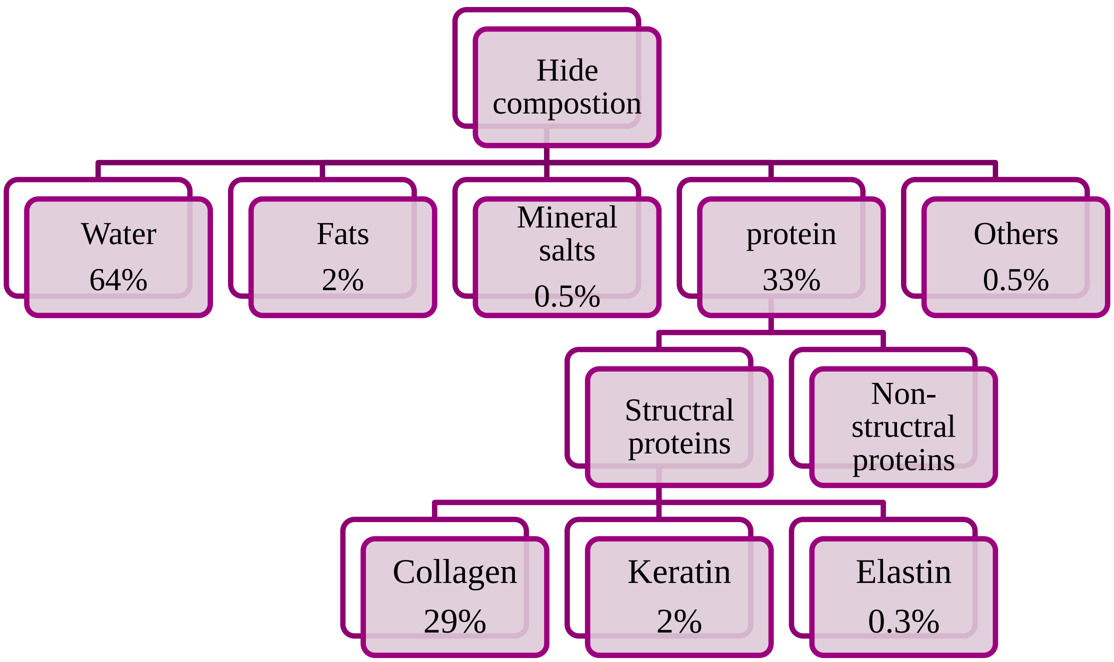

Figure 2.1: The approximate composition of animal hides [4]

Epidermis is an external, very thin layer that consists of dead cells full of keratin. Dermis (Corium) is the central layer and the most important part of the skin for leather manufacturing that comprises 70% of the protein component –mainly collagen, which is the most abundant protein, and forms a network of collagen fibers. It also contains hair roots. Dermis is made up of two layers, which are the papillary layer that supplies nutrients to the epidermis, and the reticular layer contains fiber network and proteins such as collagen, and elastin. Hypodermis is below the dermis and contains fat; this layer connects the skin to the muscle and bones [4]. Figure 2.2 shows three structural layers of skin.

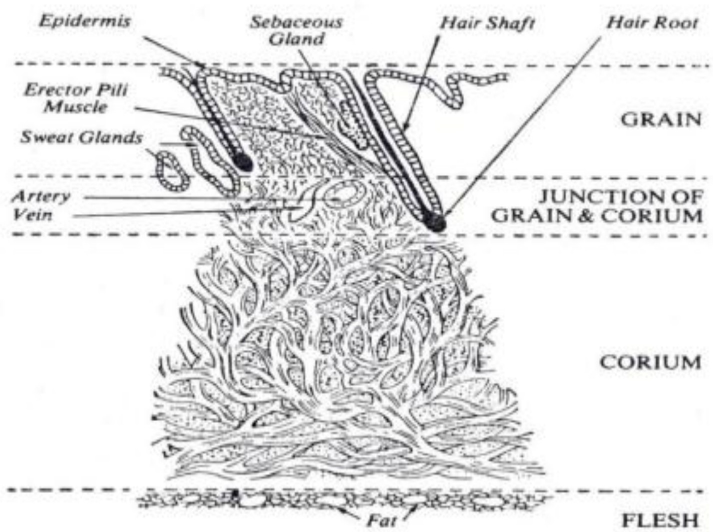

Figure 2.2: Cross section of Hide/ Skin [26]

2.1.2 Leather manufacturing processes

Leather making transforms dead animal skins into saleable leather that resists the microbial decomposition. The leather manufacturing consists of three main stages including preparation of hides in the beam house, tanning and finishing as shown in figure 2.3 [27]. During preparation of hides, pre-tanning operations are conducted, which include curing and storing, soaking, liming, deliming, bating and pickling.

Curing is a process that prevents the microbial decomposition of hides and skins by salting and drying. Hides and skins are stored on pallets in ventilated or air-conditioned area. Then stored skins are soaked, mainly to remove the salt and unwanted material such as blood, and to re-hydrate the material. Then, the soaked hides are ready for unhairing-liming step to remove the hair and epidermis. The hides are treated with an alkaline medium of sulfide and lime, and the pH of the skin being processed will rise to 12-12.5 [26] and the collagen swells, leaving a more open structure. Then the pH is adjusted in deliming process to become between 8-8.5, in order to enhance the enzymatic activity [14]. Bating is carried out to convert some of the proteins into soluble forms mainly to remove elastin. In pickling process, the pH is corrected to be suitable to the tanning operation and to prevent swelling of the leather to preserve them up to two years. In this process, acid liquor and salts are used, where pH between 2.5 and 2.8 is maintained in case of chrome tanning.

In tanning process, the most widely used mineral tanning agent is trivalent chromium. During chrome tanning, the skin structure is stabilized in its open form, where chromium penetrate the hides and react chemically with the collagen molecules making the fiber network resistant to bacteria by crosslinking with collagen, in addition to retain the skin natural properties such as flexibility and toughness [3] and basic chromium sulfate is used in chrome tanning. The pH is increased to 3.8-4.0 at the end of chrome tanning process, and the leather is called wet blue. The wet blue is then subjected to post-tanning operations, which include re- chroming, neutralization, dyeing, fat liquoring and finishing.

Re-chroming is carried out to increase the chromium content in the leather, then alkali is used to adjust pH to (4.5-6.5) to prevent deterioration of the leather. After that, the leather is colored using dyes metal complex compounds and basic dyes such as anionic dyes. Then oils are applied for fat liquoring for softness the leather. Finally, a surface coating (i.e. phenolics, polymers, naphthalene, etc.) is applied to ensure an even color and texture, and to impart fullness to the leather.

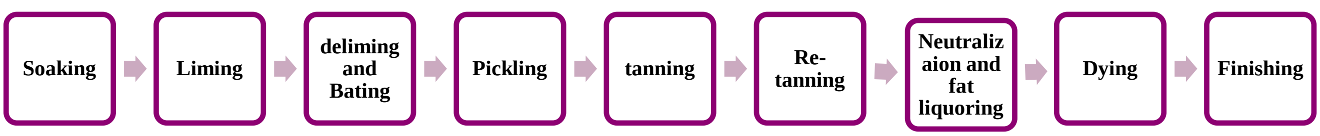

Figure 2.3: Simplified scheme of the leather manufacturing processes [28]

2.1.3 Tannery wastewater

Leather manufacturing wastewater is highly concentrated with chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), chromium, chloride, ammonia and sulfide. Liming process produces wastewater with the highest COD value [14].

Large amounts of different types of chemicals must be utilized in leather manufacturing processes are not completely fixed or exhausted by the skins, resulting in high chemical content in the tannery effluent. These chemicals discharged as a waste in tannery wastewater, leading to several environmental threats in the absence of proper treatment and disposal. Chromium is the one of major chemical constituents of the tannery wastewater; hexavalent chromium is a known inhalation irritant and associated with respiratory cancer.Table1 and 2 show the common characteristics of a tannery's wastewater.

