Wastewater characterization towards cleaner production in leather tanning industry in Palestine.

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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 parent.

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.

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Abstract

The present study aims to characterize the wastewater from leather tanning industry in Palestine in order to determine the pollution load .Wastewater samples was collected from all leather manufacturing processes released from cow hides. From various tanneries in Hebron district.

The experimental work for the characterization of wastewater presented by analyze , chemical oxygen demand (COD) , electrical conductivity (EC) , total solids (TS) , total dissolved solids (TDS) , total suspended solids (TSS), PH , ammonia (NH3) and chromium in both states Cr(III) ,Cr(VI) .

The analysis results for the physiochemical characteristics shows the following. The PH of the wastewater shows a high variation depending on manufacture process, the wastewater generated from liming&deliming process comes with alkaline properties have a PH value of (8-12) , whereas wastewater comes from pickling & tanning process have an acidic properties with PH values ranged (2-4).The highest COD value of the wastewater among the leather manufacturing process was detected in liming&Unhairing process with an average value of (8000) .studying the TS,TSS and TDS values it was found the washing process generate the wastewater that have the high value. The wastewater generate from tanning process is the only effluents that contains chromium with the amount of (3500), as a form of Cr^{+3}, also a little amount hazardous Cr^{+6} might be found. According to the mentioned results we can say that the pollution loads in the wastewater is really high. Through tracking the producing one ton of hide, the amount of wastewater generated was approximately $10m^3$.

نبذة مختصرة

تهدف هذه الدراسة الى توصيف المياه العادمة الناتجة عن صناعة دباغة الجلود في فلسطين, و قد تم جمع عينات المياه العادمة من جميع عمليات تصنيع الجلود الصادرة من جلود البقر. من مختلف المصانع في منطقة الخليل.

تم توصيف المياه العادمة من خلال عمل تجارب لتحليل الخصائص الفيزيائية للعينات المأخوذة ,حيث تم دراسة طلب الأكسجين الكيميائي , (COD) , التوصيل الكهربائي , إجمالي المواد الصلبة (TS) , إجمالي المواد الذائبة (TDS) , إجمالي المواد العالقة(TSS) , تركيز الأمونيا(NH_3), درجة الحموضة PH , تركيز الكروم الثلاثي (Cr^{+3}) والسداسي (Cr^{+6}).

بعد دراسة الخصائص الفيزيوكيميائية للمياه العادمة الناتجة عن عملية تصنيع الجلود ظهرت لدينا النتائج التالية. أولاً بتحليل درجة الحموضة للمياه العادمة ظهر لدينا إختلاف كبير في القيم بين المرحال المختلفة حيث انها في مرحلة التجير وإزالة الشعر(liming&Unhairing) كانت خصائص المياه قاعدية وبدرجة حموضة تتراوح بين (8−12) بينما عثر على خصائص حمضية للمياه العادمة في مرحلة التخليل والدباغة (pickling & tanning) وبدرجة حموضة (2−4) , ثانياً أظهرت نتائج دراسة المياه العادمة في مرحلة التجير وإزالة الشعر(liming&Unhairing) بأنها تحتوي على تركيز عالي من طلب الأكسجين الكيميائي (COD) بقيمة متوسطة تعادل 8000 ملغم/لتر. ثالثاً كانت أعلى قيم لكل من إجمالي المواد الصلبة , إجمالي المواد الذائبة وإجمالي المواد العالقة TS,TSS,TD في المياه العادمة الناتجة من عملية غسل الجلود (Washing). رابعاً في مرحلة الدباغة (Tanning) تحتوي المياه العادمة على الكروم بالشكل الثلاثي بتركيز 3500ملغم/لتر كما تظهر كمية قليلة من الكروم السداسي . بناءاً على النتائح أعلاه يتبين أن تركيز الملوثات في المياه العادمة الناتجة عن عملية تصنيع الجلود عالية . ومن الجدير ذكره بأن تصنيع طن واحد من الجلود ينتج عن ما يقارب 10 م3 من المياه العادمة .

Chapter one

" Introduction"

1.1 Introduction

Tanning industry play an important role in economic growth, employment an export, output of tannery process use as raw material in foot and leather wearing industry, and consider as a important industry in Hebron. The majority of tanneries are small in terms of employment; 57% of the tanneries employ less than 5 workers and 26% and employ 5 to 9 workers. This industry appeared in the twenties of the last century, faced many challenges and difficulties, start from raw materials and chemicals to the restrictions of the Israeli occupation and competition in the market.

Leather production done in three main stages, start with preparation of hides in the beam house stage, tanning stage and post-tanning or finishing stage. Animal skin consists of three layers – the epidermis, dermis and hypodermis. Epidermis is the outer layer and consist of hard cells. And this removing in unhairing process, hypodermis the lower layer and its consist fat and protein and is removing in fleshing process, dermis is a middle layer its consist of collagen and elastinfibre which consider a major part of hides. The basic component of the skin is collagen so only dermis layer is used in leather industry[7], collagen structure consists of twined triple units of peptide chains The amino acid are joined together by peptide links[3].

Leather industry consumes large amounts of chemicals (approximately 130 different types of chemicals) ranging from common salt (sodium chloride) to toxic chromium sulfate [4]. 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 [5]. 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 [6]. In addition to large consumption of water during the manufacturing processes, the water consumption of Palestinian tanneries is estimated at 70000 m^3 /year [7].

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 [8, 9]. 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 [4]. 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 [10].

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 [11]. 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.

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 [12].

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 [13, 23].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 [24].

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% [23].

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) [15].

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 [14, 15]. Titanium tanning agents obtained from the waste of metal industry can be used to produce eco-friendly leather with acceptable physical and chemical characteristics [17].

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 [16]. 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 [18].

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 [19]. 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 [20].

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 [21].

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 [22].

1.3 Problem Statement

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

The main question

Depending on the wastewater samples released from leather tanning industry,what are the values of the main physiochemical characteristic for the whole leather tanning process ?

The sub questions

1-how does the PH, COD , TS values changes among the leather tanning industry process , and what are the reasons behind those changes ?

2-How to apply the cleaner production principle (CP) over the wastewater released from the leather tanning production?

3-How to modify the leather tanning process in order to increase the chromium uptake within the process?

4-what is the effect of changing the tanning process parameter on the final product cost and quality?

1.4 Goals and objectives

The present study aims to characterize the wastewater from leather tanning industry in Palestine, in order to identify the best cleaner production options for minimizing the chromium uptake by the leather and decreasing the chromium concentration in the effluent.

The project specific objectives

1-Studying the possibility of applying the CP options after going over the whole leather tanning industry process.

2-Determinning the characterize of each manufacturing process in order to be able to make a full mass balance study

3-Establishing a questionnaire in order to evaluate the opportunities of applying the CP options.

1.5 Significance of Study

The significance of this study comes from the importance of protecting the environment and decreasing the financial effort resulted from the leather tanning industry. The management of this industry by characterizing tannery effluent from all process was the first step, obtaining wastewater generation rate pollutants quantities and chromium containing are the main outputs of this study in order to establish treatment plans and as a main aim to stop the Israeli occupation pressure over the manufacturers in order to dispose their wastes which highly cost.

1.6 Methodology

1- Pre-assessment phase

*walk through inspection.

*pre-assessment of the leather tanning manufacturing process.

*preparation of leather manufacturing 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

The total estimated cost for this project is 3255$ as detailed in Table 1.1:

Table 1.1: The total estimated cost for implementing the project.

Number	**Item**	**Cost($)**
1	lab tools (Beakers, flasks, cylinders, etc.)	100
2	Lab testing kits and trials	3000
3	Transportation	75
4	Glass containers	50
5	Safety requirement	30

1.8 Action Plan

Table 1.2: Action plan for the first semeste

Task	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 change										■	■	■				
Characterization of wastewater					■	■	■	■	■	■	■	■				
Documentation						■	■	■	■	■	■	■	■	■	■	
Presentation																■

Table 1.3: Action plan for the second semester

Task	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
Preparation of leather manufacturing processes flowchart																
Calculate chromium up take																
Preparation of CP implementation plan																
Documentation																
Final Presentation																

Chapter two

" Literature review"

2.1 Background

2.1.1 Skin structure

The skin is the largest and most complex organ in the body .It consist of water, proteins , fats mineral salts and others as shown in figure1. Its primary functions that protect the body from environmental factors such as bacteria, viruses, prevent water losses and thermo-regulation.

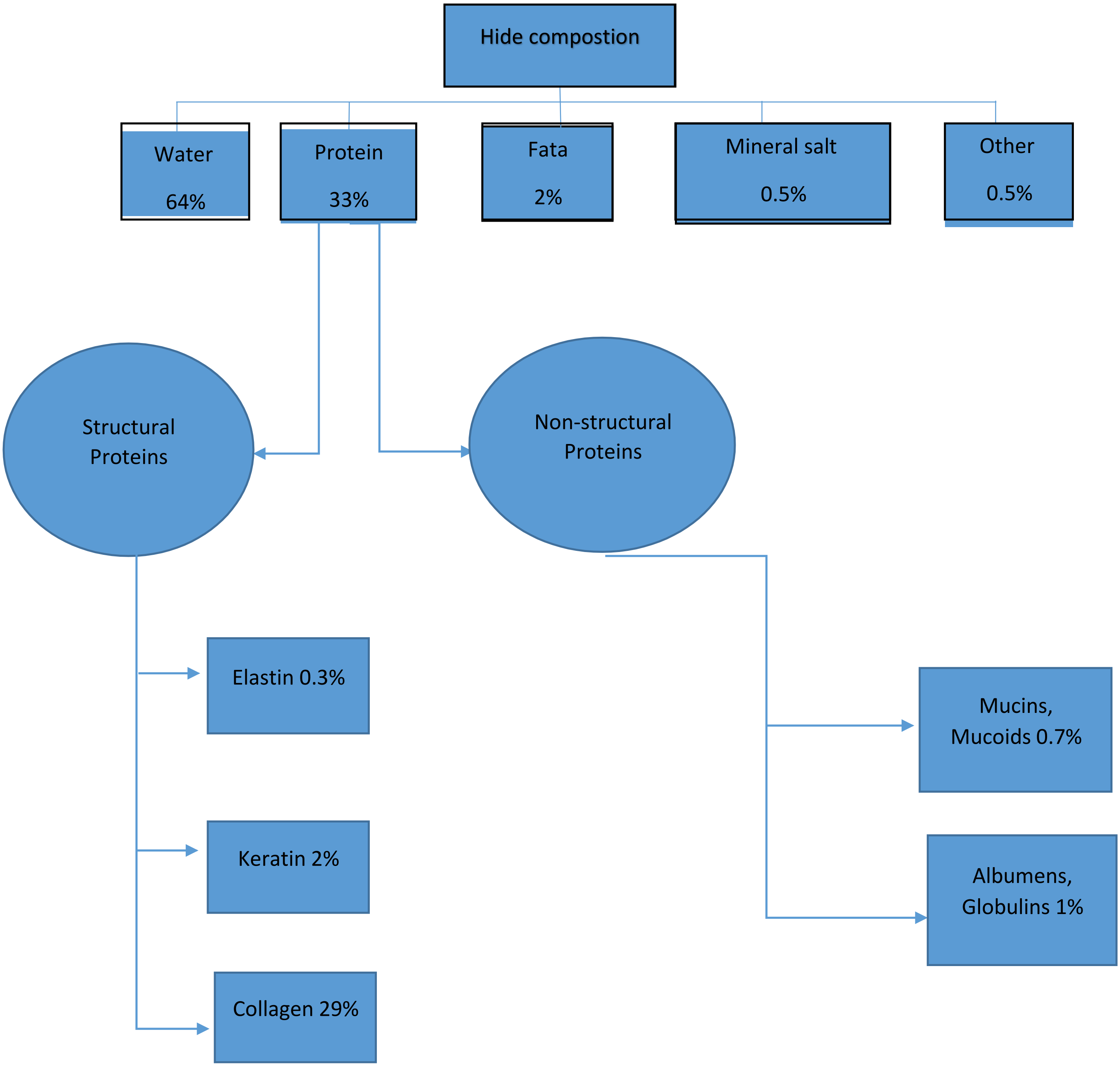

Figure 2.1: The approximate composition of animal hides.[7]

Epidermis	Epidermis
Papilary layer	Dermis
Fibernetwork layer	
Hypodermis	Hypodermis

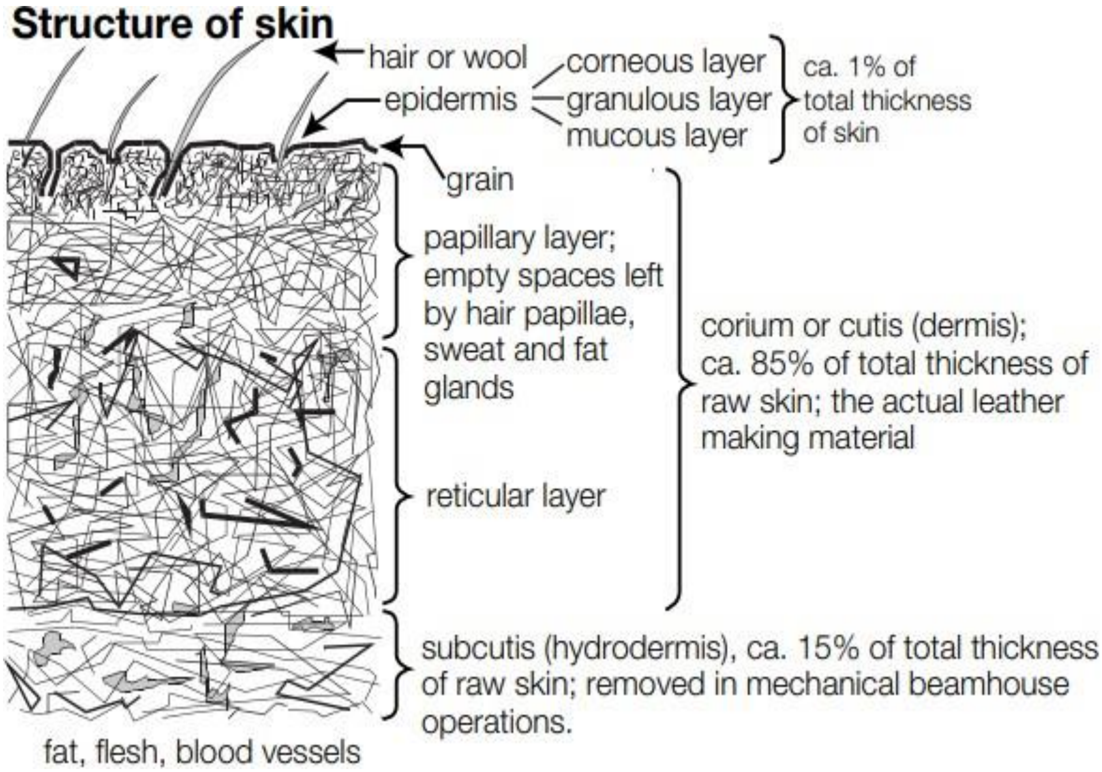

Figure 2.2: Structure of skin.[16]

2.1.2 Leather manufacturing processes

The tanning process is usually accomplished in three main stage is, first stage beamhouse, and the second stage tanning and third stage post-tanning.

First stage beamhouse fresh skins must undergo preliminary treatment (curing) before being transferred to the factory , the curing is the process of preventing the skin from rot and bacterial growth by salting or drying and the skin is stored on pallets in a well-ventilated area.

In soaking, the hides are soaked in clean water to remove the salt left over from curing and increase the moisture, in this process the preserved raw hides regain their normal water contents. Dirt, manure, blood, preservatives (sodium chloride, bactericides) are removed by adding detergent and water.

After that in unhairing and liming stage Extraneous tissue is removed , Unhairing is done by chemical dissolution of the hair, fat and epidermis with an alkaline medium of sulfide and lime, and Na2S ,. Lime blended with sodium sulphide is traditionally used to loosen wool and hair, or dissolve these into a pulp, this process is responsible for the major part of the COD load from a tannery.

Then unhairing and liming, the aim of unhairing and liming is to remove the hair, epidermis, and to some degree, during this process hair roots and pigments are removed. This results in the major part of the ammonium load in the effluents.

Then Deliming the lime in the hides is no longer required, and must be removed before chrome tanning which occur in acidic solution. Reduction in the pH of the hides, which returns to their natural thickness, is carried out in two separate stages, the first bring referred to as deliming. bating is carried out as part of the same process (in the delime float) , and uses enzymes to digest dissolve some of the remaining nonstructural proteins. During bating and pickling the skins are treated with acid and salt in preparation for tanning. During tanning the skin fibres absorb the tanning agents. That's when the skin becomes leather.

Tanning (tanyard) the actual tanning to make leather, this stage following after beamhouse stage including, tanning and Splitting In order to achieve an even specified thickness the leather is reduced in substance. The resulting split-leather can be processed further than, and shaving after the tanning stage comes the finished leather stage (In the post-tanning area). [26]