Table 2.1: Average pollution load in combined tannery's wastewater [29]

Parameter	Source	Average value in effluent
Oxygen demand (BOD, COD)	The presence of biodegradable and non-biodegradable materials.	2000, 4000 mg O_2/L respectively
Chromium (trivalent chromium)	Tanning process (main tanning agent)	150 mg/L
Total kjeldhal nitrogen (TKN)	From using de-liming material.	160 mg/L
Suspended Solids (SS)	Beamhouse operations, trimming and cutting leather, flesh and hair residue.	2000 mg/L
Sulfide (S^{-2})	From using sodium sulfide and sodium hydrosulfide in unhairing process	160 mg/L
Sulfate (SO_4^{-2})	From pickling process (H_2SO_4)	1400 mg/L
Oil and grease	Oils in finishing phase	130 mg/L
Chloride (Cl^{-1})	From using chloride containing chemicals (chloric acid)	5000 mg/L
pH		6-9

Table 2.2: Characterization of leather tanning industry wastewater from different processes [30]

Parameter /Process	Soaking	Liming	Deliming	Pickling	Chrome tanning	Retanning
COD	11640±1484.92	18578±1827.15	7485.1±1808.07	2707±687.34	1716±619.43	4487.1±1121.61
TS	36160.5±9772.95	21961.35±1695.4	25002.1±11543.58	23588±12215.97	13553.5±16899	6272.95±8345.2
TDS	27067.5±9853.5	15157±1636.24	19199.95±11596.48	23130±12204.6	13148.5±16897.7	6100.95±8342.37
TSS	9093±80.61	6804.35±59.18	5802.6±52.89	458±11.313	405±1.41	172±2.82
Ph	8.37±0.988	12.00±0.707	8.63±0.989	3.25±0.212	4.09±0.141	4.11±0.127
Chloride	31127.37±849.05	5581.2±72.14	3862.12±140.89	41568.9±1423.37	2719.7±364.202	2666.15±436.49

*All values except pH are expressed in mg/L.

2.1.4 Cleaner production

Cleaner production (CP) is defined by United Nations environmental program (UNEP) as the continuous application of an integrated preventive environmental strategy to processes, products, and services to increase overall efficiency, and reduce risks to humans and the environment [12]. CP, in industrial sectors, is considered as cost-effective strategy, which meets the need of environmental pollution mitigation at the source and reduction of production cost [14].

Cleaner production options are divided into three main groups; waste reduction at the source, recycling and product modifications [31], figure 4 shows these options.

Raw material and the used chemicals are substituted by less toxic materials to avoid environmental impacts, or by effective material to increase production efficiency. Good housekeeping is the simplest cleaner production approach. Waste stream can be recycled to reuse by company in its production processes, or after waste treatment can be sold to consumers or to other companies as by-product. Polluted products are improved by changing the product itself or its packaging.

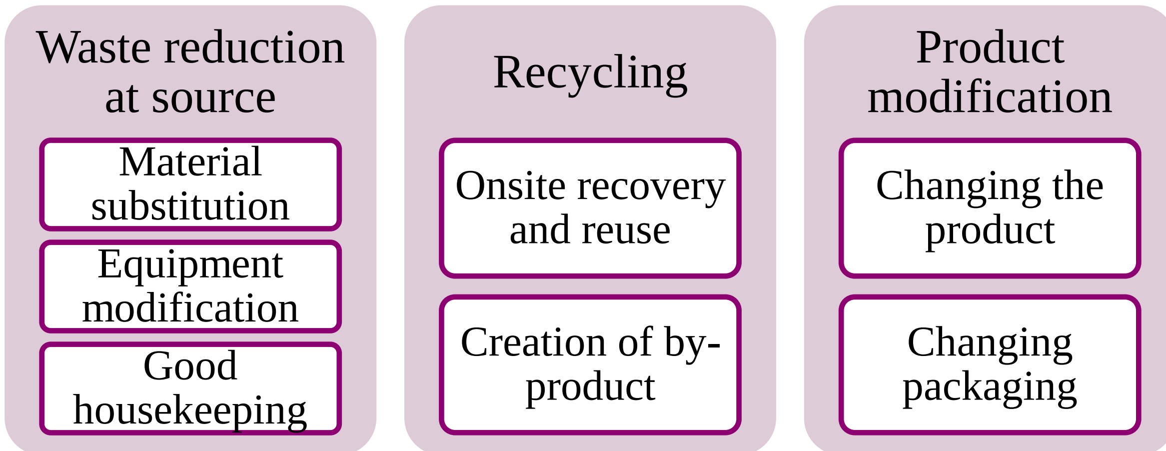

Figure 2. 4: Options of cleaner production [31]

2.1.5 Al-Waleed tannery

This study is dedicated to “Al-Waleed” and “Palestine” tanneries, which are classified as the biggest tanneries in Hebron city. They are located in the industrial zone to the south of the city. Al-Waleed tannery has a manufacturing capacity of 438 ton of hides yielding 278 ton of leather annually.

The companies have kept in pace with the latest technical and technological developments related to its work. They tend to employ modern techniques in their processes, which allow them to offer high quality leathers to the local and international markets after six decades in the business. Figure 2.5 shows the Al-Waleed tannerys’inputs and outputs of all manufacturing processes. The detailed processes of Al-Waleed tannery are shown in appendix A.

Over the past few years, these tanneries employed different techniques to manage their wastewater, such as adsorption by marlstone. However, switching to CP may allow minimization and probable elimination of wastes leading to an eco-friendly and greener industry.

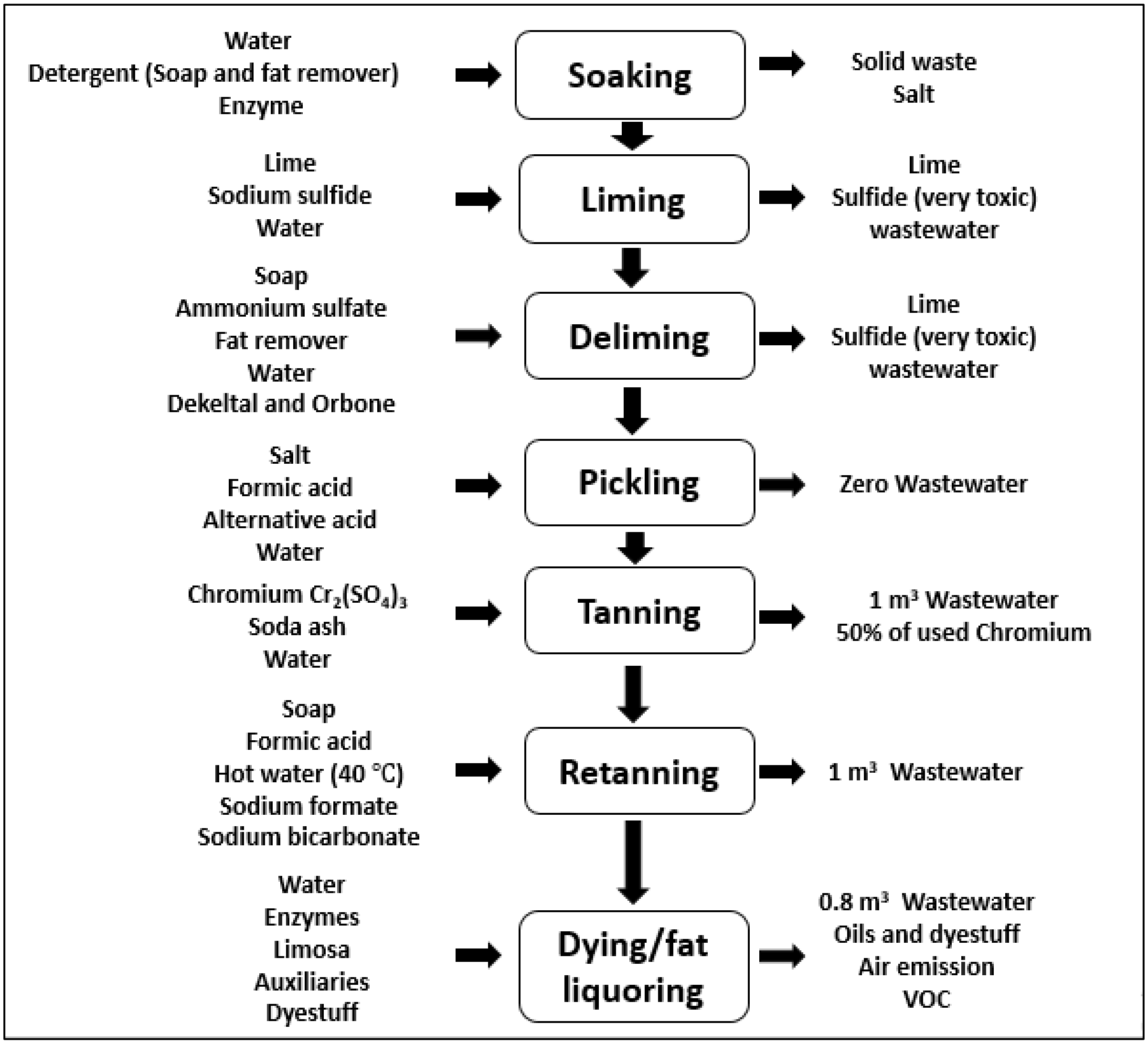

Figure 2. 5: Al-Waleed tannery leather manufacturing processes per ton hide.