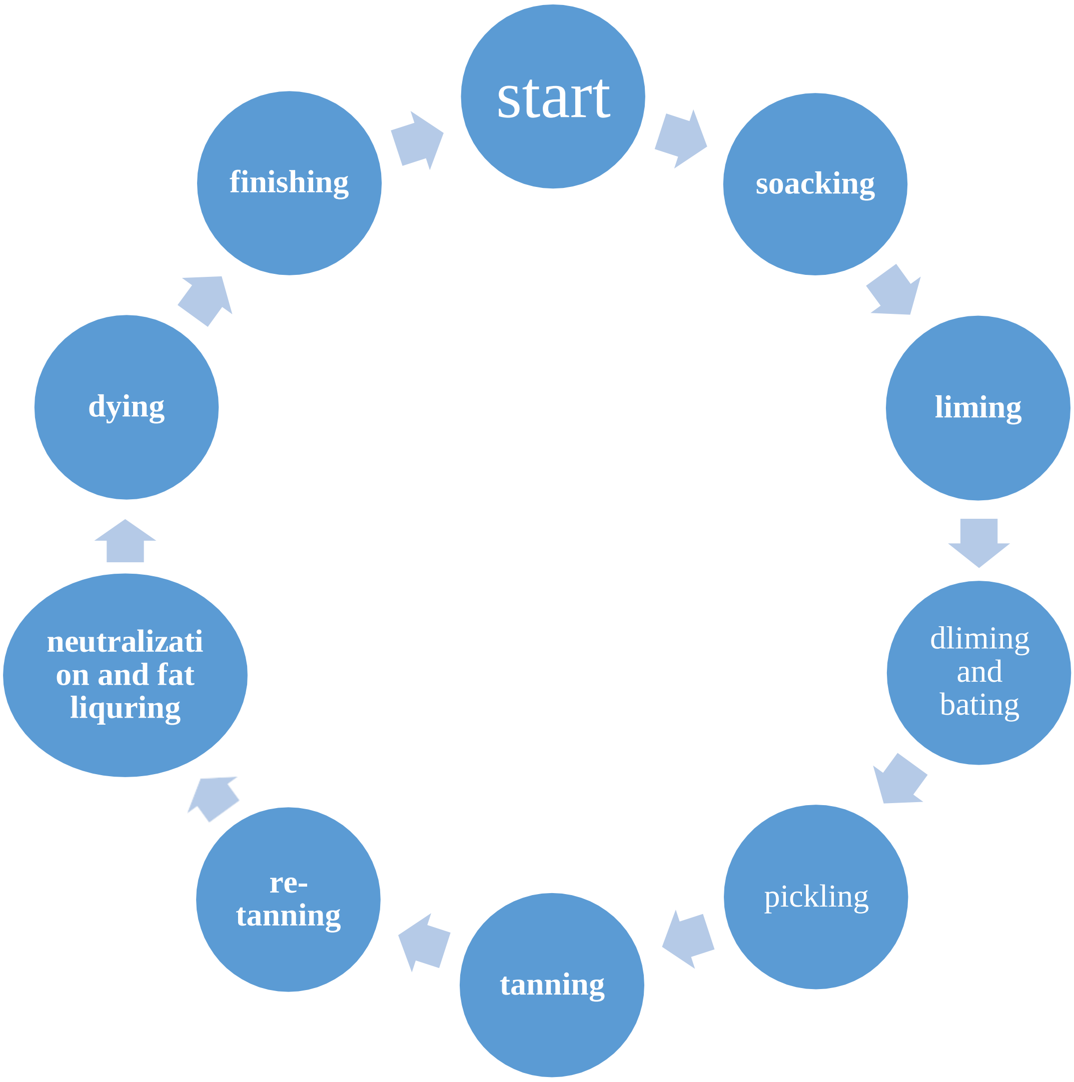

Figure 2.3 leather industry process. [36]

2.1.3 Tannery wastewater

Tannery wastewaters are highly complex and are characterized by high contents of organic, inorganic and nitrogenous compounds, chromium, sulfides, suspended solids and dissolved solids.[2] High concentration of chemical oxygen demand content (COD), Total Solids (TS), Total Soluble Solids (TDS), Total Suspended Solids (TSS), Chromium, Chloride, Ammonia and Sulfide. All these concentrations come out in the wastewater of the tanning process and the concentrations at each stage depend on the proportion of leather and raw materials involved in the process so these concentrations are not fixed Wastewater is treated in different physical, chemical or biological ways. Through research and experiments, both aerobic and anaerobic processes are used to treat tanning Wastewater [35]**.**

Table 2.1: Average pollution load in combined tannery's wastewater [36].

Parameter	**Source**	**Average value in effluent**	**Unit**
BOD	The presence of biodegradable and nonbiodegradable materials.	2000	mg O_2/L
Chromium (trivalent chromium)	Tanning process (main tanning agent)	150	mg/L
COD	The presence of biodegradable and nonbiodegradable materials	4000	mg O_2/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	1400	mg/L
Sulfate (SO4 -2)	From pickling process (H2SO4)	130	mg/L
Oil and grease	Oils in finishing phase	5000	mg/L
Chloride (Cl-1)	From using chloride containing chemicals (chloric acid)	-	mg/L
pH	-	-	6-9

Table2.2: Characterization of leather tanning industry wastewater from different processes[28].

Parameter/ process	Chloride	pH	TSS	TDS	TS	COB
Soaking	31127.37 ±849.05	8.37 ±0.988	9093 ±80.61	27067.5 ±9853.5	36160.5 ±9772.95	11640 ±1484.92
Liming	5581.2 ±72.14	12.0 ±0.707	6804.35 ±59.18	15157 ±1636.24	21961.35 ±1695.4	18578 ±1827.15
Deliming	3862.12 ±140.89	8.63 ±0.989	5802.6 ±52.89	19199.95 ±11596.48	25002.1 ±11543.58	7485.1 ±1808.07
Pickling	41568.9 ±1423.37	3.25 ±0.212	458 ±11.313	23130 ±12204.6	23588 ±12215.97	2707 ±687.34
Chrome tanning	2719.7 ±364.202	4.09 ±0.141	405 ±1.41	13148.5 ±16897.7	13553.5 ±16899	1716 ±619.43
Retanning	2666.15 ±436.49	4.11 ±0.127	172 ±2.82	6100.95 ±8342.37	6272.95 ±8345.2	4487.1 ±1121.61

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. Cleaner production is applied to increase efficiency, quality and reduce risks to humans and the environment. It is an integrated process to protect the environmental world and reduce the consumption of environmental resources and operating costs.

More than 90% of global leather production of 18 billion sq. It is through chrome-tanning process currently. The conventional methods employed for tanning lead to significant material loss and serious environmental concern. The current chrome management options like high exhaustion tannage, chrome recycling and recovery–reuse methods.

Therefore, concern about increasing concentrations of pollutants in the environmental world, risks to the environment, human health and resource consumption. In recent centuries, so-called clean production has emerged as one of the means of conservation, reduction and reuse.

In the industrial sector, clean production is mainly used. Production options are divided into reducing waste, replacing raw materials and chemicals with less toxic substances, or adding effective materials to increase production.

The practice of clean production in the tanning process improves traditional tanning processes which helps to reduce the total dissolved solids and other toxic chemical outputs. Use environmentally friendly raw materials in prepare synthetic tanning salts (syntans), thus stopping the release of toxic chemicals in liquid waste after tanning. Re-evaluating chromium and use an alternative with the same specifications to minimize environmental impact [25].

2.1.5 Options of cleaner production:

Cleaner production options relate not only to changing equipment, but also to the operation Cleaner production options can be grouped into:

1. Waste reduction at source;
2. Recycling.
3. Product modifications.

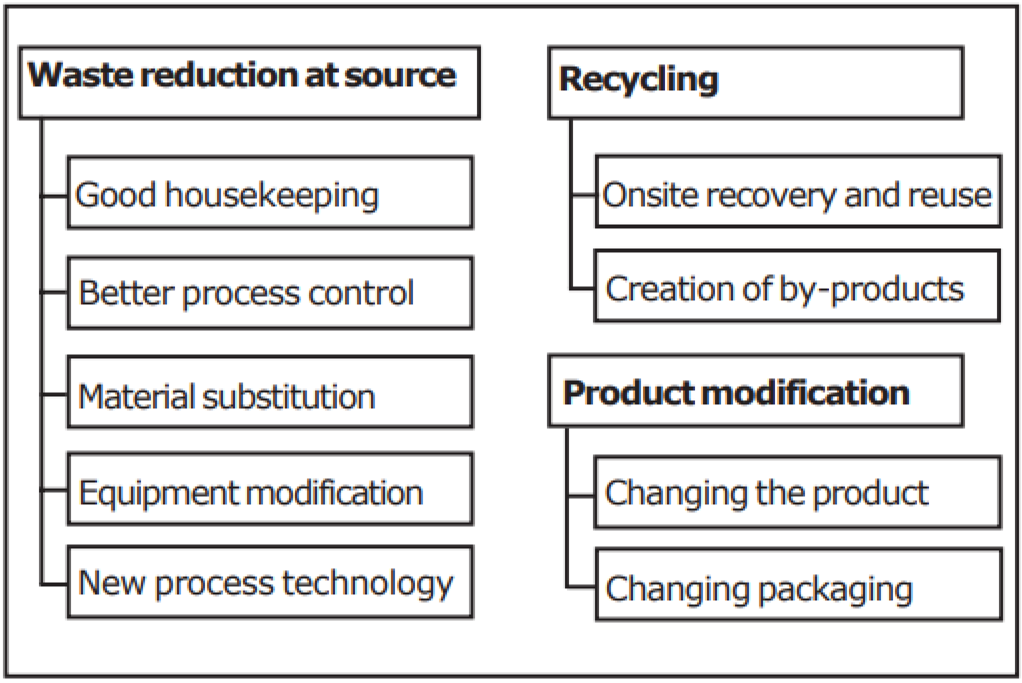

Figure 2.4: Options of cleaner production.

2.2 literature Review

2.2.1 Recovery of chromium

The leather industry is one of the main sources of water contamination with chemicals used in the tanning process. He noted that approximately 50% of the chemicals enter the wastewater and produce large quantities of toxic waste (organic and inorganic). Most existing plants use chromium to manufacture leather because it provides better skin elasticity and water resistance and prevent rot, but the presence of chromium in wastewater is a key factor in serious pollution of the environment and humans and damage to the sewage network. Therefore, several experiments were carried out to remove chromium from wastewater in order to reduce pollution, reduce chemical concentrations and improve water quality and treatability, Such as membrane technology and nanofiltration (NF).

The membrane technique has permeability and retention of many ions, especially chromium.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.

Adsorption technology is one of the experiments conducted on wastewater to remove chromium, it is low cost, it uses three types of activated carbon (C1) waste from sugar industry as waste products and (C2, C3) is a commercial granular activator.

The process or technique and its absorption depend on the physical and chemical properties, through experiments the result was the most effective or the highest area is C1 where the surface area (520.66), it is an effective economic way to remove chromium from wastewater.

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).

2.2.2.1 Titanium tanning

Titanium is an alternative to chromium salts in tanning as it is a good technology in the leather sector .The use of titanium salts in the tanning process produces skins of high quality, from the quality of the use of tanned chromium, which is abundant, cheap and non-toxic, titanium in the same system of chromium with lower concentrations in terms of the resulting chemicals and pH between 3.8-4, as well as a significant reduction in liquid waste. Therefore, titanium salts are introduced as a substitute for chromium in the leather industry [18].

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. Aluminum tanning plants were manufactured by aluminum sulfate with twelve water molecules was combined with sodium citrate. A certain amount water was added, and the mixture boiled for some time. The pH of the solution was then adjusted to 3.5 by the addition of Na2CO3 to obtain the aluminum tanning agent [18].

2.2.2.3 Zirconium tanning

Because of the use of chrome tanning agent in the leather industry, which produces wastewater that contains a high percentage of chromium and solid waste, containing wastewater from the leather industry on chrome poses a danger to the environment in terms of the conversion of Cr(III) into more toxic Cr(VI). Therefore, the leather industry faces severe environmental and social pressures. the development of sustainable chrome free tanning agents has become the focus of international leather researchers in academia and industry. Zirconium salt is regarded as a potential alternative to chrome tanning agent and has drawn renewed attention due to its relatively high tanning ability, and low environmental risk. However, traditional Zr-tanned leather has poor organoleptic properties, such as stiff handle and coarse surface. A generally accepted reason is that zirconium salt is very active to react with skin collagen fibers in the initial stage of tanning and thus precipitate on the leather surface, leading to the uneven distribution of Zr in leather and poor tanning performance. Highly-oxidized starch (HOS) with different ODs (OD, representing the amount of carbonyl and carboxyl groups) and molecular weights can be prepared using H2O2 and a copper-iron catalyst at high temperature. Remove Zr complexes using HOS with appropriate OD Through this method, zirconium with HOS is more effective and has a high quality in the tanning process, than chromium and is expressed as a good alternative in terms of quality in itself and low environmental impact [19].

2.2.3 Better uptake/exhaustion of chrome

To reduce the percentage of chromium in liquid waste due to restrictions imposed by environmental authorities, and to control pollution by modifying the process, or developing it and improving conditions by enhancing chromium penetration. Process modification includes use of masking agents and increasing collagen reactivity. 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 %. The main factors affecting the quality and efficiency of tanning: chromium concentration, temperature, pH and the method used in the industry itself.

Chromium fixation is affected by temperature as its lifting positively affects Chromium fixation. The Prefer or should the temperature rise at the beginning of the process. The pH is the second factor that affects the efficiency of tanning, as the increase in the pH causes the temperature to drop, but some problems may arise if the pH is above 5, then the chromium starts to accelerate. As for the concentration of chromium, it also affects the efficiency of tanning, which is a constant percentage on leather. The penetration of chromium increases with increasing its concentration due to the increase in the diffusion amount, but the efficiency of the process decreases with increasing chromium [32].

2.2.4 Chrome recycling method

Instead of discharging chromium into the wastewater and causing environmental problems, and problems for the sewage networks so that the use is not one time, the chrome can be recycled as well as reduce its use by 20% [30].

The recovered chromium oxide content is usually at a concentration of 100-152 Cr20 / L when used in conventional tanning Practical Indian experience has shown , that leather tanned with 70 % fresh chrome and 30 % recovered chrome has more or less the same quality as leather tanned with 100 % fresh chrome[27].

Table2.3: Comparison between cleaner production options for chrome tanning process [32].

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. Simple to 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 three

"Wastewater Characterization of Leather Manufacturing Processes"

3.1 Introduction

In leather tannery industry, animal hides are transformed into leather in a succession of many complex stages, consuming high quantities of water and using large amount of chemicals, The manufacturing process begins with Soaking In soaking, the hides are soaked in clean water to remove the salt and blood ,then, Unhairing &liming The hides are treated with sodium sulfide and hydrated lime, then, deliming stage is carried out to reduce the excess of liming agents ammonium salts are used for this purpose , then , Pickling increases the acidity of the hide to, enabling chromium tannins to enter the hide by using formic acid, then, in tanning process Chromium(III) sulfate introduced to ensure that the chromium complexes are small enough to fit in between the fibers and residues of the collagen ,Finally, Retanning , dyeing, and fat-liquoring added to impart special properties to the leather .

The wastewater from Leather manufacturing is characterized with high amount of BOD and COD. Effluent contains, suspended solids, dirt, dung, blood adhering to hides and skins, and chloride etc.

This study was conducted due to the lack of information regarding leather manufacturing process wastewater output and pollutents , in Palestine ,and aims to characterizing leather manufacturing process wastewater to provide information about the types of pollutants and chemicals existing in effluent and their concentrations. Knowing this helps in developing treatment method for the outputs of this industry.

This study will be an update for what was previously done in the literature (Hassan& maher). Sampling, lab testing and procedures as well as tabulated results and graphs pertaining to the characterization cow hides are documented in this study.

3.2 Experimental Work

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

3.3 Sampling and Materials

Samples of wastewater used in this study were obtained from 7 different tanneries in Hebron district from all leather manufacturing processes, the analyzed wastewater samples were derived from tanning process of cow leather. They were collected in glas containers, brought to the laboratory, and stored at room temperature. In the analyses, pH , TS(total solids) ,TDS(total dissolved solids),TSS (total suspended solids), COD (chemical oxygen demand) concentrations were determined .

3.4 Procedures

All Wastewater samples in all processes has been identified for their Physiochemical characteristics such as pH, chemical oxygen demand (COD), total dissolved solids (TDS), total solids (TS),and the total suspended solids (TSS).

Each Physiochemical characteristic value were determined by making a specific test as mentioned below :

PH value were determined by measuring the value for 3 samples 100 ml each using the PH Bench Meter (Milwaukee MI150, US).

The chemical oxygen demand (COD) value were determined by using the 5220 C. closed reflux titrimetric method for 100 ml sample from each 6 tanning process , this method depends on using astrong oxidizing agent such as the potassium dichromate in order to oxidize the organic matter , then samples should be digested at 150°C for 2 hours .

Total dissolved solids (TDS) value were measured for the same samples used to determine the PH using TDS meter (JENWAY 4510 bench conductivity meter, UK) , then the sample were obtained into weighted silver aluminum container(W1) to be dried in the oven at 105°C for 24 hours get the sample weight read then return to the oven again for another 24 hours to be weighted again(W2) , The total solids (TS) value were calculated by the subtraction of W2 from W1 then divided over the sample volume ($TS = \frac{W2-W1}{V}$)

Total suspended solids (TSS) value were calculated from the subtraction of TS from TDS ($TS = TDS + TSS$).

3.5 Results and Discussion

Each stage of leather manufacturing produce a different amount of wastewater, as shown in the figure3.1

These wastewater amounts obtained from Hebron tanneries for the production of 1 tons of cow leather, so the amounts of wastewater discharged per ton of cow leather as shown in figure 3.1

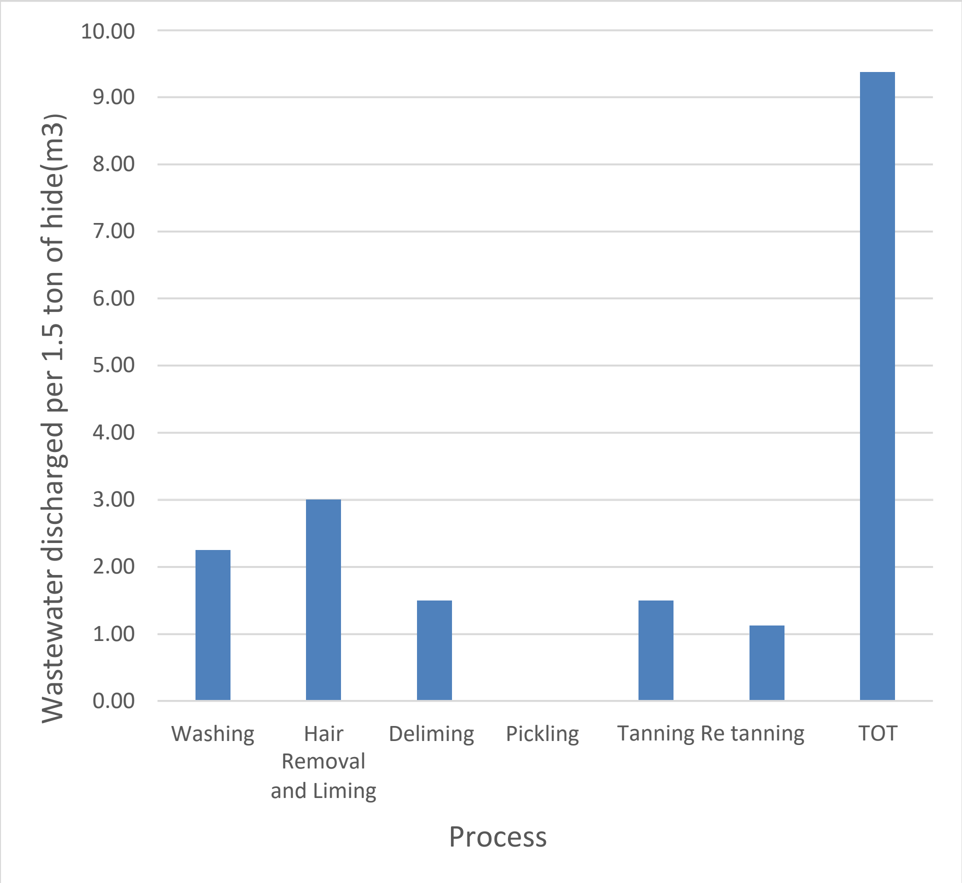

Figure3.1: The obtained wastewater discharge per 1.5 ton hide from each leather manufacturing process for cow processing from Hebron tanneries.