2.2 literature Review

2.2.1 Recovery of chromium

Currently, waste recycling and minimization have become widely important. Many efforts trend towards the recovery of Chromium (Cr (III)) from the tannery wastewater. Several recovery methods can be used, including flocculation, chemical precipitation, ion exchange, extraction, electrolysis, and membrane separation [32]. Among these methods, chemical precipitation is the most widely used technique, due to its simplicity and flexibility. To carry out this technique, segregation of post tanning solution and tanning solution is necessary to avoid possible risks, mainly formation of deadly hydrogen sulfide.

In general, this technique precipitates chromium from tanning solution as chromic hydroxide by using alkali (i.e. NaOH, Ca $(OH)_2$, Na_2O or MgO).Then Cr $(OH)_3$can be converted to chromium sulfate by dissolution with sulfuric acid for reuse in the tanning process, where chromium sulfate is suitable as a tanning solution [33].

All alkali can effectively precipitate Cr (III) at a certain pH. Sodium hydroxide (NaOH) is the most common chemical used to provide excellent Cr (III) removal. Despite that, the precipitate slowly settles making the removal expensive and difficult. Magnesium oxide (MgO) can be used instead of NaOH because of its minimum sludge volume and better settling, while MgO is too expensive. Therefore, a mixture of NaOH and MgO are used for economic and technical feasibility with high Cr (III) recovery percentage, high degree of sludge purity and minimum sludge volume [32].

Reusing the recovered chromium in tanning process has its advantages and limitations. Chromium reusing saves the chrome used and reduces the level of chromium in waste streams. However, increases the capital and running costs and additional chemicals and man power are required [24]. In Hebron the main limitation on recovery of chromium came from “Israeli” regulation which prevents the use of sulfuric acids by tanneries for political reasons.

2.2.2 Tanning alternatives

The use of alternative tanning agent has been studied intensively. There are many effective alternatives to chromium salts (i.e. aluminum, zirconium and titanium compounds) [16].

2.2.2.1 Titanium tanning

Titanium tanning is one of the most effective substitutes for chromium tanning, which produces high quality bovine upper leather, and salts of titanium are completely harmless. In general, the use of titanium salt in the tanning process produces leathers with the same quality of chrome tanned. However, titanium molecule is larger than chromium, and it cannot penetrate properly through the skin, that leads to obtain leather with greater rigidity than chrome tanned leather. The use of organic masking products is useful to aid the penetration of the titanium [15].

Combination tanning of Titanium with chromium for upper leather has been given higher chromium uptake; this combination leads to less chromium discharge in the effluent [16]. Use of titanium compounds, which are available, and non-toxic, so that this combination will overcome possible poor exhaustion levels associated with the chromium compounds.

2.2.2.2 Aluminum tanning

This mineral does not produce stable leather compared to chromium-tanned leather, and it is easily washed out by water. Aluminum can be used in combination with other tanning agent to form stable leather. Combination of aluminum with chromium is useful and can substitute some amount of chromium, also combination of aluminum salts with polyphenolic tanning form very stable tanning compounds, this combination can completely substitute chromium.

Combination of Al^{+3} and Ti^{+4} used to produce full and soft leather; tanning is processed at pH 3-5. To overcome the problem of hydrolysis, masking agents include carboxylic acid such as lactate, tartrate, citrate glutarate, phthalate and their derivatives .The choice of masking agent is determined by its ability to interact with the metal ions, and the rate at which the complex is hydrolyzed [19].

2.2.3 Better uptake/exhaustion of chrome

Optimal uptake of chromium during tanning process can be achieved by implementing two main approaches which are process modification and conditions optimization. These increase the efficiency of the process and decrease the chromium in the effluent by enhancing the penetration of chromium [24].

Process modification includes use of masking agents and increasing collagen reactivity. Masking agent is a chemical has an ability to combine with specific groups, in tanning masking enhances chromium complex penetration and reactivity. Dicarboxylic organic salts and acids can be used as masking agents, and they have high reactivity due to their carboxylic groups. Potassium tartrate is the most effective masking agent to use; it can decrease chromium from the effluent by 94.3 % [18].

The main process parameters that affect on tanning efficiency are temperature, chromium concentration, pH, reaction time and mechanical action. Increasing the temperature has a positive effect on chromium fixation, where heating must conducted at the beginning of process. pH increasing will increase shrinkage temperature which achieved by slow and regular increasing of pH lately, but some problems may arise at pH above 5 where chromium start to precipitate.

Chromium concentration affects on tanning efficiency which is defined as a proportion of chromium fixed on the hides. Chromium penetration increased by increase of its concentration due to increase of diffusion rate. In another hand, process efficiency decreases with increase of chromium concentration. There is a relation between chromium concentration and temperature, scientific study shows that 2% of chromium oxide (Cr_2O_3) is sufficient to achieve a shrinkage temperature of 110°C; actually this temperature can be achieved with Cr_2O_3about1%. Chrome content in leather, which depends on chromium concentration offer, about 3.5 % Cr_2O_3 is needed to achieve a shrinkage temperature of 100°C. This chromium offer can be achieved with more than 1.2 % of chromium oxide offer.

Mechanical action and rotation of drums is important to improve chromium penetration, the optimum speed of drum is two third of critical rate. Also, the leather content of chromium and shrinkage temperature increase with reaction time.

High exhaustion of chromium leads to reduction of chromium level in effluent, high chromium fixing and it is applicable to any type of leather, but there are some limitations including high temperature required, high running cost and longer time needed [24].

2.2.4 Chrome recycling method

Chromium can directly be recycled from chromium tanning back into processed tank. Instead of being discharged into sewer system after one use. Recycling efficiency is only 68 % and it can reduce chromium use up to 20% [24].

Table 2.3: Comparison between cleaner production options for chrome tanning process

Cleaner production option	Recovery/ reuse of chromium	Chrome recycling	Better uptake/exhaustion of chrome	Tanning Alternatives/ Titanium tanning
Advantages	Saving the chrome used and reducing the level of chromium in waste streams.	Reducing the level of chrome in waste streams and level of water consumption. Simplest form of reuse.	Saving the chrome used. Reducing level of chrome in waste streams. No change in leather quality.	The most effective substitutes for chromium tanning. Producing leathers with the same quality of chrome tanned one. Elimination of chromium discharge in the effluent.

Disadvantages	Increasing the capital and running costs. Additional chemicals and man power are required.	Some changes to tanning procedures are required. Increasing the capital cost. Some changes in leather colour.	Increasing the running costs and improved drum drive system is required. Longer running time and higher temperature are needed.	Very expensive compared to chromium compounds. Producing leather with high rigidity. Additional chemicals are required.

Chapter 3

Wastewater Characterization of Leather Manufacturing Processes

3.1 Introduction

Leather production industry transforms raw hides to salable leather, through a series of chemicals and physical processes that gives the leather stability and good market quality. The production starts with soaking where hides are soaked with water and detergents in order to remove salts and dirt. Then, lime and sodium sulfide are used to remove the hair from the surface through swelling. Then, deliming begins where ammonium sulfate is used to remove the lime. Then, pickling, were pH is lowered by using formic acid to make the hides ready for chromium reception. Then, tanning begins by adding chromium sulfate, which creates crosslinking between collagen fibers making the hide resistant to putrefaction, durable, flexible and able to be used for a wide range of purposes. Finally, they are retanned using dyes and auxiliaries for softness.