As shown in figure 3.1,Total wastewater discharge from Hebron tanneries is estimated 10 m^3/ton hides.

Wastewater amount generation various among the manufacturing processes. The largest amount of wastewater produced in liming process due to the using of water to remove epidermis layer. While, zero wastewater produced in pickling stage, due to performance tanning process in the same drum this includes the use of same water in addition to other chemicals. The amount of wastewater in the rest stages is less than liming because it needs less water.

Wastewater from leather manufacturing process contains high concentration of chemical oxygen demand (COD),total solids (TS), total dissolved solids (TDS) , total suspended solids (TSS), ,ammonia (NH3) and chromium Cr(III) .Analysis of the physiochemical characteristics of the tannery wastewater collected from various factory in Hebron district shown in table 3.1 , 3.2,3.3,3.4,3.5,3.6,3.7 respectively.

Table 3.1: Exprimental analysis of tannery wastewater for cow hide processing from Factory (1).

Source code	**Procees / parameter**	**PH**	**TDS**	**TS**	**TSS**	**COD**	**Chromium(cr^{+3})**
F1P1	Washing	6.39	3.59	64.49	60.90	2837.55	Not detected
F1P2	Unhairing&liming	12.24	2.45	43.25	40.50	9673.47	Not detected
F1P3	Deliming	8.81	3.34	35.70	32.36	5700.90	Not detected
F1P4	Pickling	3.43	3.71	89.28	85.56	3740.41	Not detected
F1P5	Tanning	3.68	3.76	57.12	53.37	3095.51	5.800
F1P6	Re-Tanning	12.00	2.29	21.51	19.22	5030.20	Not detected

All values except pH andCOD expressed in g/L*

Table 3.2: Exprimental analysis of tannery wastewater for cow hide processing from Factory 2 (F2).

Source code	**Procees / parameter**	**PH**	**TDS**	**TS**	**TSS**	**COD**	**Chromium(cr^{+3})**
F2P1	Washing	6.32	4.52	97.97	93.45	1212.41	Not detected
F2P2	Unhairing&liming	12.38	3.41	32.67	29.26	6448.98	Not detected
F2P3	Deliming	8.34	3.46	24.04	20.58	1418.78	Not detected
F2P4	Pickling	3.02	4.30	0	0	1238.20	2.500
F2P5	Tanning	3.55	4.38	0	0	1367.18	Not detected
F2P6	Re-Tanning	7.72	3.15	15.90	12.79	644.90	Not detected

All values except pH andCOD expressed in g/L*

Table3.3: Exprimental analysis of tannery wastewater for cow hide processing from Factory 3 (F3).

Source code	Procees / parameter	PH	TDS	TS	TSS	COD	Chromium(cr^{+3})
F3P1	Washing	6.33	4.66	71.16	66.50	1547.76	Not detected
F3P2	Unhairing&liming	12.30	4.37	102.57	98.20	13542.86	Not detected
F3P3	Deliming	9.33	3.73	34.5	30.32	3998.37	Not detected
F3P4	Pickling	2.64	4.67	22.61	17.95	2837.55	Not detected
F3P5	Tanning	3.77	4.59	65.99	61.39	2760.16	3.014
F3P6	Re-Tanning	7.41	4.32	48.75	44.43	386.94	Not detected

All values except pH andCOD expressed in g/L*

Table3.4: Exprimental analysis of tannery wastewater for cow hide processing from Factory 4 (F4).

Source code	Procees / parameter	PH	TDS	TS	TSS	COD	Chromium(cr^{+3})
F4P1	Washing	6.14	4.68	110.04	105.36	2476.41	Not detected
F4P2	Unhairing&liming	12.40	3.44	36.10	32.66	13026.94	Not detected
F4P3	Deliming	8.32	3.47	58.77	55.31	3224.49	Not detected
F4P4	Pickling	3.62	4.05	66.92	62.87	2966.53	Not detected
F4P5	Tanning	3.89	3.93	78.96	75.03	2579.59	.929
F4P6	Re-Tanning	7.31	3.02	53.95	50.94	1676.73	Not detected

All values except pH andCOD expressed in g/L*

Table3.5: Exprimental analysis of tannery wastewater for cow hide processing from Factory 5 (F5).

Source code	Procees / parameter	PH	TDS	TS	TSS	COD	Chromium(cr^{+3})
F5P1	Washing	6.50	4.18	60.33	56.15	2347.43	Not detected
F5P2	Unhairing&liming	7.29	3.04	21.25	18.21	1883.10	Not detected
F5P3	Deliming	8.17	2.86	15.33	12.47	2399.02	Not detected
F5P4	Pickling	3.55	4.33	83.63	79.30	2450.61	Not detected
F5P5	Tanning	3.62	4.15	49.77	45.62	2528.00	2.44
F5P6	Re-Tanning	6.69	4.16	49.06	44.90	2115.27	Not detected

All values except pH andCOD expressed in g/L*

Table3.6: Exprimental analysis of tannery wastewater for cow hide processing from Factory 6 (F6).

Source code	Procees / parameter	PH	TDS	TS	TSS	COD	Chromium(cr^{+3})
F6P1	Washing	6.38	3.60	59.01	55.40	2063.67	Not detected
F6P2	Unhairing&liming	11.77	1.68	12.17	10.49	3740.41	Not detected
F6P3	Deliming	9.10	3.73	54.46	50.73	6320.00	Not detected
F6P4	Pickling	3.64	3.85	58.86	55.10	2063.67	Not detected
F6P5	Tanning	3.49	3.69	52.85	49.16	1650.94	2.44
F6P6	Re-Tanning	8.48	2.44	10.15	7.71	1754.12	Not detected

All values except pH and COD expressed in g/L*

Table3.7: Exprimental analysis of tannery wastewater for cow hide processing from Factory7 (F7).

Source code	Procees / parameter	PH	TDS	TS	TSS	COD	Chromium(cr^{+3})
F7P1	Washing	6.37	4.55	80.05	75.50	2192.65	Not detected
F7P2	Unhairing&liming	11.98	4.06	68.82	64.76	6706.94	Not detected
F7P3	Deliming	8.93	3.81	37.82	33.62	4385.31	Not detected
F7P4	Pickling	2.95	4.57	96.50	91.93	1960.49	Not detected
F7P5	Tanning	3.31	4.48	105.32	100.84	2115.27	2.508

All values except pH and COD expressed in g/L*

The results shows that all the physiochemical characteristic of tannery effluents did not different significantly among the tanneries. This is due to the same manufacturing procedures followed by the tanneries.

Soaking: In this process the preserved raw hides regain their normal water Dirt, manure, blood, preservatives (sodium chloride, bactericides) are contents removed by adding detergent.

Liming: Extraneous tissue is removed. Unhairing is done by chemical

dissolution of the hair, fat and epidermis with an alkaline medium of sulfide and lime, and Na2S. Liming process produce the effluent stream with the highest COD value. It take 24 hours to finish.

De-liming: The unhaired, fleshed and alkaline hides are neutralized with acid ammonium salts and treated with enzymes, similar to those found in the digestive system, to remove hair remnants and to degrade proteins. During this process hair roots and pigments are removed. This results in the major part of the ammonium load in the effluents.

Pickling: Pickling increases the acidity of the hide to a pH value of 3.5 by addition of acid liquor and salts, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling .This lead to high contain of TDS,COD and ammonia concentration.

Tanning: After pickling, when the pH value is low, chromium (III) salts are added to the same effluent used in pickling. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature .Chromium concentration in the effluent is high.

Re-tanning: Re-tanning is a second, shorter tanning operation normally using a tanning agent other than chromium. After the re-tanning solution is discharged from the drum, a pigment is added in order to dye the leather to the desired color. The Next a mixture of oils is added coloring solution is also discharged from the drum and the hides and oil are rotated in the drum. This operation, called fat- liquoring, helps to produce the desired softness. After removal from retain, color, and fat- liquor drum, the leather is dried and physically conditioned. Result in high levels of COD and TS in the wastewater.

After finishing the experimental and calculation work and determining the physiochemical characteristic for the obtained wastewater samples ,Figures shows the relation between each tanning process and each physiochemical characteristic were obtained as below.

Fig 3.2 Shows the COD of the waste water generated from different tanning process in seven tanneries.

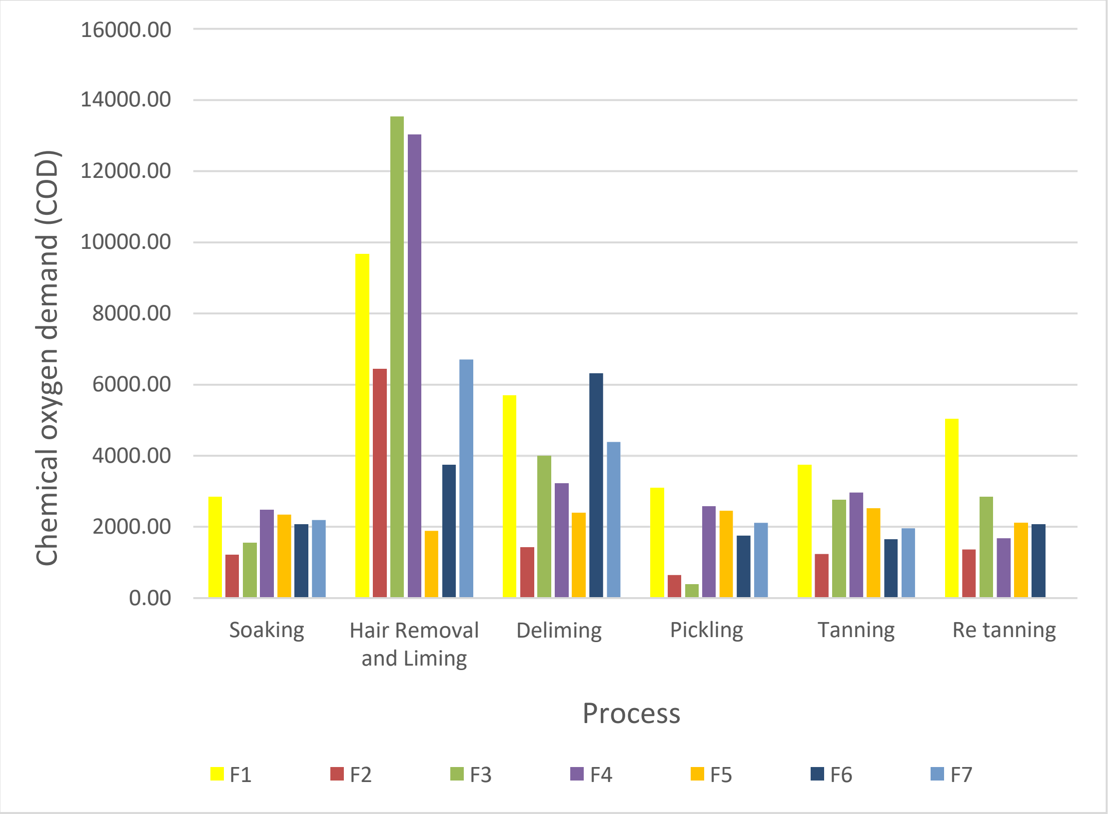

Figure 3.2: Graphical representation of measured chemical oxygen demand (COD) from each leather manufacturing process for cow processing from Hebron tanneries.

It's obvious from the figure above that there is a clear variation in the COD values for the same process in the different tanneries.

The highest COD value was detected in the liming and deliming process with an average of 8000mg/l and 4000mg/l respectively. Although the tanning process registered the lower COD value about 2000 mg/l .

Tannery wastewater contain a high amount of solids, suspended solids and dissolved solid. Fig 3.3, Fig 3.4 and Fig 3.5 show the variation of solids concentration between each process.

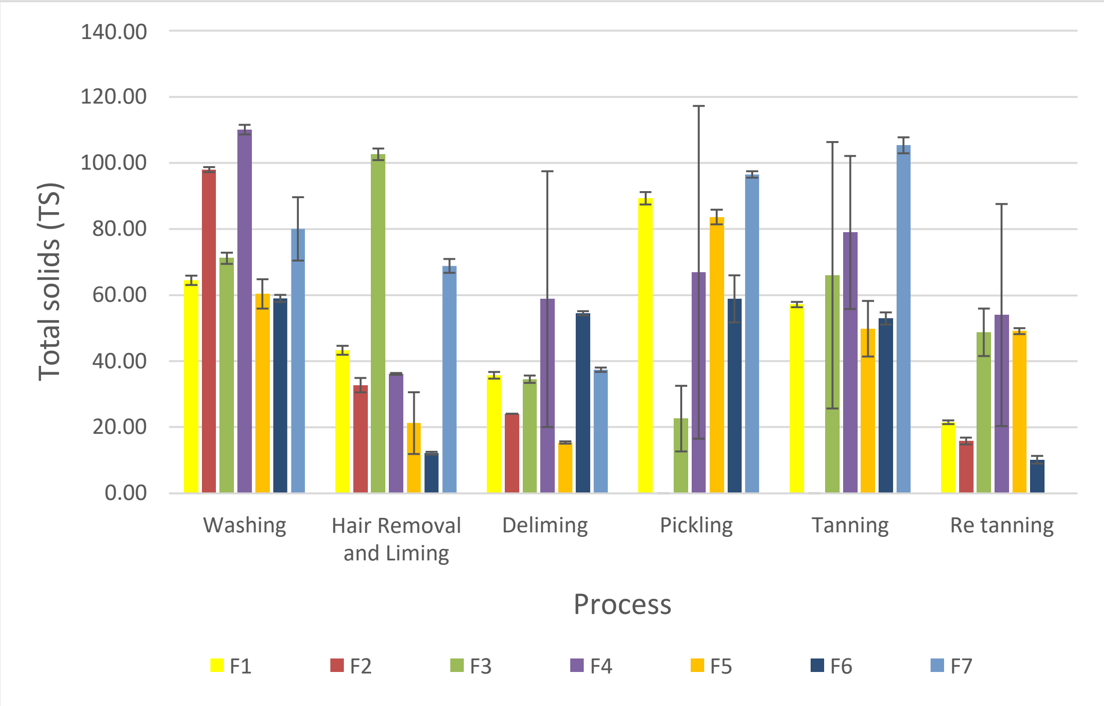

Figure 3.3: Graphical representation of measured total solids (TS) from each leather manufacturing process for cow processing from Hebron tanneries.

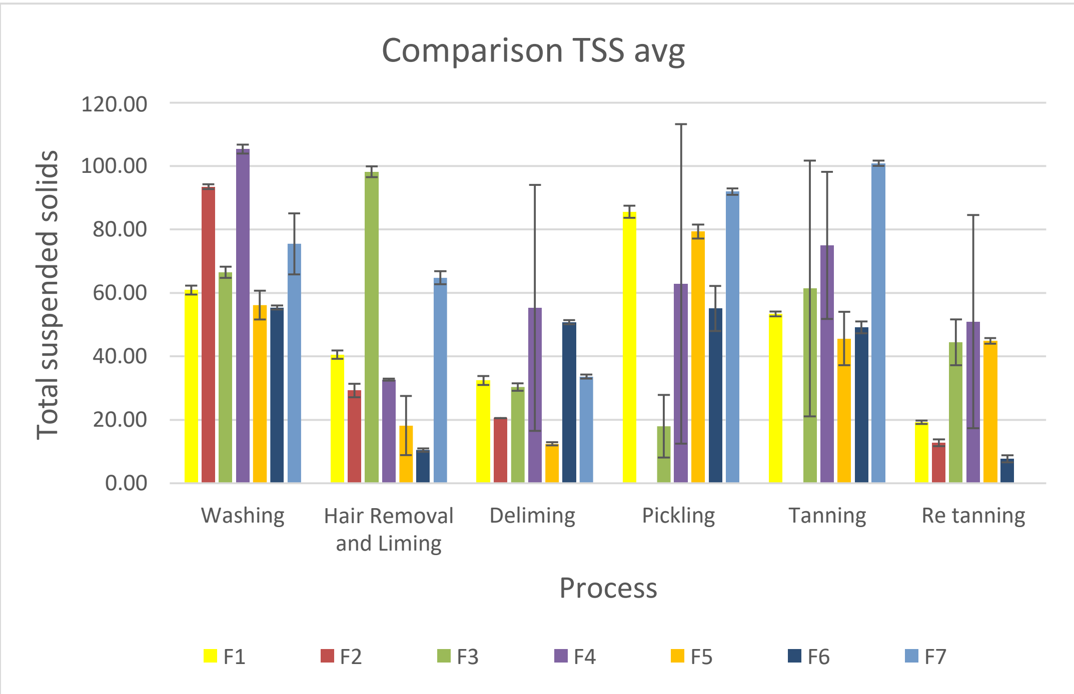

Figure 3.4: Graphical representation of measured total suspended solids (TSS) from each leather manufacturing process for cow processing from Hebron tanneries.