Leather manufacturing processes discharge large amounts of wastewater, which are highly concentrated with chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), chromium, chloride, ammonia and others. All of which differ in concentration from one tannery to another according to the practice, amounts of water used and chemical doses.

Table (3.1) lists the permissible limits stipulated by the world health organization (WHO) and the Jordanian standard 202/1991for discharges of industrial effluents to the sewer system [35].

Table 3.1: Comparison of WHO and Jordanian standards for industrial effluents discharge concentrations into the sewer system.

Parameter	**Unit**	**Value**	
		WHO	**Jordanian standards**
pH	SU	5.5-9	5.5-9.5
COD	mg/L	250	2100
TDS	mg/L	2100	3000
TSS	mg/L	600	1100
Chloride	mg/L	1000	500
Ammonia	mg/L	1	5

Chrome	mg/L	2	0.1

In Palestine, there is a lack of information regarding leather manufacturing outcomes and wastewater pollutants. This study, therefore, aims at analyzing and characterizing leather manufacturing processes wastewater to provide an insight about pollutants and concentrations, which would help developing treatment plans for this industry in the future.

This study would be the first in Palestine to exhibit a characterization for all of the leather production processes. Sampling, lab testing and procedures as well as tabulated results and graphs pertaining to the characterization of goat skins and cow hides are documented in this study.

Many efforts were made regarding tannery wastewater treatment and management. Natural marl was reported to be very efficient as an adsorbent for chromium (III). Different types of marl were tested along with the effects of contact time, doses and the state of the solid particles. Results showed high adsorption percentage (97%) at 0.003 g yellow marl /ml wastewater after only 3 days. A higher removal percentage was obtained in stirred condition; this also shortened the time required for full removal to about 7 hours [36].

Similarly, stone cutting solid waste was used to treat tanning wastewater. Adsorption was found to be at its highest percentage when stone solids were 5 g/100 ml or higher within just few days. Also, adsorption at pH above 5 gave nearly full adsorption [37].

A local study demonstrated the possibility of recycling liming/unhairing process water up to four times without affecting the quality of the leather. Experiments have shown that modifying the method followed in that step could reduce the amount of water consumption by 58%, COD by 50% and sulfide by 73% [8].

3.2 Experimental Work

This section demonstrates the work done to obtain the physicochemical characteristics for each leather manufacturing process.

3.2.1 Sampling and Materials

Industrial wastewater from all of the leather manufacturing processes in (Al-waleed tannery) in Hebron, Palestine was collected for the sake of testing. They were collected in polyethylene bottles and were brought to the laboratory and stored at room temperature. Chemicals used during the tests include silver sulfate (Sigma-Aldrich, USA), mercury (II) sulfate (Acros organics, USA), sulfuric acid (Dasitgroup, Italy). For chloride determination, titration test kit-Chloride CL 500 and visocolor Eco Chloride kits were used. For ammonia determination, eco ammonium kit was used.

3.2.2 Procedures

Effluents of all processes were characterized for their pH, temperature, chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), chromium, chloride and ammonia contents.

pH values were determined by using pH Bench Meter (Milwaukee MI150, US).The chemical oxygen demand (COD) of samples was measured by (5220 C. closed reflux titrimetric method), which uses potassium dichromate as a strong oxidizing agent to oxidize the organic under acidic conditions. Samples were then digested for approximately 2 hours at 150°C [38].

Total solids were determined with method (2540 B. Total Solids Dried at 103–105°C)by weighing the material left after the evaporation and drying of the sample in the oven at specific temperature 105°Cfor 24 hours. Similarly, TDS was measured with sample filtrate passing through filter paper (0.45μm) then evaporated in a weighed dish and dried in the oven at 105°C for 24 hours. TDS were also measures by using TDS meter (JENWAY 4510 bench conductivity meter, UK).TSS were obtained through the subtraction of TDS from TSS [38].

Ammonia and chloride concentrations were analyzed by using titration and colorimetric tests kits. PF 11 photometer was used to obtain a reading. For chloride, titration test kit-Chloride CL 500 and visocolor Eco Chloride kits were used. Eco ammonium kits were used for the analysis of ammonia content.

Hexavalent chromium was determined by method 7196A chromium, hexavalent (colorimetric) stipulated by the environmental protection agency (EPA). Dissolved hexavalent chromium reacts with 1,5 diphenylcarbazide in acidic solution. A red-violet color complex is produced, and then absorbance is measured photometrically at 540 nm by UV-visible spectrophotometer.

3.3 Results and Discussion

Tannery wastewater generation varies among processes according to their functions. A graphical representation of approximate amounts of wastewater discharged per ton hide from each leather manufacturing step is shown in figure 3.1.

These wastewater amounts obtained from (Al-Waleed tannery)for goat manufacturing and (Palestine factories) for cow manufacturing, which are with capacity of 1 ton and 1.5 tons respectively, so the amounts of wastewater discharged is corrected per ton hide as shown in figure 3.1.

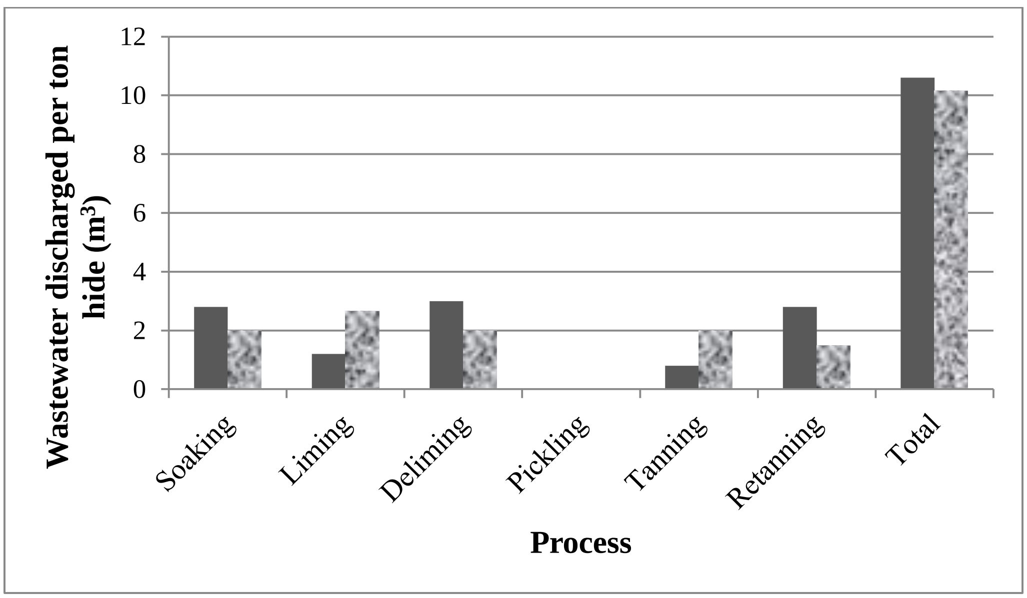

Figure3.1: The obtained wastewater discharge per ton hide from each leather manufacturing process for goat processing from Al-Waleed tannery and for cow processing from Palestine tannery

*Dark columns represent Al-Waleed tannery and lighter columns represent Palestine factory

As shown in figure 3.1, there are a noticeable variation in wastewater discharge between the two studied tanneries, according to variation of used technologies in manufacturing processes and type of raw material. Total wastewater discharge from Al-Waleed tannery is estimated between 10-12 m^3/ton hides processed. This discharge is lower than that stated in previous work, where average wastewater released is about 30-35 m^3/ton hide [40].

Wastewater generation depending on the raw material, the finishing product and the manufacturing processes. Obviously, the initial preparation and cleaning of hides from all the preserving and any non-collagen materials requires large water amounts; therefore, wastewater is generated in large amounts in the soaking process. Al-Waleed deliming process releases the largest quantity of wastewater (about 3 m^3/ton hide) throughout the entire leather manufacturing process. This is because it is conducted in three stages and every time 1 m^3water /ton hide is added among other chemicals. From previous study, the discharged wastewater from deliming is 7-9 m^3/ton hide [14]. For Palestine tannery, liming process releases the largest wastewater due to high consumption of water to remove epidermis layer. On the other hand, the pickling process releases zero wastewater, due to performance of next process in the same drum which includes the use of this water in addition to other chemicals. Water requirement in the rest of the processes is less than that in deliming and soaking, thus the wastewater generation is less.

Wastewater from leather manufacturing processes is heavily concentrated in terms of BOD, COD, TSS, TDS, in addition to chromium, chloride and ammonia. Analysis of physical and chemical characteristics of the tannery wastewater collected from Al-Waleed and Palestine tannery is shown in table 3.2 and 3.3 respectively.

Goat skins processing releases higher polluted wastewater than cow hides. Goat skin contains more grease, fatty tissues and hair which are removed in beamhouse processes and contributed in discharge of wastewater with higher level of COD and TS.

Table 3.2: Experimental analysis of tannery wastewater for goat skin processing from Al-Waleed tannery

Process/Parameter	Soaking	washing	Liming	Deliming stage1	Deliming stage2	Deliming stage 3	Pickling	Tanning	Retanning stage 1	Retanning stage 2	Retanning stage 3
COD	29000	46000	167000	14696	12672	3960	8976	7392	1548	4048	34496
TS	125100	113350	139650	14000	26600	71500	105200	77600	12700	12820	30500
TDS	110700	108667	53900	9320	19790	70900	69800	60300	15910	11320	16290
TSS	14400	4683	85750	4680	6810	600	35400	17300	1380	1500	14210
pH	6.33	6.41	12.41	10.4	9.58	9.49	4.65	3.65	3.26	4.3	3.98
Chloride	200000	22000	42500	3750	8750	19000	35000	27500	10000	6250	6250
Ammonia	0	0	0	1.7	40	40	70	150	< 0.1	1	1.7

*All values except pH are expressed in mg/L

Table 3.3: Experimental analysis of tannery wastewater for cow hide processing from Palestine tannery

Process/Parameter	Soaking	liming	Washing	Tanning
COD(mg/L)	56800	118400	6700	15040
TS(mg/L)	49400	115400	8700	31365
TDS(mg/L)	49100	35500	8590	41800
TSS(mg/L)	300	79900	110	10435
pH	9.07	13.56	13.17	3.47
Chloride(mg/L)	46875	31250	6250	31250
Ammonia(mg/L)	0	0	0	160

*All values except pH are expressed in mg/L

In soaking process, hides preservatives such as sodium chloride salt, blood and any foreign material are removed by using detergents; these materials contain high organic matter, which results in high levels of COD, TDS and chloride concentration.

Liming–hair removal process contributes to 50% of total chemical oxygen demand (COD) of tannery's wastewater. Chemical dissolution of hair and epidermis with an alkaline medium of lime and sulfide takes place, resulting in high level of organic content from hair, protein and fats. Liming wastewater is basic and highly concentrated with chloride, sulfide and TSS.

In deliming process, ammonium salts mainly ammonium sulfate are used to remove lime from hides, resulting in high concentration of ammonia in deliming effluents. In this process, hair roots and some of the protein removed, released wastewater with high level of COD and TDS. For stage 3, a used commercial chemical named "Orpone" may contain ammonium chloride due to presence of high level of ammonia and chloride in the effluent from this stage.

In pickling, to increase the acidity of hides to about 2.5-2.8, formic acid and another acidic powder are used, in addition to the use of sodium chloride salt to prevent acidic swelling, where the salt is a source of chloride and TDS. Ammonia is present in this effluent in high concentration due to the reaction between the remaining ammonia in the hides with salt, which forms ammonia-containing compounds. Here, wastewater is not discharged to the sewer system, instead it is used in the tanning process, where characterization was done to identify its content and to determine the source of ammonia and other pollutants in it.

In tanning, chromium sulfate is used as the tanning agent, soda ash or sodium bicarbonate is used to increase pH slowly for chromium fixation. Not all of the chromium added in this process is fixed on hides' surface hence; chromium concentration in the effluent is high. In this process, the same water used in pickling, which contains chloride and ammonia, is used, resulting in high concentration of ammonia and chloride.

In retanning, the used detergent-soap and formic acid release acidic wastewater. In third stage, dyestuff, oil and auxiliaries are used to color and soften the hides. The use of dyestuff and organic oil result in high levels of COD and TS in the wastewater.

The obtained physicochemical characteristics of the studied tanneries effluents are presented graphically. For multi stage processes, the characteristics were corrected and represented as one combined stage. Figure 3.2 graphically presents COD.

Beamhouse wastewater is highly concentrated with organic matter due to the preparation of hides for tanning and the removal of any unwanted material (hair, fat, unwanted proteins, etc.). Clearly, liming-hair removal process forms about 50% of the total COD. High COD means large amount of oxidizable organic material will lead to reduction of dissolved oxygen, which is deleterious to aquatic life.

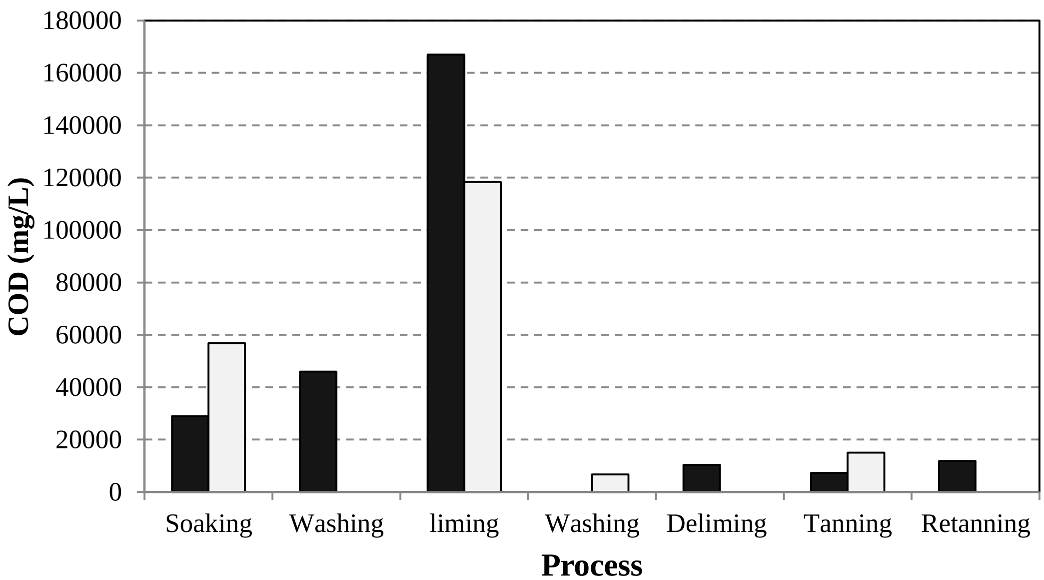

Figure 3.2: Graphical representation of the analyzed COD in different processes
*Black columns represent Al-Waleed tannery and white columns represent Palestine factory

The obtained graph has a similar trend as viewed in literature [30, 39]. As noticed from figure 3.2, liming process contributes to the highest COD value of 167000 mg/L, where Sudanic tannery releases liming effluent with 18600 mg/L COD [39]. Batu tanneryhas18578 mg/L COD for liming process [30]. The difference in amount of used water, raw material and techniques used to conduct the process causes that difference between values.

Tanneries' effluent streams are highly concentrated with solids mainly with dissolved solids as shown in figure 3.3 and 3.4. Soaking releases wastewater with high dissolved solids which mainly come from salt removal, in order to rehydrate the hides and soluble non-structural proteins. In addition to removal of some fat and dirt which contribute to presence of suspended solids.

For liming, the use of lime and sodium sulfide for hair removal results of high level of dissolved solids, in addition to suspended solids come mainly from hair other epidermal structure.

The use of acids and salts in pickling process in order to restrict the swelling of the collagen in the acidic medium, resulted in high concentration of dissolved solids in this effluent.