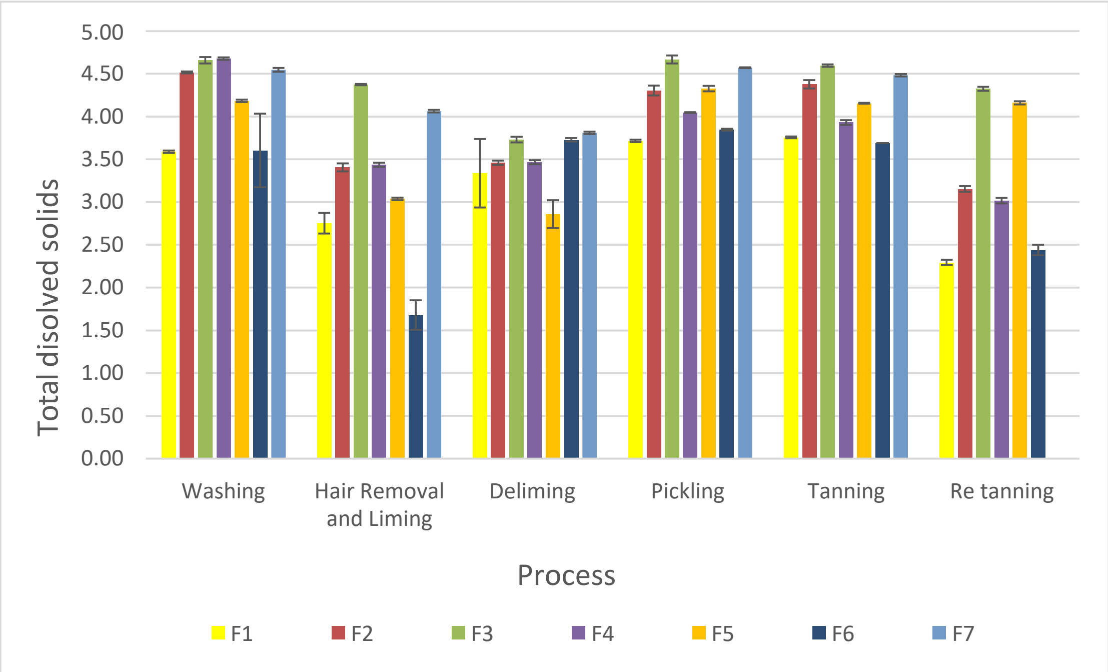

Figure 3.5: Graphical representation of measured total disolved solids (TDS) from each leather manufacturing process for cow processing from Hebron tanneries.

Wastewater resulting from soaking process have the highest value of TS, TSS and TDS because of salt and unwanted material like (blood, fat, protein, etc) are removed in this stage. Also, pickling stage effluents contains a high amount of TDS as a result of use acids and salts in order to prevent the swelling of hide. The wastewater generated from retanning process have lowest amount of solids.

There is a difference in pH values between the tanning process according to the chemicals used in each stages, these differences are shown in figure 3.6.

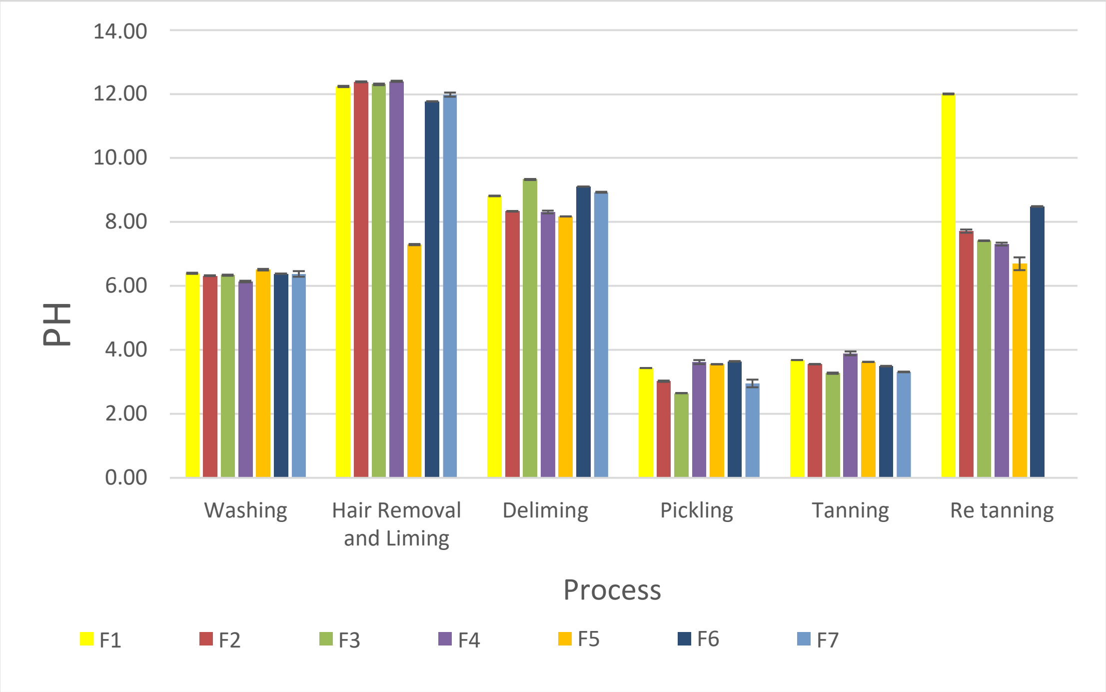

Figure 3.6: Graphical representation of measured pH from each leather manufacturing process for cow processing from Hebron tanneries.

The pH values of the effluents at various leather manufacturing stages ranged from 3 to 12. The tanning effluents had the lowest pH, 3. The low pH of the tanning effluents may be due to sulphuric acid added during the pickling stage for preparing the pickled pelt. The highest mean pH 12 was found in liming effluents because of the excessive use of lime and sodium sulphide in the production of lime pelt. Its was realized that a mean difference between the tanneries for the same process in the PH value.A large fluctuation in pH value affect adversely on aquatic environment and problems in sewer system.

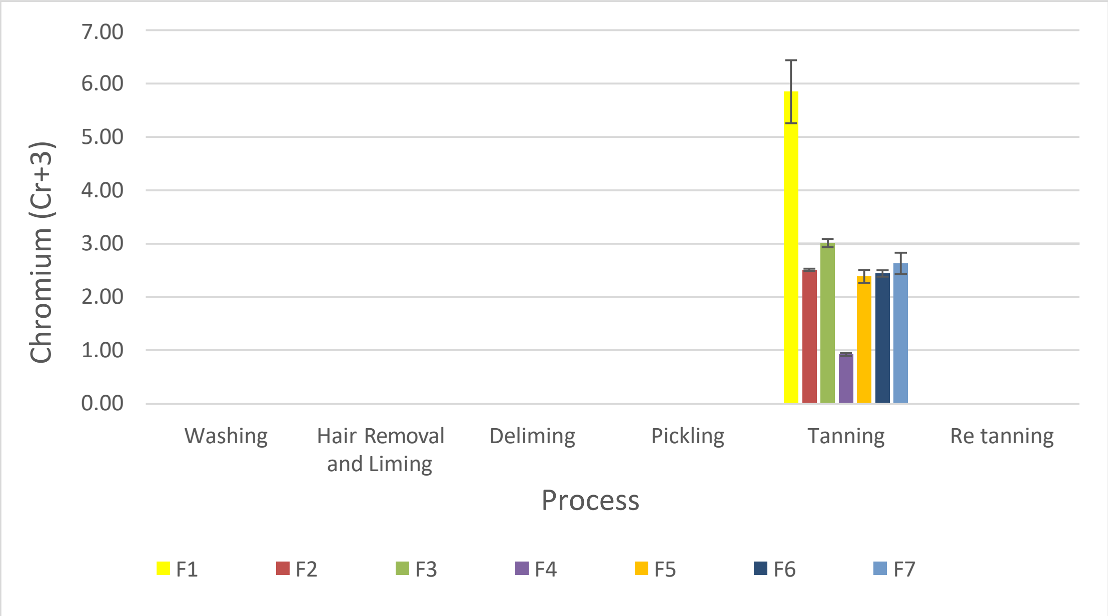

Figure 3.7: Graphical representation of measured Cr from each leather manufacturing process for cow processing from Hebron tanneries.

From the figure above it's shown that the chromium appeared in the wastewater generated from tanning process. Due to the addition of chromium in this stage with an average chromium concentration about3.500 g/l.

Chapter Four

“ Cleaner Production options “

4.1 Introuduction :

The definition of Cleaner Production that is been adopted by UNEP is the following: Cleaner Production is 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.

For production processes, Cleaner Production aims in particular at conserving raw materials and energy, eliminating toxic raw materials, and reducing the quantity and toxicity of all emissions and wastes before they leave the process.

In tanning process ,the wastewater generated from the tanning process contains a percentage of chromium salts used during this process. Therefore, many clean production technologies such as Alternative tanning agents can be used to replace chromium and chromium recovery All of these technologies improve chromium uptake.

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 4.1.

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 hazardous waste treatment	1	3	3	0	0	3	9	2	6
Reduce exposure to chemicals at work place	3	3	9	1	3	0	0	0	0
Reduce the amount of consumption chemicals of materials	3	2	6	1	3	3	9	0	0
Reduce the amount of water consumption	3	1	3	1	3	3	9	0	0
Reduce odor problems	1	3	3	0	0	0	0	2	2
Reduce noise problems	0	0	0	0	0	0	0	0	0
Reduce amount of solid waste	2	1	2	1	2	3	9	1	2
Weighted sum			20		8		27		10

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

From the previous evaluation, Shows that the use of chromium tanning alternatives is the best technique that can be implemented in the tanning process because of its ability to reduce toxic waste and reduce treatment cost.

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 Chromium uptake:

4.2.1 Introduction:

In this chapter we will apply a mass balance on the tanning process in order to measure the chromium uptake. The effct of operation condition include Ph, tempreture , chromium concentration,reaction time and mechanical action on the chromium up take will be studied.

Chromium uptake means increased chrome content in leather and reduce the chrome concentration in effluent.

Optimal uptake of chromium during tanning process can be achieved by implementing two main approaches which are process modification and conditions optimization .To improve the chrome uptake and minimize the chrome concentration in effluent.

The main parameters that affect on tanning process efficiency are temperature, chromium concentration, pH, reaction time and mechanical action. The efficiency of chrome tannin uptake depends on the concentration in the solution, The penetration of chromium into the fibers increases when the chromium concentration in the solution increases, increase of reaction time more chrome fixed on the collagen, the chrome content in leather and the shrinkage temperature increase with the tanning time, to increase chrome content in leather and shrinkage temperature, is associated with the pH in solution .