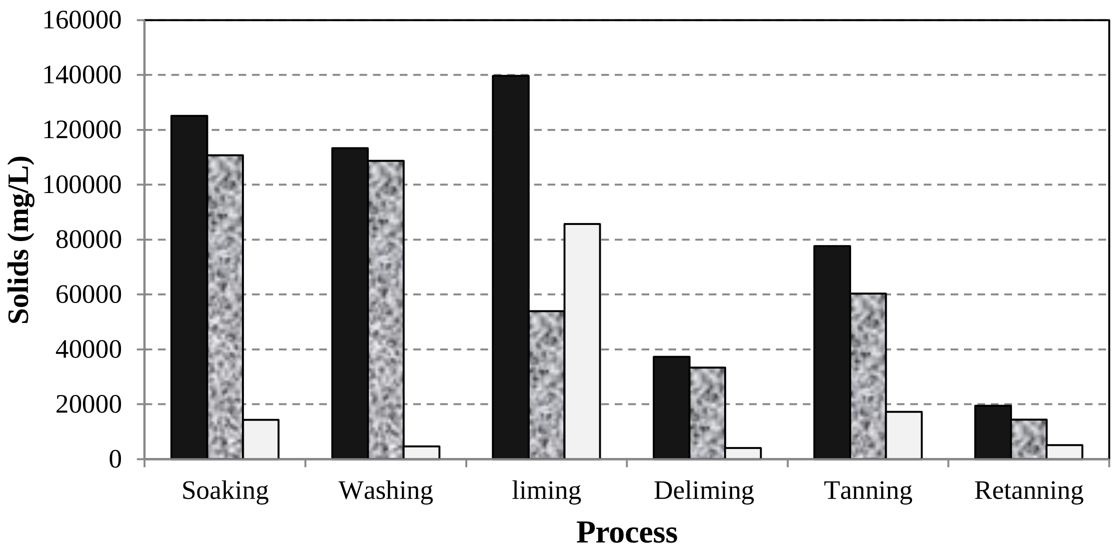

Figure 3.3: Graphical representation of solids in different processes from Al-Waleed tannery
*Dark columns represent TS, grey columns represent TDS and white columns represent TSS

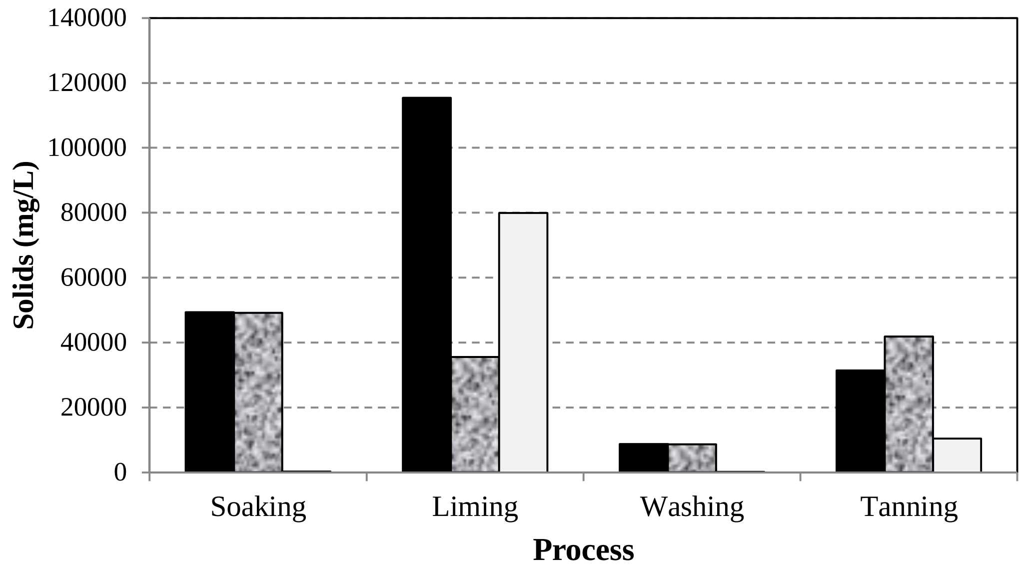

Figure 3.4: Graphical representation of solids in different processes from Palestine tannery
*Dark columns represent TS, grey columns represent TDS and white columns represent TSS

The trend of the obtained graph for representation of solids varies among tanneries, according to the used chemicals in each process. There is similarity in overall trend as viewed in Modjo tannery [30].

pH values vary according to raw materials and chemicals used in the process, depending on the required acidic/basic medium to conduct the process efficiently, this variation is shown in figure 3.5.

Liming has a higher pH due to the use of sodium sulfide and lime CaO, which are basic materials, and pH is corrected in pickling to be suitable to the tanning operation and to prevent swelling of the leather. The extreme pH of wastewater is not acceptable, as lower pH where both cause problems for aquatic life in addition to problems in sewer system.

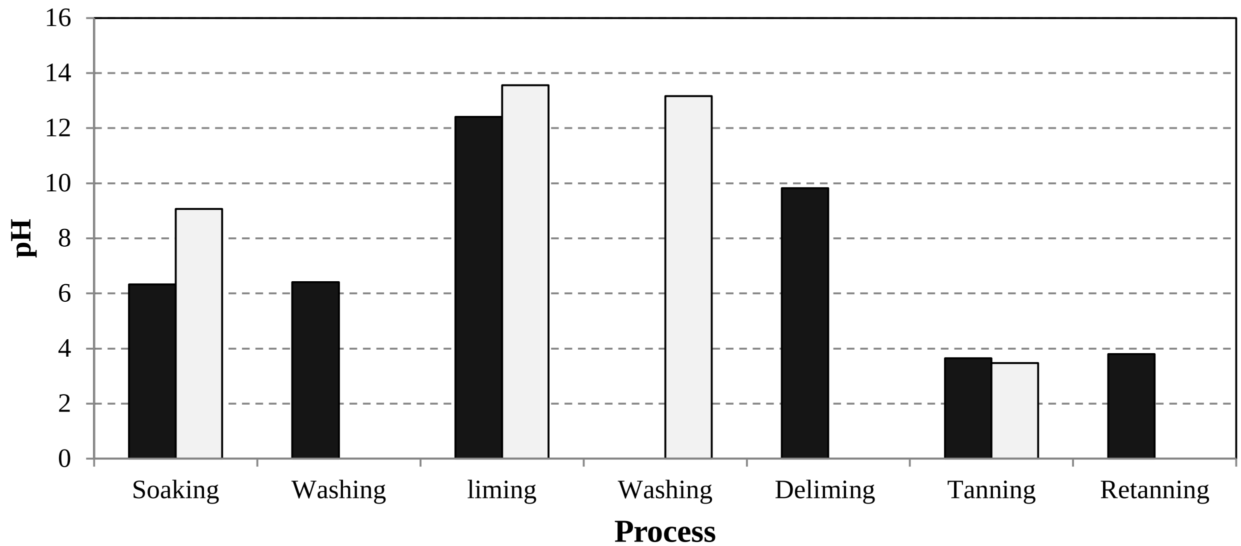

Figure 3.5: Graphical representation of measured pH in different processes

*Black columns represent Al-Waleed tannery and white columns represent Palestine factory

The obtained pH graph has a similar trend as viewed in literature [30]. Liming has a higher pH due to the use of basic materials. The measured pH of liming effluent from Al-Waleed tannery is 12.41 which is similar to Modjo tannery with pH of 12.64 [30]. As stated in literature, effluent from a tannery fluctuates between pHs of 3 to as high as 12 [39], which is similar to measured values.

Ammonia contents of wastewater samples are presented graphically in figure 3.6. For deliming, ammonium sulfate and ammonia containing chemical fertilizer, used to remove the lime from hides resulted in high concentration of ammonia in this process and other consequent processes as shown in figure 3.6. Tanning process releases wastewater with high concentration of ammonia, where pickling highly concentrated wastewater is used in this process. Ammonia forms a complex with chromium which increases its concentration. Analyzing ammonia contents in tannery wastewater is not common in the literature.

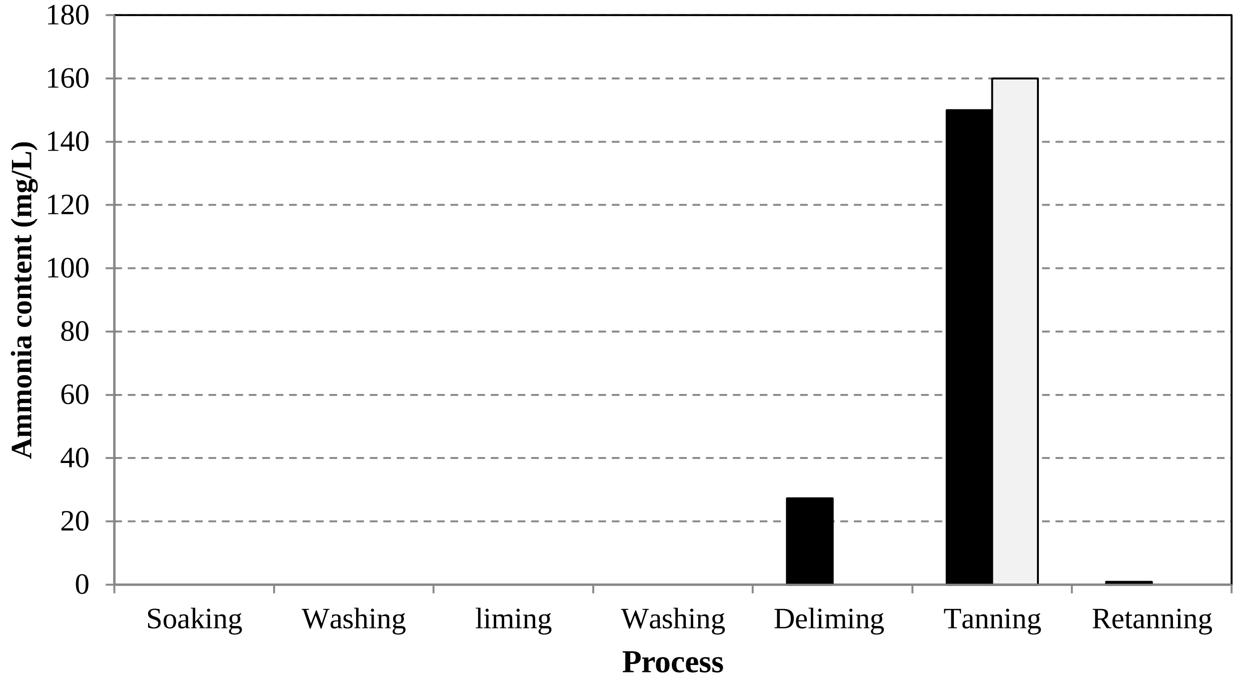

Figure 3.6: Graphical representation of measured ammonia content in different processes
*Black columns represent Al-Waleed tannery and white columns represent Palestine factory

The measured chloride contents among different processes are presented in figure 3.7. Tannery effluents are highly concentrated with chloride, mainly due to the use of sodium chloride as a preservative material. Obviously, soaking discharges wastewater with high concentration of chloride, which takes place mainly to remove the salt and to rehydrate the hides. Also tanning process releases wastewater with high level of chloride, due to the use of sodium chloride salt in pickling process where its water used in tanning process.

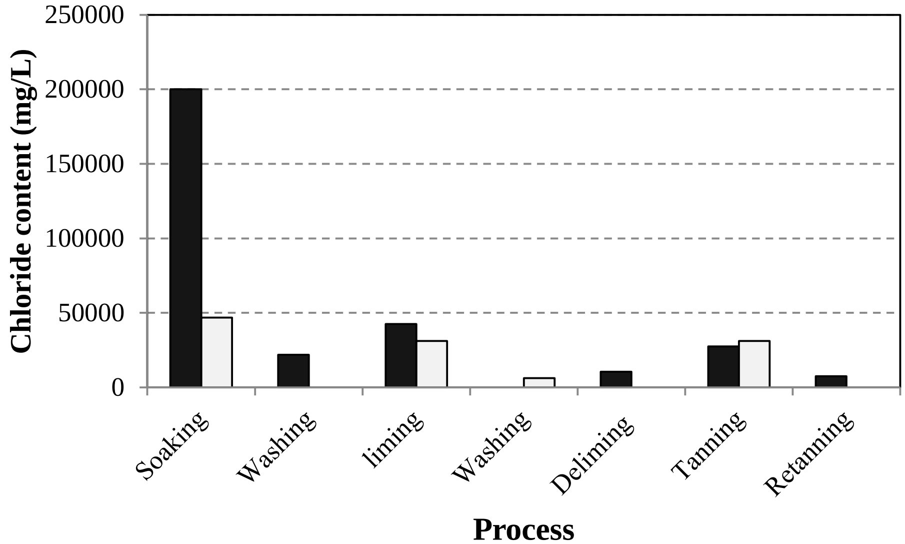

Figure 3.7: Graphical representation of measured chloride contents in different processes
*Black columns represent Al-Waleed tannery and white columns represent Palestine factory

The obtained Graphical representation of chloride has a similar trend as viewed in Batu tannery [30]. Chloride content varies according to amount of salt used for hides curing and the used chemicals in production processes and its composition.

Chromium, as hexavalent chromium, is a very toxic and carcinogenic heavy metal to the living organisms. Supposedly, hexavalent chromium should not be present in the tanning process effluent, only trivalent chromium should be, due to the use of chromium sulfate ($Cr_2(SO_4)_3$) as tanning agent. The presence of hexavalent chromium indicates that the process ideal conditions were not maintained which caused the oxidization of Cr^{+3} to Cr^{+6}. Method 7196A chromium, hexavalent (colorimetric) used for hexavalent chromium determination. Figure 3.8 shows the calibration curve/line used to determine Cr^{+6}concentration.

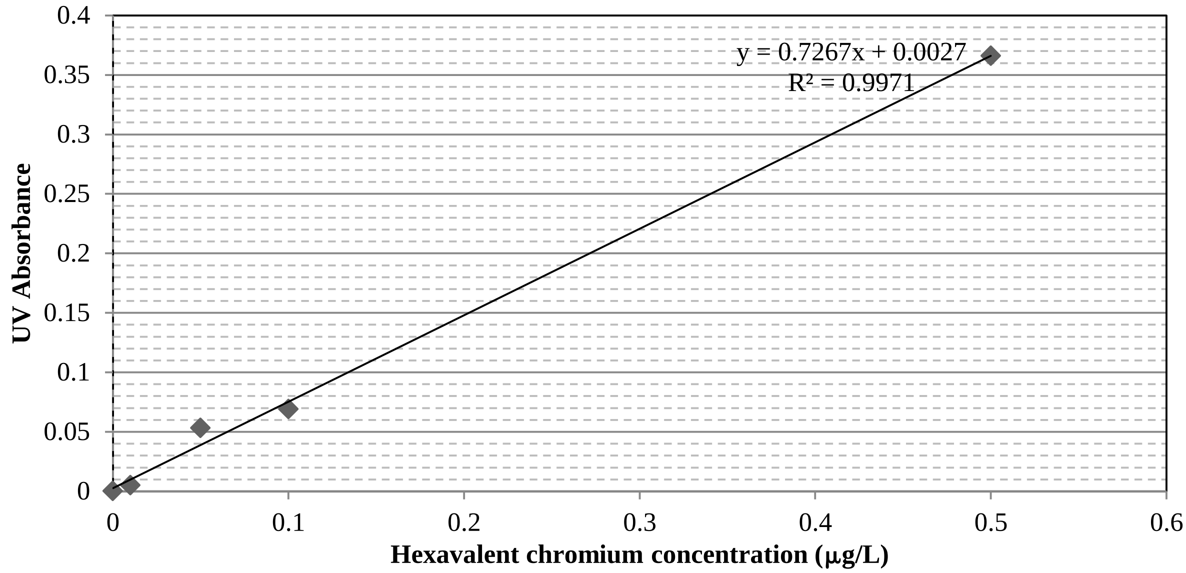

Figure3.8: The measured Calibration line of absorbance versus concentration of Cr (VI)

By use of 7196A chromium, hexavalent (colorimetric) method and the obtained calibration line, hexavalent chromium concentration from different samples were determined. Table 3.4 shows these concentrations.

Table 3.4: Experimental analysis of hexavalent chromium for Al-Waleed tannery samples

Sample	**Cr (VI)**
Chromium sulfate powder	$8.26*10^{-3}$mg/Kg powder
Pretanning sample	$1.79 *10^{-3}$mg/L
Tanning effluent	$3.2*10^{-4}$mg/L

A sample of the used chromium sulfate powder in aqueous medium, before tanning takes place, contains 1.79 μg/L Cr^{+6}, which indicates that the original chromium sulfate powder used as a tanning agent contained Cr^{+6} due to the availability of certain condition during manufacturing that allowed the oxidation of trivalent chromium. There are two main constituents in the environment, which are known to oxidize Cr (III) to Cr (VI), oxygen and manganese dioxide. It is also limited by the concentration of dissolved Cr (III) and pH. Effluent from tanning contains $3.2*10^{-4}$ mg/L Cr^{+6} which are less than the permissible limit of 0.05 mg/L according to Germany and 0.1 mg/L according to EPA [30].