4.2.2 Mass balance for tanning process:

Tanning: After pickling, when the pH value is low, chromium (III) salts are added to the same effluent used in pickling. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature .Chromium concentration in the effluent is high.

In the tanning process, wastewater from the pickling process is used, and chrome is added at a concentration of .05% for each ton of leather. Waste water samples from the tanning stage were collected and analyzed from seven factories in Hebron to determine the amount of chromium present in the effluent. The results were as shown in the table 4.1.

Table4.2: input and output of tanning process.

Components	Input	Output
Leather	1000 kg	1000 kg
Water	1000m^3	Wastewater approx.1000m^3
chromium salts (Cr_2O_3)	7-8 kg	Cr in wastewater from F1= 5.8 g/l
		Cr in wastewater from F2= 2.5 g/l
		Cr in wastewater from F3=3.014 g/l
		Cr in wastewater from F4= 0.929 g/l
		Cr in wastewater from F5=2.4 g/l
		Cr in wastewater from F6= 2.4 g/l
		Cr in wastewater from F7= 2.5 g/l

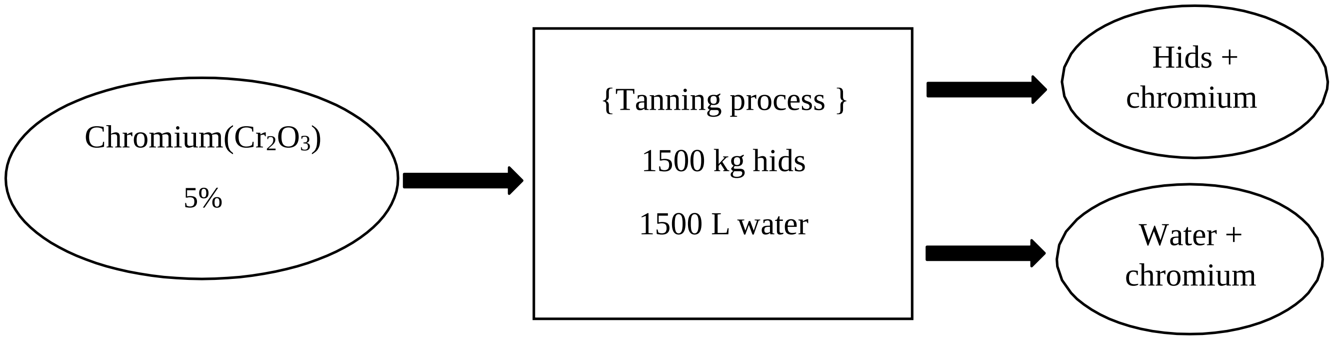

Figure4.1: mass balance in tanning process.

The figure shows the inputs and outputs of the tanning stage, as each ton of leather needs a percentage of .05 chromium and 100% of water to produce from this process wastewater and tanned hides. The process results contain an unknown concentration of chromium. The concentration of chromium in the effluent can be determined by Water analysis using ICP method, To find the chromium uptake by applying mass balance On tanning process.

4.2.3 The relations between ph and chromium uptake :

There are many factors that affect the tanning process, such as pH and cylinder speed if the pH is reduced to 2, the process temperature increase, and the cylinder speed increase.

This leads to an increase in the absorption of chromium, thus increasing the skin's absorption of chromium, improving its properties, and reducing the percentage of chromium in the wastewater resulting from the tanning process, as shown in

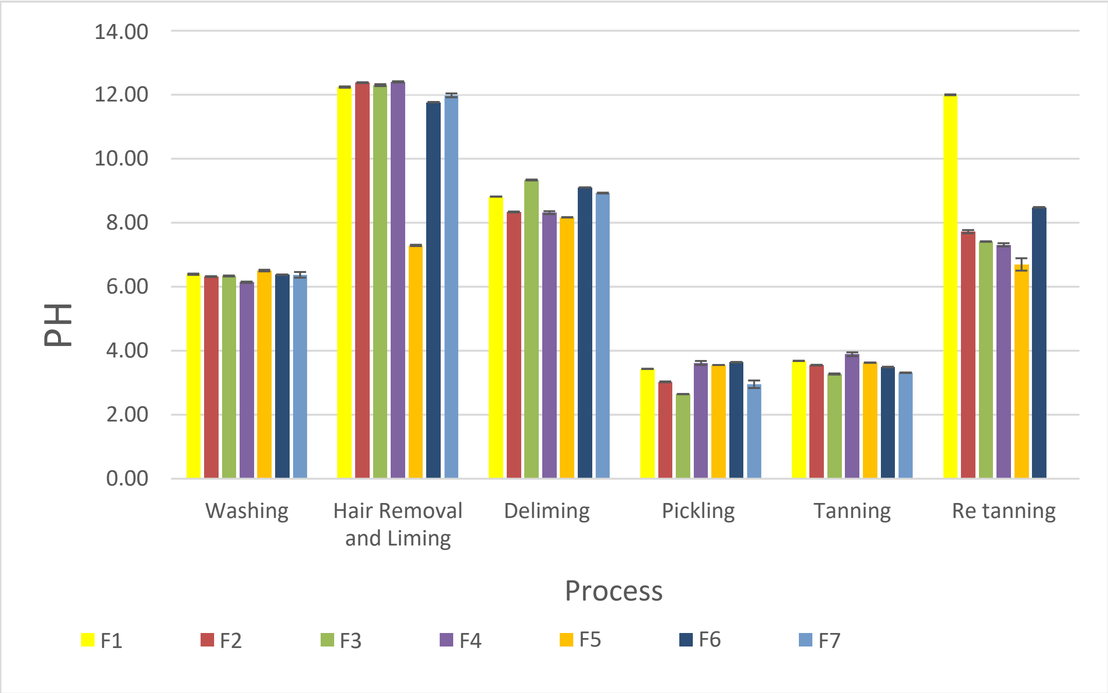

Figure4.2: Graphical representation of measured pH from each leather manufacturing process for cow processing from Hebron tanneries.

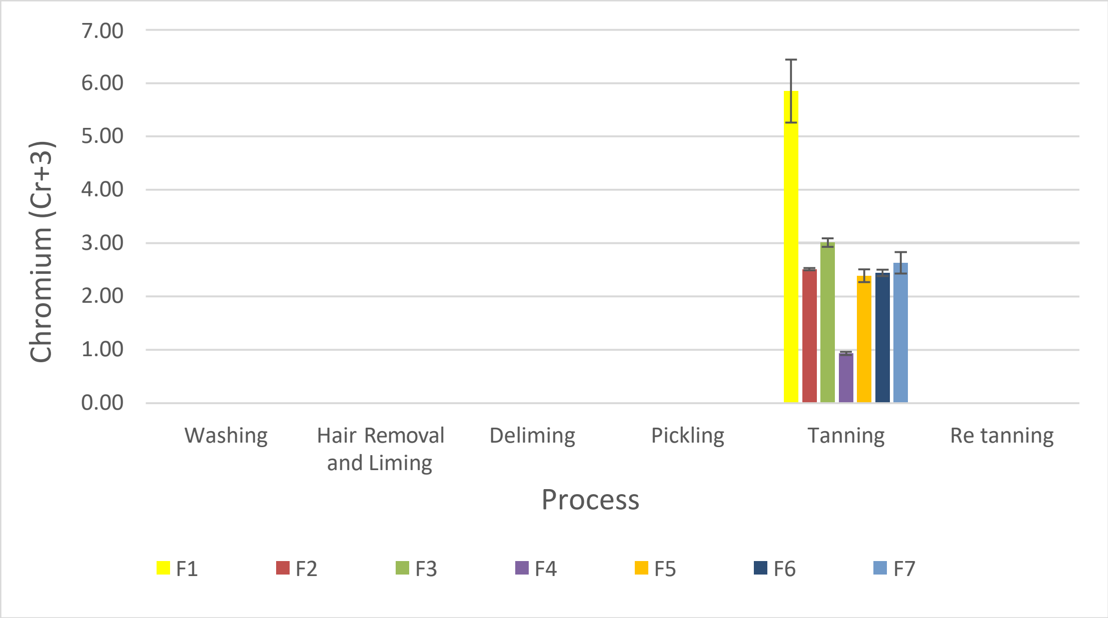

Figure4.3: Graphical representation of measured Chromium (Cr+3) from each leather manufacturing process for cow processing from Hebron tanneries.

The results are shown in figures 4.2 and figures 4.3, A decrease in the pH value leads to a decrease in the concentration of chromium present in the effluent,As a result, the chromium uptake increases during the tanning process and improves the efficiency of the process.

Conclusion:

The pollution from the effluents of the leather industries in Palestine is a major environmental and social concern. The results of the study show extremely high values of TSS, TDS, TS, COD, Cr and Ph in the effluents collected from different manufacturing stages from seven leather tanning factories were measured. The analysis results for the physiochemical characteristics shows The beamhouse operation generated high alkaline WW with high COD, TS, TDS and TSS loads, whereas, tanning operation, gave acidic WW with high chromium content. Such practices pose threats to humans, aquatic life and the entire environment. Therefore, care should be taken to check the quality of the tannery effluents at regular intervals and to make their necessary treatments, so that the pollutants may not enter the environment.

Recommendation:

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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