Comparison with literature for hexavalent chromium shows that, Batu tannery wastewater from tanning process contains $6 *10^{-3}$ mg/L Cr^{+6}, where Modjo tannery contains 1.46 mg/L Cr^{+6} [30].

Generally, all concentrations and values obtained from experimental analysis exceed the allowable limits to be discharge in the sewer system according to the Jordanian standard. The pH values of wastewater from both tanneries are between 3.26-13.56, so these samples are extremely acidic or basic. The standard limit for pH of disposed wastewater is 5.5-9.5. The discharge of this wastewater interferes with the optimum operation of wastewater treatment. Acidic wastewater may cause corrosion of the sewer structure and the release of toxic gas such as hydrogen sulfide.

COD concentration exceeds the permissible COD level of 2100 mg/L; this may accelerate the generation of sulfides in the sewer system, causing odors and corrosion problems. Total solids exceed the permissible level of 4100 mg/L. In the same manner, TSS exceed the limit of 1100 mg/L, which cause blockages and sewage overflows resulted from deposits formation.

Chapter 4

Chrome tanning process: Cleaner production implementation

4.1 Introduction

Cleaner production (CP) is defined by UNEP as the continuous application of an integrated preventive environmental strategy to processes, products, and services to increase overall efficiency, and reduce risks to humans and the environment [12].

In tanning process, there are many cleaner production technologies can be implemented to avoid chromium present in effluent or at least to reduce it. Alternative tanning agents can be used to replace chromium completely and high exhaustion technique ensures that more chromium actually affixes to the hides/skin. Chromium can be recovered by alkaline precipitation.

Advanced tanning process aims at minimizing chromium concentration on the effluent by enhancing chromium uptake up to 90% by modifying process parameter and/or tanning process [14, 24]. High exhaustion of chromium with near zero chromium discharge is called closed loop tanning system, that leads to protect environment and there is no need to further treatment [25].

The environmental evaluation of an option should take into account its impacts on the environment during the entire lifecycle of a product, also reduction in the release of hazardous and toxic chemicals and others. The economic benefits from the reductions in the quantity of waste released and resource consumption that each option can bring about should be considered reduction as shown in table 4.

Table 4.1: Environmental evaluation of cleaner production options

Evaluation criteria	**Weight**	**Recovery of chromium**		**Alternative tanning**		**Recycle**		**Exhaustion of chromium**	
		Score	Sum	Score	Sum	Score	Sum	Score	Sum
Reduction in quantity of waste released	3	1 3		3	9	1	3	2	6
Reduce expenses for waste water treatment	3	2	6	3	9	1	3	2	6
Reduce exposure to toxic chemicals at work place	2	0	0	3	6	0	0	0	0
Reduce amount of water consumption	2	0	0	0	0	2	4	0 0	
Weighted sum		9		24		10		12	

Key: 0 = no change, 3= highest rank (preferred).

The results from the previous environmental evaluation represent that chromium replacement is the most promising technology to be implemented in the tanning process due to its ability to reduce toxic waste released and eliminate treatment costs.

Substitution of chromium and use of free-chromium tanning agent is the most feasible option, due to its environmental benefits in elimination of the released hazardous and toxic wastes. The economic benefits of all the reductions in the quantity of waste released as well as associated high cost in its disposal. However, better exhaustion and uptake of chromium seems to be the favorable option for leather manufacturers in Hebron. Proposed solutions that comply with the management's vision will be further investigated and tested for full technical and financial evaluation.

4.2 Experimental work

4.2.1 Collection of leather samples

Leather samples are going to be collected from the tannery after the pickling stage is done, in coordination with the tannery owner. These samples should be cut off the processed hide two thirds down the backbone and 50 mm to the left or right side of the hide by the tannery owner. Initially, the samples are going to have random sizes, but later on, they will be adjusted in the lab. The collected leather samples are going to be kept in a plastic container containing pickling process water in it to preserve them until they are used in the lab.

The required chemicals including chromium sulfate and sodium bicarbonate are going to be collected in a plastic bag.

4.2.2 Leather testing

In order to determine the optimum tanning conditions, several tanning trials are going to take place as shown in table 4.1.

Table 4.2: tanning trials to determine the optimum conditions

A wooden drum, 2 liters in capacity, rotating at 15 RPM will be used to conduct the experiments					
	Parameters				
NO.	**Temperature C°**	**pH ($NaHCO_3$)**	**Dosage % (Chromium sulfate)**	**Time/period**	**Others**
1. 2. 3. 4. 5. 6.	20 30 40 45 50 60	3.8-4.2	7g	8 hours + overnight (no stirring)	
1. 2. 3. 4. 5. 6.	Best temperature from previous trials	3.8-4.2	3 g 3.5 g 4 g 5 g 6 g 7 g	8 h + overnight (no stirring)	
1. 2. 3.	Best temperature from previous trials	4 4.2 4.5	Best chromium dosage from previous trials	8 h + overnight (no stirring)	

4.2.3 Laboratory procedure

Laboratory tanning steps aimed to imitate the industrial practice regarding the tanning stage. A wooden drum divided into three chambers each of which has 2 liters in capacity will be used to conduct the experiments.

Sample sizes are adjusted by using a scissor to obtain approximately 100 g pieces with square shape. The wet leather samples are weighed on a balance to determine exactly the amounts of chromium and $NaHCO_3$required to be added.
60 mL of pickling water were added in addition to 20 ml of water (preheated to the specified temperature).

After that, leather samples were put in the drum, chromium was added in the specified dosage. The drum started rotating at 15 RPM as in the tannery.
After 10-20 min, 1 mL chromium liquor samples were collected and analyzed for chromium content using UV visible spectrophotometer at 540 nm wavelength. Then drum was sealed tightly to prevent any leaks.

After 6 hours, 1% NaHCO3 was added for 2 hours to reach the specified pH, after 2 hours, the drum was stopped and samples were left inside overnight. Next day,1 mL chromium liquor samples were collected and analyzed for final chromium content using UV visible spectrophotometer at 540 nm wavelength.

Finally, the hide samples were taken out, put on cork surface and left for 24 hours to dry. Then, the samples were taken to be physically tested in the "leather quality lab". Plastic containers are used to carry the samples. The Physical test of interest is the tensile test.

Conclusion

The economic importance of the leather industry and its associated environmental impacts spur us to study the chemical and the physical characteristics of the tannery wastewater as a key step of wastewater treatment and management. These analyses cover the resulted wastewater from chrome tanning process and all other processes.

The lack of proper treatment for chromium wastewater would only increase the pressure from "Israeli" legislations on this industry, so the physicochemical characteristics of the tannery wastewater and the implementation of a proper CP option is crucial to the future of this industry.

The results of the experiments for characterization of wastewater from all manufacturing processes indicate that the wastewater does not comply with the legal ranges of selected parameters, and it is highly concentrated with total solids, total dissolved solids, suspended solids, chemical oxygen demand, chloride, ammonia and chromium. Liming process has the highest COD and pH value, where chrome tanning process releases wastewater highly concentrated with chromium.

Results of preliminary evaluation demonstrated that the most feasible option would be the substitution of chromium used in this process. The option is being successfully used to produce leather with high quality with chemicals that are neither toxic nor cause adverse environmental impacts. However, better exhaustion and uptake of chromium seems to be the favorable option for leather manufacturers in Hebron.

Recommendations

Tannery should work hard in order to create a good working environment for the workers and the people surrounding the factory. In addition, awareness should be raised regarding CP and its technical, financial, and environmental significance in leather industry and all industries.

Future full technical evaluation of better exhaustion and uptake of chromium that is the most favorable option for leather manufacturers in Hebron should be conducted.

Further researches on substitution of chromium and use of free-chromium tanning agent which is the most feasible option, due to its environmental benefits in elimination of chromium in the released wastewater should take place.

Liming- hair removal process releases the highest strength wastewater which is polluted with sulfide, so further study for treatment or cleaner production implementation should be conducted in this process.

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